Users' Reports

Professor M. Kihara reporting on PF activities in Users' meeting
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ANGLE-RESOLVED PHOTOELECTRON SPECTROSCOPY OF Sb-TERMINATED GaAs(001)

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Introduction

It was recently found that antimony atoms can terminate GaAs(001)\(^1\). This Sb-terminated surface shows a very clear and streaky 2x4 reflection high energy electron diffraction (RHEED) pattern, which indicates that surface is very flat and well-ordered. For this Sb-terminated surface, the same surface atom arrangement model as As-terminated surface except the dimer consisting of Sb atoms instead of As atoms was proposed\(^3\). Since the As-dimer-origin surface state was found on the As-terminated GaAs(001)\(^2\), the similar surface state is expected for the Sb-terminated surface. Therefore, surface electronic structure is investigated by angle-resolved photoelectron spectroscopy (ARPES) on the Sb-terminated surface.

Experimental

The substrates were n-type GaAs(001) of super clean grade, doped with Si to a carrier density of 3.0x10\(^{18}\) cm\(^{-3}\). After chemical etching, the substrates were placed in a molecular beam epitaxy (MBE) growth chamber. First, GaAs about 40 Å thick was homoepitaxially grown at a substrate temperature of 575°C, showing a sharp streaky 2x4 RHEED pattern. Next, more than three monolayers of Sb were deposited on these surfaces at a substrate temperature below 200°C. Sb-terminated 2x4 surfaces were obtained by annealing these samples at 450°C. These samples were transferred from the MBE chamber in an ultrahigh vacuum to an analysis chamber connected to the BL-1A. Then, ARPES was performed on these surfaces in situ using a hemispherical angle-resolved type analyzer. The incident photon energy was 21 eV and energy resolution was determined to be about 0.1 eV by Au Fermi edge measurement.

Results and Discussion

Figure 1 shows angle-resolved photoelectron spectra taken as a function of polar angle in the [1-10] azimuth direction. Valence band maximum denoted as VBM is also indicated in Fig. 1, which is determined from the Ga 3d\(_{5/2}\) core level position at the known bulk binding energy (BE) of 18.60 eV for GaAs\(^3\).

Around 1.8 eV and 3.5 eV of BE, two dispersive peaks can be observed. The peaks located at around 1.8 eV disperse 0.2 eV toward Fermi level. This feature is similar to the surface state of As-terminated surface\(^2\), but location of BE is a little larger. The weak emissions around 3.5 eV is located at almost the same BE as that of bulk emission peaks assigned in the As-terminated surface\(^2\). Therefore, the peaks around 1.8 eV and 3.5 eV, respectively, are thought to be due to a surface and a bulk state.

References


Fig. 1 Polar angle dependence of ARPES spectra for the Sb-terminated GaAs(001) in [1-10] azimuth.
CHEMICAL STATE RESOLVED XSW ANALYSIS USING CHEMICAL SHIFT IN PHOTOELECTRON SPECTRA

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Introduction

The x-ray standing wave (XSW) technique is capable of locating the position of particular atomic species at a crystal surface or interface. We recently demonstrated the near edge x-ray standing wave (NEXSW) technique as a chemical state resolved surface and interface structure analysis technique. This was an extension of the soft-XSW technique by utilizing the chemical sensitivity of the fluorescent x-ray yield near the absorption edge of a target element. We report here a new chemical state resolved structure analysis technique that combines x-ray photoelectron spectroscopy and XSW. This photoelectron spectroscopy x-ray standing wave (PSXSW) technique allows us to investigate the distribution of a specific chemical state of a same element adsorbed on a crystal surface.

Experimental

An n-type GaAs (001) wafer was dipped into an (NH₄)₂Sₓ solution. It was then placed in an ultra-high vacuum chamber for five days to release most of the amorphous sulfur by sublimation. This left a surface covered with very thin layers of sulfur atoms. To determine the three-dimensional position of the sulfur atoms, (111) and (111) reflection XSW experiments were performed. Sulfur 1s photoelectrons excited by soft x-rays of 2.7 keV were collected with the electron energy analyzer.

Results and Discussion

Figure 1 shows the sulfur 1s photoelectron spectrum excited by 2.7 keV incident soft x-rays. We separated the spectra into only two chemical components: peak A (S-Ga chemical component) and peak B (S-As and S-S chemical components). The PSXSW results of the peak A (S-Ga chemical state component) and the peak B (S-As and S-S chemical state component) are shown in Fig.2. The results for peak A indicate that the sulfur atoms in the S-Ga chemical state order, while those for peak B indicate a random distribution of sulfur atoms in S-As and S-S chemical states. The highest binding energy chemical component in sulfur 1s core level spectra (Peak A) originate from ordered sulfur atoms which bond with Ga atoms. The sulfur atoms in the S-Ga chemical state on as-(NH₄)₂Sₓ treated GaAs(001) surface are at the bridge site while they are not highly ordered.

Acknowledgement

We would like to thank Professor H. Hashizume of Tokyo Institute of Technology for allowing us to use his analysis software. We would also like to thank Prof. Y. Nannichi and Dr. H. Oigawa of Tsukuba University, Prof. R. Uno of Nihon University and Prof. T. Kawamura of Yamanashi University for their helpful discussions.

Reference

COMPARATIVE STUDY BETWEEN MEE- AND MBE-GROWN InSb NANOCRYSTALS ON SELENIUM-TERMINATED GaAs BY PHOTOELECTRON SPECTROSCOPY

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Introduction
Semiconductor nanocrystals grown on semiconducting substrates are expected to exhibit quasi-zero-dimensional quantum effects, and are attractive materials for advanced optoelectronic. In order to clarify the crystalline quality of the nanocrystals, it is important to measure their stoichiometry. In this study, we investigated InSb nanocrystal growth on a Se-terminated GaAs(O01) surface by a migration-enhanced epitaxy (MEE) and by a conventional molecular beam epitaxy (MBE) to examine the dependence of growth methods on nanocrystal formation and stoichiometry by synchrotron radiation photoelectron spectroscopy (SRPES).

Experimental
MBE growth, Se-treatment, and in situ surface analysis using SRPES were performed in a growth chamber and an analysis chamber which are connected each other through ultra-high vacuum (UHV) at BL-1A. The sample preparation is described in detail elsewhere.1)

Results and Discussion
We prepared three kinds of samples: nominally 1-ML-thick In deposited on Se-terminated GaAs at 200°C (a), and InSb grown by MEE (b) and MBE (c) to nominally 1 ML thick on Se-terminated GaAs at 200°C and subsequently annealed at 200°C for 5 min under Sb molecular beams.2) The SRPES spectra for the three samples are shown in Fig. 1, where the intensities are normalized by the synchrotron radiation ring current. The intensity ratio (= 1.82) of Sb 4d to In 4d peaks for the MBE-grown InSb sample (c) is almost the same as that (= 1.81) for an InSb-grown sample on As-stabilized GaAs, which agrees well with the calculated value (= 1.9 to 2.0) for an InSb bulk crystal, based on photoionization cross section. Therefore, the MBE-grown InSb nanocrystals are found to be almost stoichiometric, unlike the MEE-grown ones. The difference in stoichiometry between MEE and MBE is thought to be attributed to these growth mechanisms. Sb atoms hardly migrate on the Se-terminated surface, and they re-evaporate immediately.3)

Thus, it is speculated that, in the case of MEE growth, only the Sb atoms reaching In droplets on the substrate surface are incorporated into these droplets, and that, since this incorporation efficiency strongly depends on substrate temperatures, crystal islands grown at 200°C consist of In-rich ones even post-annealing under Sb overpressure at 200°C for 5 min.

In contrast, stoichiometry for an MBE-grown sample is determined by the beam flux ratio of Sb to In at this temperature range because In and Sb atoms are simultaneously supplied on the substrate surface.

In this report, we investigated InSb nanocrystal formation on a Se-terminated GaAs(001) surface by using an MEE mode and a conventional MBE mode. The MBE-grown InSb nanocrystals are almost stoichiometric and have higher nanocrystal density than the MEE-grown ones.

References

Fig. 1 SRPES spectra of the samples: (a) In-deposited on Se/GaAs, (b) MEE-grown InSb on Se/GaAs, and (c) MBE-grown InSb on Se/GaAs.
GROWTH MECHANISM OF InSb NANOCRYSTALS ON SELENIUM-TREATED GaAs STUDIED BY PHOTOELECTRON SPECTROSCOPY
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Introduction
There have been no reports on the stoichiometry of semiconductor nanocrystals because it is difficult to evaluate the stoichiometry of these crystals that are so small. Recently, we reported the results of InSb island growth on Se-treated GaAs. In this system, the stoichiometry of heteroepitaxial InSb island crystals can easily be evaluated by using synchrotron radiation photoelectron spectroscopy (SRPES) because both the group-III and -V atoms are different from the atoms of the substrate material. In this study, we examined the effects of post annealing on InSb island-crystal formation on Se-terminated GaAs and discussed growth mechanism of InSb nanocrystals.

Experimental
MBE growth, Se-treatment, and in situ surface analysis using SRPES were performed in a growth chamber or an analysis chamber which are connected each other through ultra-high vacuum (UHV) at BL-1A. The sample preparation is described in detail elsewhere.

Results and Discussion
After growing a GaAs buffer layer, we deposited nominally 1-ML-thick InSb on GaAs at 200°C with Se treatment, and subsequently annealed at 200°C for 5 min under Sb molecular beams. The SRPES spectra at the above-mentioned two stages were measured as shown in Fig. 1. For the Se-treated sample the In 4d peak intensity is smaller by a factor of about 5 than that without Se treatment, of which result is consistent with island growth on Se-terminated GaAs, considering that the mean free path of In 4d core-level SRPES photoelectrons is estimated to be about 6 Å. The Sb 4d peak intensity is much smaller than the In 4d one, implying that In-rich InSb island crystals are formed because the calculated value of the intensity ratio of the Sb 4d to In 4d peak is 1.9 to 2.0. As shown in Fig. 2, the lack of Sb in the InSb island crystals can be explained as follows. Our recent SRPES results demonstrated the inertness of Se-terminated GaAs surfaces against impinging Sb atoms at more than 200°C, which means that surface-resident lifetimes of Sb atoms on the Se-terminated surface are very short. Thus, Sb atoms migrate little on the Se-terminated surface before they re-evaporate. This suggests that only the Sb atoms that reach InSb islands are incorporated into these crystals. On the other hand, In atoms migrate on the Se-terminated surface and prefer to form clusters because of the low surface free energy on the Se-terminated GaAs substrate. Therefore, post-annealing under an Sb molecular beam should improve the crystalline quality. As shown in Fig. 1(b), the ratio of Sb 4d to In 4d for the post-annealed sample becomes almost the same value as that of stoichiometric InSb. The stoichiometry of nanocrystals was evaluated for the first time by using in situ SRPES. We demonstrated that Sb incorporation occurs during post-annealing and that this drastically improves the stoichiometry of InSb nanocrystals grown on Se-terminated GaAs. As a result, we obtained stoichiometric InSb nanocrystals.

References
Initial Stages of Cu Surfactant Growth on Sb-adsorbed Diamond Surfaces

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Introduction

Since Cu (a=3.61496 Å) is closely lattice matched to diamond (a=3.56683 Å), Cu is expected to form an epitaxial overlayer. In this study, we investigated initial stages of Cu overgrowth on diamond films using surfactant atoms such as arsenic and antimony in comparison to the hydrogen-terminated diamond surfaces.

Experimental

Experiments with photon energy of about 100 eV were performed at beamline 1A of the Photon Factory in KEK. For C ls core levels, X-ray photoelectron spectroscopy (XPS) was used. An As or Sb flux beam from conventional K-cells was irradiated onto the polycrystalline diamond films. Cu was deposited on the H-terminated and adsorbed diamond surfaces.

Results and discussion

We have found that while no As adsorption was observed on diamond surfaces, strong Sb4d 5/2 and 3/2 peaks were clearly observed on diamond. The coverage of the surface Sb layer after 200 °C annealing was calculated to be about 35%.

Next, we deposited Cu metal on both H-terminated and Sb-adsorbed diamond surfaces at RT. As shown in Fig. 1, the Sb4d peak intensity drastically decreases for more Cu deposition, suggesting that almost all the Sb-adsorbed layer remains at the Cu-diamond interface having stable Sb-C bonds.

In order to investigate the effect of the Sb layer on metal-diamond contact formation, XPS Cls spectra were analyzed. When Cu was deposited on clean diamond surface, the Cls peak drastically shifted toward higher binding energy. In contrast, a small Cls peak shift was observed for the Cu/Sb/diamond case, indicating that the Sb atoms act as a buffer layer to prevent the Cu-diamond interfacial reaction.

The Cu surface morphology was analyzed by AFM. Figure 2 exhibits AFM images of Cu-deposited surfaces on polycrystalline diamond grains. The Cu overlayer on Sb/diamond is rougher than that on H/diamond.

In conclusion, Cu deposition on Sb-terminated diamond surfaces shows Sb surfactant effects with respect to surface morphology and electronic properties.

References


Fig. 1 Photoelectron spectra from Cu deposited diamond surfaces.

Fig. 2 AFM images of Cu-deposited surfaces on (a) H-terminated diamond and (b) Sb-adsorbed diamond. The images are 1 μm wide.
PHOTOEMISSION SPECTROSCOPY STUDY ON POROUS SILICON SURFACE

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Introduction

The mechanism leading to intense room-temperature visible photoluminescence (PL) exhibited by porous silicon is still a source of controversy. To determine this mechanism, several experiments were carried out by photoemission spectroscopy which is a very useful tool to study the band structure. However, in former research, surface effect is not considered. In this study, we examined the porous silicon surface by photoemission spectroscopy, considering band bending effect.

Experimental

The porous silicon sample was made from boron doped p-type Si(001) wafer by anodization. The PL peak energy of the porous silicon is about 1.9 eV, which is 0.8 eV wider than bulk silicon band gap. This sample was immersed in 46% HF solution for 300s to remove the oxide and then immersed in ultra pure water for 300s. To suppress oxidation by air exposure, the sample was set into a fast entry air lock chamber without drying. Photoemission spectroscopy were performed at BL-1A. He I (21.22 eV) and synchrotron radiation (138.5 eV) sources were used. The same preparation procedure was also performed on Si(001), Si(111) and poly Si.

Results and discussion

Figure 1 shows the ultraviolet photoemission spectroscopy (UPS) spectra of valence band maximum (VBM). The spectra from porous silicon is shifted to higher binding energy comparing to the other silicon surfaces. This difference is roughly estimated to be 1 eV. The origin of this shift has been explained as quantum confinement energy. However, the magnitude of this shift is different from the value derived from the PL result, therefore we should consider an additional shift caused by different origin.

Figure 2 shows the Si2p core level spectra by synchrotron radiation photoemission spectroscopy. The difference in Si2p peak position between porous silicon and others is about 0.6 eV. The core level shift is not caused by quantum confinement. Furthermore, charging effect can be neglected because the difference in Si2p peak position between porous silicon and Si(111) surface did not change even after Au deposition. This difference (0.6 eV) in Si2p is caused by band bending, which must be included in the shift (1 eV) at the valence band maximum. Therefore, the quantum confinement energy comes to 0.4 eV or less, which is consistent with the PL result and calculation. This value is in good agreement with the result which is estimated from the Si nano-ball model. In conclusion, the shift which is observed by UPS (Fig. 1) can be explained by the sum of band bending (0.6 eV) and VBM shift by quantum confinement (0.4 eV).

References

S K-EDGE XANES AND SOFT X-RAY PHOTOEMISSION SPECTROSCOPY OF SULFUR-TREATED GaAs SURFACES

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Introduction
Sulfur treatment with an (NH₄)₂Sₓ solution is regarded as an efficient surface passivation technique to reduce surface states on GaAs. Although S2p photoemission analyses revealed that sulfur-treated GaAs surfaces are terminated by Ga-S bonds, S2p spectra are not necessarily understandable because the S2p peak is split into doublet peaks by spin-orbit coupling. In this report we have measured S1s photoelectron spectra and S K-edge x-ray absorption near edge structure (XANES) by using synchrotron radiation soft X-rays to obtain detailed information about surface chemical bondings of the sulfur-treated GaAs from the S1s core-level, which has no spin-orbit splitting.

Experimental
Si-doped n-GaAs(111)A, (111)B and (100) wafers were dipped into an (NH₄)₂Sₓ solution. The S1s photoemission and S K-edge XANES experiments were carried out at the NTT beamline (BL-1A) of the Photon Factory in Tsukuba. The S1s photoelectrons excited by 2.7 keV soft x-rays were detected by a CLAM-2 analyzer. S Kα fluorescence yields counted by a solid state detector were recorded as a function of the incident energy in the S K-edge region. Both measurements were done before and after annealing the samples at 450 °C for 10 min in vacuum.

Results
Figures 1 and 2 show S K-edge XANES and S1s photoelectron spectra for (a) the as-treated and (b) the annealed GaAs(100) samples. S1s spectra similar to those in Fig. 2 were obtained for GaAs(111)A and B samples. By deconvolution of the S1s peak, four sulfur bonding states (S-Ga, S-As, S-S and S-O) on the as-treated surfaces and only the S-Ga bonding on the annealed surfaces were observed. They are resolved more clearly than in the S2p spectra. The XANES for the as-treated samples had the same fingerprint. The higher peak located at 2482 eV corresponding to the S-O peak in the S1s spectrum was assigned to the edge-jump peak of the oxyanion SO₄²⁻. The XANES spectra after annealing were slightly different between the three samples, indicating different S-Ga bonding conditions for the GaAs(111)A, B and (100) surfaces. The large spectral changes in both the S1s photoemission and S K-edge XANES by annealing are mutually consistent and suggest that annealing the sample is indispensable for the surface termination by the S-Ga bond.

References
SOFT-XSW ANALYSIS OF SULFUR INTERLAYERS IN MBE-GROWN SrF$_2$/S/GaAs(111)

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Introduction

S-passivation treatment reduces the GaAs surface states and improves the electrical properties of metal/GaAs and insulator/GaAs interfaces. These electrical properties are considered to be closely related to the interfacial structure at the overlayer/S-passivated GaAs interface. In the present paper, soft x-ray standing-wave (XSW) experiments have been performed to investigate the interface structure of MBE grown SrF$_2$/S/GaAs (111)A and B.

Experimental

Si-doped n-GaAs(111)A and (111)B wafers were used as the substrate. After chemical cleaning, the GaAs(111) wafers were dipped into an (NH$_4$)$_2$S$_x$ solution and annealed at about 430°C for 10 minutes in a vacuum. 100Å-thick SrF$_2$ epitaxial insulator overlayers were grown on the (NH$_4$)$_2$S$_x$-treated GaAs(111)A and (111)B at 430°C. The soft x-ray standing wave experiments were carried out at the NTT beam line 1A of the Photon Factory, the National Laboratory for High-Energy Physics. In these experiments, incident soft x-rays with a 2.5 keV energy just above the S K-edge were used for the {111} XSW experiments. S K$_\alpha$ (2.3 keV) fluorescent x-rays generated by the standing waves were measured as a function of sample rotation angle using a highly pure Si detector placed in the horizontal plane at a 90° scattering angle. The sample angle was scanned on a vacuum goniometer system around the {111} Bragg condition.

Results and Discussion

Figure 1 shows the XSW results of the S K$_\alpha$ fluorescent x-ray yields before and after SrF$_2$ growth on the S-passivated GaAs (111)A. The $P$ values of S atoms were not changed by the SrF$_2$ growth for both (111)A and (111)B. This indicates that S atoms on GaAs(111)A remains on top of the first-layer Ga atoms for (111)A and S atoms on GaAs(111)B remains at the first layer As atoms positions even after the SrF$_2$ growth as same as after the CaF$_2$ growth. However, the $F$ values of S atoms were slightly decreased by the SrF$_2$ growth. This suggests that disorder of the S layers is induced by the SrF$_2$ growth on S/GaAs(111)A and (111)B surfaces.

Acknowledgement

We would like to thank Professor H. Hashizume of Tokyo Institute of Technology for allowing us to use his analysis software. We would also like to thank Prof. Y. Nannichi and Dr. H. Oigawa of Tsukuba University, Prof. R. Uno of Nihon University and Prof. T. Kawamura of Yamanashi University for their helpful discussions.

References


FIG. 1. S K$_\alpha$ fluorescence yield (open circles) before and after the SrF$_2$ growth on S/GaAs(111)A; (a) (111) XSW results, and (b) (11-1) XSW results.
SR MEASUREMENTS ON SrF₂ THIN FILMS DEPOSITED ON InP
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The alkaline earth fluorides are interesting materials for insulating layers on semiconductors. We examined the growth of SrF₂ on InP, because this material combination is of special interest for MIS-device applications. The experiments using surface sensitive synchrotron radiationphotoelectron spectroscopy (SRPES) were performed at the beam line BL-1A at the Photon Factory, Tsukuba, Japan.

SrF₂ was deposited on HF etched as well as on As treated InP(100) and (111). The SrF₂ was deposited at room temperature, increasing the film thickness step by step after successive SRPES-measurements. The structural properties of these films were studied by RHEED [1, 2]. In general, the epitaxial quality of SrF₂ films deposited on As treated InP is better than that of SrF₂ on HF etched InP. On the other side, the surface roughness of films on As treated InP, as measured with AFM, is larger than that of films on HF etched InP [3].

SRPES spectra for SrF₂ on As treated InP(100) and (111) were measured. These spectra are shown in fig. 1. The most prominent difference between the two series is that on As treated InP(100) the In4d peak is still visible even after deposition of 50Å SrF₂. This is in contrast to As treated InP(111), where the In4d peak disappears after the deposition of 35Å SrF₂. A detailed study of the SRPES data shows that SrF₂ grows on As treated InP in Stranski-Krastanov mode [3]. But the thickness of the continuous base layers is significantly different between the two orientations. On As treated InP(100) the base layer is only 2 monolayers thick, while its thickness exceeds 20Å on As treated InP(111). The difference between these two orientations is simply related to the well known fact that the surface free energy of the (111) orientation is lower than that of the (100) orientation [4]. A crystallization effect of approximately 1 eV was observed in all measured SRPES spectra after annealing at 500°C.

An interfacial reaction occurs after annealing SrF₂ on HF etched InP(111) at 500°C. After this annealing step a second component is observed in the XPS Sr3d- and F1s- peaks. These peaks are related to interfacial material. A detailed study shows that the interface layer consists of SrF, while the bulk is stoichiometric SrF₂ [3]. No such reaction has been observed for SrF₂ on As treated InP(111) or for SrF₂ on InP(100).

References
Introduction

It is well known that \((\text{NH}_4)_2\text{S}_x\) treatment reduces surface states of GaAs.\(^1\) Photoemission spectroscopy studies revealed that both S-Ga and S-As bonds exist on the as-treated surfaces and that thermodynamically stable S-Ga bonds become dominant after annealing at 250-500 °C in a vacuum.\(^2\) Ohno et al.\(^3\) suggested the optimal adsorption sites for a monolayer of sulfur atoms on GaAs surfaces by minimizing the total energy. The x-ray standing wave (XSW) technique has been developed into a highly accurate technique of locating the position of particular atomic species.\(^4\) We report here the three-dimensional positions of sulfur atoms adsorbed on GaAs (001) surface analyzed by using the angle-scan soft XSW technique.\(^5\)

Experimental

An n-type GaAs (001) wafer was treated with an \((\text{NH}_4)_2\text{S}_x\) solution. This sample was then annealed at about 500 °C in a vacuum for 10 minutes. Soft XSW experiments were carried out at the NTT beamline 1A of the Photon Factory at the National Laboratory for High Energy Physics. Incident angle was scanned step by step near two different reflections, such as (1-11) and (111), for the same sample. Sulfur Ka fluorescent x-rays were collected with a highly pure Si detector.

Results and Discussion

Figure 1 shows the soft XSW results for sulfur-passivated GaAs(001). Determined P values of sulfur-passivated GaAs (001) surface indicate that sulfur atoms are at the bridge site on the Ga-terminated GaAs(001) surface forming bonds with two Ga atoms as shown in fig. 2.\(^5\) Furthermore, distance between sulfur atomic layer and 2nd Ga atomic layer is found to be 1.1 Å. This agrees well with the optimal adsorption model for a monolayer of sulfur atoms on GaAs surfaces by minimizing the total energy.

Acknowledgements

We would like to thank Professor H. Hashizume of Tokyo Institute of Technology for allowing us to use his analysis software. We would also like to thank Prof. Y. Nannichi and Dr. H. Oigawa of Tsukuba University, Prof. R. Uno of Nihon University and Prof. T. Kawamura of Yamanashi University for their helpful discussions.

References

TRANSMISSION FUNCTIONS OF THE GRATING/CRYSTAL MONOCHROMATOR
IN THE ENERGY REGION OF SOFT X-RAYS

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Introduction

The optics of the beamline 1A (BL-1A) at the Photon Factory consists of a grating/crystal monochromator (GCM) and two off-axis paraboloidal mirrors. These two mirrors are fused quartz coated by Platinum, which are located in the upper and down streams of the GCM for collimating and focusing beams. We have a plan to exchange Ni-coated mirrors for these Pt-coated mirrors in order to remove absorption structures at the Pt M-edges from the transmission function in the soft x-ray region. For the preliminary stages, we replaced the Pt-coated focusing mirror with a Cr-coated one.

Experimental

A pair of InSb(111) crystal was used as diffracting elements of the GCM for monochromatizing soft x-rays. To obtain transmission functions, Ga Lα and As Lα fluorescence yields from a GaAs wafer counted by a solid state detector were recorded as a function of the incident energy in the energy range of 2000-4000 eV. The measurements were done before and after exchanging the Cr-coated focusing mirror for the Pt-coated one at the BL-1A.

Results

Figures 1-(a) and 1-(b) show transmission functions measured by the fluorescence yield for the Pt-coated focusing mirror used so far and the new Cr-coated one in combination with the Pt-coated collimating mirror. Calculated reflectivities for these mirrors are also shown in the insets of the Figures. In Fig.1-(a) the yield decreases rapidly due to absorption of the double Pt-coated mirrors in the Pt M5-edge(2133 eV) and the low yield is kept up to the In L3-edge(3730 eV). In Fig.1-(b) absorption due to the Pt M-edges is reduced by using the Cr-coated mirror in combination of the Pt-coated one and thus the yield in the energy region of 2400 eV increases by approximately three times that in the case of the double Pt-coated mirrors. However, the yield is not obtained in the energy region over 3200 eV because of the cutoff energy of the Cr-coated mirror with 1° glancing angle. Transmission function without the absorption structure and with the improved output in the region over 3000 eV will be obtained by using double Ni-coated mirrors, since Ni has no absorption edge in this region and the higher cutoff energy than Cr.

References


Fig.1 Transmission functions of InSb(111) crystals measured by fluorescence x-ray yields from GaAs using (a) Pt-coated focusing mirror and (b) Cr-coated one in combination with Pt-coated collimating mirror. The insets show calculated reflectivities for a Pt-coated mirror, Cr-coated one and combination of these ones with incidence angle of 1 degree.
VALENCE-BAND OFFSET AT HETEROINTERFACES BETWEEN InAs NANOCRYSTALS AND Sc-TERMINATED GaAs DETERMINED BY PHOTOELECTRON SPECTROSCOPY
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Introduction
Semiconductor nanocrystals grown on semiconducting substrates are expected to exhibit quasi-zero dimensional quantum effects, and are attractive materials for advanced optoelectronic devices such as extremely efficient semiconductor lasers. In this study, we examined the valence-band offset at heterointerfaces between InAs epitaxial nanocrystals and Se-terminated GaAs substrates by synchrotron radiation photoelectron spectroscopy (SRPES).

Experimental
MBE growth, Se-treatment, and in situ surface analysis using SRPES were performed in a growth chamber and an analysis chamber which are connected each other through ultra-high vacuum (UHV) at BL-IA. The samples were Si-doped n-type GaAs(001) wafers with a carrier density of \( 1 \times 10^{18} \text{ cm}^{-3} \). The sample chemical treatment, surface cleaning, GaAs buffer-layer growth, and Se treatment were previously described in detail. The two kinds of samples were prepared by (i) depositing nominally 3-ML-thick InAs on As-stabilized GaAs at 200°C, and (ii) depositing nominally 3-ML-thick InAs on Se-terminated GaAs at 200°C by MBE. A fine streaky, As-stabilized 2x4 RHEED pattern was observed after GaAs epitaxial buffer layer growth, and also after the Se treatment the surface structure changed to show a 2x1 RHEED pattern, which implies a Se-terminated GaAs surface.

Results and Discussion
Figure 1 shows the core-level SRPES spectra for both two samples, where the intensities are normalized by synchrotron radiation ring current. For the sample without Se treatment, the peak intensity of In 4d is stronger than that of Ga 3d whereas for the Se-treated sample the peak intensity of In 4d is very weak. This difference in the ratios of Ga 3d and In 4d is also observed in the case of InSb growth. This result indicates InAs island formation on the Se-terminated GaAs surface, by considering that the height of InAs islands is larger than the photoelectron mean free path of In 4d SRPES photoelectrons, which is estimated to be about 5 Å. Thus, this result supports the interpretation that InAs islands are formed on the Se-terminated GaAs surfaces even at the very early growth stages. From the deconvoluted results in the In 4d core-level SRPES spectra, there are two peaks in the In 4d spectrum for the Se-treated sample, which are assigned as the In-Se bonding states and the In-As bonding states. There also exist the In-Se bonding states for the sample without Se treatment. This happened because the Se treatment and MBE growth were performed in the same chamber. Thus no Se-contamination can be avoided. It is noted that the Ga 3d peak position shifts forward to the higher binding energy, which is induced by Se treatment. On the other hand, no shift occurs in the In 4d peak position. This behavior can be explained by using the energy band diagrams as shown in Fig. 2. For the Se-treated sample, the Ga 3d spectrum comprises photoelectrons coming from the InAs-uncovered substrate surface area. Thus, the Ga 3d peak shift can be observed accompanying with reduction of band bending due to Se treatment. However, no change in the In 4d peak occurred. Therefore, band bending would take place again during InAs deposition, which might be caused by the residual strain and/or generation of dislocation at the heterointerface due to the lattice mismatch between InAs nanocrystals and GaAs.

References

Fig. 1 SRPES spectra with the deconvoluted results for the InAs-grown samples on GaAs with and without Se treatment.

Fig. 2 Schematic energy band diagrams at the heterointerfaces.
X-RAY ABSORPTION FINE STRUCTURE MEASUREMENTS ON SULFUR INTERLAYERS IN MBE-GROWN SrF$_2$/S/GaAs(111)

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Introduction

Sulfur treatment with an (NH$_4$)$_2$S$_x$ solution is regarded as an efficient surface passivation technique to reduce surface states on GaAs$^1$. We have grown fluoride insulator films on sulfur-treated GaAs surfaces by MBE, which is required for metal insulator-semiconductor (MIS) devices. In this report we have measured x-ray absorption fine structure (XAFS) at the S K-edge by using synchrotron radiation to investigate the relationship between the sulfur interlayer and the fluoride overlayer.

Experimental

SrF$_2$ overlayers were grown by MBE at 430 °C on (NH$_4$)$_2$S$_x$-treated GaAs(111)A and (111)B surfaces. Although reflection high-energy electron diffraction (RHEED) patterns showed that SrF$_2$ layers could be grown epitaxially on both surfaces, the SrF$_2$ epitaxial film was found to have better crystallinity on the GaAs(111)B than on the (111)A by means of x-ray diffraction. For analyzing the interfacial structure, XAFS measurements were carried out at the NTT beamline (BL-1A) of the Photon Factory in Tsukuba. X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra were recorded by monitoring S K $\alpha$ fluorescence yield with a solid state detector.

Results

Figures 3 and 4 compare the S K-edge XANES and the Fourier transform of the S K-edge EXAFS before and after growing the SrF$_2$ overlayer. In the XANES spectra after the growth, an edge-jump peak at 2472 eV based on the S-Ga bond was observed as a shoulder peak for the GaAs(111)B but not for the (111)A. The first peak of nearest neighbor Ga atoms at 1.9 Å was found in the Fourier transform after the growth on the GaAs(111)B, but again, not on the (111)A. These XAFS results demonstrate that a number of S atoms remain at the interface between the SrF$_2$ layer and the GaAs(111)B, indicating the existence of the S interlayer, while the S atoms do not exist at the same position as before the growth in case of the (111)A. This behavior of the S atoms due to the relative stability of sulfur on (NH$_4$)$_2$S$_x$-treated GaAs(111)A and (111)B$^3$ is considered to be related to the crystallinity of the SrF$_2$ epitaxial films on the GaAs(111)A and (111)B.

References

The principle of our method for measuring the mass of the electron neutrino is summarized as follows. First, the M X-rays from M-electron capture in $^{163}$Ho are measured. If $S_{\text{Mx}}^{\text{Ho}}$ stands for the photon spectrum from $^{163}$Ho, where the number of photons per atom per second is plotted as a function of the energy of photons, we have

$$S_{\text{Mx}}^{\text{Ho}} = \lambda_{M1} \cdot S_{M1}(k) + \lambda_{M2} \cdot S_{M2}(k).$$

where $S_{Mj}(k)$ ($j = 1, 2$) is the M X-ray spectrum from a Dy atom in the case where there is one vacancy in the $Mj$ subshell only; $k$ is the energy of emitted photons; $\lambda_{Mj}$ ($j = 1, 2$) is the partial M electron capture decay constant.

Next, the $S_{M1}$ and $S_{M2}$ spectra of the dysprosium atom can be obtained from fluorescence spectrum measurements as follows. If $S_E$ denotes an M X-ray fluorescence spectrum from Dy atoms excited by monochromatic photons having an energy $E$, $S_{E}$ is represented by the equation

$$S_{E}(k) = N m \sum_{i=1}^{N} \sigma_{i}(E) \cdot S_{Mj}(k),$$

where $\sigma_{i}(E)$ is the photoionization cross section for the $Mj$ subshell for an incident photon of energy $E$; $n$ is the number of dysprosium atoms in a target per cm$^2$; $N$ is the total number of incident monochromatic photons having energy $E$. In order to determine the $S_{M1}$ spectrum, we take two energies for incident photons, $E_{M1} + \Delta_1$ and $E_{M1} - \Delta_1$ where $E_{M1}$ stands for the binding energy of the $M1$ subshell and the energy $\Delta_1$ is assumed to be comparable with the level width of the $M1$ subshell. Finally we have

$$S_{M1}(k) = |S_{E_{M1}} + \Delta_1(k) - (\frac{E_{M1}-\Delta_1}{E_{M1}+\Delta_1}) \cdot S_{E_{M1}} - \Delta_1(k)| \times |N m \sigma_{1}(E_{M1} + \Delta_1)|^{-1}$$

Similarly, we get

$$S_{M2}(k) = |S_{E_{M2}} + \Delta_2(k) - (\frac{E_{M2}-\Delta_2}{E_{M2}+\Delta_2}) \cdot S_{E_{M2}} - \Delta_2(k)| \times |N m \sigma_{2}(E_{M2} + \Delta_2)|^{-1}$$

We took the values of 2.070 keV and 2.020 keV for $E_{M1} + \Delta_1$ and $E_{M1} - \Delta_1$, and 1.84 keV and 1.826 keV for $E_{M2} + \Delta_2$ and $E_{M2} - \Delta_2$, respectively. Fluorescence spectra of Dy for these incident photons from BL-2A were measured. Using equation (2) and (3), we obtained $S_{M1}$ and $S_{M2}$ spectra. Using $S_{M1}$ and $S_{M2}$ thus obtained, $S_{\text{Mx}}^{\text{Ho}}$ spectrum was reconstructed by equation (1). Then, $\lambda_{M1}$ and $\lambda_{M2}$ were determined to be $\lambda_{M1} = (0.9846 \pm 0.0492) \times 10^{-12}$ s$^{-1}$, and $\lambda_{M2} = (0.8580 \pm 0.0026) \times 10^{-12}$ s$^{-1}$.

On the other hand, the half life of the $^{163}$Ho nucleus was determined by measuring the production rate of $^{163}$Dy due to electron capture in $^{163}$Ho with isotope dilution mass spectrometry. Our result is $T_{1/2} = 4569 \pm 27$ yr or $\lambda = (4.807 \pm 0.028) \times 10^{-12}$ s$^{-1}$.

Using the values of $\lambda_{M1}$, $\lambda_{M2}$ and $\lambda$, as three constraints, $m_{\nu_e}$, the $Q$-value and the $\log(f)$ value for the decay of $^{163}$Ho $\rightarrow$ $^{163}$Dy, were determined from the formula of the electron capture rate for Gamow-Teller allowed transition as follows:

$$m_{\nu_e} = 110 \pm 35^{\oplus} \pm 90^{\ominus} \text{eV}, \quad Q = 2.710 \pm 0.005 \text{keV}, \quad \log(f) = 4.993 \pm 0.001.$$
RESONANT EMISSION SPECTRA AND RESONANT AUGER SPECTRA
IN Si-K AND Y-L\textsubscript{III} ABSORPTION EDGE

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Introduction

We have measured Si-\textit{K}\textsubscript{\alpha} Resonant X-ray Emission Spectra (RXES) and Si-\textit{KLL} Resonant Auger Spectra (RAS) in the vicinity of Si-\textit{K} absorption edge for Si single crystal, and found there is good correspondence between the peak shift and the incident photon energy in both spectra.\textsuperscript{1)} In this study, we have measured Si-\textit{K}\textsubscript{\alpha} RXES and Si-\textit{KLL} RAS in Si-\textit{K} absorption edge for Si, SiO\textsubscript{2}, and also Y-L\textsubscript{MM} RAS in Y-L\textsubscript{III} absorption edge for Y metal, YF\textsubscript{3} and YCl\textsubscript{3}. In the case of SiO\textsubscript{2}, RXES showed simple structure, however RAS showed complex structure in contrast with Si.

Experimental

RXES were measured at undulator beam line BL-2A of Photon Factory. The energy of fluorescent X-ray was analyzed by a curved crystal monochromator.

RAS were measured at BL-11B. The energy of Auger electron was analyzed by a double pass cylindrical mirror analyzer.

Results and Discussion

In this paper, we represent only for SiO\textsubscript{2}. Figure 1 shows Si-\textit{K}\textsubscript{\alpha} RXES using incident photon energy in the vicinity of Si-\textit{K} absorption edge. As far as incident photon energy reached at 1846.5 eV, it is observed that the intensity of the spectra increases resonantly. And the peak energy exhibits linear dispersion as a function of incident photon energy. Moreover these line shapes are asymmetry. Therefore these phenomena are owing to X-ray resonant Raman scattering. Above the threshold these spectra are assigned as the normal \textit{K}\textsubscript{\alpha} emission. Figure 2 shows Si-\textit{KLL} RAES of SiO\textsubscript{2}. It is observed that L and L' peak energies exhibit linear dispersion with incident photon energy, while N and N' peaks show no dispersion. The N series are assigned as a normal Auger process. In the case of L series, the dispersion lines appears above and below the threshold show discontinuity at the \textit{K} absorption region. Therefore, two processes are considered as the origin of the spectra. Above the threshold, the L series are assigned as a spectator Auger process. While below the threshold, the L series can be assigned as the Auger process which analogous to the X-ray resonant Raman process.

References

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Fig. 1 Si-\textit{K}\textsubscript{\alpha} resonant emission spectra of SiO\textsubscript{2}

Fig. 2 Si-\textit{KLL} resonant Auger spectra of SiO\textsubscript{2}
OBSERVATIONS OF POST-COLLISION INTERACTION EFFECTS USING THRESHOLD PHOTOIONIZATION METHODS

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Introduction

Post-collision interaction (PCI) effects appear in an Auger decay following inner-shell photoionization of atoms. The PCI effect is caused by a sudden change of the Coulomb field that the faster Auger electron feels on overtaking the initially ejected slower photoelectron. The faster Auger electron gains energy in the sudden change and, as its counterpart, the slower photoelectron loses energy by the same amount. As a result of this energy exchange, the PCI energy distribution for the photo- and Auger electrons obtains a characteristic lineshape; the shape is asymmetric and broadened, and its maximum is shifted in energy. Most of the previous studies on the PCI effects have concerned the single-step of the Auger decay. Hayaishi et al. recently have found the PCI effects induced by Auger cascades following Ar K-shell photoionization. The multi-step of the Auger decays gives the fact that the peak shift increases gradually according to the times of the Auger decays, but the peak broadening is almost independent of the times. The aim of the present work is to observe the PCI effects induced by Xe L-shell photoionization, in which more steps than the Auger cascades of Ar K-shell photoionization participate.

Experimental

Measurements were carried out at the undulator beam line BL-2A equipped with a double-crystal monochromator. Multiply charged ions in coincidence with threshold electrons were measured using a time-of-flight mass spectrometer coupled with a threshold-electron energy analyzer.

Results and discussion

Figure shows yields of total ions, threshold electrons and multiply charged ions near the Xe L₃ ionization limit. The yield spectrum of total ions, taken without mass analysis, corresponds to the absorption spectrum. The spectrum exhibits the L₃ edge of Xe. The yield spectra of threshold electrons and multiply charged ions exhibit the PCI shapes superimposed on the L₃ continuum ionization. It can be seen in the PCI shapes of multiply charged ions that the peak shifts increase as the charges increase and the peak widths are nearly constant.

References

NEW STRUCTURES OBSERVED IN RESONANT PHOTOEMISSION FORM THE Ni 3s LEVEL OF NiCl₂

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Introduction

Resonant photoemission is useful for confirming the existence of weak lines far from a main line of some level. For example, the photoemission spectrum of nickel metal in resonance near the Ni 2p₃/₂ absorption edge shows structures up to 50 eV above a main line of the Ni 3s level. We have made a comparatively-high-resolution photoemission experiment on the Ni 3s level of NiCl₂ in a wide-binding-energy range. In this report, new structures are revealed in the Ni 3s photoemission and resonance aspects of component structures of the Ni 3s level are briefly presented.

Experimental

Measurements were carried out using undulator radiation at BL-2B. Overall resolution was 1.0 eV at a photon energy of 850 eV. Samples used were thin films deposited on Au substrates by in situ evaporation. The pressure during measurements was typically 1 x 10⁻⁷ Pa.

Results

Figure 1 shows typical direct- (hv = 842.3 eV) and resonant- (hv = 849.2 eV) photoemission spectra for binding energies ranging from -55 to ~200 eV. Spectra shown were normalized so that the intensity of the Cl 2p line was proportional to the value of the cross section obtained from Ref. 2. CIS spectra corresponding to the binding energies a to j in Fig. 1 as well as a T.Y. spectrum are also shown in Fig. 2. Main observations obtained from Figs. 1 and 2 are summarized as follows: (1) Nine structures labelled with small letters a to j are observed in the Ni 3s spectral area of the resonant photoemission of Fig. 1. The origins of the structures a to g have already assigned. The structures h and i may be due to the 3s³p³d⁰ final state, though the intensities of these structures are a little bit high comparing with the calculated Auger decay rate of the Ni 2pγ. (2) CIS spectra after backsubtraction (Fig. 2) are in qualitative agreement with the calculated results. For example, a CIS spectrum of a main line a is scarcely enhanced on resonance. A CIS spectrum of the same line without backsubtraction is similar to the T.Y. spectrum. It is important to subtract the contribution of the background to photoemission spectra to get intrinsic CIS spectra in the core-level lines.

References

Introduction
The alloys of the rare earths and nonmagnetic elements have been well investigated to understand the microscopic magnetic behaviour of the rare earths. In particular the thin films of the rare earths have been interested because the bulk magnetic properties of them are largely altered. Recent advances in molecular beam epitaxy have made it possible to control the thickness of the thin films in atomic scale. The multilayers of the rare earths intervened by non-magnetic medium are the interesting films to obtain the information about the interaction between the 4f electrons.

In this study we investigated about the indirect exchange coupling between 4f electrons in the Gd-Lu multilayers by using the resonant photoemission technique at the 3d threshold of Gd.

Experimental
Experiments were carried out at BL 2B. The Gd-Lu multilayers were obtained by MBE at our laboratory. The films were prepared on Si (111) substrates by evaporating alternately Gd and Lu from two electron beam sources. The base pressure in the MBE was 8x10^{-11} Torr. The rate of evaporation was about 0.3 Å/sec for both elements. XPS spectra were measured at room temperature.

Results and Discussion
Valence-band and 4f spectra are shown in Fig.1 at the excitation photon energy of the 3d edge of Gd in pure Gd film and the multilayer (Gd_{10}Lu_{20})_{30}, where 10 and 20 means the thickness of Gd and Lu in Å, and 30 shows the number of the bilayers repeated in the film. In pure Gd the 4f structure and the E_f edge were observed clearly in Fig.1(a). And the satellite structure was apparently detected above the 4f peak. On the other hand for the multilayer the satellite structure disappeared as shown in Fig.1(b).

The satellite structure appeared resonantly as excitation photon energy is tuned through the energy corresponding to the 3d-to-conduction-band transition. Whenever for the multilayer exciting at this energy, the resonated structure did not appear. The XPS indicate that the 4f electrons are placed in a different circumstance in the multilayer, in which the interaction between 4f electrons is reduced because of the intervening non-magnetic Lu metal.

Fig.1. Valence-band and 4f spectra at the excitation photon energy of the 3d edge of Gd, (a) in pure Gd film and (b) the multilayer (Gd_{10}Lu_{20})_{30}

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4) Also: Nissin Software corp. Shibaurai-1-1, Minato-ku
Angular distribution of the fragment ions after the inner-shell excitation of triatomic molecules VI. High-resolution O K-edge absorption spectra of N$_2$O

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We have measured angle-resolved ion-yield spectra of some K-shell excited molecules with linear structure by using the 10-m GIM monochromator of beamline 2B. In this report, we present the high-resolution O K-edge spectra of N$_2$O and discuss the dynamics of fragmentation following the O 1s $\rightarrow$ $\pi^*$ excitation of N$_2$O, which is affected by the Renner-Teller effect.

Fig. 1 shows the O K-shell high-resolution angle-resolved ion-yield spectra of N$_2$O. The I$_{0}$ and I$_{90}$ show the ion-yield at 0° and 90° direction to the electric vector of the incident light, respectively. The FWHM (full width at half maximum) of $\pi^*$ resonance peak is 1.00eV and no fine structure is found. It is expected that the lifetime broadening of N$_2$O with an O 1s hole is comparable to that of O$_2$(180meV). The photo energy resolution of the present experiment is about 100meV and the observed peak width of a single vibronic state is estimated to be about 200meV. Therefore, $\pi^*$ resonance peak involves several vibronic states.

When the N$_2$O molecule is bent, the $\pi^*$ orbitals lose the degeneracy and have two component out-of-plane $\pi^*$ and in-plane $\pi^*$. The O 1s out-of-plane $\pi^*$ excited state has a linear stable structure as well as the ground state. On the other hand, the O 1s in-plane $\pi^*$ excited state is strongly bent. According to the Franck-Condon principle, the bending mode is not excited in the transition to the out-of-plane $\pi^*$ state but is strongly excited in the in-plane $\pi^*$ state which is lower in energy than out-of-plane $\pi^*$ state. Therefore, unresolved vibronic states in the $\pi^*$ peak arise mainly from the bending motion in the in-plane state.

It is observed that the peak top of the $\pi^*$ transition in the I$_{0}$ spectrum has slightly lower energy (about 0.17eV) than that in the I$_{90}$. This is reasonable if the fragment ions observed in the I$_{0}$ spectrum arise mainly from the bending mode which has a large contribution at the lower energy side of the vertical transition in the linear structure.

If the molecular geometry is changed to the equilibrium structure in the $\pi^*$ excited state and the axial recoil fragmentation occur after the Auger decay, one expects that the ion-yield ratio I$_{0}$/I$_{90}$ is 91 %. In the present experimental result show that I$_{0}$/I$_{90}$ at $\pi^*$ peak is about 29 %. This indicates that the Auger decay may take place on the way of starting the bending motion.

As shown in Fig. 1, the Rydberg peaks observed in the I$_{90}$ spectrum and in the I$_{0}$ spectrum are completely different; that is, the $\pi$-type Rydberg transitions are only observed in the I$_{90}$ spectrum and the $\alpha$-type Rydberg only in the I$_{0}$ spectrum. This means the bending motion has no contribution to the Rydberg states. This is consistent with the fact that the geometries of the Rydberg states are nearly the same as the geometry of the ionized state with a linear structure and the Renner-Teller effect is negligibly weak even in degenerate $\pi$-type Rydberg states. Generally speaking, "symmetry-resolved" inner-shell spectroscopy is valid for Rydberg states of linear triatomic molecules as well as for the inner-shell excited diatomic molecules.

The np$\pi^*$ (n = 3, 4 and 5) and 3d$\pi$ Rydberg peaks are observed in the I$_{90}$ in addition to the $\pi^*$ peak. The 3p$\pi$ Rydberg peak seems to have at least three components with the energy spacing about 250meV. Since the vibrational spacings of the bending, N-O stretching, and N-N stretching modes in the ground state are 73.0, 159.3 and 275.8meV, respectively, the components are probably due to the N-N stretching vibration modes.

It is found that the peak intensities of nsa Rydberg series are anomalous; the 4sa Rydberg peak is more intense than the 3sa and 5sa. In addition, the nsa Rydberg series have very large widths; the FWHM of the 3sa and 4sa Rydberg peaks are 1.07eV and 1.24eV and much wider than that of the 3p$\pi$(0.58eV). These are interpreted as the N$_2$O molecule having a $\sigma^*$ orbital below the ionization threshold and the valence-Rydberg mixing occurs, especially near the 4sa Rydberg state.

![Fig. 1 O K-edge high-resolution angle-resolved ion-yield spectra of N$_2$O. The solid line shows the ion-yield at 90° to the electric vector of the incident light (I$_{90}$) and dotted line shows one at 0° (I$_{0}$).](image)
RESONANT X-RAY EMISSION SPECTRA OF La$_2$CuO$_4$ AND CuO

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Introduction

X-ray emission spectroscopy with the excitation of monochromatic x-rays is a powerful tool to investigate the electronic structures in the initial state of the matter. The 3d $\rightarrow$ 2p resonant x-ray emission spectra (RXES) under the selective excitation from the 2p core-level to the 3d level of the transition metal reflect the initial 3d state, because the initial and final states have the same electronic configuration.$^1$ We report the results of the Cu 3d $\rightarrow$ 2p$_{3/2}$ RXES of CuO and La$_2$CuO$_4$.

These substances are materials related to the cuprous high-$T_c$ superconductors. La$_2$CuO$_4$ has the apical oxygens on the so-called CuO$_2$ plane, while CuO has no apical oxygen.

Experimental Procedure

RXES measurements were carried out at the BL2B. X-rays from the storage ring were monochromatized with a 10-m grazing-incidence monochromator of a Rowland-mount type. Fluorescent x-rays from the samples were monochromatized by a 50-cm Johansson-type spectrometer equipped with a RAP crystal and detected by a gas-flow counter with a 90%-argon-10%-methane flow gas. Overall resolution including the first and second monochromators was estimated to be about 1.6 eV. The energy of the primary x-ray was estimated by the measurements of the total photoelectric yield spectra of each sample.

Single crystalline La$_2$CuO$_4$ and polycrystalline CuO are used for measurements.

Results and Discussion

Figure 1 shows the RXES of CuO and La$_2$CuO$_4$. The origin of the abscissa indicates the excitation photon-energy which coincides with the peak of the Cu $L_3$ x-ray absorption spectra ($L_3$-XAS) of each sample. The main peaks of the RXES of both samples coincide with each other and are observed at about 1.5 eV below the peak position of $L_3$-XAS even though no peak appears at 0 eV. This implies that localized excited states gather around 1.5 eV above the ground state ($b_{1g}$ symmetry).

The full width at half maximum (FWHM) in the RXES of CuO is about 2.1 eV, while that of La$_2$CuO$_4$ is about 2.5 eV. On the other hand, the FWHM in the 3d $\rightarrow$ 2p$_{3/2}$ XES of CuO and La$_2$CuO$_4$ under the excitation of a Cu 2p core electron to a high energy continuum are about 2.6 and 3.0 eV, respectively. According to the theoretical investigation by Tanaka and Kotani,$^1$ the hybridization between the d$^9$ and d$^{10}$V states is large in these materials and the width of the emission band is wider in La$_2$CuO$_4$ due to the existence of apical oxygens, where V denotes a hole in the valence band.

It is noticed that the satellite S is observed at about -5 eV in the spectrum of La$_2$CuO$_4$. This indicates that the hybridization between the d$^9$ and d$^{10}$V states is larger in La$_2$CuO$_4$ than in CuO and that the charge transfer excited state$^1$ locates at about 5 eV above the ground state in La$_2$CuO$_4$. These results are consistent with the theoretical prediction.

Reference

Studies of angular correlation between fragment ions from inner-shell excited molecules I.

Angle-resolved photoion-photoion coincidence measurement
for the center N 1s → π* excitation of N₂O

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We carried out angle-resolved photoion-photoion coincidence measurement (ARPIPCO) without extraction field for N K-shell excited N₂O molecules to reveal the correlation with the ejection angles of fragment ions. It is found from these results that the three-body fragmentation process occurs.

A spherical sector analyzer was equipped at perpendicular direction to the electric vector of the incident light and was used to analyze the kinetic energies (KE₂) of the fragment ions. Another ion-detector can be rotatable in the perpendicular plane to the incident light direction. To obtain coincidence signals between the fragment ions, signals from the spherical sector analyzer were used to start a time-to-amplitude converter, and signals from the ion-detector were used to stop the converter. The ARPIPCO spectra were recorded in the conditions that the angle between the axes of the detectors were 180° to 120° at interval of 10°.

Fig. 1 shows the ARPIPCO spectra following the center nitrogen (N₂) 1s → π* excitation of the N₂O. The structure in the spectra can involve some coincidence signals which are due to different fragmentation patterns. The time-of-flight (TOF) of the fragment ions was calculated to assign the ARPIPCO spectra. We divide the coincidence signals into the 4 groups as shown in Table 1. The TOF's of N₀ and O⁺ and those of NO⁻ and N₂⁺ cannot be differentiated in the present measurement because of the similarity of their masses.

Fig 2 shows the polar plots of the ARPIPCO for the N₂ 1s → π* excitation of N₂O when the KE₂ is 5 eV. The count rate of ARPIPCO signals for peak A rapidly decreases as the correlation angle become small. This is because the peak A is mainly attributed to the two-body fragmentation. On the other hand, the ARPIPCO signals for the peak B are observed when the correlation angle is below 150°. This indicates that the peak B is attributed to three-body fragmentation. The result shows that peak C is affected by two- and three-body fragmentation. Thus, the origins of the ARPIPCO peaks are elucidated by examining the TOF's of fragment ions and the correlation with their ejection angles.

![Fig 1](image1.png)

![Fig 2](image2.png)

Table 1. Assignments of the ARPIPCO spectra for the N₂ 1s → π* excited state of N₂O

<table>
<thead>
<tr>
<th>peak</th>
<th>start signal</th>
<th>stop signal</th>
<th>fragmentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>molecular ion (NO⁻ or N₂⁺)</td>
<td>atomic ion (N⁺ or O⁺)</td>
<td>2 body fragmentation</td>
</tr>
<tr>
<td>B</td>
<td>atomic ion (N⁺ or O⁺)</td>
<td>atomic ion (KE₂ &lt; ca.4 eV)</td>
<td>3 body fragmentation</td>
</tr>
<tr>
<td>C</td>
<td>atomic ion (N⁺ or O⁺)</td>
<td>atomic ion (KE₂ &gt; ca.5 eV)</td>
<td>3 body fragmentation</td>
</tr>
<tr>
<td>C</td>
<td>atomic ion (N⁺ or O⁺)</td>
<td>molecular ion (NO⁻ or N₂⁺)</td>
<td>2 body fragmentation</td>
</tr>
</tbody>
</table>
Studies of angular correlation between fragment ions from inner-shell excited molecules II.

Three-body dissociation of the N K-shell excited and ionized N₂O

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We measured angle-resolved photoion-photoion coincidence (ARPIPICO) spectra of N K-shell excited and ionized N₂O. Following the report I, we present the correlation with the ejected angle of the fragment ions emitted from the K-shell excited and ionized N₂O.

The two-body fragmentation for triatomic molecules leads the correlation angle of the fragment ions 180°, whether the molecular structure is linear or bent. When the three-body fragmentation for triatomic molecules occurs, the correlation angle is not always 180°. The three-body fragmentation for the linear structure leads the correlation angle 180°; on the other hand, that for the bent structure can be influenced by bond angle of molecules.

Fig 1. shows the ARPIPICO spectrum for N₂O excited and ionized N₂O. The spectrum was measured in the condition that the angle between the axes of the detectors is 180° and the kinetic energy (KEun) of fragment ions detected as the start signal is 10 eV. Peak A can be assigned to the three-body dissociation. The intensity of Peak A is measured as a function of the correlation angle to reveal the molecular bond angle at the dissociation.

The equilibrium geometry of the N 1s ionized state is linear. On the other hand, the stable structures of two N 1s in-plane π* excited states are bent because of the Renner-Teller effect. Our calculated result shows the equilibrium bond angles for terminal nitrogen (Nₘ) and center one (Nₖ) 1s in-plane π* excited states are 136° and 114°, respectively. Therefore, it is expected that the ARPIPICO signal for Nₘ 1s → π* excitation is much strongly observed at smaller correlation angle than that for Nₘ 1s → π* excitation, and that for the N 1s ionized state the ARPIPICO signal rapidly decreases as the correlation angle becomes small.

Fig 2. shows the polar plot of the intensity of the peak A for the three excitation energies. The ARPIPICO signal for the N₁ 1s → π* excitation is spread out at the smaller correlation angle than that for N₁ 1s → π* excitation. This is qualitatively consistent with the calculated bond angle. The present results show that the ARPIPICO signal for N 1s ionized state is much more weakly influenced by the bent structure than that for N 1s → π* excited state. Although the stable structure of the N 1s ionized state is linear, the ARPIPICO signal from three-body fragmentation following N 1s ionization is affected by the bending motion.
INTRODUCTION

The light transition metal compound YTiO$_3$ has a formal d-electron number of one (3d$^1$) and its physical properties show that this compound is a Mott-Hubbard insulator because of strong correlation [1]. A Mott-Hubbard insulator usually becomes a strongly correlated metal by carrier doping. The investigation of the electronic structure of these compounds is very important to reveal the physical property related with electron correlation. In this work, we have studied the unoccupied electronic structure of the hole doped system Y$_{1-x}$Ca$_x$TiO$_3$ using oxygen K-edge X-ray absorption spectroscopy. The hole doping by substitution of Ca for Y causes an insulator-to-metal transition at about $x=0.4$.

EXPERIMENT

The experiment of X-ray absorption spectroscopy was carried out at beam line BL-2B using a 10m grazing incidence monochromator. The total-electron-yield method was used to record the spectra. The probing depth of the total-electron-yield method is about 40 Å or below [2], so that surface contamination of samples was removed by scraping with a diamond file. The pressure was about $2.0 \times 10^{-9}$ Torr during the measurement and scraping. The measurement and scraping were performed at room temperature.

RESULT AND DISCUSSION

Figure 1 shows spectra of oxygen K-edge X-ray absorption. The spectra have been normalized at a high photon energy of 550eV. These spectra reflect the oxygen 2p partial density of the unoccupied states including oxygen 1s core hole effect. However, the core-hole effect is not serious because the unoccupied density of states is consists mainly of cation site, so that the oxygen 2p contribution is relatively small [3]. The peaks at lower photon energy side of about 531eV indicate the Ti 3d t$_{2g}$ band and at about 544eV Ti 4sp band. The structures between 533eV and 540eV are probably admixture of Ti3d, Y4d and Ca3d bands. The peak intensity of the Ti t$_{2g}$ band increases as a function of hole doping and this phenomenon indicates the creation of in-gap states with hole doping. We can see a clear difference between $x=0.2$ and $x=0.4$ in the Ti t$_{2g}$ peak. The $x=0.2$ is a insulator and $x=0.4$ metal. A similar spectral change related to a metal-insulator transition is seen in the spectra of Li$_x$Zn$_{1-x}$V$_2$O$_4$ and Y$_{1-x}$Ca$_x$VO$_3$ [2][4].

REFERENCE

RESONANT M EMISSION SPECTRA IN Yb$_2$O$_3$


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Introduction

Using monochromatized soft X-ray with variable photon energy tuned near Yb M absorption edge, Yb M emission spectra of Yb$_2$O$_3$ were measured. In Yb compounds, there is a vacancy in the 4f orbital. This vacancy induces a strong self-absorption due to a dipole transition in a sample. The 4f orbital is localized, therefore, it is expected that the resonant emission line which caused by direct recombination of 4f $\rightarrow$ 3d is observed at the absorption peak energy.

Experimental

The experiments were performed with a 10m grazing incidence monochromator at undulator beam line BL-2B of Photon Factory. The sample was powder form and rubbed on to Cu plate. A curved crystal monochromator was used for energy analysis of the scattered radiation from Yb$_2$O$_3$, and a wire proportional counter was used as a detector.

Results and Discussion

Figure 1 shows the Yb M $\nu$ absorption spectra measured by means of total electron yield method. Figure 2 shows the X-ray emission spectra with incident photon energies in the vicinity of the Yb M $\nu$ absorption edge showed in Fig. 1. Dotted line shows the peak energy of M $\nu$ absorption spectrum. The intensity of these emission spectra increases resonantly, as the incident energy approaches an absorption peak energy; and below the absorption edge, the line shapes are asymmetry. These features observed in Fig. 2 are identified as same process as the resonant Raman process in Si K $\alpha$ emission spectra. Above the threshold, the intense peak is assigned as the normal M $\alpha$ emission. The resonant emission line is observed at 1521eV. However, spectrum is distorted by self-absorption effect.
BOND-SPECIFIC ION DESORPTION FROM DCOO/Si(100) BY C 1s CORE EXCITATION

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Introduction

An unresolved question is whether the state-selective core-electron excitation to a particular antibonding orbital along a unique bond within an adsorbed polyatomic molecule promotes the selective dissociation of the bond concerned.

In this work, photon-stimulated ion desorption (PSID) from formic acid chemisorbed on Si(100) has been studied by state-selective C 1s excitation. This system is considered to a suitable system for bond-selective ion desorption, because electronic excitations to each unoccupied orbital are identified with a unique bond in the adsorbed formic acid near-edge X-ray absorption fine structure (NEXAFS).

Experimental

The experiments were performed at the soft X-ray undulator beam line 2B with optical resolution of ~0.25 eV at 287 eV. The experimental details have been described elsewhere. Briefly, ions were detected and analyzed by a time-of-flight (TOF) mass spectrometer using a pulsed synchrotron radiation. As a sample preparation, a ~10L DCOOD was exposed to a clean Si(100) crystal at room temperature. Under these conditions, DCOOD dissociates with the adsorption of D* and DCOO* on Si(100)(2x1).

Results and discussion

The PSID yield curves of D+, CDO+, O+ and CD+ ions from the DCOO/Si(100) in the C 1s excitation region are shown in Fig. 1 together with Auger electron yield (AEY) curve which represents the photo-absorption cross section of adsorbed formate. The resonances observed in the AEY curve were assigned to transitions from C 1s into π*(C=O) at 288.6 eV, σ*(C-D) at 292 eV, σ*(C-O) at 297.5 eV and σ*(C=O) at 303 eV on the basis of the results on adsorbed formic acid NEXAFS. Each PSID yield shows a significant deviation from the AEY. This indicates that the PSID strongly depends on the primary excitations of the adsorbed formate. The relative abundances of desorbing ions, however, do not significantly change due to the mass effect of the leaving particles. The PSID yields of D+ and CDO+ are enhanced at the σ*(C-D) and σ*(C-O) resonances, respectively. Although the O+ yields are suffering from the effects of second order light around the π*(C=O) and σ*(C-D) resonances, an increase of the O+ yield is observed at the σ*(C=O) resonance. This finding indicates that bond-selective desorption occurs in each ion yield.

It is clearly seen that the CD+ yield is enhanced at the π*(C=O) resonance, while the CDO+ yield is suppressed. This can be explained by assuming that the CD+ ions would be produced through decay of the intermediate, core-excited D*-O-Si fragment adsorbed species, resulting from a fast neutral dissociation of an oxygen atom (from C=O). This explanation is analogous to the photodissociation of gas-phase H2S.

Fig. 1. AEY and PSID yields of D+, CDO+, O+ and CD+ from the DCOO/Si(100) as a function of excitation energy near the C K-edge.

References

RAPID PROJECTION OF CRYSTAL GRAIN ORIENTATION DISTRIBUTION IN MILD STEEL SHEETS BY SYNCHROTRON X-RAY DIFFRACTION

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Introduction
For the improvement of the formability of steel sheets, researches on the mechanism of primary recrystallization are indispensable. An investigation on primary recrystallization process of mild steel sheets was carried out by using the method developed by the present authors for rapid projection of the crystal grain orientation distribution, the pole figure, in polycrystalline materials¹).

Experimental
Measurements were made at the beamline BL-3A at the Photon Factory. Monochromatic X-radiation, 0.06 nm in wavelength, was used. It took only 100 s to record one pattern over an angle range of 50 deg. in longitude of the surface of the sphere of poles. This measurement time is one thousandth shorter than that required by conventional point-by-point pole figure measurement method²).

Results and Discussion
Fig. 1 shows the orientation distribution pattern of the [200] poles of the mild steel sheets at different steps of annealing. As the primary recrystallization proceeds, successive growing of crystal grains is reflected in the increase in the size of diffraction spots. At the end of the primary recrystallization process, the pole density becomes high at (111)<uvw> region. Magnified images were observed in the (111)<112> region indicated by an arrow in Fig. 1 (b). In a four times magnified image after 973 K annealing (Fig. 2 (a)), diffraction spots from recrystallized grains cannot be observed yet. On the other hand, in Fig. 2 (b), after 983 K annealing, a number of dark spots are seen. This shows that small primary recrystallization nuclei have become larger grains in the (111)<112> orientation area.

It can be understood that this method of rapid projection of crystal grain orientation distribution is useful for examining primary recrystallization process. Change in the number of recrystallized grains may be studied easily for various orientations.

References
A NEW "SPHERICAL-TYPE" GONIOMETER SYSTEM AT BL3A

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INTRODUCTION
The beamline BL3A where a high flux and focused beam is available by a unique x-ray optics has been widely used for various experimental purposes1). The data acquisition system based on the triple-axis/four-circle diffractometer, SIN-1 has been developed and installed.1) It has become evident, however, that a new goniometer that can mount and scan detectors toward more general directions of spherical angles is necessary to perform more easily several experiments such as fluorescence XAFS2), and various types of IP measurements3). In order to satisfy such demands, a new data acquisition system based on a "spherical-type" goniometer has been developed and installed on BL3A.

A NEW GONIOMETER SYSTEM
Some "spherical-type" goniometer systems have been developed at several SR facilities for topography measurements (HASYLAB3) & PF-BL15B4)) and for grazing incidence x-ray diffraction (GIXD) measurements (PF-BL17C5). The new spherical-type goniometer system at BL3A consists of a tandem combination of a linear stage, \( q \), and two circle goniometers, \( \kappa \) and \( \xi \) (Figure). Each axis (\( \eta, \kappa, \xi \)) corresponds to polar coordinates (\( p, \theta, \varphi \)), respectively, the origin of which coincides with the four-circle center. Since the new goniometer must "cohabit" with the original diffractometer system, a new mechanism to mount and operate a \( \kappa \)-arc on the \( \xi \)-circle was adopted. In this mechanism the \( \kappa \)-arc slides through the gear box mounted on the stage of the \( \xi \)-circle by a stepper motor rather than being fixed on the stage. Such mechanism commonly used in a \( \chi \)-circle (Euler Cradle) of four-circle goniometers was used for spherical-type goniometer systems for the first time. This mechanism enables to design the system compactly, and a detector mounted on the \( \eta \)-stage can be moved over a wide spherical angle without interference with the original goniometer. The system has been used for data acquisition with IPs or a multi-element SSD for XAFS measurements6), 8.

Figure A schematic drawing of the new "spherical-type" goniometer system. The original four circle goniometer: 1. \( \theta \), 2. \( \theta \), 3. \( \chi \), and 4. \( \varphi \). The new goniometer: 5. \( \eta \), 6. \( \kappa \), 7. \( \xi \), 8. a detector, 9 a gear box.

REFERENCES
**Introduction**

In many materials, very low amounts of elements and defects play important roles. The concentration of them usually exist at concentrations lower than atomic percent. Fluorescence X-ray absorption fine structure (F-XAFS) experiment under total reflection condition is a powerful tool for studying such defects and trace elements.

For the target of atomic percent order experiments, the authors constructed a fluorescence XAFS acquisition system by using a single solid state detector (SSD) at BL3A. With a view to observations of part per million order (ppm) elements, an additional system was constructed using a multi-elements-SSD.

**Beam Optics and Goniometer**

The total reflection F-XAFS measurement system takes advantage of high brilliance X-ray beam and a large vertical diffractometer of BL3A. It is able to focus X-ray beam onto few millimeter width range on a sample without reduction of beam intensity under total reflection condition.

BL3A has two large Pt mirrors and a double crystal monochromator. In the total reflection F-XAFS system, the collimated SR beam from the first mirror is focused horizontally by bending in the monochromator. Double small plane Pt mirrors are installed in the diffractometer, for cutting off high order harmonics.

Additional goniometers for mounting a SSD are installed in the diffractometer. They aim the SSD at the center of the diffractometer toward the sample position.

**Detector System**

A multi-elements-SSD (Canberra model GL/S) is used for the high sensitivity experiments. Figure 1 shows a block diagram of the detector system. The SSD has seven Ge detector and preamplifier pairs. The size of each Ge detector is 500mm. The thickness of the Be window of the multi-SSD is 0.5mm. Each output from the preamplifiers is connected to a shaping amplifier (Canberra 2025) and 200ns fast ADC (Canberra 8715). Two MCAs (Fast Com Tech, MCD/PC4) including a four channel router count each pulse from the ADCs. A controller (IBM-PC compatible personal computer) drives the MCAs, the monochromator, and a four channel scaler (EG&G, 974). The scaler monitors incident beam, total reflected beam, and ring current. The control software was written in C++ as a Microsoft Windows 3.1 application.

**Performance**

The CuKα peak width is lower than 200eV at integral peak intensity 10kCPS for all of the detectors. The sensitivity was checked using the fluorescence CuKα observed from Cu atoms gettered into a poly-Si thin layer. The intensities were found to agree with the concentrations from secondary ion mass spectrometer below ppm. The EXAFS oscillation was also measured for ppm order Cu atoms decorated on a Si wafer. The system will be able to observe EXAFS oscillations for very low amounts of defects and trace elements.

**References**


![Figure 1. A block diagram of the detector system](image-url)
OBSERVATION OF VOLUME CHANGE BEHAVIOR OF DNA GEL BY ULTRASMALL ANGLE X-RAY SCATTERING

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Introduction

Several polymer gels are known to undergo discontinuous volume change by the change of temperature, solvent composition, pH, ionic composition, pressure, and electric field. These phenomena can be interpreted as a phase transition in the system consisting of crosslinked polymer network and solvent. We were greatly interested in changing behavior of the structure of network during this volume phase transition. We observed a volume change process of DNA gel in acetone-water mixture by Bonse-Hart ultra-small-angle X-ray scattering (USAXS) instrument equipped in BL-3A, which is the most powerful technique to get information about the network structure of gel.

Experimental

In the DNA gels we used this time, the discontinuous volume transition occurs about 63% at 25°C, and the volume changes by 33 times. DNA gel takes collapse state at higher acetone concentration, and swollen state at lower acetone concentration.

Cylindrical shaped sample(1.28mm diameter 10mm long in swollen state) was inserted into quartz capillary(2mm diameter) in which solvent of proper concentration was filled. Then capillary was sealed by tape and set in vertical direction into a sample holder.

We measured a collapsing and swelling processes of DNA gel by USAXS. The wavelength used was fixed to 0.126nm. In case of a measurement in collapsing process, swollen sample was prepared by pure water and inserted into capillary in which acetone-water mixture of 70% was filled. On the other hand, in case of swelling process, collapsed sample was prepared by acetone-water mixture of 70% and inserted into capillary in which acetone-water mixture of 60% was filled.

In addition, we measured USAXS profiles for pure water, solvent of acetone-water mixture(75% acetone concentration), gel of swollen state in pure water, gel of collapsing state in acetone-water mixture of other concentrations.

The condition of the measurement was 0.002°-0.05° for scanning angle, 0.002° or 0.001° for step angle, and 5 or 10s/pt for integrated time.

Results and Discussion

The typical USAXS profiles are shown Figure 1. As the figure indicates, the curve of collapse sample is different from those other curves. From this fact, it is confirmed that the USAXS measurement can be one of the methods to clarify the network structure change on the transition. However, we didn't have enough time to get the data on the kinetics of the transition, and did not have enough data to determine the size of scatterers.

In a collapsing process measurements, we must be careful for a sample not to get out of a X-ray beam. So it is important to set the sample capillary in vertical direction to avoid the total reflection of X-rays. However, as the sample moves downward on the swollen-collapsing process of the transition, it is difficult to keep the volume exposed to the X-rays in constant. The farther improvement is desired for the sample setting device.

It might be done in near future to get the data on the kinetics of the transition and to analyze those data not only from the conventional view point, such as Guinier Plot, but also fractal growth theory.

Acknowledgments

This work was partly supported by the Grant-in-Aid from the Ministry of Education, Science and Culture, and also by Japanese Private School Promotion Foundation.

References


Figure 1. USAXS curves of the I(q) versus q plot for water, 75% acetone, collapse sample and swollen sample.
Introduction

Tunable synchrotron X-ray radiation has made it possible to perform various diffraction studies in relation to the use of anomalous scattering near absorption edges. The effect can distinguish two or more elements with very similar atomic numbers. It has been recognized that a chemical shift of XANES spectra occurs among different valence states and is related to anomalous scattering. Theoretical calculations which do not include pre- and near-edge effects cannot predict the chemical shift. Thus, the anomalous scattering experiments on valence states require an accurate knowledge of atomic scattering factor at wavelengths close to an absorption edge.

XANES absorption spectra

XANES absorption spectra at the Fe K edge of iron oxides were measured using a double-crystal Si(111) monochromator at the BL-3A. Powder samples mounted between polypropylene films were set between two ionization chambers filled by N2 gas. A chemical shift of about 5 eV was observed between ferrous and ferric ions in the spectra of FeO and Fe2O3 where the Fe ions coordinate in regular octahedra (Fig. 1). The spectrum of magnetite is between FeO and Fe2O3 spectra and about 2 eV higher than the FeO spectrum. An iron foil was used to calibrate the energy of the absorption edge.

Estimation of $f'$

It is well known that $f'$ can be transformed from imaginary part $f''$ by the Kramers-Kronig integral. Because the absorption measurement was made only in narrow region at the edge, the Cromer and Liberman's calculation was applied to estimate experimental $f'$ by substituting the observed cross-section data. The results are illustrated for anomalous scattering factors of Fe2+ and Fe3+ in octahedral environment (Fig. 2). The maximum difference in experimental $f'$ between ferrous and ferric ions are about 2.5 at the longer wavelength side near the Fe2+ edge.

Mixed-valence compounds

Selecting a wavelength to give the different $f'$ values, the technique promises the possibility of distinguishing ions of the same elements in a mixed valence crystal. Magnetite is an example to show electronic ordering below $T_v$. X-ray intensity data for a single crystal were collected using a four-circle diffractometer at BL-10A. Site-occupancy treatments were taken into account for such ions in structural analyses. The experimental $f'$ values are independent from the refinement procedure and can be estimated in advance. The structure calculation using $f'$ possibly gives a model in an ionic state and extracts well the distribution of valence electrons. The introduction of $f'$ into the difference-Fourier method gives valence-difference contrast for the same atomic species in a mixed valence crystal. The mapping should represent a schematic distribution of ions. A two-wavelengths technique would be useful for practical experiments.
THE MEM CHARGE DENSITY DISTRIBUTION OF Cs₃CoCl₅ BASED ON HIGH RESOLUTION SR POWDER DATA.

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Introduction

Since Sakata et al. showed that the powder diffraction data is suitable to be analyzed by the Maximum Entropy Method (MEM)11, we have been making a great effort to measure a precise powder data at the Photon Factory. We have developed the two ways of the Synchrotron Radiation (SR) high resolution powder diffractionmetry. One is the camera method using Imaging Plate (IP) as a detector at BL-6 and 18 and the other is the parallel beam reflection geometry using the long fine solar collimator at BL-33. These powder diffractions remarkably improve the angular resolution and counting statistics. Consequently, we can get accurate electron densities by the MEM even for a substance having a complicated crystal structure.

The Cs₃CoCl₅ salt has been studied to investigate the spin density in CoCl₂⁻ ion by polarized neutron diffraction (PND) experiment4). Recently, we have applied the MEM to the same PND data and visualized the three dimensional electron spin density in real space3). In order to study the bonding nature of the Cs₃CoCl₅, SR powder diffraction experiment on BL-3A using the solar collimators is carried out. The unit cell size (a=9.063Å, c=14.450Å) and symmetry (14/mcm) of this substance is suitable to perform a good quality experiment.

In this report, we present a MEM electron density of Cs₃CoCl₅ and its examination in terms of bonding nature in CoCl₂⁻ ion.

The whole powder pattern of the Cs₃CoCl₅ is shown in Fig.1. The wavelength of incident X-ray is 1.54 Å and the solar collimator having the full aperture of 0.072° is used. The collection time at each step of 2θ is 4.0 sec. After all, 113 Bragg integrated intensities (sinθ/λ<0.55Å⁻¹) are obtained.

The MEM Charge Density of Cs₃CoCl₅

The MEM density was calculated with the electron density distribution map obtained by the MEM, which is the electron density distribution map obtained by the MEM. This MEM density is used for lower density region of (110) plane in Fig.2. The MEM electron density distribution clearly shows the coordinate bonding feature between Co and Cl atoms. In Fig.3(a), the asymmetric part of the spin densities with respect to Co site is extracted from the MEM spin density based on the PND data.

The positive and negative densities are indicated by solid and dotted contour lines, respectively. The positive regions indicate the higher spin density region and vice versa. The main effects of Cl ligand fields are appeared to be the anisotropy of Co spin densities. Fig.3(a) shows the strong anisotropy of the spin densities around Co sites along the direction of Co-Cl bonds. The spin densities at the Co site are attracted toward the Cl-ions in association with the coordinate bond. In Fig.3(b), it is found that the charge density around the Co site shows the anisotropy of Co electrons which resembles to the spin density. It suggests that the covalency of Co-Cl bond causes the anisotropy of Co spin density in Cs₃CoCl₅.

We wish to thank Dr. B.N.Figgis for supplying the sample and for his interest and useful discussion.

References

TRANSVERSE COHERENCE OF SYNCHROTRON RADIATION FROM A NORMAL BENDING MAGNET SOURCE

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Introduction

Recently, speckle patterns in x-ray wave length region, that is diffraction of coherent x-rays by random media, have been observed in synchrotron radiation from a wiggler source[1] and from a normal bending magnet source[2] at NSLS, and also from an undulator source at ESRF[3]. X-ray speckle patterns would have a potential to give information about time fluctuation in matter on an atomic scale. Density-density correlations in long range, up to the coherent length of x-rays, could also be explored with atomic resolution in space.

In order to observe x-ray speckle patterns, coherent properties of x-rays have to be characterized in advance. Only a small part of synchrotron radiation from a normal bending magnet source is expected to be coherent. This report describes a measurement of coherence of the synchrotron radiation performed as a trial to observe an x-ray speckle pattern.

Experimental

Visibility of Fraunhofer diffraction patterns from a slit was used to measure transverse coherent length of the synchrotron radiation of BL-3A station[4]. Experiments were performed with a set-up as follows. X-rays of 1.39 Å were selected by a Si (111) double-crystal monochromator placed at 20 m downstream from the source. Vertical angular divergence and the third order harmonics component of the synchrotron radiation were suppressed by using a vertically collimating mirror, placed 16.2 m, of Pt-coated fused quartz plates. In order to obtain x-rays with coherent length of several μm at a collimating slit in the station located 28 m from the source, the source size had to be reduced below the value of 0.12 mm by using an upstream slit, located 15 m from the source, in front of the mirror. The Fraunhofer diffraction pattern by the collimating slit was recorded on a nuclear photo-plate (Ilford L4, 50 μm) set 0.83 m behind the collimating slit.

Results and Discussion

Achieved vertical angular divergence was estimated to be about 0.03 rad. An obtained diffraction pattern with an exposure time of 100 seconds is shown in Fig. 1. Higher order diffraction up to the 7-th can be observed. Clear visibility of the Fraunhofer diffraction shows that the transverse coherent length was larger than the collimating slit width, 6 μm, determined from intervals between the fringes in the diffraction pattern.

References


Fig. 1. An observed Fraunhofer diffraction pattern by a slit of 6 μm width.
TETRAGONAL-CUBIC PHASE CHANGE IN ZIRCONIA SOLID SOLUTIONS

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Introduction

Zirconia ceramics are attractive materials as structural ceramics with high toughness, fuel cells, oxygen sensors and refractories. These properties are strongly dependent on the crystal structures. Thus, the phase changes in the zirconia solid solutions have been extensively investigated, however there are various discrepancies and controversies in the literature. The metastable tetragonal (t'-form: \( P4_2/nmc \))-cubic (c, \( Fm\bar{3}m \)) phase transition is one of the most important keys to solve this problem. We have investigated the tetragonal-cubic phase change induced by the doping of oxides as \( \text{CeO}_2 \) and \( \text{Y}_2\text{O}_3 \) and proposed that a tetragonal form (t"-form) with an axial ratio of unity (c/a = 1) exists between the t' and c-forms. However, it is difficult to conclude that the c/a ratio of the t"-form is unity due to relatively bad resolution of the conventional tube-generated X-ray diffraction data. In the present work, high-resolution powder diffraction measurements were performed using synchrotron radiation to obtain more precise c/a ratio.

Experimental and Data Analysis

The \( \text{ZrO}_2-X\text{mol}\%\text{CeO}_2 \) samples were prepared by sintering the mixtures of \( \text{ZrO}_2 \) and \( \text{CeO}_2 \) powders at 1650°C for 5h in air (X=50, 60, 65, 70). Intensity data were collected using the synchrotron radiation (\( \lambda = 1.38 \) Å) and the triple-axis/four-circle diffractometer as a powder diffractometer at the beam line BL-3A of Photon Factory, KEK, Tsukuba. The scanning conditions were: 20 range = 61° to 64°, \( \Delta 20 = 0.01° \), fixed time = 10 s or 20 s. The diffraction profile was fitted by one, two or three reflection peaks assuming the Pearson VII type function.

Results and Discussion

The 400\( \gamma \) reflection peak splitted into 004 and 220 ones of the tetragonal phase for the composition of X=50, but showed no splitting for X=65 and 70 (Fig. 1). The precision of the c/a ratio for X=65 and 70 were estimated to be \( \pm 0.001 \) and \( \pm 0.0009 \) from the full width of half maximum of the 400\( \gamma \) peak. On the other hand, the neutron diffraction measurements clearly indicated 112\( \gamma \) reflection peak for all samples studied in the present work. The sample of X=60 is interpreted to be a mixture of the t' and t"-forms, where the t' form is defined a tetragonal phase with a c/a ratio larger than unity. These results strongly suggest the existence of the t"-form in this system. Further study for other systems and single-crystal experiments are necessary to establish this feature.

Fig. 1 Observed (+) and calculated (solid line) powder diffraction profiles of \( \text{ZrO}_2-X\text{mol}\%\text{CeO}_2 \).

References

Photoionization of Xe+ ion in the 4d shell excitation region

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Introduction
A merging-beam apparatus was developed for studies on photoionization of ions\(^1\). Recently, the results for Ba\(^+\) and Sr\(^+\) have been reported\(^2\). Here, we report the first measurement of photoionization of Xe\(^+\) in 4d ionization region. Yields of photoion with a specific charge state were determined as a function of photon energy.

Experiment
The experiment of photoionization was made by using monochromatized synchrotron radiation from a 24m spherical grating monochrometer in the BL-3B beam line. The apparatus is the same as described in Refs. 1 and 2 except for the ion source. Xe ions extracted with 2kV from an electron-impact ion source were mass analyzed with a Wien filter and deflected 90° by an electrostatic quadrupole deflector to merge into the photon beam. Then they were transported to the interaction region, whose length was 15cm, through a pair of 2mmφ orifice used to collimate the ion- and photon-beam. An electrostatic parallel plate analyzer was used as a charge state analyzer. The primary Xe\(^+\) ions were collected in a Faraday cup whilst product ions (Xe\(^{2+}\) and Xe\(^{3+}\)) were detected by two secondary electron multipliers. The background pressure was about 3x10^-10 Torr in the analyzer chamber and the typical Xe\(^+\) ion current was about 80nA.

Results
Figures 1 and 2 show measured relative photoion-yields for Xe\(^{2+}\) and Xe\(^{3+}\) as a function of photon energy. The energy resolution (\(E/\Delta E\)) for Figs. 1 and 2 are about 70 and 160, respectively. The yield spectra for Xe\(^{3+}\) reveal a giant resonance structure due to 4d\(\rightarrow\)cf transition around 100 eV. As seen in Figs. 1 and 2, some peaks are observed near 71eV. These peaks may be explained by the resonance Auger process. The excited states of Xe\(^+\) produced by 4d\(\rightarrow\)mp photoabsorption decay to Xe\(^{2+}\) and Xe\(^{3+}\). The spectra for Xe\(^{3+}\) show some structures between 75 and 87 eV and between 87 and 93eV. No such structure was observed in the photo-ion spectra for neutral Xe\(^{3}\). The origin of these structures is not clear at present. Hayaishi \(et\) al.\(^4\) observed some shake-up states just above the 4d threshold in their threshold electron spectrum for Xe. The shake-up processes may be enhanced for Xe\(^+\) case.

References

![Fig.1. Partial ion-yield spectra for Xe\(^+\) with E/\Delta E=70.](image1)

![Fig.2. Partial ion-yield spectra for Xe\(^+\) with E/\Delta E=160.](image2)

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PHOTOION SPECTROSCOPY STUDY OF Er ATOM IN THE 4d IONIZATION REGION

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The 4d giant resonances in the photoionization of rare-earth atoms are the subject of many theoretical and experimental studies. Experimental studies performed up to date have leaned toward lighter rare-earth atoms (La, Ce, Nd, Sm, Eu, Gd, Dy), and studies on heavier ones such as Ho, Er, Tm, Yb are rather few. The main reason is that radiation appropriate to these atoms (150~200 eV) has not been available with sufficient intensities. Recent developments in the synchrotron radiation technology have made possible detailed studies on these heavier rare-earth atoms.

The experiment was done at beamline BL-3B where a 24-m spherical grating monochromator provides monochromatized radiation in the 10~300 eV region. A time-of-flight mass spectrometer combined with an electron bombardment oven was used.\(^{13}\) The mass spectra obtained showed singly- to quadruply-charged ions in the resonance region. By gating each of Er\(^{n+}\) ion peaks and recording their intensities with changing the photon energy, we obtained relative partial photoion-yield cross sections, as shown in Figure 1. The accuracy in the relative intensities among the different charges is within 5 %.

The ground state of Er atom is \([\text{Kr}]\text{4d}^{10}\text{5s}^2\text{5p}^6\text{4f}^{12}\text{6s}^2\text{6p}_6\). The 4d photoionization spectrum of Er atom is dominated by the three peaks. These peaks have been assigned as \(^3\text{H}_6\text{(163.7 eV)}, \text{3H}_5\text{(166.3eV)}\text{ and }^{3}\text{G}_5\text{(169.7eV)}\) states of \(4d^24f^{13}\) configuration by Baier et al.\(^2\) The relative variation of each of Er\(^{n+}\) curves is very similar to that obtained by Baier et al., but the relative intensities among the different charges are markedly different. For example, the populations of Er\(^{+}\), Er\(^{2+}\) and Er\(^{3+}\) ions in their spectrum are 64%, 20% and 16%, respectively at the third \(^3\text{G}_5\) peak. These are appreciably different from those in the present result (57%, 29% and 13%, respectively). In addition, the present result shows apparently formation of Er\(^{4+}\) ions (1%). The former discrepancy in the population comes mostly from the difference in the detection efficiencies for ions with different charges.

As in the cases of other rare-earth atoms, the cross section curve for Er\(^{+}\) exhibits typical Beutler-Fano profile. The existence of this profile and the large Er\(^{+}\) population indicate that the photoionization in the resonance region is dominated by the strong interaction between the \(4d^24f^{12} - 4d^24f^{13} - 4d^24f^{11}_2\text{ (d,g)}\) channel and the direct \(4d^24f^{12} - 4d^24f^{11}_2\text{ (d,g)}\) channel.

We see two interesting tendencies. First, there is a tendency that the lower-energy peaks provide photoions with higher charge. Second, the peak positions depend, though slightly, on the ion charge, as has been observed in Dy atom.\(^3\) In order to obtain more detailed information about the photoabsorption and subsequent decay processes, we are going to do photoelectron spectroscopy study on Er atom.

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ANGULAR CORRELATION BETWEEN 4d PHOTOELECTRON AND NOO AUGER-ELECTRON OF XENON

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The understanding of correlation effects arising in the dynamics of electrons escaping from a charge core is a permanent goal in atomic and molecular physics. Double ionization of an atom by single photon is one of the fundamental processes of atomic dynamics. The inner shell photo-ionization of a 4d electron of Xe is well known to be followed by the subsequent NOO Auger decay processes. In order to study the correlation effects, we challenge to establish an electron-electron coincidence experimental technique for (γ,2e) process with the improved EICO apparatus1).

Figure 1 shows a block diagram of the apparatus. A rotatable parallel plate type electrostatic analyzer with a position sensitive detector to resolve emitted electron energy and two channeltron detectors with retarding grids are set in the plane perpendicular to the photon beam direction.

In the preliminary experiment for the 4d photo-ionization of Xe by linearly polarized photon beam of 110 eV, both non-coincident signals of 4d photoelectron and Auger electron measured by the rotatable energy analyzer have angular distribution oriented the electric vector direction of the incident photon beam. However, as seen in Figure 2, each angular distribution of Auger electron measured in coincidence with 4d photoelectron detected by two channeltron detectors fixed at 180 and 270 degrees against the direction of electric field vector of the incident photon beam indicates that the 4d photoelectron and NOO Auger electron way out from Xe making an angle 90 degrees to each others. In order to discuss more detailed about angular correlations, we are proceeding to improve much more the angular- and energy- resolutions of detectors.

POLARIZED B K-EMISSION FROM HEXAGONAL-BN

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Introduction
Theoretical calculations\(^1\) and the study of take-off angle dependence of the B K-emission spectrum\(^2\) predict that the valence band of h-BN is separated into \(\sigma\)- and \(\pi\)-subbands. The integrated density of states of the two components is slightly different. Recently we have measured the polarization degree of the B K-emission from h-BN and have ascertained that the \(\sigma\)-component slightly predominates. The successful polarization measurement owed much to multilayer mirrors, which we have so far developed. They are the most useful polarizing elements in the soft x-ray (SXR) region at around 45° angle of incidence.\(^3\)

Experimental
The sample was prepared by hot press from powder of 99.7% purity. Its \(c\)-axis was confirmed to be highly oriented. The experiment was carried out on BL-3B under a resolution of 0.5 eV with \(\sim 10^{11}\) photons/sec. A rotating analyzer mounted with a SXR multilayer was equipped to a SXR emission spectrometer.\(^4\) Figures 1a and 1b show B K-emission spectrum of h-BN and spectral reflectance of a Ru/B\(_4\)C 199-layer polarizer. The peak at 194 eV in Fig. 1a is due to the scattered excitation light, which is completely filtered off with the multilayer. We used the cut face of the samples, that is, the emission was observed in the direction normal to the \(c\)-axis. To raise the \(S/N\) ratio we used a slit of 1.0-mm width in front of the sample.

Results and Discussion
Figure 2 shows the output of the rotating analyzer vs its azimuthal angle measured for the B K-emission. It shows that the emission is polarized by 8.1%. It was also found to be independent of the polarization of the primary SXR's. It was polarized parallel to the inter-layer of the sample. This polarization is due to mostly the \(\sigma\)-component of the valence band of h-BN. Figure 3 shows the excitation spectra for \(\sigma\)- (solid curve) and \(\pi\)- (dashed curve) emissions. From the spectra excitation-energy dependence of the polarization degree is not evidently found.

References
INITIAL STAGE OF SOFT X-RAY STIMULATED ETCHING REACTION IN THE SF6/SiO2 ADSORPTION SYSTEM

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Introduction
The photochemical reaction of the adsorbate molecules on solid surface is important for fundamental studies of chemical elemental reactions as well as application studies of photochemical vapor deposition (CVD), photo-etching, photocatalysis and so on. The fundamental studies, however, have been rarely performed.

In the present work, the photochemical etching reaction in adsorption system of SF6/a-SiO2 at low temperature has been fundamentally studied by in situ X-ray photoelectron spectroscopy (XPS).

Experimental
The experiments were performed using soft X-ray beam line 3B. The apparatus used consisted of a double pass cylindrical miller analyzer (CMA), a sample holder system and ultrahigh vacuum pumping systems. The CMA is fixed at 75 degrees with respect to the photon beam. The a-SiO2 with thickness of 12nm was used as a sample substrate. SF6 was used as an adsorbate gas. A ~50L exposure of the adsorbate gas to substrate was carried out at -100K in order to permit a physisorbed monolayers of SF6.

Results and discussion
In order to determine the molecular structure of the etching surface, Si 2p XPS spectra were measured. Chemical shifts of Si 2p signals can be examined based on the partial atomic charge model1. Regarding the chemical bonding between Si and F, measured and estimated chemical shifts of Si 2p XPS signals can be plotted against the electronegativity sum of mSiFm molecules2, where m and n denote the number of the nearest neighbor oxygen and fluorine bonds, respectively. Of course m + n = 4 must hold for satisfying the fourfold coordination of the silicon atom. Fig. 1 shows the dependence of Si 2p chemical shifts on irradiation time along with assignments of molecular structure of the etching surface. This indicates that the SiO2 substrate is stepwise fluorinated.

The excitation of SF6 adsorbate can bring about its dissociation into SFx (x=1-5) fragment in this energy region. Since SF3 (x=1-3,5) fragment has higher electron affinity3, it is possible that the reaction is initiated by the transfer of an electron from the SiO2 to the SFx (x=1-3) radical.

An equation from Benson4 can be used to determine the stability of this metathesis complex. From the equation, for example, a critical distance of 2.36 Å between an SF3 radical and an SiO2 substrate is calculated to give the maximum distance at which the charge-transfer complex can be stable and the electron can be transferred. The large distance of an intermediate charge-transfer complex would explain the fast reaction of SF3 with the SiO2 and not need such encounters to strong collisions and high temperatures. This supports the etching reaction occurring at low temperature. Finally it should be noted that photochemical charge-transfer excitation5 on the SiO2 may occur and cause the dissociation of SF6 adsorbate.

Fig. 1. The dependence of Si 2p chemical shifts on irradiation time along with assignments of molecular structure of the etching surface.

References
X-RAY MAGNETIC DIFFRACTION OF ACTINIDE COMPOUND OF UTE

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Introduction

X-ray magnetic diffraction (nonresonant magnetic Bragg scattering) is known to give us directly information about orbital and spin moment in a ferromagnetic material. S. P. Collins and D. Laundy, who developed the white beam method of X-ray magnetic diffraction, applied it to rare earth compounds and obtained the form factor ratio of the orbital moment to the spin moment.

In the present study we apply the white beam method to an actinide compound of UTe for the first time. UTe is ferromagnetic below 104K and has very strong magnetic anisotropy (the easy axis is <111> in the NaCl type crystal structure). These features are closely related to the electronic state of 5f electrons of uranium which is thought to be partly delocalized, but details are not yet revealed. Such features of 5f electrons will be reflected to the orbital moment. The aim of this study is to measure the form factor of orbital moment of uranium by X-ray magnetic diffraction.

Experimental

The measurement has been performed at PF-BL3C with white X-rays. The beam position was 0.4mm above the orbital plane where the polarization factor $f_p$ showed its maximum. A specimen of single crystal UTe prepared by the Bridgman method was a disc with diameter of 6mm and thickness of 2mm. The experimental geometry is shown in Fig.1. Reflection intensities of (h00) planes $(h=2, 4, 6, ...)$ are measured simultaneously by the white beam method. The specimen was magnetized with an electric magnet prepared for diffraction experiment. The flipping ratio $R$'s for (h00) planes were measured with the same method as was used for Fe at 80K.

Results and Discussion

The observed $R$ is related to form factors of the orbital and spin moment, $L(k)$ and $S(k)$ respectively, as $R = (1.158)f_p(L(k)+0.3S(k))/n(k)$, when the angle between the directions of magnetization and incident beam is $10^\circ$. Here $n(k)$ is the charge structure factor of UTe. Using the observed $R$ and the calculated $f_p$ by the program we obtained the magnetic form factor of $L(k)+0.3S(k)$, which is shown in Fig.2 together with the magnetic form factor of $L(k)+2S(k)$ observed by neutron diffraction. The difference between these two magnetic form factors arises clearly from the difference in the coefficient of $S(k)$ in the form factors. The X-ray form factor is decreasing more rapidly with increase of $k$ and is much closer to the orbital form factor $L(k)$ itself than the neutron one.

Here we obtained the magnetic form factor which is very close to the orbital form factor, which will contribute to reveal the electronic state of 5f electrons in UTe.

Acknowledgements

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X-RAY MAGNETIC DIFFRACTION OF SINGLE CRYSTAL FE AT PF-BL3C

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Introduction

X-ray magnetic diffraction (nonresonant magnetic Bragg scattering) with white beam technique and a single crystal specimen was developed recently and successfully applied to the magnetic form factor measurement of Fe and Ni. The white beam method utilizes both linearly and circularly polarized X-rays, and the cross section for X-ray magnetic diffraction is related to the specific polarization factor \( \rho = P_c/(1 - P_L) \), where \( P_L \) and \( P_c \) are degrees of linear and circular polarization of incident X-rays respectively. The polarization factor is known to be critically dependent on a vertical emittance of a storage ring of synchrotron radiation.

The purpose of this study is to reveal the value of vertical emittance of the storage ring of Photon Factory by the X-ray magnetic diffraction with a single crystal of Fe. The vertical emittance has not yet been measured so far at least for BL3C, where the experiment was made.

Experimental

The specimen of a single crystal Fe is a rectangular plate of 0.27 mm thickness. The surface normal direction is <110>. The experimental configuration is shown in Fig.1. Reflection plane was {110} and the Bragg angle was fixed to 45°. Diffracted X-ray intensity was measured with a pure Ge solid state detector (SSD).

The specimen was magnetized along <100> axis with an electric magnet of closed circuit type. We measured the diffraction intensities of the positive and negative magnetization direction \( \mu (L, \mu_L) \) by reversing the magnetic field alternatively every 10s. Then we obtained the so called flipping ratio \( R \), which is defined as \( R = (\mu_L - \mu_{-L})/(\mu_L + \mu_{-L}) \). We have measured the \( R \) values for various beam positions above and below the orbital plane of the PF ring by varying vertically the position of the slits and the specimen together.

Results and Discussion

The obtained values of \( R \) for (220) reflection is plotted as a function of the beam position and shown in Fig.2. From the theory of X-ray magnetic diffraction the flipping ratio \( R \) is expressed as \( R = \mu(k)\nu(n(k))^2 \) when the angle between the directions of incident X-rays and magnetization of the specimen equals to 45°, where \( \mu(k) \) and \( n(k) \) are the magnetic and charge form factor of Fe respectively. Here the orbital moment of Fe is assumed to be completely quenched. In Fig.2 is also shown the curve of calculated \( R \) with the theoretical \( \mu(k) \) for (220) and calculated values for \( P_L \) and \( P_c \) by the program. The vertical emittance was determined so as that the calculated curve of \( R \) well reproduced the observed data of \( R \), and the value of 1.4 mm-rad was obtained. This value will be used for studies of X-ray magnetic diffraction of other ferromagnetic materials.

Acknowledgements

The authors would like to express their thanks to Prof. H. Kitamura, Prof. F. Itoh, and Dr. T. Iwazumi for their helpful discussions. This research is partly supported by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Culture (No.05640427).

References

X-RAY MICRO-DIFFRACTION MEASUREMENT OF LOCAL LAYER RESPONSE OF SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTALS TO ELECTRIC FIELD

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Introduction

The layer structure in thin surface stabilized ferroelectric liquid crystal (SSFLC) cells is characterized by the "chevron" structure. A zig-zag defect is the local layer structure (LLS) defect observed in SSFLC cells and corresponds to walls between the two possible chevron directions1). The zig-zag defect consists of broad and narrow walls. In a previous report, we have described the direct observation of the LLS of the broad wall boundary using synchrotron X-ray micro-diffraction2). Since the LLS response to external electric field is one of the most important characteristics of SSFLC cells, further experiments were done to study the LLS deformation under applied electric field.

Experimental

The experiments were done on the BL-4A. An X-ray microprobe system used was described elsewhere3). The X-ray energy used was 8 keV. The beam size at the sample was about 5 x 5 μm.

The sample used was CS-1014 (Chisso). The sample cell was prepared by sandwiching the FLC material between two glass plates of 80 μm thick with thin ITO electrodes on which the polyvinylalchol layer was coated and unidirectionally rubbed. The thickness of the sample cell ranged from 1.5 μm to 6 μm.

Results and Discussion

Fig.1 shows rocking curves (θ-scan) obtained at the broad wall for 6 μm thick SSFLC cell before, during and after the application of AC square wave (±16 V, 10 Hz). Two sharp peaks (PL and PH) appeared at around θ=± 18 correspond to the chevron structure. The central peak (PC), which indicates the bookshelf LLS, appeared only at the broad wall. Before an AC application, PC was the multiple. During the AC application, PC became stronger in intensity and narrower in FWHM. After the AC application, PC split again into multiple peaks but the intensity profile was slightly different from the initial state. The applied voltage and frequency dependences of the central peak intensity were also measured. These experimental results suggest that the perfection of the bookshelf structure at the broad wall is remarkably improved due to the field induced torque.

MICRO XANES MEASUREMENTS OF NICKEL DISSOLUTION INTO SYNTHETIC DIAMOND CRYSTALS

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Introduction
Quantification of trace impurities inside synthetic diamond crystals grown under high pressure and high temperature has been carried out using SR x-ray fluorescence (XRF) analysis. Selective dissolution of nickel from the metal solvent into {111} growth sector has been visualized by using XRF imaging techniques. The dissolved Ni concentration ranges up to 170 ppm as far as we know, and the relation between the concentration and the solvent composition is under discussion. Beside the quantitative information of trace impurities, chemical state information of dissolved Ni has been investigated using small area x-ray absorption near edge structure (XANES) measurements.

Experimental
Experiments were carried out on the BL-4A. A small area XRF system equipped with an xy sample scanning stage was used. To minimize background caused by the scattered x-rays, a Si(Li) detector was placed in the orbit plane normal to the incident beam. Incident beam energy was calibrated within the accuracy of 10 eV.

Results and Discussions
Ni XANES measurements were carried out at several positions on a Ni XRF image of a sample with the spatial resolution of 100 μm. Figure 1 shows typical Ni XANES spectra measured at {111} growth sector and at the inclusion. Figure 1(c) shows Ni XANES of metal Ni measured under the same condition as a reference. Considering the self-absorption effects with the fluorescence detection method, it can be understood that the Ni XANES at the inclusion is similar to that of the metal. The difference of Ni XANES between the {111} growth sector and the inclusion denies the possibilities of small inclusion in the {111} growth sector but confirms the dissolution into the diamond lattice. A pre-edge peak marked in the figure suggests that Ni is in a tetrahedral site in the diamond lattice.

References

Figure 1. Ni micro XANES spectra measured a) at the {111} growth sector and b) at the inclusion of the synthetic diamond grown in the Ni solvent. Fig. 1c) shows a reference spectrum of Ni foil (8μm) measured with the transmission method.
DISTRIBUTION OF TRACE ELEMENTS IN THE RENAL TUBULE OF MERCURY-EXPOSED RATS BY SR-XRF IMAGING WITH X-RAY MICROPROBE.

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1) Environmental Health Sciences Division, National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaraki 305, 2) Graduate School Doctoral Program in Medical Sciences, 3) Institute of Community Medicine, University of Tsukuba, Ibaraki 305, 4) Faculty of Science, Department of Applied Chemistry, Science University of Tokyo, Shinjuku-ku, Tokyo 162

Introduction
Mercury is a nephrotoxic metal and thought to cause more serious damage to the proximal convoluted tubule than to the distal tubule. Thus a simple and convenient method for determination of two-dimensional distribution of mercury after exposure is required to clarify relationship between the distribution and the morphological change. In this study, using SR-XRF imaging technique with X-ray micro probe, we examined detailed distribution of not only mercuric compounds after administration but also endogenous trace elements (copper and zinc) in rat kidney.

Experimental
Mercuric chloride (HgCl2) and methylmercury chloride (MMC) (5 mg as Hg /kg s. c.) were administered to five male rats, respectively, and then these animals were sacrificed 24 h after the injection. One of each rat kidney was fixed in 10% buffered formalin and embedded in acrylic resin, then cut into 20 μm-thick cross section for the specimens of SR-XRF analysis. The other kidney was digested with concentrated nitric acid, and then mercury level was measured by flameless atomic absorption spectrometry (FAAS) and copper and zinc were by inductively coupled plasma atomic emission spectrometry (ICP-AES).

XRF measurements were made at BL-4A, PF utilizing energy dispersive SR-XRF system with monochromatic X-ray microbeam obtained by multilayer monochromator and K-B type focusing optics. Energy of X-ray used was 14.38 keV. Two dimensional analysis was carried out by placing a sample on a XZ stage under the following condition: beam size, 5 x 6 μm2; step size, 5 μm/step; counting time, 10 sec/point.

Results and Discussion
Under the conditions described above, the lower limit of detection for elemental imaging was around 20 μg/g in all cases. As shown in Fig. 1, both mercury and zinc were more accumulated in the renal tubule compared to the glomerulus. The elemental map for copper was not clear because of its minimal content (Table 1). Similar results were observed in the MMC-treated rats.

Because the SR-XRF imaging used in this study can be performed without destroying the samples, we are able to examine the same sample histologically after the elemental analysis. Therefore, this method appears to be a powerful technique for the simultaneous determination of two-dimensional distribution of toxic metal and histochemistry in biological samples. The experiment of the staining to evaluate the renal damage is now in progress.

References

Fig. 1. Imaging of mercury and zinc in the HgCl2-treated rat.
Kidney section specimen (a) and fluorescent X-ray intensity distribution of mercury (b) and zinc (C). G: glomerulus, T: renal tubule

Table 1 Metal concentration in the rat kidney.

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<th>MMC</th>
<th>non-treatment</th>
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<td>Hg</td>
<td>70.7 ± 14.7**</td>
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<td>Cu</td>
<td>6.05 ± 0.39b</td>
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<td>Zn</td>
<td>19.7 ± 1.4b</td>
<td>17.3 ± 0.5</td>
<td>18.3 ± 0.9</td>
</tr>
</tbody>
</table>

Values indicate mean ± S. D. for 5 rats.
Significant difference between: a: HgCl2 and non-treatment, b: HgCl2 and MMC. *p<0.01, **p<0.05
SR-XRF IMAGING OF TRACE ELEMENTS ON HAIR OF THE RAT EXPOSED TO METHYL MERCURY

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Introduction

We previously reported a biomedical application of SR-XRF imaging with X-ray micro probe to the hair of the smelter workers1). It was consequently shown that determination of two-dimensional distribution of trace elements in the hair cross section provide us an useful information for monitoring environmental and industrial metal exposure. To investigate whether methylmercury administered endogenously shows localized distribution in hair or not, the detailed dynamics of the metal in hair of rats was examined by SR-XRF analysis in the present study.

Experimental

Methyl mercury chloride (5 mg as Hg/kg, p.o.) was given to six rats every day for 5 days. The hair was embedded in acrylic resin and cut into 25 μm-thick cross section. For determining Hg contents, rat hair was harvested at appropriate days as shown in Fig. 1.

XRF measurements were made at BL-4A, PF utilizing energy dispersive SR-XRF system with monochromatic X-ray microbeam obtained by multilayer monochromator and K-B type focusing optics2). Energy of X-ray used was 14.38 keV. Two dimensional analysis was carried out by placing a sample on a XZ stage under the following condition: beam size, 5 x 6 μm²; step size, 5 μm/step; counting time, 10 sec/point.

Results and Discussion

While Hg levels in the blood and hair reached a maximum at 7 and 8.5 days, respectively, these elimination curves exhibited a similar pattern (r=0.97), indicating that the concentration in hair appears to be extrapolated to that in blood. Also, significant accumulation (5-10 fold) of the metal in hair compared to the blood was observed (Fig. 1). SR-XRF imaging revealed selective accumulation of Hg in the cortex (Fig. 2). Appreciable difference in the site-specific distribution of Hg was not detected even if hair samples of rats which are cut at different positions (2 to 11 mm each) from the root end, were employed; however, the Hg levels of these samples were different. By contrast, the imaging result of exogenous exposure of human hair to Pb indicated that the metal accumulated only in the cuticle. Taken together it is found that SR-XRF analysis enables us to distinguish between endogenous and exogenous metal exposure of hair. Development of the exogenous model by this method are now in progress in our laboratory.

References


Fig. 1 Hg concentration of hair and blood

Fig. 2 Imaging of hair cross section at 1 mm from the root end of the No. 4 rat.
a) light microscopic photograph of the sample, and distribution of b) Hg, c) S, and d) Zn.
X-RAY FLUORESCENCE ANALYSIS OF TRACE CL ACTIVATORS IN CARBONATITE

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Introduction

The preference of minor elements including activators of cathodoluminescence between calcite and dolomite in carbonatite has been decided by using two-dimensional imaging analyses of X-ray fluorescence technique. Calcite [Ca(CO₃)] and dolomite [CaMg(CO₃)₂], which are major components of carbonatite, show cathodoluminescence caused by activation ions. Calcite and dolomite emit yellow and reddish orange luminescence respectively both activated by Mn⁺² ion. Cathodoluminescence of these minerals are observed most intensively when the activators are included about a few thousands ppm in them.

Experimental

Samples of sovite carbonatite from Jacupiranga, Brazil was polished to thin section to enable to transmit of visible light under the polarization optic microscopy. Previously, the position of the exsolution lamellae of dolomite from calcite was decided by the optical microscope and the cathodoluminescence. The X-ray fluorescence apparatus equipped in BL-4A station of PF was used for scanning two-dimensionally on thin section and measured intensity of fluorescent X-rays of characteristic elements from it. Beam size was 100 μm x 100 μm, step width was 75 μm x 75 μm, and intensity was measured for 10 seconds per one step. Scanning of 43 x 43 steps made the two-dimensional imaging map covering 3,225 mm x 3,225 mm range. XANES spectra of Mn were recorded for the determination of chemical state of manganese atom which is activator of both calcite and dolomite.

Discussion

Fig.1(left) is the grayscale map showing enrichment of Ca, which is main components of both calcite and dolomite. Three water droplet-like exsolution lamellae of dolomite, where is thicker in grayscale than the calcite region around them, it means dolomite is poorer in Ca than calcite. The dark area in right side of Fig.1(left) is magnetite particle which is lack of Ca. For the same area as Fig.1(left) the fluorescent X-rays of Mn, Fe, Sr, P, Ti and Zr were collected. Consequently the slight differences of these minor elements between calcite and dolomite were detected in the two-dimensional visual map. The smaller cations as Mn and Fe than Ca are more enriched in the dolomite. On the other, Sr which is larger than Ca is more enriched in calcite. These three cations are able to substitute Ca or Mg atom and could be main components in the calcite (or dolomite) structure. Other cations are richer in calcite. Those cations have the smaller ionic radius and the larger valency, which means they have the larger ionic potential. The chemical state of Mn was determined by the chemical shift of XANES of Mn K-edge. The valence of Mn is found to be +2, which is consistent with the wavelength value of CL emission. The form of XANES spectra is just like as that of rhodochrocite and kutnohorite, both are the carbonate minerals including Mn as main component. This suggests minor amount of Mn in calcite and dolomite substitute the Ca or Mg sites in these structures.

Fig.1 Two-dimensional imaging map of Ca (left), Mn (center) and P (right) of Jacupiranga carbonatite.
DISTRIBUTION OF STRONTIUM IN THE BODY OF EEL LEPTOCEPHALI
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Introduction
Eels are known to pass through a leptocephalus larval form. Leptocephalus is unique in their leaf-like transparent, laterally compressed body which includes a large gelatinous matrix. The gelatinous matrix is composed mainly of a glycosaminoglycan (GAG) which possesses an affinity to Sr and is broken down and consumed during the metamorphosis from leptocephalus to juvenile. Otake et al.\(^{1}\) reported that leptocephali had high Sr contents in the body and otolith which dramatically decreased during the metamorphosis, and suggested that the changes of Sr content related with GAG formation and breakdown in the body. This study is focused on making clear (1) the distribution pattern of Sr in leptocephalus body, (2) changes of Sr content in tissues, and (3) the relationship between the body Sr content and GAG dynamics.

Materials and methods
Four Conger myriaster leptocephali of full grown and late metamorphic stages, collected in the coastal waters of Oarai, Ibaraki Prefecture, Japan, in April and May 1994, were used for this study. Cryo-cross-sections (75\(\mu\)m in thickness) of the body of the specimens placed on a Myler membrane backing fixed on a plastic frame were prepared for the SRXRF analyses. Two dimensional and point analyses were carried out on the BL-4A at the Photon Factory. Point analyses were performed on the tissues of gelatinous matrix, notochord, muscle, and intestinal organs including gut and liver. The sample was excited by monochromatized X-rays of 19.5keV under 10\(^{-2}\) torr. The beam size was adjusted to the dimension of 60x60\(\mu\)m\(^{2}\). For two dimensional analyses samples were scanned horizontally with 36-50 points, vertically 21-50 points (150-200\(\mu\)m step size). Each point was exposed for 7-30 seconds. Exposure time for point analyses was 1000 seconds. Each count data was converted into the relative intensity to the Compton scattered peak which was calculated as follows:
\[
\text{(Net count of Sr-\(k_a\) peak area / Net count of Comp. scattered peak)} \times 10^3
\]

Results and discussion
Relatively high intensity of Sr distributed in gelatinous matrix in full grown leptocephalus. In metamorphosing leptocephali Sr distribution was partial in notochord, which related to bone development (Fig.1). Relative intensity of Sr in the gelatinous matrix of metamorphosing leptocephali was distinctly lower than that in the full grown leptocephalus (Fig.1), indicating that Sr content in gelatinous matrix decreased during the metamorphosis. There found no distinct changes in Sr relative intensity of muscle and intestinal organs between leptocephalus and metamorphosing specimens. Although sample number is small, the findings seem to suggest that GAG dynamics is involved in the changes in Sr content in tissues in leptocephali. We thank Dr. A. lida for helping the SRXRF analysis.

Reference
Introduction
We previously reported the detailed distribution of trace elements on the hair cross sections of the smelter workers by SR-XRF imaging with monochromatic X-ray microbeam obtained by K-B type focusing optics. This technique has enabled us to provide high spatial resolution by a small microbeam (approximately 5 x 5 \( \mu \text{m}^2 \) size) with an appropriate photon flux; however, it is hard for the system to change beam size at every specimen. To solve this problem, we attempted biomedical application of SR-XRF imaging with white X-ray microprobe to kidney of the mercury-administered rat in the present study.

Experimental
Mercuric chloride (HgCl\(_2\)) (5 mg as Hg /kg s. c.) was administered to a male rat, and then the animal was sacrificed 24 h after the injection. One of the rat kidney was fixed in 10% buffered formalin and embedded in acrylic resin, then cut into 20 \( \mu \text{m} \)-thick cross section for the specimens of SR-XRF analysis. The other kidney was digested with concentrated nitric acid. Then mercury and zinc levels were measured by flameless atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), respectively.

XRF measurements were made at BL-4A, PF utilizing energy dispersive SR-XRF system with white X-ray microbeam obtained by a slit system. Two dimensional analysis was carried out by a placing sample on a XZ stage under the following condition: beam size, 10 x 6 \( \mu \text{m}^2 \); step size, X=10 \( \mu \text{m} \)/step and Z=5 \( \mu \text{m} \)/step; counting time, 10 sec/point. For histopathological determination, the same sample was stained by the method of periodic acid Schiff reaction (PAS).

Results and Discussion
Clear imaging of mercury distributed in rat kidney was successfully carried out with white X-ray microprobe while the metal concentration was 67.8 \( \mu \text{g/g} \) (Fig. 1). Result of PAS staining for mercury-treated kidney revealed that appreciable tissue damage was not observed after the analysis. In the proximal tubules, mercury was higher in the damaged tubules than in the normal tubules whereas the distribution of zinc, an endogenous trace element, was opposite.

Though white X-ray microprobe is thought to cause a damage to the sample, no significant damage was observed for the kidney specimen in the present SR-XRF imaging technique. Consequently, it is found that white microbeam analysis is a useful technique to obtain two-dimensional metal distribution in biological sample because beam size is easily adjusted by the slit in short time.

References
SUB-μm X-RAY MICROBEAM BY KIRKPATRICK-BAEZ OPTICS

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Introduction

The recent development in synchrotron radiation instrumentation has enabled the realization of hard X-ray microprobes of less than a few μm beam size. On BL-4A, the X-ray microbeam system using Kirkpatrick-Baez (K-B) optics has been used for spectroscopy and X-ray diffraction experiments.1,2,3) A practical beam size was around 5 x 5 μm². In order to reduce a beam size with a sufficient photon flux, two types of experiments were performed: 1) K-B optics has been newly designed for BL-16X to fully utilize radiation from a multipole wiggler, and 2) the BL-4A microbeam system has been improved in the beam size.

BL-16X: sub-μm X-ray microbeam system

The experimental arrangement was essentially the same as that installed on BL-4A.1) Synchrotron radiation from the multipole wiggler was monochromatized by either a double crystal monochromator or a multilayer monochromator. A pair of elliptical mirrors made of fused quartz coated with Pt was used. The demagnifications of the vertical and horizontal mirrors were 1/200 and 1/750 respectively and the expected beam size at the focusing point was about 2 x 2 μm². The knife edge scanning was used to measure the beam size. The X-ray energy was 9 keV. The beam size of 1.6 x 1.7 μm was obtained with the photon flux of about 4 x 10^8 ph/sec/300 mA by the multilayer monochromator. By reducing the opening of slits located at about 24 m from the source point, the beam size of 0.7 (horizontal) x 0.9 (vertical) μm² with a photon flux of about 1 x 10^7 ph/sec/300 mA was obtained by the multilayer monochromator. Fig. 1 shows the Ni Kα fluorescent and transmitted X-ray intensity distributions from a Ni 2000 mesh per inch grid. Fig. 1(c) is the detailed intensity distribution along the vertical direction.

BL-4A: Improvement of the microbeam system

To reduce the beam size of the X-ray microbeam system being used on BL-4A, the use of a slit close to the source point is practically effective. A series of 5 rectangular slits, ranging from 700 x 280 μm² to 200 x 60 μm², was placed at 3 m from the source point. A W thin wire of 2.5 μm in diameter was scanned at the focusing point to measure the beam size. The beam size was reduced from 5 μm to 2.5 μm.

Authors would like to thank Prof. H. Maezawa and Mr. S. Asaoka for the installation of the slit in the beam line.

3) A. Iida et al., Ferroelectrics, 149(1993)117

Fig. 1. Ni Kα (a) and transmitted (b) X-ray intensity distributions from a Ni 2000 mesh per inch grid. 121 x 121 steps, 0.25 μm / step. The darker regions correspond to higher intensities. (c) detailed intensity distribution in the vertical direction.
DETECTION OF TRACE COBALT AND MANGANESE IN SYNTHETIC DIAMONDS BY SR XRF METHOD

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b)Department of Applied Chemistry, Faculty of Engineering, University of Tokyo, Tokyo 113, Japan

Introduction

High quality single crystals of diamond are grown in the metallic solvent, and it is required to know about impurities in them incorporated from the solvent, as the basic data for the impurity-controlled crystals. Main elements used for composing the solvents are Fe, Ni, Co, Mn and Co. Other elements such as Al, Ti, Zr and Cu are occasionally added. Some of these elements are incorporated into the diamond lattice as well as being contained as inclusions. We have detected dissolved Ni, and determined its concentrations. Dissolution of Fe has not yet been confirmed in spite of repeated trials of analyses, because of its very low level of dissolution, which is easily masked by unexpected, low level contamination.

We are continuing efforts of detecting, and determining concentration of, other 3d elements. Recently, we succeeded in detecting Co and Mn in crystals grown in pure Co and an alloy of Ni-Mn-Co (68:27:5 by wt).

Experimental

Inclusion-free crystals were grown at a pressure of 5.5 GPa and temperatures of 1200~1400 °C. Then, they were cut parallel to the direction of a (110) plane, and formed into wafers of about 0.2mm in thickness. XRF measurement was carried out on the BL-4A, using a monochromatized 9 keV beam. The beam was concentrated with the ellipsoidal mirror and limited to a size of around 100/μm x 100/μm. The detailed method of the concentration determination is reported elsewhere[1]. A sample was mounted on the x-y scanning stage, and point analyses were carried out at selected positions of interest on the XRF images.

Results and discussion

The x-y concentration mapping and point analyses for Sample R, grown in pure Co, showed detectable Co in the (111)-sectors and in the (311)-sector. It was not detected in the (100)-sector. Results of the point analyses are illustrated in Fig.1. This behavior looks the same as that of Ni[2]. Absolute concentration determination has not yet been finished for the sample R, but measurement on another Co-grown sample, N (performed in 92G-247), shows concentrations up to 17 ppm. Solubility of Co in diamond seems a little less than that of Ni. Based on XANES spectrum and the similarity of the distribution behaviors of Co and Ni, Co is thought to be dissolved in the diamond lattice [3].

Point analyses on Sample O, grown with the Ni-Mn-Co alloy solvent, has shown the similar behaviors of concentration distribution for Ni and Co. Ti data are shown in Table 1.

Mn was also detected in Sample O. However, no correlation was found between the concentration of Mn and that of Ni (or Co). The XANES spectrum for Mn, measured on the region free from inclusions, was different from that measured on the inclusion. This suggests a possibility that Mn is also dissolved in the diamond lattice, though it should be confirmed by other methods, such as CL, PL and EPR.

References


Table 1 Concentrations of Ni, Co and Mn, determined for Sample O. (grown in Ni-Mn-Co alloy)

<table>
<thead>
<tr>
<th>Position</th>
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<th>Mn(ppm)</th>
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<td>(110)</td>
<td>2.9</td>
<td>0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Fig.1 Point analyses on Sample R.
O: Co is not detected
●: Co is detected
Secondary Structure of N-Acetylglutamic and N-Acyl-L-glutamic Acid Oligopeptides in the Solid State

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Introduction

A great number of structural studies for polyglycine (PG) and poly-L-glutamic acid (poly(Glu)) have been made by various techniques. According to the X-ray studies, PG I is in the β structure and PG II in the helical structure. For poly(Glu), it is well known that this polymer takes up α-helix, β-structure and random coil in the solution and in the solid state. In particular, for the β-structure of poly(Glu) in a gel state the presence of two β-forms (β1 and β2) has been confirmed by X-ray diffraction. However, conformational studies on the oligomers are very few. In the present work N-acetylglycine oligomers, and their potassium salts, N-octanoyl-L-glutamic acid oligomers were prepared and the conformations of these oligomers in the solid state were investigated by X-ray diffraction powder patterns.

Experimental

N-Acetylglycine oligomers (residue number n=3~5) were prepared by a method similar to that of Ingersal and Bubcock. Two crystalline modifications for these glycine oligomers were obtained. N-Acetyl glycine oligomers [A-series] treated in saturated LiBr aqueous and the samples [B-series] treated in dichloroacetic acid were prepared. N-Octanoyl-L-glutamic acid oligomers (residue number, N=3~12 and 14) were prepared by the method described in our previous paper. X-ray diffraction powder patterns were obtained by the use of an RAD-RC diffractometer with countermonochromator (CuKα, 60kV, 220mA) and Synchrotron radiation X-ray beamline optics (BL-4B) with double crystal Si(III) monochromater, and photon energy 4~34 eV.

Results and Discussion

For N-Acetylglycine Oligomers, the X-ray diffraction powder patterns of N-acetylglycine oligomers were measured and compared with those of PG I and PG II. For the A-series, very intense reflections at 4.18-4.20 Å and weak ones at 3.12-3.17 Å were observed, corresponding to the 4.14- and 3.09- Å reflection of PG II, respectively, while the patterns of the B-series contained very intense reflections at 3.36-3.37 Å and medium ones at 4.35-4.39 Å, corresponding to the 3.42- and 4.36- Å reflections of PG I respectively. Thus, the A-series oligomers gave only the PG II-like reflection.

For N-octanoyl-L-glutamic acid, reflections at 2.30-2.34, 2.61-2.66, 3.11-3.19, 3.57-3.62, 3.91-3.96, 4.70-4.74 and 7.66-7.84 Å are observed for the shorter oligomers (N=3~6). These reflections are closely related to those at 2.31, 2.60, 3.17, 3.61, 3.90, 4.74 and 7.83 Å for β2-type poly(Glu). For the longer oligomers (N=8~12 and 14), reflections at 2.61-2.80, 3.89-3.93, 4.63-4.64 and 9.00-9.32 Å are observed, and correspond to those of the β1-type poly(Glu) at 2.80, 3.89, 4.73 and 9.03 Å. Moreover, the diffraction pattern features of the shorter oligomer samples are very similar to those of the β2-type poly(Glu) and the patterns of the longer oligomer samples to those of the β1-type poly(Glu). These observations suggest that the shorter oligomers take a conformation similar to the β2-type poly(Glu) and the longer oligomers that similar to the β1-type poly(Glu).

References

DEPTH PROFILING OF ZIRCONIA-TOUGHENED ALUMINA USING MULTI-WAVELENGTH X-RAY DIFFRACTION DATA

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Introduction

Diffraction methods are being used to characterise phase abundance and residual strain in zirconia-toughened alumina (ZTA) ceramics. Laboratory-based x-ray and neutron diffraction measurements have indicated substantial differences in character between the near-surface and the bulk (1,2,3). Synchrotron radiation offers the possibility for determining depth profiles of phase abundance and strain in the alumina matrix and the monoclinic (m) and tetragonal (t) ZrO\textsubscript{2}.

Experimental

The instrument employed was the high-resolution powder diffractometer described by Ozawa et al (4). Full-pattern data sets were collected at wavelengths 0.73, 0.87, 1.07, 1.52 and 2.00 Å provide information depths for low-angle data ranging from about 2 to 35 μm from the surface. Data were collected in symmetric reflection mode with a 0.5 mm incident beam slit. The specimen suite comprised a sintered alumina, and six ZTA specimens containing, respectively, 4.5, 7.3, 9.0, 11.7, 14.9 and 18.4% zirconia by weight. The samples were examined as-sintered, i.e. without surface treatment and after grinding and polishing.

Results and Discussion

The results so far have indicated the following: (1) Depth profiles for the t-ZrO\textsubscript{2}/m-ZrO\textsubscript{2} phase composition ratio by weight showing substantial variations in the level of transformed zirconia with ZrO\textsubscript{2} loading, depth and surface treatment (2) Residual strain depth profiles showing that the non-linear strain associated with the monoclinic grains passes through a pronounced maximum as the ZrO\textsubscript{2} concentration increases beyond about 10% by weight. This behaviour, which is consistent with Young's modulus data in the literature, seems to indicate the onset of micro-cracking in the matrix (3) Uniform residual strain depth profiles demonstrate a negative, or compressive, strain near the surface (2.00Å) which increases with ZrO\textsubscript{2} loading and depth below the surface (Fig. 1.); and (4) Detection, for the first time, of β-alumina in ZTA specimens.

![Fig. 1. Variation of uniform strain in alumina with different ZrO\textsubscript{2} levels at three wavelengths. Rietveld refinement of the data was used to determine the strain from shifts in the a cell parameter shift.](image)

References

INDEPENDENT DETERMINATION OF THE TEMPERATURE FACTOR
OF A GA ATOM IN GaAs POWDER SAMPLE (III)

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The temperature factor of a Ga atom in GaAs powder sample was determined independently of that of As atom by the use of the anomalous dispersion.

Results and Analysis

Eleven diffraction measurements were carried out near the K absorption edge of Ga(1.19578 Å), on the longer wavelength side in the range from 1.19735 to 1.21116 Å. The results are shown in Fig. 1. The values of structure factor were smoothed against the wavelength by the use of the third order power series.

The scale factor of data in each measurement was determined by the conventional method using the theoretical values of the anomalous dispersion correction terms(ABC)[1]. The error of F(311) is within ±2%, which shows good accuracy of our measurements.

Experimental ADC of Ga near the K absorption edge of GaAs was obtained by T. Fukamachi from absorption coefficient measurement[2], and recently by M. Yoshizawa from pendelloesung beat due to X-ray resonant scattering[3].

The temperature factors were estimated using the same kind of parameters as previously, those are K, L and Bq shown in

\[ \text{K} = \frac{F_L(hkl)}{\overline{F_{\text{G}}}} \]

\[ \text{L} = \frac{F_{\text{G}}(hkl)}{F_L(hkl)} \]

\[ \text{Bq} = \frac{1}{\text{R}} \]

where \( s = (\sin \theta / \lambda)^2 \), \( F_L \) and \( F_{\text{G}} \) are the structure factors at longer and shorter wavelength, \( f_0 \) is the atomic scattering factor of Ga and \( f'_{\text{G}} \) the real part of ADC of Ga. When K was changed parametrically, L and Bq were estimated by the least mean squares method. The value of Bq was determined when the R-factor was about 0.01 and indicated saturation.

Although values of ADC are somewhat different between each other, the temperature factors were about 1.5 Å² from Fukamachi's ADC and Yoshizawa's ADC, and 1.6 Å² from the theoretical one, as shown in Table 1.

Table 1. Temperature factor of Ga atom obtained from pairs of diffraction measurements.

<table>
<thead>
<tr>
<th>Pairs(A)</th>
<th>Theoretical Bq(Å²)</th>
<th>Fukamachi's Bq(Å²)</th>
<th>Yoshizawa's Bq(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.19735-1.19826</td>
<td>1.5 0.009</td>
<td>1.4 0.009</td>
<td>1.4 0.009</td>
</tr>
<tr>
<td>1.19826-1.19918</td>
<td>1.5 0.013</td>
<td>1.5 0.013</td>
<td>1.5 0.013</td>
</tr>
<tr>
<td>1.19918-1.20168</td>
<td>1.6 0.036</td>
<td>1.6 0.036</td>
<td>1.6 0.036</td>
</tr>
<tr>
<td>1.20168-1.20356</td>
<td>1.6 0.010</td>
<td>(1.6 0.014)*</td>
<td>1.6 0.010</td>
</tr>
<tr>
<td>1.20516-1.21100</td>
<td>1.7 0.010</td>
<td>(1.8 0.010)*</td>
<td>-</td>
</tr>
</tbody>
</table>

* using extrapolated values of f' and f''.

Discussion

Increasing the number of data and smoothing the values of structure factors against the wavelength, saturation of R-factors was attained when the values of K were about 1.1 which should be 1.0 if the errors in experimental data were negligible. However the obtained temperature factor was about 1.6 Å². This value is very much larger than 0.912 Å² obtained at CuKα by the conventional method.

References

STRUCTURE OF ONE-DIMENSIONALLY DISORDERED COMPOSITE CRYSTAL (LaS)$_{1,18}$VS$_2$

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1) National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305
2) The Institute of Science and Industrial Research, Osaka University, 1-8 Mihogaoka, Ibaragi, Osaka 567
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4) Mineralogisch-Petrographisches Institut der Universität Hamburg, Grindelallee 48, 20146 Hamburg 13, Germany

Introduction

The structure of the composite crystal (LaS)$_{1,18}$VS$_2$ consists of interleaved incommensurate layers parallel to (001) of LaS and VS$_2$, each of them forming a substructure based on a C-centred orthorhombic lattice with $a_1 = 5.705(1)$, $b = 5.828(1)$, $c = 22.32(2)$ Å, $Z = 8$ for LaS and $a = 3.366(3)$, $b = 5.828(1)$, $c = 22.32(2)$ Å, $Z = 4$ for VS$_2$. The $b$ and $c$ axes are common to both substructures. The structure of the (100) projection (Fig. 1) is isotypic with that of the orthorhombic (PbS)$_{1,18}$TiS$_2$ plane group $pgm$, $b' = b/2$, $c' = c$. The La and S atoms of LaS are arranged like Na and Cl in the NaCl structure. The V atom is surrounded by six S atoms octahedrally.

Experimental

While the 0kl reflections are sharp, all the other reflections are more or less diffuse and connected to each other through diffuse streaks parallel to $c^*$. The intensities of 0kl reflections were collected on a CAD4 diffractometer using MoKα radiation; $1 < \theta < 30^\circ$. After applying an absorption correction, the intensities were reduced assuming an mm symmetry. The profiles of the diffuse reflections and streaks within the 1kl planes of both substructures were measured on the equi-inclination Weissenberg patterns taken at BL-4B using monochromatized synchrotron radiation of wavelength 1.180 Å.

Structure Determination

The structure of the (100) projection was refined by the least-squares method based on 94 $F^*_h$'s. Using anisotropic atomic displacement factors, the refinement converged to $R = 0.067$, $R_w = 0.084$. The LaS and VS$_2$ layers have the symmetry of $Cmm(a)$ and $P(3)2/m$ respectively. In the orthorhombic milieu, however, the latter is lowered to $C2/m1(1)$. The layers are not stacked right over their neighbours of same kind, but are shifted by $\pm a/2$ or $\pm a/2$ for LaS or VS$_2$ respectively. Since these two possible shifts (up and down) for each kind of layers are equivalent owing to the mirror planes perpendicular to [100], stochastic change of the signs leads to a disordered structure. A method for calculating the diffraction intensities of such disordered layer structures has been given by Kakinoki and Komura. Some trial calculations with two probability parameters $A$ for uu-ud or dd-dd and $B$ for ud-ud or du-uu sequences lead to the best agreement between the observed and calculated intensity profiles at $s = 0.64$ and $t = 0.5$. The probability parameters were determined by the least-squares method; $A = 0.88$, $B = 0.77$ for the LaS and $A = 0.88$, $B = 0.83$ for the VS$_2$ substructures. Fig. 2 shows the observed and calculated intensity profiles of 1kξ of the LaS substructure. Each substructure forms an OD structure for itself, but the composite structure as a whole does not. Detailed discussions are published elsewhere.

References

ELECTRON DISTRIBUTION AND CHEMICAL BONDING OF A15-TYPE Cr OBTAINED BY MAXIMUM ENTROPY METHOD

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Introduction
The A15-type Cr exists only in fine particles or thin films together with bcc Cr and further this structure easily translates to bcc above 450°C. Therefore almost all investigations hitherto reported were limited to a crystal facet and magnetic properties. The present report gives the results of the study of the electron-density map and the bonding character of the A15-type Cr obtained by a combination of powder x-ray diffraction data and the maximum-entropy method (MEM).

Experimental
The Cr fine powder used was prepared by evaporation of bulk Cr with purity 99.995% in an Ar atmosphere at about 1.3 kPa pressure. The x-ray diffraction experiments were carried out using both the powder diffractometer installed at the experimental station BL-4B and a Rigaku RINT 1500-type diffractometer. The wavelength of the incident beam in the synchrotron radiations (SR) was selected to be approximately 1Å in order to obtain an optimum diffraction condition. Diffraction intensity data were collected by step scanning with a sampling interval of 0.02° in 2θ. The accumulation time and scan range was 12 s and 2θ=28° to 33° for the former, and 50 s and 2θ=28° to 45° for CuKa radiation for the latter, respectively.

The average particle size of the A15-type Cr was determined as about 700Å from the dependence of the full width at half maximum on the value of the scattering vector for each Bragg reflection by the Scherrer equation.

Analysis
In order to determine the accurate integrated intensities of respective reflections from powder x-ray intensity data, a whole-powder-pattern fitting was carried out with the computer program WPPF by Toraya13. 29 and 13 integrated intensities of the A15-type Cr for SR and CuKa radiation, respectively, were determined. However, the reliability of the integrated intensities for SR was fairly poor because a peak-to-background ratio is somewhat small. Therefore the integrated intensities determined from CuKa radiation were used for the following analyses. The refined unit cell parameter was 4.60089(3)Å. Next, the scale factor was determined by an ordinary least-squares method in order to convert the integrated intensities into the structure factors on an absolute scale. The electron density ρ(r) at a certain pixel located at r was calculated by the MEM. The calculation was done in the region of the minimum asymmetric unit of the point symmetry m̅3m within the divided 64x64x64 pixels.

Results
In the present calculation, the values of R and Rs factors attained at the final MEM map were 0.21% and 0.29%, respectively, and therefore excellent MEM maps were obtained. The electron-density-distribution map of the lower-density region for the (001) plane is shown in figure, where 2x2 unit cells are drawn in order to demonstrate the bonding character. The contour lines (eÅ⁻³) are drawn from 0.4 to 2.0 with 0.1 intervals. The electron-density distribution around 6c-site Cr atoms (Cr(2)) is quite different from that around 2a-site Cr atoms (Cr(1)). The tight covalent bonding between the adjacent Cr(2) atoms within the infinite linear chains is clearly found, and the peak height at the middle point between adjacent Cr(2) atoms is 0.9 eÅ⁻³. The electron densities observed around the points such as 0 1/2 0 show a cross section of the linear chains along the z axis. Furthermore, the electron-density distribution about the Cr(2) atoms spreads in the direction perpendicular to the linear chain.

On the other hand, the asphericity of the electron-density distribution around Cr(1) atom is characterized by the spread toward the centre of the adjacent Cr(2) atoms. These facts may be an indication of the existence of a weak bond between the Cr(1) atom and Cr(2)-Cr(2) bond. In contrast to the valence-electron distribution, the core-electron distribution is perfectly spherical. The peak height at the Cr(1) atoms is 349.1 eÅ⁻³, and at the Cr(2) atoms, the height is slightly smaller, i.e. 343.6 eÅ⁻³.

References
Introduction
The parallel-beam optics using synchrotron radiation for high-resolution powder diffraction experiments can be most effectively used by combining it with either horizontal parallel slits (hereafter called HPS) or crystal analyzer mounted on the diffracted beam side. The crystal analyzer generally gives higher angular resolution, while the HPS is advantageous in obtaining high intensity. Two main purposes of the present study (Toraya et al., 1995) are: to achieve the 0.03° angular resolution and to stack the foils to the 25 mm height, which is required for asymmetric 2θ scanning at a fixed incident angle (Toraya et al., 1993).

Instrumentation and Experimental
Two sets of HPS (hereafter called HPS1 and HPS2 for HPS’s with 0.032° and 0.065° apertures, respectively) were constructed. Some specifications (for HPS1 and HPS2) were: transmission efficiency (%) = 67 & 80, spacing between the two foils (mm) = 0.1 & 0.2, number of foils = 167 & 100, thickness of foil (stainless steel) (mm) = 0.05, length (mm) = 353, effective window size (mm²) = 15 (width) x 25 (height).

The powder diffractometer PFPD at a BL-4B experimental station was used for testing the HPS. The profile intensity was step-scanned at step intervals of 0.005 ~ 0.02° and the counting time of 2 ~ 5 s at each step.

Results and Discussion

Intensity) Table 1 gives a comparison of the peak maximum intensity (counts/sec) and the FWHM (°) of the (111) reflection from CeO₂, observed in various slit settings. These intensities were corrected for the decay of incident beam, background, and the absorption by the air. The peak maximum intensity obtained by using HPS1 is 8.6 times higher than that obtained by 0.1 mm receiving slit (RS). The intensity will become strong more than one order in magnitude if intensities by HPS1 and RS are compared at the same resolution of 0.032°. The intensity is decreased to 59% by replacing the HPS2 with HPS1. The relative transmission efficiency of HPS1 against HPS2 is considered quite good if we take into account the ideal value of 84% (Table 1) and a technical difficulty in stacking parallel 167 very long thin foils of stainless steel.

Table 1. Comparison of peak maximum intensities (I_max) and FWHM’s

<table>
<thead>
<tr>
<th>Slit</th>
<th>I_max</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPS1</td>
<td>14223</td>
<td>0.0319</td>
</tr>
<tr>
<td>HPS2</td>
<td>24236</td>
<td>0.0582</td>
</tr>
<tr>
<td>RS = 0.1 mm</td>
<td>1655</td>
<td>0.0385</td>
</tr>
<tr>
<td>RS = 0.2 mm</td>
<td>5199</td>
<td>0.0564</td>
</tr>
<tr>
<td>RS = 0.5 mm</td>
<td>15348</td>
<td>0.1153</td>
</tr>
</tbody>
</table>

Angular variation of resolution function) Variations of FWHM with 2θ, observed with HPS1 and HPS2 for the reflections from CeO₂, are shown in Fig. 1. The FWHM for (200) reflection at 2θ of 32.810(1)° gave the minimum of 0.030(1)° for HPS1, achieving a primary purpose of the present study.

Fig. 1. Variations of FWHM with 2θ.

References
Introduction

Through the electron density analysis on γ-Fe₂SiO₄, Marumo et al. (1) suggested the possibility that small amount of Fe²⁺ ion in octahedral site is substituted by Si⁴⁺ ion. In the system γ-Fe₂SiO₄-Fe₃O₄ which has also spinel structure, it is interesting to investigate such disorder state because three ion species of Fe²⁺, Fe³⁺ and Si⁴⁺ are to be considered for the cation distribution to tetrahedral and octahedral sites. We performed powder diffraction intensity measurements of γ-Fe₂SiO₄-Fe₃O₄ solid solution synthesized under high pressure in order to determine the cation distribution in this system.

Experimental

The mixture of α-Fe₂SiO₄ and Fe₃O₄ powders was charged in a gold capsule and treated at 10GPa and 1200°C for 5 h. with a 6-8 split sphere type high pressure device. Three kinds of Fe₃-xSiₓO₄ solid solution (x=0.28, 0.49 and 0.70) with spinel structure were prepared. A powder diffractometer PFPD designed for high angular resolution study was used for the data collection. Using a monolithic Si (111) monochromator with fixed beam position, the incident X-ray source with the precise wave length of 1.790 Å, which is similar to the characteristic X-ray of CoKα, was adopted. All optical paths including the sample chamber were evacuated in order to reduce background noise. Sample spinner with 3 rpm was employed for the randomization of sample orientation. The step counting technique of 0.02°/10 sec was applied. Integrated intensities of 111, 330, 400 and 220 diffraction were obtained.

Data analysis and result

Because Si⁴⁺ often has octahedral coordination under high pressure as in Stishovite (2) and that Fe²⁺ prefers octahedral site to tetrahedral one when crystal field stabilization energy is considered (3), we assumed that Fe³⁺ in octahedral site is exclusively substituted by Si⁴⁺. Accordingly we proposed a following structural formula in order to determine the cation distribution;

\[
\{Si^{4+}_{x+y}(1-x)Fe^{3+}_{1-x+y}\}[Fe^{2+}_{1+x}Fe^{3+}_{1-x-y}Si^{4+}_{x+y}]O_4
\]

where y is (Si⁴⁺ in octahedral site)/(total Si⁴⁺). Powder diffraction patterns for various y were simulated with the RIETAN program (4) and compared with those observed. Simulated diffraction intensity ratios of 111/220, 330/220 and 400/220 are plotted against y and by using thus obtained calibration curves, we determined y of each sample.

Obtained y and structural formulas for three samples are shown below. This result strongly indicates that Si⁴⁺ is substituted in octahedral site of γ-Fe₂SiO₄-Fe₃O₄ solid solution. Because of rather large experimental errors, however, the relation between y and x has not been determined. Further investigation by Rietvelt method as well as Mössbauer method which can analyze distribution of Fe²⁺ and Fe³⁺ ions are now in progress.

\[
x=0.28 \quad y=0.30 \pm 0.1
\]

\[
\{Si^{4+}_{0.23}Fe^{3+}_{0.77}\}[Fe^{2+}_{1.33}Fe^{3+}_{0.57}Si^{4+}_{0.10}]O_4
\]

\[
x=0.49 \quad y=0.07 \pm 0.05
\]

\[
\{Si^{4+}_{0.47}Fe^{3+}_{0.54}\}[Fe^{2+}_{1.49}Fe^{3+}_{0.47}Si^{4+}_{0.04}]O_4
\]

\[
x=0.70 \quad y=0.18 \pm 0.1
\]

\[
\{Si^{4+}_{0.57}Fe^{3+}_{0.43}\}[Fe^{2+}_{1.70}Fe^{3+}_{0.17}Si^{4+}_{0.13}]O_4
\]

References

XANES STUDY ON THE Mn-CLUSTER IN PHOTOSYNTHETIC WATER OXIDATION ENZYME DEPLETED OF FUNCTIONAL Cl-

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Hiroyuki Oyanagi3)

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Introduction

Photosynthetic water oxidation is catalyzed by the tetranuclear Mn-cluster located in the photosystem II (PSII) core complex, and proceeds through four stable intermediate reaction states, denoted as S(i = 0 to 3), by use of the energy of four photons (1). Cl- is an indispensable inorganic cofactor for the normal cycling of the S-state mechanism and structural stabilization of the cluster (2). In the absence of Cl-, the capability of photosynthetic O2 evolution is lost and a limited number of oxidizing equivalents for water oxidation could be accumulated on the donor side of PS II (3), but the chemical identity responsible for the charge accumulation is still matter of debate. In this report, we probe the electronic state of the Cl- depleted Mn-cluster by measuring Mn K-edge XANES spectra.

Experimental

PSII membranes with 600-800 μmoles O2/mg Chl/h were isolated from spinach, and prepared for XANES as described (4,5). For Cl- depletion, the membranes were washed with 2 M NaCl for removal of the 16 and 24 kDa extrinsic proteins, in which Cl- release is facilitated. After three washes with a Cl- free buffer containing 400 mM sucrose, 20 mM MES-NaOH (pH 6.5), the resultant Cl- depleted membranes were suspended in the same Cl- free medium supplemented with 20 mM Mes-Ca(OH)2 (pH 6.5) at 5 mg Chl/ml. An 18 μl aliquot of sample applied on a membrane filter was illuminated with a saturating Nd-YAG laser flash at 10°C, and then immediately cooled to 77 K in liquid N2 (4). XANES spectra were measured at the Photon Factory of the National Laboratory for High Energy Physics beamline 4B using Si (111) monochromator. Fluorescence X-ray was detected with a modified silicon (lithium) solid-state detector placed 10 mm away from the sample which was kept in darkness at 30 K during data collection (5). Energy calibration was performed using the pre-edge peak at 6543.3 eV of the KMnO4 spectrum simultaneously measured with an absorption mode. For each spectra, seven to ten scans were averaged. Processing of the data was carried out with IGOR software (Lake Oswego, Oregon, U.S.A.).

Results and Discussion

The second derivatives of the Mn K-edge region in the control and the Cl- depleted membranes were shown in Fig. 1 in order to emphasize the effects of Cl- depletion and flash illumination on the edge features. The overall features of the second derivatives of the spectra in the control membranes were in good agreement with those previously reported (6) although the sample concentrations used in the present study were much lower than those reported. The characteristic features found in the control spectra (a) were also seen in the Cl- depleted spectra (b), but Cl- depletion resulted in some changes in the spectra, indicating that subtle conformational changes were induced in the Mn-cluster by Cl- depletion. A flash illumination, however, induced a quite similar changes in the spectra both in the control and in the Cl- depleted membranes. In the control membranes, it has been indicated that the changes in the oxidation state of the Mn atom from Mn (III) to Mn (IV) is responsible for the changes in the features of the second derivatives of the spectra upon S1-to-S2 transition (6). The present results, therefore, implied that the Mn-cluster is oxidized from Mn (III) to Mn (IV) after 1 flash in the absence of Cl- as the normal S1-to-S2 transition.

Fig.1. The second derivatives of the Mn K-edge spectra. (a) and (b) are control PS II membranes after 0 and 1 flashes, (c) and (d) are Cl- depleted membranes after 0 and 1 flashes.
STUDY ON THE SHORT-RANGE ORDERING IN DISORDERED CU-PT ALLOYS BY DAPS TECHNIQUE

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The X-ray diffuse scattering intensity from disordered Cu-Pt alloys whose compositions were 7.0, 10.0, 15.0, 24.5, 32.0 and 75.0 at.% Pt has already been measured at room temperature (1). Twofold and fourfold splittings of diffuse scattering due to short-range order were observed at 100, 110 and their equivalent positions (X points), respectively, for Cu-16.0, 24.5 and 32.0 at.% Pt alloys, where the separation of split diffuse maxima increases monotonically with increasing Pt content. On the other hand, no splitting of diffuse scattering was observed at Cu-<16.0 at.% alloys. Extra diffuse maxima were observed at 1/2 1/2 1/2 and its equivalent positions (R points) for all samples, the intensity being related to the concentration. The SRO parameters were determined from all six alloys. The sign and magnitude of 200-parameter strongly depend on the ratio of R- to X-point diffuse intensities. Synthesized data indicated that the first few SRO parameters dominate the R-point maxima, though the sign and magnitude of higher-order parameters play an important role in causing the appearance of split diffuse maxima. We have proposed that there are two types of correlation in the disordered state of Cu-Pt alloy system, i.e. between the consecutive (111) atomic layers and due to Fermi surface imaging.

Recently, Stragier et al. (2) have developed a new X-ray technique, diffraction anomalous fine structure (DAFS), which combines the long-range order sensitivity of diffraction techniques with the short-range order sensitivity of absorption techniques. In fact, they have demonstrated that the synchrotron DAFS measurements for the Cu(111) and Cu(222) Bragg reflections provide the same local structural information as X-ray absorption fine structure and described how DAFS can be used to provide enhanced site and spatial sensitivities for polyatomic and/or spatially modulated structures. We, have, therefore, planned to observe the DAFS spectra at the X and R points in the reciprocal space, mentioned above, for single crystals of Cu-Pt alloys. We will understand whether the two types of correlations exists in the disordered state or not, after analyzing the experimental results. It is now in preparation.

References
Introduction
It is known that fcc-Fe in epitaxially grown thin films on Cu single crystal substrates by MBE (molecular beam epitaxy) is ferromagnetic, whereas the fcc-Fe precipitated in a supersaturated solid solution of Cu(Fe) alloy shows antiferromagnetism [1, 2]. A model for fcc-Fe which was first suggested by R.J. Weiss and theoretically calculated by Moruzzi et al. explained the ferromagnetism and non-ferromagnetism of fcc-Fe [3, 4]. Moruzzi et al. reported that the magnetic moment of Fe atom in fcc-Fe depends on interatomic distance of Fe atoms and there are two magnetic (high and low spin) states and one non-magnetic (low spin) state. Since these magnetic states are thermodynamically at nonequilibrium, their precise magnetic properties and the threshold interatomic distance of the transition were not explained. In this work we investigate the MBE grown fcc-Fe samples by fluorescence EXAFS. Since the EXAFS measurement can reveal the interatomic distances in samples, it was expected that the relationship between the interatomic distance of Fe atoms in fcc-Fe and their magnetic property can be discussed from the results.

Preparation of Samples
Three fcc-Fe samples were prepared by MBE. First of all, on Cu (100) substrates, Ni-doped Cu buffer layer, Au-doped Cu buffer layer, and non-doped Cu buffer layer, were grown for each samples, respectively, to control the distance of Fe atoms in the following layers. On the buffer layer, 7ML thick Fe layer was grown, and then capped by 14ML thick doped or non-doped Cu layer, respectively. The Fe(7ML)/Cu(14ML) structures were repeated 10 times. Finally, 400Å doped or non-doped Cu cap layers were grown. The growth rate and substrate temperature were about 1.2 ~ 2.2Å/min and 60 ~ 90°C, respectively.

Experiments and Discussions
Magnetization was measured by VMS and SQUID. All samples show ferromagnetism. In spite of our expectation that the magnetic moment should be controlled by the lattice constants of the buffer layers, the magnetic moment per Fe atom in fcc structure was estimated about 1.0μB for all the samples.

EXAFS measurement was conducted at BL4C in Photon Factory, and analyzed the distance between Fe atoms in fcc-Fe layer. Back scattering amplitude and phase factor calculated theoretically by A.G. McKale et al. were used to analyze the measured EXAFS data [5]. Two shell model was assumed, in other words, it assumed that two Fe-Fe distances exist in the fcc-Fe layer.

Fig. 1 shows the calculation results of Moruzzi et al., and experimentally determined Fe-Fe distances by the present EXAFS measurement were plotted in the figure. As shown in this figure, there are two phases of fcc-Fe with long and short Fe-Fe distances. The Fe atoms with long Fe-Fe distance take high magnetic moment (~ 2.4μB). The Fe atoms with short Fe-Fe distance take almost 0 magnetic moment. The ratio of these two phases was almost equal. Thus the mean magnetic moment of all samples were nearly equal to 1.0. This value agree with the measured magnetic moment.

Acknowledgments
Authors would like to thank Prof. M. Matsui. All fcc-Fe samples were offered from his laboratory.

References

Figure 1: The results of calculation and experiment
FLUORESCENCE EXAFS STUDY ON LOCAL STRUCTURE OF LATTICE-MISMATCHED HETEROEPITAXIAL SEMICONDUCTOR LAYER AS A FUNCTION OF THICKNESS

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Introduction
Heteroepitaxially grown semiconductor layers are used as a base of various functional electrical and optical devices. For example, semiconductor laser diodes consist of double heterostructure, and HEMTs (high electron mobility transistors) also make use of the heteroepitaxial structure.[1, 2]

In order to obtain device quality heteroepitaxial layers, combinations of lattice-matched materials are usually selected. When we combine two or more materials in a continuous heteroepitaxial layer, the condition of lattice matching among these materials is a more important factor than other characteristics of the materials. In a lattice-mismatched heterostructure, the crystalline quality of the layer thicker than a critical thickness is degraded by the generation of misfit dislocations.[4]

Thus, it is important to investigate the crystalline quality of the layer around the critical thickness in detail to realize the lattice-mismatched heteroepitaxial layer of device quality.

In this work, heteroepitaxial InPAs layers grown on InP substrates are investigated by EXAFS (extended X-ray absorption fine structure) measurement. InPAs/InP system is one of the lattice-mismatched systems. InP_{0.4}As_{0.6} contains at most 3.2% of lattice mismatching to InP at As composition x = 1, i.e., InAs.

Preparation of Samples
InPAs and InAs layers were grown on InP substrates with 1000Å-thick InP buffer layers. InPAs and InAs layers were covered with 20Å InP cap layers to protect the surface of InPAs and InAs layers and to assure the thicknesses of them. All InPAs and InAs layers were grown on (100)-oriented InP wafers by OVMPE (organometallic vapor phase epitaxy) at 620°C. Trimethylindium(TMIn), arsine(AsH₃), and phosphine(PH₃) were used as source gases.[3]

The As composition of prepared InP_{1-x}Asₓ layers were x = 0.6 and x = 1.0. The lattice mismatch between InP substrate and InP_{0.4}As_{0.6} is 1.9%, and that between InP substrate and InAs is 3.2%. The critical thicknesses of these systems are calculated to be about 85Å and 40Å, respectively.[4]

Experiments and Discussions
These samples were measured by EXAFS at the As K-absorption edge. EXAFS can reveal the bond length between As atom and its nearest neighbor In atom.[5] Fig. 1 shows As–In bond lengths measured by EXAFS as a function of layer thickness. Dash-dotted-line in the figure indicates the As-In bond length in a free standing InP_{0.4}As_{0.6} alloy. 2.60Å in the thinnest samples is nearly equal to the As-In bond length of the dilute As in InP matrix.[5] Beyond the critical thicknesses, InPAs and InAs show gradual bond accommodation in the crystals. The mechanism of the gradual bond accommodation is discussed in [6].

Acknowledgments
The authors would like to thank Mr. H. Kamei, for his cooperation in preparing samples.

References

Figure 1: Bond lengths of As–In in InP_{0.4}As_{0.6} layers grown on InP substrates measured by EXAFS. Dash-dotted-line at 2.61Å in the figure indicates the As-In bond length in a free standing InP_{0.4}As_{0.6} alloy.
EXAFS STUDY OF MBE GROWN CuInSe₂

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Introduction
CuInSe₂ (CIS) has been considered to be a promising material for the solar cells with high conversion efficiency, although the structure of this material has not been established. The improvement of the efficiency can be realized if the microscopic structure is clarified as a function of composition. In this study the structures of CIS grown by molecular beam epitaxy (MBE) were characterized by EXAFS for the local structure, changing the Cu/In ratio systematically.

Experimental
CIS epitaxial layers grown on GaAs(001) with Cu/In ratios (g) ranging widely from g = 0.81 to 1.53 were measured. From the X-ray diffraction study these epitaxial layers are highly oriented single crystal. In spite of a lattice mismatch in a-direction, 2.3% between CIS layer and GaAs substrate, the a-spacing of CIS nearly agreed with the values in bulk CIS data, which suggests that these epitaxial layers are almost relaxed. The EXAFS measurements¹) were performed at the beamline BL4C and BL13B1 of the Photon Factory, National Laboratory for High Energy Physics using synchrotron radiation.

Discussion
The results revealed the local structure of chalcopyrite CIS epitaxial layer, such as bond lengths (R₁In-Se, R₉Cu-Se) and mean square relative displacement (σ₁In-Se, σ₉Cu-Se). From σ₉Cu-Se values the structural disorder is minimized around the stoichiometry (Fig. 1). The result agrees with that of X-ray diffraction: the narrow region of the chalcopyrite phase around the stoichiometry. The anion displacement, u-values was obtained experimentally according to the following equation where lattice parameter (a) obtained by X-ray diffraction is used.

\[ u = \frac{1}{4} - \frac{R₉^{2}In-Se - R₉^{2}Cu-Se}{a^2} \]

Figure 2 indicates that the deviation of the Se position from the ideal zinc-blend structure takes the maximum value around the stoichiometry which is closest to the value of the ideal zinc-blend structure; 1/4. It shows that the deviation from the stoichiometry increases the distortion in the chalcopyrite unit cell.

References

Fig. 1 The bond length and mean square relative displacement of Cu-Se bond at 80 K with various Cu/In ratio.

Fig. 2 The u value obtained from the EXAFS measurement of Se-edge at 300K with various Cu/In ratios.
STRUCTURAL ANALYSIS OF MOLECULAR ORIENTATION IN THIN FILM OF PENTACENE DOPED WITH IODINE

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Introduction

It is well known that highly ordered thin films of pentacene (PEN) having quasi-two dimensional shape, are fabricated by a sublimation method. The author found that the intercalated structure was formed and the film was transformed into two-dimensional conductor due to doping with iodine. However, the information concerning molecular orientation of iodine in the intercalated structure has hardly been obtained so far. The author reported that molecular orientation of polyiodides in a conducting LB film based on TTF derivatives has been determined by XANES spectra using polarized SOR beam. In this study, molecular orientation of iodine was surveyed from the analysis of angular dependence of 1-Ll XANES spectrum using polarized SOR beam.

Results and discussion

Measurements are performed with the alignments of the system as shown in Figure 1, where E is the incident beam. M indicates the molecular axis of iodine. 1-Ll edge spectra were measured by changing the electric field vector of incident beam angle θ. The measurements were carried out at room temperature in air and the measured sample was covered with polyester thin film with the thickness of 10 μm in order to avoid the elimination of iodine.

XANES spectra of the iodine doped film with the incident beam angle of 10, 55, 80 degrees, are shown in Figure 2. The intensity of half filled 5p(σ*) peak at 5.183 keV decreased with increasing the angle θ, which indicated that the long axis of iodine molecule was parallel to the substrate plane. The normalized intensities of the peak to the intensity of edge jump at 5.2 keV corresponding to the molecular density of iodine in the film, are plotted to the angle of incident beam: θ (Figure 3). The plots are in good agreement with the calculated values of both parallel orientation to the plane and randomly oriented in the plane. These results are consistent with the previous results from X-ray diffraction pattern where the change in the spacing along the c-axis; 4A, corresponded to the ionic diameter of iodine, and from electron diffraction where the molecular orientation of iodine did not affected to the diffraction pattern. It concludes that iodine molecules are oriented with the long molecular axes parallel to the plane in the intercalated PEN film.

References


Figure 1. Schematic representation of measurement alignment

Figure 2. 1-Ll XANES spectra of iodine doped PEN film with angle of incident beam (a) 10 deg., (b) 55 deg., and (c) 80 deg.

Figure 3. Normalized peak intensity as a function of incident beam angle.
Anomalous scattering of single crystal Cu/Ni superlattices

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Introduction

There has been much interest in elastic features in multi-layer materials. In 1983, Tsakalakos et al.1 reported the elastic anomaly of the system with the modulation wavelength in the vicinity of 17 Å. We have to stress that their samples were textured ones. On the other hand, Davis et al. and Kumar et al.2-4 reported no elastic anomalies were seen by various methods in 1991. We have synthesized single crystal CuNi superlattices. Origin of the elastic anomaly is still unknown. One of the candidate is coherency strain of each layer. It is difficult, however, to obtain the information of the lattice spacing along the growth direction in diffraction method. Only we can do is to fit the measured intensity profile of superlattice and to extract the various parameters. A small angle reflection provides the information without the lattice deformation. It is, however, difficult to detect the small angle scattering because of small contrast between two constituents. Reflection at the interface is related to the Fresnel reflectivity,

$$N = \frac{\tilde{n}_v - \tilde{\eta}_w}{\tilde{n}_v + \tilde{\eta}_w}, \quad (1)$$

where $N$ is the complex reflectivity of the interface and $\tilde{\eta}_v$ is the complex optical constant of the v layer ($v = A$ or B).1 Calculation of the reflectivity is performed as such the sum of the reflectivity times the phase factor. The summation is taken over the whole layer. The diffraction data are compared with the result of the dynamical theory considering absorption.

Experimental

Samples were prepared on a GaAs substrate for (001)-Cu Ni superlattice and on a YSZ substrate for (111)-Cu Ni by MBE method5 with the modulation wavelength (A) ranging from 8 Å to 80 Å. Wavelength of the used radiation was determined so that the contrast between two layers became high, that was between 1.30 Å to 1.54 Å. These parameters were determined by the anomalous scattering factors by the literature 6. Measurements were performed in the BI-4C.

Results and Discussion

Figure 1 shows the profile of small angle diffraction from [Cu Ni] superlattice with A = 36 Å. Many satellite peaks are observed between $\lambda = 1.38$ Å to $1.50$ Å, which are correspondent to the region of high contrast between two constituents. The even order reflection is seen to be slightly weak compared with the odd one. This is acceptable because of almost equi-thickness superlattice structure. fluctuation in the superlattice from the profile of the large-angle diffraction in the laboratory. The thickness of the distinct layer is two or three layers (4 to 6 Å) and the fluctuation of the period was only 1 layer. However, there is some uncertainty in the fitting of so-called step model calculation because of lattice strain. From the measurement, we can obtain the detailed information of the fluctuation of the superlattice. We are planning to extract the structural parameters consistently with the large angle diffraction.

References

X-RAY DIFFRACTION STUDY OF TYPE-B CaF$_2$/Si(111) INTERFACE.

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INTRODUCTION

Heterostructure of CaF$_2$/Si(111) has been providing us interesting subjects on epitaxial growth of insulator on semiconductor surfaces. Especially interface of this system shows a complex structure which depends on the details of growth condition. For example, two kinds of interface structures, type-A and type-B are known to exist [1]: type-B interface is obtained at high growth temperature above 700 °C, where the CaF$_2$(111) layer is rotated 180° with respect to the Si(111) substrate [2]. We studied the structure of type-A interface by X-ray crystal truncation rod (CTR) scattering technique [3,4]. In the present study, type-B interface with long interface spacing has been investigated.

EXPERIMENTAL

Epitaxial layers of CaF$_2$ on Si(111) were grown in a molecular beam epitaxy (MBE) system of A.F.Ioffe Physico-Technical Institute.

X-ray measurements were carried out by using the Weissenberg camera at BL-6A2 so as to obtain the whole pattern of X-ray diffraction in reciprocal space and intensity of 00l specular CTR scattering. Type-B interface with long interface spacing (= distance between the middle of the top Si layer and the first Ca layer = 4.60 Å) of the sample was confirmed.

A vertical type of four-circle diffractometer with a Si(111) crystal analyzer at BL-4C was also used for observing the non-specular CTR scattering which is necessary to determine the lateral structure of CaF$_2$ layers. Consequently we collected the integrated intensity of the CTR scattering around 003, 015, 014, 0-15, and 0-14 Bragg points indexed in hexagonal lattice unit.

RESULTS AND DISCUSSION

To analyze the CTR intensity we adopted the formula based on the kinematical scattering theory. Figure 1 and 2 show the observed and calculated CTR scattering. The best fitted model is the interface structure in which the Ca atom occupies the T-site (top Si atoms in the first Si layer [2]). For other sites, T4 and 1H sites proposed so far [2], we could exclude them because of ill agreements between observation and calculation in these models. This result is in accordance with our study on the type-A interface [4], but shows a sharp contrast to the structure of the type-B with short interface spacing [2,5,6]. In [2,5,6] the Ca occupies on the T4 site for type-B with short interface spacing.

Physical meaning of the refined parameters describing the structure of thin film, morphology of the interface and the surface will be discussed thoroughly in near future. Further observation is necessary to reveal the relation of the interface structure and growth condition.

Figure 1: Observed and Calculated (01l) CTR scattering.

Figure 2: Observed and calculated (0-1l) CTR scattering.

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REFERENCES

There is little direct information about the atomic structure around a vacancy or vacancy clusters in quenched fcc metals, because experimental investigations have proved to be difficult as a result of the small sizes of vacancy clusters.

X-ray diffuse scattering methods are capable of providing detailed information on small clustered defects when scattering models are available. We have observed small vacancy type dislocation loops in quenched copper by X-ray diffuse scattering. In gold, well investigated by electron microscopy, the formation of vacancy clusters can be followed from the very beginning up to the final form of the large stacking fault tetrahedra.

In this study, we have tried to make diffuse scattering measurements for the detection of small vacancy clusters and stacking-fault tetrahedra in quenched pure gold crystals.

The specimens of single crystal plates of 5 x 7 x 0.4 mm in size with their surfaces parallel to the (111) crystallographic plane were spark-cut out of single crystal rods (nominal purity 99.99%). Specimens were quenched from 940°C into 4°C water in atmosphere of argon + 10% hydrogen gases.

X-ray diffuse scattering experiments were performed on a Huber 5020.4 four circle diffractometer at room temperature installed at BL-4C. A wavelength of 0.15405 nm (corresponding to CuKα) was selected by the double crystal Si 111 monochrometer with sagittal focusing.

The quenched specimens were kept at room temperature. Diffuse scattering measurements near the (111) reflection in [111] direction (θ-2θ scan) was carried out at room temperature for the quenched and annealed specimens. Fig 1 shows the Huang diffuse scattering intensities as a function of q in a double logarithmic scale. The q^-2 dependence line is also shown in the figure, which means the characteristic features of scattering from single point defects or small clusters. The results of the intensities would rather indicate near q^-3 dependence. This may be associated with small dislocation loops [1].

Detailed analysis is in progress.

β-galactosidase from E. coli is a classic enzyme in molecular biology. There is a large amount of biochemical and genetic data available, but, until recently nothing was known of the structure of the enzyme.

The structure of the native enzyme was determined by Jacobson et al. in 1994. It is homotetramer of 460,000 daltons. Each subunit is 1023 residues long and folds into 5 different domains. Tetramerization is required for activity because each of the four active sites is completed by a loop that reaches across from a neighboring subunit.

Recently we have analyzed the binding modes of four inhibitors in order to establish a structural basis for catalytic activity of the enzyme.

The natural substrate for β-galactosidase is lactose with hydrolysis leading to two possible outcomes. In one outcome glucose and galactose are produced. In the other outcome or the glucose is reattached to the galactose to form allolactose. Allolactose enhances β-galactosidase expression. In this way a cell that has only lactose as a food source can both digest lactose and produce more β-galactosidase.

Kinetic experiments have shown that the catalytic mechanism is a two step reaction with a possible covalent intermediate. The inhibitors we studied are two substrate analogs (phenyl-thio-β-D-galactoside and 2-F-lactose) a covalently bound ‘intermediate analog’ (2-F-galactosyl-enzyme) and an inhibitor thought to be a transition state analog (galactonolactone).

The space group of the crystals is P21 with cell dimensions 107.5 Å, 207.9 Å, 509.9 Å, 90.0°, 94.7°, 90.0°. There are four tetramers per asymmetric unit. Data were collected and processed on the four inhibitors to 2.6, 2.6, 2.6, and 3.0 Å resolution. R-merges were 0.08, 0.09, 0.09, and 0.09.

The electron density maps clearly show that the two substrate analogs bind in nearly identical positions in the active site. The binding interactions include hydrophobic stacking with a tryptophan and some hydrogen bonds between protein side chains and hydroxyls on the galactosyl part of the inhibitor.

The covalently bound inhibitor binds in the same orientation as the ‘transition state’ analog. Thus there appears to be two binding modes - the substrate, (disaccharide) mode and the intermediate (single ring) mode. In both modes the 6' oxygens point in the same general direction and make similar contacts with the protein. However the single ring ligands are rotated 90° about the 6' hydroxyl to a position deeper in the active site. The single rings also make different protein contacts with 3 of the 5 hydroxyls of the galactosyl ring.

The “single ring” modes also show a that a loop of about 10 amino acids swings about 9 Å toward the active site. The effect of this shift is to occlude part of the substrate binding site.

The implications for catalysis are, at present, uncertain. Glutamate 537 has been identified biochemically as the catalytic nucleophile. The substrate analog complexes, however show that this residue is 6 Å from the C1 carbon and it is not immediately obvious how nucleophilic attack by Glu 537 on this carbon could occur.

Another mechanism discussed in the literature is an electrophilic attack on the glycosidic oxygen by the active site magnesium. However, the magnesium is 8 angstroms from the glycosidic oxygen.

There is, of course, the possibility that the binding seen in the crystals may not represent productive binding. On the other hand, both substrate analogs bind the same way even though they are quite different in nature. This conformation is also consistent with the stereochemistry of the reaction by leaving the β side of C-1 open for water to attack. Furthermore, binding seems to be determined by the same sort of interactions that would be expected for a protein substrate complex. Thus it seems reasonable to suppose that the observed mode of binding for the substrate analogs resembles the Michaelis complex.

Resolution of these questions must await completion of the crystallographic refinement of these complexes.

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References
CRYSTAL STRUCTURE OF STREPTOMYCES ERYTHRAEUS TRYPsin AT 1.9Å RESOLUTION

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Introduction

Some of the authors had already reported the crystal structure of Streptomyces erythraeus trypsin (abbreviated as SET) at 2.7Å resolution(1). The structure analysis of SET suggested that the quality of the X-ray data for the native crystal was poor beyond 2.85Å resolution. Therefore it was hardly difficult to make a comparison of the structure between SET and other trypsins in detail. Re-collection of the X-ray data of SET and the crystal structure analysis were carried out, in order to determine the precise spatial arrangement of the active sites at pH 7 and to compare the tertiary structure with the other crystal structures of trypsin.

Experimental

A new data set to 1.8Å resolution was recollected on the station BL6A2 at the Photon Factory synchrotron radiation facility using a screenless Weissenberg camera (2) cooled to 283K. The X-ray wavelength was 1.04Å. The radius of a film cassette of 287mm and the collimator size of 0.2mm were used. The oscillation range of 6° with an overlap of 1° and the Weissenberg coupling constant of 3°/mm were adopted. One crystal was used to collected 17 packs of Fuji imaging plates. A total of 46,035 reflections between 25 and 1.8Å resolution were obtained, of which 17,947 reflections were independent. An Rmerge was 0.117. The completeness of the data set between 7 and 1.9Å resolution is 69.2%.

Rotation parameters were determined with the fast-rotation function. The search model adopted was the structure of Streptomyces griseus trypsin(SGT) from the Protein Data Bank (entry number 1SGT). The SGT model is refined to an R value of 0.230 at 1.7Å resolution. The optimum result was obtained using data between 7 and 3.5Å resolution with an outer radius of Patterson integration of 20.4Å and a 5° step in all three spherical polar angles (ψ, φ, χ). Unambiguous and symmetry related peaks were obtained.

Translation parameters for the correctly oriented model were determined with the X-PLOR program system.

The SET model excluding three C-terminal residues (Gly225 to Val227) was built from a IF^-F^ or omit maps. In the last step of the X-PLOR refinement the model consisted of the 224 amino acid residues and 99 water molecules gave an R factor of 0.193. In order to optimize the structural geometry, 25 cycles of restrained least-squares refinement were performed, using the program PROLSQ. The final model contains 1,619 protein atoms and 92 water molecules. No Ca2+ ion was assigned in the crystal structure. The final R factor is 0.203 for12,860 reflections with a 3 σ (F) cut-off between 7 and 1.9Å resolution.

Results and discussion

The disposition of the catalytic triad is compared with those of bovine trypsin(BT) and SGT in Fig. 1. The side-chains of the catalytic triad are mutually of similar conformation among these three proteases. The χ1 torsion angles of His42(57), Asp88(102) and Ser179(195) distribute within ±5° from each mean value. The good coincidence for the positions of both the His and Asp residues is observed between SET and BT, though the positions of these residues in SGT shift by more than 0.5Å from those of SET or BT (Fig. 1). A rather small positional difference of 0.38Å occurs on Ser1790 in BT and SGT. On the other hand, the position of Ser1790 in SET differs from that of BT by 0.82Å or from that of SGT by 0.84Å. In spite of these structural differences among SET, BT and SGT, the hydrogen bond distances concerned with the side-chains in the catalytic triad coincide fairly well. Only the Asp880 δ2 atom is hydrogen bonded to the His42Nδ1 atom, which is also hydrogen bonded to the Ser194(214)Oδ1 atom in the three proteases.

Fig. 1. The disposition of the catalytic triad. SET(Thick lines), BT(medium lines) and SGT(thin lines).

References

We have determined X-ray crystallographic structure of bar-headed goose oxyHb to a resolution of 2.0Å. The R value of the model is 19.88%. The overall structure is similar to those of mammal R state Hbs. The r.m.s. differences of the main chain coordinates between the tetramers of bar-headed gooses oxy Hb and human oxy−, co−, horse met Hb are 1.099Å, 1.016Å and 0.949Å respectively.

The "switch region" of the alb2 interface has a wider gap than those of human R state Hbs, due to the residue Gln replaces Thr at the position 38a in goose Hb. This amino acid substitution also cause slightly quaternary structure change.

Compared to human oxyHb, the stereochemistry of the haem group region of both the a and b chains show some difference. Particularly in the b subunit, the rotation of the distal HisE7(63)imidazole ring about the Ca−Cβ bond and its large distance from the haem plane make a hydrogen bond possible between E7 Ne and the terminal binding oxygen atom, while in human oxyHb this hydrogen bond either does not exist or is only very weak.

The B chain N and C termini are well-localized, and together with the other neighbouring basic groups, they form a strong positively charged pocket at the entrance to the central cavity around the molecular dyad. The well-ordered conformation and the three-dimensional positive charge distribution confirm that this area is the bird IPP binding site. Residue pairs from two b chains; ValNAl(1), HisNa2(2), LysE6(82), HisH17(139), ArgH21(143) and HisHC3(146) involve in IPP binding.

The penultimate tyrosine residues of both the a and b chains (140a, 145b) stay in the pocket formed by the F and H helices as in human Hbs. However, in the a chain, TyrHC2(140) contact closely with both the haem proximal F helix and the alb2 interface FG corner. In the b chain TyrHC2(145) locates at the Hb IPP binding site and its phenolic oxygen atom from strong hydrogen bond with the alb2 interface ValFG5(98) b carbonyl oxygen atom. These two penultimate residues TyrHC2(140)a and TyrHC2(145)b seem to play a more important role in propagating structural changes between different part of the molecule, such as the molecular surface, alb2 interface and the haem proximal side in bar-headed goose Hb.

From the model, the substitution of Pro(119a) to Ala in bar−headed goose Hb alb1 interface, which is unique among bird and mammal Hbs and thought to be critical for the enhanced oxygen affinity in bar−headed goose Hb, cause no significant change in protein structure. The Ala(119)a adopts a proline−like main chain conformation in Ramachandran plot, which suggests the structure of this area is very conserved. The Pro(119)a to Ala substitution may impose its effect on the interchain contact in the T state Hb.
**Introduction**

Aminoacyl-tRNA synthetases (aaRS) are a class of enzymes that catalyze the first step in protein biosynthesis. In this reaction, each amino acid is attached to the 3' end of its cognate tRNA chain. An ester linkage is formed between the amino acid and a hydroxyl group of the 3'-terminal adenosine of tRNA. The energy required for formation of the ester bond is supplied by the hydrolysis of ATP according to the reaction

\[
\text{aa + ATP + tRNA } \rightarrow \text{aa-tRNA + AMP + PPi}
\]

where aa denotes amino acid. Mg\(^{2+}\) ion is also required in this reaction.

We propose a new reaction mechanism as follows. At first, Mg\(^{2+}\) ion is coordinated tetrahedrally with two water molecules and residues of aaRS. Then P\(\beta\)=O and P\(\gamma\)=O in ATP approaches Mg\(^{2+}\) ion and two water molecules are displaced.

Methionyl-tRNA synthetase (MetRS) was reported to recognize strictly anticodon of tRNA. When the CAU anticodon of tRNA\(^{\text{Met}}\) have been transformed to the UAC anticodon of tRNA\(^{\text{Val}}\) and the CAT anticodon of tRNA\(^{\text{Leu}}\). MetRS catalyzes methionylation of those tRNA mutants sufficiently. Therefore, MetRS could be a good example to know the mechanism of the anticodon recognition.

In order to know the reaction mechanism of aminoacylation and molecular recognition, dimerization-domain-truncated MetRS from Thermus thermophilus HB8 of molecular weight 58,000 have been analyzed by X-ray crystallography.

**Experimental and Results**

Crystals were obtained in a PEG6,000 solution at pH7.5, 20°C by the hanging drop vapor diffusion method. The crystal is space group \(P2_12_12_1\), and unit cell dimensions \(a=83.1, b=117.4, c=56.7\) Å. The measured density \(D_c=1.22\) g/cm\(^3\) gives a calculated solvent content of 48.1 % and \(V_m=2.37\) Å\(^3\)/Dalton. Isomorphous heavy atom derivatives were prepared by a soaking method. Intensity data for native and derivative crystals were collected using Weissenberg camera at wavelength of 1.00Å by synchrotron radiation source at Photon Factory in Tsukuba. A data set for native crystals with 25611 independent reflections, 5.95% R-merge and 88.7% complete to 2.2Å was obtained. The data collection statistics are shown by Table 1.

The multiple isomorphous replacement (MIR) method was applied using PROTEIN program package. After refinement of metal parameters for CH\(_3\)CO\(_2\)HgC\(_6\)H\(_4\)N\(_2\), K\(_2\)PtCl\(_4\) and Sm(OAc)\(_3\) derivative crystals, the overall figure of merit was 0.65 by PROTEIN to 3.5Å resolution. Heavy atom parameters are shown by Table 2.

The phase obtained was improved by solvent flattening method using the program DM. The last figure of merit was 0.72 to 3.5Å. The electron density map calculated from this phase gave obvious molecular boundary against solvent region.

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<th>Table 1. Data collection statistics</th>
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<td>Crystal</td>
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<th>Table 2. MIR heavy atom phasing statistics</th>
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<td>Derivative</td>
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<td>Phasing power</td>
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<td>Cullis R factor</td>
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soaking conditions

Hg\(_1\) : CH\(_3\)CO\(_2\)HgC\(_6\)H\(_4\)N\(_2\) 1.25 mM 1.5days
Hg\(_2\) : CH\(_3\)CO\(_2\)HgC\(_6\)H\(_4\)N\(_2\) 1.3 mM 1days
Pt\(_1\) : K\(_2\)PtCl\(_6\) 10mM 8days
Pt\(_2\) : K\(_2\)PtCl\(_6\) 10mM 4days
Sm : Sm(OAc)\(_3\) 2mM 2days
DATA COLLECTION AND PROCESSING OF BASIC PHOSPHOLIPASE A$_2$ FROM THE VENOM OF AGKISTRODON HALYS PALLAS

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Introduction

Phospholipase A$_2$ (PLA$_2$) [EC 3.1.1.4] catalyzes specifically the hydrolysis of the C-2 ester bond of 3-sn-phosphoglycerides to produce lysophosphatidylcholine and fatty acids. In addition to this esterasic activity, snake venom PLA$_2$ possesses various pharmacological activities. The venom of *Agkistrodon halys* pallas contains three homologous PLA$_2$. The acidic PLA$_2$ exhibits activity of inhibiting platelet aggregation. The neutral PLA$_2$ is a presynaptic neurotoxin, designated as Agkistrodotoxin. The basic one, in common with numerous basic phospholipase A$_2$ from other sources, has ability to hemolyze erythrocytes. Moreover, compared with most of other phospholipase A$_2$, this basic enzyme is unique in their behaviour toward natural substrates concerning the hydrolysis of *E. coli* membranes in the presence of a bactericidal permeability increasing (BPI) protein from neutrophil source [1] [2]. Thus it is of interest to understand the structural bases of the functional variety of these PLA$_2$. The crystal structure of acidic PLA$_2$ has been determined at 2A resolution [3].

Experimental and Results

Basic PLA$_2$ from *Agkistrodon halys* pallas was kindly provided by Professor Y.C. Zhou group in Shanghai Institute of Biochemistry. Two crystal forms of basic PLA$_2$ have been crystallized in the basic conditions using vapour diffusion techniques. One belongs to monoclinic system, another orthorhombic. The details of crystallization will be published elsewhere. Diffraction data of both forms have been collected to moderate resolution using synchrotron radiation-imaging plate-Weissenberg camera system [4] at BL6A2 station in Photon Factory. The wave length of 1.0A and camera radius of 286.5mm were used.

(a) Monoclinic form. Only a few crystals were obtained. The crystal is small and fragile. The crystal was carefully mounted with long crystal edge parallel to the spindle axis of Weissenberg camera. The oscillation range ($\Delta$\phi) and the ratio (C) of crystal rotation to the detector movement was 5.0$^\circ$ and 2.0$^\circ$/mm respectively. Diffraction patterns were recorded on Fuji Film imaging plate and digitized on a Fuji Film BA100 photo reader system. The symmetry and cell dimensions of the crystal was determined by auto-indexing program in WEIS program package [5] on computer FACOM using two sheets of imaging plate which recorded small-angle oscillation patterns with $\phi$ angle of 45$^\circ$ and 90$^\circ$ respectively. The results show that the crystal belongs to C2 space group with unit cell dimensions of $a$=100.24A, $b$=54.16A, $c$=117.39A and $\beta$=120.74$^\circ$. The predicted positions of reflections, calculated based on the crystal setting matrix obtained by auto-index, match well with the observed. More than 90% reflections have deviations of <0.05 for index $h$, $k$ and $l$. The data processing was done using program package WEIS (UNIX version) on SGI workstation and then scaled and combined using the program package ROTAPREP, ROTAVATA, AGROVATA and TRUNCATE in CCP4 suite [6]. The data processing gave 14419 unique reflections. The merging $R$ factor is 6.2%. The crystal volume per unit of protein molecular weight is calculated to be 10.31A$^3$/dalton, implying that each asymmetric unit contains probably four molecules, and the solvent content in the unit cell of basic PLA$_2$ is about 52% [7]. The further studies is in progress.

(b) Orthorhombic form. Preliminary identification by 4-circle diffractometer and Rigaku-Axis IIC system indicates that the crystals belong to orthorhombic system, 222 point group. The data has also been collected with Weissenberg camera in Photon factory and processed by using program package of WEIS and CCP4 suite, similar to those used for the monoclinic crystal. The final $R$merge is 8.0% within 20-2.5A resolution range. The crystal contains two molecules in each asymmetrical unit. Structure determination of this crystal by the molecular replacement method is in progress.

The structure determination and comparison of different crystal forms will reveal the possible flexible region in the structure of this enzyme.

We thank Prof. N. Sakabe for his kind invitation to work in Photon Factory and Dr. N. Watanabe for his various help in data collection and processing. We also thank Dr. S. Ikemizu for his help in auto-indexing. The project is supported from Chinese Academia Sinica.

References

X-RAY STRUCTURE STUDY OF ACTIVE-SITE MODIFIED D-GLYCERALDEHYDE-3-PHOSPHATE DEHYDROGENASE FROM PALINURUS VERSICOLOR

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D-glyceraldehyde-3-phosphate dehydrogenase (GAPDH) is a typical allosteric enzyme. The active-site carboxymethylated reaction of GAPDH from muscle is an 'all-of-the-sites' reaction, whereas the reaction which leads to the formation of a fluorophore carrying NAD derivative is 'the-half-of-the-sites' [1]. Structure analysis of carboxymethylated GAPDH (CM-GAPDH) from P. versicolor at high resolution will explore this reaction from the structure point of view. CM-GAPDH crystal is isomorphous to that of holo-GAPDH [2]. The 1.8A resolution diffraction data of CM-GAPDH used in the refinement were collected at the synchrotron radiation-Fuji imaging plate-Weissenberg camera system at BL6A2 station in Photon Factory of KEK. The data were processed using the WEIS program. The merging R factor is 0.079 for the data set including 78030 reflections at 1.8A resolution. The structure refinement of CM-GAPDH at 1.8A resolution was carried out on the basis of structure of holo-GAPDH at 1.8A resolution, using program X-PLOR, and model building on SGI workstation using program Turbo-Frodo [3]. The current model, containing 2 NAD$^+$ molecules, 4 sulfate ions and 388 ordered water molecules in the red and green subunits, gives a crystallographic R-factor of 0.183 for reflections within 6.0-1.8A resolution and a stereochemistry with r.m.s. deviations from ideal geometry of 0.013A for bond lengths and 2.794 for bond angles. The electron density map of CM-GAPDH at high resolution reveals clearly the atomic positions of carboxymethylated group (Fig.1), which is parallel to the nicotinamide ring of coenzyme NAD$^+$ and has a charged interaction with that moiety of NAD$^+$. It is notable that the structure of modified active site and the mode of its interaction with NAD$^+$ are nearly identical for green and red subunits, implying that 'the-half-of-the-sites' reaction leading to the formation of fluorescent NAD derivatives unlikely results from pre-existing structural asymmetry. Further and detailed analyses of CM-GAPDH structure are underway.

Acknowledgment

We are particularly indebted to professor Noriyoshi Sakabe for his kind invitation, which made our working in BL6A2 station possible. Also most grateful to Dr. N. Watanabe for various help in experiment and computing.

References


Fig.1. Fitting of carboxymethylated group at modified active site of GAPDH and corresponding electron density
STRUCTURAL STUDIES ON PROTEINS OF MEDICAL IMPORTANCE

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Introduction
This proposal covers a range of different protein crystallographic projects from the groups of Drs D. Stuart and Y. Jones in Oxford and their collaborators including Dr D. Stammers. The unifying theme is the relevance of each project to medical research. We report here on three projects which benefited from data collection on BL6A2 at the Photon Factory in 1994.

HIV-1 Reverse Transcriptase
The multifunctional enzyme reverse transcriptase (RT) from HIV-1 is a key target for anti-viral therapies to combat AIDS. Data collected at the Photon Factory have yielded the highest resolution (2.2 Å) structural information available to date for this molecule.1) In total Photon Factory data have enabled us to determine, and fully refine at high resolution, the structures of three RT/inhibitor complexes in addition to an apo enzyme structure. The structures of the complexes with the non-nucleoside inhibitors (nevirapine, 1051U9 and α-APA) reveal a common mode of binding for these chemically diverse compounds.2) Comparison of these complexes with the unliganded structure suggests that these inhibitors act by locking the polymerase active site in an inactive conformation.3)

Vascular Cell Adhesion Molecule-1
The cell-surface glycoprotein Vascular Cell Adhesion Molecule-1 (VCAM-1) mediates intercellular adhesion by specific binding to the integrin Very-Late Antigen-4 (VLA-4). VCAM-1, with the intercellular adhesion molecules ICAM-1, ICAM-2, ICAM-3 and the mucosal vascular addressin MAdCAM-1, forms an integrin-binding subgroup of the immunoglobulin superfamily (IgSF). We were able to collect high resolution data at the Photon Factory for native and selenomethionyl forms of a functional, integrin-binding, fragment composed of the first two domains of VCAM-1.4) These data were central to the subsequent structure determination at 1.8 Å resolution.5) Structure/function analysis reveals a key integrin-binding motif situated on a distinctive, highly exposed loop between β-strands C and D of the N-terminal Ig-like domain.

Tissue Factor
Tissue factor is a cell-surface glycoprotein receptor which initiates the blood coagulation cascade after vessel injury by interacting with blood clotting factor VII/VIIa and which is implicated in various pathological processes. Native data collected at the Photon Factory enabled us (in collaboration with Dr K. Harlos, Univ. Oxford and Dr B. Boys, Univ. Edinburgh) to determine the crystal structure of the extracellular region of tissue factor at a resolution of 2.2 Å.6) Tissue factor consists of two Ig-like domains associated through an extensive, novel, interdomain interface region. The binding site for factor VII lies at the interface region and involves residues from domain 1 and an extended loop (binding 'finger') of domain 2.

Acknowledgements
We gratefully acknowledge the invaluable assistance of Dr A. Nakagawa and Professor N. Sakabe during data collection at the Photon Factory.

References
CRYSTAL STRUCTURE OF THE U1A PROTEIN-RNA COMPLEX

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Introduction

U1A protein is a component of U1 snRNP, which is one of five U snRNPs involved in pre-mRNA splicing. The protein of U1A protein contains two copies of an RNA-binding domain called the RNP domain. Only the amino-terminal RNP domain of U1A protein is required for binding U1 snRNA hairpin II\(^1\), which is the protein's binding site on U1 snRNA\(^2\). The amino-terminal RNP domain of U1A protein has been solved previously\(^3\), and consists of a 4-stranded antiparallel \(\beta\)-sheet flanked on one side by two \(\alpha\)-helices.

Although there are now many structures of protein-DNA complexes only four structures of protein-RNA complexes have been solved. The RNP domain is found in over 200 distinct proteins involved in RNA processing and transport\(^4\) which bind a wide variety of RNA sequences.

Data Collection

We crystallised a complex of the amino-terminal RNP domain of U1A protein with a 21 nucleotide hairpin RNA molecule representing hairpin II of U1 snRNA. The crystal space group is \(P6_522\) with unit cell edges \(a=b=97.0\,\text{Å},\ c=255.3\,\text{Å}\). The crystals diffract to 1.7 \(\text{Å}\), but the length of the \(c\)-axis prevented reflections being resolved on many conventional x-ray detectors. For this reason we used the 40 x 20 cm\(^2\) Fuji IPs with the Weissenberg camera on Photon Factory beamline BL-6A\(^5\) which could resolve the reflections. Data sets of native crystals and an isomorphous derivative were collected on BL-6A with 1.000\(\text{Å}\) wavelength x-rays. The derivative was of an engineered serine\(^{29}\rightarrow\) cysteine mutant covalently bound to methyl mercury\(^6\). A second data set was later collected at the SERC Daresbury Laboratory on synchrotron beamline PX9.6 using a 30cm MAR IP scanner and 0.882\(\text{Å}\) wavelength x-rays. All data sets were collected from crystals frozen at 100 K.

Data Reduction and Structure Determination

Data from Photon Factory BL-6A were reduced using DENZO; data from Daresbury PX9.6 were reduced with MOSFLM. 3 mercury sites were identified in the asymmetric unit with the SHELXS-90 program; the positions of these sites were refined and phases calculated with MLPHARE using derivative data sets collected at two wavelengths (see previous section). An electron density map was calculated and solvent flattened with the SOLOMON program to 2.4\(\text{Å}\) resolution. Model building was carried out in the graphics program O, and the structure refined using TNT to 1.92\(\text{Å}\) with an R-factor of 21.5\% and a free R-factor of 26.6\%. (For details of references for these programs, see Ref. 7).

Structure of the complex\(^7\)

3 U1A-RNA complexes are found in the asymmetric unit, and there are no significant differences between them. The loop of the RNA hairpin binds to the 4-stranded antiparallel \(\beta\)-sheet of the protein as an open, effectively single-stranded structure. The carboxy-terminal residues of the RNP domain lie across the \(\beta\)-sheet, and together with a loop from the protein which protrudes from the \(\beta\)-sheet's surface, form a groove in which the RNA loop nucleotides lie. The stem of the RNA hairpin makes few interactions with the protein. Extensive interactions within the complex are mediated by RNA bases stacking to protein side chains and many hydrogen bonds\(^8\) (Figure 1). The structure reveals the stereochemical basis for sequence-specific RNA recognition by the RNP domain.

Fig. 1 Structure of the U1A-RNA complex.

References

STRUCTURE OF THE CATALYTIC CORE OF THE FAMILY F XYLANASE FROM PSEUDOMONAS FLUORESCENS.

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Introduction

Sequence alignment suggests that xylanases evolved from two ancestral proteins and therefore can be grouped into two families, designated F and G. Family F enzymes show no sequence similarity with any known structure and their architecture was unknown. Studies of an inactive enzyme-substrate complex will help to elucidate the structural basis of binding and catalysis in the family F xylanases.

Results

We have therefore determined the crystal structure of the catalytic domain of a family F enzyme, Pseudomonas fluorescens subsp. cellulosa xylanase A, at 2.5Å resolution and a crystallographic R-factor of 0.20. The structure was solved using an engineered catalytic core in which the nucleophilic glutamate was replaced by a cysteine. As expected, this yielded both high-quality mercurial derivatives and an inactive enzyme which enabled the preparation of the inactive enzyme-substrate complex in the crystal. We show that family F xylanases are eight-fold α/β-barrels (TIM barrels) with two active-site glutamates, one of which is the nucleophile and the other the acid-base. Xylopentaose binds to five subsites A-E with the cleaved bond between subsites D and E (Figure 1). Ca²⁺ binding, remote from the active-site glutamates, stabilizes the structure and may be involved in the binding of extended substrates.

Conclusions

The architecture of P. fluorescens subsp. cellulosa has been determined crystallographically to be a commonly occurring enzyme fold, the eight-fold α/β-barrel. Xylopentaose binds across the carboxy-terminal end of the α/β-barrel in an active-site cleft which in the native enzyme contains the two catalytic glutamates1.

Reference


Fig. 1 The eight-fold α/β-barrel architecture of the catalytic domain of xylanase A from P. fluorescens subsp. cellulosa drawn using MOLSCRIPT. The eight β-strands are shown as arrows and the eight α-helices are also shown. Ca²⁺ binding stabilizes the loop after strand 7 and the substrate-binding subsites are formed by loops after strands 4-7. The substrate is shown using solid bonds. The active-site nucleophile (Glu246) resides on strand 7 and the acid-base catalyst (Glu127) on strand 4.
High-Resolution Crystal Structure of Intermediate Liganded State of 
\((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) Hybrid Hemoglobin.

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\textsuperscript{§}Photon Factory, National Laboratory for High Energy Physics (KEK), Tsukuba, Ibaraki 305, Japan

1. Introduction
Several metal substituted hybrid hemoglobins (Hbs), 
\((\alpha \text{Fe}(\text{II}))_2(\beta M\text{G}(\text{II}))_2\) and where \(M\) denotes 
metal ions other than \(\text{Fe}(\text{II})\), have been studied. Among 
them \(\text{Mg}(\text{II})\)-Fe(II) hybrid Hbs show very low ligand 
affinity implying that \(\text{Mg}(\text{II})\)-porphyrin stabilizes deoxy 
quaternary structure. The crystals of both unliganded and 
liganded forms of grown from ammonium sulfate (AS) solution (space group \(P2_1\)) and 
from polyethylene glycol (PEG) solution (space group \(P2_12_12\)) are isomorphous to those of deoxyHbA grown 
from the same solutions. Taking advantages of these 
facts, we determined to compare the structures of 
unliganded and liganded \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) within deoxy 
quaternary structure.

2. Experimental Procedures
Crystallization of \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) was carried out in 
AS (pH 6.5) and PEG solution according to the method 
described by Perutz (1968) and Ward (1975) for human 
deoxy HbA. X-ray refraction data to about 1.5 Å resolution 
were collected at the Photon Factory, KEK using the 
Weissenberg Camera (Sakabe, 1983) for macromolecular 
crystallography with Fuji imaging plate (IP). Crystals 
of \((\alpha \text{Fe}(\text{II})-\text{CO})_2(\beta \text{Mg}(\text{II}))_2\) and \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) from 
AS solution yielded a totals of 297677 \(I_{\text{obs}}\) and 283630 \(I_{\text{obs}}\) respectively, which gave 112896 \(I_{(hkl)}\) and 108411 \(I_{(hkl)}\) independent reflections with the 
iables of 7.79% and 7.07%. The crystals from PEG solution yielded totals 
of 132210 \(I_{\text{obs}}\) and 173737 \(I_{\text{obs}}\), which gave 43553 \(I_{(hkl)}\) and 47371 \(I_{(hkl)}\) independent reflections with the 
iables of 5.76% and 6.66% for unliganded and liganded cases 
respectively. The structures were refined with the 
Hendrickson and Konnert restrained least-squares program 
PROLSQ (Hendrickson, 1985). The \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) and \((\alpha \text{Fe}(\text{II})-\text{CO})_2(\beta \text{Mg}(\text{II}))_2\) model for the crystals from 
AS solution resulted in a \(R\) factor of 17.5% for 47348 and 50333 reflections respectively between 10.0-1.7 
Å with magnitudes greater than 3.0\(\sigma\). In the case of the 
crystals from PEG solution the unliganded and liganded models resulted in a \(R\) factor of 19.3% for 34907 and 
37380 reflections between 10.0 and 1.9Å with magnitudes 
greater than 3.0\(\sigma\).

3. Results
There are no significant differences between the 
structures obtained for the crystals from the different 
solution conditions. With the exception of the immediate 
vicinity of the \(\alpha\)-heme, the \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) and 
\((\alpha \text{Fe}(\text{II})-\text{CO})_2(\beta \text{Mg}(\text{II}))_2\) structures are very similar to each 
other and to deoxyHbA. Comparison of the two structures 
in a graphics viewers showed that there are no significant differences between \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) and deoxyHbA. In \(\alpha 1\) subunit, Fe(II) atom moves 0.5 Å into the heme plane 
upon CO binding. The F and E helices are slightly 
displaced relative to the heme.

Our study confirms partially liganded structures in the T 
state as follows: (1) Mg in the \(\alpha\) subunits of deoxy 
and CO liganded \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) is five coordinated and 
stereochemically almost identical to ferrous ion in 
deoxyHbA, (2) the structure of the \(\alpha \beta 1\) \(\alpha \beta 2\) interface of 
\((\alpha \text{Fe}(\text{II})-\text{CO})_2(\beta \text{Mg}(\text{II}))_2\) is that of the T quaternary 
structure, and (3) the tertiary structure changes upon CO 
binding to the \(\alpha\) subunit of \((\alpha \text{Fe}(\text{II}))_2(\beta \text{Mg}(\text{II}))_2\) are such 
that the CO molecule and the Fe atom with the same 
conformation as that of COHbA are fitted into the T 
quaternary structure.

We are deeply indebted to Professor Sakabe N. and Dr. 
Watanabe N. for advises in the data collection and the 
structure refinement at the Photon Factory. We would like 
to thank Drs Miyazaki G., Hori H., Shibayama N., Fugii 
M. and Unzai S. for helpful discussions and suggestions.

Figure 1. The comparison of the \(\alpha\) heme environments of 
\((\alpha \text{Fe}(\text{II})-\text{CO})_2(\beta \text{Mg}(\text{II}))_2\) (filled bonds), and deoxyHbA 
(open bonds). The \(\alpha\) heme environments of the models 
have been superimposed in the BGH frame (Baldwin & 
Chothia, 1979).

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Ward, K.B. (1975) J. Mol. Biol. 98, 161
CRYSTAL STRUCTURE REFINEMENT OF RECOMBINANT MURINE INTERFERON-β

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**Introduction**

Interferons (IFNs) are proteins showing antiviral, antitumor and immunomodulator activities with potential therapeutic value. The IFNs have been classified into two categories on the basis of their biological and physical properties. Type I IFNs include fibroblast interferon (IFN-β) and the leukocyte family of interferons (IFN-α) which is composed of at least 10 subspecies. Each member of the Type I IFNs contains ~165 amino acid residues, and competes for the same receptors, furthermore, identical amino acids occupy invariant position in 23 % of their amino acid sequences. In contrast, Type II IFN (IFN-γ) contains ~146 amino acid residues and displays no measurable binding to Type I interferon receptors.

**Experimental**

Data collection were carried out using the macromolecule-oriented Weissenberg camera installed at BL6A devised by Prof. Sakabe. To collect high resolution data with high completeness, we used three crystals. The three set of data were scaled using the program package WEIS developed by Dr. T. Higashi. The obtained data were of good quality with the Rmerge value of 4.78 % and the completeness of 91.0 % at 2.15 Å resolution. We used the program XPLOR for the crystallographic refinement. The final R-factor at 2.15 Å resolution is 19.1 % (free R-factor is 25.8 %) with 48 solvent molecules.

**Results**

Based on the fully refined crystal structure of MuIFN-β, we deduced model structures for some Type I interferons: HuIFN-αD, HuIFN-β and BoIFN-τ. These theoretical studies combined with the site-directed mutagenesis studies by Uzé et al. (1) have revealed the detailed features for the receptor binding of Type I interferons as follows (2). (A) There are two receptor binding regions on the Type I interferon molecules, one is the so-called "hot area" composed of Loop AB and Helix D, and the other region is composed of Helices A and C. (B) The hot area is composed of two parts: the conserved area ("Cv-area") and the non-conserved area. The "Cv-area" seems to be responsible for the binding to one of the receptor molecules which shows common binding activity for all Type I interferons.

**References**


X-RAY STRUCTURE OF ALKALINE PROTEASE FROM PSEUDOMONAS AERUGINOSA IFO 3455

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Introduction

Alkaline protease from Pseudomonas aeruginosa IFO 3455 is a zinc requiring metalloprotease consisting of 470 amino acid residues. It is thought that alkaline protease may play a key role in infection of the bacteria to their host cells through inactivation of various physiological activators such as some complement components, immunoglobulins A and G, and many protease inhibitors. In order to obtain the structural information in more detail for understanding the proteolytic mechanism of the enzyme, we have solved the crystal structure of alkaline protease and refined it at 2.0 Å resolution.

Experimental

The lyophilised sample of alkaline protease was crystallized as described before. All X-ray intensity data were collected with a screenless Weissenberg camera at the BL6A2 station of Photon Factory in National Laboratory for High Energy Physics, Tsukuba, Japan. The conditions for data collections were already reported. Two native crystals were mounted with the crystallographic b* and c* axes parallel to the spindle, respectively. The Rmerge between the native data sets was 5.28% for 44,289 independent reflections (/>o(/)) at 2.0Å resolution. For heavy-atom derivative crystals, the c*-axis mounting was applied. The intensity data were all processed with the program WEIS.

Model building and Refinement

An initial model of the enzyme was built with a computer graphics system, IRIS Indigo ELan using the program package TURBO-FRODO. The initial crystallographic R value was 43.5% for 16,182 independent reflections within the resolution of 10.0 to 2.8 Å. The model was refined by simulated annealing and conventional positional refinement using the molecular dynamics program X-PLOR installed on a CRAY Y-MP2E/264 supercomputer. Several cycles of refinement were carried out after manual model rebuildings using 2Fo-Fc and Fo-Fc maps. Then, water molecules and calcium ions were added to the model. Finally, temperature factors of individual atoms were refined. The crystallographic R value was dropped to 19.8% for 33,698 independent reflections (/>o(/)) within the resolution of 8.0 to 2.0 Å. The final model consists of 470 amino acid residues, 308 water molecules and nine ligand ions. It exhibits a reasonable conformation with excellent geometry. No residues fall into the disallowed region, and 88.8% of the total residues lie in the most favoured region.

Results and Discussion

The molecule has an elongated ellipsoidal shape with approximate dimensions of 90 × 42 × 35 Å. It consists of two distinct structural domains (Fig. 1). The N-terminal domain is the proteolytic domain which contains the active site zinc atom in the inside of the large cleft. The overall structure of the domain is similar to that of astacin, a metalloprotease belonging to a superfamily different from that of the alkaline protease. The C-terminal domain has a two-layer β-sandwich structure consisting of 19 β-strands. In the central region of this domain, an unusual parallel β-helix wound like a right-handed spiral through the short turns between the adjacent strands. Ca2+ ions bound internally within the turns formed by a repeated GGXGD sequence motif may play an essential role in stabilizing this β-helix structure.

Fig. 1) An overall view of alkaline protease(A) and its folding topology (B).

References

CRYSTAL STRUCTURE OF PHOSPHOLIPASE A2 FROM TRIMERESURUS FLAVOVIRIDIS (HABU SNAKE) VENOM IN ITS ACTIVE PH STATE AT 2.0Å RESOLUTION

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Introduction
Some of the authors have been determined the crystal structure of dimeric phospholipase A2 (abbreviated as PLA2) from a venom of Habu snake (Trimeresurus flavoviridis) at 1.5Å resolution(1). The crystals were however grown at pH 4.9, and do not contain Ca^{2+} ions which is indispensable to its enzymatic activity. The Ca^{2+} ion binding ability of PLA2 increases rapidly at alkaline pH, especially above pH 8.5. Therefore the crystallization of PLA2 at pH 9 was tried and its structure study has been carried out to compare the structural changes between the active pH state and inactive one.

Experimental
Crystallization - crystallization was carried out by the hanging-drop vapor-diffusion method. A 10mM Tris-HCl buffer (pH 9) containing 12% polyethylene glycol 6000 was used as a reservoir solution. Rhombic crystals were grown at 4°C after 2days.. The crystallographic data are given in Table 1. Two molecules, Molecule A and B respectively, are contained in an asymmetric unit.

Data collection - Two native data set were collected on the station BL6A2 at the Photon Factory using a screenless Weissenberg camera (2) cooled to 283K. The X-ray wavelength was 1.00Å. The radius of a film cassette of 287mm and the collimator size of 0.2mm were used. The oscillation range of 12° with an overlap of 0.5° were adopted. For Native 1 data the exposure time of 120s per Fuji imaging plate (IP) was selected to collect high-resolution data. The a* axis of the crystal was rotated with the Weissenberg coupling constant of 3° /mm. For Native 2 data the exposure time was set to 60s and the c* axis was rotated with the coupling constant of 1.5° /mm. 17 packs of IP were processed with WEIS program system (3) for Native 1 and 2, respectively. A summary of the data collection was given in Table 2.

Structure determination and refinement - Rotation parameters were determined with the Crowther's fast-rotation function. The search model adopted was the structure of PLA2 at pH 4.9. Two peaks related with a local 2-fold symmetry were obtained unambiguously, using Native 1 data between 8 and 3.5Å resolution with an outer radius of Patterson integration of 20.4Å. Translation parameters for Molecule A and B were determined with the Crowther and blow's translation function, using 8-3.5Å resolution data.

by for Molecule B was determined with R-factor search method. At this stage the crystallographic R is 0.371.

Refinement of the model was performed with the program X-PLOR, using merged data set. The final model contains 1,918 protein atoms and 126 water molecules. The final R factor is 0.176 for 14,243 reflections with a 3σ(F) cut-off between 10 and 2Å resolution.

Table 1. Crystal data
| Space group | P2_1 |
| Cell constants | a=65.20Å |
| | b=55.35Å |
| | c=35.11Å |
| g=90.23° |
| Asymmetric unit | PLA2 dimer |
| Density | 1.30g/cm³ |
| Sloven content | 43.5% |
| V_m | 2.30Å³/dalton |

Table 2. Summary of data collection statistics
| Native 1 | Native 2 | Total |
| Resolution(Å) | -2.0 | -2.7 | -2.0 |
| Total observations | 40,030 | 25,998 |
| Unique reflections | 13,085 | 8,984 | 15,519 |
| Completeness(%) | 74.5 | 93.3 | 88.1 |
| R_merge(%) | 9.03 | 5.82 | 10.42 |

Results
The three-dimensional structure of PLA2 at pH 9 is essentially similar to that at pH 4.9, as shown in Fig. 1.

Fig. 1. Comparison of the Ca^-backbones of PLA2. The structure at pH 9 (thick lines), and that at pH 4.9 (thin lines).

References
X-RAY CRYSTALLOGRAPHIC STUDY OF NON-PEPSIN-TYPE ACID PROTEINASE A FROM ASPERGILUS NIGER VAR. MACROSPORUS

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Introduction

Aspergillus niger proteinase A is a non-pepsin-type acid proteinase, distinctly different in various properties from the family of pepsin-type proteinases. It is insensitive to the inhibitors specific and common to the pepsin family and shows substrate specificity fairly different. It is not homologous in primary structure with pepsin at all.¹)

There is no information on which residues participate in the catalysis and how the mechanism operates. To elucidate these properties of proteinase A on the basis of three-dimensional structure, X-ray crystallographic analysis has been started.

In the present study, we got three good heavy-atom derivatives and calculated the electron density map of proteinase A. It is in progress to determine the structure of polypeptide chains to explain the electron density map.

Experimental and Results

Three types of proteinase A crystals have, so far, been obtained for X-ray crystallographic study. Among the three types of the crystals, type 1 crystals are grown more rapidly under less strict conditions than the other two types of crystals.²)

Heavy atom derivatives were, therefore, searched for type 1 crystals by the soaking method to solve the structure of proteinase A by multiple isomorphous replacement (MIR) method. Intensity data were collected by using a data collection system at the BL6A station in the Photon Factory, by combining the Weissenberg camera for macromolecular crystallography, an imaging plate, a Fuji image reader BA100, and a data reduction program WEIS with a synchrotron radiation (λ = 1.00 Å).³, ⁴)

Since the solvent content (V_wat) of type 1 crystals was very low (26%) and hence the crystals were less reactive to heavy atom reagent, we used extremely high concentrations of heavy atom solutions for soaking crystals and found two kinds of Pt-derivatives and one kind of Hg-derivative.

The initial phases were determined by multiple isomorphous replacement with anomalous scattering (MIRAS) method using CCP4 program suite.⁵) After the refinement of heavy-atom parameters, the overall figure of merit was 0.57 for reflections to 2.0 Å resolution. The phases were improved using solvent flattening procedure. The resulting 2.5-Å electron density map is shown in Fig. 1.

Although the relative molecular mass of proteinase A is 22,300, which is about half the size of pepsin-type proteinases, the proteinase A molecule has the shape of a croissant, that is similar to pepsin-type proteinases.

We thank Prof. Noriyoshi Sakabe (Tsukuba University) for his encouragement and interest during the experiments.

Fig. 1. 2.5 Å electron density map of proteinase A

References

CRYSTAL STRUCTURE ANALYSIS OF GLUTATHIONE SYNTHETASE - REFINEMENT OF TRIS-NATIVE STRUCTURE -

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Introduction
Glutathione synthetase (EC 6.3.2.3; GSHase), the second enzyme in the glutathione biosynthetic pathway, catalyzes the synthesis of glutathione from γ-L-glutamyl-L-cysteine and Gly in the presence of ATP and magnesium ion. GSHase from Escherichia coli B is a homotetramer, 316 amino acid residues each monomer. The X-ray structure of the native enzyme has been determined at a resolution of 2.0 Å. The ATP-binding site of the GSHase is located in the cleft formed between two domains, each of which consists of an antiparallel β-sheet, helices, and a loop. The site has no typical mononucleotide-binding motif; β-strands are antiparallel in the ATP-binding site of the GSHase, while they are parallel in the motif. The dipeptide-binding site is assigned close to the ATP-binding site. The interactions of ATP and the dipeptide substrates with amino acid residues at their bind sites are only speculated from the kinetic analysis of mutant GSHases. The binding site of the third substrate glycine has never identified, because the substrate is missing with crystallographic analysis. Another functional, structural element of the ATP-binding site in the GSHase is a loop of 16-residue long. Proteolytic cleavage of the loop at Arg233 or substitution of the loop with a short turn resulted in fatal loss of the GSH synthetic activity. In the mutant enzyme with the loop-substitution, γ-L-glutamyl-L-cysteine dependent ATP-hydrolytic activity increases to almost same extent as the synthetic activity. Mutations of the glycine residues on the loop increased the Km value for glycine.

Phosphate buffer at pH 6.0 was previously used for the crystallization of the GSHase. The crystals from phosphate buffer, however, diffracted badly at higher resolution ranges. Other buffers were screened for crystallization of the GSHase. Tris-HCl buffer at pH 7.5 is optimal for the catalytic activity. In the present study we refined the model of Tris-native GSHase at 2.0 Å resolution. This model reveals the active site structure at the optimal catalytic conditions.

Methods and results
Tris-native crystals were obtained by microdialysis method using the same procedure reported previously. Diffraction patterns of the crystals at one α- and two c-axis crystal settings were recorded on imaging plates by using a large Weissenberg camera installed at the BL-6A2 station of Photon Factory. The diffraction images recorded on imaging plates were digitized using BA100 photo-reader system (Fuji Film), and processed to indexed intensity data sets with the programs XViewer and WEIS. The complete data set was obtained by merging three data sets; 61,869 observed reflections, 30,967 unique reflections with Rmerge of 7.01% and 90.3% complete to 2.0 Å (F > 2σ(F)).

All the refinement procedures were performed using X-PLOR on a Cray Y-MP2E at the Institute for Chemical Research, Kyoto University. The initial model, the phosphate-native GSHase, was refined as rigid-body. Simulated annealing refinement was performed from 3000 K to 300 K at a time step of 0.5 fsec with slow-cooling protocol. After B-factor refinement, 95 water molecules were added by using WATER.

The crystallographic R-factor of the final model is 20.8% for 24,108 unique reflections between 10.0 and 2.0 Å (F > 2σ(F)). In our previous phosphate-native model, the main-chain dihedral angles at Asn114 were out of the allowed regions in Ramachandran plot. In the present refinement, the peptide bond between Val113 and Asn114 was modeled in a cis configuration instead of a trans configuration. That configuration has much improved the stereochemical quality of the Tris-native model. RMSDs from the ideal geometry are 0.012 Å in bond lengths, 2.77 deg in bond angles, 25.36 in dihedral angles, 1.01 in improper angles. Average B factors are 18.27 Å² for the main-chain atoms and 21.41 Å² for the side-chain atoms.

We also refined the previously reported model of the phosphate-native GSHase by using the final model of the Tris-native GSHase as the initial model. The new phosphate-native model is of good quality in stereochemistry and in geometry. Tris- and (new)phosphate-native structures are almost in the main-chain folding of subunit but slightly different in subunit assembly. Structural bases of the optimal catalytic conditions will be revealed by comparing the side-chain conformations of the residues in the active site between the two structures.

The coordinates of the two structures will be deposited to Protein Data Bank.

References
7) Fuji, Private communication.
10) Sugio, Private communication.
ELUCIDATION OF THE CATALYTIC MECHANISM OF 7α-HYDROXYSTEROID DEHYDROGENASE BASED ON X-RAY CRYSTAL STRUCTURE ANALYSIS

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Introduction

7α-Hydroxysteroid dehydrogenase (7α-HSDH; EC 1.1.1.159), the most abundant hydroxysteroid dehydrogenase in human intestinal flora, has been found in numerous genera of bacteria and in mammalian livers. Two kinds of 7α-HSDH have been cloned, sequenced, and characterized. One is the NAD+-dependent 7α-HSDH from E. coli HB101 (Yoshimoto et al., 1991, 1993) and the other is the NADP+-dependent 7α-HSDH from Eubacterium sp. strain VP112708 (Baron et al., 1991). Each of them is a homo-tetrameric enzyme having a similar molecular weight and exhibits similar substrate specificity. The deduced amino acid sequences of the enzymes show that both of them belong to the short-chain alcohol dehydrogenase family. In order to elucidate the common catalytic mechanism and the origin of differences among substrate specificities of the enzymes belonging to the short-chain alcohol dehydrogenase family, we have begun crystallographic studies on 7α-HSDH from E. coli.

Experimental

Two native crystals (P41212 with dimensions a=b=81.66 Å and c=214.6 Å) of 7α-HSDH prepared as described by Tanaka et al. (1995) were used for X-ray data collection by a Weissenberg method at the beamline BL6A (Sakabe, 1991). Detailed experimental conditions for the data collection are summarized in Table 1. The data sets were processed with the program WEIS (Higashi, 1989). Three heavy-atom derivatives were prepared by transferring native crystals into heavy-atom solutions each containing HgCl2, K3PtCl4, or KAu(CN)2. X-ray data collections for the derivative crystals were performed by an oscillation method at 20 °C using a Rigaku R-AXIS IIe area detector with CuKα radiation, which was generated by a Rigaku RU200 rotating-anode generator operating at 45 kV and 110 mA and focused by a Superc double focusing mirror. The derivative data sets were collected from a single crystal each up to 2.8 Å resolution and processed with a Rigaku data processing software PROCESS. The native and derivative data sets were further processed with the CCP4 suite (Collaborative Computational Project, Number 4, 1994). The heavy atom positions were determined by a Patterson method with RSPS (Knight, 1989) and the heavy atom parameters were refined with MLPHARE (Otwinski, 1993).

Results

Statistical details of the diffraction data are presented in Table 2. A difference Patterson map for the Au derivative (Figure 1) shows that there are two major heavy-atom binding sites per asymmetric unit. Electron density maps calculated with phases obtained by multiple isomorphous replacement techniques turned out to be good enough to interpret. We are now building a protein model for 7α-HSDH.

Acknowledgements

We thank Professor N. Sakabe and Drs A. Nakagawa and N. Watanabe for help with data collection and processing at the Photon Factory, Tsukuba, Japan. NT is supported by the JSPS fellowship fund.

Table 1. Experimental conditions of Weissenberg data collection for the native crystals of 7α-HSDH

<table>
<thead>
<tr>
<th>Data set number</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common conditions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Collimator aperture (μm)</td>
<td>100 x 100</td>
<td>100 x 100</td>
</tr>
<tr>
<td>Crystal-to-Imaging Plate distance (mm)</td>
<td>429.7</td>
<td>429.7</td>
</tr>
<tr>
<td>Number of oscillations / Imaging Plate</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

Specific conditions

- Rotation axis
- α angle / Imaging Plate movement (°/mm): 1.07, 1.27
- β angle / Imaging Plate °: 5.07, 6.07
- Total number of Imaging Plates: 18, 18
- Total α scan range °: 91.5, 91.5
- Exposure time / Imaging Plate (sec): 40, 48
- Ring current (mA): 311, 306

For the first 8 Imaging Plates. For the last 10 Imaging Plates.

Table 2. Data collection statistics for 7α-HSDH

<table>
<thead>
<tr>
<th>Source</th>
<th>Native</th>
<th>HgCl2</th>
<th>K3PtCl4</th>
<th>KAu(CN2)</th>
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<tbody>
<tr>
<td>Resolution limit (Å)</td>
<td>1.80</td>
<td>2.80</td>
<td>2.82</td>
<td>2.81</td>
</tr>
<tr>
<td>Number of observed reflections</td>
<td>164,209</td>
<td>50,703</td>
<td>39,912</td>
<td>49,995</td>
</tr>
<tr>
<td>completeness (%)</td>
<td>91.6</td>
<td>85.7</td>
<td>91.2</td>
<td></td>
</tr>
<tr>
<td>merging R-factor based on intensity (%)</td>
<td>5.84</td>
<td>7.24</td>
<td>8.52</td>
<td>7.24</td>
</tr>
</tbody>
</table>

References

DATA COLLECTION OF XANTHINE OXIDASE ISOLATED FROM BOVINE MILK ON THE 6A2 BEAM LINE

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Introduction
Xanthine oxidase or xanthine dehydrogenase isolated from mammals is a component of the nucleotide catabolism pathway. The active enzyme, a 290kdal homodimer, catalyzes the oxidation of hypoxanthine to uric acid. Each subunit contains one FAD, two 2Fe/2S centers, and one molybdopterin group. The enzyme is synthesized in vivo as xanthine dehydrogenase (type D enzyme). This form uses NAD as the catalytically preferred primary electron acceptor for the oxidation reaction. Alternatively, the dehydrogenase form may be converted to the oxidase form of the enzyme (type O enzyme) either during normal cell growth or during certain types of interruptions to normal cell growth. This conversion occurs either by reduction of disulfide bonds, generating the "reversible" type O enzyme, or limited proteolysis, generating the "irreversible" type O enzyme. This new form of the enzyme differs in its internal electron transfer kinetics, accessibility of some cofactor sites to priming from external electron sources, and the preferred cofactor as the ultimate electron source during the oxidation reactions. Instead of using NAD as the kinetically preferred electron acceptor, the type O enzyme exhibits a kinetic preference for dioxygen. The product of this electron transfer to oxygen is the formation of highly reactive hydroxide radicals. These species have been shown to cause severe cell damage and have been implicated in neuronal cell death that is a characteristic of amyotrophic lateral sclerosis.

Extensive studies on the mechanism of electron transfer between the cofactor sites have been made on both the oxidase and the dehydrogenase forms. During steady state catalysis, electron transfer between the cofactor sites is in rapid equilibrium. The electrons move into the cofactor sites through the molybdopterin center and, in the case of the xanthine oxidase, exit to the oxygen through the FAD center. Thus, the oxidative half reaction occurs at the molybdopterin center and the reductive half reaction occurs at the FAD center. Elucidation of the three dimensional structure of the enzyme is an important step in the study of electron transfer between the cofactor and the substrate binding sites.

Experimental
Xanthine oxidase preparations of exceptional purity have been obtained using newly perfected purification techniques. This highly purified xanthine oxidase forms crystals using polyethylene glycol 4000 as a precipitant. Crystals form rapidly, but diffract too weakly for high quality data collection on a laboratory x-ray source. Preliminary low resolution data using a rotating anode x-ray source show that the space group is C222(1) with unit cell dimensions of a = 119.1 Å, b = 166.5 Å, c = 156.3 Å. A Matthews parameter of 2.7 indicates that there is one monomer of M protein per asymmetric unit. The data are 82% complete to 4.5 Å with an R factor of 18%. A medium resolution native data set has been obtained using the Weissenberg camera on beam line BL-6A2 (Figure 1). The image plates were scanned using a BA-100 image plate reader and the data were analysed using the WEIS® computer package. The crystals diffracted to 3.0 Å resolution and data processing is in progress. Additional cocrystallization experiments with several heavy atom compounds have yielded small crystals, with unit cell parameters similar to those of native crystals. Data sets have been collected on the BL-6A2 beam line and data processing is in progress.

References

Acknowledgements
We would like to thank Prof. N. Sakabe, Drs. N. Watanabe, A. Nakagawa and S. Ikemizu for their expert assistance on the BL-6A2 equipment and the National Laboratory for High Energy Physics, KEK.

Figure 1: Diffraction of native xanthine oxidase crystals (distance= 429.7mm, coupling constant= 1.3, wavelength= 1.0 Å, oscillation= 2.5deg, ring current= 325mA, speed= 2.0deg/sec, number oscillations= 50)
Introduction

The great mobility of B-chain N-terminal is one of the prominent features of insulin molecules. The study of rhombohedral 2 zinc and rhombohedral 4 zinc insulin crystal structures indicated that Zn\(^{2+}\) took an important role in stabilizing insulin hexamer, while the study on the phase relationship in phenol-insulin crystal growth system shows that phenol is also very important to the stabilization of insulin hexamer. The larger the amount of \(\alpha\)-helix of B-chain N-terminal in hexamer, the more stable insulin hexamers will be. We report here the structure of the form B monoclinic porcine insulin crystallized in the presence of phenol.

Experiments and Results

In the sodium citrate buffer with 1% zinc chloride, keeping phenolic content between 0.76-1.25%, form B monoclinic insulin crystals are obtained. The crystals were indexed as monoclinic, space group \(P2_1\) with cell dimensions: \(a=49.24\, \text{Å}, b=60.94\, \text{Å}, c=48.18\, \text{Å}, \beta=95.8^\circ\), and there is a hexamer in the asymmetric unit \(^1\). The first data set with 7422 independent reflections were measured on X-200B Area Detector system equipped in our laboratory, using CuK\(\alpha\) radiation to a resolution of 2.7Å and yield of a total of 5024 independent reflections to a resolution of 3.0Å. (88.9% of unique data to 3.0 - 10.0Å) with a Rmerge of 5.01%. Data processing was performed by using the "XENGEN" package (V1.3), supported by the Siemens Company. The second data set collected with Synchrotron Radiation using a Weissenberg Camera with an imaging plate at BL6A2 equipped in National Laboratory for High Energy Physics, extended to 2.1Å. IP data was indexed and reduced by using WEIS program package. Data were further processed by using the CCP4 program package.

The form B monoclinic insulin crystal structure was determined by the molecular replacement method supplemented with the molecular packing method. The crystal structure of 4 zinc bovine insulin at 1.9Å resolution was chosen as the model. The molecular replacement and initial refinement calculation were carried out on the data collected on the X-200B Area Detector. Refinement of the atomic positions and thermal parameters were carried out on a combined Area Detector and Synchrotron Radiation data set (Rmerge=6.04%).

The initial phase was obtained by using rotation function program of x-plor package and molecular packing program of our laboratory. After the preliminary refinement by using the macromolecular rigid body refinement technique, the molecular model was further refined and adjusted by using the energy-minimizing stereochemically restrained least-square refinement on the difference Fourier maps(2Fo-Fc). The final R-factor is 22.4% at 3.0Å resolution, the r.m.s. deviation from standard bond length and bond angle are 0.022Å and 4.7° respectively. The backbone of six molecules is fitting well with the electron density map and electron behavior well on the electron density map(Fig. 1, Fig. 2). The structure information of form B monoclinic insulin at 3.0Å resolution shows that the hexamer structural state of R6 as that in form A crystal solved by Derewenda et al. \(^2\). More detailed structural information will be obtained soon after the final refinement of structure.

References

HIGH RESOLUTION CRYSTAL STRUCTURE OF THERMOSTABLE \( \alpha \)-AMYLASE FROM BACILLUS LICHENIFORMIS

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Introduction
\( \alpha \)-Amylase is an enzyme which hydrolyzes the \( \alpha \)-1,4-glucosidic linkage of starch components, glycogen, and various oligosaccharides. It is widely found in bacteria, plants, and animal secretions. Thermostable \( \alpha \)-amylase from Bacillus species is of great industrial importance in the production of corn syrup. The crystal structures of four \( \alpha \)-amylases, Taka-amylase, porcine pancreatic \( \alpha \)-amylase, Aspergillus niger \( \alpha \)-amylase, and barley malt, have been reported, but none of bacterial origin has been determined. \( \alpha \)-Amylase from Bacillus licheniformis (BLAA) is among the most thermostable natural enzymes used in biotechnological processes. Therefore, this enzyme provides an attractive model for investigating the nature of thermostability of proteins. Here we report the crystal structure of a thermostable \( \alpha \)-amylase from Bacillus licheniformis determined at 1.8 A. This study will provide the basis of designing the amylases with enhanced thermostability and other improved properties such as acid stability by protein engineering.

Experimental Methods
\( \alpha \)-Amylase from Bacillus licheniformis was purified and crystallized as described in a preliminary paper [1]. Diffraction data were measured at 14 °C on the image plate, using a Weissenberg camera for macromolecular crystallography at the BL-6A2 [2]. The wavelength of synchrotron X-rays was 1.000 Å and 0.1 mm collimator was used. A Fuji image plate (type BAIII, 20 x 40 cm) was placed at a distance of 429.7 mm from the crystal. The oscillation range per image plate was 4.5 to 6.0 degree with a speed of 2.0 degree/s and a coupling constant of 2.2 to 1.5 degree/mm. An overlap of 0.5 degree was allowed between two contiguous image plates. The diffraction patterns recorded on the image plates were digitized by a Fuji BA100 scanner. The raw data were processed using the program WEIS [3]. The native data set collected from two crystals were merged. Statistics of Photon Factory data are given in Table 1.

<table>
<thead>
<tr>
<th>Resolution (Å)</th>
<th>Measurement (Unique)</th>
<th>Completeness (%)</th>
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<tr>
<td>1.6</td>
<td>504,225</td>
<td>85.5</td>
</tr>
<tr>
<td>1.8</td>
<td>(59,730)</td>
<td></td>
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</table>

Table 1. Native data of BLAA

Results and Discussion
The three-dimensional structure of BLAA has been determined by multiple isomorphous replacement using five heavy atom derivatives. And we have refined the structure at 1.8 A. The R-factor is 21 % for reflections in the range of 8.0 - 1.8 A with \( F > 3 \sigma_F \). The polypeptide chain folds into three distinct domains. The first domain of \( \beta \)-barrel structure consists of 307 amino acid residues. The second domain, inserted between the third \( \alpha \)-helix of domain A, forms a separate structural domain that consists of residues from 108 to 180. The third C-terminal domain, consisting of residues 395 to 483, forms a distinct globular unit in which the chain folds into an eight-stranded antiparallel \( \beta \)-barrel. By analogy with other \( \alpha \)-amylases, important active site residues are identified as Asp231, Glu261, and Asp328, which are all located at the C-terminal end of the central \( \beta \)-barrel. The Ca-atoms of the BLAA structure are shown in Figure 1. The details of the crystal structure of BLAA will be described elsewhere [4].

Acknowledgements
We thank Professor N. Sakabe and Dr. A. Nakagawa for their assistance with data collection at beamline BL-6A2. A travel fund from Pohang Light Source is acknowledged.

References

Figure 1. A Ca representation of the model of BLAA.
STRUCTURE DETERMINATION OF SEMICONDUCTOR DOUBLE HETEROSTRUCTURES IN SUB-ATOMIC SCALE BY X-RAY CTR SCATTERING

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Introduction

In order to realize the high functional devices, a technique to grow heteroepitaxial semiconductor layers as thin as several Å is strongly required. In such thin layer structure, the thickness of each layer must be controlled to the order of 1ML and the interface layers must be confined as thin as 1ML to obtain the grown layer to work well as designed.

For III-V semiconductors, OMVPE (organometallic vapor phase epitaxy) and MBE (molecular beam epitaxy) became available to grow such thin layer under control and to make well defined interfaces. However, it is still difficult to obtain the well defined interfaces of thin layers which contain different group-V atoms. Because the vapor pressure of group-V atoms is relatively high, the group-V atoms easily diffuse or exchange across the interface.

In this work, we investigate the interfaces of InPAs/InP grown by OMVPE measuring the X-ray CTR (crystal truncation rod) [1, 2] scattering. The X-ray CTR measurement is expected to reveal the layer structure of the epitaxially grown samples in the atomic scale.

Preparation of Samples

Two samples were prepared by OMVPE [3]. All samples were grown on InP (001) substrate and capped by 20Å InP layer. The first sample was 1ML grown InAs (sample-a), and the second one was prepared by exposing the surface of InP substrate to AsH₃ for 8[sec] (sample-b).

Experiments and Discussions

The X-ray CTR measurement was conducted at BL6A2 in Photon Factory. The wavelength of the X-ray was set at 1.6082Å. The diffraction spot of (002) plane was used in this work. The theoretical curve can calculate when a proper model of sample structure is assumed. The X-ray CTR spectra were analyzed by curve fitting to the calculated curves. Fig. 1 shows the X-ray CTR spectra of 1ML-grown InAs sample and the theoretical curve calculated with the best fit parameters for the example.

The curve fitting calculation went on very well. For example, the thicknesses of the InP cap layers are nearly equal to what we designed.

The distribution of As atoms and the amount of As atoms in each sample were obtained. The results show that the As atoms extended only into the upper layer, and not extended into the lower layer. The amounts of As atoms in sample-a and -b are about 0.45[ML] and 0.72[ML]. This means that contrary to our design As atoms only for 0.45[ML] were contained in sample-a, and that InP exposed to AsH₃ for 8[sec] contained As atoms as much as 0.72[ML] of InAs. The amount of As atoms in each sample was investigated also by As characteristic X-ray fluorescence yield measurement [4] The result of the measurement agreed well with the result of X-ray CTR measurement. These results indicate that X-ray CTR measurement can sense the layer structure as thin as 1ML and can reveal the distribution of the composition in the resolution of atomic layer.

Acknowledgments

The authors would like to thank Mr. H. Kamei. All OMVPE-grown samples were prepared by him.

References


Figure 1: Measured X-Ray CTR spectra. ℓ is index of k-space.
X-ray Studies of Macrophage Migration Inhibitory Factor from Human Lymphocytes

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Introduction

Lymphocytes secrete a large number of soluble protein mediators, known as lymphokines, in response to antigenic or mitogenic stimulation. The first lymphokine discovered was macrophage migration inhibitory factor (MIF), which was originally identified by its ability to prevent the migration of guinea pig macrophage out of capillary tubes in vitro (1,2). MIF was suggested to concentrates macrophages at the infection site and make them function in antigen processing and phagocytosis. MIF is also a potent activator of macrophages and is likely to be critical in cell-mediated immune host defenses (3). The cDNA of human lymphocyte MIF was cloned (4). The protein encoded by human lymphocyte MIF cDNA has a molecular weight of about 12.5 KDa with 115 amino acid residues.

Experimental

The crystals of MIF from human lymphocytes appeared when ammonium sulfate was used as a precipitant. Best ordered crystals were obtained after 3-5 days when a droplet of protein solution (5 mg/ml) containing 1.05 M ammonium sulfate and 50 mM Tris-HCl (pH 8.5) was equilibrated against a 2.1 M ammonium sulfate. The crystals were regularly shaped prism with dimensions of about 0.3 x 0.3 x 0.2 mm. These crystals belong to space group P3₁21(P3₂21) with a=b=96.4 Å and c=105.5 Å.

Intensity data were collected with synchrotron radiation at 2.5 GeV at the BL-6A2 of Photon Factory, the National Laboratory for High Energy Physics, Tsukuba, Japan. The X-ray beam was monochromatized to 1.00 Å by Si (111) monochromator system. A screenless Weissenberg camera with a 0.2 mm aperture collimator and a cylindrical cassette of 286.5 mm was used. The diffraction intensities were recorded on 200 x 400 mm imaging plates (Fuji Photo Film Co. Ltd), which were digitized at 100 μm intervals on a Fuji BA100 read-out system. The intensity data were processed using the WEIS program (5). The total oscillation range of 90.5° was covered by 20 serial Weissenberg photographs. Oscillation range of 5.0° was employed throughout of the data collection. The exposure time was 20 sec. per degree. The crystals were stable towards X-ray exposure and the diffraction was recorded beyond 1.9 Å resolution. The merging R factor was 0.061 for 77,199 measurements. A total of 21,552 independent reflections (up to 2.0 Å) were obtained.

We thank Professor N. Sakabe and the Photon Factory, National Laboratory for High Energy Physics (BL-6A2) for his kind help in data collection. This work was supported in part by grant-in-aid of Ministry of Education, Science and Culture of Japan (No. 05244105).

References

Glucose dehydrogenase (EC. 1.1.1.47) from Bacillus megaterium is tetrameric enzyme with four identical subunits. Each monomer consists of 261 amino acids with Mr=28200. The enzyme is inactivated in alkaline solution and is stabilized by the addition of NaCl. The inactivation is due to the reversible dissociation of the tetramer into inactive monomers. We have obtained 7 kinds of stability-increasing mutant enzymes by single amino acid substitution. The amino acid substitution in them must have much information about the role of these amino acid residues in the stabilization of the intersubunit interaction and/or tertiary structure of the protomer. In order to elucidate the mechanism of increasing stability, we started the X-ray crystallographic structure analysis of this enzyme.

Glucose dehydrogenase (GlcDH) was purified according to the procedure of Nagao et al. from Escherichia coli KP3998 cells harbouring the over-expression plasmid pGDA2, a hybrid plasmid containing a glucose dehydrogenase gene from B. megaterium 1WG3. The crystal suitable for the X-ray analysis were obtained from solutions of polyethyleneglycol by vapor diffusion in hanging drop, followed by a microseeding technique. The best crystals were obtained by mixing 5 μl of a protein stock solution containing 10mg/ml GlcDH and sodium phosphate buffer with 5 μl of a reservoir solution. Crystals developed of size up to 0.2x0.2x1.2 (mm) within one month.

The crystals belong to the monoclinic, space group C2 with unit cell dimensions of a=119.57Å, b=66.05Å, c=120.83Å and β=93.05°.

The diffraction data for native crystals were collected on Weissenberg camera at Photon Factory with the imaging plates as a detector. The latent image in the imaging plates were digitized on a Fuji-Film BA100 scanner and processed with program WEIS to evaluate integrated intensities. The data collection statistics are summerized in Table 1.

On the other hand, two heavy atom derivatives (Hg, Pt) were obtained by soaking native crystals. The data collection statistics are also given in Table 1.

Heavy atom positions were determined from difference Patterson and cross Fourier maps. Heavy atom parameters were refined at 3.2Å resolution. The MIR electron density map allowed discrimination between the protein and solvent region. There is one tetramer in an asymmetric unit. It is likely that each protomer is related by three twofold axes. Further analysis is in progress.

Acknowledgement
We are so much thankful to Dr. Nakagawa for his assistance in the data collection and processing.

References
Cytochromes c' are small electron transfer proteins with 120-130 amino acid residues and a single protohaem IX group attached through an invariant Cys-X-Y-Cys-His motif which provides the fifth iron atom ligand through His $\text{Ne}^2$. Unique features of these proteins are the absence of any sixth ligand to the iron and their ability to bind small neutral ligands (NO, CO) at the vacant coordination site. The cytochromes c' are invariably isolated as soluble dimers.

Crystallographic analyses of the cytochromes c' from three bacterial species (refs 1, 2, 3) have established that they have a classic 4 helix bundle topology with the haem filling a cleft at one end. Little homology exists between members of the group (typically 25-30% identity) and interhelix angles within the bundles also vary. Monomer-monomer contacts are mediated principally through helix A but again the A-A' angle can vary by as much as 12° according to species.

Crystals of cytochrome c' from Alcaligenes sp have cell dimensions $a = b = 54.4$ Å, $c = 181.1$ Å, $\gamma = 120°$, space group $P6_522$, $Z = 12$. Despite extensive screening only one heavy atom derivative ($K_2PtCl_4$) has been obtained.

Structure solution by molecular replacement on its own failed and the correct AMORE solution was eventually identified from the anomalous phasing of the iron atom (obtained from a lower resolution Cu-K$^+$ data set) combined with considerations of dimer formation (ref 4). Density modification, model building and L.S. refinement could not define the interhelix loops so phase information from the single isomorphoiis derivative was used to completely define the structure.

A 1.8 Å native data set was collected on beamline 6A2 of the Photon Factory synchrotron source, courtesy of Dr N. Sakabe (ref. 5). Intensity data were measured by screenless Weissenberg photography with image plates using X radiation of 1.0 Å wavelength. Two crystals were used; one oriented along [c] and rotated in all through 60° (65 min. total exposure) and the second with an [a] axis mount rotated through 90° (84 min. exposure). Images were processed using the program WEIS and after scaling and merging the complete data set comprised 18,500 unique reflections (89% complete) with an overall $R_{merge}$ of 0.054.

2.35 Å data for the derivative were collected locally and processed to give 4950 unique reflections with $R_{merge} = 0.045$.

Phases calculated from one major and two minor substitution sites gave a mean FOM of 0.44 and the SIR phased map correlated well with that obtained from anomalous iron scattering. Point by point addition of (1) the anomalous iron map, (2) the SIR phased map and (3) a Wang, phase-extended map gave a combined map in which the interhelix loops could be traced. Refinement employing initially XPLOR and then TNT proceeded without difficulty.

The final structure containing 1045 atoms gives a final $R_{value}$ of 0.184 for all data between 20.0-1.86 Å with RMS deviations from accepted geometries of 0.015 Å and 2.0° for bonds and angles respectively. The average coordinate error is 0.15 Å.

Structure analysis and comparison of this cytochrome c' with others confirms that there is much variability within the 4 helix bundle motif, due mainly to the absence of inter helix hydrogen bonds. In all structures the haem is surrounded by non conserved hydrophobic residues, one of which occupies the site of the "6th ligand". There is a network of conserved hydrogen bonds to the haem propionate in which a conserved arginine (Arg 112) plays a key role. The large B-C loop which provides many essential haem contacts shows many deletions and insertions but nevertheless maintains a conserved structure of [310 helix-two $\beta$ bonds-310 helix]. The angle between helices A and C is the most conserved whereas those involving B and D, which have least interaction with the haem, are the most variable.


Cytochrome c'

The haem is shown as a ball-and-stick model
THE CHARGE DENSITIES OF C₆₀ AND ALKALI METAL DOPED C₆₀ BY THE MAXIMUM ENTROPY METHOD.

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Introduction

Alkali metal doped fullerenes are attractive substances as superconductors. So far, many experimental and theoretical studies have been done to examine the mechanism of superconducting behavior. For the fundamental crystal structure, it is well known that the C₆₀ molecules form fcc positions and alkali metal atoms locate at tetrahedral and octahedral sites.

Recently, a new method has been developed for accurate structure analysis, that is, the Maximum Entropy Method (MEM). The MEM is the promising since the high resolution electron density can be obtained directly from the limited number of X-ray data without using a structural model. The charge density study of metal doped fullerene superconductors has a potential to give useful information for the study of superconducting mechanism.

In this report, the results of the MEM analysis based on the SR powder data of alkali metal doped fullerenes, Li₂CsC₆₀ (Tc=0K) and K₂RbC₆₀ (Tc=23K), are presented.

Experiment

The X-ray powder data was collected by the large Debye-Scherrer camera (radius 572mm) using Imaging Plates (IP) at the Photon Factory BL-6A2, BL-18B and BL-16B. The wavelength of the incident X-ray was 1.542Å (C₆₀) and 1.0Å (Li₂CsC₆₀ & K₂RbC₆₀). In order to have a X-ray powder pattern with good counting statistics, the diffracted intensities were accumulated on IP for 3-4 hours, which is rather long as exposure time for IP experiment. The obtained powder patterns are shown in Fig.1.

Charge Densities in C₆₀, Li₂CsC₆₀ and K₂RbC₆₀

The details of the procedure to obtain MEM density distributions from powder data are given in elsewhere. In Fig.2, the MEM electron density maps are shown for the lower density region of (110) plane. The MEM charge density of pure C₆₀ reveals the image corresponding to the free rotation of C₆₀ molecule. For Li₂CsC₆₀, the characteristic concentration of the charge densities in the direction of <111> are found on the C₆₀ cage. On the other hand, the charge distribution of K₂RbC₆₀ is found to have strongly localized density of C₆₀ cage in accordance with merohedral disorder. It is concluded that there are distinct difference with regard to the charge distribution of C₆₀ molecule which should be related to superconducting behavior.

The authors thank Prof. N.Sakabe and Drs. A.Nakagawa, N.Watanabe, S.Adachi and S.Ikemizu for their kind help in data collection at PF.

References

STRUCTURAL STUDY of FLUORITE - HYDROGEN TERMINATED Si(111) INTERFACE by X-RAY CTR SCATTERING TECHNIQUE

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CaF$_2$/Si(111) structures became a model object for studies of fluoride on semiconductor heteroepitaxy owing to close lattice matching and relative simplicity of their growth by molecular beam epitaxy (MBE)[1]. The heating at high temperature used to obtain clean Si surface is undesirable for future device applications and 7x7 superstructure on Si(111) makes it difficult to form the perfect interface. In the present work we applied the technique of x-ray crystal truncation rod (CTR) scattering to study thin MBE grown CaF$_2$ films on H-terminated Si(111) surface and atomic structure of the interface.

All the studied samples were grown in Physico-Technical Institute (St. Petersburg) in a small research MBE system. The H-terminated silicon surface was obtained by chemical etching according to [2]. Reflection high energy electron diffraction measurements before the fluorite growth showed that the silicon surface was flat and did not have any superstructure. The usual growth process was as follows:

1. deposition of CaF$_2$ 3 ML (monolayer) on H-Si(111) at 200°C;
2. anneal at 700-850°C for 10 minutes;
3. growth of 15 to 22 ML of CaF$_2$ at 200°C.

The low temperature at the last stage provides the coherent growth mode of the film [3].

X-ray diffraction measurements were carried out at BL-6A2 using Imaging Plate technique [4]. The radiation wavelength was 1.00 Å, the beam was 0.1 mm in diameter. All the presented data are background subtracted integrated intensities of CTR scattering versus the normalized angle, measured in Si(111) reciprocal lattice units $X$.

All the data were fitted using one-dimensional scattering model:

$$I(X) = \frac{1}{A_{sub}(X)} + Q \exp \left( \frac{2\pi i X d}{A_{film}(X,R)} \right)^2$$

where $I(X)$ is the reflected intensity, $A_{sub}$ and $A_{film}$ are Si substrate and CaF$_2$ film contributions to the scattering amplitude, $d$ is the interfacial distance [5], $Q$ is the factor representing crystal quality of the film and $R$ is the average deviation from the mean film thickness (ML).

Curves (a) and (c) in Fig. 1 show the CTR profiles from the CaF$_2$ films grown on H-Si(111) and annealed at different temperatures. The curve (d) relates to the film grown on 7x7 reconstructed clean Si(111) surface. All these curves indicate that the films are of high crystal quality ($Q = 0.9$). The interfacial distances are very close to $d = 0.9$ and correspond to the interface where Si atoms of the last substrate layer are bonded to Ca ions in the first layer of the film [6]. As it is seen from the damping of thickness oscillations, the film with annealing at 850°C (a) is much smoother and has the best fit roughness parameter $R = 3$.

The obtained values of the interface distance correspond to the so-called "short interface" ($d = 0.9$) which is metastable and transforms to the "long interface" ($d = 1.45$) within a day in thin (15 ML) film [6]. We found the "short interface" in the sample with 15 ML of CaF$_2$ in the measurements one week after the growth (curve (a)) and then a week later again (curve (b) $d = 0.92$). Thus we conclude that the "short interface" remains unstable at least within two weeks in the film grown on H-terminated Si(111) surface.

REFERENCES


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Fig. 1 CTR profiles from CaF$_2$/Si(111) structures
(a) 15 ML on H-Si(111), anneal at 850°C, (b) the structure of (a) measured a week later, (c) 22 ML on H-Si(111), anneal at 700°C, (d) 21 ML on 7x7 Si(111), anneal at 850°C.

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CRYSTAL STRUCTURE OF THE COMPLEX BETWEEN BOVINE TRYPsin AND WHEAT GERM TRYPSIN INHIBITOR (I-2) AT 2.3Å RESOLUTION

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Introduction
A trypsin inhibitor I-2 from wheat germ contains 123 amino acid residues and 10 disulfide bridges, its molecular weight being 12,600. The amino acid sequence of the first 56 residues was determined by Odani et al.\(^1\) The known sequence and the amino acid composition of I-2 are very similar to those of barley rootlet trypsin inhibitor (BRTI).\(^2\) Both I-2 and BRTI consist of two domains of approximately 60 residues, each of which can inhibit one trypsin molecule. In order to determine the tertiary structure of I-2 which belongs to a new family, the structure study has been carried out.

Experimental
The crystallization and the data collection of the 2:1 complex between trypsin and I-2 have been described previously.\(^3,4\) The crystals belong to space group \(P2_12_12_1\), \(a=73.49(2), b=120.56(3), c=70.04(2)\AA\) and \(V=6.206(5)x10^8\AA^3\). High resolution X-ray data were collected using Weissenberg camera at the BL-6A, station at the Photon Factory. The structure was determined by the molecular replacement method based on the structure of bovine trypsin (BT). The poly-alanine model of I-2 was initially traced using a 2Fo-Fc map at 2.5Å resolution, on the basis of the structure of adzuki inhibitor (AB-1). Most of the unknown amino acid residues could be assigned, judging from the electron density map calculated at several refinement stages. The final model of I-2 includes 115 amino acid residues of which eight are not identified. Four N-terminal residues and four residues in a flexible loop could not be built because of the very diffuse electron density in the corresponding regions of the map.

The structure was refined using X-PLOR to an R-factor of 0.178, in which two trypsin molecules, two \(\text{Ca}^{2+}\) ions and 220 water molecules are also included.

Results and discussion
The structure of the two domains, A and B, are essentially similar to each other (Figure). Each domain has an anti parallel \(\beta\)-sheet of three strands (sub domain 1 or 3), a small anti parallel \(\beta\)-sheet of two strands and two flexible loops (sub domain 2 or 4), which are related by a pseudo two-fold rotation axis. The loop which connects the two strands in sub domain 2 or 4 is very flexible and four residues in the loop of sub domain 4 could not be built. The sub domains 1 and 3 include an arginyl residue for the reactive site, respectively. The structure of sub domains 1 and 3 is basically similar to that of the trypsin binding domain of Bowman-Birk type inhibitors (BBI). The reactive site of sub domain 1 or 3 interacts with BT in the same manner as BBI.

References
Introduction

Cyclophilins (CyPs) have been originally identified as soluble intracellular receptor proteins for immunosuppressants cyclosporin A (CsA) and subsequently shown to have peptidyl-prolyl cis-trans isomerase (PPIase) activity in vitro. CyPs are classified into two families: CyPa present in the cytoplasm and CyPb in the membrane. CsA has been revealed to be immunosuppressive in the formation of drug-receptor complex which blocks T-cell activation and/or proliferation. A variety of mechanistic probes have led to the proposal of enzymatic catalysis by the distortion. Which residues in the CyP are critically important for initiating catalysis remains somewhat unclear. We report the crystal structure of yeast CyPA with molecular weight of 17400 consisting of 162 residues at 1.9 A resolution. From structural comparison with human CyPA and E. coli CyPA attached with a small peptide we propose a model in which the interaction between particular residues of hydrophobicity and proline ring of the substrate initiates cis to trans isomerization.

Experimental

Crystals of yeast CyPA were obtained using hanging drop vapor diffusion technique. They belong to triclinic, space group P1 with cell constants of \( a = 44.45(2), \ b = 53.11(2), \ c = 32.018(6) \) A, \( \alpha = 84.91(2), \beta = 95.22(4), \gamma = 108.56(4) \). The unit cell contains two crystallographically independent molecules. X-ray intensity data were collected with Weissenberg camera in the wavelength of 1.00 A with BL6A2 beamline at Photon Factory in Japan. 65303 reflections were observed using two crystals at 1.6 A resolution and \( R_{merge} \) of 4.74% was obtained for 22622 independent reflections. Human CyPA was used as a search model for molecular replacement calculation using XPLOR. PC refinement of the highest rotation function peaks gave two peaks related by a local two-fold axis. Translation function for the position of molecule B produced the highest peak at 0.269, 0.962, 0.692 in fixing the position of molecule A at origin. The rigid body refinement for this model reduced \( R \) to 34%. The model was built and improved on the basis of 2Fo-Fc Fourier maps using O. The final \( R \) factor for the model containing of 126 water molecules was 18.5% at 1.9 A resolution.

Result and Discussion

The yeast CyPA has \( \beta \)-barrel structure consisting of antiparallel eight \( \beta \)-strands with two \( \alpha \)-helices at the top and the bottom. As observed in human and E. coli CyPAs. \( \beta \)-barrel is composed of two orthogonal \( \beta \)-sheets. There exists the cleft in the surface of the first \( \beta \)-sheet. The second \( \beta \)-sheet stabilizes overall \( \beta \)-barrel structure by the hydrophobic residue core making with the first \( \beta \) sheet. The hydrophobic pocket consisting of Phe-58, Met-59, Phe-111, Trp-119, Leu-120. His-124 is in the cleft and acts as the receptor site. These residues are conserved in human CyPA while the tryptophan and histidine residues are replaced by the phenylalanine and tyrosine residues with the hydrophobic property respectively in E. coli CyPA. These side chains take at the same orientation.

Fig. 1 Ribbon diagram of yeast CyPA. Hydrophobic residues in the receptor site are represented by stick model.
X-RAY CRYSTALLOGRAPHIC ANALYSIS OF $\alpha$-AMYLASE INHIBITOR

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Introduction

$\alpha$-Amylase inhibitors ($\alpha$-AIs) are known to distribute widely in plants. In wheat two types of AIs, endogeneous and exogeneous ones, are present. The exogeneous AIs in wheat inhibit enzymes of animal and insect origin, and are classified as to molecular weight (60 K, 24 K, and 12 K) into three families. The AIs with molecular weights of 60 K and 24 K are composed of several subunits with molecular weights of 12 K. The amino acid sequences of some of the exogeneous AIs are homologous. The exogenous AI coded 0.19 is one of the most studied inhibitors from wheat kernel, and belongs to the 24 K family. The amino acid sequence of this AI is composed of two identical subunits, each of which consists of 124 amino acid residues. This AI has five disulfide bonds. To date, however, little is known about the three-dimensional structures of these AIs. Here we report the X-ray intensity measurement of 0.19 $\alpha$-AI and preliminary X-ray crystallographic analysis.

Experimental and Results

$\alpha$-AI was purified from wheat flour and crystallized in 20 mM PIPES buffer (pH 7.0) containing 100 mM NaCl. The crystals belong to space group $P3_1$ or $P3_2$, and have unit-cell dimensions of $a=b=79.3 \text{ Å}$, and $c=60.8 \text{ Å}$. The $V_m$ value is 2.0 $\text{Å}^3$/dalton assuming that two dimers are present in an asymmetric unit. Heavy-atom derivatives were prepared by the soaking method and analysed preliminary using low-resolution data collected with a four-circle diffractometer and CuKa radiation.

For the mercury and uranium derivative crystals as well as the native ones, high resolution intensities were collected with synchrotron radiation at BL6A2 and Weissenberg camera for macromolecular crystals. The radius of cassette used was 429.7 mm. The diffraction intensities recorded on the imaging plates were read out by a Fuji film BA-100, and processed by WEIS program. Conditions and results of the measurements are given in Table 1. For the native crystal, two sets of the camera data and the diffractometer data were merged and scaled to yield 19,167 independent reflections.

One major mercury site was determined by the difference Patterson map. Four uranium sites were determined by the difference Fourier and Patterson maps. Their coordinates and occupancies were refined using the program PHASES. The mean figure of merit was 0.56 for the data between 15 and 3.5 Å resolution. Interpretation of the best Fourier map is currently underway.

Table 1. Experimental conditions and results

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We thank Drs Atsushi Nakagawa and Shinji Ikemizu and Prof. Noriyoshi Sakabe for their kind help in the data collection using the Weissenberg camera.

References

Three-dimensional structure of "BphC" enzyme from Pseudomonas sp. KKS102 having polychlorinated biphenyl (PCB)-degrading activity.

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Introduction
Polychlorinated biphenyls (PCBs) are widely distributed environmental pollutants. Because of their chemical stability, PCBs are recalcitrant to biodegradation. Since 1973, many microorganisms that could degrade PCBs have been isolated and characterized. Pseudomonas sp. strain KKS102 is one of the PCB-degrading microorganisms and the "BphC" enzyme (2,3-dihydroxybiphenyl dioxygenase) is a key enzyme in the PCB degradation pathway of the microorganism. The BphC enzyme is characterized as one of the extradiol type dioxygenases which have one Fe(II) ion in their active sites. To gain insight into the catalytic mechanism of the BphC enzyme, we undertook X-ray crystallographic analysis of BphC enzyme from Pseudomonas sp. strain KKS102. The BphC enzyme is an oligomeric enzyme made up of eight identical subunits each of 292 amino acid residues. The total molecular weight of the BphC enzyme is ca. 250kDa.

Experimental
Three-dimensional structure of BphC enzyme was solved using multiple isomorphous replacement method (MIR) with selenomethionyl proteins used as one of the heavy atom derivatives. The high resolution native data were collected using the macromolecule-oriented Weissenberg camera devised by Prof. Sakabe installed at BL6A2. We used XPLOR for the crystallographic refinement. Current R factor at 2.3 Å resolution is 18.6 % with 41 solvent atoms and one MPD molecule.

Results
The BphC enzyme is a thick-walled cylinder that has a diameter of ca. 110Å and a height of ca. 93 Å. It contains a substantial central cavity or channel which is barrel shaped, the inner diameter being ca. 25 Å at the top of the cylinder, and ca. 50 Å at the middle part of the cylinder. The octamer can be regarded as a stack of two planar rings each of which is composed of four subunits arranged with a four-fold rotational symmetry. The subunit of BphC enzyme is composed of two domains (Fig.1). Each domain contains two repetitions of a unique folding motif consisting of ca. 55 amino acid residues. The repetitive motif has a "ββββ" motif which appears to be the novel one. In terms of this "ββββ" motif, the subunit of BphC enzyme is composed of four repetitions of the "ββββ" motifs.

In the active site, we found an Fe ion which was coordinated by side chains of three amino acid residues, His145, His 209 and Glu 260. The crystallographic analysis of the BphC enzyme complexed with 2,3-dihydroxybiphenyl (2,3-DHBP) showed two hydroxyl groups of 2,3-DHBP coordinated to the Fe ion resulting in a five-coordination geometry roughly arranged in a trigonal bipyramid form (1).

Fig.1 Schematic drawing of a subunit of the BphC enzyme.

Reference
HIGH RESOLUTION DIFFRACTION STUDIES ON RUBISCO FROM SPINACH AND SYNECHOCOCCUS

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Ribulose-1,5-bisphosphate carboxylase/oxygenase (Rubisco) catalyzes the initial reaction of the two competing metabolic pathways of photosynthetic CO$_2$ fixation and photorespiratory carbon oxidation. As a result, CO$_2$ and O$_2$ compete for the same catalytic site. Oxygenation of RuBP leads to a decreased net efficiency of photosynthesis. In order to understand the catalytic mechanisms and the role of individual residues during catalysis, a detailed knowledge of the three-dimensional structure of reaction intermediates and mutant enzymes is required to the highest possible resolution. This could pave the way for site directed mutagenesis experiments aimed at suppressing the unwanted side reaction.

The enzyme in eukaryotes and the majority of prokaryotes is a hexadecamer (L$_8$S$_8$, 550 kD) composed of eight large, (L, 55 kD) and eight small, (S, 14 kD) polypeptide chains. Despite the obvious difficulties involved in crystallizing such large molecules, crystal quality is generally high with crystals often diffracting to 2 Å resolution or beyond. Our project at the Photon Factory aims at capturing the highest possible resolution at a high speed.

EXPERNIMENTAL

Spinach enzyme

Our initial structure of this enzyme is of an activated quaternary complex with 2-carboxyarabinitol-bisphosphate (2-CABP), an analogue of an intermediate halfway in the carboxylation reaction mechanism (1). The crystals of the very stable 2-CABP complex were obtained using ammonium sulphate. In order to crystallize other less stable complexes, it was necessary to replace ammonium sulphate with another precipitating agent, because sulphate ions compete with the ligand in the active site. We have managed to overcome a certain disorder problem and have obtained crystals from the unliganded and activated form of spinach Rubisco into which substrates can be diffused. The crystals are grown from polyethylene glycol, are isomorphous with the crystals of the 2-CABP complex and diffract to at least 2 Å. These crystals could be ideal for time-resolved diffraction experiments under conditions when the enzyme turns over. Preliminary experiments in the home laboratory showed that the active site loops have opened up and that these crystals can withstand soaking of ligands without loosing diffracting power.

Two different starting crystals were used with slightly different loop structures: the unliganded activated crystals, and crystals of a complex with the product phosphoglycerate (PGA) from which PGA can be washed out. One dataset was collected on the PGA complex. Another dataset was collected on crystals where PGA was washed out and replaced with the substrate RUBP. In this case it was necessary to use calcium as an activator metal to prevent the enzyme from turning over in the crystal. We used a Weissenberg camera for macromolecular crystallography at BL6A2 (2) with an IP radius of 860 mm and a 100 mm collimator. Four Fuji BASIII imaging plates were used giving a total detector area of 80 cm x 40 cm. Diffraction data to about 2.1 Å resolution were collected (wavelength = 1.00 Å; I = 270 mA; E = 2.5 GeV) with an oscillation range of 3 deg/exposure. These data were processed and merged with data collected at Daresbury using DENZO (3). Refinement of the RUBP complex is nearly completed and the structure shows clear density for the activator carbamyl, the metal and RUBP in the active site.

Synechococcus enzyme

A different approach is to use site directed mutants of Synechococcus Rubisco to investigate the role of individual residues in catalysis (a collaboration with Prof J. Andrews, Research School of Biological Sciences, Canberra, Australia). The mutant T65V shows an altered relative specificity and different partitioning of side-reactions. It crystallizes in isomorphous with the crystals of the 2-CABP complex in spacegroup P2$_1$ with unit cell dimensions 169.9 Å, 169.6 Å, 108.9 Å, β=98.6°. Diffraction data from three crystals collected in the previous allocation period have been processed with DENZO: the final merged data set contained 258,749 unique reflections to 2.2 Å resolution (R merge = 0.111). The structure was solved by molecular replacement and refined with a final R factor of 0.186 for all reflections between 7.0-2.2 Å.

ACKNOWLEDGEMENTS

We are greatly indebted to Prof. N. Sakabe and Drs A. Nakagawa and N. Watanabe for their assistance with the use of Beam line 6A2. The work was supported by NFR, SJFR, MRC and OCMS.

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STRUCTURAL STUDIES OF GLUTATHIONE S-TRANSFERASES

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The Ian Potter Foundation Protein Crystallography Laboratory, St Vincent's Institute of Medical Research, 41 Victoria Parade, Fitzroy, Victoria 3065, AUSTRALIA

Introduction

Glutathione S-transferases (GSTs) are a key component of an organism's defence against toxic chemicals.\(^1\) GSTs have been implicated in the development of the resistance of cells and organisms towards drugs, pesticides, herbicides and antibiotics and hence have been the subject of intense research over the last few years.\(^1\) We have obtained crystals of GSTs from a diverse range of organisms\(^2,3\) as a first step towards structure-based design of new GST inhibitors.

Methods

Crystals of four GSTs were taken to the Photon Factory. Human placental crystals grow in space group \(P4_2_1_2\) with cell dimensions \(a=b=60.0\,\text{Å}\), \(c=239.0\,\text{Å}\) and diffract beyond 2.5 Å. Insect GST crystals grow in space group \(P4_2_2_2\) with cell dimensions \(a=b=88.0\,\text{Å}\), \(c=66.9\,\text{Å}\) and diffract to about 2.2 Å. Liver fluke GST crystals grow in space group \(I4_2_2\) with cell dimensions \(a=b=160.0\,\text{Å}\), \(c=77.8\,\text{Å}\) and diffract to approximately 3.0 Å. Bacterial GST crystals grow in space group \(P4\) with cell dimensions \(a=b=90.9\,\text{Å}\), \(c=117.3\,\text{Å}\) and diffract to 2.3 Å resolution. Crystals were mounted in X-ray capillaries and fixed to the Weissenberg camera on beam line 6A2. Diffraction data were collected on Fuji image plates and scanned on a Fuji BA100 image plate reader. Processing of the X-ray diffraction data were undertaken using the program WEIS.

Results and Discussion

We had previously solved the structure of the human placental GST.\(^4\) A number of data sets were collected of the human GST in complex with various inhibitors and substrates. The data sets have been processed and are currently being analysed. One native and two heavy atom derivative data sets of the insect GST were collected and processed. The insect GST structure has now been solved by the multiple isomorphous replacement method.\(^5\) The liver fluke GST crystals have proved radiation-sensitive and hence are a candidate for cryocrystallography. A search for suitable cryoprotectants is currently in progress. A native data set for the bacterial GST has been collected and a search for suitable heavy atom derivatives is in progress.

Acknowledgements

We thank KEK National Laboratory for High Energy Physics and the Australian Nuclear Science and Technology Organisation for supporting the project, and Prof. N. Sakabe and Dr. A. Nakagawa for their assistance with use of beam line 6A2. We thank the Biomolecular Research Institute for their help and advice with the program WEIS.

References

STUDY ON PRECISE STRUCTURE OF SCORPION NEUROTOXIN: DIFFRACTION DATA COLLECTION AT 1.2Å RESOLUTION*

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Introduction
Scorpion toxins are a family of small neurotoxic proteins. Generally, most of the toxins are a group of basic homologous polypeptides containing about 60-80 amino acids except BmK IV[1] whose pI is 5.3. It has been reported that they bind to various ion channels[2] with high affinity and selectivity. In spite of the significant sequence similarity found among different toxins, they display various degrees of toxicity and specificity to different animal species. Therefore it is a good system for studying the structure-function relationship.

Chinese scorpion Buthus martensi Karsch, summarized as BmK, widely distribute all over China and East Asia. An acidic scorpion neurotoxin BmK8, which displays the lowest toxicity to mammals among the purified eight neurotoxins[1], has been successfully crystallized[11]. Then two other toxins (BmK4 and BmK1) with a medium and a high toxicity respectively were crystallized so as to establish an activity-sensitive crystallographic system. On basis of this, a 3-D structure series of toxicity-different toxins with homology may be established, furthermore, the detail comparison between activity and structure can be performed. Obviously, high resolution data is important to perform this procedure in order to finally explain the relationship between the various toxicity of the complicated molecules and the structures of them.

Experiments and Results

Crystals of BmK1 used in the data collection was crystallized from a recipe containing 2.8M NaH2PO4 (pH~4.53) described as Li et al[14]. The crystals belong to a space group P212121 with cell dimensions a=27.12Å, b=52.77Å, c=76.39Å and two molecules per asymmetric unit. Two very high quality crystals with the size about 0.7 x 0.2 x 0.1mm³ selected from a batch crystals were mounted along a and b axes for two data sets, respectively. The diffraction data collection was carried out with a screenless Weissenburg Camera and Image Plates[5] at the beam line BL6A2 of Photon Factory in KEK. A wavelength of 1.0Å and a film cassette with radius of 429.7mm were used in data collection. The intensity were read out by Fuji Film BA100 Scanner System and processed using the WEIS program system[6]. The experimental conditions and data evaluation are listed in Table 1. Two data sets with a and b rotation axes were collected and then were combined so as to overcome the loss of reflections due to the blind zones. A total of 78828 reflections were measured which were merged into 24712 independent reflections. A statistical analysis of this data set is listed in Table 2 which shows a high quality data With a very high resolution of 1.2Å has been available. The structure analysis is now in progress.

We would like to thank Professor Sakabe for the use of camera and Dr. Watenabe for the helps in the data collection procedure.

References

Table 1. Experimental Conditions and Data Evaluation

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<td>No. of reflections</td>
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Table 2 Statistical Analysis of the Merged Data

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<td>Rmerge</td>
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Supported by National Foundation of Nature Science (39370153).
** Corresponding author
Crystal Structure of Holliday Junction Resolvase RuvC Protein from *E. coli*


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INTRODUCTION
Holliday junction, which results from homologous pairing and strand exchanges between two DNA molecules, is a central intermediate in genetic recombination or DNA repair. At the final stage of recombination, the intermediate is required to be resolved into recombinant DNA duplexes. In *E. coli* cells, the RuvC protein (M.W. 19kDa) catalyzes the resolution of the Holliday junction through the endonucleolytic mechanism. The RuvC dimer introduces nicks at or crossover the junction with both identical polarity and symmetry. This process requires a homologous sequence at the junction point and Mg^{2+} cations.

EXPERIMENTS
The RuvC crystals were obtained using the microdialysis method. The crystals belong to the monoclinic space group P2₁, with unit cell dimensions a=72.8Å, b=139.6Å, c=32.4Å, and β=93°, and contain four molecules per an asymmetric unit. The RuvC structure has been solved by the MIR method and the molecular averaging. Intensity data sets for native and derivative crystals were collected using a Wissenberg-type imaging plate diffractometer mounted on a beam line BL-6A2 or BL-18B3. The statistics of data collections are shown in Table 1. The intensity data were evaluated using the program WEIS.

<table>
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<th>Table 1. Statistics of data collections at PF</th>
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<tr>
<td>Completeness</td>
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<td>Rmerge</td>
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RESULTS
The model was refined with the programs XPLOR and PROLSQ, resulting in an R factor of 15.7% for 15,545 reflections from 6Å to 2.5Å. The RuvC subunit consists of a five stranded mixed β-sheet with α-helices on both sides. The folding topology shows similarity to that of RNaseHI from *E. coli*. The crystal structure reveals a dimer formation of RuvC subunits related by a dyad axis (Fig.1). Combined with results from mutational analyses, the refined structure allows us to define the catalytic center, which is constituted by four acidic residues, Asp7, Glu66, Asp138 and Asp141, at the bottom of a large cleft. In the dimer structure, the catalytic sites lie 30 Å away from each other. The distance and steric hindrance between the active sites in the dimer imply that the substrate binding of RuvC would cause large structural changes to the junction point.

ACKNOWLEDGMENT
We are grateful to Prof. N. Sakabe, Drs. A. Nakagawa and N. Watanabe for their assistance in using the facilities at Photon Factory. Dr. K. Katayanagi, Mr. T. Kashiwagi and Mr. S. Sugiyama are also acknowledged for their help in data collection.

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Introduction
Hammerhead ribozyme is being watched with great interest as a new nucleic acid medicine, which can break down the mRNA of tumor cell products.\(^1,2\) To reveal the mechanism of the catalytic reaction, several research groups are challenging to clarify the crystal structure. The structure of a complex between hammerhead ribozyme and its substrate analogue was reported by Mckay and his colleagues\(^3\) But the substrate of the complex is not RNA but DNA, and has no Mg\(^{2+}\) which is essential for the reaction. We succeeded to crystallize the enzymatic part of the hammerhead ribozyme which is consisted in two chains (Chain 2,3) (Fig.1).

Experimental
We have already reported the crystallographic data and experimental conditions for data collection.\(^4\) To clarify the structural composition of hammerhead ribozymes, the complex formation between the component RNA chains was investigated in several combinations by electrophoresis experiments.

Results
Hammerhead ribozymes have been defined including the substrate chain, without any evidence for the structural composition. It was not clear whether they always require the substrate chain to assemble a rigid structure. Our results show that the two catalytic strands formed a rigid complex, and it is possible that the catalytic binary complex forms a ternary complex when mixed with the substrate chain in solution. Hammerhead ribozymes may be thus defined in two parts, the catalytic and the substrate parts, like an enzyme protein in principle. If this is the case, comparative studies of the three-dimensional structures of the binary and the ternary complexes will be most interesting.

Fig. 1 Sequence of hammerhead ribozyme

Acknowledgement
We thank Dr. N. Watanabe, Dr. A. Nakagawa, and Prof. N. Sakabe of the Photon Factory for their assistance with the data collection.

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Structural Studies for Time Resolved Reaction Mechanism on Ribonuclease

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Introduction
According to the development of Laue method, we are understanding enzymatic reaction on the view of dynamic chemistry. Ribonuclease A is one of the well-known enzyme, but the detail of the catalytic mechanism is not clear so far. We employed ribonuclease A as a sample of such a time resolved Laue experiment. Well-understood knowledge of the mechanism on atomic level will give us a key to design an artificial enzyme for human life.

Experimental
A crystal was mounted in a flow-cell with cotton fibers. After injection of substrate, dinucleotide CpA (3 mM), Laue diffraction patterns were recorded on an imaging plate. The crystal was fixed at the same orientation during all data collections, because we wanted to collect reflection data which would be changed with time under the same condition. The exposure time was 20 m second for each shot. All the data was evaluated by the program LAUE written by Higashi.

Results
The change of Laue patterns was monitored with the number of observed reflections and Rmerge, as seen in Fig. 1 and 2. Until 50 minutes after injection, the numbers of reflection decreased but Rmerge increased gradually. Then these changes were reversed. These facts suggest that a "structural change" in the crystal is progressed during 50 minutes and then it goes back to the initial state before injection. The "change" would be caused by the catalytic reaction of ribonuclease A. Now we are evaluating the intensity data exactly and making electron density maps. The data will give us an interesting information on the reaction mechanism.

![Fig.1 A time course of number of observed reflections](image1.png)

![Fig.2 A time course of Rmerge](image2.png)

Acknowledgement
We thank Dr. N. Watanabe, Dr. A. Nakagawa, and Prof. N. Sakabe of the Photon Factory for their assistance with the data collection.
Ribosomes are the universal cell organelles facilitating the translation of the genetic code into proteins. They are riboprotein assemblies (m.w. 2.3x10^6 daltons), containing 60-73 different proteins and 3 RNA chains, of ca. 4500 nucleotides. Crystals diffracting best to 2.9 Å were grown from ribosomal particles of halophilic and thermophilic bacteria. The large unit cell dimensions, the extremely weak diffracting power, the relatively large mosaicity and the shape of the crystals (very thin plates or needles) dictate the performance of all steps in X-ray analysis with bright and highly collimated synchrotron radiation. At ambient temperature ribosomal crystals decay upon the first instance of X-irradiation. To overcome this unusual sensitivity, we developed cryo data collection techniques. Data of reasonable quality have been collected from crystals of ribosomal particles of wild-type and mutated bacteria; chemically modified particles; complexes of ribosomal particles with components of protein biosynthesis (mRNA, tRNA and nascent protein chains).

For phasing by MIR and MAD, heavy atom derivatization is being performed either by soaking crystals in solution of multi-metal salts, or by covalent attachment of monofunctional reagents of dense organo-metal clusters prior to the crystallization. The suitability of both approaches for intermediate resolution phasing has been clearly demonstrated in the recently obtained MIR and two SIR electron density maps: at 9 Å, 16 Å & 26 Å respectively, of the large and the small subunits, by soaking in heteropolyanion W salts: K$_3$Na$_2$W$_{18}$O$_{62}$ & (NH$_4$)$_6$(P$_2$W$_{18}$O$_{62}$)14H$_2$O or by pre-crystallization specific binding of an undecagold cluster. All three maps could be further refined by solvent flattening.

These progress has been made because of the availability of intense and focused SR beam and of the recent improvement of the quality of the crystals, which are of lower mosaicity and higher stability. The soaked crystals diffracted to 4-5 Å. Because of lack of sufficient beam time, data were collected only to 7-8 Å. Even at this resolution 1-1.5 hours were needed for rotation of 1 degree.

A projection of half of the unit cell of the 9 Å SIR map of the halophilic large ribosomal subunits.

A projection of half of the unit cell of the 16 Å MIR map of small thermophilic ribosomal subunits.
A NEW METHOD FOR ANALYZING THE PERIODIC STRUCTURE OF MULTILAYER
BY DIFFERENTIAL ANOMALOUS SMALL-ANGLE X-RAY SCATTERING

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Introduction

Small-angle x-ray diffraction in the reflection geometry is widely used for characterizing the periodic structure of a multilayer. Their peak intensities are proportional to the square of the difference between the average x-ray atomic scattering factors of each layer. Thus, only weak diffraction peaks are observed in some multilayers composed of elements with close atomic numbers, such as, the multilayers with the gigantic magnetoresistance (GMR). In such cases, the anomalous x-ray scattering (hereafter referred to as AXS) effect has been often applied in order to enhance a contrast of x-ray scattering power between layers.

On the other hand, the intensity of the higher order peak is drastically reduced because of the Lorentz-polarization and absorption effects. This prevents us from evaluating their accurate integrated intensity, which sometimes makes difficult to determine the concentration profile with sufficient reliability. This is more serious in the above GMR multilayers. Therefore, a new method to evaluate an accurate peak profile even for the higher order peaks has been tested.

Theoretical Background

Due to a large variation of anomalous dispersion terms (Fig.1a), the peak intensity shows a distinct change near their absorption edges (Fig.1b). As observed in Fig.1b, the peak intensity becomes almost equal to zero in the region just above the Cu K absorption edge, and the intensity is strongly amplified in the vicinity of the Co K absorption edge.

Let us choose the two incident energies of \( E_1 (7.69\text{keV}) \) and \( E_2 (9.20\text{keV}) \) in Fig.1b. This figure implies that large peak intensities are observed at \( E_1 \) and almost no peak is observed at \( E_2 \). By taking a difference between them, the peak profile would be accurately determined without being disturbed by large back-ground. This would greatly improve the signal to noise ratio especially at the higher order peak.

Results

Intensity profiles of the Cu/Co multilayer observed at \( E_1 \) and \( E_2 \) are compared in Fig.2. The intensity profile, corrected for the fluorescent radiations and absorption, and converted to the absolute units is shown in (a). Since these peaks may have some analogy with those from a single crystal along the depth, the Lorentz factor for single crystals, \((\sin 2\theta)^{1/2}\), is applied to the intensities of (a). The results are shown in (b). On the other hand, the intensities in (c) are the results with the Lorentz factor for powders, \((\sin \theta \sin 2\theta)^{1/2}\). It is found in (b) and (c) that the background profiles in (c) shows an extremely good coincidence though the background intensity at 9.2keV in (b) is shifted towards a larger value and its slope is slightly steeper than that at 7.69 keV. This suggests that the Lorentz factor for powders, \((\sin 2\theta \sin \theta)^{1/2}\), should be used in the present analysis. However, it should also be noted that we cannot give this conclusion any universality applying to all multilayered samples. The difference between these two intensity profiles in (c) will give accurate peak profiles from the Cu/Co multilayer. Further details will be explained in elsewhere (K.Kato et al., Mater. Trans. JIM, 36 (1995), to be printed).
LOCAL STRUCTURE AND OPTICAL PROPERTY OF ZrF₄-BASED GLASS DOPED WITH Ni²⁺

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**Introduction**

Recently several papers on heavy metal fluoride glasses doped with 3d- and 4f-transition metal ions have provided details of the optical properties that make these glasses attractive for use as laser host materials and optical fiber amplifiers. Most of the studies on the optical characteristics of these glasses have centered on ZrF₄-based glasses. Local structure analysis around transition metal ions in these attractive glasses is interesting in the viewpoint of clarifying controlling factors of their optical properties. However, systematic studies about the local structure around doped ions in fluoride glasses are few. In this study, the local structures around Zr⁺⁺ and Ni²⁺, being glass network forming cation and emission center 3d-ion, respectively, in ZrF₄-based glasses are clarified by measuring Zr and Ni K-EXAFS, and are related to ligand field strength around Ni²⁺ obtained from optical absorption spectra.

**Experiments**

Glasses of (95-x)ZrF₄-xBaF₂-2LaF₃-3NiF₂ (x=20–35) are prepared by a conventional melting method under an Ar atmosphere. Li₂ZrF₆ and NaNiF₃ were taken as reference for EXAFS analysis. EXAFS spectra were measured in a transmission mode at room temperature in Photon Factory, KEK; Zr K-edge (17.99keV) at beam line 10B and Ni K-edge (8.33keV) at beam line 6B. Because of low Ni concentration, Ni K-EXAFS measurements were carried out 3–5 times, and spectra were averaged to improve S/N ratio.

**Results & discussion**

Figure 1 shows the inter-ionic distances of Zr-F and Ni-F pairs as a function of glass-modifying BaF₂ content. The Ni-F inter-ionic distance remarkably changed with glass composition in contrast to the Zr-F inter-ionic distance. This means that local structure around Ni²⁺ is greatly affected by glass composition. The F⁻ coordination numbers around Ni²⁺ obtained from EXAFS analysis are almost 6 in all glasses. The spectral profiles of Ni²⁺ optical absorption also indicated that F⁻ coordination number around Ni²⁺ are 6, and NiF₆ polyhedra have O₆ symmetry configuration.

The ligand field strength around Ni²⁺ decreased with increasing Ni-F inter-ionic distance, as shown in figure 2. This fact agrees with the ligand field theory.

![Fig.1 Inter-ionic distances of Ni-F and Zr-F pairs as a function of BaF₂ content.](image)

![Fig.2 Relationship between Ni-F inter-ionic distance and ligand field strength.](image)

**References**

X-RAY ABSORPTION STUDY OF SUPERCRITICAL CF$_3$Br

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Department of Physics, Kyoto University of Education, Fukakusa, Fushimi, Kyoto 612, Japan
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Introduction

The local structure of supercritical fluid (SCF) state, i.e., the state beyond the critical temperature and pressure, is an interesting subject which is not well understood to date. In the case of gaseous molecules in ambient temperature and pressure, it is known that molecular clusters of various sizes are formed in the SCF state. However, little is known about the structure of the SCF state of molecules to date. With the x-ray absorption fine structure (XAFS) spectroscopy technique one can expect to observe the difference in the structure of liquid and that of the SCF state, and the effect of intra- or interatomic interaction in the SCF state as well as the size and the structure of the formed clusters.

For this purpose we have developed a cell equipped with gas handling system with which in-situ measurement of the SCF state can be made in the experimental station of the synchrotron radiation facility. The results of the x-ray absorption measurements on CF$_3$Br molecule are presented.

Experimental

The sample cell and gas-handling system which fulfill the following conditions was designed. a) The sample cell which is able to make absorption measurements of gas, liquid, and SFC states among which the molecular densities are different in several order of magnitude. b) The length of the x-ray path through the sample can be controlled from outside. c) The in-situ change of the states from liquid to SCF can be controlled. d) The total gas-handling system is compact enough to accommodate to a small space in the hatch of the experimental station.

Results and Discussion

X-ray absorption measurements were performed at BL-6B and BL-7A. Figure 1 shows the x-ray absorption spectra of Br K edge of gaseous, liquid and SCF states of CF$_3$Br with 600 μm in thickness. The differences in the edge jump reflect the change in the density of each state. In Fig. 2 are shown the Fourier transforms of the k$^3$ weighted oscillatory XAFS spectra of gas, liquid, and SCF states. The Fourier spectra of liquid and SCF states are almost identical. This means no apparent difference in the local structure around Br ion between the liquid and the SCF states in the CF$_3$Br. It seems that no intra or inter molecular interaction is observed in the XAFS spectra.

Reference

A XAFS STUDY ON THE LOCAL STRUCTURES OF TITANIA-SILICA MIXED OXIDES

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2Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyoku-ku, Kyoto 606, Japan

Introduction

Titania-silica mixed oxides have attracted much attention as ceramic glasses and catalysts. We have been studying the relationship between the local structures of mixed oxides and selectivity of epoxidation of olefins with tert-butyl hydroperoxide catalyzed by titania-silica mixed oxides.

Experimental

Titania-silica with a known content was prepared by a rapid hydrolysis from a mixture of Ti(OPr')4 and Si(OEt)4 followed by heating in air at 823K for 3 hr. Epoxidation of 1-octene and cyclohexene were carried out with tert-butyl hydroperoxide at 90 °C under a nitrogen atmosphere. Mixed oxides were sealed in a Q-pack pouch in a dry box and X-ray absorption spectra were obtained with the Beam Line 6B and 7C Stations by a fluorescence and a transmission methods.

Results and Discussion

XANES

Deconvolution of XANES spectra indicated that TiO2-SiO2 with no more than 40 mole% Ti have a singlet pre-edge peak, while triplet peaks were observed for mixed oxides with more than 40 mole% Ti. The high pre-edge peak area of the former oxides is responsible for tetrahedral structure.

EXAFS

Fig. 1 shows Fourier transforms of k3-weighted EXAFS at the Ti K-edge measured in a transmission mode. The spectra of mixed oxides with ≤ 40 mol% Ti are very similar indicating a single peak attributed to Ti-O bond. The first-shell peak shifts to a longer position and the second-shell clearly appears for mixed oxides with ≥ 50 mol% Ti which corresponds to the Ti-O-Ti interaction. The structural parameters derived from the curve-fitting for the first-shell peaks show that the bond distance and coordination number in mixed oxides with ≤ 40 mol% Ti are in fairly good agreement with those of tetrahedral structure(Ti(OPr')4), and the bond elongation in mixed oxide with 50 mol% Ti is due to the mixing of an octahedral structure. (Table 2) The tetrahedral species of mixed oxides is concluded to be responsible for the selective formation of epoxides from olefins with tert-butyl hydroperoxide.

<table>
<thead>
<tr>
<th>Table 1 Pre-edge peaks of titania-silica mixed oxides measured by the fluorescence method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti mol%</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
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<tr>
<td>20</td>
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<tr>
<td>40</td>
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* Relative to the inflection point of the continuum.

<table>
<thead>
<tr>
<th>Table 2 Structural parameters for Ti-O bonds in the first-shell of titania-silica mixed oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti mol%</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
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<tr>
<td>20</td>
</tr>
<tr>
<td>40</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>Ti(OPr')4</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
</tbody>
</table>

*The coordination number is estimated on the basis that the coordination number of Ti-O bond of Ti(OPr')4 is 4.00.

Fig. 1 Fourier transforms of titania-silica mixed oxides.
Crystal Structures and Phase Transitions in La@C₈₂ and C₇₆

Tetsu Watanuki, Hironori Nakao, Hajime Kawada, Kenji Ishii, Yasuhiro Fujii, Hiroyoshi Suematsu, Youichi Murakami, Yasuhiro Nakao, Kouichi Kikuchi, Youji Achiba, Isao Ikemoto, and Yukata Maniwa

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Introduction

In the previous x-ray diffraction (XRD) study of metallofullerenes, we used the powder crystals cocrystallized with some solvent such as CS₂. In this case, the solvent makes the crystal structure analysis so complicated that the precise position of the metal atom inside the carbon cage could not be determined. In this present study we prepared solvent-free powder crystals of La@C₈₂ (< 1 mg) by the sublimation method, and performed XRD study.

In addition, we have investigated the structural phase transition of higher fullerene, C₇₆. The crystal structure of C₇₆ is f.c.c. or hexagonal at room temperature (RT). At low temperatures the crystal undergoes phase transitions in relation to the orientational change of molecules, as is the case of C₆₀ and C₇₀. In our previous study, however, we observed no change in the temperature dependence of diffraction pattern (7.6K-600K) corresponding to these transitions. In this study we used the solvent-free crystals prepared by the sublimation method, and performed low temperature powder XRD measurements.

Experimental Procedures

Powder XRD measurements were carried out at BL6B. The incident beam (the wavelength 1.100 Å) was collimated to 0.2 mm in diameter, and an imaging plate was used as a detector, which enables us to get Debye rings, even for less than 1 mg of powder crystals. For low temperature experiments (7.8-300K), we used a closed-cycle He refrigerator and cryostat.

Results and Discussion

a. La@C₈₂

Figure 1 shows the XRD spectrum of La@C₈₂ at RT. All diffraction peaks can be assigned to the major crystals with the f.c.c. lattice and the minor crystals with the hexagonal lattice. The lattice constant was determined as a=15.82 Å ± 0.01 Å for the f.c.c. crystal, and a=11.14 Å and c=18.40 Å for the hexagonal crystal. The exact determination of atomic positions is not yet completed, but our present model calculation shows that the La atom is located inside the carbon cage. The R-factor is about 11%.

b. C₇₆

Figure 2 shows the XRD spectrum of C₇₆ at RT. All diffraction peaks can be assigned to the major crystals with the f.c.c. lattice and the minor crystals with the hexagonal lattice. At 7.8K, there are some extra peaks which cannot be assigned to these ones. Figure 3 shows the temperature dependences of lattice constant of the f.c.c. and hexagonal crystals, (7.8K-300K). The temperature dependence shows two anomalies at about 200K and 150K, which possibly correspond to two successive phase transitions in relation to the orientational change of molecules. The latter anomaly is also observed as a change of ¹³C-NMR line shape, which can be interpreted in terms of an orientational transition of molecules.

References

3) Y. Maniwa et al., private communication
Local Atomic Structures of Zr$_7$Ga$_{10}$Ni$_{20}$ Amorphous Alloys by the Anomalous X-ray Scattering Method

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$^2$ Institute for Advanced Materials Processing, Tohoku University, Sendai 980 Japan.

Introduction

New metallic amorphous alloys with an extremely wide supercooled liquid region, e.g. La-Al-Ni$^{[2]}$, Zr-Al-Ni$^{[3]}$, etc., have been found by Inoue et al. The origin of such an extremely good thermal stability is one of our greatest concerns. As a result of the previous structural studies in La-Al-Ni$^{[2]}$ and Zr-Al-Ni$^{[3]}$ amorphous alloys, it is found that their thermal stability is closely related with large variations of local atomic structures around certain atomic pairs during crystallization. In the present study, the local atomic structures around Zr, Ga and Ni have been determined in Zr-Ga-Ni amorphous alloys by the AXS method.

Experimental

Zr$_7$Ga$_{10}$Ni$_{20}$ amorphous ribbons were produced by a single-roller melt-spinning technique. The glass transition and crystallization temperatures of the as-quenched sample are 674K and 724K, respectively. The anomalous x-ray scattering (AXS) intensities were measured at the 6B beam line in the Photon Factory. By obtaining energy differential intensity profiles just below Zr, Ga and Ni K absorption edges, the environmental radial distribution functions (RDFs) around Zr, Ga and Ni have been determined.

Results

The ordinary and environmental RDFs for the as-quenched sample and the sample annealed for 120s at 700 K in the supercooled liquid region are shown with solid and dotted curves in Fig.1. By referring the Goldschmidt radii of the elements, the first peaks in the environmental RDFs are attributed to the pairs indicated in the figure. The coordination numbers and atomic distances at these peaks for the as-quenched and annealed samples are summarized in Table 1.

The amorphous sample was crystallized by annealing the as-quenched amorphous sample for 180ks at 700K in the supercooled liquid region. It has been determined by comparing the experimental energy differential intensity profiles with the ones calculated in various Zr compounds that the precipitation phases are a mixture of Zr$_7$Ga$_{10}$Ni$_{20}$ and Zr$_7$Ni$_{20}$. The average atomic distances and coordination numbers of Zr-Zr and Zr-Ga pairs in Zr$_7$Ga$_{10}$Ni$_{20}$ and Zr$_7$Ni$_{20}$ phases are larger than those in the amorphous state and the atomic distance of Zr-Ni pairs is nearly equal to the value in the amorphous state. The coordination number for Zr-Zr pairs is larger in the crystallized sample than in the amorphous sample. Consequently, it seems that the values of the atomic distances and coordination numbers in the amorphous state come closer to those in the crystalline phases by annealing in the supercooled liquid region. The DSC traces of the as-quenched and annealed amorphous alloys suggest that the present amorphous alloy is thermally destabilized by annealing in the supercooled liquid region.

These AXS and DSC measurements suggest that the thermal stability of the present amorphous alloy is closely related with the local atomic structure in the amorphous state and that the change of the local atomic structure in the amorphous alloy toward that in the precipitated phases makes the present amorphous alloy thermally destabilized. This is consistent with the results obtained in the previous structural studies in the La-Al-Ni and Zr-Al-Ni amorphous alloys$^{[4]}$.

References

2) A. Inoue et al., Mater. Trans. JIM, 31 (1990), 177.
4) E. Matsubara et al., Mat. Trans. JIM, 33 (1992), 873.

Table 1 Coordination numbers and atomic distances for Zr$_7$Ga$_{10}$Ni$_{20}$ amorphous alloys as-quenched and annealed for 120s at 700K in the supercooled liquid region.

<table>
<thead>
<tr>
<th>pairs</th>
<th>as-quenched</th>
<th>annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Zr</td>
<td>0.32</td>
<td>0.325</td>
</tr>
<tr>
<td>Zr-Ga</td>
<td>0.288</td>
<td>0.292</td>
</tr>
<tr>
<td>Ga-Zr</td>
<td>0.288</td>
<td>0.292</td>
</tr>
<tr>
<td>Zr-Ni</td>
<td>0.276</td>
<td>0.277</td>
</tr>
<tr>
<td>Ni-Zr</td>
<td>0.276</td>
<td>0.277</td>
</tr>
</tbody>
</table>

Fig.1 Ordinary and environmental RDFs for Zr, Ga and Ni of the Zr$_7$Ga$_{10}$Ni$_{20}$ amorphous alloys as-quenched (solid) and annealed for 120 s at 700 K.
INTRODUCTION

For the past few years, we have attempted to apply the XAFS technique to elucidate the microstructure of Co-Cr films [1,2], which have been important materials for magnetic recording media since the original proposal by Iwasaki [3]. One of the issues on Co-Cr films has been on possible existence of two-phase structure consisting of Co-rich and Cr-rich portions; this view originated from the early electron microscopic observations of sputter-etched Co-Cr films [4] and was followed by many experiments including the observations of chemically etched films [5,6], spin echo NMR [7] etc.

Chrysanthemum-like patterns observed in chemically etched Co-Cr films under the electron microscope have been interpreted as evidence of phase separation. The present study aims to obtain further information on local structures of Co-Cr films by means of XAFS.

EXPERIMENTAL

Co-Cr films were formed on PET web by DC magnetron sputtering by use of a target of 80 at.% Co and 20 at.% Cr. Reference samples of Co-Cr films were obtained from Thin Film Research Laboratory of Teijin Limited; these films were prepared by roll coater equipped with a pair of facing targets. Co and Cr foils were purchased from Goodfellow Corporation.

Measurements of XAFS were made at BL-10B, 68 and 7C of the Photon Factory. Temperature of the samples were changed from about 10K to room temperature.

RESULTS AND DISCUSSION

First, Co and Cr foils were analysed to obtain reference data. Co crystal is hcp with a=5.512Å and c=4.107Å by diffraction data. Difference of 0.01Å is difficult to distinguish by EXAFS; hence we treated 6 atoms located at 2.499Å apart from a central atom and 6 atoms placed slightly further at 2.512Å, as 12 nearest neighbours all together. An EXAFS analysis gave a result, with an assumption that Debye-Waller type factor σ’s are equal in all shells, that R1=2.50Å (σ=0.06Å, N1=12), R2=3.55Å (N2=6), R3=4.02Å (N3=2), R4=4.37Å (N4=18), R5=4.87Å (N5=12).

For simplicity, we took up only R1 and at best R2 when compared with Co-Cr alloy films.

Co-Cr films of several origins were measured by EXAFS at K-edge of Co and interatomic distances were obtained. There was virtually no difference in the first and second nearest interatomic distances between Co and Co-Cr films. This was expected at least for the reference samples since the lattice constants of Co-Cr was known to be almost the same for the Cr concentration between 12 and 30 at.% [8]. Actually, other Co-Cr samples also brought similar results.

Before doing detailed analyses, we compared, in this study, the patterns of Fourier transforms of EXAFS of various origins, whose examples are shown below. Those patterns were apparently similar each other as long as the crystal was hcp (namely, for Cr contents less than 40%); Co-Cr films which did or did not exhibit chrysanthemum patterns revealed little difference in the Fourier transform patterns.

XANES spectra showed some difference between Co and Co-Cr, if the Cr contents were 10%; but, there was little difference in XANES between Co-Cr films with and without chrysanthemum patterns.

Situation was similar at the K-edge of Cr, although the spectra of Cr foils were of course definitely different from Co-Cr, since the crystal structure is different.

Thus, so far, the existence of phase separation in the Co-Cr films has not been proved from the difference in the XAFS patterns. Further efforts are being made to find the evidence by XAFS.

I describe the preparation of 'interfacial clusters' on CeO₂ as an extracted model of catalytic active site. The structure transformation was followed by EXAFS.

EXPERIMENTAL

Two kinds of CeO₂ were prepared. CeO₂ synthesized from Ce(NO₃)₂·6H₂O was heated in vacuum at 673 K, then in O₂ at 293 K (CeO₂-ox). A few amount of Ni(NO₃)₂·6H₂O was impregnated on CeO₂-ox (Ni 0.25 wt %) and in H₂ at 773 K (12h) (CeO₂-red). Ru₃(CO)₁₂(1) was reacted with each CeO₂ in purified THF (Ru 1.7 wt%). Ru K-edge EXAFS was measured at beamline 10B and 6B, and analyzed on code EXAFSH by Yokoyama et al. by using empirical parameters extracted from Ru and RuO₂ powders, (1), and [Ru(CO)₃Cl₂]²⁻. All the procedure was carried out in Ar or vacuum.

RESULTS AND DISCUSSION

The EXAFS studies on supported Ru, Rh, Pd, Re, Os, Ir, or Pt clusters were well summarized in ref 2. Different from the examples of these clusters, cluster (1) was transformed to monomeric species [Ru(CO)₃Cl₂(μ-O₂)₅] (2) by the reaction with CeO₂-ox [Figure 1(1)] or CeO₂-red in THF at 290 - 337 K.

As the species (2) was supposed to be homogeneous based on EXAFS, IR, and TEM measurements, it can be used as starting material to prepare 'interfacial' cluster catalysts. By the reduction in H₂ around 373 - 600 K, (2) was transformed to monolayer-like 'interfacial' model cluster (3) in size of ca.11 Å both on CeO₂-ox [Figure 1(4)] and CeO₂-red. In contrast, (2) was transformed to [Ru₃(μ-O₂)₅Cl₂] [Figure 1(2)], and to Ru oxide cluster in size of ca.20 Å (oxidized in the absence of O₂) [Figure 1(3)] by heating in vacuum at 673 and 813 K, respectively.

I am under the investigation of origin of extreme absorption capacity {H(a)/Ru = 4 - 5} and excellent ammonia synthesis activity of (3) on CeO₂-red.

REFERENCE

Figure 1. Ru K-edge EXAFS for cluster (1) on CeO₂-ox. Incipient(1), heated in vacuum at 673 K(2), heated in vacuum at 813 K(3), and in H₂ at 573 K(4). (a) k³-weighted χ(k) and (b) its associated Fourier Transform.
Introduction

Photoabsorption of atoms has been generally treated as a single-electron excitation process. However, the existence of the multielectron excitation process, where the removal of a core electron by photoabsorption causes excitation of additional electrons in the same atom, has been known in x-ray absorption spectra for a long time. With the recent advent of synchrotron radiation facilities, this process has been studied extensively [1] and has received special interest in fundamental atomic and molecular physics as well as in applied fields, such as solid-state physics and chemistry, because it is a sensitive probe to study atomic and molecular structures and excitation dynamics.

Most of the experiments have been performed for isolated atoms, such as noble gases [2,3], where the influence of neighboring atoms can be neglected.

It was pointed out by Kodre and co-workers [4] and Frahm et al. [5] that for solid targets it is difficult to identify weak transitions corresponding to multielectron excitation in x-ray absorption spectra. The reason is that in condensed matter, the oscillation due to the x-ray absorption fine structure masks small signals in the energy region where multiple electron excitation (KLL) occurs.

In the case of solution, the EXAFS is dominated by a simple coordinate bond, which can be modeled and removed from the spectra. Therefore, aqueous solutions are appropriate samples to study multielectron transition processes in the x-ray absorption spectra including structural signals from surrounding atoms.

The aim of the present work is to study whether the multielectron excitation process, which we have observed for Kr [2], can be detected for elements not in gas phase.

Experimental

The sample used were 0.2-mol/mm² propylene carbonate solution of tetra-n-octylammonium bromide (NBr) and 0.01-mol/mm² ethanol solution of EuBr, (EuBr). These samples were contained in a sealed Teflon cell of 8 mm length. The contribution of higher harmonics in the x-ray radiation was negligible due to the critical energy of the synchrotron radiation spectrum. We also confirmed the absence of signals from surrounding atoms.

The sample used were 0.2-mol/mm² propylene carbonate solution of tetra-n-octylammonium bromide (NBr) and 0.01-mol/mm² ethanol solution of EuBr, (EuBr). These samples were contained in a sealed Teflon cell of 8 mm length. The contribution of higher harmonics in the x-ray radiation was negligible due to the critical energy of the synchrotron radiation spectrum. We also confirmed the absence of signals from surrounding atoms.

Results

In the Br [1s3d] excitation edge, it is easy to detect the onset of this edge. The measured [1s3d] excitation cross section is quasiquantitatively shown in Fig.1. The onset of the [1s3d] transition occurs at 91 eV for NBr and 80 eV for EuBr. The measured energy agrees with the present theoretical calculation. For the Br [1s3p] transition, the onset of the measured values occurs at 205 eV for NBr and 203 eV for EuBr. These values also agree well with the calculated value. As indicated in Fig.1, the [1s3p] cross section is seen to rise much more gradually with photon energy than the [1s3d] cross section and $\alpha(1s3d)/\alpha(1s)$=5.0x10^3 for the [1s3d] transition. These values are in better agreement with the calculated shake-up probabilities in Table I than with the shake-up-plus-shake-off probabilities obtained by Mukoyama and Taniguchi [6]. Combining this fact with the energy dependence of the shake-up and shake-off probabilities, we can confirm the conclusion of our previous work that the multielectron excitation edges observed in x-ray absorption spectra are ascribed mainly to shake-up process. However, the measured cross section is larger than the calculated value for the [1s3p] excitation, but smaller for the [1s3d] transition. The discrepancy in the cross section between theory and experiment is due to the error of subtracting the sudden approximation, which is valid for the high-energy limit of the incident photon.

![Fig.1](image)

Measure (a) Br 1s3d and (b) 1s3p double-electron cross sections in NBr.

References

EXAFS study of Zr$_{0.80}$Gd$_{0.20}$O$_{1.90}$

Tsuneo Matsui$^1$, Hiroto Yokoi$^1$, Yuji Arita$^1$, Hideo Ohno$^1$ and Katsumi Kobayashi$^1$

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3) Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305-0801, Japan.

Introduction

An anomalous increase in the heat capacity curve of each (U, M)$_3$O$_9$ sample, (M = Lanthanides), was observed at temperatures from about 550 to 1300K depending on dopant and its concentration[1]. This anomalous increase was interpreted as due to the formation of Frenkel pair-like defects of oxygen and the dependence may have some relation with formation of clusters in this structure. Therefore, in this study we have used EXAFS spectroscopy to obtain the temperature dependence of local structure around Zr and Gd in gadolinia-stabilized zirconia (Zr$_{0.80}$Gd$_{0.20}$O$_{1.90}$) which have the same fluorite structure as YO$_2$ and to discuss the changes of distribution of dopant, oxygen vacancy and oxygen interstitial above the onset temperature of the anomalous increase in the heat capacity of doped UO$_2$. The EXAFS study of stabilized zirconia at high temperature has been performed only for Y-stabilized one[2].

Experimental

The X-ray absorption measurements near Zr-K edge at room temperature, 573K, 873K and 1073K and Gd-L$_3$ edge at room temperature were made with Synchrotron Radiation by use of the EXAFS facilities on the beam lines 7C and 6B. The powder sample of single cubic Zr$_{0.80}$Gd$_{0.20}$O$_{1.90}$ phase was prepared by heating a mixture of ZrO$_2$ and Gd$_2$O$_3$ powders at 1673K in air for 48h.

Results and Discussion

1. Room temperature : The average cation-oxygen interatomic distance calculated from lattice constant was 0.224nm, whereas the Zr-O and Gd-O interatomic distances calculated from the least-square fitting were 0.214nm and 0.233nm respectively. This result is attributed to the anion vacancies being preferentially sited adjacent to smaller Zr$^{4+}$ cation which, with ensuing relaxations, permits a closer contact between Zr$^{4+}$ and its oxygen neighbors. However, coordination number for the first-neighbor oxygen shell of Gd calculated from the least-square fitting was less than 8-coordination and slight smaller than that of Zr. Thus, from the result on coordination number, the position of oxygen vacancies can not be clearly determined.

2. Temperature dependence : The Zr-O interatomic distance calculated from the least-square fitting slightly decreases with temperature, showing the inconsistent results with the effect of thermal expansion. Fig. 1 shows the variation in the area of the radial distribution function of Zr-O and Zr-Metal peaks with temperature, which we use as a measure of the relative disorder in the sample. The decrease in Zr-O area (arising from thermal induced disorder within the shell of oxygen or cation neighbors) is smaller for Gd-stabilized zirconia than for pyrochlore La$_2$Zr$_2$O$_7$ with order configuration of oxygen. The variations in the area of Y-stabilized zirconia with temperature obtained by Catlow et al [2] are also shown in fig. 1. These data are normalized with the amplitudes of Zr-O or Zr-Metal at room temperature. The amplitudes of Zr-O and Y-O shells converge at higher temperatures, whereas latter are larger than former at low temperature, indicating Y-O shell is more ordered at low temperatures relative to Zr-O. There seems to be similarities between the variation

References

STRUCTURAL ANALYSIS OF AMORPHOUS Zr-Y-Al-Ni ALLOY
BY THE ANOMALOUS X-RAY SCATTERING METHOD
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Kozo SHINOUDA1, Tomomi KOSAKA1 and Eiichiro MATSUBARA2

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Introduction
Amorphous alloys in the Zr-Y-Al-Ni system indicate a wide range of supercooled liquid region and are quite promising for the engineering materials1). This report describes the structure of Zr60Al15Ni25, Zr33Y27Al15Ni25 and Y60Al15Ni25 amorphous alloys (hereafter denoted as Zr60, Zr33Y27, Y60, respectively) obtained by the anomalous X-ray scattering(AXS) method 2).

Experimental and Results
Amorphous ribbons of Zr60, Zr33Y27 and Y60 were produced by a single roller melt-spinning technique in an Ar atmosphere3). The AXS measurements were carried out at the BL-6B station. Fig.1 shows the environmental Qi(Q), QiY(Q) of Y60 together with ordinary Qi(Q), as an example. The RDFs of Y60 are given in Fig.2. Since the peak at 0.28nm is found in three RDFs, this peak is allocated to the Y-Ni pairs. The peak at around 0.36nm is not detected in environmental RDF around Ni. Thus, the peak at 0.36nm may be attributed to Y-Y pairs. The structural parameters of Y60 was refined by using the interference refining technique coupled with the structural information on Y3Al2 and Y3Ni2. After several iterations of least-squares calculation, the interference functions denoted by dots in Fig.1 were obtained. The structural parameters of Z33Y27 and Z60 were obtained by a similar manner.

Discussion
The structural parameters indicate that Y-Al pairs is rather distinct than the Y-Ni pairs in Y60, although the first saturated crystal is Ni2Y when Y60 is annealed. The difference in the atomic arrangements between Ni2Y and Y60 may be one of the reason for a wide supercooled liquid region. Similar discussion is also possible in the case of Z60, where Zr5Al3 is the first crystal appeared by annealing while Zr-Al pairs is quite rare in the amorphous structure. As for Zr33Y27, the Zr-Y pair is recognized even if Y and Zr have the insoluble character. This feature should be another significant factor for obstructing crystallization.

References
BEHAVIOR OF WURTZITE-TYPE BORON NITRIDE AT ULTRAHIGH PRESSURES

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Osamu SHIMOMURA
Photon Factory, National Laboratory for High Energy Physics
Kenichi TAKEMURA
National Institute for Research in Inorganic Materials

Introduction
Boron nitride is similar to diamond in that the phase relations of the two materials are quite corresponding to each other: they exist in the graphitic and rhombohedral forms at ambient pressure as well as in the diamond and wurtzitic forms at high pressure. The high-pressure forms can all be metastably retained to the ambient conditions and, hence, quenching technique has been applied in most cases to study the phase relations. Such relations, however, can be much more precisely known by in-situ observations.

For the wurtzitic form of boron nitride (w-BN), both the quenching and in-situ studies have shown a conversion to the diamond-like form (c-BN) upon heating to about 1000°C under pressure exceeding 8 GPa. The temperature for the conversion decreases with an increase in the pressure, leading to an expectation that w-BN would transform into c-BN at relatively low temperatures when pressurized to beyond 50 GPa.

This study was undertaken to know the behavior of w-BN in-situ under pressure as high as 90 GPa.

Experiment
Our w-BN sample was synthesized from graphitic BN either by static or by dynamic compression. The sample was pressurized with a gasketed diamond-anvil cell and afterwards heated to several hundreds centigrade by a Pt wire heater placed near to the diamond anvils. Pressure was measured by fluorescence of ruby chips incorporated with the sample or, otherwise, by equation of state of the gasket. X-ray-diffraction was carried out at room temperature using monochromatized radiation from BL-6B. The diffracted x-rays were recorded by an imaging plate.

Results and discussion
Figure 1 shows x-ray-diffraction patterns of w-BN pressurized to 90 GPa. Pattern A was recorded before heating while pattern B was obtained after being held at 700°C for 30 min. A small peak labelled G in pattern A is the gasket line. There is essentially no change in the two diffraction patterns. Quite similar behavior was observed from experiments undertaken at lower pressures and temperatures. These observations show that w-BN persists stable at least to 90 GPa and 700°C.

Fig. 1. X-ray-diffraction patterns of w-BN at 90 GPa. A: before heating, B: after heating.

The conversion from w-BN to c-BN involves a change from eclipsed to staggered conformation. Since such a conformational change requires relatively large transition-state volume, the kinetics of the conversion can be retarded at higher pressures despite the heating to enhance the kinetics.

References
MICROSTRUCTURAL CONFIGURATIONS OF MOLYBDENUM OXIDES ON ALUMINA

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Introduction

It is reported that tetrahedral Mo oxide species and polymolybdate with an octahedral configuration are present in the monolayer region. The structure of molybdenum oxides is much affected by the nature of supports such as silica, alumina and titania. The selectivity of 2,3-epoxypropan-1-ol over the low Mo-loading region was low, but it increased remarkably after the coverage of the monolayer. The present study deals with the microstructure of Mo oxides supported on α-, γ-, and χ-alumina in relation to their activity in the epoxidation of allyl alcohol using t-butyl hydroperoxide as an oxidant.

Experimental

Alumina-supported molybdenum oxides were prepared by impregnation of hexaammonium heptamolybdate tetrahydrate on alumina, followed by calcination at 500 °C in air for 3 h. Epoxidation of allyl alcohol was carried out at 90 °C under a nitrogen atmosphere. Mo samples were sealed in a Q-pack pouch in a dry box and X-ray absorption spectra were obtained with the Beam Line 6B station by a transmission mode.

Results and Discussion

XANES ESCA analysis indicated that the monolayer of Mo oxides was covered with ca. 1 wt%, 20 wt%, and 15 wt% of Mo oxide loading for α-, γ-, and χ-alumina, respectively. IR and XRD analyses indicated that MoO₃ was formed after the coverage of an Mo monolayer. The pre-edge peaks did not give any information about the configuration of supported Mo species when compared with those of standard Mo samples with tetrahedral and octahedral configurations. XANES spectra indicated that tetrahedral species predominated in the monolayer region while octahedral ones began to appear with an increase in Mo-loading.

EXAFS Fig. 1 shows Fourier transforms (FT) of the EXAFS spectra of Mo oxides supported on α-alumina. FT for 0.5 wt% Mo oxide shows a single peak which corresponds to the Mo-O bond (1.77 Å) of isolated tetrahedral species. FT for 2 wt% Mo oxide shows two kinds of Mo-O bonds plus Mo-Mo which is due to adjacent Mo species of polymolybdate or MoO₃. The selectivity of 1,2-epoxypropan-1-ol is also shown in the figure; the higher the Mo-loading, the higher the selectivity. The results for γ- and χ-alumina supported Mo oxides were similar to that for α-alumina supported one: the predominant species was isolated tetrahedral Mo oxide in the monolayer region especially with low Mo-loading, and the adjacent Mo (octahedral) oxide species began to appear with an increase in Mo, and finally MoO₃ was formed over the monolayer coverage. When isolated tetrahedral Mo oxide was observed, the selectivity of epoxide was very low showing that epoxidation occurs with aggregated Mo oxides and that the most active species is MoO₃ spreaded on alumina. MoO₃ layer easily apperas on α-alumina (the lowest surface area) with lower Mo oxide loading.

Fig. 1 EXAFS-FT of Mo/α-Al₂O₃

AN EXAFS INVESTIGATION OF DENATURATION PROCESSES IN HORSE HEART FERRICYTOCHROME C

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Introduction

The heme attached coaxially to Fe (III) ion and its axial ligands are essential not only for the conformation of horse heart ferricytochrome c (CYT-C) but they also play a crucial role in the folding-process. Acid denaturation of CYT-C occurs in a single cooperative transition around pH = 2.5 at low ionic strength. On the other hand, under the condition of acidification at high ionic strength or in high HCl solution with pH lower than 2.0 the CYT-C leads to a compact high-spin state lacking the Met-80 ligand which has been called as the molten-globule (MG) state. However, there is no direct information of local structure around Fe (III) ion in CYT-C in the MG and unfolding states (denatured state).

In the present paper, we have determined local structure around Fe (III) ion of CYT-C in denatured state using 20.0 x 10^{-3} mol dm^{-3} HCl (pH = 1.80) and compared its local structure with that in MG states generated by the increase of NaCl concentration by means of EXAFS method.

Experimental

All chemicals (analytical grade) were employed without further purification. The concentration of CYT-C was kept at 5.0 x 10^{-3} mol dm^{-3} during all EXAFS measurements.

EXAFS measurements were performed using synchrotron radiation from the Photon Factory at the National Laboratory for High-Energy Physics (KEK, Tsukuba). Fe-edge X-ray absorption spectra were collected in a fluorescence detection mode, using BL-6B with two Si(111) crystal monochromators under ring operating condition of a positron energy of 2.5 GeV, and a ring current of 350-200 mA. The magnitude and imaginary parts of Fourier transform, \( \Phi(r) \), were obtained from EXAFS oscillation \( k^2 \Phi(k) \).

In order to determine the structural parameters, the Fourier filtering technique was employed. A non-linear least-squares fitting was applied to the filtered data according to the EXAFS formula. The three-shell fitting was employed for the parameter fitting. The shells were divided into a shell of the Fe-N scattering between the Fe (III) ion and four imidazole N atoms in porphyrin ring that between the Fe (III) ion and an N atom in His-18, and a shell of Fe-S scattering between the Fe and an S atom in Met-80. The scattering atoms in the first, second and the third shells are N atom in the porphylin ring, and an S atom in poiphyrin ring, respectively.

The three-shell fitting was also applied to the inverse Fourier-transform spectrum derived from the \( \Phi(r) \) in the range of 1.26 A to 2.27 A. The shape of \( \Phi(r) \) in the r-range of 1.26 A to 2.27 A for CYT-C in 0.1 mol dm^{-3} phosphate buffer solution of pH = 7.00. In a case of application of the EXAFS formula, the three-shell fitting was employed for the parameter fitting. The shells were divided into a shell of the Fe-N scattering between the Fe (III) ion and four imidazole N atoms in porphyrin ring that between the Fe (III) ion and an N atom in His-18, and a shell of Fe-S scattering between the Fe and an S atom in Met-80. The scattering atoms in the first, second and the third shells are N atom in the porphylin ring, and an S atom in poiphyrin ring, respectively.

From the XANES spectra, heme-Fe ions of CYT-C in all solutions are confirmed as Fe^{3+}.

Results and Discussion

The three-shell fitting was also applied to the inverse Fourier-transform spectrum derived from the \( \Phi(r) \) in the range of 1.24 A to 2.27 A for CYT-C in 0.1 mol dm^{-3} phosphate buffer solution of pH = 7.00. In a case of application of the same N's as those of CYT-C powder, \( \sigma(2) \) converges to negative values. When N's are fixed to 4, 2, and 1 for the respective shells, \( \sigma(2) \) converged to positive and reasonable values. \( k \) has been determined to be 0.652k A for all shells under the values of N mentioned above. The least-squares fitting was performed by employing \( A(k) = 0.652k A \) for all the data of CYT-C in solutions. When N's in the second and the third shells were parametrized under the condition mentioned above, the best fitted values of \( N_{N(ax)} \) and \( N_{S(ax)} \) in the second and the third shells are found to be 1.8(1) and 0.99(5), respectively.

The value of \( N_{S(ax)} \) shows that in addition to the N atom in His-18 an atom with a similar atomic number to N atom coordinates to the Fe (III) ion. This atom is supposed to be O atom in H2O. The value of \( N_{S(ax)} \) in the third shell shows that only an S coordinate to Fe (III) ion. In the three-shell fitting, \( N_{N(eq)} \) and \( N_{S(eq)} \) have been determined to be 1.962(1) A, 1.963(3) A and 2.271(3) A, respectively. \( o(2) \) in the shells are parameterized under the constrain of the three \( o(2) \) being equal.

The shape of \( \Phi(r) \) in the 20.0 x 10^{-3} mol dm^{-3} HCl aqueous solution of pH = 1.80 is similar to that in the buffer solution. N's in the second and the third shells have been determined to be 1.7(5) and 0.81(6), respectively, from the inverse Fourier-transform spectrum of \( \Phi(r) \) in the range of 1.26 A to 2.27 A. The least-squares fitting was performed by employing \( A(k) = 0.652k A \) for all the data of CYT-C in solutions. When N's in the second and the third shells are N atom in the porphylin ring, and an S atom in poiphyrin ring, that between the Fe (III) ion and an N atom in the porphylin ring, that between the Fe (III) ion and an N atom in His-18 an atom with a similar atomic number to N atom coordinates to the Fe (III) ion.

*Fig. 1. Plots of (a) \( N_{N(ax)} \) and (b) \( N_{S(ax)} \) versus [NaCl].
1) J. Babul and E. Stellwagen, Biochemistry, 11, 1195(1972).
EXAFS STUDY ON THE DEBYE-WALLER FACTOR IN KTaO₃ AND SrTiO₃

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Introduction

Many cubic perovskite crystals undergo phase transition, where they transform to slightly distorted structures from the ideal perovskite structure. The aim of this study is to investigate a local structure of crystals in which the soft phonon mode was observed. We investigate the Debye-Waller factor of KTaO₃ and SrTiO₃, which are regarded as quantum paraelectrics, by using the EXAFS (Extended X-ray Absorption Fine Structure) technique. We previously reported the Debye-Waller factors of the Ta-O atomic pair in KTaO₃ at low temperatures [1]. Here we report anharmonic thermal vibration of the Ta-O atomic pair in KTaO₃ above room temperature and that of Ti-O atomic pair in SrTiO₃.

Experiment

The sample of KTaO₃ was prepared as a thin film by precipitating on a BN disk for measurements at high temperatures. X-ray absorption spectra were measured using an EXAFS facility installed at the beam line 10B. EXAFS spectra near the Ta-L₃ edge were obtained from room temperature up to 700 K. The powder sample of SrTiO₃ was dusted onto scotch tapes and held by Al foils to keep temperature uniformly. EXAFS spectra were measured near the Ti-K edge from room temperature down to 60K at the beam line 6D.

Results and discussion

The EXAFS function g(κ) was extracted from the absorption spectrum following the standard procedure. The programs XAFS93 and MB93 were employed for the EXAFS data analysis. To determine local structure parameters taking account of an anharmonic thermal vibration, we used an EXAFS formula based on the single scattering theory and expressed by the cumulant expansion up to fourth-order term [2]. We examined the local structure around a Ta atom which locates on the center of an O octahedron in KTaO₃. The fourth-order cumulant $\langle \chi^4 \rangle$ was found to be almost negligible within the estimated standard deviation at temperatures from 24 to 700 K. On the other hand, the third-order cumulant $\langle \chi^3 \rangle$, which referred to an asymmetric atomic motion and responsible for the thermal expansion, appears above 500 K as shown in Fig. 1. Although the Ta and O atoms locate statistically on the centro-symmetric position, we can detect the third-order cumulant of the potential between the Ta and O atoms by the EXAFS technique. This is a feature of the EXAFS technique in comparison with the diffraction technique.

We examined the local structure around a Ti atom which locates on the center of an O octahedron in SrTiO₃. SrTiO₃ undergoes a phase transition $T_c = 110$ K due to the condensation of B25 phonon mode at the Brillouin zone boundary [3]. Although the $\langle \chi^2 \rangle$ of the Ti-O atomic pair in the harmonic model shows no anomaly around $T_c$, discrepancy factors between the theoretical and experimental EXAFS functions increase below 150 K, implying that an anharmonicity of atomic vibration increases. Thus we adopted an anharmonic vibration model. Figures 2 and 3 show the temperature dependence of the Debye-Waller factors $\langle \chi^2 \rangle$ and $\langle \chi^4 \rangle$ of the Ti-O atomic pair. The Debye-Waller factors clearly show an anomaly around $T_c$. However, the Debye-Waller factor of EXAFS observes an atomic vibration in <100> directions which are orthogonal to the direction of the atomic displacement of the O atom due to the soft mode at the Brillouin zone boundary. These anomalies don't indicate the softening of phonon mode directly. We are still considering these anomalies of $\langle \chi^2 \rangle$ and $\langle \chi^4 \rangle$ near the phase transition temperature.

References

LOCAL ATOMIC STRUCTURE OF FERRIC HYDROXIDE $\text{Fe(OH)}_3$
IN AQUEOUS SOLUTION BY AXS AND EXAFS METHODS

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Introduction
Various Fe oxides, oxyhydroxides and hydroxides are widely distributed in soils, minerals, rivers, seawater, etc., and playing an important role in our environment, biological actions and industrial activities. The atomic structure of ferric hydroxides, however, is little known in the early stage of the hydrolytic behavior of ferric ions. In the present study, the ferric hydroxide $\text{Fe(OH)}_3$ in aqueous solution was studied by the anomalous x-ray scattering (AXS) and EXAFS methods.

Experimental
A ferric hydroxide $\text{Fe(OH)}_3$ was precipitated from $\text{Fe(NO}_3\text{)}_3$ solution by adding $\text{NaOH}$ aqueous solution. The precipitated $\text{Fe(OH)}_3$ was rinsed with distilled water in order to remove free $\text{NO}_3^-$ and $\text{Na}^+$ ions. The AXS and EXAFS measurements at Fe K absorption edge were carried out at the beam line 6B.

Results
The Fe K EXAFS RDF for the $\text{Fe(OH)}_3$ solution in Fig.1 consists of three peaks indicated with arrows. By consulting the crystalline data of some Fe$^{3+}$ hydroxides and oxides, these three peaks are attributed to the first near neighbors of Fe-O and Fe-Fe pairs, and the overlapped second near neighbors of Fe-Fe and Fe-O pairs. The environmental RDF for Fe$^{3+}$ in the $\text{Fe(OH)}_3$ solution is also shown in Fig.2. The structural parameters in Table 1 have been determined so that they explain the EXAFS and environmental RDFs in Figs. 1 and 2, simultaneously.

Table 1 Coordination numbers and atomic distances of $\text{Fe(OH)}_3$ in aqueous solution.

<table>
<thead>
<tr>
<th>Pairs</th>
<th>$\text{Fe(OH)}_3$ in aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r$ / nm  $N$</td>
</tr>
<tr>
<td>Fe-O(1st)</td>
<td>0.209 5.5</td>
</tr>
<tr>
<td>Fe-O(2nd)</td>
<td>0.367 7.0</td>
</tr>
<tr>
<td>Fe-Fe(1st)</td>
<td>0.316 3.6</td>
</tr>
<tr>
<td>Fe-Fe(2nd)</td>
<td>0.341 2.2</td>
</tr>
</tbody>
</table>

By carefully examining the structural parameters in Table 1 and the atomic structures of some Fe$^{3+}$ hydroxides and oxides crystals, such as goethite, akageneite, lepidocrocite and hematite, the following structural features of $\text{Fe(OH)}_3$ in aqueous solution have been reduced.

The fundamental unit structure is FeO$_6$ octahedra. They are connected by edge and double-corner sharing linkages and form a network consisting of double octahedral chains. It appears that in aqueous solution, water molecules may exist in vacant sites between these chains.

STRUCTURAL PHASE TRANSITION OF ALUMINUM ANTIMONIDE AT HIGH PRESSURE

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Osamu SHIMOMURA
Photon Factory, National Laboratory for High Energy Physics
Kenichi TAKEMURA
National Institute for Research in Inorganic Materials

Introduction

The III-V compounds are known to undergo pressure-induced phase transition from tetrahedrally coordinated structure into basically octahedral coordination. The octahedrally (and quasi-octahedrally) coordinated structure is either β-Sn or NaCl-type. Appearance of the types is to a great extent governed by ionicity of the compounds; β-Sn type prevails at high pressure in covalently bonded compounds while NaCl type appears in much more ionic compounds. A critical ionicity for separation between β-Sn and NaCl structures is around 0.3 on Phillips scale[1].

Earlier studies[2] on AlSb have unanimously uncovered pressure-induced transition at about 8 GPa, but the structural assignment for the high-pressure phase has been controversial: β-Sn, NaCl, or otherwise, orthorhombic. The appearance of the latter two structures, if correct, is interesting in view of the ionicity 0.25 for AlSb and the critical value.

Experiment

A commercially obtained AlSb sample was pressurized in a gasketed diamond-anvil cell and x rayed with a synchrotron radiation from BL-6B at a wavelength of 0.6888 Å. Diffracted x rays were recorded by an imaging plate.

Results and discussion

Typical x-ray-diffraction patterns are shown in Fig.1. The pattern taken at 0.5 GPa can be basically interpreted by zincblende-type structure. There appear several extra lines (marked by closed circles) arising from impurities originally contained in the sample. These lines however merge into stronger peaks at higher pressures. At 9.3 GPa, a drastic change is recorded in the pattern, indicating an occurrence of a structural phase transition into a new phase (AlSb-II). The pattern at 9.3 GPa can be assigned to an orthorhombic lattice. The lattice parameters for AlSb-II at 21.8 GPa was a=5.27286Å, b=4.96749Å, and c=5.76600Å. At approximately 28 GPa, AlSb-II transformed into AlSb-III. This new transition has not been reported earlier. The 35.3 GPa pattern for AlSb-III can tentatively be assigned to a body-centered orthorhombic structure.

References

EXAFS studies on diluted magnetic semiconductor Cd$_{1-x}$Mn$_x$Te
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Introduction
Diluted magnetic semiconductor Cd$_{1-x}$Mn$_x$Te has attracted considerable attention because of its novel magnetic and magneto-optical properties derived from a hybridization of Mn 3d and sp band states. Recently, photoemission measurements have revealed that the Mn 3d contribution to the valence bands of Cd$_{1-x}$Mn$_x$Te is almost unchanged with $x$. This result suggests that the local coordination around Mn atoms is almost independent of $x$. In this study, we have performed EXAFS experiments for Cd$_{1-x}$Mn$_x$Te.

Experimental
Cd, Mn and Te K-edge EXAFS spectra of Cd$_{1-x}$Mn$_x$Te ($x = 0.10, 0.18, 0.32, 0.40, 0.48, 0.60$ and $0.69$) were measured in the transmission mode at BL-10B, 6B and 14A, respectively. All measurements were performed at 50 K. Samples were prepared using a Bridgman method. The samples were checked by x-ray diffraction and electron-microprobe analysis. The analysis of EXAFS data was performed by means of the well-established procedure.

Results and Discussion
Figure 1 shows Cd-Te (closed circles) and Mn-Te (open circles) bond lengths in Cd$_{1-x}$Mn$_x$Te obtained from Cd and Mn K-edge EXAFS spectra. Solid line exhibits the averaged cation-anion bond length obtained from x-ray diffraction. One notice that the Cd-Te and Mn-Te bond lengths in the alloys are almost unchanged with $x$ and nearly equal to those in pure CdTe ($2.80$ Å) and hypothetical zinc-blende type MnTe ($2.74$ Å), respectively. These results are in contrast to those by x-ray diffraction.

Figure 2 shows the Fourier transform of Te K-edge EXAFS function $k^2\chi(k)$ for Cd$_{0.82}$Mn$_{0.18}$Te. The first peak at 2.5 Å is assigned to a mixed contribution of Cd and Mn coordination. We can also recognize a second peak at 4.3 Å, which is attributed to the 12 Te coordination (second nearest neighbors around absorber Te atoms). Te-Cd and Te-Mn bond lengths in the alloys obtained by analyzing the first peak are consistent with those in Fig.1 within ±0.01 Å.

Present EXAFS results well explain $x$-independent Mn 3d states in Cd$_{1-x}$Mn$_x$Te revealed by photoemission measurements. In order to determine detailed coordination around Mn atom such as bond angle of the MnTe$_4$ cluster, the analysis of the second shell around the Te atoms is now in progress.

References
THE STRUCTURE OF AMORPHOUS PLATINUM DISULFIDE
AS STUDIED BY ANOMALOUS X-RAY SCATTERING
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Introduction
Crystalline dichalcogenides with a transition metal are known to have a layered structure. Many interesting properties of these compounds, such as charge density waves and intercalation chemistry, arising from their low dimensional structure, have been extensively studied. On the other hand, the amorphous state frequently shows better catalytic and electrochemical properties than the crystalline state. However, little is known about the structure and physical properties of these amorphous chalcogenides. The main purpose of this work is to present a new structural information of amorphous platinum disulfide (a-PtS2) by applying the anomalous X-ray scattering (AXS) method.1

Experimental
Amorphous PtS2 was prepared by passing H2S gas through H2PtCl6 aqueous solution at room temperature. The ordinary X-ray scattering measurement was carried out with Mo Ka radiation. The AXS measurements at the energies of -300 eV and -25 eV away from the Pt L absorption edge were carried out at the beam line 6B.

Results and Discussion
Figure 1 shows the ordinary and environmental RDFs for Pt in a-PtS2. Referring to the crystal structure of PtS2, the coordination numbers and atomic distances at the near-neighbor region were determined by the least-squares variational method. The resultant structural parameters are summarized in Table 1. It is found that a Pt atom is surrounded with 5.3 S atoms at 0.235 nm, and the atomic distances of the first and third nearest neighboring S-S pairs are 0.300 and 0.353 nm, respectively. No significant difference is detected in these parameters between the crystalline and amorphous states. This indicates that a fundamental structural unit of PtS6 octahedron in c-PtS2 remains in a-PtS2. On the other hand, it should be stressed that the structure of a-PtS2 is characterized by an additional correlation of the second nearest neighboring Pt-Pt pairs. The number of the first nearest neighboring Pt-Pt pair is 4.4 which is less than 6.0 in c-PtS2. The second nearest neighboring Pt-Pt pair at 0.398 nm, which is not present in the c-PtS2, shows its coordination number of 1.1. The first and second nearest neighboring Pt-Pt pairs correspond to the edge sharing linkage and the corner sharing linkage of PtS6 octahedron, respectively. It is suggested from the structural point of view that the open structure associated with a lower packing density of corner sharing linkage is probably one of the significant factors in determining the catalytic and electrochemical properties of a-PtS2.

References

![Fig. 1: Ordinary and environmental RDF for a-PtS2. Vertical lines indicate the peak positions found in crystalline PtS2 of CdI2-type structure.](image)

Table 1: Comparison of near neighbor correlations for a-PtS2 with those of crystalline PtS2.

<table>
<thead>
<tr>
<th>Pairs</th>
<th>c-PtS2 (P3m1)</th>
<th>a-PtS2</th>
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<tr>
<td></td>
<td>r / nm</td>
<td>N</td>
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<tr>
<td>Pt-S</td>
<td>0.234</td>
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<tr>
<td>S-S</td>
<td>0.307</td>
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<td>S-3</td>
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<td>3</td>
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<tr>
<td>S-S</td>
<td>0.354</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>0.354</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt-S</td>
<td>0.425</td>
<td>6</td>
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</table>

Table 1: Comparison of near neighbor correlations for a-PtS2 with those of crystalline PtS2.
PRESSURE DEPENDENCE OF INTER- AND INTRAMOLECULAR DISTANCES IN TRIGONAL SELLENIUM

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Introduction

Recently, inter- and intramolecular distances in trigonal selenium under high pressure have been investigated by an X-ray diffraction method using conventional X-ray source (MoKα, λ = 0.71069 Å, 50kV, 200mA). However, the sufficient results have not yet been obtained at pressure above 5 GPa because of a low signal-to-noise ratio of the diffraction pattern. In order to know the precise atomic position parameter in trigonal selenium at pressure above 5 GPa, the X-ray diffraction pattern has been measured using synchrotron radiation as an intense X-ray source.

Experiment

Trigonal selenium was prepared by annealing of an amorphous form with 99.999% purity in high vacuum at 160 °C for two hours. For the high-pressure experiments, the diamond anvil cell technique was used. Pressure was measured by the ruby fluorescence method. Angle-dispersive powder X-ray diffraction experiments were performed using the synchrotron radiation on beam line 6B at the Photon Factory National Laboratory for High Energy Physics. The X-ray beam is monochromatized to a wave length of 0.6888 Å and was directed to the sample through a pinhole collimator 80 μm in diameter. The X-ray diffraction data at pressures up to 18 GPa were collected with imaging plate detector. The details are described elsewhere.

The structural analysis was carried out by the Rietveld-refinement program Rietan.

Results and Discussion

A previously reported phase transition from trigonal form (Se-I) to intermediate one (Se-II) has been observed at about 15 GPa. As the Rietveld analysis for the Se-II has not yet been performed, the result for only trigonal form is described hereafter.

Figure 1 shows the observed and calculated X-ray diffraction patterns obtained at about 7 GPa by using conventional X-ray source (previous data) & synchrotron radiation (present data), respectively.

Figure 1 shows the observed and calculated X-ray diffraction patterns obtained by using conventional X-ray source (previous data) and synchrotron radiation (present data), respectively. Labeled G indicates a diffraction peak of metal gasket. The signal-to-noise ratio of the present data is much higher than that of previous data. The diffraction peaks in the present data are sharp and clear over a wide diffraction angle and the gasket peak is very weak compared with that of previous data. However, an agreement between observed and calculated diffraction patterns is not so good for the present data. The half-height-width of the calculated diffraction peak at high diffraction angle is larger than that of the observed one. The standard deviation for the atomic position parameter is about 0.004, which is comparable to that obtained before.

The pressure dependencies of lattice constants a and c obtained at this time agree well with those obtained before. That is, with increasing pressure, the lattice constant a decreases rapidly while the lattice constant c increases gradually. The pressure dependence of atomic position parameter x is shown in Fig.2 and compared with earlier data. The pressure dependence of this atomic parameter change near 5 GPa, that is, the parameter increases rapidly at pressure up to 5 GPa, becomes to be almost constant near 5 GPa and increases gradually afterwards. Since the trigonal selenium becomes from an indirect gap semiconductor to a tellurium-like direct gap one near 5 GPa, the change in pressure dependence of atomic parameter may be related to the change in band structure of trigonal selenium.

The pressure dependencies of inter- and intramolecular distances which are calculated from lattice constants and atomic parameter are in agreement with that obtained before. With increasing pressure, the intermolecular bond distance decreases rapidly while the intramolecular bond distance increases gradually at pressure up to 5 GPa. At pressure above 5 GPa, it is not clear whether the intramolecular bond distance increases or not with pressure because of large experimental error.

References

Observation of Phase Variation in the Rocking Curve in the Laue Case

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Introduction

By turning the X-ray energy from synchrotron radiation very close to the K absorption edges of Ga and As, the rocking curves were measured of GaAs 200 diffracted and transmitted beams in the symmetric Laue case. The rocking curves of transmitted beam are asymmetric with respect to the Bragg condition. It is found that the asymmetry of the transmitted rocking curves is due to the phase of the crystal structure factor.

Experiment

SR at KEK-PF BL6C1 beam line was monochromated by the two crystal monochromator using Si 111 reflection. The intensities of the diffracted and transmitted beams from the sample were detected by a scintillation counter or an SSD. Fig.1 (a) and (b) show the observed rocking curves. The thick solid line is the curve of the transmitted beam and the thin solid line that of the diffracted beam. The X-ray energy of (a) is 10502eV which is above Ga K absorption edge and (b) is 11805eV which is below As K absorption edge. The intensity curve of the transmitted beam (a) is asymmetric: The intensity in the low angle side is lower than that in the high angle side. The intensity increase is quite steep. On the other hand, the asymmetry of the curve in (b) is opposite.

Conclusion

If we denote the Fourier transform of the real part of the X-ray polarizability as \( \mathbf{x}_{br} = |\mathbf{x}_{hr}| \exp(i \alpha_{hr}) \), the corresponding imaginary part as \( \mathbf{x}_{hi} = |\mathbf{x}_{hi}| \exp(i \alpha_{hi}) \), then the phase difference is given by \( \delta = \alpha_{hi} - \alpha_{hr} \). Fig.2 shows the calculated rocking curves in the symmetric Laue case based on the dynamical theory of X-ray diffraction. The parameter \( W \) of the horizontal axis is proportional to \( \Delta \theta (\theta: \text{diffraction angle}) \). The thick solid line shows the rocking curve of transmitted beam for \( \delta = \pi \) and the dashed line that for \( \delta = 0 \). The thin solid line is the rocking curve of diffracted beam for \( \delta = 0 \) and \( \pi \). By comparing the curves in Fig.1 and Fig.2, we obtain that Fig.1(a) corresponds to the case \( \delta = \pi \) and (b) to the case \( \delta = 0 \). In this way, we can determine the phase factor \( \delta \) from measured rocking curves. This approach is generally applicable to the phase determination of crystal structure factor.

References

Linear Cu\(^{2+}\) \((S = \frac{1}{2})\) inorganic chain compound CuGeO\(_3\) exhibits a spin-Peierls (SP) transition at 14 K. The present report describes the existence of the strong fluctuation and/or the formation of short-range order above 80 K associated with the appearance of the Bonner-Fisher law. The temperature dependence of the b lattice constant and the integral breadth at 0\(\bar{4}0\) reflection is consistent with the observation of the softening of the LA phonons along the b axis and the spontaneous strain \(\Delta b\) by Lorenzo et al.

In the structural aspects there exist interesting properties above \(T_{SP}\) as indicated by Pouget et al. [2]. From the viewpoint of the precursor phenomena of SP transition, organic compounds could be classified into two categories [4]. The first group includes charge-transfer (CT) complexes such as TTF-CuBDT and MEM(TCNQ)\(_2\) which exhibit quasi-3D precursor phenomena and their magnetic susceptibility \(\chi(T)\) perfectly obeys the formula by Bonner and Fisher (B-F) (Class 1). The second one is composed of CT salts as \((D)_2X\) \((D=\text{TMNDF} \text{ or } \text{BCPPTF}, X=PF_5\) and \(\text{AsF}_5\)) which exhibit quasi-1D structural fluctuation and it affects the B-F type \(\chi(T)\) below \(T_{SP}\) \((H=J_{2S}(S_{AB})\) (Class 2). Pouget et al. [2] have emphasized that CuGeO\(_3\) resembles the Class 2 compounds. In CuGeO\(_3\), structural fluctuations are decoupled between neighboring chains around 15-19 K and the dimerized domains were observed up to at least 40 K from the x-ray diffuse scattering study at 1/2 \(3/2\). However, one of the remaining problems is quantitative disagreement between the measured \(\chi(T)\) and the B-F law as reported by Hase et al. [1]. In the study of single crystal, the search in the reciprocal space was performed by using the selected wave numbers as the incident x-ray, \(k=\frac{1}{\lambda}, 0.653-1.886 \text{ Å}^{-1}\). X-ray diffraction measurements using the synchrotron radiation was carried out at BL-6C, at the Photon Factory. The Si (111) monochromator was used under the negligible intensity of the \(\lambda/3\) contamination. The incident x-ray is running parallel to the a axis. The diffraction beam was projected on the imaging plate.

X-ray diffraction patterns taken at 300 and 80 K \((k=1.230 \text{ Å}^{-1})\). At 80 K, satellite spots were observed and they were assigned as \(h/2 k/2 (h+1: \text{ even}, k: \text{ integer})\) with the reduced wavevector \(q=(1/2,0,1/2), \) where the notation of the crystallographic axes follows the space group \(Pbmm\) in which the unique axis is taken as the c axis. The observed selection rules are in good agreement with those for the reported SP dimerized structure [3]. The reflection spots with \(h+1: \text{ even}\) such as \(1/2 0 1\) were also observed. Such types of reflections can be observed even at room temperature. Its origin is not clear at the present stage.

The remarkable feature of the present result at 80 K is the sharpness of the satellite reflections at 1/2 \(k/2 (k=0,1,2,3)\) etc. On the reflection at 1/2 \(k/2 (k=3,5,6)\) the temperature dependence of the satellite intensity has been already reported by neutron diffraction [2,3], in which these peaks clearly show the critical behavior at \(T_{SP}\) and x-ray diffuse scattering at 1/2 \(1/2\) \(3/2\) shows the quasi 1D structural fluctuations above about 19 K [2]. In our study, the integrated intensity at 1/2 \(3/2\) gradually increases with decreasing temperature below 80 K and it is enhanced below \(T_{SP}\). In contrast to the previous results the present observation of satellite at 80 K shows the existence of some kind of the formation of order. It is natural to consider that it may strongly correlate to the deviation of the \(\chi(T)\) from the B-F law [5]. In CuGeO\(_3\), the value of \(J\) is 120.4 K and up to around \(J\), \(\chi(T)\) may deviate from the B-F law due to the onset of quasi 1D structural fluctuation as reported by Pouget et al. [2] and above \(-120.0 K\) \(\chi(T)\) may be inherently affected by the structural instability triggered by the present satellite reflections. In this respect, CuGeO\(_3\) rather belongs to a new type of the SP transition other than two categories. The persistence of the present satellite peaks up to high temperatures also indicates the existence of a mode with low frequency.

In summary, the present report exhibits the existence of the strong fluctuation and/or the formation of short-range order above 80 K associated with the appearance of the satellite spots at h/2 k/2 \((h=\text{odd}, k: \text{ integer})\), which may give an explanation of the difference between the observed \(\chi(T)\) and the B-F law.

The present work has been performed as a part of a project (Proposal 93-G284) approved by the Photon Factory Advisory Committee.
Study of search for the structural change and the stability of CeNiSn as the Anisotropic Semiconducting Dense Kondo Lattice

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Introduction

CeNiSn is a semiconducting compound which is known as a dense kondo system. The electronic specific heat coefficient is 210 mJ/K·mol from which the compound classified into the heavy electron system. From the electrical resistivity measurement, the gap of the semiconducting band structure was estimated to be between 5K and 8K. At present the origin of this energy gap of the electronic band structure is not known. One possibility is that the gap is formed by the occurrence of the CDW transition at low temperatures. CeNiSn has the ε-TiNiSn type orthorhombic crystal structure with the lattice constants of a=7.542 Å, b=4.6009 Å, c=7.617 Å. The purpose of this experiment is to observe the crystal structure change, if it occurs, by the SR X-ray diffraction of CeNiSn single crystal and energy dispersive X-ray diffraction at low temperatures below 1K.

Experimental Procedures and the Results

The single crystal was grown by a Czochralski method. A thin specimen was cut from the single crystal. The specimen was attached to the sample holder of the dilution refrigerator which is installed at BL-6C1. The lowest temperature at which we took the Laue photograph of CeNiSn was 240 mK.

The enlarged Laue spots are shown in Fig 1(a) and (b). Fig 1(a) shows one of the expanded Laue spot taken at 4.2 K with a beam size of 0.5x3.0 mm. Fig 1(b) shows the expanded photograph of the same Laue spot taken at 240 mK with a beam size of 0.5x2.0 mm. In these result the crystal possesses mosaic structure to a great degree, we cannot find any special difference. We could not observe any crystal distortion in either Laue photographs or energy dispersive X-ray diffraction at various temperature down to 240mK.

Very recently Takabatake et al. pointed out the possibility of the coexisting of two phases which showed anomalous temperature dependence of the electrical resistivity and also the specific heat. From our experiment we could not say the existing of two phases because that the quality of the crystal was not so good to say it.

Reference

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AMORPHIZATION FROM THE QUENCHED HIGH-PRESSURE PHASE IN TERRAHEDRALLY-BONDED MATERIALS

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Introduction

Recently, amorphization from the quenched high pressure phase on decompression has been studied for many semiconductors [1-3]. Results were analyzed by using a configuration-coordinate model. The temperature dependence of the intensity of the diffraction peaks gives information concerning the potential barrier $\Delta U$ between the two phases of the before- and after-phase transitions. As the amorphization depends on $\Delta U$, it is interesting to study the path dependence of the phase transition in III-V compounds with different strength and ionicity of bonds.

Experimental

X-ray diffraction measurements at high pressures and low temperatures were carried out by an energy dispersive method using a synchrotron radiation from a bending magnet (BL-6C1)[4]. Pressure was generated by a diamond anvil cell with bellows which enabled us to change pressure continuously even at low temperatures.

Results and discussion

When pressure was released at low temperature, the high-pressure phase was quenched. In GaAs, amorphization from the quenched high-pressure phase occurs from 140 K to 260 K when temperature is increased at 5 GPa. Fig. 1 shows some examples of x-ray diffraction patterns for GaAs measured at $\theta = 11.5^\circ$. Results are summarized in Fig. 2.

In GaP, similar amorphization was observed on decompression from 27 GPa at constant temperature; from 8 GPa to 6 GPa at 90 K, from 11 GPa to 6 GPa at 130 K, and from 17 GPa to 14 GPa at 300 K. At 300 K, however, diffraction peaks from the zincblende phase were also observed. The transition pressure decreases with decreasing temperature.

Fig. 2 Phase diagram for phase transitions from the quenched high-pressure phase along various paths for GaAs.

References

RESPONSE OF NB-BASED TUNNEL JUNCTIONS TO SYNCHROTRON RADIATION

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Introduction
Superconducting tunnel junctions are expected to exhibit an excellent energy resolution for x-ray detection. The energy resolution has already been reported to reach values by a factor of 2 to 4 better than silicon detectors.1) Synchrotron radiation is capable of producing intense x-rays. Monochromatic x rays of different energies are available in high intensity beams, and they are useful in wide fields of science and technology. We are interested in the application of superconducting tunnel junctions to synchrotron radiation experiments. Nb-based tunnel junctions are tested at x-ray energies of 4 to 15 keV by means of synchrotron radiation.

Tunnel junctions
The junctions were fabricated at the Electrotechnical Laboratory (ETL) with a photolithographic method. We followed the method that had been developed by Nakagawa et al. The junctions are constituted by a trilayer of Nb/Al/AlOx/Nb. The thickness of base Nb, Al and top Nb was 50, 10 and 650 nm, respectively. The junction area is 100x100 μm² in size.

Measurement of synchrotron radiation
The experiment was carried out at the BL6C1 of Photon Factory of KEK. The junction experiment was made at a temperature of 0.4 K by the use of a 3He cryostat having a Be window for x-ray entrance. Spectra obtained by the 100 μm junction are presented in Fig. 1 for x rays of 4 to 15 keV. A full energy peak is seen for irradiation of 6-keV x rays, but it becomes more unclear with increasing x-ray energy. Although the junctions were suffered from very noisy circumstances, the energy resolution was 520 eV for 6-keV x rays. When the noise shielding is made more completely, the energy resolution will be improved.

Fig. 1 Spectra obtained by 100 μm x 100 μm junction for x rays of 4 to 15 keV.

Conclusion
The Nb-based tunnel junction was demonstrated to work in the circumstances of the synchrotron radiation facility.

References
EVALUATION OF PARABOLOIDAL FOCUSING MIRRORS
BY USING PARTIALLY COHERENT X-RAYS
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Introduction
An x-ray microprobe has been expected to be a promising analytical tool for spectroscopic and structural studies of the elemental constitution of matters with spatial resolution. Detectable signals are fluorescent x-rays, photoelectrons, EXAFS and so on. Although these signals are examined rigorously in the spectroscopic study, only a few experiment on micro-analysis have been reported.

Recent advances in x-ray optical elements made it possible to design various types of x-ray microprobes. Among them grazing incidence mirrors are the most convenient focusing elements because they can be used for the wide spectral range.

Very accurate fabrication techniques for focusing elements are required to obtain a small x-ray spot less than one micron. Aspheric mirrors answer this purpose because these are now being rapidly developed in the study of x-ray microscopy.

In this report we show that partially coherent x-rays are useful to evaluate the aspheric grazing incidence mirror which is designed for producing x-ray microbeam.

Experimental and Results
We examined focusing test with a paraboloidal mirror at BL-6C2. A schematic diagram of microbeam optics is shown in Fig.1. Instead of using an ellipsoidal mirror a paraboloidal mirror was used because it does not require a long source-to-mirror distance.

Incidence x-rays to paraboloidal mirror were monochromatized 1.377 Å (9 keV) by a Si(311) channel-cut monochromator, and collimated by a single Si(333). The energy spectrum of the collimated beam was examined with the SSD (pure Ge). The result showed that high energy x-rays (27 keV) which reflected from the first monochromator were cut by the Si(333). The beam divergence of the collimated beam is estimated about 6 μrad by DuMond diagram.

In this focusing test, the spot split into four when the incidence beam size was 160(meridional)x400(sagittal) μm (Fig.2). As the result of selecting best focusing spot with Slit III, the spot size was 5.5(meridional)x5.0 (sagittal)μm (Fig.3). Then the incidence beam size was 30x150μm.

Discussion
In this focusing test, the spot split into four. This result was caused by the figure error of the mirror. When highly collimated beam was used for the evaluation of mirror surface, we must consider the spatial coherence. The spatial coherence of the horizontal axis is approximated by the product of the wavelength and the inverse of the beam divergence. In our case it is about 24 μm. The meridional spot size was roughly limited by the numerical aperture of the mirror. The vertical - spatial coherence is determined by the widths of three slits. The well defined evaluation of mirror surface can be made by considering these limits.
KINETIC ENERGY RELEASED DISTRIBUTIONS OF H\(^+\) IONS DESORBED FROM H\(_2\)O/Si(100) ADSORPTION SYSTEM BY O 1s EXCITATION

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Introduction

It has been reported that the core level excitation to a \(\sigma\)-type of unoccupied orbital results in high ion-desorption probability in some adsorbate systems.\(^1\),\(^2\) To clarify the role of the core-excited states involving the \(\sigma^*\) orbital in the ion-desorption process, the kinetic energy released distribution (KERD) of H\(^+\) ions desorbed from H\(_2\)O-chemisorbed Si(100) was measured at O 1s \(\rightarrow\) \(\sigma_{O-H}\) resonant.

Experimental

The experiments were performed using soft X-ray beam line 11A. Ions were detected and analyzed by a time-of-flight (TOF) mass spectrometer\(^3\) using a pulsed synchrotron radiation. The resolution of excitation and kinetic energy were about 6 and 3 eV, respectively. The sample was cleaned by standard procedures to form the (2x1) surface. 10L saturation exposure of the substrate to H\(_2\)O was carried out.

Results and discussion

The KERDs calculated from the TOF profiles of H\(^+\) ions obtained with the photon energies of 500 and 535 eV are shown in Fig. 1. To investigate details of changing the KERDs with the primary excitation energy, the KERDs were decomposed into four Gaussian distributions. Using a least-squares fitting method, the parameters of the distributions were determined; The peak energies (and full widths of half maximums) of each component are 2.8(1.29), 5.0(1.44), 7.8(2.23), and 11.3(3.16) eV, which are denoted as \(\alpha\) to \(\delta\), respectively. Figure 2 (a)-(d) show intensities for these components as a function of photon energy. All the intensities of the kinetic energies components markedly depend on the primary excitation energy, and exhibit some characteristic thresholds, which are features of 1(Si L-shell excitation), 2(O 1s \(\rightarrow\) \(\sigma_{O-H}\) resonant), 3(shake-up ionization), and 4(shake-off ionization) depicted on the top of Fig. 2. These findings indicate that several different desorption channels open at these thresholds. In particular, the highest kinetic energy [Fig. 2(d)] component significantly increases at O 1s \(\rightarrow\) \(\sigma_{O-H}\) resonant. This can be explained by the fact that the two-hole one-electron final states through the spectator Auger process are repulsive.

Moreover, a delayed onset of Fig. 2(d) at about 570 eV is consistent with those of H\(^+\) total yields and O\(^+\) total yields. The onset can be explained by the formation of multiple charged cation following shake-off ionization, where their strong localization and repulsiveness lead to desorption.\(^2\)

References


![Fig. 1 Decomposition of the kinetic energy distributions into four components which are expressed by Gaussian distributions.](image1)

![Fig. 2 (a)-(d)the intensities of four kinetic energy components, (e)O\(^+\), (f)H\(^+\), (g)Auger electron, and (h)partial electron yield spectra.](image2)
ELECTRONIC PROPERTIES OF SO$_2$ ADSORBED ON Ni(100) STUDIED BY UPS

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Introduction

Adsorption of sulfur dioxide SO$_2$ has recently become an attractive subject. We have investigated surface structures of SO$_2$ on Ni(111) and Ni(100) surfaces by means of S K-edge XAFS spectroscopy [1], and have clarified that the SO$_2$ molecule is lying nearly completely flat and the S atom locates at the bridge sites on both the Ni(111) and Ni(100) surfaces. In the present work, we have measured UPS of submonolayer SO$_2$ adsorbed on Ni(100). On the basis of the present results, the nature of the chemical bonds between SO$_2$ and Ni are discussed.

Experimental

A clean and (1 x 1)-ordered Ni(100) crystal was dosed with 5 L SO$_2$ at 170 K. The S coverage can be estimated to be ~0.4 ML. UPS measurements were carried out at the plane grating monochromator station BL-7A. UPS data were taken with polar angles $\theta$ of an electric-field vector $\mathbf{E}$ of the incidence photon (49 eV) were chosen as 90° (normal incidence) and 20° (grazing incidence). The photoemission polar angles $\alpha$ with respect to the surface normal were 70° (glancing emission) for $\theta$=90° and 0° (normal emission) for $\theta$=20°, respectively.

Results and Discussion

Figure shows differences of ultraviolet photoemission spectra between submonolayer SO$_2$/Ni(100) and clean Ni(100). Peaks A, B and C can be assigned to the one-electron orbitals of adsorbed SO$_2$ molecules. Peak C is derived from the $6a_g$ (S3s) orbital, which lies lower by ~0.8 eV than that of solid SO$_2$. This lower-energy shift can be ascribed to initial-state charge transfer and final-state relaxation effects of submonolayer SO$_2$. Peaks A and B show significant angular dependence because of contributions of different states depending on detection geometries. Peak B appears in the normal emission spectrum at a lower energy side than in the grazing incidence. Taking account of the selection rule, this implies that the $2b_1$ orbital is more significantly shifted to a lower binding energy side, indicating stronger interaction of the $2b_1$ orbital with the substrate Ni than the other $\sigma$ orbitals in peak B. This can be easily understood since the $2b_1$ orbital is of out-of-planar $\pi$ bonding character and the molecule is lying flat on the surface. It should be also noted that a new feature labeled N was found at ~3 eV as a shoulder. In the previous studies [2] the band was assigned to the $3b_1$ level, which corresponds to the lowest unoccupied molecular orbital in a free molecule and is of $\pi^*$ character. The observation of the $3b_1$ level thus provides a direct evidence for a partial occupancy of the $\pi^*$ orbital due to the charge transfer from the substrate.

The bonding nature between SO$_2$ and the Ni surface should be exclusively of $\pi$ interaction; the S lone-pair orbital, which is regarded as a highest occupied molecular orbital and is important for the interaction of $\sigma$ donation, does not play an essential role for the present bonding nature, and SO$_2$ acts dominantly as a $\pi$ acceptor.

References

Proposal No. 94-G363

**O K-EDGE NEXAFS STUDIES OF SO$_2$/Ni(100)**

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**Introduction**

Structural and electronic properties of SO$_2$ adsorbed on metal surfaces are quite interesting because of bifunctional natures of a $\pi$ acceptor and $\sigma$ donor. Recently we have investigated surface structures of SO$_2$ on Ni(111) and Ni(100) surfaces by means of S K-edge XAFS spectroscopy [1], and have clarified that the SO$_2$ molecule is lying nearly completely flat and the S atom locates at the bridge sites on both the Ni(111) and Ni(100) surfaces. In order to obtain further information around the O atom, we have measured O K-edge NEXAFS of submonolayer SO$_2$ on Ni(100).

**Experimental**

A clean and (1 x 1)-ordered Ni(100) crystal was dosed with 5 L SO$_2$ at 170 K. The S coverage can be estimated to be ~0.4 ML. Angular dependent O K-edge NEXAFS measurements were carried out at the plane grating monochromator station BL-7A. A partial electron yield mode with a retarding voltage of -400 V was employed.

**Results and Discussion**

Figure shows O K-edge NEXAFS spectra of submonolayer SO$_2$ on Ni(100), together with that of multilayer SO$_2$. Since multilayer SO$_2$ is randomly oriented, only the 55° incidence spectrum was measured and is shown in Figure. Two intense resonances in the spectrum of multilayer SO$_2$ were observed at 530.7 and 535.9 eV and are ascribed to the transitions of O1s-to-$\pi^*$ and O1s-to-$\sigma^*(O-S)$, respectively. Submonolayer spectra, on the contrary, exhibit noticeable polarization dependence. Comparing those to the multilayer spectrum, we can easily assign the two features at 530.7 eV and 534.9 eV to the $\pi^*$ and $\sigma^*(O-S)$ transitions, respectively.

The $\sigma^*(O-S)$ resonance at 534.9 eV is most enhanced at normal X-ray incidence and almost diminished at grazing incidence, while the $\pi^*$ resonance is maximized at grazing incidence. These facts directly imply the flat-lying orientation of the molecular plane, being consistent with the S K-edge XAFS results [1]. The lower energy shift of the $\sigma^*(O-S)$ resonances by 1.0 eV was observed compared to the multilayer one. It is well known that the energy position of the $\sigma^*$ resonance is strongly correlated to the corresponding bond length; as the bond length is greater, the energy position is getting lower. The present result indicates the elongation of the S-O bond. The S K-edge NEXAFS has given a similar lower-energy shift of 1.7 eV and moreover the S K-edge SEXAFS has revealed the elongated S-O bond length by 0.08 Å [1], being in good accordance with the present finding.

The $\pi^*$ resonance in the 55° incidence spectrum is more than two times of magnitude suppressed compared to the solid one. The suppression should originate from a partial occupancy of the $\pi^*$ orbital (charge transfer from the Ni 3d bands to the SO$_2$ $\pi^*$ orbital) or, in other words, from strong mixing between the $\pi^*$ orbital and Ni 3d bands.

The bonding nature between SO$_2$ and the Ni surface should be exclusively of $\pi$ interaction; the S lone-pair orbital does not play an essential role for the present bonding nature, and SO$_2$ acts dominantly as a $\pi$ acceptor.

**References**

ELECTRONIC STATES OF STEPPED Ni(7 5 5) SURFACES STUDIED BY ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY

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Introduction

It has been shown that surface states strongly depend on the atomic structure of surfaces. A stepped single crystal surface can be formed where steps are periodically arranged. Each row of steps is separated by a terrace plane that is composed of several atomic rows. This makes one dimensional arrays of step rows on the surfaces. As a function of localization of electrons, new electronic states (electronic step states) must appear at the steps. Such electronic states exhibit more or less one dimensional character of the surface. Up to now, it has been believed that no electronic step states exist on stepped metal surfaces, because of delocalized nature of electrons in metals. Recently, we found the direct proof of the existence of the electronic step states on the stepped surface of Ni(7 9 11) by means of angle resolved photoemission spectroscopy (ARUPS). In this report, we show a new evidence of the electronic step states of Ni(7 5 5) surfaces by ARUPS, although the present experiment is still preliminary.

Experimental

ARUPS measurements were performed using the beam line type of ADES-400 (VG) installed at BL-7B. The incident angle of synchrotron radiation was 70° from the surface normal. The sample surface of Ni(7 5 5) was cleaned by repeated cycles of Ar ion bombardment and annealing at the temperature of ~1000 K. The clean surface was confirmed by Auger electron spectroscopy and low energy electron diffraction.

Results & Discussion

Figure 1 shows the photoelectron spectra measured at the normal emission on the clean and the oxygen adsorbed surfaces. On the clean surface, three peaks denoted as S, T, and B are observed. By the adsorption of oxygen, the peak intensities of S and T decrease, but peak B is invariant. Referring the previous ARUPS results of the surfaces Ni(7 9 11) and (111), peaks S and T can be assigned to the step and terrace electronic states, respectively. Peak B is due to the bulk bands. The change of the peak intensities of S and T is more clearly shown in Fig. 2. At the present stage of the experiments, the quenching rate of both peaks is probably similar. In the case of the Ni(7 9 11) surface, the electronic step states is much surface sensitive than the terrace one. These results show one of the characteristic nature of the surface steps with the different structures. The dispersion relation of the electronic states of the Ni(7 5 5) surface is still under investigation. It was also found that the electronic step states shows no dispersive feature, along the direction perpendicular to the step.

References

Temperature-Dependent EXAFS Study on Oriented YBa2Cu3Oy,.5 Superconductor

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INTRODUCTION

In spite of intense effort, no consensus has been reached on the microscopic mechanism of superconductivity in Cu-oxide materials. The anomalous temperature dependence of structure parameters has been reported by EXAFS measurements around for YBa2Cu3O7.5 and the related materials[1,2]. It is, however, important to verify quantitatively the dependence. To confirm our previous results, we made the polarization-dependent EXAFS measurements on the magnetically oriented YBa2Cu3Oy,.5 under two configurations of parallel (\(\ell \parallel c\)) and perpendicular (\(\ell \perp c\)) to the c-axis, where \(\ell\) denotes the X-ray polarization vector.

EXPERIMENTAL

The polarization-dependent Cu K-edge EXAFS spectrum was taken in the transmission mode on the beamline 7C. A Si(111) double-crystal monochromator was used by detuning to reject higher harmonics. The photon energy \(E\) was calibrated by assigning 8.9788KeV to the pre-edge peak at the K-edge in Cu foil. The temperature variation was measured using the closed-cycle He refrigerator. The temperature was monitored using the Si diode sensor attached to an Al holder.

DATA ANALYSIS

The EXAFS function \(\chi (k)\) was extracted from the observed spectrum by using the program "XAFS93"[3]. Improved background subtraction and normalization methods were used. A nonlinear least-squares fit for both Cu-O\(_{2,3}\) and Cu-O\(_{1}\) contributions was performed over \(k=3.7-14.7\AA^{-1}\) on Fourier-filtered data (filtered over the range \(k=2.5-18.0\AA^{-1}\)) a backtransformed over \(R=1.0-1.9\AA\) from 20K to room temperature. Since the three distances of Cu-O\(_{2,3}\) and Cu-O\(_{1}\) in the a-b planes are very close, we treated their average distance as the equatorial bond distance Cu-O\(_{eq}\) (single-shell model).

RESULTS AND DISCUSSION

According to the polarized EXAFS formula[4], we analyzed \(\chi (k)\) on the following parameters:

\(R_{j}\), the radial vector from an absorbing atom to \(j\)-th neighbor; \(\sigma^{(i)}\) (\(i=2,3\)), the 2nd- and 3rd-order moments, and \(\sigma^{(4)}\), the 4th-order cumulant. To determine accurately these values, the number of neighboring atoms was fixed the crystallographic value. The parameters of \(\Delta R_{j}\) and \(\eta\) were first determined so as to fit to the spectrum at 20K, and then they were fixed for the spectrum at higher temperatures. Figure 1(a)-(d) shows \(R_{Cu-O}\) and \(\sigma^{(i)}\) (\(i=2-4\)). These parameters monotonically decrease with decreasing temperature from 300K to 100K. It clearly shows, however, that they yield an anomalous behavior in a limited temperature range around \(T_{c}\): \(R_{Cu-O}\) anomalously increase, whereas \(\sigma^{(3)}\) and \(\sigma^{(4)}\) show a peculiar decrease. This overall feature is in agreement with our previous results[1-3]. It suggests that the anharmonicity in lattice vibration correlates with the superconductivity.

References

Electronic and Intracrystalline Structure of Mercury Halide Intercalated into High-T\textsubscript{c} Superconducting Phase of Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y}

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Introduction
Recently, we have developed new superconducting intercalation compounds of (HgX\textsubscript{2})\textsubscript{6}Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y} (X = Br and I)\textsuperscript{7}. According to the previous communication\textsuperscript{7}, it was found that the mercuric halide molecules intercalate inbetween Bi\textsubscript{2}O\textsubscript{3} slabs along with remarkable lattice expansion and a slight decrease in T\textsubscript{c}. In order to elucidate the origin of T\textsubscript{c} evolution upon intercalation, we have investigated systematically on the electronic and crystalline structures of HgX\textsubscript{2}-intercalates using the X-ray absorption spectroscopy (XAS).

Experimental
HgX\textsubscript{2} (X = Br, I) - intercalated Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y} composites were prepared by the vapor transport reaction of guest molecule and the pristine Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y} described previously\textsuperscript{1}. X-ray absorption experiments for the HgX\textsubscript{2}-intercalates were carried out on the beam lines 7C and 10B at the Photon Factory, KEK-PF with a storage ring providing a 2.5 GeV electron beam at a current of ca. 300–360 mA. The curve fitting analysis for the Hg Lm-edge EXAFS spectra was carried out for the inverse Fourier transformed k\textsuperscript{3}X(k,\kappa) of the first shell corresponding to the Hg-X bonding pair in the Fourier transform (FT).

Results and Discussion
In the I L\textsubscript{2,3}-and Br K-edges XANES spectra of the HgX\textsubscript{2}-intercalates, a sharp white line, associated with transitions from ns core level into unoccupied final np states above the Fermi energy level (E\textsubscript{F}), is observed. Compared to that for unintercalated HgX\textsubscript{2} molecule, the intensity of this peak is reduced upon HgX\textsubscript{2} intercalation as observed in iodine intercalation\textsuperscript{1}. As the intensity of this peak is proportional to the density of unoccupied final np states, the observed intensity decrease apparently indicates that the electron is only slightly transferred from the host lattice to the guest HgX\textsubscript{2} layer. In the viewpoint of charge transfer, we have also examined the effect of intercalation on the electronic and geometric structure of host lattice by comparing the Cu K- and Bi Lm-edge spectra of the pristine Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y} and its HgX\textsubscript{2}-intercalates. In the Cu K-edge spectra, there is no prominent change in the peak position and intensity, indicating that the electronic structure and the local symmetry of copper site are hardly changed upon HgX\textsubscript{2}-intercalation. However, a comparison of Bi Lm-edge XANES spectra for the pristine and its HgX\textsubscript{2}-intercalates obviously demonstrates some characteristic variations in spectral feature after HgX\textsubscript{2}-intercalation. First of all, the edge energy is remarkably increased upon HgX\textsubscript{2}-intercalation, indicative of the oxidation of Bi\textsubscript{2}O\textsubscript{3} layer. Secondly, the pre-edge peak near 13418 eV, whose intensity is proportional to the density of unoccupied 3d\textsubscript{xy} orbital, is enhanced upon intercalation, confirming the oxidation of Bi\textsubscript{2}O\textsubscript{3} layer. At third, the energy difference between the main-edge peaks which correspond to 2s \rightarrow 6d_{xy} and 2s \rightarrow 6d_{xy} transitions\textsuperscript{13} is decreased upon intercalation, which is due to the elongation of axial oxygen ligand to the bismuth resulting in the stabilization of 6d\textsubscript{xy} orbital compared to 6d\textsubscript{xy} one.

In addition to the evolution of electronic structure, the intracrystalline structure of mercuric halide molecule in the interlayer space of Bi\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{y} lattice was investigated by the EXAFS analysis. The Fourier transforms (FT) of k\textsuperscript{3}-weighted Hg Lm-edge EXAFS spectra for the HgX\textsubscript{2}-intercalates show the prominent FT peaks at the R range of 2.0 Å and 2.6 Å, which are attributed to the Hg-X shell. For the curve fitting analysis, these peaks are back Fourier transformed into k space as present in figure 1, together with the simulated EXAFS signal. From the result of EXAFS curve fitting, the coordination number of mercury in HgX\textsubscript{2}-intercalate is found to be two for both intercalates and the bond length of Hg-X is determined to be 2.46 Å for HgBr\textsubscript{2}-intercalate and 2.65 Å for HgI\textsubscript{2}-one, those which are slightly larger than that for gaseous species.

Acknowledgments
This work was supported in part by the Korean Ministry of Education (BSRI-94-3413) and the KOSEF (92-25-00-02).

References
EXAFS STUDY ON THE INTRACRYSTALLINE STRUCTURE OF AgI INTERCALATED INTO Bi$_2$Sr$_2$CaCu$_2$O$_y$

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INTRODUCTION

Recently, we reported that mercury or silver halides could successfully intercalate into the 2-dimensional Bi$_2$Sr$_2$CaCu$_2$O$_y$ superconductor. Among these new series of intercalates, we have found that the AgI-intercalated system could exhibit mixed conductivity with a substantial ionic contribution. In this paper, we report the intracrystalline structure of AgI which was determined by the extended X-ray absorption fine structure (EXAFS) spectroscopy.

EXPERIMENTAL

The (AgI)Bi$_2$Sr$_2$CaCu$_2$O$_y$ intercalate was prepared as described previously. X-ray absorption measurements were carried out at BL 10B and 7C in Photon Factory, National Laboratory for High Energy Physics (KEK-PF, Tsukuba, Japan). The EXAFS data were processed with IBM PC version of UWXAFS II.

RESULTS AND DISCUSSION

Figure 1 shows the Fourier-filtered EXAFS spectra of Ag K and 1 L$_{III}$ for the AgI intercalate, which are compared with those of β-AgI within the photoelectron wavevector range of k = 2 - 10 Å$^{-1}$. For the Ag K-edge spectra, both amplitude and frequency for the AgI intercalate are almost identical with those for β-AgI (Fig. 1a). In case of the 1 L$_{III}$-edge EXAFS (Fig. 1b), even though there is little change in frequency between (AgI)Bi$_2$Sr$_2$CaCu$_2$O$_y$ and β-AgI, however, the amplitude for AgI intercalate is reduced in the entire range of k space and especially the amplitude depression at low k space is more pronounced than at high k one, which indicates clearly the reduction of coordination number around the central iodine after intercalation. The non-linear least square curve fitting results have shown that the bond distance of 2.78 Å between silver and iodine of the intercalated AgI was almost the same as that of β-AgI (2.78 ~ 2.79 Å). The fitted coordination number (C.N) of silver in (AgI)Bi$_2$Sr$_2$CaCu$_2$O$_y$ is nearly identical with that in β-AgI. On the other hand, the C.N of iodine in (AgI)Bi$_2$Sr$_2$CaCu$_2$O$_y$ becomes smaller than that in the free AgI, which is due to the fact that the iodine of the intercalated AgI should interact with the Bi atom in the interlayer surface of Bi$_2$Sr$_2$CaCu$_2$O$_y$. Therefore, we propose that the intracrystalline structure of the intercalated AgI is formed as β-like structure in the 2-dimensional interlayer space of Bi$_2$Sr$_2$CaCu$_2$O$_y$.

Acknowledgments. This research was supported by the Korean Ministry of Science and Technology (MOST) for the high-Tc superconductivity research (1994), the Korean Ministry of Education (BSRI-94-3413), the Photon Factory (proposal No. 92G196) and the Pohang Light Source (proposal No. 92-012).

REFERENCES

EXAFS STUDY ON THE DEACTIVATION OF Co-Mo/Al2O3 HDS CATALYSTS DURING ONE-YEAR COMMERCIAL RUN

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Introduction

To meet an increasing demand for low-sulfur petroleum products, there have been lots of studies aimed at the improvement of the hydrodesulfurization (HDS) catalysts. From the practical point of view, another important issue lies in the suppression of catalyst deactivation during the hydrotreating processes. We have prepared a series of Co-Mo catalysts with various loadings and exposed them to a commercial HDS run. In this study EXAFS method was applied to the characterization of the freshly sulfided and used catalysts to discuss the catalytically active sites and their changes during the run.

Experimental

Four kinds of Co-Mo catalysts were prepared by coimpregnation of Al2O3. The Mo loadings were 9.3, 14.7, 20.7 and 34.7 wt% as MoO3 with a constant Co/Mo molar ratio of 0.5. Each catalyst was loaded in a stain-less steel basket and then exposed to a commercial HDS run for a year. As a reference to the used catalyst, each fresh catalyst was sulfided in a stream of 5%-H2S/H2 (673K-2h). Mo and Co K-edge EXAFS measurements were carried out in the transmission mode at BL-10B and 7C of the Photon Factory.

Results and Discussion

Fig.1 shows the coordination numbers of S (N(S)) and Mo (N(Mo)) around Mo obtained from the magnitudes of the two peaks in the Fourier transformed Mo K EXAFS spectra, which were assigned to Mo-S and Mo-Mo in MoS2. The N(S) and N(Mo) for each used catalyst are much larger than those for the corresponding fresh catalyst. These changes are attributed to deeper sulfiding of Mo species and larger MoS2 stacks in the used catalysts. Transmission electron microscopy (TEM) observation revealed no change in the average number of layers per a MoS2 stack during the run, in contrast to the increase in the MoS2 stack size which is consistent with the EXAFS results. These results indicate that MoS2 stacks grow in the lateral direction but do not grow in the normal direction to the layers during the run.

Fig.2 shows Fourier transforms of the Co K EXAFS of the fresh and used catalysts (MoO3= 34.7 wt%), together with that of CosSs which is thermodynamically the most stable species under the reaction conditions. Considering the XANES results, the shift of the main peak from the fresh catalyst to the used one suggests that the oxide species in the fresh catalyst was converted into sulfide during the run. However, the formation of CosSs is not clearly observed. Thus, in spite of the aggregation of MoS2, the major part of Co atoms are not released from the edge of MoS2 in the used catalysts.

In the present study, more active catalysts gathered larger amounts of C, Ni and V depositions, which have long been claimed to be the major cause of the catalyst deactivation. Recently, however, the aggregation of MoS2 stacks was claimed to be the main cause of the catalyst deactivation [1]. Further study is needed to conclude to what extent the structural change contributes to the catalyst deactivation.

Reference

LOCAL STRUCTURES AROUND Co AND Mn IONS IN ZnO-BASED VARISTORS BY XAFS
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Introduction

ZnO ceramics containing 1-3mol% of Bi₂O₃, La₂O₃, Pr₂O₃, CoO, MnO and Cr₂O₃ etc. to ZnO exhibit highly nonlinear current-voltage characteristics, which are called varistors. The varistor effect takes place at grain boundaries within the ceramics. It is known that the role of Bi₂O₃, La₂O₃ or Pr₂O₃, whose ionic radius of cation is much larger than that of Zn⁺, is to form the grain boundary layers. CoO and MnO are reported to improve nonlinear ohmic coefficient. However, the coordination states of Co and Mn ions, i.e., whether they exist in the ZnO matrix or in the boundary layer, are not clarified. In this study, the local structures around Co and Mn ions in ZnO:M₁, Co, Mn (M₁=Bi, La, Pr) are analyzed.

Experimental

Samples were prepared by a solid-state reaction among constituent metal oxides. The amount of additives was fixed to be 1mol% to Zn. The as-sintered samples were divided into three. One was oxidized in an O₂ flow, another was reduced in an Ar flow, and the other was annealed in an ambient atmosphere. Each treatment was performed at 500°C for 1h. The Co and Mn K-absorption spectra were measured in a fluorescent mode at the BL-7C station using the Lytle-type fluorescence detector. Signals were accumulated for 3sec per point. The XAFS data analyses were performed by using the Program Library provided by Sakane.

Results and Discussion

Table 1 shows the Co-O distance obtained by curve-fitting analyses for ZnO:M₁, Co, Mn varistors (M₁=Bi, Pr, La). In all the systems, the distance was calculated to be 0.196-0.197nm and did not change even after various treatments. If the Co ions take a divalent state and are coordinated tetrahedrally by oxide ions, the distance would be 0.196nm, calculated from their effective ionic radius. These results suggest that the Co⁺ ions are occluded in the wurtzite-type ZnO matrix.

Our X-ray diffraction studies have indicated that Mn ions in the ZnO:Bi, Co, Mn varistor exist as a form of Mn₂O₃ and those in the ZnO:La, Co, Mn sample exist as a form of LaMnO₃+x. This difference appeared in the shape of the respective Mn K-XANES spectrum. It is of interest that the Mn-O distance in the La-system varied with the oxidized/reduced treatments. That is, the oxygen content of LaMnO₃+x varied. Whereas that in the Bi-system was calculated to be 0.197nm and did not change after the treatments. In the Bi-system, Mn ions are also confirmed to take a trivalent state and a 6-folded coordination by XAFS. In the La-system, the ratio of Mn⁴⁺/Mn³⁺ was estimated by assuming that the distance varied in accordance with Vegard's law, which is shown in Fig 1. After the oxidized treatment, approximately 60% of Mn ions were found to have a tetravalent state.

Table 1. Co-O distance obtained by curve-fitting analyses for ZnO:M₁, Co, Mn varistors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C. N.</th>
<th>R/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁=Bi</td>
<td>oxidized</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>sintered</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>0.197</td>
</tr>
<tr>
<td>M₁=Pr</td>
<td>oxidized</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>sintered</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>0.197</td>
</tr>
<tr>
<td>M₁=La</td>
<td>oxidized</td>
<td>0.196</td>
</tr>
<tr>
<td></td>
<td>sintered</td>
<td>0.197</td>
</tr>
<tr>
<td></td>
<td>reduced</td>
<td>0.196</td>
</tr>
</tbody>
</table>

Fig. 1 Ratio of Mn⁴⁺ ions in ZnO:La, Co, Mn varistors.
XAFS STUDIES ON TITANIUM OXIDES INCLUDED WITHIN ZEOLITES FOR THE PHOTOCATALYTIC DECOMPOSITION OF NO
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Introduction
We have reported that the highly dispersed titanium oxide catalyst with tetrahedral coordination is prepared in the pore structure of transparent Vycor glass and the catalyst exhibits a quite high photocatalytic activity compared to the bulk TiO$_2$ powder. Along these lines, titanium oxides included within zeolite cavities and frameworks are prepared and utilized as the photocatalysts for the direct decomposition of NO molecules at 275 K. In the present studies, we deal with the characterization of these catalysts using XAFS measurements.

Experimental
Two types of Ti-silicalite having different Ti contents (TS-2A: 2.3 wt%, TS-2B: 8.1 wt% as TiO$_2$) were prepared hydrothermally. The Ti-oxide/silicalite (imp. Ti/SL: 8.0 wt% as TiO$_2$) sample was prepared by impregnating of silicalite with an aqueous solution of TiCl$_3$. The Ti-oxide/Y-zeolite (ex. Ti/Y: 1.1 wt% as TiO$_2$) sample was prepared by ion-exchange with an aqueous titanium ammonium oxalate solution. The photocatalytic reactions of NO molecules were carried out at 275 K using a 75-W high-pressure Hg lamp (λ>280 nm). The XAFS spectra (XANES and EXAFS) were measured at the BL-7C facility of the Photon Factory. The Ti K-edge absorption spectra were recorded in the transmission mode or fluorescence mode at 295 K.

Results and Discussion
UV irradiation of various titanium oxide catalysts in the presence of NO at 275 K led to the formation of N$_2$ and N$_2$O. The photocatalytic efficiency and selectivity for the formation of N$_2$ are much higher on the Ti-oxide/Y-zeolite catalyst prepared via an ion-exchange method (ex. Ti/Y) and Ti-silicalite (TS-2A) catalyst than those of other catalysts. While the formation of N$_2$O was found to be the major reaction on the Ti-silicalite with a high Ti content (TS-2B) and Ti-oxide/silicalite prepared by the impregnation method (imp. Ti/SL).

Figure 1 also shows the FT-EXAFS spectra of the catalysts. All data are presented without phase shift allowances which can be estimated to be about 0.4-0.5 Å. All catalysts exhibit a strong peak at around 1.6 Å which can be assigned to the neighboring oxygen atoms (Ti-O). The Ti-oxide/Y-zeolite prepared by an ion-exchange method (ex. Ti/Y) and Ti-silicalite (TS-2A) catalysts exhibit only Ti-O peaks indicating the presence of the isolated titanium oxide species. These results together with the results obtained by XANES studies, indicate the formation of isolated tetrahedral TiO$_4$ species on the Ti-oxide/Y-zeolite and Ti-silicalite catalysts.

On the other hand, Ti-silicalite (TS-2B) catalyst with a high Ti content and the Ti-oxide/silicalite prepared by an impregnation method (imp. Ti/SL) exhibit an intense peak at around 2.7 Å. This peak can be assigned to the neighboring titanium atoms (Ti-O-Ti) as well as a Ti-O peak, indicating the aggregation of the titanium oxide species in the catalysts. The titanium oxides overflowed from the framework of the Ti-silicalite (TS-2B) aggregated and formed octahedral titanium oxide species.

From these results, it is concluded that a high photocatalytic efficiency and selectivity for the formation of N$_2$ in the decomposition of NO molecules was achieved on the Ti-oxide/Y-zeolite (ex. Ti/Y) and Ti-silicalite (TS-2A) catalysts which are consisted of the highly dispersed isolated tetrahedral titanium oxide species. While, the formation of N$_2$O from NO molecules proceeded on the Ti-silicalite (TS-2B) and Ti-oxide/silicalite (imp. Ti/SL) catalysts which involve the aggregated octahedral titanium oxide species.
XAFS cumulant and ligand exchange reaction rate constant for metal ion in aqueous solution

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Introduction
There exist a few EXAFS applications to the study of chemical reactivity of metal complexes in solution. A correlation of the self-electron exchange rate constant with the difference in the metal-ligand bond distance between two oxidation states was reported[1]. Recently, it has been reported that the ligand exchange reaction rate constant, $k_1$, of hydrated metal complexes in aqueous solution is closely related to the EXAFS Debye-Waller factor, $\sigma^2$[2,3] and is also related to the higher order cumulant in EXAFS[3].

In this report, the relation between $\sigma^2$ and $\log k_1$ is predicted by combining a simple Arrhenius equation and an expression for the Debye-Waller factor developed recently[4].

Experimental
All the K-edge absorption spectra were recorded in a transmission mode at BL-6B and BL-7C in Photon Factory. Si(111) double crystal monochromators were used. In order to reduce the higher order components in X-ray, the second crystal was detuned or a quartz mirror was inserted into the X-ray beam.

The solution samples were prepared by dissolving the metal perchlorate salts. Perchloric acid was added into the solution in order to prevent the hydrolysis.

The EXAFS interference function was extracted from the absorption spectrum and was Fourier transformed according to the procedure described in ref. 5. The backscattering amplitude and the phase shift are those calculated by McKale et al. using curved-wave method[6]. In the EXAFS interference function is included the third order cumulant $C_3$.

Results and Discussion
The anharmonic potential between the metal ion and water oxygen is assumed to be of the Morse function as $V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x})$, where $x$ is the relative displacement in the interatomic distance, $\alpha$ is the parameter for the width of the potential and $D$ is the dissociation energy. The theoretical approach to the EXAFS Debye-Waller factor using the Morse interatomic potential leads to a simple expression[4], $\sigma^2 \propto a^2 h/(8\pi\alpha\sqrt{2D})$, where $a$ is the lattice constant.

To the ligand exchange reaction in aqueous solution, we apply the Arrhenius theory, then $k_1 = A \exp(-E_a/k_BT)$, where $E_a$ is the activation energy and $A$ is the frequency factor. For simplicity, we assume here that $E_a$ is approximated by $D$. If the parameter $\alpha$ is assumed to be constant, then $\sigma^2/\alpha^2$ is proportional to $1/\sqrt{D}$ and we obtain a simple expression. $(\sigma^2/\alpha^2) \propto C(\log A - \log k_1)$, where $C$ is an arbitrary constant at a given temperature. In Fig. 1 are plotted the $(\sigma^2/\alpha^2)^2$ values against $\log k_1$ for the metal ions in aqueous solution, where $r$ is the nearest neighbor distance. The straight line in Fig. 1 corresponds to the $C$ and logA values of 0.11 and 10.0, respectively. The parameter $A$ is the important parameter indicating the maximum value of the ligand exchange reaction rate pertaining to the zero activation energy. It is remarkable that the value of $A$ coincides with that for the diffusion-controlled reaction in water (the order of $10^{16}$ s$^{-1}$).

References
FLUORESCENCE XANES MEASUREMENTS FOR AMORPHOUS Al-Ce ALLOYS UNDER HIGH PRESSURE

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Introduction
Many alloys and compounds of Ce exhibit anomalous features such as the dense Kondo effect. The anomalies are associated with partial delocalization of 4f-electron due to strong hybridization of the 4f orbital with the conduction band, and to partial charge transfer to the partner element. Recently, some of the present authors performed high pressure experiments for amorphous Al-Ce alloys and found that the dense Kondo effect in the amorphous alloys are suddenly enhanced by external pressure. Such a sudden change in the dense Kondo state with pressure has not been observed in crystalline alloys. In this work, fluorescence XANES spectra for amorphous Al-Ce alloys under high pressure were measured by our developed technique, and the changes in Ce valence with pressure were estimated in order to understand the dense Kondo state in the amorphous alloys.

Experimental
Amorphous Al-Ce thin ribbons were prepared by a melt-spinning technique under pure argon atmosphere. Ce-L\textsubscript{III} XANES spectra were measured under various high pressures using a beryllium gasketed diamond anvil cell and the focused synchrotron radiation source at the BL-7C of the Photon Factory, KEK. We recorded fluorescence x-rays of Ce-L\textsubscript{III} radiation in order to estimate the absorption of Ce-L\textsubscript{III}, or the excitation of electrons from the 2p\textsubscript{3/2} core level into the 5d\textsubscript{5/2} or 5d\textsubscript{3/2} conduction bands. The spectra were analyzed in the manner similar to that proposed by Rohler. The detailed method of analysis was described in our separate paper.

Results and Discussion
Figure 1 shows fluorescence Ce-L\textsubscript{III} XANES spectra for amorphous Al\textsubscript{12}Ce\textsubscript{80} under ambient and high pressure. The solid lines are our theoretical fits. At ambient pressure (A.P.), the spectrum (a) exhibits only a single white line, corresponding to Ce\textsuperscript{3+} (4f\textsuperscript{1}). As the external pressure is applied, another white line assigned to Ce\textsuperscript{4+} (4f\textsuperscript{0}) is clearly appearing, and then the spectrum (b) at 1.5 GPa exhibits a typical doublet-profile which is characteristic of the mixed-valence. Analysis of the L\textsubscript{III} data yields the Ce valence of V=3.07 at A.P. and V=3.19 at 1.5 GPa, respectively. This indicates that the electron transition from 4f\textsuperscript{1} to 4f\textsuperscript{0} in the amorphous Al-Ce alloy is rapidly promoted by only a little external pressure. We already confirmed that pressure-induced 4f electron transition occurs in crystalline PdCe and GaCe alloys. However, the pressure dependence of Ce valence in the amorphous Al-Ce alloy is incomparably larger than that in the bulk crystalline alloys.

Fig. 1 Fluorescence Ce-L\textsubscript{III} XANES spectra for an amorphous Al\textsubscript{12}Ce\textsubscript{80} at (a) A.P. and (b) 1.5 GPa.

References
ON THE ROLE OF Ga IN NANO CRYSTALLINE FORMATION FOR THE MELT-QUENCHED Fe$_{73}$Ga$_4$Nb$_3$Si$_{11}$B$_9$ ALLOY

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Introduction

Reduction of crystalline size to nano scale sometimes drastically changes physical properties of materials. For example soft magnetic properties are significantly improved by decreasing grain size due to reduction of magnetic anisotropy. Small amount of additives often play key roles to form nano scale crystallites which are precipitated from amorphous by appropriate annealing melt-quenched amorphous ribbons. A well known example is Cu and Nb in Fe$_{73}$Cu$_{10}$Nb$_{3}$Si$_{11}$B$_{9}$ [1]. Cu in this alloy is believed to promote nucleation of α-Fe(Si) because Cu is insolvable in Fe. Our previous XAFS work have proved that fcc Cu clusters precipitate prior to α-Fe precipitation [2]. On the other hand Tomida [3] has found that Ga addition to Fe$_{73}$Ga$_4$Nb$_3$Si$_{11}$B$_9$ also causes nanocrystalline formation even though Ga is soluble to α-Fe. The aim of this study is to know how Ga behaves during α-Fe precipitation in order to know the role of Ga on the nanocrystalline formation.

Experiments and Results

XAFS measurements of Ga K-edge have been done at BL 7C by transmission method using Si(111) monochromator for the as-quenched and annealed at 623K, 693K, 723K, 783K and 893K for 1 hour. After usual background subtraction and normalization procedures using EXAFS2 [4], $\chi(k)$ was obtained. Curve fittings were carried out using theoretical parameters such as background amplitudes, phase shifts and photo electron mean free paths which are calculated by FEFF5 [5]. The details of the data analysis will be described elsewhere [6]. Fig.1 and Fig.2 show the results of coordination number and mean square variation as a function of annealing temperature, respectively. It is noteworthy that coordination number around Ga decreases sharply at just the beginning of crystallization (723K). Coordination number is estimated assuming all atoms are iron in the analysis. Therefore it seems reasonable to think that the decrease in coordination number around Ga atoms can be attributed to the increase in Si or B. B is more likely than Si. These XAFS results suggest that at the beginning of α-Fe precipitation Ga is excluded from α-Fe nuclei toward grain boundary where Si or B are more abundant than the average. Such a transient exclusion of Ga toward grain boundary of α-Fe nuclei probably reduce surface energy of nucleus and then promotes nucleation of α-Fe.

References

(4) N. Kosugi, H. Kuroda, PROGRAM, EXAFS2/V3, Research Center for Spectrochemistry, Faculty of Science, Univ. Tokyo.
AN EXAFS INVESTIGATION OF LOCAL STRUCTURE AROUND Rb+ IN AQUEOUS SOLUTION

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Introduction
The local structures around various metal ions in aqueous solutions have been studied by use of NMR, X-ray and neutron diffraction techniques.1,2 Vorgin et al. have reported that the coordination number, N, of H2O around Rb+ is 3.5 on the basis of NMR spectrum of RbOH aqueous solution. However, it has been pointed out that the N is underestimated owing to the weak magnetic interactions between Rb+ and H2O molecules.2 The interatomic distance, r, around Rb+ in aqueous solution has not been experimentally determined so far.

In the present communication, the local structure around Rb+ in dilute aqueous solution determined by Rb K-edge EXAFS method is reported.

Experimental
EXAFS measurements were performed by using synchrotron radiation from the Photon Factory (PF) at the National Laboratory for High Energy Physics (KEK, Tsukuba).3 The concentration of the solution was 1.0 x 10⁻⁴ mol dm⁻³. As reference samples, we measured the EXAFS spectra of solid RbOH and rubidium hydrogen succinate (RbC4H5O4; RHS). EXAFS spectra were collected in transmission mode, using beamline BL-7C with two Si(111) flat crystal monochrometers. The programs "XAFS93" and "MBF93" were employed for the EXAFS data analyses.4 Figs. 1(a) and (b) show the Fourier transforms, Φ(r), of the EXAFS oscillations, k²Φ(k), of RbOH aqueous solution and solid RbOH at 300 K, respectively. Φ(r)'s of both samples exhibit a pronounced peak around the r of 2.2 Å corresponding to the nearest neighboring atoms. The X-ray structural analysis of solid RbOH shows that the Rb+ is coordinated by six O atoms.5 Thus, the peaks are attributed to the Rb-O scattering. The coordination number, N, and the Rb-O distance, r, around Rb+ in solid RbOH were obtained by applying the filtering technique6 to the pronounced peak which corresponds to the range of 1.640-2.510 Å. A non-linear least-squares fitting was applied to the filtered data according to the EXAFS formula.7

Results and Discussion
The analysis of EXAFS spectrum of RbOH aqueous solution was carried out with λ(k) = 1.486k estimated from the EXAFS spectrum of RbOH powder. The N and r around Rb+ in the RbOH aqueous solution have been determined to be 6.6(1.2) and 2.88(5) Å, respectively. Furthermore, we try to determine the N and r with λ(k) = 1.677k estimated by using the structural parameters of RHS, in which the Rb+ is coordinated by eight O atoms.8 Similar results of N = 6.3(1.1) and r = 2.92(2) Å were obtained. The present results are comparable with those reported for K+ and Cs+ in aqueous solutions by means of X-ray and neutron diffraction methods; N = 6-8 and r = 2.60-2.95 Å for K+, and N = 6-8 and r = 2.95-3.15 Å for Cs+. It is worthwhile to point out that the present EXAFS investigation is performed on dilute aqueous solution. The previous investigations of the local structure around alkaline metal ions in aqueous solution were made at the concentration higher than ca. 1.0 mol dm⁻³, in which case the counter anion might affect the local structure.9 Consequently, it can be concluded that the N and r around Rb+ in aqueous solution is approximately six and 2.90(3) Å, respectively; the O atoms can be attributed to those of H₂O molecules. The effective ionic radius, r_eff, is estimated to be 1.66 Å. The value is in good agreement with that determined by Heyrovská.10

References
4) H. Maeda, to be published.
We investigated Fe-K X-ray absorption near edge spectra in order to identify iron-containing species giving rise to the magnetism in a nanocomposite (NC) composed of iron-oxide dispersion in a silver matrix. This NC has been shown to be superparamagnetic by previous magnetization measurements [1], which suggests the possibility of the occurrence of giant magnetoresistance and magnetic refrigeration. The NC sample pellets of 50 at.%Fe were synthesized by an inert gas condensation method in a batch. One of them was post-annealed in He gas at 250°C for 1 h, and another in 10%-O2 at 230°C for 15 h. Average grain sizes both of iron-oxide and silver grains determined by TEM were 10-30 nm before and even after the heat treatments. Specimens for XANES were prepared by mounting on a tape the powder obtained from grinding the pellet. To obtain reference data, measurements were made on pure iron-oxides as well. The room temperature measurements were performed in the transmission mode on the beam line of 7C with a scanning step of 0.4 eV. Harmonics were removed by detuning the monochromator. The focusing mirror was not used. The background-subtracted absorption coefficient, µ, has been normalized to the absorption step at the edge. The energy of all of the spectra were carefully calibrated by using an Fe foil reference and are accurate to 0.1 eV.

Figure 1 shows the Fe-K near edge spectra along with those of the reference materials, in which the derivative spectra dµ/dE are plotted to emphasize the energy shifts and feature changes in the near edge region. It should be pointed out that (1) the spectra of both the annealed samples are quite similar to that of α-Fe2O3, (2) the spectrum of the as-compacted sample shows significant differences from γ-Fe2O3. They indicate that some iron-containing phases coexist in the as-compacted sample. We modeled the as-compacted spectrum by a linear combination of the reference spectra. Very good agreement between the spectrum was obtained with contents of 5%Fe, 53%Fe3O4, 42%γ-Fe2O3, as shown in Fig.2. The present agreement is far better than that obtained from the previous measurements in the fluorescence mode [2]. This improvement in modeling of the as-compacted spectrum would be due to that the transmission mode measurement less involves surface effects than the fluorescence mode and is more reliable.

References
STUDY OF LOCAL LATTICE STRUCTURE OF NiMn ALLOY BY EXAFS

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Introduction

It has been proved that the magnetic properties of NiMn alloy change as annealing conditions, that is magnetization increases with annealing time. It seems that the magnetism is related to the atomic arrangement of Ni and Mn or short range order.

In this report, we studied local lattice changes structure of NiMn alloys for various annealing times by using EXAFS, which has an advantage that the structure around individual atoms of Ni and Mn can be investigated.

Experimental

All the K-edge absorption spectra were recorded in transmission mode at BL6B and BL7C. Si(111) double crystal monochromators were used. The storage ring was operated at 2.5 GeV and the ring current was 200~300 mA.

All samples were ground to fine powder. Ni(75, 77, 80 at%)-Mn alloy were annealed at 400°C for 200 hours and 1000 hours. The sample powders were interposed between adhesive tapes.

The method of data analysis has been described in ref. 2 in detail.

Result and Discussion

Fourier transforms of Ni K-edge for Ni(75 at%)-Mn alloys are shown in Fig.1 for various annealing times (as reserved, 200 hours, 1000 hours). Fourier transform of Ni powder is also shown in the figure for comparison. Ni has an f.c.c. structure. NiMn alloys which studied in this report has similar f.c.c. structure and the lattice constant is ca. 3.5Å. First peak at ca. 2.5Å is assigned to first nearest neighbor. The peaks at 4.2Å and 5.0Å are correspond to third and fourth nearest neighbors, respectively. The atomic distance is for NiMn alloys are longer than that of Ni powder. The height of peaks increases and the peaks becomes clearly with annealing time. This result indicates that the statistical disorder of atomic distances becomes smaller with annealing.

From the viewpoint of magnetism, it is reported that the magnetic property of Mn-Mn becomes antiferromagnetic when the distance of Mn-Mn is 2.2~3.0Å and that becomes ferromagnetic when the distance is 3.0~3.9Å. In Ni(75%)-Mn alloy regularly arranged Ni and Mn atoms are located at the face center and the corner of f.c.c. lattice, respectively. In this case, the distance of Mn-Mn is ca. 3.5Å. The present EXAFS result is consistent with that the regularity of arrangement of Ni and Mn atoms raises with annealing time.

Fig.1 Fourier Transforms of Ni K-edge EXAFS of Ni powder and Ni(75%)-Mn (As Reserved, 200hours, 1000hours)

Curve-Fitting results for the distance between the nearest neighbor atoms are shown in Table. 1. According to this result, we can easily estimate that the lattice constant (f.c.c. structure) is about 3.54Å. The nearest neighbor distance for 80% alloy is shorter than that for 75% alloy.

The analysys of Mn K-edge EXAFS must provide interesting information. That is now in progress.

Table 1. Result of Curve-Fitting

<table>
<thead>
<tr>
<th>r/Å</th>
<th>75%</th>
<th>77%</th>
<th>80%</th>
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<tr>
<td>As Reserved</td>
<td>2.51</td>
<td>2.51</td>
<td>2.50</td>
</tr>
<tr>
<td>200hours Anealed</td>
<td>2.49</td>
<td>2.49</td>
<td>2.49</td>
</tr>
<tr>
<td>1000hours Anealed</td>
<td>2.51</td>
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References

Total-Conversion-Electron Yield EXAFS Applied to Deposited Thin Films.

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Introduction
EXAFS spectra for deposited thin films on single-crystal substrates were obtained by using a new apparatus which works under an atmospheric gas. It gives the spectra of not only thin films but scattered powder on a tape very easily.

Experimental
The apparatus is shown in Fig.1. The incident angle and the vertical and horizontal positions to X-ray beam is able to be set up arbitrarily. The cell is constructed from plastics and conductive carbon tape and is filled with He gas. The measured current, I, consists of Auger electrons, photoelectrons and secondary electrons produced by high energy Auger or photoelectrons in the surface layer of the film. Moreover the cell acts as a gas ionization chamber since the electron emitted from the film creates a bunch of He⁺ ion-electron pairs, which operates until it loses its energy. By reversing the polarity of the bias at the electrode, He⁺ ion current is obtained which had been considered to be more surface sensitive in comparison with the electron-yield mode. The measurements were performed at the BL-7C. The beam intensity, I₀, was monitored with a gas ionization chamber (17cm, 100% N₂).

Results and Discussion
Using the apparatus, the sample can be easily exchanged because the inside of the apparatus need not be evacuated and the sample has only to be put on a conductive carbon tape. There were no obstacles to obtain the EXAFS spectra for insulating materials, if a wide carbon tape was used for the sample holding electrode. Fig.2 shows the EXAFS spectra for SrTiO₃ powder by the transmission method and the powder on a tape by the He⁺-yield method. There is little difference between them. This indicates that EXAFS spectra can be easily obtained without the adjustment of sample concentration or thickness. With the highest possible bias voltage, 1kV, the best spectra with least noise were obtained. The smaller the incident angle was, the higher the S/N and S/B ratios were obtained. The peaks due to the diffraction were observed for the epitaxially grown films on a single-crystal substrate as shown in Fig.3. The peaks moved with the incident angle.
XAFS STUDIES ON THE LOCAL STRUCTURE OF THE EMITTING SITES ON TITANIUM SILICALITE (TS-1, TS-2) CATALYSTS

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Although the unique catalytic properties of titanium silicalite has already been reported by many researchers, the characterization of their active sites has not yet been carried out sufficiently. This is an unprecedented report on the observation of the photoluminescence (PL) of titanium silicalite (TS-1, TS-2) and the characterization of the PL active sites by the XAFS measurements.

TS-1 (24-TS-1; Si/Ti = 24, 12-TS-1; Si/Ti = 12) and TS-2 (85-TS-2; Si/Ti = 85) were hydrothermally synthesized. MFI and MEL structures of these samples were identified by XRD measurements. An IR band at ca. 960 cm⁻¹ was observed with all samples indicating the insertion of Ti atom into the zeolite framework.

After the 85-TS-2 was calcined at 723 K and degassing at 523 K, it exhibited a PL band at ca. 480 nm by the excitation at ca. 280 nm. This PL band is attributed to the radiative decay process from the charge transfer excited state of the highly dispersed Ti-oxide species with a tetrahedral coordination. As shown in Fig. 1, both 24-TS-1 and 12-TS-1 showed a weak PL band at ca. 450 nm different from the wavelength of PL band observed with 85-TS-2. The TS zeolite with the higher Si/Ti ratio exhibited the stronger PL band; 85-TS-2 > 24-TS-1 > 12-TS-1. These PL band can be effectively quenched by the addition of O₂, NO and H₂O, respectively, indicating that PL active species locate at positions accessible to small reactant molecules. As shown in Fig. 2, in the XANES spectra, a strong pre-edge peak was observed with all of the TS zeolites indicating the presence of Ti-oxide species with 4- or 5-coordination. In the FT-EXAFS spectra, a small peak due to neighboring Ti atoms (Ti-O-Ti) was observed as well as a peak due to neighboring O atoms (Ti-O). The intensity of Ti-O-Ti peak became larger for TS zeolite with the smaller Si/Ti value, indicating the partial aggregation of Ti-oxide species. These results conclusively indicate that most of Ti-oxide species in the TS zeolite are PL active isolated Ti-oxide with a tetrahedral coordination, however, in the TS zeolite with a low Si/Ti ratio the aggregated Ti-oxide species coexist.

**XANES Study of Eu Species Encapsulated in Potassium Y-Type Zeolite**

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**Introduction**

Recently Baba et al. found that fixation of europium amide complex onto potassium-exchanged Y-type zeolite (K-YZ) generates the strong basic sites [1]. The same phenomenon was already observed for Yb-amide complex encapsulated in K-YZ [1,2]. Its catalytic performance is very similar to Yb/K-Y-zeolite although the electronic configurations of Yb and Eu are different from each other. We report here the active species in Eu amide complex in K-YZ.

**Experimental**

Sample was prepared by immersing K-YZ in liquid ammonia dissolving Eu at 196 K as described elsewhere [1]. The samples were first evacuated at room temperature to remove ammonia and heated in vacuo at various temperatures.

X-ray absorption (XA) experiments were carried out on beam line 7c at Photon Factory in National Laboratory for High Energy Physics (proposal no. 93-175). XA spectra were collected in a fluorescence mode with a two-crystal Si(111) monochromator with a stored current of 300 - 250 mA and a ring energy of 2.5 GeV. In situ cell was used because the samples are moisture- and oxygen-sensitive. The normalization of XANES was carried out as described elsewhere [3].

**Results and Discussion**

Eu L₃ XANES spectra of the samples evacuated at 303 - 973 K exhibit two absorption maxima at 6972 and 6979 eV, so called white lines. The ratio of the peak heights changes for each spectrum, indicating that at least two kinds of chemical species are present as a mixture on the Eu/K-Y. From the peak positions, these peaks are assignable to 2p₃/₂-5d transition in Eu⁷⁺ and Eu⁶⁺, respectively [6]. This indicates that valence of Eu ions varies during evacuation. However, successive desorption of hydrogen, chemisorbed ammonia, and nitrogen was observed with elevating temperature (TPD) in vacuo [1], showing that not only the valence variation of Eu but also the change of chemical species of Eu surface complex take place. In any event, it requires to estimate the fraction of Eu²⁺ and Eu³⁺, quantitatively.

We carried out deconvolution of XANES with two sets of curves of a Lorentzian for white lines and an arctangent for continuum absorption [2]. Table 1 shows that thus obtained ratios of integrated areas of Eu²⁺ and Eu³⁺ white lines in percentage. The sum of the absolute values of those areas for Eu²⁺ and Eu³⁺ for the samples of each temperatures were found to be constant within two significant figures. This indicates that the ratios reported in Table 1 are the same values as those for the composition of Eu²⁺ and Eu³⁺. The desorption of NH₃ was found in the TPD profile in the temperature range of 400 - 470 K. In this temperature range, the decomposition of Eu²⁺(NH₂)₂ into Eu⁴⁺NH and NH₃ has been reported [5]. In addition, we observed that imide formation by Infrared spectroscopy (IRS) after evacuation at 423 K. These strongly suggest that the Eu²⁺(NH₂)₂ decomposition takes place also in the present case in the temperature range of 400 - 470 K, where the maximum of Eu²⁺ fraction is found in table 1. On the other hand, in the temperature range of 300 - 420 K, where reduction of Eu⁷⁺ is suggested by XANES, the simultaneous desorption of H₂ and N₂ was observed in TPD experiment. Since the dissolution of Eu in liquid ammonia causes the formation of Eu²⁺(NH₂)₂ and Eu³⁺(NH₂)₃ mixture [5] and there has been no report that Eu³⁺(NH₂)₃ directly decomposes to EuNH, reduction of Eu³⁺ should be owing to the following process: Eu³⁺(NH₂)₃ → Eu²⁺(NH₂)₂ + H₂ + (1/2)N₂. In the temperature range of 423-673 K, oxidation of Eu²⁺ proceeds and H₂ desorption is found. The evaporation of Eu³⁺ is supported by the report of Usuki et al. [6]. The evaporation at the temperature above 673 K increases the Eu²⁺ fraction again and there is no evidence of the formation of Eu⁴⁺. TPD experiments clarified N₂ desorption and hydrogenation activity of the sample reaches maximum at 973 K. These results strongly suggest that another nitride phase with Eu⁴⁺ has been formed by heating the sample at the temperature above 673 K.

**References**

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XAFS STUDY OF FERROCENE - RELATED DERIVATIVES

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**Polymer Research Laboratory, Toyobo Research Institute, Kaata, Ohtsu, Shiga 520-02
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Introduction

Compounds sandwiching transition metals such as a ferrocene and its ring-substituted derivatives are now developing owing to their peculiar behavior in an electron reservoir and/or high redox potential, and catalytic activity. The application as a novel material may cover the wide scientific and engineering regions. In cyclopentadieny1-Fe-phenyl-X (CpFePh-X) complexes, it is recently found that the redox activity is strongly affected by substituents, X. For the investigation of the change of the redox activity in the viewpoint of the electronic state, several experimental and theoretical studies have been achieved. The aim of this work is to give the bond distances between Fe-C (Cp) and Fe-C(Ph) with the various substituents as fundamental quantities for the theoretical calculation of the electronic states.

Experimental

X-ray absorption spectra around Fe K-edge were observed in the transmission mode at BL-7C beamline in Photon Factory (KEK, Tsukuba) at room temperature. The storage ring was operated at ring current of 350 - 25 mA and positron energy of 2.5 GeV. The radiation was monochromatized with Si(111) double crystals. Higher harmonics were reduced by means of a reflection on two Si mirrors.

The specimens were prepared in following procedure. A ferrocene solution added with AI powder and powdered AICI3 is stirred in benzene solvent. After refluenting for 6 hours, the mixture was cooled, and the yellow aqueous layer was separated, washed out with light petroleum, and treated by an aqueous solution of PF6NH4. The resulting precipitate, benzene-cyclopentadieny1-iron(II) is filtered off. The other iron complexes are produced in the same manner by adding some anion.

For the analysis of the observed absorption spectra in order to obtain the local structure around Fe ions, the programs "XAFS93" and "MBF93" were employed. A ferrocene is used as a standard substance.

Results and Discussion

In Fig.1, the analyzed distance deviations from Fe ions to C of the nearest neighbor rings are shown. Here, deviations are expressed in values relative to the distances of Fe-C's of CpFePh-H, and 1 shell indicates the deviations from Fe to C of Cp and 2 shell those from Fe to C of Ph.

In the case of halogen substituents, the bond distances of Fe-C(Ph) become shorter and those of Fe-C(Cp) longer slightly. The larger ionic radii show the larger deviation. CN substituent shows elongation in both the first shell and the second shell. The deviations are considerably large for Br substituent in the second shell. This large shrinkage of the Fe-C(Ph) suggests that the electronic states are remarkably modified, especially in the excited states (or chemical reaction intermediate states), resulting in the change of the redox activity. The electronic states of CpFePh-X are in calculation, based on the observed distances.

Fig. 1. The deviation of the bond distances from Fe ion to C ion in the various substituents. The values are relative to the distance of Fe-C of CpFePh-H.

References

STUDY OF STRUCTURAL ANISOTROPY IN AMORPHOUS TbFe MULTILAYERED FILMS VIA EXAFS

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Introduction

We have investigated the magnetic and magneto-optical(MO) properties of Rare Earth-Transition Metal multilayers (RE-TM MLs) for several years. In result the magnetic anisotropy of RE-TM MLs was found to depend on the bilayer period showing a peak at bilayer period of 1nm[1]. The origin of the magnetic anisotropy of RE-TM amorphous alloy was debated and several models were proposed.

Recent study using Synchrotron Radiation indicated that local structure in amorphous RE-TM alloy is correlated with the magnetic anisotropy[2]. In this paper the EXAFS study of amorphous Tb/Fe multilayers is presented and the mechanism of magnetic anisotropy is discussed.

Experiment

Samples were prepared by rf magnetron sputtering method. Magnetic properties were measured by VSM and Torque magnet meter. In photon Factory, X-ray absorption measurement at the Fe K-edge of Tb/Fe MLs was carried out utilizing the XAFS station at the BL-7C. All XAFS measurements were made at room temperature by transmission mode. Structural anisotropy is obtained by measuring the angle dependence of EXAFS.

Result and conclusion

Figure 1 show the Fourier transformed Fe EXAFS signal of Tb/Fe MLs whose bilayer period is 1.5nm. In this figure 'E in-plane' indicate the information of in-plane structure and 'E out of plane' show the information of the structure perpendicular to the film plane. The peak at 2Å shows Fe-Fe correlation. In this figure Fe-Fe correlations of 'E in-plane' is larger than that of 'E out of plane'. We suggest that the change of magnetic anisotropy with various bilayer period is correlated to the change in the ratio of Fe-Fe coordination number.

Table 1 show the coordination number ratio and magnetic anisotropy energy of Tb Fe MLs and TbFe alloy[2]. The magnetic anisotropy energy are varied with the change of coordination ratio. We can consider that the change of magnetic anisotropy depending on bilayer period is affected by coordination ratio of Fe atom.

Table 1 Magnetic anisotropy and coordination number ratio

<table>
<thead>
<tr>
<th>bilayer period</th>
<th>((C_\perp - C_\parallel)/C_\parallel)</th>
<th>(K_u(\times 10^3 J/m^3))</th>
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<tr>
<td>alloy</td>
<td>0.071</td>
<td>1.58</td>
</tr>
<tr>
<td>1.5nm</td>
<td>0.101</td>
<td>4.2</td>
</tr>
<tr>
<td>3.0nm</td>
<td>0.062</td>
<td>2.74</td>
</tr>
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</table>

\(C_\parallel\) : coordination number of Fe for 'E in-plane'
\(C_\perp\) : coordination number of Fe for 'E out of plane'

References

STRUCTURAL CHANGES IN THE PROCESS OF Cu-PHOTODOPING IN AMORPHOUS GeSe₂

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Introduction
When an amorphous (a-) chalcogenide thin film is deposited onto a clean surface of Cu or Ag metal and irradiated by visible light, metal atoms rapidly diffuse into the amorphous film. This photodoping phenomenon has been well known since the discovery in 1966 [1], and is very interesting because it takes place only in amorphous chalcogenides, not in crystal ones. The atomic structure of fully photodoped a-GeSe₂ by the Ag atoms was investigated by the EXAFS and the anomalous x-ray scattering measurements [2]. On the contrary, there is little study on the structural changes in the process of the photodoping. In this paper, we report the structural change of Cu photodoped a-GeSe₂ investigated by the Ge, Se and Cu K-edges EXAFS measurements.

Experimental
We have measured the EXAFS spectra in the total electron yield (TEY) mode at the beam line BL-7C of Photon Factory in the National Laboratory for High Energy Physics. The sample film of a-GeSe₂ of 7000 Å in thickness was evaporated onto a clean Cu substrate of about 500 Å in thickness in the dark condition. We investigated the photodoping process by the repeated cycle of measuring TEY-EXAFS spectra in a vacuum chamber and irradiating the sample by visible light emitted from a 1000-W tungsten lamp through a viewing window of the chamber. Taking the surface sensitivity of the TEY method into account, the EXAFS signals come only from the upper amorphous layer of about 1000 Å, not from the metal underneath.

Results and Discussion
Figure 1 shows the Cu and Se K-edges EXAFS functions at the irradiation time of 0 and 240 min. Despite the TEY signal was very weak (~10⁻¹¹ A), distinct oscillations were observed. The magnitude of the edge jump of the Cu K-edge spectrum at 0 min is already about 50% of that at 240 min. This would originate from the photodoping by weak light emitted from the filament during the evaporation of a-GeSe₂ or the thermal diffusion of Cu into a-GeSe₂. Each spectrum for the irradiated sample seems to be very similar to that for the corresponding initial one. However, from the preliminary analysis of these spectra, some structural changes, for example the slight elongation of the bond-length only around the Se atoms, were clarified. The detailed analysis using theoretical backward scattering amplitude and phase-shift functions calculated by the FEFF software [3] is now in progress.

This study was partly supported by The Japan Securities Scholarship Foundation and Nissan Science Foundation.

References
STRUCTURAL STUDY OF LOW Z ELEMENTS BY X-RAY RAMAN SPECTROSCOPY

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Introduction

X-ray Raman spectroscopy (XRRS) has been proposed as a complementary tool to soft x-ray spectroscopy. It employs an inelastic scattering of hard x-rays to obtain spectra in soft x-ray region, thus eliminating various experimental difficulties associated with the use of soft x-rays. The greatest disadvantage of XRRS is its very small scattering cross section. Therefore excitation source must be as strong as possible and the spectrometer used has to be extremely efficient. In this study a spectrometer using cylindrically bent graphite crystal was tested to obtain XRRS of several compounds.

Experimental

Measurements were carried out at BL7C. The energy of the incident beam was tuned to about 5 keV. Beam size was around 0.8 × 5 mm². The scattered radiation was collected and analyzed by a cylindrically bent, 5 cm × 5 cm super graphite (SG) crystal with a 200 mm radius of curvature. (004) reflection was employed. Dispersed X-rays were detected with a position sensitive proportional counter of 10 cm in length. Similar experimental setup has already been reported by Ice and Sparks. Since a significant variation in efficiency along the detector position has been observed, the response function of the analyzer-detector combination was determined each time by scanning the beamline monochromator energy while monitoring the intensity of the elastic peak. Spectra were then corrected with the measured response function.

Results and Discussion

Fig. 1a shows an XRRS of diamond obtained at scattering angle of 90°. Measurement time was 10 hrs. Although not shown here, FWHM of the elastic peak shows that the resolution of this spectrometer is 6 eV, which is almost identical with that achieved with Ge(333) crystal spectrometer at around 8 keV. In Fig.1b shown is an extracted EXAFS oscillation by applying a routine used for EXAFS analysis. A comparison with the result reported previously and the soft x-ray absorption spectrum reveals the following. Firstly, the fine structure of XRRS reported here is the same as that of soft x-ray absorption spectrum. Secondly, nearly 10 times increase in efficiency was achieved with the use of bent SG monochromator crystal compared with the Ge(333) crystal spectrometer employed previously.

In addition to XRRS of carbon in diamond and graphite, XRRS of fluorine in LiF and those of boron and nitrogen in BN was also obtained, suggesting that XRRS can be applied to various other elements.

Attempts to increase the resolution by the use of (006) reflection and to extend the target materials by the use of lower wavelength excitation are now in progress.

![Fig. 1.](image)

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References

THE STRUCTURE OF Fe CLUSTERS IN MELT-QUENCHED La-Fe ALLOYS BY FLUORESCENCE XAFS

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Introduction

Melt-quenched La-Fe(8-12 at% Fe) alloys exhibit interesting structural and magnetic properties. Results of structural and magnetic measurements of the melt-quenched La-Fe alloys can be well explained by the formation of Fe clusters embedded in fcc β-La. Below about 300K, their ferromagnetism is induced by inter cluster coupling. Between 300K and 400K, ferromagnetic inter cluster couplings disappear and super paramagnetic state arises due to intra cluster ferromagnetic coupling. The ferromagnetic couplings in cluster fade out above 400K and it turns to paramagnetic state. X-ray diffraction for the as-quenched La-Fe shows fcc La(β-La) diffraction peaks with no α-Fe peaks. Lattice constants of β-La for the as-quenched La-Fe alloys do not show any concentration dependence of Fe. In order to elucidate the structural properties of the Fe clusters embedded in β-La, we have carried XAFS measurements of the Fe K-edge for the melt-quenched La-8 and -12 %Fe alloys.

XAFS experiments and Results

Because of large X-ray absorption of La, transmission method is not available in the present case: \( \mu = 7.7 \) for the as-quenched La-8%Fe (about 25 μm in thickness). We adopted fluorescence method as an alternative method. Fluorescence intensity \( I(E) \) for a thick sample can be represented as

\[
I(E) = \frac{\mu(E)}{\mu(E) + \mu(E) + \mu(E)}
\]

where \( \mu(E) \) is absorption coefficient for a dilute target element. \( I(E) \) is proportional to \( \mu(E) \) only if \( \mu(E) \) can be considered as independent on photon energy. For La-8%Fe, energy dependent portion of the denominator in eq.(1) consists of only about 0.4%, which allows to apply fluorescence method for the present La-Fe alloys.

Fluorescence XAFS measurements were done at BL 7C using a Si(111) monochromator with a total reflection mirror at R.T.. An ion chamber was used as a detector combined with the Lytle collimating slit. Mn(3 μm) was used as the Z-1 filter.

After usual background subtraction and normalization procedures, \( \chi(k) \) is deduced and the results are shown in Fig.1 in terms of \( k^2 \chi(k) \) vs k for the as-quenched La-8% and -12% Fe, and La-12%Fe annealed at 673K for 30 min together with that of α-Fe. The Fourier transforms for these curves are shown in Fig.2.

The characteristic features of these XAFS results can be summarized as follows.

1. The results for annealed La-12%Fe agrees with that of α-Fe. This indicates that Fe clusters embedded in β-La precipitate as α-Fe above 673K.
2. The local structure of Fe for the as-quenched La-8% and -12%Fe show highly disordered states with a broad and low amplitude of \( \chi(k) \) as shown in Fig.1. This means that amorphous Fe clusters are formed in crystalline fcc La. The Fourier transforms for these curves are shown in Fig.2.

Quantitative analysis such as curve fitting is now underway.

References

XAFS STUDIES ON THE BEHAVIOR OF METAL ATOMS DURING PYROLYSIS OF THE ION-EXCHANGED BROWN COAL

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Introduction
The particle size of the catalyst has a strong effect on the activity and the selectivity of the coal pyrolysis process. Smaller particles are desirable because they have a larger percentage of unsaturated surface sites that are readily accessible for catalysis. The ion exchanging method is one of the simple method for dispersing metal ions atomically on the coal surface.

In this study, the behavior of metal atoms of ion exchanged coal during its pyrolysis process were studied by EXAFS spectroscopy under in-situ conditions.

Experimental
Loy Yang coal from Australia was used in this study. The metal-loaded samples were prepared by an ion exchange method using nickel chloride in aqueous solution. The Ni loadings were 1.4 and 6.4 wt%.

Samples were pyrolyzed in vacuum. After a sample was heated to a desired temperature at the rate of 5 K/min, then the sample was cooled to room temperature.

Ni K-edge EXAFS measurements were carried out by a transmission mode at BL-7C of Photon Factory. The data were analyzed by a curve fitting method using program "EXAFSH". Ni metal and NiO were chosen as standard materials for Ni-Ni bond and Ni-O bond, respectively.

Results and Discussion
Fig. 1 shows the Fourier transforms of Ni K-edge EXAFS data for the pyrolyzed Ni-coal (Ni loading: 1.4 wt%). There is only one peak between 1 and 2 Å assigned to Ni-O in the Fourier transforms of EXAFS spectra of the Ni-loaded coal pyrolyzed at 623 K. There is no bond between 1.8 and 2.5 Å which is assigned to Ni-Ni bond. It shows that nickel ions are supported to oxygen anions of functional groups on the coal surface. Ni-Ni bond began to appear in the Fourier transforms of EXAFS spectra of Ni-loaded coal pyrolyzed at 773 K. It means that functional groups coupled with nickel are decomposed and small nickel metal clusters are formed at 773 K. In the Fourier transforms of the spectra of the Ni-loaded coal at 6.4 wt%, on the other hand, Ni-Ni bond was observed for specimen pyrolyzed at 673 K (Fig. 2). It means that small Ni particles were formed at 673 K. Moreover, the coordination number of Ni-Ni bond of 6.4 wt% coal pyrolyzed at 673 K is larger than that of 1.4 wt% coal pyrolyzed at 773 K.

These results indicate that the thermal stability of nickel exchanged surface functional groups and the aggregation of Ni atoms depends on the Ni loadings on the coal.

Fig. 1. Fourier transforms of k^2-weighted EXAFS data for pyrolyzed Ni-coal (Ni loading: 1.4 wt%).

Fig. 2. Fourier transforms of k^2-weighted EXAFS for pyrolyzed Ni-coal (Ni loading: 6.4 wt%).

References
1) Program "EXAFSH" coded by T.Yokoyama and T.Ohta, The University of Tokyo (1993).
XAFS STUDY ON LOCAL STRUCTURE OF IRON(III)-SACCHARIDE COMPLEXES
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Introduction
Saccharides play important roles in various forms of living systems as parts of diverse biological molecules. Saccharide molecules possess several hydroxyl groups that may bind with transition metal ions to form various metal-saccharide complexes in their nature and utility.

One of the authors (C.P.R.) has synthesized various iron(III) complexes of mono-, di-, tri-saccharides and alcohols. We have determined their local structures from XAFS measurements.

Experimental
X-ray absorption spectra around the Fe K-edge were measured in transmission mode for the iron(III)-saccharide complexes in solution and in the solid state at BL7C station of the Photon Factory at the National Laboratory for High Energy Physics (KEK).

Results and Discussion
The Fe K-XANES spectra of a reference Fe(NO₃)₃ solution and of the iron(III)-saccharide complexes showed the shape and intensity of which are typical for an octahedral coordination of iron(III). However, the spectra for the saccharide complexes exhibit considerably broad peaks just above the absorption edge, compared with that for the Fe(NO₃)₃ solution which contain an octahedral [Fe(OH₂)₆]³⁺ moiety. It may be an indication of distorted octahedral Fe-O bonds resulting in a splitting of degenerate energy levels of iron(III) atom in the saccharide complexes.

Figure 1 shows the Fourier transforms (uncorrected for the phase shift). The first peak at 1.6 Å is due to Fe-O bonds within the Fe(III)-saccharide complexes.

Table 1 shows the results of the curve-fitting analysis for Fourier filtered EXAFS modulation of the iron(III)-saccharide complexes in aqueous solution and in the solid state. From these results we proposed the structures of the iron(III)-saccharide complexes in Figure 2.

![Fig. 1. Fourier transforms.](image)

![Fig. 2. Proposed structures of the iron(III)-saccharide complexes.](image)
EXAFS STUDIES OF FERRITIN PARTICLES

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Introduction

Iron, an essential nutrient for many cellular processes is stored in the form of two proteins, ferritin and hemosiderin. Both proteins contain small iron oxide cores, usually less than 10 nm in diameter. The core of ferritin is completely surrounded by a well-characterized soluble protein shell, while hemosiderin is insoluble and the associated protein is irregular and poorly characterized. The genetic diseases thalassemia and hemochromatosis result in the accumulation of iron oxide particles.

In order to understand the structure of such particles we have investigated ferritin. Iron K-edge x-ray absorption spectra were recorded for a sample of freeze dried horse spleen ferritin over a range of temperatures from 40 K to 300 K. Gaussian-type radial distribution functions were fitted to the data from all temperatures simultaneously and the obtained mean-square relative displacements $\sigma^2$ were fitted using an Einstein model. For iron atoms in the second and/or third coordination shell an Einstein temperature of $330 \pm 20$ K was obtained. If oxygen was assumed in the second or third shell, its Einstein temperature was $460 \pm 20$ K. This indicates that the core of ferritin may have a more rigid structure than those of previously studied ferritin analogs (nanocomposite polysaccharide iron complexes).

Results and discussion

The ferritin radial distribution function with respect to iron consists of a first oxygen peak, which is not considered in this analysis, and two further peaks whose nature is not known exactly. The second and third coordination shells around the absorbing iron atom may consist of (a) oxygen and iron, (b) iron and iron or (c) iron and oxygen. Using the harmonic approximation we have analyzed the EXAFS data in R-space by curve fitting with a routine developed by one of the authors [1]. We have employed the amplitudes and phase shifts calculated with the single-scattering version of the FEFF code (version 3.1.1) [2]. Five datasets, each corresponding to a different temperature, were fitted simultaneously and the coordination numbers were constrained to be the same for all datasets. For all of the above three cases good fits with reasonable fit results were obtained. The quality of the fits decreased only slightly in the order (a) to (c). At present we cannot yet determine which of the three cases is the correct one but we can already determine the Einstein temperatures. The mean-square relative displacement $\sigma^2$ of a coordination shell was measured as a function of temperature and can be fitted with an Einstein model. In this analysis we employ differences of Debye-Waller factors:

$$\sigma^2(T) - \sigma^2(T_0) = \frac{h^2}{8\pi^2\mu k_B\Theta_E} \left[ \coth\left(\frac{\Theta_E}{2T}\right) - \coth\left(\frac{\Theta_E}{2T_0}\right) \right]$$

Here, $T$ is the temperature, $\Theta_E$ the Einstein temperature and $T_0$ is a reference temperature. $T_0$ was chosen as the lowest temperature for which EXAFS spectra were measured (40 K). $\mu$ is the reduced mass of the absorber-backscatterer pair. Irrespective of the choice (a), (b) or (c) we obtain for iron backscattering atoms an Einstein temperature of $\Theta_E = 330 \pm 20$ K and for oxygen backscattering atoms an Einstein temperature of $\Theta_E = 460 \pm 20$ K. This shows that the phonon spectrum describing the oscillations of the second- and third-shell atoms is dominated by a peak. Mohie-Eldin et al. [3] have measured a Debye temperature of $248 K \pm 12 K$ for a ferritin analog, polysaccharide iron complex using the Mössbauer effect. This implies that the iron(III) oxyhydroxide core of their analog may be less rigid than that of horse spleen ferritin.

We are grateful for the assistance of Prof. Nomura.

References

STRUCTURE OF Cr-DOPED MULLITE CERAMICS

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Introduction

Mullite is a ceramic that has high strength at high temperature. It is therefore of great interest in industrial applications. The general composition of mullite is $\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ $(0.2 \leq x \leq 0.4)$ [1]. Mullite can be doped with Cr, leading to an incorporation of up to 12 wt% $\text{Cr}_2\text{O}_3$. It has been concluded that Cr is incorporated by replacing Al [2].

Results and discussion

We have measured EXAFS spectra of the Cr K edge of Cr-doped mullite at BL-7C. For all measured spectra the magnitude of the Fourier transform, which is related to the pair distribution function (PDF), is characterized by two pronounced peaks (Fig. 1). The first peak is ascribed to the nearest-neighbour oxygen atoms making up the octahedra surrounding the central Cr atoms and the second peak is assumed to be due to aluminum. In order to get a more quantitative view, the EXAFS spectra were least-squares fitted [3] to a model function, which was based on standard Gaussian lineshapes for the PDFs of oxygen and aluminum. It turned out that the aluminum peak could not be fitted satisfactorily with a single Gaussian PDF alone. The discrepancy was reduced by assuming an additional Gaussian contribution to the PDF of aluminum. In order to reduce the number of variable parameters per dataset three datasets were fitted simultaneously: an 11.5 wt% $\text{Cr}_2\text{O}_3$ mullite sample measured at 300K and 150K and a 7.3 wt% $\text{Cr}_2\text{O}_3$ sample measured at 300K. For these datasets it was assumed that the energy corrections $\Delta E$ were identical for each atom type and that the coordination numbers were temperature independent. Figure 1 shows a typical fit, carried out in this way, for the 11.5 wt% sample. In Fig. 2 the PDF obtained from the fit is shown. It consists of 6 oxygen atoms at 1.98 Å with $\sigma^2 = 0.004$ Å$^2$ and of aluminum peaks at 2.91 Å (1.8 Al atoms) and 3.30 Å (5.4 Al atoms). The smaller Al peak is broader ($\sigma^2 = 0.007$ Å$^2$) than the bigger peak, for which $\sigma^2 = 0.004$ Å$^2$. From these results we are trying to determine the crystallographic sites of the Cr atoms in the mullite structure.

Fig. 1: Fourier transform magnitude for a mullite sample measured at 300K. Shown is the result of a simultaneous fit to three datasets with three coordination shells each. The shoulder at ~1 Å could not be fitted.

Fig. 2: Pair distribution function of Fig. 1.

References

X-RAY DIFFRACTION STUDY OF OXYGEN MONOLAYERS ON XENON PLATED GRAPHITE

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Introduction

An oxygen molecule ($O_2$) has spin $S=1$ and monolayer crystals form a two-dimensional (2D) antiferromagnet. Various phases have been observed depending on coverage ($C$) and temperature ($T$). We have used hexagonal boron nitride (hBN) as a substrate so far and in dilute $\delta$-phase we observed an antiferromagnetic phase which has not been observed when graphite is used. We find that the substrate plays an important role on the magnetic and crystal structures of monolayers: especially the electronic structure of the substrate possibly affect the exchange interaction between $O_2$ molecules. In order to elucidate such an effect of the substrate, we have used xenon (Xe) monolayers, which is an insulator. Monolayer Xe has a $\sqrt{3} \times \sqrt{3}$ commensurate structure on graphite, on this we could grow $O_2$ monolayers. The surface potential is weaker than that of graphite or hBN substrate and we could expect more essential character of $O_2$ monolayers in this system.

Experimental

X-ray diffraction measurements were performed at BL-7C. Monochromatized incident beam ($\lambda=1.000\AA$) was diffracted by samples mounted in a cryostat and an imaging plate (IP) was used for detection. Because the diffraction intensity from $O_2$ monolayers is small, the optical system was carefully constructed to reduce the scattering from the beryllium (Be) sample cell, the Be shroud of a cryostat, and also from air. We spent typically one hour for one spectra with a wide q range ($0 - 4\AA^{-1}$) and better resolution compared with conventional scintillation counter system.

Results and discussion

When Xe monolayer was physisorbed on grafoil, we observed three peaks at $q=1.68,2.89,$ and $3.37\AA^{-1}$, assigned as (10), (11), and (20) of triangular lattice respectively. The lattice parameter is $a=4.32\AA$, which gives slightly more dilute structure than $\sqrt{3} \times \sqrt{3}$ one. When $O_2$ was adsorbed at $C=0.6$, these peaks shifted to higher $q$ value and Xe and small amount of $O_2$ form $\sqrt{3} \times \sqrt{3}$ lattice, which is stable even above the melting temperature ($T_m$) of $O_2$. As we increase $C$, we observed a peak at $q=2.25\AA^{-1}$, increasing the intensity with $C$ (Fig.1). Here the diffraction from grafoil and Xe layer was subtracted from the data. This peak is seen in all the temperature range below $T_m$.

Fig.2 shows $T$ dependence of spectra for $C=2.93$. A peak is observed at $q=2.25\AA^{-1}$ for low $T$ phase. In addition to this, at $30K$ a broad peak appears at $q=2.45\AA^{-1}$. When we increase $T$, the peak at $2.45\AA^{-1}$ disappears and a new peak appears at $q=2.08\AA^{-1}$.

The peak position is close to that of 3D $O_2$, however, simple 3D $O_2$ cannot explain the $T$ dependence of magnetization and also we observed melting transition below $50K$, lower than 3D case, so we conclude this peak is from $O_2$ films.

In the present experiments we have first obtained a spectra from monolayer crystals using IP technique.

![Fig.1](image1.png)

![Fig.2](image2.png)

Fig.1: C dependence of x-ray diffraction spectra at 8K.
Fig.2: T dependence of x-ray diffraction spectra for $C=2.93$.
SOLVATION STRUCTURE OF BR⁻ ION AT STEARYLTRIMETHYLLAMMONIUM BROMIDE AQUEOUS SOLUTION SURFACE STUDIED BY TOTAL-REFLECTION EXAFS

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Introduction
The X-ray absorption spectra of Br⁻ at aqueous solution surface were obtained by using a new method, total-reflection total-conversion-electron-yield XAFS. Because this technique is inherently surface sensitive, it may provide us with the information of the surface structure of solution.

Experimental
The measurements were performed at BL-7C. The design of the sample cell has been described. The spectra at Br K-edge were recorded under the condition of total external reflection at an incident angle of 1 mrad. The samples studied were aqueous solutions of stearyltrimethylammonium bromide (STAB), LiBr, and KBr. The spectra were obtained with the bias voltage of -150 V (He⁻ yield) at +1°C.

Results and Discussion
The signal intensity from STAB solution is larger than that of KBr while the concentration of Br⁻ in STAB solution is 1000 times as small as that in KBr. STA⁺ is a cationic surface active ion, and thus, this technique is proved to be highly surface sensitive. The EXAFS \( \chi \) spectra are compared in Fig. 1. The EXAFS oscillation in the spectrum of KBr solution is monotonous and can be fitted with a single shell model, while that of STAB solution is complex and needs to be fitted with a two shell model. The curve-fitting calculations were performed by using the phase shift and the back-scattering amplitude parameters generated by the FEFF. The coordination distance \( r \) value for the 1st shell of STAB solution corresponds to the Br-O (in water molecule) distance, and is found to be shorter than that for KBr solution of 3.23 Å. Thus the solvation structure of Br⁻ present at the STAB solution surface must be different from that in the bulk. The coordination number \( N \) value for the 1st shell of STAB solution is larger than that for KBr solution. Since the EXAFS amplitude is proportional to \( \cos^2 \theta \), where \( \theta \) is the angle between an X-ray polarization vector and the bond of X-ray absorbing atom to the photoelectron scattering atom, the horizontally polarized X-ray from the synchrotron strongly detects horizontally coordinating atoms but not vertically coordinating atoms with respect to the solution surface. Thus the larger \( N \) value for the STAB solution surface indicates that the probability of finding water at the same level as Br⁻ is fairly larger than in the bulk as is illustrated in Fig. 2.

Table 1. Curve-fitting results for Br⁻ aqueous solutions.

<table>
<thead>
<tr>
<th>solute</th>
<th>method</th>
<th>( \frac{c}{mM} )</th>
<th>( r/Å )</th>
<th>( N )</th>
<th>( \alpha/Å )</th>
<th>( \Delta E_\text{g} / eV )</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAB (1st shell)</td>
<td>HeY</td>
<td>0.1</td>
<td>3.12</td>
<td>9.6</td>
<td>0.283</td>
<td>-10.4</td>
</tr>
<tr>
<td>(2nd shell)</td>
<td></td>
<td></td>
<td>5.22</td>
<td>2.6</td>
<td>0.209</td>
<td>-2.1</td>
</tr>
<tr>
<td>LiBr</td>
<td>HeY</td>
<td>500</td>
<td>3.23</td>
<td>5.5</td>
<td>0.145</td>
<td>-6.2</td>
</tr>
<tr>
<td>KBr</td>
<td>T</td>
<td>100</td>
<td>3.23</td>
<td>6.0*</td>
<td>0.160</td>
<td>-6.8</td>
</tr>
</tbody>
</table>

1 M = 1 mol dm⁻³. *This spectrum is used as a reference and its \( N \) value is assumed to be 6. HeY and T are the He⁺-yield and the transmission method, respectively.

References
TOTAL PHOTOELECTRON IMAGING OF SUB-MICRON STRIPE PATTERNS USING A SOFT X-RAY MICROBEAM FORMED BY A WOLTER-TYPE MIRROR

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Introduction

Photoelectron microscopes are promising tools for microanalysis both in surface science and in industrial applications. We have been developing a scanning photoelectron microscope using a Wolter-type grazing incidence mirror. In the present study, we have performed one-dimensional imaging of sub-micron-sized stripe patterns by detecting total photoelectron signals.

Experimental

The design of the Wolter-type mirror is shown in Fig. 1. The demagnification of the mirror is 1/29.8. The mirror was fabricated using vacuum replication and its mirror surface was then reproduced with epoxy resin. The mirror was installed in the bending-magnet soft x-ray beamline BL-8A. A 30-μm pinhole was positioned at F₁ to determine the source size. A 1.8-μm focal spot was formed on the sample surface at F₃. The energy of the incident soft x-ray was 150 eV and photon flux at the focal point was about 10⁴ photons/s.

The samples were Al stripe patterns formed on a SiO₂ layer on a Si wafer. These Al stripes had the same width and spacing. We prepared three stripe patterns with 4, 1, and 0.7-μm line widths. Five Al lines were drawn for the 4-μm and 1-μm-line-width stripe patterns and ten lines for the 0.7-μm-line-width pattern. The microbeam scanned the sample surface across the stripes. Photoelectrons emitted from the sample were detected with a microchannel plate.

Results and Discussion

The variations of total photoelectron intensity when the microbeam scanned the stripes are shown in Figs. 2(a)-(c). In Fig. 2(c), we show only a limited part of the variation curve. Arrows in the figures denote the position of the Al lines. As shown, each stripe was clearly detected with modulations of 0.33, 0.12, and 0.08, respectively, for the 4-μm, 1-μm, and 0.7-μm stripes.

Recently, we have developed a 0.6-μm microbeam. According to our imaging simulation, it should be possible to resolve 0.3-μm-line-width pattern with a modulation of 0.08 using this beam. We are now planning to conduct total photoelectron imaging at a lateral resolution of 0.1-0.3 μm as well as two-dimensional imaging.

References


Fig. 1 Wolter-type mirror design.
NEW FABRICATION METHOD OF WOLTER-TYPE X-RAY FOCUSING MIRRORS FOR SCANNING PHOTOELECTRON MICROSCOPES

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Introduction

Scanning photoelectron microscope (SPEM) uses a focused X-ray microbeam to investigate the chemical and physical properties of material surfaces with high lateral resolution. Our SPEM uses a Wolter-type grazing incidence mirror for microbeam formation. 1) Wolter-type mirrors have so far been fabricated by vacuum replication and were successfully used in X-ray microscopes. However, the vacuum replication method has practical difficulties in maintaining surface roughness at high replication-temperatures and in controlling the shape of the mirror surface during the cooling down process.

We have developed a new fabrication method of Wolter-type mirrors to overcome such problems.

Mirror Fabrication

The fabrication method 2) consists of two processes. The first process is a conventional vacuum replication process, where a glass replica of the mirror is fabricated using a master mandrel. Then, in the second process, epoxy resin is used for forming the X-ray reflecting surface of the mirror. A small amount of epoxy resin is injected into a thin gap between the replicated mirror and another mandrel with the same contours as that of the first one. The surface of the mandrel is coated with a 200-nm-thick gold film, which adheres to the epoxy resin as it hardens. Since the second process can be completed at room temperature, we had none of the problems mentioned for vacuum replication. We have improved the surface roughness to less than 6 nm (peak-to-valley) and the figure displacement to less than 1 \( \mu \)m.

Evaluation Using Synchrotron Radiation

The focusing characteristics of the mirror were investigated by knife-edge test at the BL-8A beamline. Monochromatic X-rays (150 eV-1 keV) passing through a 1mm-diameter-pinhole were focused by the Wolter-type mirror. Figure 1 shows the change in X-ray intensity caused by knife-edge movement in the meridional plane of the mirror. All lines observed at different photon energies are superposed on each other, indicating that the mirror has no significant X-ray scattering on the surface.

Figure 2 shows the beam profiles of a 150 eV X-ray microbeam observed when the X-ray source was formed with a 20 \( \mu \)m-diameter-pinhole. The beam size, determined as the full width at half maximum of the profile, reaches the range of 1 \( \mu \)m. In previous experiments, 3) the meridional beam size saturated at 20 \( \mu \)m due mainly to the figure displacement of the mirror surface. The profile shown in Fig. 2 indicates that the epoxy resin process improved the fabrication accuracy of the mirror.

References
**XAFS STUDY FOR AMORPHOUS \(\alpha\)-QUARTZ**

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2 Faculty of Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162
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**Introduction**

Amorphous \(\text{SiO}_2\) may be considered as the simplest model substance for a multicomponent oxide glass. Its behavior as the function of pressure and temperature may therefore shed some light on structural variations in other highly polymerized but chemically more complex silicate glasses and melts such as acid magmas.

Recently, pressure-induced crystalline-to-amorphous transformation in the solid state is the subject of intense study. Höfler et al.\(^1\) reported that amorphous \(\text{SiO}_2\) can be also recovered in a partially densified state after compression at elevated pressures and temperatures. It does not return to its normal density (2.20 g cm\(^{-3}\)) at 1 atm (10\(^5\) Pa) and room temperature, but retains densities up to about 2.6 g cm\(^{-3}\), depending on the \(P-T\) conditions of compaction. Seifert et al.\(^2\) and McMillan et al.\(^3\), reported that in the low pressure range, the compression mechanism cannot be due to a variation of the stiff Si-O mean bond distance but must be assigned to change in the Si-O-Si bridging angle or the number of tetrahedra per ring. The high-pressure X-ray diffraction data at 25-35 GPa were measured by Hemley et al.\(^4\). They found amorphization of crystalline silica. The structural data of \(\alpha\)-quartz in high pressure region were, however, not obtained.

It is expected that X-ray absorption near edge structure contributes to characterization of the compaction mechanism of amorphization in \(\alpha\)-quartz. This study shows the experimental results of Si K–XANES analysis of \(\alpha\)-quartz, stishovite and amorphous \(\alpha\)-quartz which was synthesized by using a 6-8 anvil at 36 GPa.

**Experimental**

The Si K-edge XANES spectra were measured in X-ray fluorescent mode at BL-8B using InSb(111) double crystal monochromator. The samples were finely powdered and homogeneously deposited on the PVF membrane. Intensity of the fluorescent X-rays was measured by two SSD with three Si(Li) crystals.

**Results and Discussion**

The Si K-edge XANES spectra and their differential profiles are shown in Figs. 1 and 2, respectively. The spectra of \(\alpha\)-quartz and amorphous \(\alpha\)-quartz in Fig. 1 are very similar to each other and show small differences only in the energy region at 1855 eV. The spectral shape of stishovite shown in Fig. 1 is different from other ones, because stishovite has rutile type structure and each Si is surrounded by six O, while it is surrounded by four O in \(\alpha\)-quartz. The XANES spectra of amorphous \(\alpha\)-quartz is similar to \(\alpha\)-quartz and it is estimated that the Si atom in amorphous \(\alpha\)-quartz is coordinated by four O, and not six O. A small modification in the peak position between \(\alpha\)-quartz and amorphous \(\alpha\)-quartz spectra is indeed evident in Fig. 1. The peak at 1855 eV disappeared with densification. This effect probably due to the minor decrease of the Si–O–Si angle. This results are also supported by Fig. 2, and are in good agreement with those of recent shock–recovery studies.\(^5\) In this way, it was possible to measure Si K–XAFS spectra of bulk samples, and the structural information of amorphous \(\alpha\)-quartz was obtained by the XANES spectra.

**References**

XAFS STUDY FOR SULFIDE MINERALS

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Introduction

The sulfur takes various oxidation states depending on its existing environment. Therefore, it is expected that mineralogical samples exhibit a diversity of sulfur X-ray absorption spectrum. So far, XAFS analysis of light elements has been mainly applied to surface analysis, and few data were reported on bulk state samples. But in the case of geological samples, bulk data is required rather than the data from sample surface.

This study aimed to collect fundamental data in XAFS analysis of sulfur and applies it to the study of the chemical state of sulfur in sodalite group minerals. The crystal structure of the sodalite group minerals can be described as having an aluminosilicate (AlSiO₄) framework. Chemical state of sulfur is interesting, because their cavities are occupied by various forms of sulfur atoms. The samples used in this work were: haiyne: (Na,Ca,K)₂(Al₂Si₂O₈)(SO₄)₂, lazurite: Na₂Ca₂(Al₂Si₂O₈)₂S₄, and helvite: Mn₅(B₈Si₆O₂₁).X-ray absorption spectra were measured at BL-8B using an InSb(111) double crystal monochromator. S K-edge XANES spectra of sulfide and sodalite group minerals were measured in X-ray fluorescent mode. The EXAFS spectra of β-ZnS (sphalerite) were measured in a transmission mode.

Results and Discussion

S K-edge XANES spectra of sulfide minerals are given in Fig. 1. The absorption-edge energies were defined by the first intense peak of their differential spectra. The absorption-edge energies are: As₂S₃: 2464.3 eV, m-HgS: 2465.8 eV, MnS: 2466.3 eV, CuS: 2462.8 eV and elemental sulfur: 2465.8 eV. In spite of the variety of the structures of these minerals, the absorption edge energies were similar to each other and were almost equal to that of elemental sulfur.

S K-edge XANES spectra of the sodalite group minerals are given in Fig. 2. These spectra exhibited characteristic chemical shifts, as well as unique spectral shapes. The spectra of haiyne and helvite exhibited typical peaks of sulfate ions and sulfide ions, respectively. Although the spectrum of lazurite showed the peaks of sulfide and sulfate sulfur, the ideal formula of lazurite is reported as Na₂Ca₂(Al₂Si₂O₈)₂S₄. The existence of sulfate ion was first found by this study.

The extracted EXAFS oscillations weighted by k³ and its Fourier transform (uncorrected for the phase shift) are shown in Fig. 3 (a) and (b), respectively. The first intense peak at 2.0 Å in the |F(r)| curves is due to the S-Zn bonds in β-ZnS. Peak at 3.5 Å in Fig. 3 (b) corresponds to the non-bonding S-S interaction. The sulfur atom in the structure is surrounded by four zinc atoms and has a tetrahedral structure.

The structure parameters r, n and σ of the sulfur atom were determined by a least-squares calculation applied to the Fourier filtered k³χ(k) values over the k range of 4.75 - 12.55 Å⁻¹. The inverse Fourier transformation was performed over the r range of 1.585 - 2.582 Å. The best fit values are listed in Table 1. The S-Zn bond length agrees well with the literature values.³ The solid lines calculated using the obtained parameter values well reproduce the experimental points, as depicted in Fig. 3(c). In this way, the quality of the XAFS spectra obtained from these experiments were found to be satisfactory.

Table 1 The S-Zn bond length r, the Debye-Waller factor σ and the coordination number n for the sulfur atom in β-ZnS.

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>σ (Å²)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.32 (0.4)</td>
<td>0.077 (0.8)</td>
<td>3.9 (0.8)</td>
</tr>
</tbody>
</table>

Reference


Fig. 1 S K-XANES spectra of sulfide minerals and elemental sulfur.

Fig. 2 S K-XANES spectra of haiyne, helvite, lazurite and sulfur standard.

Table 1 S-Zn bond length r, the Debye-Waller factor σ and the coordination number n for the sulfur atom in β-ZnS.

Table 3 (a) χ(k) weighted by k³ for β-ZnS, (b) The Fourier transforms F(r) of the k³χ(k) for β-ZnS, uncorrected for the phase shift, (c) The Fourier filtered k³χ(k) curves and its least-squares parameter fit for β-ZnS. The observed values are shown by dots and calculated ones are shown by solid lines.
INTRODUCTION

Amorphous Co-Nb-Zr thin films are used as magnetic materials in VCR heads. The films are formed by sputter evaporation method and known to be amorphous\(^{(1,2)}\). However, there have not been enough investigations on structure changes of the materials in manufacturing process. The authors have analyzed the structure of the Co-Nb-Zr thin films by fluorescent XAFS method.

EXPERIMENTAL

**Samples:**

Co-Nb-Zr thin films with different process conditions were prepared for XAFS analyses as listed in Table 1. Co\(_{0.835}\)Nb\(_{0.124}\)Zr\(_{0.041}\) thin films with thickness of 20 \(\mu\)m were deposited on substrates of (Mn,Zn)Fe\(_2\)O\(_4\) single crystal. The sample (c) and (d) were annealed and surface of the sample(b) was slightly ground by so-called “lapping” treatment. Cobalt (f) and Niobium (g) metal foils were prepared as references. The samples were measured by powder X-ray diffractometer beforehand. It was proved that sample (a), (b) and (c) were amorphous, and (d) and (e) were crystalline. A lattice constant, \(c\), of the sample (e) was larger than that of the sample (d) by 2%.

**Measurement:**

Co, Nb and Zr Ka fluorescent yield spectra were measured at BL-8B. XAFS of reference foils, (f) and (g), were measured by transmission method.

RESULTS

Figure 1 shows an example of a measured XAFS spectrum of the Co-Nb-Zr thin film. The measured spectra were analyzed by one-electron scattering approximation method and results are shown in Table 2 and Fig. 2. The sample (d) was annealed at 873K and known to have two phases of \(\alpha\)-Co and Nb-Zr alloy. Therefore, it was expected that the sample (a) without heat treatment and the sample (c) annealed at 733K have amorphous structure similar to \(\alpha\)-Co phase. Results of EXAFS analyses were consistent to the foresight and the analyses also suggested the growth of Nb-Zr clusters by heat-treatment. Coordination numbers of Nb and Zr around Co are decreased by heat-treatment, however that of Co-Co, Zr-Nb and Nb-Nb are increased. Effect of lapping process was estimated using the sample (b). Coordination numbers of Nb and Zr atoms are decreased and that of Co atoms are increased by lapping. It suggests that Nb and Zr atoms are separated from Co atoms and Co clusters are grown by lapping.

REFERENCES

EXAFS Study on LPCVD Tantalum Pentaoxide Films

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Introduction

Silicon dioxide and silicon nitride have been utilized as dielectric capacitor films in dynamic random access memories (DRAMs). Materials with higher dielectric constants are required for highly integrated devices such as 256 Mbit DRAMs. CVD Ta2O5 thin films have been extensively studied because of its high dielectric constants and excellent step coverage characteristics1). However, the problem remains that the current leakage of the capacitor film is not as good as those of the conventional silicon compounds capacitor. Some oxidation treatments should be necessary because there are relations between the leakage current characteristics and oxygen defects in Ta2O5 structure. The authors have investigated on amorphous Ta2O5 films by XAFS method to reveal the relation between local structure of the Ta2O5 and the oxidation treatments.

Experiments

Four samples were prepared for XAFS measurement as shown in Table 1. Tantalum pentaoxide films with thickness of 10nm were deposited on poly crystalline silicon film on silicon wafer by low pressure chemical vapor deposition (LPCVD) using Ta(OC2H5)5 and O2 gas mixture source. After the deposition, each film was annealed by the different processes. L-type tantalum pentaoxide was used as a reference material. Well ground Ta2O5 powder was annealed at 1273 K in dry O2 to make L-type Ta2O5.

TaLIII-edge fluorescent yield spectra were measured at BL-8B. An incident x-ray beam was monochromatized by a Si(311) double crystal monochromator.

Results and Discussion

The Radial Distribution Functions (RDFs) obtained by Fourier transformation of \( \chi(k)k^3 \) are shown in Fig. 1. The largest peak of each RDF was assigned to oxygen atoms around a tantalum atom. Results of curve fitting analyses2) are listed in Table 1. The coordination number (C.N.) of O atoms around a Ta atom and the Ta-O interatomic distance (R) increased after the annealing. The C.N. and R of the sample (c) which had lower leakage current are close to those of the reference material (d). The oxidation treatment caused the local structure change to the L-type Ta2O5 and current leakage reduction of Ta2O5 capacitor film. It suggests that L-type Ta2O5 structure is essential for the capacitor film.

References


<table>
<thead>
<tr>
<th>sample</th>
<th>C.N.</th>
<th>R(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) as-deposited</td>
<td>3.9(2)</td>
<td>0.196(1)</td>
</tr>
<tr>
<td>(b) annealed O2 873K,15min. Ar 1073K,10min.</td>
<td>5.7(2)</td>
<td>0.197(1)</td>
</tr>
<tr>
<td>(c) annealed O2 623K,10min.</td>
<td>6.4(2)</td>
<td>0.204(1)</td>
</tr>
<tr>
<td>(d) L-type Ta2O5</td>
<td>6.4*</td>
<td>0.205(1)</td>
</tr>
</tbody>
</table>

*Fixed parameter determined by X-ray diffraction.

Fig. 1. Fourier transform of TaLIII-edge EXAFS.
A NEW MONOCHROMATOR SYSTEM AT BL-8B
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Introduction

A new tandem type monochromator has been installed in the beam line BL-8B. Monochromator crystals of InSb(111), Si(111) and Si(311) are used in the energy regions of 1.68 to 21.8 keV. The main application of the beam line is measuring x-ray fluorescent spectra for XAFS analyses of solid state materials such as silicon compounds and ferroelectric oxides. Therefore the authors did not strive high energy resolution, \( \Delta E/E < 10^{-5} \), however rapid scanning time and sufficient resolution for XAFS of \( 10^{-4} \) order were aspired.

Design features

Schematic illustrations of the monochromator is shown in Fig. 1. A new type of monochromator was designed to accomplish the main objective which provides XAFS spectra rapidly. The first and the second crystals were set on the \( \theta \)-stage and the crystals are rotated simultaneously. The height of monochromatic x-rays is adjusted only by using a z-stage which defines the distance between two crystals. This type of monochromator has following advantages; (1) that provides thermal stability of the first crystal because an incident beam always radiate the center of the first crystal, (2) that decreases an angular deviation between angles of two crystals because the second crystal moves only along the z-stage.

Table 1 shows the features of main axes of the monochromator. The \( \theta \) axis is driven from 10 to 80 degrees with angular resolution of 0.36 arc sec. A monochromatized energy is defined by the \( \theta \) angle. The \( \Delta \theta_2 \) axis is rotated to align the Bragg angle of the second crystal with resolution of 0.1 arc sec. The \( z \) axis, which defines a distance between two crystals, moves from 10 to 60 mm.

All the optics of the beam line were installed in a high vacuum condition to decrease x-ray absorption and scattering by windows and a beam-path especially in low energy region less than 5 keV. High vacuum-type stepping motors were used to drive the axes of the monochromator and a base pressure was less than \( 1 \times 10^{-5} \) Pa.

No focusing mirror was used in the beam line while the monochromatic beam had been focused by a bent cylindrical mirror before.

Two monochromators were connected tandem as shown in Fig. 2. Usually one is equipped with InSb(111) crystals and the other is Si(311). Wide energy range can be used easily by choosing a monochromator.

Thermal instability

The monochromatic energy is described by the \( \theta \) angle, however it shifts with a temperature changes of the first crystal heated by a synchrotron radiation in proportion to a ring current and its projection, \( \cos \theta \). The energy shift has not been measured precisely yet, however the shift caused by the ring current variation was estimated to be less than \( 5 \times 10^{-4} \) during a half-day long measurements of TaL edge spectra.

![Fig. 1 Schematic illustrations of the monochromator](image_url)

![Fig. 2 Side view of the tandem type monochromator](image_url)
Fabrication and testing of hard x-ray sputtered-sliced zone plate

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Introduction

Recently, Fresnel zone plates (FZPs) have been widely used as microfocusing optical devices in the soft x-ray region and are usually fabricated using electron-beam lithographic patterning techniques. This patterning technique can produce very high-resolution structures, for example, a spatial resolution of 300 Å has been reported for x-ray, with a wave length of 30 Å, but is limited in its aspect ratio (height/width) to around unity. It is recognized that FZPs fabricated by this technique are difficult to use in the hard x-ray region because the absorber thickness is usually insufficient for stopping x-rays. While optics such as the grazing incidence total-reflection mirror, the bent crystal, and the multilayer mirror, have been developed, the availability of these elements for widespread practical use is still limited.

Hard x-ray zone plates (ZPs) with high aspect ratios have been fabricated previously by several groups using physical vapor deposition (to produce alternating transparent and opaque layers on a fine wire core) which is so called sputtered-sliced ZPs. However, a submicron beam has not been realized by either of these ZPs.

We are currently making sputtered-sliced ZPs by physical vapor deposition, with alternating transparent (carbon) and opaque (silver) layers on a fine gold wire core to improve the spatial resolution and light-collecting efficiency in the hard x-ray regions. In this report, we describe the results of the focusing test with a brief description of the fabrication process.

Zone Plate Fabrication

Alternate multilayer zones were constructed by dc planar magnetron sputtering. 2 The silver and carbon concentric multilayers (28 layers) were deposited onto rotating Au wire substrate of 47 μm at a rotation speed of 15 rpm. 3 The designed focal length of the ZP was 158 mm for 8.05 keV x-ray. The film thickness of the first inner layer (carbon) was 0.4 μm and 0.29 μm for the outermost layer (silver). After deposition, the wire sample was fixed into a melt solder, tightened and sliced into a plate 1 mm in thickness normal to the wire axis. Finally, the ZP was polished mechanically. The thickness obtained was estimated at about 40 μm. A scanning electron micrograph of the present ZP is shown in Fig. 1.

X-ray Focusing Test

The characterization of the ZP was performed on BL-8C at the Photon Factory using 8 keV synchrotron x-rays. For this experiment, SR beam from the normal bending magnet was used with the beam monochromatized using a Si(111) double-crystal monochromator and confined by 0.12 x 0.12 mm aperture in front of the ZP. The ZP was located 28 m from the radiation source point. The pinhole (0.05 mm) was placed 11 m in front of the ZP, with an order selecting aperture (OSA: 20 μm) made from thin tantalum plate (thickness: 0.2 mm) located after the ZP.

The wire (0.2 mm) edge-scan profile is differentiated to give a line spread function of the optical system. The finest focused beam size obtained was 0.9 μm at the first order focal point (158 mm from the ZP). Figure 2 shows the integrated x-ray intensities and the focused beam profile. The efficiency of this ZP was determined to be ~ 4% in the 8 keV x-ray, which is about one half of that of the ideal FZP.

To improve spatial resolution of the ZP, it is necessary to reduce the thickness error and irregular structure of the zone boundaries.

References

Refractive Index of Human Blood Measured with an X-Ray Interferometer

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* Institute of Clinical Medicine, University of Tsukuba, Tsukuba, Ibaraki 305

Introduction

Phase-contrast X-ray imaging is sensitive to light elements, such as carbon, nitrogen, and oxygen. Demonstrative observations of biological specimens have been reported, and the possibility of an application to medicine has also been suggested. Thus, it is experimentally clear that organic matter, which is difficult to observe with absorption contrast, is observable with phase contrast. As the next step, it is necessary to find out what produces the image contrast. In a physical sense, the origin of phase contrast is the distribution of the refractive index inside a sample. To pick up biological information from a phase-contrast X-ray image, however, we must know how a histological structure is reflected in the image. It has been reported that lipid distribution can produce a structure in a phase-contrast image. Here, we concentrate on the effect of blood on phase contrast. If the refractive index of blood is different from those of other parts of a body, blood contrast is expected in a phase-contrast X-ray image.

Experimental

We measured the refractive index of human blood for 0.7 Å, 0.8 Å and 0.92 Å X-rays with an X-ray interferometer. We added 3.3% of heparin to a human blood sample to prevent coagulation during the measurement. In addition, the blood sample was tested by being separated into serum and corpuscles with 0.8 Å and 0.92 Å X-rays. For comparison, distilled water, physiological salt solution, and acrylic resin were also tested. Samples were put in a liquid cell made of acrylic resin. The X-ray exit side window of the cell was inclined against the entrance side, and therefore interference fringes of a regular interval appear. The fringe interval is inversely proportional to the refractive index decrement δ from unity. By measuring the fringe interval, the absolute value of δ is determined.

Results and discussion

In Figure 1, δ/λ² is plotted versus λ using the measured δ-values listed in Table I. This is consistent in that δ is proportional to λ². The difference of δ between samples is significant. The δ of corpuscles is especially large. This is consistent in that corpuscles contain high concentration of iron. On the contrary, the δ of serum is comparatively small. In line with this, the δ of blood is about 3% larger than that of serum due to the corpuscular ingredient in blood.

The above results suggest that blood distribution should produce a structure in a phase-contrast X-ray image. So if phase-contrast X-ray imaging is applied to medical diagnosis, blood vessels and internal bleeding might be detected without contrast enhancement.

References

2) A. Momose and J. Fukuda, Med. Phys. in press.

Table I. Measured values of δ ($x 10^{-6}$).

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>distilled water</th>
<th>physiological salt solution</th>
<th>serum</th>
<th>corpuscles</th>
<th>blood</th>
<th>acrylic resin</th>
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<tr>
<td>0.7</td>
<td>0.747</td>
<td>0.751</td>
<td>-</td>
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<td>0.775</td>
<td>0.861</td>
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<td>0.8</td>
<td>-</td>
<td>0.949</td>
<td>0.999</td>
<td>1.049</td>
<td>1.036</td>
<td>1.129</td>
</tr>
<tr>
<td>0.92</td>
<td>-</td>
<td>1.306</td>
<td>1.321</td>
<td>1.385</td>
<td>1.353</td>
<td>1.486</td>
</tr>
</tbody>
</table>

Fig. 1 Plot of δ/λ² versus λ using the measured values of δ in Table I.
Observation of Cancer Tumor with Phase-Contrast X-Ray Computed Tomography

Atsushi MOMOSE, Tohoru TAKEDA*, and Yuji ITAI*

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* Institute of Clinical Medicine, University of Tsukuba, Tsukuba, Ibaraki 305

Introduction

X-ray computed tomography (CT) reveals structures inside an object nondestructively; the origin of the image contrast is heavy elements with high X-ray absorbance. Biological specimens consisting of light elements with low X-ray absorbance therefore cannot be observed practically without image enhancement with a contrast medium. Phase-contrast X-ray computed tomography (PCX-CT)\textsuperscript{25} has been developed to overcome this problem. PCX-CT uses the X-ray phase shift for its input data instead of \( \mu \). So, reconstructed sectional images from PCX-CT map the distribution of the refractive index inside the sample. The image sensitivity of PCX-CT is estimated to be almost a thousand times larger than that of the conventional X-ray CT using absorption contrast. Therefore, PCX-CT is promising for observing the structure inside organic matter, such as a biological sample.

Experimental

We observed a cancerous rabbit liver. The liver was fixed in 10% formalin. A sample was cut away from the liver and was put in a sample cell filled with formalin.

PCX-CT uses an X-ray interferometer cut from a silicon perfect crystal, and its experimental setup is shown in Figure 1. When the Bragg diffraction condition is satisfied, two beam paths are created. In one of the beam paths, the sample cell was inserted. The sample was rotated in the cell, which was fixed to the sample rotation stage. Interference fringes caused by the sample were detected with an X-ray sensing pickup tube. A wedge-shaped phase shifter was inserted in another beam path to superpose the external phase shift. This is necessary to read the X-ray phase shift from interference patterns. The phase-shift data sets read at each angular position of the sample were input in a CT reconstruction algorithm.

Results and discussion

Figure 2 is one of the phase-contrast sectional images of the cancerous sample. We used 0.92 Å X-rays. A cancer tumor is clearly observed in the center to upper-right area of the image. Furthermore, structures in the tumor are detected; the bright and marginal dark area might indicate degenerative and active cancer cells. In the corresponding absorption-contrast CT image (not shown), no structure was detected. Thus, not only the position of a cancer tumor but also the condition inside the tumor were visualized by using phase-contrast X-ray computed tomography.

References

PHOTON ENERGY DEPENDENCE OF SYNCHROTRON RADIATION INDUCED GROWTH SUPPRESSION IN ALUMINUM CHEMICAL VAPOR DEPOSITION
- CHEMICAL SHIFT ANALYSIS OF AUGER ELECTRON SPECTRA -
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INTRODUCTION
In our previous paper, we found clear photon energy dependence in the synchrotron radiation induced growth suppression effect in aluminum chemical vapor deposition (CVD) on a Si surface. The Al growth was suppressed perfectly by inner shell electron excitation. However, the suppression effect was little in the case of the valence electron excitation. The origin of the photon energy dependence of the suppression effect is studied by the chemical shift analysis of the suppression layer.

EXPERIMENTAL
SR irradiation experiments was carried out at the beam line BL-9B. The photon energy was varied by cutting away high energy photons by means of changing the incident angle of SR to mirrors equipped in the beam line. To compensate the photon intensity change when the cut off wavelength was varied, the irradiation experiment of full wavelength region was carried out in single bunch operation of the storage ring.
Dimethylaluminum hydride(DMAH) was used as CVD gas. The suppression layer was formed on a Si(100) clean surface by the 10 minutes irradiation with various spectrum region at a temperature of 200°C. The Al LVV chemical shift of the each suppression layer was measured by in-situ Auger analysis.

RESULTS AND DISCUSSION
Figure 1 shows the photon energy dependence of (a) suppression efficiency and (b) Al LVV chemical shift of suppression layer. The suppression efficiency in Fig.1(a) is defined as the film-thickness ratio between SR irradiated and non-irradiated area. The horizontal axis shows the upper limit of the photon energy utilized for irradiation. The inner shell energy of the related elements such as Al, Si, and C, are also indicated in the same figure for reference.
As shown in Fig.1(a), suppression effect is remarkable in the core electron excitation region. Even the Al 2p excitation, corresponding to the shallowest core level, is sufficient to cause almost perfect suppression. The photon energy dependence of the Al LVV chemical shift shown in Fig.1(b) shows a good correlation with that of the degree of suppression effect shown in Fig.1(a): The chemical shift of the surface layer formed by valence electron excitation is observed at 68 eV. This value means that metallic aluminum is formed on the surface. On the other hand, the chemical shift in the core electron excitation case is 64 eV which corresponds to the value of aluminum carbide. Consequently, the cause of the wavelength dependence of SR irradiation effect on the CVD reaction is explainable as the change of chemical nature of the suppression layer from elemental aluminum to covalent type aluminum carbide.

The detail of the photochemical reaction of the DMAH molecules adsorbed on the Si surface is not clear. However, the gas phase experiment on dissociative ionization for DMAH, increase of H intensity and decrease of AlC_H and AlCH intensity according to the wavelength change from valence to Al(2p) core excitation. We think that this means the Al(CH) bond breaking is notable in valence electron excitation while C-H bond breaking is remarkable in the core electron excitation. If this reaction occurs on the surface decomposition, the change of chemical nature from elemental aluminum to AlC is explainable, since Al formation requires Al(CH) bond breaking and AlC requires C-H breaking.

REFERENCE

Fig.1. Photon energy dependence of (a) the degree of the SR induced growth suppression effect and (b) the Al LVV chemical shift of the suppression layer on a clean Si surface.
PHOTON ENERGY DEPENDENCE OF SYNCHROTRON RADIATION INDUCED
GROWTH INITIATION IN ALUMINUM CHEMICAL VAPOR DEPOSITION
- CHEMICAL SHIFT ANALYSIS OF AUGER ELECTRON SPECTRA -

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INTRODUCTION

As stated in the previous article of this issue, we found clear photon energy dependence in synchrotron radiation (SR) irradiation effect for Al-CVD reaction on Si surface and the cause of the energy dependence can be explained by the chemical nature change of surface layer formed in photochemical reaction. When the surface is changed to SiO$_2$, initiation effect is observed and this effect also shows clear photon energy dependence. In the case of the valence electron excitation, only the Al growth initiation was observed, while both the initiation and suppression effects were observed in the case of the inner shell electron excitation. To clear the origin of this wavelength dependence of initiation effect, we measured the photon energy dependence for the surface layer composition formed by SR irradiation by means of the Auger chemical shift analysis.

EXPERIMENTAL

The experimental procedure is the same as the previous articles. Silicon dioxide film was formed by thermal oxidization of silicon substrate. Two kinds of initiation layers were examined by in-situ Auger electron spectroscopy: one was the layer formed by 10 minutes irradiation, and the other was 90 minutes irradiation. The CVD temperature was fixed to 200 °C.

RESULTS AND DISCUSSION

Results are shown in Figure 1, where (a) is the photon energy dependence of the film thickness after 90 min CVD time, which is the measure for the degree of initiation effect and (b) is the Al LVV chemical shift of the initiation layer. Closed circle corresponds to the data for 10 min irradiation and the closed triangle to those of the full irradiation of the 90 min CVD. In the case of the 10 min irradiation, only the Al growth initiation was observed independently to the excitation photon energy. On the other hand, in the case of the 90 min irradiation, clear difference between valence and core electron excitations was observed, i.e., initiation effect was observed in valence excitation, while both suppression and initiation effects are observed in core electron excitation region.

The Al LVV chemical shift of the initiation layer formed by 10 min irradiation was 68 eV, corresponding to metallic Al. The bonding nature of the CVD film formed by core electron excitation is changed to covalent (64 eV: carbide-Al).

The difference between 10 min irradiation and 90 min one can be understood by the change of surface chemical nature from SiO$_2$ to Al due to CVD growth. In the initial stage of irradiation, the surface is SiO$_2$, where metallic aluminum growth is dominant. When the surface changes from SiO$_2$ to Al by CVD growth, photochemical reaction shows photon energy dependence like as silicon surface, i.e., metallic aluminum is formed in valence excitation and AlC is formed in core excitation.

These observations show good agreement with the result of CVD features shown in Fig. 1(a). Consequently, the wave length dependence of the SR irradiation effect on SiO$_2$ surface can be explained by that of photochemical reaction on SiO$_2$ and grown Al surface and succeeding thermal reaction.

REFERENCE

1) F. Uesugi and I. Nishiyama, the previous article of this issue.

![Fig. 1](image-url)
INTRODUCTION

In the last several years, we have reported unique photochemical effects of synchrotron radiation (SR) on Al chemical vapor deposition (CVD), i.e., suppression effect on Si surface and initiation effect on SiO₂ surface. This effect is very sensitive to the surface chemical reactivity and the substrate temperature. In the last year’s report¹, we reported the suppression effect observed on hydrogen terminated Si surface which has intermediate chemical reactivity between clean Si and SiO₂ surfaces. The temperature range, however, where clear inverse patterning was observed, is different from clean Si surface. On the other hand, we found a strange temperature dependence in the growth rate on Si surface, i.e., increase and decrease dependence². As the mechanism of oscillatory temperature dependence, we proposed a model in which hydrogen termination by CVD gas has an important role. To clarify the temperature range where SR irradiation effect is remarkable, and the mechanism of oscillatory temperature dependence, we examined the substrate temperature dependence of SR induced CVD reaction characteristics on hydrogen terminated Si surface.

EXPERIMENTAL

Experiments were carried out at the beam line BL-9B. Hydrogen terminated silicon surface was prepared by dipping the APM-cleaned Si(100) wafers in 1.6 % diluted HF solution. No contamination was observed on the surface in Auger electron spectroscopy (AES). The hydrogen termination was checked by thermal desorption spectroscopy. Two desorption peaks were observed clearly.

Non-monochromatized SR light (E<310 eV) was exposed to the H-Si surface through a line-and-space steel mask. Dimethyl aluminum hydride (DMAH) was used as the CVD gas, which was supplied by molecular beam source. Substrate temperature was varied from 150 to 700 °C. The film thickness of deposited aluminum was measured by a step-height meter, Dektak 3030ST (Saloam Co.).

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of Al film thickness grown on hydrogen terminated Si surface. The CVD time was 90 min constant through experiment so that film thickness in this figure is proportional to the deposition rate. Characteristic features were found: 1) The deposition rate for non-irradiated area, which means pure thermal reaction, showed increase and decrease dependence, and formed a peak near 300 °C. 2) SR irradiation showed almost complete suppression effect below 400 °C. The peak near 300 °C in thermal deposition reaction disappear in the case of SR irradiation.

The oscillatory temperature dependence observed here is essentially similar to those of clean Si case. However, in the Si case, we observed two peaks, at 200 °C and 300 °C. We explained the peculiar dependence as the combination of several elementally reactions and the change of surface composition. We assumed that hydrogen termination by DMAH is responsible to the deposition-rate decrease from 200 to 250 °C and the formation of first peak, since this effect was caused from the AES-non-detectable species. The assumption based on indirect evidence is confirmed by the present experiment. Namely, the first peak disappeared in the experiment using the hydrogen pre-terminated Si surface.

The temperature range where SR irradiation effect is observable is clarified to be below 400 °C, i.e., peak region in temperature dependence. From the Auger analysis, we confirmed that film composition formed by thermal CVD is pure metallic aluminum and that aluminum carbide is formed on Si surface in the initial stage of SR irradiation. Therefore, we concluded that this chemically inactive AlC layer formed by SR photochemical reaction is the cause of suppression effect. Over 400 °C region, the film composition of thermal CVD is aluminum carbide, so that SR effect is hidden and disappear in this high temperature range.

REFERENCE

2) F. Uesugi and I. Nishiyama, ibid, #8 (1990) 163.
Energy-Dispersive Grazing Incidence In-plane Diffraction of Very Thin Ta$_2$O$_5$ Films with Synchrotron Radiation White X-rays

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1. Introduction

Energy-dispersive X-ray diffraction using synchrotron radiation (SR) is applied to very thin polycrystalline films. We perform energy-dispersive grazing incidence in-plane diffraction with synchrotron radiation white X-rays (SR-EDGID) against a 95Å thick Ta$_2$O$_5$ film. Ta$_2$O$_5$ is a candidate for high-dielectric films in the next generation LSIs.

2. Experiment

Two thicknesses (95 and 860Å) of Ta$_2$O$_5$ films were deposited on (100)Si substrates by low-pressure chemical vapor deposition (LPCVD). The as-grown films were amorphous, and were made polycrystalline by subsequent annealing at 800°C.

SR-EDGID experiments were carried out at beam line 9C of Photon Factory. Figure 1 shows the setup. The glancing angle (θo), made by the sample surface and the X-ray beams, was set at 0.24 degrees. The in-plane diffraction beams at 34.9 degrees (2θ) from the incident beams through a slit and a Soller slit were measured with a Ge solid-state detector (SSD).

After the SR-EDGID measurements, X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS) were performed to identify any anomalous peaks in the SR-EDGID spectrum.

3. Results

The SR-EDGID spectra of the Ta$_2$O$_5$ films contained many diffraction peaks and Ta fluorescence peaks, as shown in Fig. 1. Almost all diffraction peaks were identified as orthorhombic-Ta$_2$O$_5$ peaks (JCPDS: 25-0922). However, we found an anomalous peak at 6.39keV (d=3.24Å), which could not be identified as reported Ta oxides (Fig. 2, a). The peak appeared only in the 95Å thick film, and clearly differs from the normal diffraction peak of the 860Å film at 6.5keV (d=3.17Å).

XPS measurements indicated the presence of Si on the 95Å Ta$_2$O$_5$ film, and its absence on the 860Å film. RBS could detect the surface Si of the 95Å film. The spectrum contains a very small and sharp peak indicating that Si precipitated just at the surface. The amount of Si at the surface is estimated at about 5Å or less by fitting with theoretical curves, assuming the precipitates to be Ta-Si.

Based on the above results, it was shown experimentally that SR-EDGID can detect 5Å thick Ta silicide precipitates on a Ta$_2$O$_5$ film. The results indicate that SR-EDGID as a crystallographic analysis method yields an unparalleled high sensitivity for polycrystalline materials. Energy-dispersive X-ray diffraction has not been applied sufficiently to non-organic polycrystalline materials until now. After this study, we expect SR-EDGID shall be applied to polycrystalline substances in many fields.

References

ENCLOSED SYSTEM WITH HELIUM GAS FOR XAFS AND DIFFRACTION EXPERIMENTS

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Introduction

Transition metal oxides are really fascinating elements, since they show fruitful electronic properties from ferroelectrics, magnetism to superconductors, moving from light to heavy elements. Since the energy of K-absorption edge in the light transition metal elements such as Ti, however, is less than 5keV, XAFS and/or diffraction experiments employed with anomalous dispersion on samples consisting of Ti are not allowed in an air-atmosphere. The transmission and fluorescence XAFS measurement could be performed with an evacuated flight path in order to reduce the air-path length as short as possible. On the other hand, since the diffraction experiment requires the several X-Y slits, soiller slits and sometimes analyzer crystal, more windows compared with the case of XAFS experiment should be installed before the diffracted X-rays reaches a detector. As a consequence, the absorption by the windows, even if a thin capion film (8nm in thickness is available) is used, kills the X-ray intensities. In this report we will show a newly developed enclosing system with He gas which allows to carry out XAFS, DAFS and diffraction employed anomalous dispersion with an energy over than 4 keV.

Experimental

Figure 1 shows the block diagram of the system. The whole equipments of a θ-2θ table, ion chambers, Lytle and solid state detectors are covered with an ethylene vinyl alcohol copolymer, named EVAR (Kuraré Corp.), which is used in order to keep the system under the He atmosphere. The size of this "coffin" is 1700(l) x 600(w) x 600(h) mm³.

Fig. 1 Block diagram of the enclosed system with He gas for XAFS and diffraction experiments.

As it can be seen, there is no chance for incident and diffracted X-rays to experience the air. At first the air in the "coffin" is evacuated roughly by a rotary vacuum pump for a couple of minutes, and then the He gas is subsequently introduced. It takes almost 30 minutes to reach the oxygen concentration of 0.1 at% in He ambient atmosphere. It was observed by oxygen sensor that the oxygen concentration of less than 0.5 at% was kept constant for 24 hours under the closed condition. Less than 0.1 at% oxygen concentration, if it is desired, can be achieved by keeping He gas flowing. As an examination of this system, the EXAFS spectra on TiO and thin film SrTiO₃ were observed with and without the system.

Results

Figure 2 shows the result of the fluorescence XAFS measurements on TiO observed with the system, together with the data taken without the system. As seen in the figure, the oscillation in the extended region as well as the edge step was observed clearly in the spectrum taken with the system, but not without the system. Then, it can be concluded that the system works very well.

Fig. 2. TiO XAFS spectrum with and without the system

Also, the thickness of 80nm of SrTiO₃ thin film was found to be good enough for getting the XAFS spectrum with reasonable statistics.
NEAR EDGE STRUCTURE OF DAFS SPECTRUM ON YIG

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Introduction
It is well known that x-ray absorption near edge structure (XANES) at Fe K-edge of various Fe-oxide generally shows the so-called pre-peak structure. Recently, site-specific XANES spectra from a \( \text{[Y}_3\text{Fe}_2(\text{FeO}_4)_3] \) YIG single crystal under a standing wave field was observed and it was reported that the pre-peak structure for XANES are mainly produced by Fe\(^{3+} \) at the tetrahedral site in ferrimagnetic YIG.\(^{1} \)

The diffraction anomalous fine structure (DAFS) study gives also site-specific information for the inequivalent sites of a single atomic species within the unit cell without any requirement for crystal perfectness.\(^{2} \) In this paper the diffraction anomalous near edge structure (DANES) spectrum of each site Fe\(^{3+} \) ion in YIG single crystal is presented.

Experimental
The sample was a YIG single crystal film grown epitaxially on a GGG (111) substrate.

The DANES measurements were carried out with a Si(311) double crystal monochromator at BL-9C. The DANES signals were measured around the Fe K-edge for the three different Bragg peaks listed in Table I. Figure 1 shows the DANES spectrum of the (332) Bragg peak from YIG.

Results and Discussion
The DANES intensities were corrected for absorption using the measured substrate peak intensity at the same energy range. The variation of peak intensity of substrate around the Fe K-edge can be regarded as the absorption of the YIG film.

The DANES spectrum of each site Fe\(^{3+} \) ion in YIG was determined. Figure 2 shows the DANES spectrum of tetrahedral site Fe\(^{3+} \) ion extracted from Fig.1. It was confirmed that the pre-peak structure for XANES of YIG are mainly produced by tetrahedral site Fe\(^{3+} \) ion.

Table I. The crystallographic weights for three Bragg reflections of YIG. Where \( f(\text{Td}) \), \( f(\text{Oh}) \) and \( f(Y) \) are form factor of the tetrahedral site Fe\(^{3+} \) ion, the octahedral site Fe\(^{3+} \) ion and Y\(^{3+} \) ion, respectively.

<table>
<thead>
<tr>
<th>((h,k,l))</th>
<th>( f(\text{Td}) )</th>
<th>( f(\text{Oh}) )</th>
<th>( f(Y) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(332)</td>
<td>-8</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>(422)</td>
<td>8</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>(444)</td>
<td>-24</td>
<td>16</td>
<td>-24</td>
</tr>
</tbody>
</table>

Fig.1 DANES spectrum of (332) Bragg peak from YIG.

Fig.2 DANES spectrum of Tetrahedral site Fe\(^{3+} \) ion.

References
Structural transition layer of silicon oxide at the SiO$_2$/Si interface studied by x-ray diffraction

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Introduction

For future LSI devices with high density memories, the necessary gate oxide thickness is estimated to be around 5-10 nm. For this thickness regime, a rapid decrease of the breakdown charge ($Q_{bd}$) of SiO$_2$ films has been observed in constant current time dependent dielectric breakdown (TDDB) measurements. The electronic properties of such thin films are affected by the structure of the SiO$_2$ films. The existence of a structural transition layer at the SiO$_2$/Si interface has been reported. Even a crystalline phase has been found at the SiO$_2$/Si interface. In spite of a number of structural studies of the SiO$_2$/Si interface, there are many remaining problems, such as the difference in the production processes or the initial oxidation mechanism.

In this report, the x-ray intensity of the silicon substrate 311 reflection in an extremely asymmetric scheme of small incident angle and large exit angle has been observed in constant current time dependent dielectric breakdown (TDDB) measurements. The existence of a structural transition layer at the SiO$_2$/Si interface has been reported. In spite of a number of structural studies of the SiO$_2$/Si interface, there are many remaining problems, such as the difference in the production processes or the initial oxidation mechanism.

In this report, the x-ray intensity of the silicon substrate 311 reflection in an extremely asymmetric scheme of small incident angle and large exit angle has been observed in constant current time dependent dielectric breakdown (TDDB) measurements. The x-ray intensity of the silicon substrate 311 reflection was measured in an extremely asymmetric scheme. By using successive asymmetric 311 reflections from the monochromator crystals, the angular divergence of the x-rays impinging on the sample was less than 0.1 arcsec. The 311 reflection was used in a parallel setting to avoid wavelength-dispersion effects.

Results and Discussion

The integrated intensity is obtained from incident-angle scans by summing the data of intensities from -160 arcsec to 160 arcsec. All the experimental results and fitted curves are shown in Fig. 1. The fitting parameters for the theoretical curves in Fig. 1 are only the density of the SiO$_2$ films and an overall scale factor. In Fig. 1, data for samples having only the native oxide formed during the wafer cleaning process are also shown and labeled "clean". These data were not included in the fits, yet the fitted curves for various fabrication processes accidentally pass through them.

We found it impossible to find a single curve which would fit all the data for the same fabrication process. This clearly shows the existence of a degraded layer of SiO$_2$. The thick SiO$_2$ films are composed of two layers with different densities; a low density (2.37-2.40 g/cm$^3$) structural transition layer next to the Si substrate and an upper layer with bulk SiO$_2$ density (2.55-2.60 g/cm$^3$). Thinner films consist of the structural transition layer only. The densities of the structural transition layer agree with the value 2.45 g/cm$^3$ for films 1.59-5.57 nm thick obtained with a nuclear reaction method using dry $^18$O gas. In thick films, the thickness of the structural transition layer films is 7.8 nm. This thickness coincides with the thickness at which a rapid decrease of the breakdown charge ($Q_{bd}$) occurs in constant current time dependent dielectric breakdown (TDDB) measurements.

In order to investigate stress in the silicon substrate around the SiO$_2$/Si interface. The half width at half maximum (HWHM) of the x-ray rocking curves of all the samples are shown in Fig. 2. We find that in the thinnest SiO$_2$ films, the HWHM value on the low angle side is far from the expected value (dashed line). The origin of the broadness at the low angle side is a lattice expansion in the [311] direction. The $d/d$ is roughly estimated to be the order of $10^{-3}-10^{-4}$. Thus, the degraded SiO$_2$ layer is indeed stressed. This may also be the reason for the existence of the degraded layer of SiO$_2$.

Reference

PEROVSKITE-TYPE SmAlO₃: ANALYSIS OF TWINNING ORIGINATED BY VERY SLIGHT DEFORMATION FROM AN IDEAL CUBIC LATTICE.

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3) Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980-77, Japan

Introduction

A series of crystalline phases of RAIO₃(R=rare earth elements from La through Lu) crystallize in perovskite-type structures with slightly deformed lattices from the ideal cubic structure. RAIO₃ with lower atomic numbers show trigonal symmetry with rhombohedral lattices, and those for higher atomic numbers are orthorhombic. CeAlO₃ exceptionally takes tetragonal system. Most of phases of RAIO₃ have twinned textures which are supposed to be due to a phase transition. Deformation from the ideal cubic to rhombohedral or orthorhombic lattice of each phase is smaller in the phase with smaller atomic number. Thus, the values of a and c of orthorhombic SmAlO₃ are very close to each other because of the smallest deformation in the orthorhombic lattices. Therefore, it is very difficult to decide for SmAlO₃ to be orthorhombic and to analyze twin structure. The analysis of such a twinning will be important in order to know the actual physical properties of the crystals, and also to predict its higher temperature structure. In this investigation, the parallel property of synchrotron radiation (SR) was applied to analyze twinning of SmAlO₃, and the results were compared with those obtained by conventional laboratory X-ray source.

Experiments

Single crystals used in this experiment were synthesized by flux method and crystals are almost cube with 10μm in edge. Single crystal diffractometer of BL-10A at KEK-PF using wave length 0.70Å monochromatized by Si(111) and conventional four-circle diffractometer using 0.71Å (MoKα) monochromatized by pyrolytic graphite were used in this experiment. In BL-10A, the distances from monochromator to specimen and specimen to detector are 250cm and 50.2cm, respectively. The front slit(SL2) which is 65.2cm apart from the specimen is 0.5mmφ, and that the rear slit(SL3) which is just before the detector is 10mmφ which is large enough to detect both reflections of twinned domains. Schematic diagram of reciprocal lattices of twinned crystal is shown in Fig.1. The numbers I and II denote the first and the second domains, respectively. The b axes are common in both twin domains. If we scan along the c-axis using conventional four-circle diffractometer, the 008 reflection gives a profile shown by A in Fig.2. However, scanned result by SR with the same specimen and the same reflection as used above gives a doublet shown in Fig.3. The peaks of lower and upper angles correspond to 008 of the first domain and 800 of the second domain, respectively. If we put this result on the former profile as shown in B of Fig.2, the split of 008 and 800 is much smaller than the split of Kα₁ and Kα₂. On the other hand, 0 12 0 reflections are not splitted as shown in Fig.4.

Results and discussion

The results of a=5.295(2)Å and c=5.279(2)Å were obtained by independently analyzing each lattice of twin domains by SR X-ray sources. As a result, obtained twin relationship between two domains are

\[
\begin{pmatrix}
a \\
b \\
c \\
\end{pmatrix} = \begin{pmatrix}
0.0024 & 0.0005 & 1.0041 \\
-0.0001 & 0.9990 & -0.0004 \\
-0.9980 & -0.0004 & -0.0007
\end{pmatrix}
\]

Comparing with these results, the lattice constants obtained by a four-circle single crystal goniometer and powder diffractometer using laboratory X-ray sources were 5.286(1)Å for both a and c, and b=7.475(1)Å. Thus, it will be worthy to note the excellent diffraction peak resolution by SR X-ray sources. For the structure analysis, however, some improvement will be needed for the collection of integrated intensities from the independent domain.

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2) M.Tanaka et al., J.Alloys & Comp., (1993)1271,
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A STUDY OF PARTIAL PATTERSON USING X-RAY ANOMALOUS DISPERSION
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• Fachrichtung Kristallographie, der Universität
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Introduction
An exact structure analysis of superlattice materials has been
still difficult problem because of extremely weak intensities of
superlattice reflections. The method proposed by Soejima and
Fischer1) has been applied to superstructure determination of
PbZrO₃ using X-ray anomalous dispersion at PbL₂ and ZrK
absorption edges. Intensities of several superlattice
reflections were observed as a
function of incident energy and the result indicated that Zr
atom has displacement which contributes to the superlattice
along c direction2). This
contradicts the models reported before3, 4, 5, 6).

Experimental
To determine the superstructure which can well explain the
energy dependence of super-
lattice reflections at
absorption edges, the data
collections were made near the
edges within $\sin \theta / \lambda \approx 0.7$ Å⁻¹,
assuming lower symmetry of space
group reported in the refer-
ences. After the collections
for monitor intensity,
absorption and Lorentz factor,
structure factors were obtained.
The program to search a
reasonable atomic coordinates in
minimum R-factor has been coded
in FORTLAN.

Results and discussions
As a result, the minimum R-
factor was found to be 0.197.
The superstructure is
illustrated in the figure(a),
comparing with those given by
Jona et al.3), and Glazer et
al.6), shown in (b) and (c),
respectively. Though the result
in the present work does not
satisfy us with large R-factor,
it is emphasized that the model
in the figure (a) is an possible
structure to explain the effect
of anomalous dispersion on the
superlattice reflections.

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(1992)
Soc.Jpn., 51 2635-2640 (1992)
6) Glazer A.M., Roleder K. and Dec J. Acta
Single crystals of superhydrous phase F were synthesized by Kanzaki (1) using a multi-anvil high pressure device. The effect of pressure on phase F is of primary importance for its possible occurrence in the subducting slab at transition zone depths (410-660 km) of the earth's mantle but its true unit cell and structure have remained unknown to date. This paper reports the results of our structural study at room pressure with the synchrotron radiation on a small single crystal of phase F synthesized at 17 GPa and 1000 °C.

Two crystals (specimens #1 and #2) were selected and were identified as phase F by their chemical composition and X-ray diffraction patterns obtained with a Gandolfi camera. Since these crystals were of about 30 μm in diameter and were too small for characterization with a conventional X-ray source, they were examined with the synchrotron radiation using the vertical type four-circle diffractometer at the beam line BL-10A. From the results of peak search procedure, crystal #1 proved to be twinned. Crystal #2 was untwinned and used for X-ray measurement. A set of X-ray diffraction intensities up to sinθ/λ=0.71 were measured with the monochromatized synchrotron radiation of the wave length of 0.7065 Å by the Si(111). The results of X-ray measurement are summarized in Table 1. The crystal structure was determined based on the three-dimensional Patterson synthesis and was refined with the full-matrix least-squares method. Final agreement factors for 85 F0's used were R=11.5% and wR=12.3%. This high value of R reflects a problem associated with the X-ray diffraction intensity measurement on a very small crystal of low degree of crystallinity. The structure is based on the ABCBAC type doubled cubic closest packing arrangement of oxygens. Mean bond distances are 2.07(8) Å, 2.08(8) Å and 2.16(8) Å for (Mg, Si)O6 octahedra and 1.89(7) Å and 1.79(4) Å for SiO4 tetrahedra.

Table 1. Crystallographic data for phase F

<table>
<thead>
<tr>
<th>Size of the specimen</th>
<th>30x24x18 μm (specimen #2)</th>
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</thead>
<tbody>
<tr>
<td>Unit cell parameters</td>
<td>Hexagonal, P63cm</td>
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<tr>
<td></td>
<td>a=5.073(3) Å, c=14.013(9) Å, V=312.3(5) Å³</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>Mg_{3.35}Si_{5.51}H_{7.26}O_{18}, Z=1</td>
</tr>
<tr>
<td></td>
<td>(the difference of the total weight is ascribed to H₂O)</td>
</tr>
<tr>
<td>No. of independent I₀ measured (sinθ/λ &lt;0.71)</td>
<td>I₀&gt;3.0 o I₀: 118, No. of I₀ used: 85</td>
</tr>
<tr>
<td></td>
<td>R=11.5 %, wR=12.3 %</td>
</tr>
</tbody>
</table>

References

STRUCTURE ANALYSIS AND DIFFERENCE ELECTRON DENSITY OF CaFeO₃ CONTAINING Fe⁴⁺

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Introduction

After the excitement of high-Tc superconductor since 1986¹, perovskite and perovskite-related oxides containing transition metal cation have been drawn special attention.

The octahedrally coordinated Fe⁴⁺ in the high spin state having one e_g electron is expected to provide the cooperative Jahn–Teller effect. A strong electron–phonon coupling is anticipated in the oxides containing Fe⁴⁺. CaFeO₃ and SrFeO₃ are known as oxides containing octahedrally coordinated Fe⁴⁺, and which are having simplest chemical composition. The Mössbauer spectrum of CaFeO₃² suggests that Fe⁴⁺ in CaFeO₃ exhibits a charge disproportionation reaction into Fe³⁺ and Fe⁵⁺ below 290K in contrast to that in SrFeO₃ having its valence state in decreasing temperature down to 4.2K.

All reports on CaFeO₃ were using a powder sample because of difficulties in synthesizing of single crystal. We have prepared a single crystal under high oxygen partial pressure and examined the crystal structure and the difference electron density of CaFeO₃ at room temperature(293K) and 113K, which is enough low temperature to occur the charge disproportionation reaction of Fe⁴⁺.

Experimental

A single crystal of CaFeO₃ whose size is 60 x 60 x 50 μm³ was synthesized utilizing a reaction under high oxygen partial pressure applying 2 GPa and 1273K by means of a piston cylindrical device. Collection of diffraction intensities was performed using the vertical–type four–circle diffractometer at the BL-10A station with the monochromated synchrotron radiation of λ=0.6985Å by monolithic Si(111) crystal. A cold nitrogen–gas blower was employed in the low temperature experiments. A set of intensities up to sinθ/λ = 1.01Å⁻¹ were measured at the ω–2θ scan mode. Isotropic thermal treatment was applied for all atoms. Final R–factor values were 0.033 and 0.036 at 293K and 113K respectively. The electron density maps were obtained using the difference Fourier method.

Results and Discussion

CaFeO₃ has a tetragonal unit cell in which contains four formula units and whose dimensions are: a=5.348(1)Å, c=7.573(1)Å and a=5.341(1)Å, c=7.559(1)Å at 293K and 113K, respectively. The crystal structure of CaFeO₃ at 293K and 113K has been determined as an orthorhombic perovskite structure (Pbnm(No.62)) having orthorhombic symmetry. No structural change at 113K from 293K was observed. The observed Fe⁴⁺–O distances is similar to that of SrFeO₃. No cooperative Jahn–Teller distortion of Fe⁴⁺O₆ octahedra is observed. Fe–O–Fe angle of ca. 160° in CaFeO₃, in contrast to that of 180° in SrFeO₃, might change the Fe–O–Fe interaction and cause the charge disproportionation reaction.

The difference electron density map on the (110) plane at 293K is shown in Fig.1. A positive peak with 1.2eÅ⁻³ height observed at the middle of Fe–O bonds suggests its strong covalency.

References


Fig.1. The (110) difference–Fourier map of CaFeO₃ at 293K. Contour lines are drawn at intervals of 0.2eÅ⁻³; positive contour are solid; negative contours are dashed.
XANES Study on Pt L-Edges in Transition-Metal Pt Alloys

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INTRODUCTION

The magneto-optical sum rules proposed by Carra et al.[1] of magnetic circular X-ray dichroism (MCXD) are powerful tool for studying magnetism because of a possibility of direct separation of orbital and spin magnetic moments. As we apply the MCXD data to the sum rules, several difficulties in actual analysis restrict the reliability of result. In particular, estimation of white-line intensity is a serious problem. Even at the L-edge of transition metals or rare-earth elements, it is generally difficult to do the estimation. It leads to the uncertainty of hole population in valence d-bands. In this report, we present the procedure to estimate the integrated intensity of white-line in the Pt L-edge XANES spectra. The Pt L-edges have also attracted interest in connection with the anomalous feature in the white-line spectra.

EXPERIMENTAL

The TM-Pt (TM=Cr, Mn, Fe and Co) alloys were prepared by arc-melting method under an Ar atmosphere. The Cu$_2$Au-ordered phase was realized by a suitable thermal treatment and verified by X-ray powder diffraction. The XANES spectrum was measured on the beamline of 10B equipped with a Si(311) channel-cut monochromator.

RESULTS AND DISCUSSION

Figure 1 shows the normalized XANES spectrum at the Pt $L_2$- and $L_3$-edges in the MnPt$_3$ compound. For an estimation of the integrated intensity of white-line, we adopted the standard procedure composed of the following two steps: First, to rescale the spectrum, the $L_2$ XANES spectrum is multiplied by a factor of 2.52, which is defined as a rescaling factor, so as to coincide with the $L_3$ XANES spectrum at 40 eV above the aligned edges. The present value deviates significantly from the factor of 2.22 in pure Pt[2].

Second, an arctangent curve as a continuum background was subtracted from the normalized spectrum. Actually, the observed XANES spectrum can be well reproduced by the superposition of a resonant absorption with a Lorentzian line shape and a continuous one represented by the arctangent curve, as shown in Fig.2. The white-line profile decomposed by a Lorentzian with FWHM~7 eV gives an adequate amount of integrated intensity. The branching ratio is evaluated to be $I(L_3)/[I(L_2)+I(L_3)]=0.82\pm0.02$ in the series. The observed ratio indicates a deviation from the statistical value (2/3=0.67) of the atomic branching ratio. Although such a deviation has been interpreted as the dominant d$_{sp}$-character of the 5d-states due to a large spin-orbit interaction,[3] it is inconsistent with the results of MCXD that Pt 5d-bands possess no orbital moment in the MnPt$_3$ compound.[4]

References


![Fig.1. XANES spectra at the $L_2$- (left) and $L_3$-edges (right) in the MnPt$_3$ compound.](image1.png)

![Fig.2. The XANES spectrum at the Pt $L_3$-edge. The broken line shows an arctangent curve.](image2.png)
INTRODUCTION

X-ray absorption spectrum at the Fe K-edge in various Fe compounds generally exhibits the so-called pre-peak structure interpreted as the 1s→3d dipole-allowed transitions[1-3]. This characteristic structure has attracted interest in connection with the electronic states of Fe$^{2+}$ or Fe$^{3+}$ ions lying at tetrahedral ($T_d$) or octahedral ($O_h$) environment. Since the ferrimagnetism in Fe-oxides is ruled by the Fe-ions, the information about site contribution to the spectrum is useful to understand the local environment of the Fe ions for the magnetic ordering. In this report, XANES spectrum at the Fe K-edge in several ferrimagnetic Fe-oxides is presented.

EXPERIMENTAL

The following Fe-oxides were prepared: YIG and Ho-IG (a notation of Fe ion configuration is $[3\text{Fe}^{2+}]_{T_d}[2\text{Fe}^{3+}]_{O_h}\text{O}^{2-}$) with garnet structure, magnetite ($[\text{Fe}^{3+}]_{T_d}[\text{Fe}^{2+}]+{\text{Fe}}^{3+}]_{O_h}\text{O}^{2-}$) and Li-ferrite ($[\text{Fe}^{3+}]_{T_d}[1.5\text{Fe}^{2+}]_{O_h}\text{O}^{2-}$) with inverse spinel structure, maghemite ($\gamma$-Fe$_2$O$_3$) with spinel structure, Ba-ferrite ($\alpha$-Fe$_2$O$_3$) with magneto-plumbite structure, and hematite ($\alpha$-Fe$_2$O$_3$) with corundum structure. XANES spectrum was recorded on the beam-line 10B equipped with a Si(311) channel-cut monochromator. The energy calibration was carefully made at the shoulder of K-edge in Cu foil.

RESULTS AND DISCUSSION

The Fe K-edge normalized XANES ($\mu\epsilon$) spectra in the Fe-oxides and pure Fe are shown in Fig.1. The pre-peak structure is commonly observed at the energy specified as 7.11±0.001 keV for the present Fe-oxides. In pure Fe, a bump on the lower energy side is just located on the position of the pre-peak, which suggests that these structures should be ascribed to the similar origin and the difference results from the difference of electronic states, i.e., metal and insulator. Moreover, it seems that the pre-peak structure is not sensitive to chemical structure and Fe ion configuration, because it shows no remarkable variation except for the intensity.

On the other hand, the main absorption shows a variety of structure; that is, garnet exhibits a flat crest on the higher energy side, the other oxides yield a white-line like enhanced absorption, whose position and structure vary with the coordination number of ligand and the degree of distortion from the inversion symmetry[3].

From a comparison between garnet and inverse spinel about Fe-ion configuration and magnetic ordering, one can conclude that the pre-peak structure is completely originated in the Fe$^{2+}$ ion lying at the $T_d$-sites, and the main absorption is mainly ascribed to the Fe$^{3+}$ and/or Fe$^{3+}$ ion lying at the $O_h$-sites. The pre-peak structure can be interpreted as the 1s→3d dipole transitions allowed at a $T_d$-site by the mixing between Fe 3d-4p orbitals through the hybridization with O 2p orbitals[4]. However, several questions remain for the spectrum: Chemical shift of about 10 eV between the pre-peak structure and the main absorption, the white-line like enhanced absorption in spinel, the flat crest in garnet, and so on.

References


Fig.1. XANES spectra at the Fe K-edge in the Fe-oxides and pure Fe.
Effect of Metal Atoms in Sodalite Cage on the Coordination Number for Metal Clusters Supported on NaY Zeolite

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Introduction

Metal clusters supported on zeolites attract much attention due to very unique changes in physicochemical properties such as the electronic structure, adsorption and catalytic activity as the cluster size decreases below 1 nm. The small metal cluster size in zeolite can be estimated from the coordination number (CN) obtained using curve fitting of the extended x-ray absorption fine structure (EXAFS). However, recent theoretical studies pointed out that the EXAFS curve fitting can underestimate the CN for very small metal clusters as much as 30%, due to static disorder and vibration anharmonicity coming from a large fraction of the surface atoms. More recently, we have compared the CN from EXAFS for small metal clusters entrapped inside the supercage of NaY zeolite with that derived from the number of the metal atoms per cluster using a xenon adsorption technique. Both techniques indicated similar precision. However, the CN from EXAFS was approximately 30% less than that from the xenon adsorption, indicating a significant difference in their accuracy.

The present work was undertaken in order to evaluate the accuracy of the xenon adsorption technique and EXAFS curve fitting method. To this end, we have measured EXAFS and xenon adsorption for Pt/NaY and Pt/alumina samples. The results are discussed in this report with the location of metal atoms determined using a hydrogen chemisorption difference between room temperature and high temperatures.

Experimental

The preparation of Pt clusters supported on NaY zeolite (Pt/NaY) is reported elsewhere. Hydrogen chemisorption on the Pt cluster was performed at both 296 K and 473 K, using conventional volumetic adsorption apparatus. X-ray absorption was measured at the Pt LIII edge at room temperature with a self-supporting sample wafer placed in an in-situ XAFS cell using Beam Line 10B. The XAFS spectrum thus obtained was analyzed with UWXAFS2 and Eff5 codes. Static disorder and vibration anharmonicity have been taken into account in the data analysis.

Results and Discussion

Results of the H chemisorption measurement and the CN from XAFS curve fitting are shown in Table 1. The CN of the Pt/NaY is much smaller than the average coordination number, n, calculated from the xenon adsorption measurement using space-filling models. The H chemisorption on the Pt/NaY increased by 12 - 13% while the sample was heated at 473 K for 2 h and subsequently cooled down to 296 K. The H-chemisorption increase was found to come from diffusion of H2 into the sodalite cage containing a Pt cluster followed by the chemisorption on the cluster. This has been confirmed with H chemisorption on Pt clusters supported inside the sodalite cages and Pt clusters supported on γ-Al2O3. The preparation of a Pt/NaY sample with Pt clusters mostly inside the sodalite cage is described elsewhere. EXAFS data for the Pt/NaY indicate that the cluster in the sodalite cage compromises of 4 to 6 Pt atoms. The Pt clusters chemisorbed very little H at 296 K, but the chemisorption increased markedly at 473 K. The Pt/Al2O3 did not indicate any increase in the H chemisorption upon the heating. The chemisorption increase upon heating is not due to adsorption of H2 inside the sodalite cage, since the NaY zeolite without Pt cluster does not adsorb H2 at 473 K.

The H chemisorption data in Table 1 indicate that a Pt/NaY sample, which was thought to have all Pt clusters inside the supercages, contains ca. 10% Pt atoms inside the sodalite cages. Temperature programmed desorption of H2 led to the same conclusion. Xenon adsorption did not occur on the Pt clusters located inside the sodalite cages.

In conclusion, the xenon adsorption can probe only the metal clusters located inside the supercage while EXAFS does all the clusters located inside both the supercages and the sodalite cages. This information resolves the discrepancy between the xenon adsorption technique and EXAFS, and more importantly, confirms experimentally the accuracy of EXAFS for the measurement of the CN for very small metal clusters consisting of 40 - 50 atoms. The CN from EXAFS for small metal clusters should be very accurate if the static disorder and anharmonicity are fully taken into account as in the present work.

Table 1 Hydrogen chemisorption and the Coordination Number from EXAFS for Pt/NaY

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNa</th>
<th>nb</th>
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<th>%d</th>
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<tr>
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<td>---</td>
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</table>

a from XAFS curve fit, b from xenon adsorption method, c total hydrogen chemisorption per Pt atom, d percent increase of hydrogen chemisorption at 473 K and relative to that at 296 K.

References

INTRODUCTION

Pt-Mo bimetallic catalysts have been shown to exhibit higher activities in the reactions such as hydrogenation of alkanes [1,2], dehydrogenation of cyclohexane [3] and CO hydrogenation than Mo or Pt alone. Yet, the structure of the catalysts has not been studied much. There has been a study on Mo deposited epitaxially on Pt clusters when Mo(CO)₅ vapor was deposited on preformed Pt/Y-zeolite [4]. We have performed XAFS study of alumina-supported (PtMo) catalysts in order to elucidate the structure of the catalysts and their relationship with the activity of CO hydrogenation reaction.

EXPERIMENTAL

Three kinds of samples were prepared by incipient wetness impregnation with the variation of the order of Mo and Pt loading onto the support. For Pt-Mo/Al₂O₃, Pt/Y-Al₂O₃ was prepared with H₂PtCl₆·6H₂O, dried at 380K for 5h, calcined at 770K for 12h, and then the calcined sample impregnated again with (N₁₄)₅Mo₇O₄⁺₄H₂O with the 1:1 atomic ratio of Mo to Pt. The resulting bimetallic catalysts were then treated by the same drying and calcination procedure. Mo-Pt/Al₂O₃ was prepared by adding Mo first and Mo+Pt/Al₂O₃ by a coimpregnation.

For XAFS measurements, the prepared catalysts were palletized into disc shape and sealed by a flame in a cell with a Kapton window under the same gas as for their pre-treatments. The spectra were taken for K-edges of Mo and L₃-edge of Pt at beamline 10B of Photon Factory in Tsukuba, Japan. The collected data were analyzed by R-space method based on a standard analysis procedure.

RESULTS AND DISCUSSION

EXAFS showed unequivocally the formation of bimetallic bond between Mo and Pt for all bimetallic catalysts. The variation of reduction temperature was shown to affect the extent of the bimetal formation. Based on the relative magnitudes of coordination numbers of metals, it was concluded that Mo segregates to the surface irrespective of the sequence of the impregnation. The Mo-Mo distance became longer than the one found in monometallic catalysts treated under same conditions. Platinum concentrated in the core region of the bimetallic particles showed the normal Pt-Pt distance. Such a structure was also confirmed by spectra of air-opened sample, which showed oxidized Mo state but nearly same Pt state as in in-situ samples.

In Mo/Al₂O₃, a strong interaction of molybdenum with the support was identified with EXAFS and XANES. The strong interaction between molybdenum and the support alumina was also shown in all the bimetallic catalysts.

The general structural feature of all bimetallic catalysts prepared in this study by different sequence of impregnation is identical to that of Pt-Mo/Y-zeolite prepared by vapor deposition [4]. The formation of this bimetallic particles appears to be a factor responsible for the observed synergy between Pt and Mo in CO hydrogenation.

| Table 1. Coordination numbers of the bimetallic catalyst |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | N₁₄MoMoMoMoMo | N₁₄MoMoMoMoPt  | N₁₄MoMoPtPtPt  | N₁₄PtPtPtPtPt  |
| Pt-Mo           | 6.9            | 0.6            | 1.6            | 1.2            |
| Mo-Pt           | 6.8            | 0.7            | 2.4            | 1.7            |
| Mo+Pt           | 6.5            | 0.06           | 1.1            | 0.5            |

REFERENCES
CRYSTAL STRUCTURE OF ALKOXY SUBSTITUTED IRON OXYCHLORIDE

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Introduction
In synthetic chemistry point of view, the surface modification of FeOCl by intercalating the organic molecules or substituting them with chlorides would be a potential way of preparing various new 2-dimensional organic derivatives of FeOCl, and their detailed crystal structures are prerequisite for understanding the physical and chemical properties. However it is very difficult to obtain single crystals of such organic derivatives, since they are easily broken into fine powders due to the considerable elastic deformation during the intercalation and substitution reactions. In this regard, X-ray absorption spectroscopy is a useful way of determining the structure of such materials due to its sensitivity to the local environment around specific atoms, irrespective of crystallinity or dimensionality of solids. In the present work, we report, for the first time, the detailed structural changes around the iron of an alkoxy substituted FeOCl by using the Fe K-edge XAS.

Experimental
X-ray absorption measurements were carried out by using the EXAFS facilities installed at the beam line 10B of the Photon Factory, the National Laboratory for High Energy Physics, operated at 2.5 GeV with ca. 260 ~ 370 mA of stored current. All the data were recorded in a transmission mode at room temperature, using a Si(311) channel-cut monochromator. Intensities of the incident and transmitted beams were measured.

Result and Discussion.
EXAFS spectra in the range of ~ 2.5 Å⁻¹ < k < ~14 Å⁻¹, were Fourier-transformed as shown in Figure 1. It should be noted that the EXAFS spectra for alkoxy-substituents and γ-FeOOH are very similar in shape except for FeOCl. The peaks at ~1.5 Å and ~2 Å can be assigned, respectively, to the Fe-O bonding pair and the Fe-Cl one. The third-shell peaks in the region of 2.4Å < R < 3.2Å are originated by the nearest Fe--Fe interactions including the Fe--Fe ones which correspond to b-axis parameter. The small peaks beyond 3.2 Å could not be simply assigned due to complex contributions by various interactions with oxygen, chlorine, and iron atoms. And it is clearly seen that the first-shell peak by the Fe-O interaction gradually increases with the simultaneous decrease of the second-shell peak corresponding to the Fe-Cl interaction as the substitution ratio increases. Such experimental results could be adequately explained by the fact that the replacement of the chloride of FeOCl by alkoxy group enhances the first-shell peak in the FTs due to the introduction of oxygen scatterer in this region.

The analysis of EXAFS data for the methoxy substituent has been performed. Under an assumption that a- and b-cell parameters as well as the space group are the same as FeOCl, the backscattering amplitude and phase shift functions for all paths were calculated by FEFF code, using c-axis cell parameter (10.00 Å) by our powder XRD data. The fitted structural parameters were used again to determine the new a- and b-cell parameters and fractional coordinates on Pmnn space group. The curve fitting was carried out again, using backscattering amplitude and phase shift functions newly calculated on the basis of the modified structural data. This analytical procedure was repeated until the fitting results became self-consistent. According to the fitting result, the Fe-O bond distances in FeOCl0.13(OCH3)0.87 become similar one another, resulting in more regular octahedral symmetry around the iron compared to FeOCl. In addition, the Fe--Fe(b) bond distance is fitted to be equal to the nearest Fe--Fe(1) one at 3.09 Å, which is normally observed in iron oxides and alkoxy complexes with an edge-shared octahedral linkage. Three different bond distances within the octahedron become similar one another upon the substitution, and furthermore 89.2° of the bond angle Cl-Fe-Cl in FeOCl increases to 106° (CH3O-Fe-OCH3) in the methoxy derivative. The bond angles of O(1)-Fe-O(1) and O(2)-Fe-O(2) change from 152° to 154° and from 103° to 97°, respectively. These changes represent that the local symmetry around central iron atom of substituents is higher than that of FeOCl.

Figure 1 Fourier transforms of experimental k²-weighted Fe K-edge EXAFS spectra of (a) FeOCl, (b) ethoxy substituent, (c) methoxy substituent and (d) γ-FeOOH

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References
EXAFS STUDY ON THE OSMIUM COMPOUNDS WITH PEROVSKITE STRUCTURE

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Introduction

The complex perovskites, SrLaScOsO$_6$, SrScOsO$_6$, SrCaOsO$_6$, and SrLiOsO$_6$, have been prepared by conventional solid state route and their X-ray absorption spectroscopic studies have been performed on the Os K$_{III}$-edge. Quantitative EXAFS analysis involving more distant shells beyond the first coordination one becomes very complicated since the total number of adjustable structural parameters increases, and the multiple scattering (MS) paths must be often considered in addition to the single scattering (SS) ones. Therefore, in order to obtain the physically meaningful parameters, some of the variables must be constrained at reasonable values for the higher-order shells and the multiple scattering paths. In this regard, it is of great interest that the present osmium perovskite compounds might be good model compounds, for which the reliability of EXAFS analysis with some constrained parameters can be tested. In this work, comparisons between EXAFS spectra for the present four perovskite compounds are expected to be able to reveal how the structural distortion and MS effects contribute to EXAFS spectra.

Experimental

Polycrystalline samples of A$_2$BoO$_6$ (A = Sr; B = Li, Ca, and Sc) and SrLaScOsO$_6$ were prepared by calcining stoichiometric mixture of SrO, La$_2$O, Li$_2$O, CaO, Sc$_2$O$_3$, and Os metal. For the synthesis of Sr$_2$LiOsO$_6$, small excess amount (5%) of Li$_2$O was used to compensate for the loss during the high temperature treatment. X-ray absorption experiments were carried out at the beam line 10B of Photon Factory, National Laboratory for High Energy Physics (KEK-PF). All the data were recorded in a transmission mode at room temperature using Si(311) channel-cut monochromator.

Results and Discussion

Fourier transforms (FTs) of the k$^3$-weighted Os K$_{III}$-edge EXAFS spectra in the range of $-3 \, \text{Å}^{-1} \leq k \leq -14 \, \text{Å}^{-1}$, and their best fits are shown in Figure 1. In order to determine the structural parameters from the Os K$_{III}$-edge EXAFS spectra, the nonlinear curve fittings were carried out in R space of FTs. The first peak in $-1 \, \text{Å} \leq R \leq -2 \, \text{Å}$ of the FTs is attributed to backscattering from the octahedrally coordinated oxygens. Its large intensity and high symmetry might imply undistorted osmium octahedron. The Os-O bond distances for each oxidation state of Os$^{IV}$, Os$^{V}$, Os$^{VI}$, and Os$^{VII}$ are 1.961, 1.948, 1.923, and 1.883 Å, respectively, which represent a linear variation against the oxidation states of osmium. In addition, the variation of Debye-Waller (DW) factors for Os-O bond is proportional to the bond distance. DW factor reflects the mean square relative displacement (MSRD) of the equilibrium of the Os-O bond distance due to the vibration and/or the static disorder. Therefore a larger bond distance results in a larger DW factor due to the stronger thermal vibration$^{15}$, and the present result is in good agreement with this expectation. On the other hand, the peaks in $-2.5 \, \text{Å} \leq R \leq -4 \, \text{Å}$ of FTs, those which show different patterns for each compound, are attributed to backscattering from A site cations and the competing B site ones as well as MS contributions along B-O-B path and within OsO$_6$ octahedron. It is seen from Figure 1 that the peaks in the higher R range ($-2 \, \text{Å} < R < -4 \, \text{Å}$) of the spectra for Sr$_2$LiOsO$_6$ and Sr$_2$CaOsO$_6$ are considerably reduced, compared with those for the others. In case of Sr$_2$LiOsO$_6$, these reduced amplitudes are mainly due to lowered backscattering of the third nearest neighbor, Li (Z=3), but in case of Sr$_2$CaOsO$_6$, such an phenomenon can be explained by the abnormally large DW factor for single scattering contribution from stronitrium atoms in the second shell, which is caused by the structural distortion from cubic symmetry. It should also be noted that collinear double and triple scatterings in the linear chain of Os-O-Ca for Sr$_2$CaOsO$_6$ are less than those in the linear chain of Os-O-Sc for Sr$_2$ScOsO$_6$, despite that almost the same backscattering amplitude of Ca and Sc would be expected to give similar MS contributions. This difference suggests that the crystal structure of Sr$_2$CaOsO$_6$ is also a little distorted from the cubic one, thereby decreasing the Os-O-Ca bond angle. Therefore, combined with X-ray powder diffraction, the results of EXAFS analyses indicate that the crystal structure of Sr$_2$CaOsO$_6$ is rhombohedral.

Acknowledgment

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References

X-RAY ABSORPTION SPECTROSCOPIC EVIDENCE ON THE PARTIAL FORMATION OF Cu⁺ IN THE SUPERCONDUCTING La₂CuO₄₀.₈

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Introduction

X-ray absorption spectroscopic study has been carried out on the Cu K-edge in the superconducting La₂CuO₄₀.₈ samples, which were prepared by oxidizing La₂CuO₄₀₀ electrochemically or chemically with KMnO₄, in order to examine the orbital character of the charge carrier introduced into CuO₂ layer by the excess oxygen incorporation. Since the inner shell absorption measurements have provided valuable information on the local orbital character of the carriers in hole-doped cuprates, X-ray absorption spectroscopy (XAS) has been intensively studied at the Cu K-edge. However, earlier studies on the Cu K-edge XANES spectra for La₂CuO₄-related compounds, could not reach at the general consensus for the spectral interpretation due to the absence of adequate Cu⁺-reference spectrum as well as its complexity. In the present work, we present the clear spectroscopic differences between the nonsuperconducting phase and superconducting one by means of the Cu K-edge XAS. And these differences are for the first time suggested to be attributed to the partial formation of Cu⁺ in superconducting phase through the comparison with the Cu K-edge spectra for the chemically well-defined Cu⁺ references.

Experimental

The undoped La₂CuO₄ was prepared by a conventional solid state reaction. For the doped La₂CuO₄₀.₈, electrochemical and chemical oxidation experiments have been carried out under the conditions for obtaining the maximum value of δ. The X-ray absorption experiments were carried out at the beam line 10B of the Photon Factory in Tsukuba, operated at 2.5 GeV, 260~370mA.

Results and Discussion

EXAFS analyses: The structural parameters are summarized in Table 1. It is worthy to note here that the chemical oxidation of La₂CuO₄ by KMnO₄ could induce the same doping effect as the electrochemical one. EXAFS analyses clearly show that the axial Cu-O(2) bond distance is significantly decreased by the oxidation.

XANES analyses: Figure 1 (a) represents the Cu K-edge XANES spectra for the present compounds together with La₂Li₀.₅Cu₀.₅O₄ and LaCuO₂ for comparison. It is obvious that there is an overall spectral shift of about 0.5 eV to a higher energy side after the electrochemical or chemical oxidation. In addition to the overall peak shift, we could observe a remarkable difference in the Cu K-edge XANES spectra. Namely, an additional shoulder (A’) was appeared reproducibly at ~8986 eV for the oxidized compounds. This difference can be more clearly seen in the corresponding second-derivatives of Figure 1 (b). The peak A’ has been generally accepted as a 1s→4pₓ transition accompanied by a shake-down process through the ligand to metal Cu (3d hole) charge-transfer (LMCT). On the other hand, our previous study on the Cu K-edge of the chemically well defined Cu⁺-compounds would give us some clues about the origin of A’ peak. We have pointed out that the enhanced attractive potential of trivalent copper favors the charge transfer from oxygen ligand to copper, so that the shake-down transition is expected to appear at somewhat higher energy side. Moreover, La₂Li₀.₅Cu₀.₅O₄ exhibits the splitting (A and A’) of transition by the shake-down process, which corresponds to the transitions to the final states of 1s→3d² L¹⁻¹ 4px and 1s→3d² L¹⁻¹ 4py, respectively. It can be seen from Figure 1 that the peak position of A’ for the present oxidized La₂CuO₄₀.₈ is well consistent with that of the peak A’ for La₂Li₀.₅Cu₀.₅O₄. It is therefore concluded that the doping with excess oxygen gives rise to a partial formation of trivalent copper, resulting in the stronger covalency in the Cu-O σ bonds with an increase of hole density in the Cu-O planes.

Table 1. Fitted structural parameters to the Cu K-edge EXAFS spectra.

<table>
<thead>
<tr>
<th>Atom</th>
<th>as-sintered</th>
<th>electrochemically oxidized</th>
<th>chemically oxidized</th>
</tr>
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<tbody>
<tr>
<td>La₂CuO₄₀₀</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R/A</td>
<td>σ² + Δ²</td>
<td>R/A</td>
<td>R/A</td>
</tr>
<tr>
<td>4 O(1)</td>
<td>1.90, 0.002</td>
<td>1.89, 0.004</td>
<td>1.89, 0.006</td>
</tr>
<tr>
<td>2 O(2)</td>
<td>2.41, 0.011</td>
<td>2.34, 0.010</td>
<td>2.33, 0.009</td>
</tr>
</tbody>
</table>

Figure 1. (a) Cu K-edge XANES spectra for La₂CuO₄ as sintered (—), electrochemically (---) and chemically (—-) oxidized La₂CuO₄₀.₈ together with Cu⁺-reference compounds, La₂Li₀.₅Cu₀.₅O₄ (—) and LaCuO₂ (---), and (b) their second derivatives.

Acknowledgment

This work was in part supported by the KOSEF (92-25-00-02) and the MOST for the high Tc superconductivity research (1994).

References

X-RAY ABSORPTION SPECTROSCOPIC STUDIES ON THE COPPER COMPLEXES INTERCALATED IN 2-DIMENSIONAL LAYERED SILICATE

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Introduction
There has been an increased interest in the coordination chemistry of polyaza macrocycles including cyclam and their derivatives due to their significant catalytic activities in many reactions. And in layered aluminosilicate such as montmorillonite, the interlayer cations can be easily ion-exchanged with a variety of organic and inorganic cations. It is therefore expected that the intercalation will alter electronic configuration, mobility, and orientation of the complex cation in the interlayer surface. Therefore, the characterization of chemical bonding state as well as local structure of transition metal ion within the charged layers has been one of the most attractive problems. X-ray absorption spectroscopy is very useful to examine the electronic and local environment of the probed metal ion absorbed in the interlayer due to its element-selectivity and no requirement of long-range ordered structure.

In the present work, we have examined the changes of local geometry and electronic structure around the copper ion for Cu²⁺, [Cu(en)₂]²⁺ (en=ethylenediamine), and [Cu(cyclam)]²⁺ (cyclam = 1,4,8,11-tetraazacyclotetradecane) ions-exchanged clays and compared with those of their free complexes by means of the Cu K-edge X-ray absorption spectroscopy.

Experimental
X-ray absorption measurements were carried out with synchrotron radiation by using the EXAFS facilities installed at the beam line 10B of the photon Factory. All the data were recorded in a transmission mode at room temperature, using a Si(311) channel-cut monochromator. Intensities of the incident and transmitted beams were measured with N₂- and (25% Ar - 75% N₂)-filled ionization chambers, respectively.

Results and Discussion
The intercalation of Cu²⁺, [Cu(en)₂]²⁺ and [Cu(cyclam)]²⁺ ions in the montmorillonite was confirmed by the powder X-ray diffraction, in which (00₁) diffraction peak appeared at d = 12.618 Å, 12.932 Å, and 13.463 Å, respectively.

Figure 1(right) shows the Fourier transforms (FTs) of the Cu K-edge EXAFS oscillations, χ(k) weighted by k³ in the range of ~2 Å⁻¹ < k < ~13 Å⁻¹. It is clearly seen in FTs that Cu²⁺ ion-montmorillonite exhibits only the first intense peaks at ~1-2 Å corresponding to the interactions between the copper ions and oxygen atoms in the first coordination sphere, while [Cu(en)₂][ClO₄]₂ and [Cu(cyclam)][ClO₄]₂ and their intercalated forms with the montmorillonite exhibit more distant peaks due to the square planar Cu-N interaction.

Figure 1(left) shows the normalized Cu K-edge XANES spectra for the present compounds. Although each XANES spectrum exhibits a characteristic feature of a copper(II) ion square-planarly coordinated with oxygen or nitrogen ligands, the spectra for copper ions with nitrogen ligands show the clear difference from that for the copper ions with oxygen ligands. The main peak B can be assigned to the 1s → 4p transition, based on the dipole selection rule of Δl = ±1, and especially the shoulder peak A is definitely assigned to the shakedown satellite by means of the polarized Cu K-edge XANES studies for well oriented Cu(II) complexes. It is obvious that the position of peak A shifts to lower energy upon the intercalation into montmorillonite. This observation indicates that the charge transfer from 2p orbitals of nitrogen ligand to 3d orbitals of copper metal occurs more effectively as stated above, and thus the Cu-N bonding character becomes more covalent. Moreover, the peak A for the cyclam complex (A = 1.7 eV) is shifts to lower energy compared to that for the ethylenediamine one (A = 0.7 eV), even though this peak for both free complexes is present at almost the same energy position.

Acknowledgment
This work was supported in part by the Korean Ministry of Education (BSRI-94-3413) and by the KOSEF (92-25-00-02).

References
XAFS Studies of Iron Catalyst in Coal Liquefaction Residue

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Introduction
The development of the efficient catalyst is a very important subject in coal liquefaction process. The feasibility of catalyst recovery from liquefaction residue should be considered because the efficient catalysts are very expensive. From this point of view, fundamental study on the properties of catalyst in the residue is necessary for the efficient recovery of catalyst from the residue. In previous studies1)-3), we have analyzed the chemical form and state of iron catalyst in the residue by using X-ray absorption fine structure (XAFS) spectroscopy. In general, coal contains inherent inorganic constituents as mineral matter, which possibly causes deactivation of liquefaction catalyst and several other problems in liquefaction process. It is, therefore, strongly recommended that coal is demineralized before use, if economical situation allows to do so. In the present study, we try to clarify the effect of coal demineralization on the chemical form of iron catalyst for liquefaction.

Experimental
Raw or demineralized Newstan coal and synthetic FeS2 were used as feedstock and catalyst, respectively. The liquefaction conditions are as follows; 450°C, 5MPa(H2 gas), 20 wt% loading of FeS as catalyst. The liquefaction products were washed with THF and liquefaction residue was obtained as insoluble fraction. The XAFS spectra at Fe K-edge of the resultant residue were recorded in a transmission mode on a beam line BL-10B at KEK-PF at room temperature using Si(311) monochromator.

Results and Discussion
The spectrum of synthetic iron catalyst before liquefaction is given in Fig. 1(a). Three peaks appeared at 1.9, 2.8 and 3.8 Å. These are attributed to Fe-S (1.9 and 2.8 Å) and Fe-Fe (3.4 Å) derived from FeS2, respectively. Fig. 1(b) and (c) show FT-EXAFS spectra of iron catalyst in the two types of residues. There is almost no difference in the profile of FT-EXAFS spectra between the two residues. The 2.8 and 3.4 Å peaks, observed clearly in FeS2 catalyst, diminished or disappeared in liquefaction process. These findings indicate that the demineralization does not influence the chemical form of iron catalyst and iron species do not exist as raw FeS2 catalyst in liquefaction residue.

References

Fig. 1. FT-EXAFS spectra at Fe K-edge. (a) synthetic FeS2; (b) and (c) iron catalysts in residues from raw and demineralized coals, respectively;
INTRODUCTION

Metal clusters can be applied in various fields of chemistry, such as catalysis, colloids, electrochemistry, etc. Metal cluster with controlled particle size has an advantage to optimize the chemical properties. Recently, we reported the catalysis on supported [Ru6N] clusters.1 In this paper, we report in-situ EXAFS of [Ru6N] clusters on MgO and Cs+-doped MgO in relation to promoted catalysis.

EXPERIMENTAL

The samples were prepared from [P(PPh3)3][Ru5N(CO)11]Cl. The Ru K-edge EXAFS was measured at BL10B at 30 - 293 K. The analysis was performed on the program EXAFS by Yokoyama et al. by using empirical parameters of amplitude and phase shift.

RESULTS AND DISCUSSION

The curve fitting data for N_Ru-Ru were always about four in Table 1, similar to four of (1), suggesting that the [Ru6N] unit remained on support in catalytic conditions. Based on the increase of N_Ru-Os (O_s: oxygen atom at surface) from 0.5 to 1.2 by changing Ru wt% from 2.5 to 0.48 for [Ru6N]/MgO (Table 1), two coordination models of [Ru6N] can be drawn on flat MgO (2.5 wt%) and on stepped MgO surfaces (0.48 wt%) (Figure 1).

The cluster structures in H2/N2 were investigated. The changes of r_Ru-Ru (0.03 - 0.08 Å) in Table 1 and adsorption measurements indicated that the cluster framework expanded by the adsorption of five to six H atoms on Cs+/MgO, and by three to four H on MgO. The expanded [Ru6N] shrunk to initial structure by the evacuation. N2 was found to be adsorbed as μ_2-coordination on [Ru6N]. We propose promoted catalysis mechanism based on these structure changes and coordination style.2

REFERENCES

(2) Y. Izumi and K. Aika, to be published.

Table 1: Curve fitting analysis of Ru K-edge EXAFS for supported [Ru6N(CO)11] clusters

<table>
<thead>
<tr>
<th>support</th>
<th>Ru wt%</th>
<th>gas</th>
<th>T_ambient /K</th>
<th>N</th>
<th>r</th>
<th>Δ(σ²)_Ru-Ru</th>
<th>N</th>
<th>r</th>
<th>Δ(σ²)_Ru-O</th>
<th>Rf</th>
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<td>MgO</td>
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<td>-2.2</td>
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<td>vac</td>
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<td>2.09</td>
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<td></td>
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<td></td>
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<td>193</td>
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<td>0.5</td>
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<td>100</td>
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<td>2.71</td>
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<tr>
<td>Cs+/MgO</td>
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<td>vac</td>
<td>293</td>
<td>4.2</td>
<td>2.63</td>
<td>3.6</td>
<td>0.6</td>
<td>2.03</td>
<td>0.94</td>
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<td>100</td>
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<td>0.6</td>
<td>2.06</td>
<td>-2.1</td>
<td>3.8</td>
</tr>
</tbody>
</table>

a Incipient cluster was heated at 813 K and in H2 at 588 K. b Incipient cluster was heated at 673 K and in H2 at 588 K. Cs+/[Ru6N] = 12 in mol. c in Å. d in 10⁻³ Å².
Ag K EDGE EXAFS OF AMORPHOUS Gd$_{30}$Ag$_{70}$

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Introduction
From EXAFS analysis on amorphous Gd$_{68}$Cu$_{32}$ and Gd$_{67}$Ni$_{33}$ alloys, we found that they have two kinds of interatomic distance between Gd and transition metal: one is about 2.8 Å and the other is about 3.4 Å. To know whether it is characteristic of Gd-rich system, in this report, we investigate the local structure of Gd-poor amorphous Gd$_{30}$Ag$_{70}$ by means of EXAFS measurements.

Experimental
Amorphous Gd$_{30}$Ag$_{70}$ ribbon was prepared from 3N Gd and 4N Ag by melt spinning technique. X-ray diffraction confirmed the amorphous state. EXAFS experiments were carried out with a transmission mode at the BL-10B station of Photon Factory (KEK, Tsukuba). The measurement was done near the K edge of Ag at 300 K in the operation of 3GeV.

Results and Discussion
Figure 1 shows $k^2 \chi(k)$ for Ag K edge of amorphous Gd$_{30}$Ag$_{70}$. Fourier transform of $k^3 \chi(k)$ is presented in Fig. 2, where the distance is not corrected for phase shifts. The thick line denotes the imaginary part of the radial structure function $\Phi(R)$ and the thin curve is its absolute. We make the Fourier filtered $k^3 \chi(k)$ from $\Phi(R)$ between a couple of broken lines in Fig. 2 and analyse it with data by McKale. The analysis gives information on the interatomic distance as follows: 2.69 Å for the Ag-Ag distance; 2.87 Å and 3.36 Å for the Ag-Gd distance. Two kinds of Ag-Gd distance are consistent with the result for the Gd-rich amorphous alloys. Peak positions of the imaginary part of $\Phi(R)$ correspond to the distances of Ag and Gd neighbours around the central Ag atom, which are shown by the arrows in Fig. 2. Thus we obtain that the Gd-poor Gd-Ag amorphous alloy shows two sorts of Gd-Ag distance as well as the Gd-rich system. The analysis for Gd L$_3$ edge is now in progress.

References
XAFS STUDIES ON THE Ag⁺/ZSM-5 PHOTOCATALYST FOR THE DECOMPOSITION OF NO

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Department of Applied Chemistry, University of Osaka Prefecture, 1-1 Gakuen-cho, Sakai, Osaka 593

Introduction
Ag/zeolites have been reported to show very high activity for the disproportionation of ethylbenzene and the selective reduction of NO by ethylene at around 823 K. In the present work the photocatalytic decomposition of NO has been undertaken on the Ag⁺/ZSM-5 catalyst at 298 K and the characteristics of the photocatalyst have been investigated by in-situ X-ray absorption near edge structure (XANES), ESR, and a diffuse reflectance spectrum (DRS) technique.

Experimental
The Ag⁺/ZSM-5 zeolite catalyst was prepared by an ion-exchange method with an aqueous Ag(NH₃)₂⁺ solution. Silver loading was determined as 6.7 wt% metal. Prior to the measurements of the spectra and photocatalytic reactivity, the samples were treated with O₂ at 673 K, then degassed at 473 K. Photocatalytic reactions were carried out at 298 K using a high pressure Hg lamp through a water filter. XANES spectra were obtained at the BL-10B facility of the Photon Factory at the National Laboratory for High Energy Physics, Tsukuba.

Results and Discussion
UV irradiation of the Ag⁺/ZSM-5 catalyst in the presence of 10 Torr of NO at 298 K led to the formation of N₂ and N₂O with a good linearity against the UV irradiation time, while under dark conditions the formation of N₂ and N₂O was not detected. On the H⁺/ZSM-5 catalyst, the formation of N₂ and N₂O was not observed. These results indicate that the Ag⁺ ions play a significant role in the photocatalytic decomposition of NO on the Ag⁺/ZSM-5 catalyst. The rate of N₂ formation on the Ag⁺/ZSM-5 catalyst is 10 times faster than on the Cu⁺/ZSM-5 catalyst. Under UV-irradiation of the catalyst through the UV-25 filter (λ > 250 nm), the photocatalytic decomposition of NO proceeded at 15% the rate without the UV-cut filter. This indicates that the UV-light effective for NO decomposition lies in the wavelength regions of 200 nm to 250 nm.

Figure 1 shows the XANES spectra of the Ag⁺/ZSM-5 catalyst (a), Ag foil (b), and bulk Ag₂O (c), respectively. As shown in Figure 1, the XANES spectra of the Ag foil and bulk Ag₂O exhibit several well-defined bands due to multiple-scattering (A) at around 25530 eV and other bands arising from continuum resonances involving a multiple-scattering effect in the region above 25550 eV, while the XANES spectrum of the Ag⁺/ZSM-5 catalyst scarcely exhibits any remarkable band due to this effect. This implies that silver ions are anchored onto the inner surfaces of the micro pores of the ZSM-5 zeolite in a high dispersion state without the formation of any large clusters or crystals of the Ag metals or oxides.

The dispersion state of Ag⁺ species was investigated by DRS measurements. The Ag⁺/ZSM-5 catalyst exhibits an intense absorption band at around 220 nm which is attributed to the 4d¹⁰→ 4d⁵s¹ electronic transition on the Ag⁺ ions. The Ag⁰ atoms, and Ag₅⁻ and Ag₅⁺ clusters are known to exhibit absorption bands in wavelength regions longer than 250 nm. However, the Ag⁺/ZSM-5 catalyst does not exhibit any absorption bands in this region. Furthermore, no ESR signals assigned to the Ag⁰ atoms or Ag⁺ species were observed with the Ag⁺/ZSM-5 catalyst. These results support the conclusion that silver ions are included within the ZSM-5 zeolite as isolated Ag⁺ ions. The most effective UV lights for the photocatalytic decomposition of NO was found to lie in the same wavelength region as the absorption band of the Ag⁺/ZSM-5 catalyst which is attributed to the presence of the isolated Ag⁺ ions.

From these various findings, it was concluded that the photo-exited electronic state of highly dispersed isolated Ag⁺ ions (4d⁵s¹) plays a significant role in the photocatalytic decomposition of NO while an electron transfer from the photo-excited Ag⁺ into the π anti-bonding molecular orbital of NO leads to the weakening of the N-O bond and initiates the decomposition of the NO molecule.

Figure 1. The XANES spectra of the Ag⁺/ZSM-5 catalyst (a), Ag foil (b), and Ag₂O powder (c).

Reference
**Introduction**

The Nd-Fe-B alloy is one of the most promising materials with outstanding magnetic properties that is usually produced either by melt-spinning\(^1\) or by sintering\(^2\). In the melt-spinning approach\(^3\), the amorphous intermediate is converted into crystalline hard magnetic phase by hot pressing so that the crystallization behavior in heating process, especially the structural change in atomic scale, is very important to optimize the process. However, for the amorphous alloys such atomic scale information was hardly available by the conventional structure analysis technique such as X-ray powder diffractometry (XRD). This study deals with the Nd L\(_3\) XAFS structure analysis of the title alloy to reveal the crystallization behavior in atomic scale structure.

**Experimental**

In rapid quenching by melt-spinning (R.Q.) technique\(^4\) we prepared two kinds of samples with the compositions of Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) and Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\). Each sample was heated at three different temperatures, 823 K, 893 K and 973 K under argon atmosphere. All specimens were characterized by XRD.

We made the Nd L\(_3\) XAFS measurements of the alloys at the BL-1OB station by means of transmission mode. Typically the spectra were measured within the range of 300 eV before and 510 eV after the absorption edge. The data analysis was done with the procedures proposed by Maeda et al.\(^5\).

**Results and Discussion**

Differential scanning calorimetry (DSC) for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) and Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\) samples indicates that single exothermic peak at about 870 K due to amorphous-crystal transition was found for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) while double peaks at about 890 K and 910 K for Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\).\(^6\) All Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) specimens except for the samples heated at 893 K and 973 K showed very broad XRD pattern. In contrast the variation of XRD pattern for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) sample in heat treatment shows that broad peaks assigned to \(\alpha\)-Fe were found for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) samples treated at 890 K while as-quenched Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) sample and that heated at 973 K showed the amorphous and the crystalline XRD patterns with no such peak, respectively.\(^7\) With TEM analysis, a particulate \(\alpha\)-Fe phase was revealed in the continuous alloy matrix of Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) at 890 K.\(^8\)

Figs. 1 and 2 show the variation of radial distribution function (RDF) with no phase shift correction in the thermal treatment for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) and Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\), respectively. There appears to be no significant difference in local structure between Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) and Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\) at each temperature. Therefore, we made the curve fitting analysis to the first peak assigned mainly to the Fe atoms. As for Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) the first peak shifts to longer distance below 893 K by about 0.01 Å, and then decreased by about 0.02 Å with increase of the heating temperature up to 973 K while small difference is observed between 893 K and 973 K.

The variation of the peak of Nd\(_{5}\)Fe\(_{77}\)B\(_{12}\) during the heat treatment shows that the "frozen" structure imposed by rapid quenching would relax to somewhat "expanded" amorphous structure before the crystallization peak in the DSC curve; after the crystallization temperature where the amorphous-crystal transition occurs, only the crystal growth of crystallite would proceed. In the case of Nd\(_{5}\)Fe\(_{77}\)Bi\(_2\) the variation behavior of the peak distance indicates that the relaxation of the frozen structure would not occur up to 893 K. The structure would be gradually rearranged to meta-stable structure similar to that at 973 K.

**Acknowledgments**

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**References**

EXAFS EVIDENCE ON UNDERPOTENTIAL DEPOSITION OF Rb⁺ ON CARBON-SUPPORTED Pt IN AQUEOUS SOLUTION

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**Introduction**

EXAFS spectroscopy is the excellent in-situ tool for investigating the underpotential deposition (UPD). However, no studies have been contributed to the underpotential deposition of alkaline metals in the aqueous solutions. This is because the subtle current arising from UPD can not be distinguished under cover of that of the bulk electrolysis and, additionally, the application of the spectroscopic methods seems to be given up at the formation of hydrogen bubbles.

We have used a spectroelectrochemical cell, by which good spectra can be obtained in the gas evolution potentials, and measured spectra of Pt L₃ and Rb K edges under potential control. In this report we show the evidence of the deposition of Rb at very positive potential.

**Experimental**

The electrode preparation and cell are described in ref 1. The loading of platinum was 3.5 % and the average particle size was 1.5 nm. The spectra were recorded in a transmission mode at the beam line BL-10B at room temperature. The solutions was 2 x 10⁻⁴ M Rb⁺ + 0.5 M H₂SO₄. The potential was represented against Ag/AgCl.

**Results and discussion**

Figure 1 shows EXAFS oscillation. Fourier-transform and curve fitting result of Rb K edge at -0.8 V. k^2χ(k) at -0.4 V is shown for comparison. No EXAFS oscillation was observed at -0.4 V. On the contrary, clear oscillation appeared at -0.8 V. Fourier-transform of the EXAFS oscillation at -0.8 V showed a significant peak around 0.35 nm. This was inverse Fourier-transformed to k^2χ(k) after filtering of the peak at 0.2 < r/nm < 0.43. This can be fitted quite well with one Rb-Pt shell. This demonstrates that the deposition occurs above -0.8 V. This is much larger than the UPD potential reported in aprotic solvent, -1.65 V (vs SHE).

The bond length obtained by the curve fitting agreed well between Pt-Rb (0.367 nm) and Rb-Pt (0.364 nm). These agree also with that of Rb₂PtH₄ (0.363 nm). The similarity of the chemical environment of Rb on Pt particle and in Rb₂PtH₄ is possible. And this may be a reason why UPD potential in aprotic solvent is much more negative than the result obtained in this study.

Fig. 1: EXAFS oscillation and Fourier transform of Rb K edge in 0.0002 M Rb⁺ + 0.5 M H₂SO₄.

**References**

CHARACTERIZATION OF SUPPORTED PLATINUM CATALYSTS PREPARED BY THE REDUCTION OF ADSORBED METAL PRECURSORS WITH SODIUM TETRAHYDROBORATE SOLUTION AT ROOM TEMPERATURE

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INTRODUCTION
Supported metal catalysts are prepared by a variety of ways and many of them require high-temperature treatments like activation and reduction. These treatments often give a crucial impact on the activity of catalysts. One can naturally expect that non-heat-treated catalysts will show different activities. In a recent work, we prepared an alumina-supported platinum catalyst by the reduction of an adsorbed metal precursor with sodium tetrahydroborate solution at room temperature. The catalyst prepared is highly active to the selective production of cinnamyl alcohol (unsaturated alcohol) in the liquid-phase hydrogenation of an α,β-unaturated aldehyde, cinnamaldehyde. Such a high activity was not observed for a catalyst prepared by the reduction of the same adsorbed precursor by hydrogen at 400°C or above, as expected from the literature data. In the present work, we have studied the nature of those non-heat-treated catalysts by several techniques.

EXPERIMENTAL
Supported platinum catalysts were prepared from porous alumina and silica gels as support and platinum tetraamine dichloride and chloroplatinic acid as precursor. Metal precursors were adsorbed by the supports under controlled pH conditions. The precursor/support samples obtained were reduced by a 0.1 M sodium tetrahydroborate solution at 35°C and pH 11.6 for 30 min or by flowing hydrogen at 500°C for 3 h. The catalysts reduced by the former and latter procedures are referred to as LR and HR catalysts, respectively. Activities of the catalysts prepared were tested for liquid-phase cinnamaldehyde hydrogenation. The bulk structure of platinum crystallites formed was studied by Pt LIII-edge EXAFS spectra measured at room temperature at the BL-10B station. The surfaces of the crystallites were examined by chemisorption of hydrogen and carbon monoxide and X-ray photoelectron spectroscopy (XPS). Experimental details have been described elsewhere.

RESULTS
The alumina-supported LR catalysts from the two precursors showed higher activities and selectivities to the unsaturated alcohol compared to the corresponding HR catalysts. The platinum crystallites of the LR catalysts were slightly smaller than those of the HR ones from EXAFS and chemisorption data. However, the difference was small so that this could not explain the difference in the catalytic actions. The EXAFS and XPS did not indicate a difference in the bulk structure (Pt-Pt distance and coordination number) and in the electronic state of the surface of the crystallites between the LR and HR catalysts. Thus, we think that the LR catalysts have a different atomic arrangement at the crystallite surface that is not achieved for HR ones. In the case of silica support, the LR and HR catalysts indicated similar very low activities compared with the alumina-supported catalysts.

REFERENCES
Alkali-doped C$_{60}$ is known to exhibit superconductivity. We report new chemical application of fullerene as catalyst support utilizing the conductivity when doped with alkali.

**EXPERIMENTAL**

Crude C$_{60}$ was purified by carbon column method. Obtained C$_{60}$ was reacted with Ru$_3$(CO)$_{12}$ in toluene (24h). Cs$^+$-doped SiO$_2$ was added to the solution (6h). Solvent was evaporated, evacuated at 723 K, and in H$_2$ at 588 K (Ru 2.7 wt%). The molar ratio Cs$^+$:Ru$_3$:C$_{60}$ was 3:2:3 (cat-1). Reference without C$_{60}$ was prepared in the same procedure (cat-2). Ru K-edge EXAFS was measured at beamline 10B, and analyzed on code EXAFSH by Yokoyama et al. by using empirical parameters extracted from Ru and Ru$_2$O$_3$ powders.

**RESULTS AND DISCUSSION**

EXAFS oscillation was weaker for cat-1 (Figure 1(1b)), and the coordination around 1.9 Å in (1c) was stronger than in the case of (2c). As TEM measurements (Topcon) suggested that Ru was situated on C$_{60}$ bulk judging from the stripe pattern (7.4 Å interval, 1st & 2nd layers of C$_{60}$) and the color contrast, curve fitting analysis was performed with Ru-Ru & Ru-C waves for cat-1, and with Ru-Ru & Ru-O waves for cat-2 (Table 1). The N$_{Ru-Ru}$ was 3.9 for cat-1, but far larger (10) for cat-2. The Ru clusters on C$_{60}$ bulk can be electronically affected by doped Cs$^+$ (on SiO$_2$) through C$_{60}$ bulk as if through 'electron conductive medium' as suggested by XPS. Further investigation is needed to explain the catalytic difference (ammonia synthesis) with/without C$_{60}$ (160 and 25 μmol h$^{-1}$g-cat$^{-1}$, respectively).

**REFERENCES**


**Table 1: Curve Fitting Analysis of EXAFS**

<table>
<thead>
<tr>
<th>sample</th>
<th>N</th>
<th>r</th>
<th>Δ($\sigma^2$) N</th>
<th>r</th>
<th>Δ($\sigma^2$) N</th>
<th>r</th>
<th>Δ($\sigma^2$) N</th>
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<td>Ru-C$_{60}$-Cs$^+$/SiO$_2$</td>
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<td>6.6</td>
<td>2.15</td>
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<td></td>
<td>1.3</td>
<td>2.21</td>
<td>-2.2</td>
<td>0.09</td>
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</tbody>
</table>

Figure 1. Ru K-edge EXAFS for cat-1(1) and cat-2(2). (a) raw spectrum, (b) $k^3 \chi$, (c) its associated FT, and (d) CF.
EXAFS OF GERMANIUM OXIDE MONOLAYERS PREPARED BY CHEMICAL VAPOR DEPOSITION METHOD ON METAL OXIDES
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Introduction
Thin oxide layer with a homogeneous structure is promising as a model of mixed-oxide catalyst. The silica monolayers were prepared by the CVD (chemical vapor deposition) of Si(OCH₃)₄ (tetramethoxysilane) on several metal oxides [1, 2]. However, few spectroscopic methods are available for SiO₂. Since germanium is included as the same group of the periodic table as silicon, the CVD of germanium alkoxide is expected to form the monolayer of germanium oxide. We will now report the EXAFS of deposited germanium, which will give valuable information about the structures of oxide monolayers.

Experimental
The vapor of Ge(OCH₃)₄ (germanium tetramethoxide) was admitted at 473 K on γ-alumina, titania and zirconia, and the samples were calcined at 673 K in 27 kPa of oxygen. The GeO₂ loading was determined from the weight gain.

The Ge-Κ edge EXAFS was measured on a self-supporting disk molded from the sample powder at the Beam Line 10B of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF). The synchrotron radiation from the electron storage ring (25 GeV, average current 100 mA) was monochromatized with a channel-cut Si(311) monochromator. The incident- and transmitted-beam intensity was measured by an ionization chamber filled with a gaseous mixture (15 % argon and 85 % nitrogen) and with 100 % argon, respectively. The k³ weighted EXAFS was extracted by the method according to Tanaka et al. [3], and Fourier transformed.

Results and Discussion
The Fourier transform of EXAFS shows the obvious difference in the structures between the GeO₂ deposited on alumina and the α-quartz type GeO₂ (Fig. 1). The α-quartz type GeO₂ showed both of the Ge–O and Ge–O–Ge bonds, whereas the deposited GeO₂ revealed only the Ge–O bond. This suggests a structure of ultra thin layer of the deposited GeO₂. Similar transforms were obtained by the depositions on titania and zirconia.

![Fourier Transform of EXAFS](image)

The BAT method (benzaldehyde–ammonia titration) [1] showed that the deposited layer covered 1 nm² of the alumina surface with 13 atoms of Ge. This suggests that the monolayer of germanium oxide consisting of 1 : 1 of Al–O–Ge bond. The CVD of germanium alkoxide is concluded to form the monolayers of germanium oxide on the metal oxides.

References
EXAFS STUDIES OF SODIUM BORATE GLASSES DISPERSING SMALL Bi METAL PARTICLES

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Introduction

It is interesting that nature of ultra fine particles of metals or semiconductors is different from their bulk states because of the size effect. There are many methods to prepare ultra fine particles such as vapour phase method. But the particles made by vapour phase method are aggregated by their cohesion, so it is difficult to investigate the particle nature individually. Then the method to grow the particles in the solid matrix was devised. We made Bi metal particles whose diameters were about 1 nm to 200 nm in sodium borate glasses by heat treatment. By using these glass samples we investigate the local structures around Bi atoms during the precipitation process of the particles.

Experimental

We prepared the glass samples containing Bi metal particles by the conventional melting and the heat treatment processes. A 28Na2O-72B2O3 glass with 3SnO and 1Bi2O3 was fused at 1300K. After quenching the melt quickly, Bi metal particles were precipitated by the heat treatment for 300 hour. The heat treatment temperature was 748K. The shapes of the samples were slabs. The particles precipitated in the glasses were checked by the wide angle X-ray diffraction measurements and confirmed as Bi metal crystal.

The EXAFS absorption spectrum of Bi LIII edge was measured at the BL-10B station at the Photon Factory. The measurements were carried out at room temperature.

Results and Discussion

The states of the glass samples before and after the heat treatment process are shown in figure 1. There are no particles in the glass without heat treatment. In contrast, some spherical particles are shown in the glass after 300 hour heat treatment. The heat treatment temperature was 748K. The shapes of the samples were slabs. The particles precipitated in the glasses were checked by the wide angle X-ray diffraction measurements and confirmed as Bi metal crystal.

Figure 2 shows the Fourier transforms of the k^3–multiplied EXAFS data of the glass samples. One is the glass without heat treatment, and the other is with 300 hour heat treatment. Figure 2 also contains the data for the Bi2O3 crystal as a reference sample. The spectrum for the glass without heat treatment has only one peak. This fact shows that Bi atoms are dissolved uniformly in the matrix glass and there are no middle to long range order around Bi atoms. To contrast with the spectrum of the Bi2O3 crystal, the peak in the glass spectrum is almost the same position as the shortest Bi–O correlation in the Bi2O3 crystal. The result shows that the peak can be assigned to the nearest Bi–O correlation around Bi atoms in the glass. Similarly, in the spectrum of the 300 hour heat treated glass only one peak is observed. It is obvious that this peak has the same origin with the peak in the as quenched glass. There is no peak corresponding to the Bi–Bi correlation, because the amount of the Bi atoms which precipitate as Bi metal particles is too small. Namely, the most part of Bi atoms still remain in the glass matrix. This result is supported by our thermal analysis.
STRUCTURE OF HIGHLY DISPERSED MOLYBDENUM SULFIDES SUPPORTED ON ZEOLITE

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Introduction
In the previous study [1,2], we demonstrated that highly dispersed Mo sulfide species are synthesized by using Mo(CO)6 encaged in zeolite as a precursor and that they exhibit high activity for the HDS of thiophene. The dispersion of the Mo sulfide species were estimated on the basis of NO adsorption capacities. In the present study, the structure and dispersion of zeolite supported Mo sulfide species were examined, in the presence or absence of Co, by EXAFS techniques.

Experimental
Molybdenum hexacarbonyl, Mo(CO)6, was adsorbed on a NaY zeolite which had been evacuated at 673 K. Mo(CO)6/NaY was sulfided at 673 K. The resultant Mo sulfide catalyst is denoted MoSx/NaY. MoO3/NaY was prepared by a conventional impregnation method and the sulfided form is denoted MoS2/NaY here. Cobalt was introduced into MoSx/NaY by using Co(NO)(CO)3 as a precursor, followed by a second sulfidation at 673 K (CoSx-MoSx/NaY). A Mo-Co sulfide catalyst was also prepared by a reversed order of Co and Mo adsorptions (MoSx-CoSx/NaY). The EXAFS spectra were measured at room temperature on a BL-1OB instrument at PF without exposing the sulfided sample to air by using an in situ cell with Kapton windows.

Results and Discussion
The catalytic activity of MoSx/NaY for the HDS of thiophene was found to increase as the Mo loading increased up to 2 Mo/super space, which fact suggests a formation of a uniform Mo sulfide species in the concentration range. MoSx/NaY showed 2-3 times higher HDS activity than MoS2/NaY in line with the previous observations [1,2]. The k3-weighted Fourier transforms of the Mo K-edge EXAFS for MoSx/NaY. In the case of MoSx/NaY, only Mo-S and Mo-Mo bondings were observed and the Mo-Mo coordination number was calculated to be close to unity, suggesting a formation of highly dispersed Mo sulfide species. On the other hand, Mo-O bondings were detected for MoS2/NaY as well as Mo-S and Mo-Mo bondings due to Mo sulfides (not shown), suggesting that only a part of Mo is sulfided in MoS2/NaY. This was corroborated by XPS. The higher activity of MoSx/NaY is explained in terms of a higher dispersion of the Mo sulfide species.

The catalytic synergy between Co and Mo sulfides was found to generate for the HDS of thiophene for CoSx-MoSx/NaY. The maximum activity was obtained at the composition of about Co/Mo = 1. The k3-weighted Fourier transforms are shown in Fig.1 for the Co-Mo binary catalyst. It is clearly demonstrated that Mo-Co bondings are observed at 0.282 nm in addition to Mo-S and Mo-Mo bondings. The formation of binary sulfide species was also confirmed by the Co2p XP spectra of the catalyst. MoSx-CoSx/NaY showed the same HDS activity as MoSx-MoSx/NaY at the identical composition. The formation of the Mo-Co bondings were also observed for MoSx-CoSx/NaY. On the other hand, an addition of FeSx to MoSx (FeSx-MoSx/NaY) significantly decreased the HDS activity of MoSx. In this case no Mo-Fe bondings were observed as shown in Fig.1.

In conclusion, it is demonstrated by using EXAFS techniques that highly dispersed Mo sulfide species are formed on zeolite by using Mo(CO)6 and that highly dispersed Mo-Co binary sulfide species are synthesized on zeolite. We suggest that Mo-S-Co bondings are required for the generation of catalytic synergies, taking into consideration the catalytic activities of variously prepared model Co-Mo catalyst systems [3].

References

Fig.1 k3-weighted Fourier transforms of the Mo K-edge EXAFS for MoSx/NaY, FeSx-MoSx/NaY and CoSx-MoSx/NaY.
STRUCTURES OF Mo/SiO₂ CATALYSTS DURING ETHANOL OXIDATION REACTION

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Introduction

For Mo/SiO₂ catalysts prepared by fixing Mo₂(C₃H₅)₄ onto silica, we proposed structure models, which basically based on the idea that on those fixed catalysts strong bonds between Mo and SiO₂ keep initial dimeric nature of the precursor complexes. [1] Usually only little Mo-Mo peaks were observed with EXAFS measurement of the catalysts in oxidized state. Once when measured at 80K, they could be detected with strong intensity. [2] We concluded that large thermal Debye-Waller-like factor had blurred the Mo-Mo peaks at room temperature. At 433K the fixed dimer catalysts were reduced with ethanol. Formation of acetaldehyde reached a plateau with a certain reduction level. EXAFS spectra of the catalysts at that point showed 0.26nm Mo-Mo bonds with coordination number 0.5. Catalytic ethanol oxidation over the catalysts was thought to proceed with a redox cycle between those two dimer structures. In this time we reconsider those structure models and propose other ones.

Experimental

Mo/SiO₂ catalysts were prepared from MoO₂(acac)₂, (NH₄)₂Mo₇O₂₄ (AHM), [Mo₃O₂(OAc)₆(H₂O)(OH)₂] xH₂O and Mo₂(C₃H₅)₄. Ethanol oxidation activity of those catalysts was measured by a closed circulating system. EXAFS spectra were taken at BL-10B.

Results and Discussion

All prepared Mo/SiO₂ catalysts of c.a. 2wt% loadings have no significant Mo-Mo EXAFS peaks in oxidized form without contacting air. It is also confirmed that even the fixed catalysts show polymolybdate-like Mo-Mo peaks when exposed to moist air. [3] So it is unable to say unequivocally that the peak observed previously at low temperature was dimer structures. The formed polyaniions should be Keggin type silicomolybdicacids, as determined by comparison of the catalysts' and the anions' spectra.

Fig.1 shows EXAFS Fourier transform spectra of Mo/SiO₂ catalysts from various precursors reduced by ethanol at 433K. Peak of Mo-Mo bond at 0.26nm can be seen for all of them with almost the same coordination number 0.5. Fig.2 depicts that the peak grow further with higher temperature reduction. From these spectra and the result of UV-VIS DRS measurements, it is thought that this Mo-Mo bonds are not that of isolated dimers and that it cannot build up in a single step. We propose a new structure model that on Mo/SiO₂ catalysts in general dominant species are aggregates of Mo. At the initial stage of reduction with ethanol, gained electrons are delocalize in the aggregates and no change can be observed in EXAFS 2nd. shells, maybe because at this stage they have diverse Mo-Mo distances and static Debye-Waller factors are large. When the reduction proceeds further, strong bonds are created by then localized electrons and that can be detected in EXAFS spectra. Kinetic results show that the catalytic ethyl alcohol oxidation reaction at 433K may proceed by redox mechanism, but the reduction level with the 0.26nm Mo-Mo bond cannot be involved in the redox cycle.

References

Local strain in single crystal Cu/Ni superlattices

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Introduction

Recently, much attention has been drawn by the specific features in metallic multilayers. Magnetoresistance and reflectivity are the most important application of multilayers. In 1983, Tsakalakos et al.\(^1\) reported the anomalous feature of elastic property in the system with the modulation wavelength in the vicinity of 17Å. On the other hand, Davis et al. and Kumar et al. reported no elastic anomalies were seen by various methods in 1991.\(^2,3\) YYg synthesized single crystal Cu/Ni superlattices in order to clarify the presence and the origin of the elastic anomaly in the Cu/Ni superlattice. Coherency strain is one of the candidate for the elastic anomaly. It is difficult, however, to obtain the information of the lattice spacing along the growth direction in diffraction method. We have to apply the non-diffraction method to observe the lattice spacing of each layer.

Experimental

Samples were prepared by removing the GaAs substrate selectively by chemical etchant. In order to support the films, substrate was remained on the edge. Furthermore, the samples were stacked each other and 5μm myler film. Samples were held on the rotational stage in order to incline against the X-ray beam. Measured samples were listed in table 1. Measurements were performed at the BL-10B. In order to suppress the statistical fluctuation, iterative measurement were performed.

Analysis of the EXAFS data was performed by subtracted with the background, Fourier-transformed, filtered and fitted with calculation.

\[\chi(k)\]

\[k (\text{Å}^{-1})\]

\[d\text{-spacing}(\text{Å})\]

\[\Lambda (\text{Å})\]

Table 1 Measured samples and calculated lattice spacing along the growth direction.

<table>
<thead>
<tr>
<th>(\Lambda(\text{Å}))</th>
<th>L.S. in Cu (Å)</th>
<th>L.S. in Ni (Å)</th>
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<tr>
<td>7.2</td>
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<td>14.4</td>
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<tr>
<td>160</td>
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Results and Discussion

Figure 1 shows the observed and calculated \(\chi(k)\) curves of Ni atoms in the \([\text{Cu}_{10}/\text{Ni}_{10}]\) superlattice. Extracted parameters were also listed in table 1. It is interesting that the spacing of Cu along the growth direction is deformed from the bulk lattice spacing. On the other hand, that of Ni increases and is close to bulk lattice spacing with \(\Lambda\). This result suggests that the large strain remains at \(\Lambda\) smaller than 36 Å. We are planning to calculate the elastic constant and to compare with the experimental result.

References


Fig. 1 Observed and calculated of EXAFS function.

Fig. 2 Distance of Cu-Cu and Ni-Ni in the growth direction calculated by the fitted data.
STABILIZATION OF COPPER METAL CLUSTERS IN MORDENITE NANOPORES: WATER TREATMENT OF EVACUATED COPPER-ION-EXCHANGED MORDENITE AT 300 K

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Introduction
Small metal clusters have attracted great interest during the past decade. Optical and electronic properties of clusters are expected to change from "bulk" properties to "molecular" properties within a certain size range. With reference to electronic properties, this change is represented by the transition of the electronic band structure of a crystal to the molecular orbital levels of a smaller size substance. Furthermore, since the cluster size determines the relative population of coordination sites and its molecular symmetry, a heterogeneous catalytic reaction at a metal surface is affected not only by the electronic properties of the metal but also by the structure of coordination sites, and the cluster size is suggested to be responsible for the modified selectivities in a number of catalytic reactions. Controlled synthesis and examination of clusters in the intermediate size range is of particular interest, because this would allow controlling the properties of electronic materials and catalyst systems.

We found that the small copper metal clusters of low crystallinity have been prepared in the cavities of mordenite via ion-exchange processes, followed by heat treatment, and subsequent H2O treatment at 300 K. In the present investigation, XAFS techniques are used to obtain the electronic and structural properties of metal particles formed in the mordenite nanopores.

Results and Discussion
Figure 1 shows the EXAFS and XANES spectra for copper-ion-exchanged (215%) mordenite (CuM-215) which was evacuated at 300 K (a) and at 873 K (b), and reevacuated at 300 K after exposing the 873 K-evacuated CuM-215 sample to saturated H2O vapor for 12 h at 300 K (c), respectively. Using CuO as the reference substance, we attributed the first and second major peaks centered at 1.54 Å and 2.85 Å (no phase-shift correction) to the backscattering from the nearest neighbor oxygen atoms and from the second nearest copper ions, respectively. After evacuating this sample at 873 K, the second peak disappears. This fact is explained quite naturally that the species formed upon evacuation at 873 K have a large static or dynamic disorder. The new feature is observed on the spectrum (c); it shows a new band at 2.18 Å in addition to the band at 1.42 Å. This new band may be due to the Cu-Cu interaction in metal by comparison with the spectra for the reference metal sample. This result suggests that copper metal fine particle is formed in zeolite matrix through the treatment of sample with H2O at 300 K.

As to the XANES spectra, the presence of a weak peak at 8.978 keV (1s-3d) and the lack of an intense band below 8.985 keV for 300 K-evacuated sample both indicate that this sample contains predominantly Cu(II) species. The strong peak at 8.984 keV in the 873 K-evacuated sample has been observed in a number of Cu(I) compounds and is ascribed to the 1s-4p transition. This finding implies that treating the sample at higher temperatures in vacuo reduces the divalent copper ion to the monovalent state. After exposing this sample to H2O vapor, the main feature of XANES is the decrease in intensity of Cu(I) edge; the resulting pre-edge spectral pattern is similar to that for Cu metal. Taking account of the above EXAFS results, this spectra can be reasonably accounted for by the existence of copper metal. Furthermore, the presence of the weak shoulder around 8.978 keV indicates the existence of divalent copper ion. This consideration is also supported from the ESR data; the ESR peak intensity of the 873 K-treated sample was increased by exposing this sample to H2O vapor.

EXAFS has been used to investigate the structure of metal microclusters. When small metal clusters are examined by EXAFS, the apparent average coordination number is smaller than that observed in the bulk metal because of the high proportion of surface atoms. This effect is dependent on the size of the metal cluster. Therefore, we can estimate the size of formed metal particle from the data of coordination number. From our data, it is found that microclusters (10-15 Å mean diameter) were formed in the sample by treating the 873 K-evacuated CuM-215 with saturated H2O vapor at 300 K. The XANES spectrum also supports the above conclusion; the absence of two peaks at 8.994 and 9.004 keV in the XANES for microclusters, in contrast to that for the bulk metal, indicates the absence of higher-shell atoms in the cluster, as described by Montano et al.9 The reason for the formation of metal cluster is ascribed to the stability of Brønsted acid sites in copper-ion-exchanged mordenite. IR spectroscopic data has provided similar evidence.

Reference
EXAFS STUDY ON STRUCTURAL CHANGE OF Ni-W/SiO$_2$-Al$_2$O$_3$
CATALYSTS USED IN A ONE-YEAR COMMERCIAL RUN

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INTRODUCTION

In catalyst studies some conflicting conclusions are reported, because the support or the preparation method employed in each study is different. In the present study, we prepared a series of Ni-W/SiO$_2$-Al$_2$O$_3$ catalysts with different SiO$_2$/Al$_2$O$_3$ ratios using a common support and preparation method, and then introduced them into a commercial hydrodesulfurization (HDS) unit for a year. The main purpose of this report is to discuss the dependence of structural changes on the SiO$_2$ content in the support during the one-year run.

EXPERIMENTAL

Ni-W/SiO$_2$-Al$_2$O$_3$ catalysts with 6 mol% of Ni and 12 mol% of W loadings were prepared by impregnation using supports with different SiO$_2$/Al$_2$O$_3$ molar ratios of 0/100, 30/70 and 50/50. A caracker packed by the prepared catalysts was located in a commercial HDS unit for vacuum gas oil for one year. Corresponding freshly sulfided catalysts were also prepared as references. Structural changes were analyzed by the W L$_{33}$ edge EXAFS spectra measured at the BL-10B of the Photon Factory.

RESULTS AND DISCUSSION

The FT magnitudes of W-W and W-S peak are shown in Fig.1 as a function of SiO$_2$ content in support. Both FT magnitudes of the W-W and W-S peak increase as the SiO$_2$ content in the support increases, indicating that the WS$_2$ slabs on the SiO$_2$-rich supports are larger than those on the Al$_2$O$_3$ support for the fresh catalysts.

During the HDS run, the WS$_2$ slabs are found to grow in the lateral direction, as indicated by the increase in the W-W and W-S magnitude. Among the spent catalysts, the WS$_2$ slabs on the SiO$_2$-rich supports were larger than those on the Al$_2$O$_3$ support in contrast to the fresh catalysts.

The interaction between W and Al$_2$O$_3$ leads to less aggregated tungsten sulfide structure on the Al$_2$O$_3$-rich support during the sulfiding procedure. However, the WS$_2$ slabs on Al$_2$O$_3$ are more mobile during the run as compared to those on the SiO$_2$-Al$_2$O$_3$ supports.

The relative change in the size of the WS$_2$ slabs is represented by the ratios of the magnitude of W-W peak in the spent catalysts to that in the fresh catalysts, which is also shown in Fig.1 with dotted line. It shows that the growth of the WS$_2$ slabs is suppressed by the addition of SiO$_2$ in the support. The XPS and TEM studies on the same catalysts have supported the above discussion. It can not be determined with the present study whether the SiO$_2$ support alone or the interface between SiO$_2$ and Al$_2$O$_3$ has such effect. The growth of the WS$_2$ in the lateral direction leads to the decrease of the number of catalytically active sites located at the edges of WS$_2$ slabs, which likely cause the catalyst deactivation.
SOLVATION STRUCTURE OF SILVER(I) ION IN NON-AQUEOUS SOLVENTS

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Introduction
The solvation structure of metal ions is indispensable for understanding their reactivity in solution. For the first-row transition metal(II) and -(III) ions in aqueous solution, the hydration structures are determined by the X-ray diffraction method to be 6-coordinate octahedral. Recently, the solvation structures in non-aqueous solvents have been also investigated by the EXAFS method. According to these results, the solvation structure is influenced by the size of metal ion and solvent molecule and the charge of metal ion. For instance, the solvation number in the bulky solvent, 1,1,3,3-tetramethylurea (TMU), is 5 and 6 for the Mn(II) and In(III) ion, respectively, although the ionic radius for both the ions is similar [1]. In order to evaluate the relationship between the solvation number and the size of metal ions, it is useful to know a solvation structure of Ag(I) ion.

It is known that the Ag(I) ion forms 2-coordinate linear complexes with ammonia, imidazole, and pyridine in the crystalline and aqueous phases [2,3]. On the other hand, the structure of solvated Ag(I) complexes prepared in pyridine and acetonitrile is 4-coordinate tetrahedral. According to the studies for aqueous solution of Ag(I) ion by using X-ray scattering, neutron scattering, and EXAFS, the hydrated Ag(I) ion has the 4-coordinate tetrahedral structure with Ag(I)-O bond length of 231 ~ 245 pm. However, there are no data of solvation structure of Ag(I) ion in non-aqueous solvents.

Experimental
We have performed the EXAFS measurements for 0.3 ~ 0.4 mol kg⁻¹ AgNO₃ solutions of H₂O, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), TMU, trimethylphosphate (TMP), acetonitrile (AN), n-propylamine (PA), and ethylenediamine (EN) at the BL10B with a channel-cut Si(311) monochromator and ion chamber detectors filled with Ar and Kr gases for I₀ and I measure-ments, respectively.

Results and Discussion
Fourier transforms are represented in Figure 1 together with the structure parameters determined by using aqueous solution as a standard sample. The coordination number is decided to be 4 for all solutions presented in this study. Interestingly, the large Ag(I) ion has the lower coordination number than 6. This is due to the low charge of the central Ag(I) ion, i.e., the steric repulsive force in the 6-coordinate solvation for the Ag(I) ion would be large and may not be compensated by the electrostatic attraction between the Ag(I) ion and surrounding solvent molecules.

A DMSO molecule has potentially two coordinating sites and it is expected that an S atom of DMSO binds to the Ag(I) ion from a measure of the softness of Ag(I) center. However, there is no difference in the k²g(k) curves for H₂O, DMF, DMSO, TMU, and TMP solutions, thus we can conclude that the DMSO molecule coordinates to the Ag(I) ion at the O site. For DMF, TMU, and TMP as well as DMSO, the donor atom should be oxygen and the Ag(I)-O bond lengths are the same, ~238 pm. This distance is in a good agreement with those in many tetrahedral Ag(I) compounds, thus the solvation structures of Ag(I) ion in DMF, DMSO, TMU, and TMP are tetrahe-dral.

In the AN solution, obtained Ag(I)-N distance is consistent with the value in a crystalline phase. This supports that the Ag(I) ion is surrounded by four AN molecules in T₄ symmetry.

For the EN solution, the second sphere peaks due to the Ag(I)-N-C non-bonding interactions appear in the Fourier transform, whereas the corresponding peaks are not seen in the PA solution, although the molecular structures of these two solvents are similar. This clearly indicates that the EN molecule binding to the Ag(I) ion acts as a bidentate solvent to form the [Ag(en)₂]⁺ complex. The fact that the Ag(I)-N bond length in EN is longer by 2 pm than that in PA reflects the chelate formation of EN because of the rather large ionic radius of Ag(I) ion compared with the chelate size of EN.

For the Ag(I) ion, the Ag(I)-N distances in AN, PA, and EN are shorter than the Ag(I)-O distances in H₂O, DMF, DMSO, TMU, and TMP. On the contrary, the distance of M(II)-O interaction for the first-row transition metal ions is shorter than the M(II)-N distance. This is due to the softness character of the Ag(I) center, i.e., the covalency for the Ag(I)-N bonding interaction is more effective.

Figure 1. Fourier Transforms of Ag(I) Ion Solutions. The figures in parenthesis are the coordination number and bond length in pm.


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XAFS STUDY ON THE EFFECT OF COMPLEXANE TYPE LIGANDS ON THE STRUCTURE OF Mo AND W COMPOUNDS IN AQUEOUS SOLUTIONS I. Preparation of nickel--tungstate solutions and catalysts

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Introduction
Environmental regulations on emissions have been tightened, and lead to low aromatics and sulfur specifications for diesel fuels. Highly active hydrogenation catalysts are desirable for aromatics saturation. Extensive studies on the hydrotreating catalysts reveal that dispersion and geometric configuration of MoS2-like crystallites on the catalyst support as well as location of Co and Ni on these crystallites influence their hydrogenation activities and selectivity. We showed that the citric acid was an effective agent to control the Mo structures and to increase the HDS activities.1-3 Tungstate catalysts are known to be highly active in hydro-treating/hydrocracking of middle distillates and upgrading coal-derived oils, which contains low concentration of sulfur. Therefore, innovation of the development of NiW catalysts would impact on their use as aromatic saturation catalysts in spite of their price and limited reaction atmospheres compared with NiMo catalysts.

We prepared the NiW impregnating solutions by using citric acid as a complexing agent, and characterized of the tungsten structure in the impregnation solutions and in the sulfided catalysts by EXAFS.

Experimental
The NiW catalysts were prepared by an incipient wetness impregnation method. The impregnating aqueous ammoniacal (am) solutions were prepared using solution of ammonium tungstate (NH4)2H2W12O42·nH2O and nickel nitrate, and aqueous citrate(cit) solutions were prepared using the former tungstate solution, nickel carbonate and citric acid. γ-Al2O3 was supplied by Catalysts & Chemicals Industries Co., Ltd(surface area=209 m2/g, pore volume=0.81 cm3/g). The impregnated catalysts were dried at 393 K for 4 hours and then calcined at 773 K (standard) for 3 hours in dried air(flow rate=3 1/min). Amounts of the active components were 4.2 wt% of NiO and 29.0 wt% of WO3 for the NiW catalysts and 29.0 wt% of WO3 for the W catalysts. The calcined catalysts were sulfided with a gas containing hydrogen and hydrogen sulfide(H2S(5%)/H2(95%)) at 673 K for 2 h prior to test reactions and characterization. The EXAFS measurements of impregnating solutions and sulfided catalysts were done at the Photon Factory(BL 10B, 7C).

Results and discussion
Figure 1 shows the Fourier transforms of the EXAFS spectra(W L3-edge) for the sulfided NiW(am) and NiW(cit) catalysts, two main peaks were observed at 0.241 nm and 0.315 nm for both of the catalysts, which corresponds to the first W–S and W–W coordinations in WS2 crystallites. Table 1 shows the average coordination numbers for sulfur(N(S)) and tungsten(N(W)) atoms. The N(W)/N(S) values3 suggested that the size of the (002) basal planes of the WS2-like crystallites was larger for the NiW(cit) catalyst than that of the NiW(am) catalyst. In other words, crystallization of WS2-like sulfides was more advanced for the NiW(cit) catalysts, though about 65 % of WO3 was converted into the WS2-like sulfides for both of the NiW catalysts(XPS data).

Table 1 Tungsten coordination in the sulfided NiW catalysts

<table>
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<tr>
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<th>N(W)</th>
<th>N(W)/N(S)</th>
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<td>4.9</td>
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References
XAFS STUDIES ON THE LOCAL STRUCTURE OF THE INTERLAYER ION IN SYNTHETIC FLUORINE MICA ION EXCHANGERS

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Introduction

Some synthetic fluorine mica has a very high selectivity in ion-exchange reactions. A sodium type tetrasilicic mica, sodium taeniolite (NaT, NaMg\(_2\)Li\(_4\)Si\(_8\)O\(_{20}\)F\(_2\)), exchanges its Na\(^+\), the interlayer cation, for K\(^+\), Rb\(^+\), Cs\(^+\), and other cations in solutions. NaT shows specially high selectivity for K\(^+\), Rb\(^+\), Cs\(^+\), and NH\(_4\)\(^+\). It takes up these cations selectively in the presence of much excess of Na\(^+\). Na\(^+\) of NaT and micas with similar composition was exchanged for Rb\(^+\) and other cations and XAFS of the exchanged ions were measured. The structural changes were studied with powder X-ray diffraction patterns to characterize their ion-exchange selectivity.

Experimental

Fluorine micas were used after removing impurities such as \(\alpha\)-cristobalite by washing with water and separation with centrifugation. Rb, Cs, Sr, and Ba chloride solutions were used for the reactions under 25°C. Exchange ratios of Rb\(^+\) were varied from 0.2% to 55% (the maximum exchange ratio) of Na\(^+\) in NaT, and of other cations were ca. 40% and 55%. X-Ray absorption spectra of K or L\(_2\)-edge of exchanged ions were obtained at BL-10B and BL-7C. X-Ray powder diffraction patterns were measured by Rigaku RINT 1100V. Samples were prepared to be wet with the exchange reaction solution for both measurements because of their structural changes under dry conditions.

Results and Discussion

Figure 1 shows XANES spectra of Rb and Sr K-edge and Cs and Ba L\(_{3}\)-edge uptaken into NaT and their 0.1 mol/dm\(^3\) nitrate or chloride solutions. XANES of Rb and Cs samples are apparently different whereas those of Sr and Ba samples are similar. It shows that Rb and Cs take another local structure than in the solution state. All of the exchanged NaT for each ion-exchange ion showed same XANES spectra. EXAFS Fourier transforms of exchanged NaT for are shown in Fig. 2. There is a large peak at the identical position with that in aqueous solution in the transform of Sr and Ba-exchanged NaT. The cations are hydrated as if they are in aqueous solutions. Rb and Cs-exchanged NaT show many peaks in the transform. According to the crystal structure of K-type taeniolite, KMg\(_2\)Li\(_4\)Si\(_8\)O\(_{20}\)F\(_2\), these peaks can be assigned as Fig. 2 (a) indicates. There is no peak or shoulder for the hydrated water oxygen at the position for their aqueous solution. These alkaline cations are held as an anhydrous form. Fourier transforms of all of Rb and Cs-exchanged NaT look very similar one another.

X-Ray diffraction patterns around (001) diffraction of NaT after Rb-exchange reaction for exchange ratios of ca. 40% and 55% are shown in Fig. 3. The peak around 2\(\theta\) = 5.8° can be assigned to the two-water layer form of NaT. This peak decreases with increasing the exchange ratio and disappears when the ratio reaches at the maximum. The peak around 2\(\theta\) = 8.7° becomes clearer with increasing the ratio. This peak can be assigned to the anhydrous form of Rb\(^+\)-type taeniolite. From the diffraction pattern changes with the exchange ratio for Rb\(^+\) and K\(^+\), only NaT having the two-water layer form of NaT can exchange its Na\(^+\) and it becomes an anhydrous form. The dehydrated layer never exchanges its residual Na\(^+\).

From the information of XAFS and powder diffractions, a following mechanism of Rb-exchange reaction can be depicted. At the first stage, Na\(^+\) in a two-water layer is exchanged for Rb\(^+\). In this exchange reaction, Rb\(^+\) detaches its hydration waters. When the ratio of Rb\(^+\) in the two-water layer reaches at certain critical value, the layer begins excluding its interlayer waters until it become an anhydrous form. Finally, all the layers in a sample become anhydrous forms and then the whole exchange reaction stops.

Reference

I. INTRODUCTION

Recently, it has been found that several crystalline materials are transformed into an amorphous state by compression. These amorphization have received considerable attention. However, the structural aspects of most pressure-amorphized materials are still unknown.

This paper shows the XAFS results on pressure-amorphized (a-) GeO₂. There are some polymorphs of GeO₂. For convenience's sake, a-quartz type, rutile type and melt quenched glass GeO₂ are abbreviated to q-, r- and m-GeO₂, respectively. Both q- and m-GeO₂ are built up of network of GeO₄ tetrahedra by bridging oxygen, although the long range periodicity is lost in m-GeO₂. On the other hand, r-GeO₂ has octahedral coordinated Ge.

II. EXPERIMENTAL

Syntheses of a-GeO₂ were carried out using a uniaxial split-sphere apparatus. Samples of q-GeO₂ were compressed and quenched from 12, 16 and 20 GPa (q-GeO₂ is transformed into amorphous state at about 6.5 GPa).

All Ge K-edge XAFS measurements were carried out in transmission mode at BL-IQB.

III. RESULTS AND DISCUSSION

The observed Ge K-edge XANES spectra are shown in Figure 1. The lowest energy absorption (peak-A marked in Figure 1) of a-GeO₂ shifts toward higher energy side as increasing synthesized pressure. On the other hand, the peak of m-GeO₂ is observed at 11.106 keV as its of q-GeO₂ is. For m- and q-GeO₂ have almost same short range order of atomic arrangement, the energy of peak-A is affected by the first nearest neighbor of Ge atom. Therefore, it is considered that a-GeO₂ has lost the short range order of starting material.

The Fourier-transforms of k^3-weighted EXAFS spectra are shown in Figure 2 and the bond distances of the first nearest (Ge-O) and the second nearest (Ge-Ge) atoms determined by curve fitting analyses are summarized in Table 1. We can see two Ge-Ge peaks of a-GeO₂ in Figure 2 and these two bond lengths approach to those of r-GeO₂ by compression.

It is suggested that an increase in pressure for the synthesis of a-GeO₂ results in making its structure closer to r-GeO₂.

![Figure 1: The Ge K-edge XANES spectra of some polymorphs of GeO₂](image)

![Figure 2: Magnitude of the radial structure function \(\phi(R)\) of some polymorphs of GeO₂](image)

| Table 1: Bond distances from curve fitting calculation |
|----------|----------|----------|
| \(R_{Ge-O}\) (Å) | \(R_{Ge-Ge}\) (Å) | \(R_{Ge-C-H}\) (Å) |
| q-GeO₂ | 1.75 | 3.15 | - |
| 12 GPa | 1.76 | 2.95 | 3.20 |
| 16 GPa | 1.78 | 2.95 | 3.45 |
| 20 GPa | 1.76 | 2.98 | 3.40 |
| r-GeO₂ | 1.88 | 2.86 | 3.42 |
in situ XAFS STUDY OF BIUNCLEAR Ru COMPLEXES.
STRUCTURES AND ELECTRONIC STATES

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Introduction
The redox reactions of metallic cluster complexes are important from a biochemical point of view. However, the intermediate products in these reactions are so unstable that they must be stabilized electrochemically and be kept under an inert atmosphere. These intermediate products have been little characterized before. An in situ electrochemical cell for use in synchrotron radiation XAFS experiments has been developed to investigate these structures and electronic states. The structures and electronic states of intermediate products of a Ru complex, \([\text{Ru}_2(\mu-O)(\mu\text{CH}_3\text{COO})_2(bpy)_2(\text{Him})_2]^{2+}\) (bpy = bipyridine, Him = imidazole), in acetonitrile solution have been studied with this new cell by XAFS measurements combined with this new cell.

Experimental
Fig. 1 shows a typical cyclic voltamogram measured at 25°C for an acetonitrile sample solution which contained 1mM Ru and 0.1M \((\text{n-Bu})_4\text{NPF}_6\). Ru K-edge XAFS spectra were recorded on BL10B in the Photon Factory, National Laboratory for High Energy Physics. The concentration of Ru was 20mM.

Results and Discussion
In Fig. 1, an oxidation wave at +0.9V is assigned to the oxidation from Ru \((\text{II}, \text{III})\) to Ru \((\text{II}, \text{IV})\). Two reduction waves at -0.4V and -0.6V are assigned to the coupled reduction from Ru \((\text{II}, \text{III})\) to via Ru \((\text{II}, \text{III})\) to Ru \((\text{II}, \text{II})\). The XANES spectra for Ru \((\text{II}, \text{III})\) and Ru \((\text{II}, \text{IV})\) species are approximately identical whereas that for Ru \((\text{II}, \text{III})\), is different. The EXAFS spectra for the Ru \((\text{II}, \text{III})\) and Ru \((\text{II}, \text{IV})\) species are shown in Fig. 2. The least-squares fitting of the EXAFS spectra have shown that on oxidation the Ru–N and Ru–O distances are decreased, whereas the Ru–Ru distance is increased by almost 0.1Å (see Table 1). This result is in accordance with reported crystal structures. The Ru \((\text{II}, \text{III})\) spectrum will be measured.

Table 1 Structural data of \([\text{Ru}_2(\mu-O)(\mu\text{CH}_3\text{COO})_2(bpy)_2(\text{Him})_2]^{2+}\)

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<th>(E_0(\text{eV}))</th>
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References
INVESTIGATION OF STRUCTURE OF THE SOL-GEL DERIVED SODIUM GERMANATE GLASSES BY EXAFS
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Introduction
It has been reported by Ivanov et al. that, in the relation between composition and physical properties such as density and refractive index of alkali germanate glasses, a peak appears when the alkali content is increased, which is now known as "germanate anomaly". The structure of melt-derived germanate glasses is known to be constructed by two types of coordination polyhedron, i.e., GeO₄ and GeO₆. Melt-derived GeO₂ glass consists of four-fold coordinated Ge atoms, and the addition of alkali oxide such as Na₂O to GeO₂ glass causes the formation of six-fold coordinated Ge atoms till alkali content amounts to 20 mol% where the fraction of the six-fold coordinated Ge is 25%. In general, structure with ions or atoms in low coordination state is favorable at high temperatures, and at low temperatures structure with high coordination state is preferred. Therefore, it is expected that Na₂O-GeO₂ glasses prepared by sol-gel method, which enables the low temperature processing of glasses, may contain larger amount of six-fold coordinated Ge atoms than melt-derived one. With such a background, sodium germanate glasses were prepared by sol-gel method, and the coordination state of Ge atoms in the glasses was examined by Ge-EXAFS using high luminous X-ray at the Photon Factory.

Experimental
High purity Ge(0-C_H₂NaOCH₃ (28wt% in methanol) and NaOCH₃ (99.999 %) and NaOCH₃ (28wt% in methanol) were used as starting materials. The alkoxide mixture corresponding to the oxide composition of xNa₂O-(100-x)GeO₂ (x=10,15,20 mol%) was diluted with anhydrous ethanol, and then another solution consisting of water, HCl and ethanol was added dropwise to the former solution while stirred and cooled in the water/ice bath. The molar ratio of water, ethanol and HCl to Ge alkoxide was 2.0, 20 and 0.005, respectively, in the final solutions. The mixed solutions were kept standing in the room for gelation in a tight-sealed container. These solutions set to gels in two days. After aging in the room for one day, these gels were transferred to 60°C oven for drying. These xerogels thus obtained were heat-treated to 400°C with a heating rate of 10°C/min, and held there for 20 min. The heated specimens were X-ray amorphous. In the neighborhood of the Ge K-absorption edge (11.1036keV), X-ray absorption measurement of the 400°C-heated samples were performed at BL-10B. White X-ray generated by synchrotron was monochromated using channel cut Si(311) crystal monochromater. Two ionization chambers were used to detect the incident and transmitted beams. Hexagonal GeO₂ (h-GeO₂) crystal was used as reference of four-fold coordinated Ge⁺ ion, and tetragonal GeO₂ (t-GeO₂) crystal as that of six-fold coordinated one.

Results
Figure 1 shows the RDF curves of 400°C-heated xNa₂O-(100-x)GeO₂ (x=10,15,20) gels, together with those of t-GeO₂ and h-GeO₂ crystal. Since phase shift parameter is not taken into consideration in the radial distribution function (RDF) curves, RDF peaks appear at lower r position than real position. In the figure, each sample except t-GeO₂ crystal has a peak at 1.40Å. The first peak for t-GeO₂ crystal is located at larger distance as 1.55Å, because the Ge-O distance in octahedral GeO_6 is longer than that of tetrahedral GeO_4. Peaks for 400°C-heated gels are broader than that of h-GeO₂ crystal, suggesting that two types of coordination states exist in these samples. At the lower side of the second peaks of 400°C-heated gels, a small and broad peak appears with increase of Na₂O content. The phenomenon may be explained in terms of the edge-shared GeO₆ octahedra in those samples. Table 1 shows the coordination number of Ge⁺ atom, the corrected inter-atomic distances and Debye-Waller factors, respectively, obtained from non-linear least square fitting of the first RDF peak. The fraction of six-fold coordinated Ge atoms is much more than that of melt-derived glass of the same composition.

References

Table 1. Result of non-linear least square fitting

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<th>Na₂O (mol%)</th>
<th>r₁ (Å)</th>
<th>r₂ (Å)</th>
<th>s₁</th>
<th>s₂</th>
<th>Nc</th>
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HYDROGEN ADSORPTION INDUCED STRUCTURE IN Pt L₃ XANES

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Introduction

Adsorbed hydrogen on metal particles play an important role in the catalyses. However, a little techniques available to characterize the adsorbed hydrogen. XANES spectra of Pt L₃ edge have been found to suffer change by the adsorption of hydrogen. But the origin of the change is still at issue. Three possible mechanisms are proposed for a moment, i.e., change in direct interaction with support oxygen, to create a new bonding between metal particle and surface OH groups and adsorbed H changes the electronic states of Pt particle. The purpose of this work is to find a plausible origin for that new peak associated with hydrogen adsorption.

Experimental

XANES spectra were measured at BL10B using Si(311) channel cut monochromator. The sample was produced by an ion exchange and an impregnation method. The supports were SiO₂ and Al₂O₃. The particle size was determined by an uptake of hydrogen under the assumption of H/Pt_surface =1 and the spherical shape. The sample was reduced at 773 K for 1 h and then evacuated at 773 K for 0.5 h. Hydrogen was adsorbed on the same Pt particles at room temperature.

Results and Discussion

Fig.1 shows the XANES spectra of Pt L₃ edge of Pt/SiO₂. The new peak appears at 8 eV above the white line peak top. The peak height increases with the increase of the dispersion as shown in Fig.2, indicating that the peaks is due to the introduction of hydrogen. The triangle in the Fig.2 shows the height of the peak in the L₃ edge of Pt/Al₂O₃ which is on the same lines those of Pt/SiO₂. The position of the new peak also appeared at 8 eV above the white line peak top. No dependence of the supports indicates that the new peak does not arise from the metal support interaction. Probably the interaction of H will push up some of the vacant d-band to higher energy which is the origin of the new peak. We are now planning to carry out the experiment for other supports and other adsorbates to confirm this point.

References

CHARACTERIZATION OF Cu-AI CATALYST'S PRECURSOR BY XAFS
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Introduction
Cu catalysts are useful for methanol synthesis and water gas shift reaction. They are prepared as hydroxides or basic carbonates, and mixed or co-precipitated with Al, Zn, Mg. Moreover, they are prepared after calcined and/or reduced. The activity and life of the catalysts depend largely on the preparations. Therefore, it will be very important to investigate the formation mechanism of the hydroxides or basic carbonates from the precipitates. In this note, the Cu atomistic structure of malachite, compound like hydrotalcite, and their precursors containing Cu and Al ions are investigated using a XAFS spectrometry.

Experiments
Sample preparation: Samples of the basic carbonate like hydrotalcite containing Cu and Al (sample: 1), malachite (sample: 2) and their precursor (sample: 3) were prepared using the method by C. Busetto et al. Because the precursor of this system was easy to change, the precipitates were handled carefully.

XRD measurements: The results of XRD measurements for the sample-1 and -2 were similar to No. 37-630 and No. 10-399 of JCPDS card files, respectively. However, the sample-3 showed amorphous diffraction pattern.

ESR measurements: The ESR measurement for the sample-3 showed the hyperfine structure, which implied that the Cu compound existed as isolated unit instead of complex 3-D network structure.

XAFS measurements: The XAFS spectra of a Cu foil, CuO, sample-1, -2 and -3 were measured around Cu K-edge at BL-10B of Photon Factory in National Laboratory for High Energy Physics. The XAFS spectrum of sample-3 was measured instantly after prepared at neighbor laboratory within the Photon Factory.

Results and Discussion
Figures-a, -b and -c show the Fourier transforms of the EXAFS around the K-edge/Cu weighted by \( k^2 \) of the sample-1, -2 and -3, respectively. The phase shift were corrected by using the deviations for CuO.

It was known that cupric ion showed distorted octahedral structures in many compounds. According to L.E. Orgel et al., the distances between Cu and 6 oxygens in malachite were 1.96 or 2.01 A at the 4 short bonds in a plane and were 2.41 or 2.71 A at the residual 2 weaker bonds on lines normal to the plane. The distance between Cu and 6 octahedral oxygens in the hydrotalcite-like compound would be similar to those in malachite.

In all figures, a dominant peak at \( R = 1.6 \) A could be identified with the corresponding Cu-O bonds (1.96 or 2.01 A) in the square-planed positions. However, any other peaks with the corresponding Cu-O bonds (2.41 or 2.71 A) in the positions on lines normal to the plane were not observed. In figures-a and -b, the other peaks could be observed at the distances more than 2.0 A (which corresponded to >2.9 A in the case of malachite). In figure-c only one peak could be observed at \( R = 1.6 \) A, so there would be no constant structures at the range longer than \( R = 1.6 \) A. This is consistent with the results of the XRD and ESR measurements.

References
INTRODUCTION

Recoverin is a 23 kDa EF-hand, calcium regulatory protein found in bovine retinal rod as a calcium-dependent modulator of retinal guanylate cyclase. A homologous protein, S-modulin, was isolated from frog retinal rod as a Ca-dependent modulator of phosphodiesterase. Recently, the physiological function of these EF-hand proteins is established as the Ca-dependent terminator of the transduction cascade via regulation of rhodopsin phosphorylation.

A further important and interesting feature of recoverin is that its N-terminus is acylated with one of four types of fatty acyl residues including myristoyl (C14:0), C14:1, C14:2 and C12:0. N-terminal acyl residues would be expected to play a role in protein-membrane interactions, rather than in protein-protein interactions.

In this study, we investigated the conformational change in recoverin upon binding of calcium, as well as the effect of myristoylation on its solution structure by solution X-ray scattering. The study reveals the Ca-dependent conformational change, as well as the alteration of its surface properties depending on calcium and N-terminal myristoylation.

EXPERIMENTAL

Both myristoylated and unmyristoylated recoverins were expressed in E. coli and purified by an ordinary method. The purified recoverins were generous gifts from Dr. L. Stryer. Both recoverins were dialyzed against either buffer containing 1 mM CaCl2 or buffer containing 5 mM EGTA. Solution X-ray scattering experiments were performed with a SAXES camera installed at BL10C.

RESULTS AND DISCUSSION

SAXS measurements were performed under four different conditions, with both myristoylation and calcium, with myristoylation and without calcium, without myristoylation and with calcium, without both myristoylation and calcium. Proteins are monomeric under two conditions, without myristoylation and with calcium, and with myristoylation and without calcium, while proteins tend to aggregate under the other conditions. The Ca-dependent monomerization and aggregation were reversible. Similar results are obtained for S-modulin. The observed structural parameters are listed in Table I. In retinal rod, recoverin is bound to membrane under high calcium concentration, while it becomes soluble under low calcium concentration. The present results indicate that physiologically soluble state is monomeric. The aggregation is mainly due to hydrophobic interaction. We concluded that recoverin alters its surface hydrophobicity depending on both calcium and myristoylation, which would be common properties for recoverin-like proteins.

<table>
<thead>
<tr>
<th>Protein</th>
<th>Shape</th>
<th>$R_c$ (Å)</th>
<th>$d_{max}$ (Å)</th>
<th>$\alpha$-helical content (%)</th>
<th>Effect of melittin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristoylated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Ca$^{2+}$</td>
<td>Aggregated</td>
<td>nd$^a$</td>
<td>nd$^b$</td>
<td>65</td>
<td>None</td>
</tr>
<tr>
<td>- Ca$^{2+}$</td>
<td>Globular, monomeric</td>
<td>21.2 ± 0.3</td>
<td>63 ± 3</td>
<td>52</td>
<td>Induced aggregation</td>
</tr>
<tr>
<td>Unmyristoylated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ Ca$^{2+}$</td>
<td>Globular, monomeric</td>
<td>20.3 ± 0.3</td>
<td>57 ± 3</td>
<td>65</td>
<td>None</td>
</tr>
<tr>
<td>- Ca$^{2+}$</td>
<td>Aggregated</td>
<td>nd$^a$</td>
<td>nd$^b$</td>
<td>52</td>
<td>None$^c$</td>
</tr>
</tbody>
</table>

$^a$The values could not be determined because of aggregation. $^b$Melittin possibly stimulates aggregation in this state.
UNFOLDED STATES OF APOCYTOCHROME c STUDIED BY SOLUTION X-RAY SCATTERING

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INTRODUCTION

Removal of the covalently bound heme group from cytochrome c produces apocytochrome c. The conformation of apocytochrome c has been assumed to be unfolded under aqueous conditions of neutral or acidic pH, but an α-helical structure in the presence of lipids. Although horse cytochrome c and several other proteins are largely unfolded in the absence of salt in the vicinity of pH 2, they adopt a molten globule state in the presence of anions either from salt or acid.

Horse cytochrome c is a basic protein with pI=10.1. Goto and coworkers indicate that the addition of anions to the acid-unfolded state, either from salt or acid, or an increase in pH decrease the repulsive forces which arise from the protein net charge and, as a consequence, increase the folding forces. Comparison of the intermediate conformations of holo- and apoproteins may reveal the role of heme in stabilizing the folded and molten globule states.

We have studied the conformation of apocytochrome c and a fluorescence-labeled derivative under various conditions of pH and salts. Consequently, we have found that apocytochrome c adopts an intermediate state (the A state), resembling the molten globule of the holoprotein, at acidic pH in the presence of anions. The term, molten globule, is proposed for the compact denatured state which retains a most part of the secondary structure but loses its tertiary structure. We have shown that solution X-ray scattering is the best technique to describe compactness and shape of non-native conformation such as molten globule state (1). In this report, we describe solution scattering from several conformational states of apocytochrome c.

EXPERIMENTAL

Small-angle X-ray scattering (SAXS) measurements were performed with SASES installed at BL10C. Horse cytochrome c was purchased from Sigma. The heme group linked to the two cysteine residues by thioether bonds was removed by reaction with silver sulfate. Apocytochrome c was passed through a column of Sephadex G-25 equilibrated with 5mM sodium acetate buffer at pH 4 containing 0.1mM EDTA. The extrapolated scattering curve to zero protein concentration was obtained through the measurements at at least 5 different protein concentrations between 5 and 25mg/mL.

RESULTS

We have carried out SAXS measurements on the different conformational states of apocytochrome c. However, the specimens at pH above 4 or in the presence of salt show distinct aggregation. We could not obtain structural information on molten globule and collapsed states of apocytochrome c. Figure A shows Guinier plots of apocytochrome c at pH 3 in the presence and absence of 4M guanidine(Gdn)-HCl, and at pH 6 in 4M Gdn-HCL There are no substantial differences in 4M Gdn-HCl between at pH 3 and at pH 6. The Rg of Gdn-HCl-induced unfolded state is 30Å. The acid-unfolded state without denaturant or salt has a smaller Rg of 22.5Å, which is similar to the acid-unfolded state of holocytochrome. Therefore, the acid-unfolded state of cytochrome c is compact compared to the denaturant-unfolded state. The result suggests that there are variety in structure even for the unfolded state, and that unfolded state cannot be generalized as "random coil".

Figure A: Guinier plots of apocytochrome c in 10mM glycine HCl buffer at pH 3 (○), in 10mM glycine HCl buffer at pH3 and 4M Gdn-HCl (△), and in 10mM phosphate buffer at pH 6 and 4M Gdn-HCl (□).

REFERENCE

APPLICATION OF IMAGING PLATE TO SOLUTION X-RAY SCATTERING

Yoshinobu IZUMI, Kazuyoshi SAKAI, Hidenori YOSHINO, Yoji INOKO, Mikio KATAOKA, Hiroshi URATA, Tetsuro FUJISAWA, Katsumi KOBAYASHI and Yoshiyuki AMEMIYA

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Introduction
The solution X-ray scattering (SOXS) technique using an imaging plate (IP) has been recently developed and applied to study the conformations of calmodulin (CaM) in solution under different sample conditions. The comparison with data obtained from the PSPC system demonstrated the excellent performance of the IP system (1).

Experimental
In developing the SOXS technique with IP, it has been required to measure a pair of scattering intensities from the solution and solvent in the same experimental condition. For this aim, the minimization of the following points has been made: (a) the time decay of the ring current of PF, (b) the effect induced by the utilization of two of IPs and (c) the time decay of the data accumulated on these IPs. The size of the IP was 250x200mm².

Results and Discussion
Fig. 1 shows the scattering profiles of the horizontal and vertical directions from cholesterol. The distance between peaks indicated by arrows is 407 pixels irrespective of direction. The peak width of the vertical direction is 2 times that of the horizontal direction depending on the convergent condition of the torroidal mirror. Using the peak distance, the value of pixel is transformed into the s value, which is defined by \( s = \frac{2 \sin \theta}{\lambda} \). Fig. 2 shows the comparison between the profiles of the IP and PSPC for the Ca²⁺-saturatedCaM in solution. The comparison demonstrates the excellent performance of the IP system. Details on these results will be published elsewhere.

References
SMALL-ANGLE X-RAY SCATTERING STUDIES OF THE SOLUTION STRUCTURE OF PROTEINS UNDER PRESSURE

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Introduction

It is well known that most proteins are denatured by pressure up to 1000 bar while some of them are renatured by moderate pressure up to ~2000 bar. Those characteristic phenomena are among the effects of pressure on proteins. However, there are limited studies of pressure effects on the molecular structure of protein due to experimental difficulties. Quite recently high pressure infrared spectroscopic studies and NMR studies have been started, which investigate secondary and local tertiary structures of proteins, respectively. The purpose of the present work is to perform solution X-ray scattering (SOXS) under high pressures up to 4000 bar, which give information on the global tertiary structure of proteins.

Methods and Results

It is of critical importance for the scattering measurement at high pressure to correct for the background scattering from the cell and solvent, since increasing pressure increases the pathlength and the density of water. Therefore, we employed a hydrostatic cell in a piston-cylinder type for the high pressure measurements. The present cell, which is designed to reach 7000 bar, has two synthetic diamond (Type 1b) windows (1.0 mm thick and 5.0 mm diameter). The pressure generated is directly controlled by the transmitting fluid of a hand hydraulic pump (Hikari Co., max. Press. 10 kbar). The pressures were measured by a Heise pressure gauge with an accuracy of 1 MPa. Thus, we can measure the X-ray scattering of the sample and reference under high pressures in the same instrumental conditions to accurately correct background scattering. The cell is designed to be very compact, measuring 55 mm (long-parallel to the light path) by 86 mm (height). It was used in a BL-10C instrument which was installed at the Photon Factory, without special instrument modifications. It took 600 sec to obtain the scattering profile of proteins at high pressures.

No radiation damage to samples was detected during each measurement.

We measured SOXS of egg-white lysozyme at high pressure up to 4000 bar, where the protein is not denatured. Figure 1 shows the Guinier plots at 1 atm and 4000 bar, at 25 °C, which are obtained from the scattering curves after the background correction. Further, we corrected the scattering intensity on the basis of the pressure dependence of X-ray absorption of water by measuring direct beam attenuated by 0.6 mm Al plate. The linearity of both plots in the relatively wide region of scattering angle indicates the high accuracy of this measurement using the present high pressure cell. This means that this cell allows qualitative measurement of SOXS under high pressure. From the slopes, we obtained the radius of gyration of lysozyme (Rg)=15.35±0.12Å for 1 bar, 14.71±0.25Å for 4000 bar. An increase in pressure induces a significant decrease in Rg. More detailed experiments, e.g., determination of volume of proteins are now in progress.

![Guinier plots for lysozyme in 10 mM MES buffer (pH 5.7) at 1 atm and 4000 bar.](image)
Structural Study on the subunit configuration of oligomeric proteins by using solution X-ray scattering technique

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2) MAC Science Co., Ltd., Midori, Yokohama, Kanagawa 226

Introduction

We have been studying on the positional change of subunit packing upon enzymatic reaction. In previous report, lactate dehydrogenase (LDH) from pig heart (MW 146,000) and glyceraldehyde-3-phosphate dehydrogenase (GAPDHase) from chicken muscle were found to show a gross change in medium scattering region. The change, however is very subtle so that we developed the ring-cathode detector [1] and checked its performance.

Experimental

In order to clarify the performance, we collected wide angle scattering of LDH solution by using ring-cathode detector as well as PSPC under the same condition. The camera length was about 55 cm and collection time were 1200 sec and 900 sec for PSPC and Ring-cathode detector, respectively. The high voltage was applied up to 2.15 KeV. Total count rate was $1.2 \times 10^5$ cps.

Results and Discussion

It is apparent from Figure 2 that the quality of data in medium angle scattering region was greatly improved compared to PSPC. It is also good at collecting data under identical condition between sample and buffer condition, which is essential to solution X-ray scattering measurement. We intend to apply this detector to time resolved measurement.

Reference

STUDIES ON MECHANICAL PROPERTIES OF CALCIFIED COLLAGEN
BY SMALL ANGLE X-RAY DIFFRACTION
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Introduction
Bone has often been regarded as a two phase composite of hydroxyapatite (HAP) minerals embedded in collagen matrix. From the HAP content dependence of mechanical properties of bone, it was expected that collagen matrix around HAP particles had modulus larger than that of collagen without HAPs<sup>1</sup>. This expectation suggests the reinforcement of collagen matrix by HAP particles. There are, however, no immediate empirical evidences for the reinforcement. The purpose of this work is to show the difference between the moduli of collagen with (bone) and without mineral (tendon).

Experimental
Bone samples were prepared from matured (around 20 months) bovine femur. Specimens were shaped in rectangular plates whose longer axes were parallel to bone axis of the femur. Collagen specimens were obtained from bovine Achilles tendon. The Young's moduli of collagen and bone collagen were estimated by measuring the strain for the characteristic D-period of collagen as a response to the macroscopically applied force. Small angle X-ray diffraction method was employed to determine the strain, where synchrotron orbital radiation was used as a strong X-ray beam source. Mechanical loading apparatus was constructed and set in the small angle X-ray diffractometer build at BL10C station in PF of High Energy Physics Institute. Measurements were made in saline solution at room temperature (22°C).

Results and Discussion
The 3rd order reflection of D-period was investigated. Figure 1 shows the stress-strain relation for tendon collagen and bone collagen thus measured. The vertical (stress) axis was calculated from applied force divided by the cross sectional area of the specimen. Taking account of the data scattering, the stress-strain relations of the D-period for bone collagen and tendon collagen were revealed to be Hookean, where the slope of the plot is proportional to the apparent Young's modulus. It is clear that the apparent Young's modulus of bone collagen is far larger than that of collagen without mineral. If we assume the Young's modulus of collagen as 1 GPa, the apparent Young's modulus for bone collagen under the existence of mineral particles is about 20 GPa. The value is similar to the Young's modulus value of bone itself. Results by X-ray diffraction method are generally regarded as a weighted average information over all of the scatterer in the system. This result evidences the existence of strain distribution in bone and a simple numerical calculation reveals that the mechanical structure of bone would be described by an equi-strain model.

References

![Fig. 1 Stress-strain curves for bone and tendon.](image-url)
EFFECT OF VARIATION OF pH ON GANGLIOSIDE MICELLAR STRUCTURE IN SOLUTION STUDIED BY USING SMALL-ANGLE X-RAY SCATTERING

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1Department of Physics, Gunma Univ., Maebashi 371, 2Faculty of Engineering, Gunma Univ., Kiryu 376, 3Faculty of Textile Science and Technology, Shinshu Univ., Ueda 386, 4Photon Factory, KEK, Tsukuba-shi 305.

Introduction
Gangliosides are glycosphingolipids which contain a ceramide linked to glucosylgalactosylsialic acid, found in the highest concentration in the nervous system, particularly in gray matter, but are widely distributed in other tissues. Gangliosides are concerned in the self organization of tissues, immune response and cell differentiation through the molecular recognition carried out by various polysaccharide chains of ganglioside molecules. Gangliosides can be thought to form micelles in solution rather than vesicles or bilayers because of the presence of large head groups, and actually is found to form micellar structures as shown elsewhere.1 Here we will show the experimental result on the effect of variation of pH on ganglioside micellar structure obtained by use of synchrotron radiation X-ray scattering methods.

Experimental
As described elsewhere,2 gangliosides used were extracted with hot chloroform-methanol from acetone-ethanol-light petroleum extracted residue of cephaline preparation. The crude gangliosides were further purified and fractionated according to the modification of Svennerholm's method. The lyophilized ganglioside powder was dissolved in citrate buffer adjusted to various pH and used for the scattering experiments. The ganglioside sample used here was the di-sialogangliosides (Gdi). The ganglioside concentration was adjusted 0.5wt%. X-ray scattering experiments were carried out by using the small-angle X-ray scattering spectrometer SAXES installed at BL10C line of the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan. The wavelength used was 1.49 Å and the sample-to-detector distance was 87 cm. The exposure time was 300 s for each measurement. Temperature of samples was kept at 25°C. The standard analyses were carried out in the same way as shown elsewhere.3

Results and Discussion
As shown in Figure 1, by lowering pH the scattering profile of ganglioside changes from that for a spherical micelle to that for a elongated one. This situation is also clearly seen in Figure 2 showing the distance distribution function p(r) obtained by the Fourier transformation of the scattering curves in Figure 1. At low pH, the maximum diameter of the micelles is enlarged greatly. It can be assumed that the variation of pH affects the extension of acid sugar head of ganglioside very sensitively.

References
THERMAL STABILITY OF GANGLIOSIDE MICELLAR STRUCTURE IN SOLUTION STUDIED BY USING SMALL-ANGLE X-RAY SCATTERING

Mitsuhiro Hirai,^1 Toshiharu Takizawa,^1 Sadato Yabuki,^1 Hiroshi Mitomo,^2 Toshihiro Hirai,^3 Katsumi Kobayashi,^4 and Kouhei Hayashi.^1

1Department of Physics, Gunma Univ., Maebashi 371, 2Faculty of Engineering, Gunma Univ., Kiryu 376, 3Faculty of Textile Science and Technology, Shinshu Univ., Ueda 386, 4Photon Factory, KEK, Tsukuba-shi 305.

Introduction

Gangliosides are found in the highest concentration in the nervous system, particularly in gray matter, but are widely distributed in other tissues. Gangliosides are assumed to play a role in a variety of surface events such as specific recognition of external ligands and biotransduction of membrane mediated information. In gangliosides, the most complex sphingolipids, an oligosaccharide chain containing at least one acidic sugar, called sialic acids, is attached to ceramide. Owing to such characteristics, gangliosides show marked amphiphilic property resulting in high solubility in aqueous solution. To clarify the various physiological functions of gangliosides in connection with those structural properties, we have studied the structure of ganglioside in solution by using neutron and synchrotron radiation X-ray solution scattering methods.

Experimental

The preparation of gangliosides was described elsewhere. The ganglioside powder was dissolved in Hepes buffer adjusted at pH6.8 and used for scattering experiments. The solute concentration was 1.0 wt%. The ganglioside sample used here was disialogangliosides (G_{2}A). X-ray scattering experiments were carried out by using the small-angle X-ray scattering spectrometer SASES installed at BLIOC line of the Photon Factory of the National Laboratory for High Energy Physics, Tsukuba, Japan. The wavelength used was 1.49 Å and the sample-to-detector distance was 87 cm. The exposure time was 300 s for each measurement and the integrated exposure time was below 2000 s. Temperature of samples was controlled in the range of 20-60 °C by circulating water within the precision below 0.5 degree. The Guinier and the distance distribution function analyses were carried out in the same way as shown elsewhere.

Results and Discussion

The temperature dependence of scattering profile of ganglioside is shown in Figure 1. The distance distribution functions p(r) obtained by the Fourier transformation of the scattering curves are shown in Figure 2. The scattering and p(r) profiles can be well described by shell-modeling. In the process of temperature elevation, the ganglioside micellar structure changes from an ellipsoidal shape to a spherical one, which can be assumed to result from the change of packing factor of ganglioside molecule. Detailed analysis and discussion will appear elsewhere.

References

STRUCTURE DETERMINATION OF THE Si(111)/3x3-Bi SURFACES
BY X-RAY REFLECTIVITY METHOD

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Introduction
Absolute reflectivity of x-rays diffracted from the surfaces brings us valuable information such as the coverage of adsorbed atoms which is unavailable by the usual kinematical data analysis because intensity scale is not changed in the data analysis process of absolute reflectivity. In this time we measured absolute reflectivity from the Si(111)/3x3-Bi surfaces and analyzed the data using a newly developed dynamical theory.1,2

Experimental
We made experiment in BL10-C using the UHV chamber for surface X-ray diffraction. In the chamber the Si(111)/3x3-Bi surfaces were prepared by vacuum deposition following the surface cleaning by electron beam heating.

Because of the temperature gradient of the surface at Bi deposition, two phases of the Si(111)/3x3-Bi surface appeared: a low-coverage phase (α-phase) grown at a higher temperature place and a high-coverage phase (β-phase) grown at a lower temperature place. Structure models of these two phases are shown in Fig.1. We measured reflectivities from these two phases along 00 reciprocal lattice rod. In Fig.2 measured reflectivity from α-phase is shown in open circles and that from β-phase is shown in full circles. Two phases are clearly distinguished by the drastically different reflectivities.

Result
It is noteworthy that the ordinate value in Fig.2 is not arbitrary but absolute. By the new dynamical theory the absolute reflectivity R from the crystal surface is given as

\[ R = \frac{r_c^2 A^2 C^2}{\cos \theta_{in} \cos \theta_{out}} |S|^2 |F_{tot}|^2 \]  

(1)

The meanings of symbols in eq.(1) are explained in refs 2,3.

The fitting curves calculated using eq.(1) are depicted in Fig.2. The fairly well agreement between experiment and theory indicates that absolute reflectivity method is useful for structure study of surfaces.

References
ANOMALOUS SMALL-ANGLE SCATTERING EXPERIMENT OF FERRITIN SOLUTION

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Introduction
Anomalous X-ray scattering is a new technique in structure determination of macromolecules in solution. The merit of this technique is the capability to change the scattering densities of the target atoms in the molecules without any chemical modifications. However, so far the application only has been found with a few proteins [1–3] because of the demerit that the contribution of the anomalous scattering to the total scattering is very small. We have performed an anomalous small-angle scattering experiment of ferritin which is known to be a protein giving an extremely large anomalous effect as a whole.

Ferritin is a roughly spherical molecule consisting of a protein shell surrounding an iron oxide core. The central cavity of the molecule has a capacity for up to 4500 iron atoms. The molecular weight has been reported to be about 460,000 for iron-free ferritin (apo-ferritin) and about 900,000 for full ferritin.

Experimental
Horse spleen ferritin was obtained from Sigma Chemical Co. and used in 50mM phosphate buffer (pH7.0) containing 0.15M NaCl after gel filtration to remove dimer components. The protein concentration were 0.23\% for scattering measurements and 2\% for absorption measurements.

The experiments were carried out at bending magnet beam line BL–10C consisting of a fixed exit double Si(111) crystal monochromator followed by a bent cylindrical mirror. The calibration of the X-ray wavelengths selected by the monochromator was done by use of the iron K absorption edge (1.743 Å) of iron foil.

Results and Discussion
Absorption measurements using the SAXS camera were done for ferritin solution and iron foil. The K absorption edge of ferric iron in ferritin was found to appear at 1.740 Å, suggesting that the anomalous scattering from iron atom depends strongly on its chemical environment. Fig.1 shows the variation of the radius of gyration, R_g, of ferritin molecule with X-ray wavelength. The magnitude of change in R_g owing to anomalous scattering is proportional to the magnitude of the real part with negative sign, f_1, of anomalous scattering factor [1]. As can be seen from Fig.1, ferritin molecule exhibits the increase in R_g near the absorption edge because the anomalous scatterers are distributed in the center of the molecule.

Fig.2 shows Guinier plots of the differences in intensity between two scattering curves at different wavelengths, compared with the plot of the scattering curve at the edge. The difference intensity curves, which are approximately expressed by the product of the scattering amplitude functions of ferritin with off–resonance and of the iron core, gave an apparent R_g of about 35 Å. From this value, the R_g of the iron core was estimated to be about 28 Å, yielding a constant density sphere with a diameter of about 72 Å. This size is in good agreement with an inner diameter of 76 Å of the hollow structure revealed by X-ray crystallographic analysis of apo–ferritin [4].

References
DEVELOPMENT OF THE SIMULTANEOUS CALORIMETRY AND TIME RESOLVED SMALL ANGLE X-RAY SCATTERING INSTRUMENT

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Introduction
Calorimetry gives macroscopic thermodynamic information of the system, on the other hand, X-ray scattering gives micro-structure or fine structure of the system. Several attempts are reported for combined measurements of calorimetry and X-ray scattering method, however, they have problems for the sensitivity of calorimetry. Although we have reported the simultaneous differential thermal analysis/small angle X-ray scattering (DTA/SAXS) apparatus and its applications [1-3], the sensitivity of DTA is not sufficient to discuss thermodynamic quantities of the system. In this study, the newly developed simultaneous differential scanning calorimetry/small angle X-ray scattering (DSC/SAXS) apparatus which had the comparable DSC sensitivity and accuracy with the conventional DSC was reported.

Simultaneous DSC/SAXS instrument
Detailed structure of the simultaneous DSC/SAXS apparatus was reported [4]. The cell structure of DSC/SAXS instrument was essentially similar to that of conventional DSC, Seiko DSC 200. The DSC sensitivity of DSC/SAXS was almost the same with conventional DSC 200. The sample cell structure of DSC/SAXS is shown in Fig.1. Both sample and reference holders with a 2mmφ hole for X-ray beam were made of platinum. Heat flow at sample holder was detected by four pairs of thermocouples.

Experimental
Hexatriacontane (C36H74) with 99.8% purity supplied from Tokyo Kasei Co. Ltd. was used through the experiment. Simultaneous DSC/SAXS instrument was installed on SAXS optics with 2.0 m camera length at BL-10C. DSC/SAXS measurement was carried out in the temperature range from 337 K to 351 K at 0.5 K/min.

Results
DSC curves and (001) plain distance, D(001), were observed as a function of temperature on real time. C36H74 showed two solid state transition below its melting temperature (Tm). D(001) changed clearly at transition temperatures and varnished completely at Tm.

References
STRUCTURE ANALYSIS OF QUASI-AND STABILIZED XANTHAN HYDROGELS

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Introduction
Multi-helical polysaccharides, such as gellan and xanthan, form thermo-reversible hydrogels. Sol-gel transition temperature and dynamic shear modulus (G') of these hydrogels are influenced by annealing at the sol-state [1,2]. The hydrogels with insufficient annealing show the frequency dependence of G' (quasi-gel). With increasing annealing time, hydrogels show high G' value which is almost constant at frequency from 10^-3 to 1 Hz (stabilized gel). In this study, structural information of quasi-gel and stabilized gel was observed by small angle X-ray scattering (SAXS).

Experimental
Sample used in this study was xanthan sodium salt supplied from Mitsubishi Chemical Co. Ltd. 2wt% of xanthan aqueous solution was obtained by previously reported method [1]. The obtained sample solution was annealed at 363 K for various periods in the instrument.

SAXS was measured by SAXS optics with 2.0 m camera length at BL-10C in PF, KEK, Tsukuba equipped with the simultaneous differential thermal analysis/SAXS apparatus (DTA/SAXS) [3]. X-ray wavelength was 0.16 nm. Annealing of sample was carried out in DTA/SAXS apparatus.

Results
Observed scattering intensity functions were corrected for back ground (water in the cell) and transmission. The reduced distance distribution function was obtained by the Fourier transformation of the scattering function according to the following equation:

\[ G(r) = \frac{2}{\pi} \int I(q) \sin(qr) dr \]

The obtained G(r) for 2wt% quasi-gel and the stabilized gel at 290 K were shown in Fig.1. The first correlation peak of the stabilized gel was at r=20 nm, whereas that for quasi-gel was at r=15 nm. The long range ordered structure may be proceeded in the stabilized gel.

References

Fig.1 Reduced distance distribution function G(r) for quasi-gel and stabilized gel of 2wt% xanthan hydrogels.
Solution X-ray scattering analysis of denatured states of *Streptomyces* subtilisin inhibitor.

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Introduction

In order to investigate little known global properties such as compactness and chain shape of the cold-denatured state of protein in comparison with the native and heat-denatured state, solution x-ray scattering analysis is employed on *Streptomyces* subtilisin inhibitor (SSI), which at low pH is known to exist in at least three distinct thermodynamic states, namely the native (N), cold-denatured (D'), and heat-denatured (D) states¹).

Results

Using small-angle X-ray scattering technique, we determined the radius of gyration ($R_g$) and shape of the molecule of N, D', D and also urea-denatured state (Durea). $R_g$ values for the N (pH 3.0, 20 °C), D' (pH 1.8, 3 °C), D (pH 1.8, 35 °C) and Durea (5 M urea, pH 1.8, 3 °C) were 22.9±0.7, 20.7±1.3, 25.8±1.5 and 35.9±4.2 Å, respectively. Estimates of molecular weight deduced from $I(0)$, the extrapolated intensity at 0 scattering angle, indicated that the N state is in the dimeric form while the three denatured states are monomeric. These results have shown that the D', D and Durea states are largely expanded than the native state. Kratky plot of scattering profiles has shown that the N and D' states have globular-type conformations while the D state is in a chain-type conformation (Fig.1). Kratky plot of Durea indicated that Durea has more randomized chain-type conformation than that of D. X-ray scattering analysis of N, D' and D states in a high-angle region was also examined and demonstrated existence of rigid inner structures in the N, D' and D states. However, the profile of the three states is different from one another, indicating that the inner structures of the N, D' and D states are all different from one another.

Conclusions

The most striking conclusion is that the D' state, although rather expanded, contains significant amount of rigid inner structures and its chain shape is globular. This is quite unique for the denatured protein. On the other hand, the D state lacks globularity, although there remains some intrachain interactions in the expanded chain and contains a small amount of secondary structures. As compared to the D' and D state, Durea is more highly denatured and close to the random conformation.

References

PHASE BEHAVIOR AND STRUCTURES OF Semi-
INTERPENETRATING POLYMER NETWORKS PREPARED BY
PHOTO-CROSSLINKING

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I. Introduction

We have performed in situ photo-crosslinking of polymer chains in the miscible region of binary polymer blends. By optical microscopy and small-angle X-ray scattering, the phase behavior and structures of these IPNs are elucidated and discussed.

II. Experimental Section

1) Samples: Polymer blends used in this work are the mixtures of poly(styrene-co-chloro methyl styrene) (PSC, $M_w = 2.6 \times 10^5$) and poly(vinyl methyl ether) (PVME, $M_w = 2.6 \times 10^5$) [PSC/PVME]. To induce the crosslinking reactions among PSC chains, anthracene was labeled to the polymer chains according to the procedure reported previously. Photo-crosslinking reactions of the blends were carried out at 90°C by using the 365nm line of a 500W mercury-xenon lamp (Hamamatsu Photonics). This temperature is located in the one-phase region and ca. 40°C below the binodal line of the blend. Only the blends with an off-critical composition (50/50) are used in this work.

2) Experimental Results:

Anthracene-labeled PSC/PVME (50/50) blends were irradiated at 90°C over different time intervals ranging from 5min to 8hrs. Under this condition, ca. 70 % of the anthracenes on PSC chains was reacted. Up to the first 3hrs of irradiation, no structures can be clearly observed by phase-contrast optical microscopy. However, as irradiation time exceed 3hrs, concentric bi-continuous structures clearly appear and grow slowly with irradiation time. As an example, the optical micrograph of a PSC/PVME (50/50) blend which was irradiated over 3hrs at 90°C, is shown in Figure 1. Eventually, the time evolution of these structures are stopped upon irradiation over long time. To monitor the phase separation in the early stage of the process, we measure, at room temperature, the SAXS profiles of the PSC/PVME (50/50) blends after irradiation over 10, 15 and 20mins. The temperature of the irradiation experiment is 90°C. In Figure 2, these results are shown in the form of Kratky plot. The scattering profile of the as-cast blend without irradiation does not exhibit characteristic features. However, upon irradiation, the scattering in the large q region ($4 \times 10^{-4}$ Å⁻¹ - $6.5 \times 10^{-4}$ Å⁻¹) increases and exhibits a broad peak which slightly moves toward the low q range upon increasing irradiation time.

These experimental results indicate that at 90°C, the blend becomes unstable after irradiation over 10min, and continuation of irradiation will push the system deeply into the two-phase region. These structures will grow with increasing irradiation time until the PSC chains gain enough crosslink density to freeze the phase separation. Under this experimental conditions, these bi-continuous structures are frozen by the time their sizes reach the micrometer scale.

References

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2) T. Tamai, A. Imagawa and Q. Tran-Cong Macromolecules 27, 7486 (1994)
CRystallization of polymer networks is very different from that of linear polymers because diffusion of molten polymer chains participating in crystallization is greatly restricted due to the presence of cross-links. Recently we reported a slow crystalization kinetics of end-linked poly(tetrahydrofuran) (PTHF) having a narrow inter-cross-link molecular weight distribution. It took about one week to complete crystallization at 20 °C. Spherulitic crystal super-structures were also observed in this network polymer by light scattering and optical microscopy. This slow crystallization enabled us to study the crystallization kinetics with differential scanning calorimetry (DSC). This finding was verified by an independent method, i.e., infrared absorption spectroscopy. We discuss here the molecular weight dependence of crystallization kinetics of polymer networks based on the results obtained by DSC, optical microscopy, and small-angle X-ray scattering experiments.

Experimental Section

A series of PTHF networks were prepared by a two-step reaction: prepolymer polymerization and chain coupling with a four-functional cross-linker. The range of Mn's is from 2.54 x 10^3 to 10.2 x 10^3, where Mn is the number average molecular weight of PTHF between successive cross-links. The polydispersity index, Mw/Mn, was equal to or less than 1.22, where Mw is the weight average molecular weight. Real-time crystallization kinetics of the PTHF networks and prepolymers were studied by small-angle X-ray scattering (SAXS). The SAXS experiments were conducted with a high brilliant X-ray beam from synchrotron orbital radiation, National Laboratory for High Energy Physics, Tsukuba, Japan. Sample films of 500 µm thick were heat treated at 60 °C and then quickly transferred to a temperature controlled chamber kept at 15 °C, followed by a time-sliced SAXS experiment. The wavelength of the X-ray was 1.488 Å. The sampling time was either 5 min or 1 min each, depending on the rate of crystallization.

Results and Discussion

Figure 1 shows the Lorentz-factor-corrected scattered intensity function q^2I(q) vs. q plots of the networks, U052 (Mn = 5.2K). The quantity q is the magnitude of the scattering vector. Although no peak evolution with time was detected for U025, an evident peak growth due to crystal formation and its ordering was observed for U052, U065, U079, and U102. These scattering peaks indicate presence of an ordered structure, namely stacked lamellae having a long spacing of about 200 Å, irrespective of inter-cross-link molecular weight, Mn. No systematic variation in the spacing was found in the network samples.

Fig. 1 Lorentz-factor-corrected SAXS intensity profiles of U052 during isothermal crystallization.

Fig. 2 Mn dependence of crystallization half time.

As shown in Figure 2, a strong Mn dependence of crystallization kinetics is observed. The decrease in the crystallization rate with decreasing the inter-cross-link molecular weight is accounted for by decreasing of the supercooling and an increase in the activation energy for transferring liquid-solid interface.

References:
SOLUTION STRUCTURAL CHARACTERIZATION OF THE MOLTEN GLOBULE STATE OF GLOBULAR PROTEINS

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INTRODUCTION
The molten globule state is a compact denatured state with a significantly native-like secondary structure but a largely flexible and disordered tertiary structure, and has been proposed to be a common folding intermediate of globular proteins. Further, the molten globule state is considered to play important roles in protein targeting and sorting in a cell. To reveal the structural properties of molten globule is important cytophysiologically as well as protein physicochemically.

Although the molten globule is defined as "compact" and "globular", the degree of compactness and globularity has not been discussed quantitatively with a few exceptions, because few techniques have been available for the quantitative measurements on these properties. We have shown that, solution X-ray scattering is useful and effective to characterize solution structure of the non-native conformational states of proteins. Since the size and shape is critical properties to define molten globule, we intensively investigated molten globules of various proteins by solution X-ray scattering.

EXPERIMENTAL
The molten globule state or the compact denatured state of α-lactalbumin, cytochrome c, apomyoglobin and the staphylococcal nuclease fragment were selected for the present purpose.

RESULTS AND DISCUSSION
The obtained Rg values were listed in Table 1. The molten globule is expanded from the native state. The increase in Rg is up to 30% of the Rg of the native state. The degree of the increase in Rg for α-lactalbumin is smaller than the other three proteins. α-lactalbumin possesses intramolecular disulfide bonds, while the other three do not. Therefore, we consider that the tendency of the molecular expansion at the molten globule would be restricted by intramolecular disulfide bonds.

Kratky plots indicate that these molten globules or compact denatured states are globular in shape, while P(r) functions can be classified into two types. The molten globule of cytochrome c and α-lactalbumin give a unimodal P(r), and the molten globule of apomyoglobin and the SNase fragment give a bimodal P(r). Further studies suggest that the former is rather close to the native state, while the latter is close to the unfolded state. A bimodal P(r) would be a common structural property for the intermediate appearing in early stage of folding.

Table 1. Comparison of Radius of Gyration between Native State and Molten Globule State

<table>
<thead>
<tr>
<th>Protein</th>
<th>Rg (Native) (Å)</th>
<th>Rg (MG) (Å)</th>
<th>ARg/Rg(Native) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cytochrome c</td>
<td>13.5</td>
<td>17.4 (NaCl)</td>
<td>28.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.0 (Acetylation)</td>
<td>25.9</td>
</tr>
<tr>
<td>Holomyoglobin</td>
<td>17.5</td>
<td>14.9 (Holo→Apo)</td>
<td>14.9</td>
</tr>
<tr>
<td>Apomyoglobin</td>
<td>20.1</td>
<td>22.2 (NaTCA)</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.9 (Holo→MG)</td>
<td></td>
</tr>
<tr>
<td>SNase</td>
<td>16.2</td>
<td>21.2 (Fragment)</td>
<td>30.9</td>
</tr>
<tr>
<td>α-Lactalbumin</td>
<td>15.7</td>
<td>17.5 (Apo)</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.9 (Acid MG)</td>
<td>14.0</td>
</tr>
</tbody>
</table>
SMALL-ANGLE X-RAY SCATTERING STUDIES OF THE GLASS-CRYSTALLIZATION PROCESS IN EGG WHITE

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Introduction
Opaque egg white gel is known to become transparent (glasslike egg white) in a dry atmosphere by the loss of the inner water; the change is called "gel-to-glasslike transition". As mentioned in the last activity report, we performed the time-resolved SAXS measurements during the dehydration process of the heat- and the pressure-treated egg white gels simultaneously with the weight measurements, which revealed the analogous evolutions of the volume and the gyration radius.

In addition to the kinetic feature in the gel-to-glasslike transition mentioned above, we have been also investigating the properties of the glasslike specimen and, in the previous study, found the heat-induced partial crystallization. However, the formation mechanism could not be made clear because of the weak X-ray source intensity in our labo. Therefore in the present study, with utilizing the synchrotron radiation source, the time-resolved SAXS measurements were performed during the crystallization process of the dehydrated egg white in order to make clear the features of the crystal growth.

Experiments
The egg-white glass was prepared by dehydrating the heat-treated egg white gel at 25°C and 65% in humidity. During the measurement, the temperature of the dehydrated specimen was kept at 60°C. The time-resolved SAXS measurement was carried at BL-1OC in the Photon Factory. The wavelength of the incident X-ray beam was 1.488 Å.

Results and Discussion
During the SAXS measurements, the transparent glasslike egg-white became turbid with the progress of the crystallization, and correspondingly, the intensity of the profiles increased with time.

An almost linear dependence was observed in a q-region in the plot of the ln |I(q)| vs. q², below which the Guinier's law held, indicating that the crystalline particles were cylindrical. The radius, R, of the cylindrical particle was calculated from the slope of the plots. The height of the cylindrical particle, H, could be calculated with R and the gyration radius Rg which was calculated from the initial slopes of the Guinier plots, by the following equation:

\[ R_g^2 = \left( \frac{R^2}{2} + \frac{H^2}{12} \right). \]

Acknowledgements
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References
SMALL-ANGLE X RAY SCATTERING FROM SOLUTION OF BILE SALT

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Introduction

The micelle formation of three isomeric taurin conjugated bile salts, sodium taurodeoxycholate (NaTDC), sodium taurochenodeoxycholate (NaTCDC), and sodium tauroursodeoxycholate (NaTUDC) in aqueous solution was previously investigated at various concentrations of the bile salts ($C_B = 5$-$100 \text{ mM}$) and added sodium chloride ($C_S = 0$-$1.0 \text{ M}$) by small-angle X-ray scattering. The results showed that NaTDC and NaTCDC micelles grow from disc-like to rod-like micelles with increasing $C_B$ and $C_S$, whereas NaTUDC forms only disc-like micelles with the present $C_B$ and $C_S$ range. The purpose of this experiment is to examine whether or not the micellar growth from disc-like to rod-like micelles with increasing $D_2O$ composition. The effect of $D_2O$ on the micellar formation may be a measure of the hydrophobic effect on the micellar growth.

Experiment

The 100 mM bile salt solutions having different $D_2O$ (0, 25, 50, 75, 100%) and different concentrations of added sodium chloride ($C_S = 0.5$ and $1.0 \text{ M}$) were measured by small-angle X-ray scattering at BL10C of KEK-PF. The analysis of the data was done by the Guinier method.

Results and Discussion

The radius of gyration $R_g$ and the radius of the intersection $R_c$ obtained are shown in Fig. 1. In 100% $H_2O$ solution all bile salts form disk-like micelles as has previously been described.1) With increasing $D_2O$ composition disk-like micelles of NaTDC and NaTCDC did not grow, however, NaTUDC disk-like micelles increase in $R_g$ and $R_c$. In 100% $H_2O$ solution NaTDC and NaTCDC micelles grow from disc-like to rod-like micelles with increasing $C_B$ and $C_S$, whereas NaTUDC forms only disc-like micelles present within the present $C_B$ and $C_S$ range. It is interesting the $D_2O$ effect on micelle formation of NaTUDC is in contrast with the effect of $C_B$ and $C_S$.

References

ANOMALOUS SMALL-ANGLE SCATTERING EXPERIMENTS ON THE PRECIPITATION STRUCTURE OF Fe-BASED ALLOYS

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Introduction
Small-Angle X-ray scattering experiment utilizing the anomalous dispersion effect is one of the powerful methods to examine inhomogeneous structures such as precipitation structure consisting of elements with neighboring atomic numbers, or more complicated structures such as multiphase shell structures. The ASAXS results of the Fe-Cu based alloys has been presented in this report.

Experimental
Fe-Cu binary alloys and Fe-Cu-Ni-Mn alloys have been investigated in the present experiments. The samples were aged at 773K for 600s to form uniform precipitates with the size of 2-4nm. The samples of about 5mm thickness were mechanically thinned down to 30-50 microns for transmission SAS measurements. The ASAXS experiment has been carried out at BL-10C of Photon Factory. The incident X-rays of the energy near Fe K-edge and Mn K-edge were used to obtain enhanced contrast in SAS profiles. The ASAXS profiles have been compared with the small-angle neutron scattering (SANS) data.

Results and Discussion
The photon energies used in the present experiments are shown in Fig.1. The contrast in the scattering factor is enhanced by 3.3 times compared with the measurement at the photon energy near Cu Kα. For FeCuNiMn alloys, energies near the Mn K absorption edge were also used. From the SANS experiments, it was found that Mn tends to segregate at the precipitate/matrix interface, which causes disagreement between the Guinier radius for nuclear scattering intensity and that for magnetic scattering intensity. If the discrepancy between the two radii comes from the surface segregation of Mn, it should be clearly seen by the scattering contrast variation when one measures around the Mn absorption edge. Figure 2 shows the scattering intensities of an Fe-CuMnNi alloy aged at 773K for 600s, obtained for the photon energies around the Mn K absorption edge. The scattering profiles have two distinct part, i.e., the monotonically decreasing part at low-k region and the hump in higher (k~0.4nm⁻¹) scattering vector region. The lower q-region is not strongly affected by the photon energy. On the other hand, the profiles at higher scattering vector are strongly affected by the photon energy, suggesting that this part comes from the precipitates. The Guinier radius obtained at Mn edge is larger than that at Fe edge, suggesting the interfacial segregation of Mn at the precipitates.

References
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Fig.1 $f_0+f'$ near K abs. of Fe and Mn.

Fig.2 The scattering intensity profiles for Fe-CuMnNi near the Fe and Mn K-abs. edge.
SMALL ANGLE X-RAY SCATTERING OF LONG CHAIN POLY(OXYETHYLENE) SURFACHTANTS IN AQUEOUS SOLUTION

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Introduction

Deca-, eicosa-, triaconta-, and tetracontaoxyethylene dodecyl ethers, C_{12}H_{25}O(CH_{2}CH_{2}O)_{n}H abbreviated as C_{12}E_{n}(n = 10, 20, 30, and 40), are nonionic surfactants which are widely used as emulsifying, washing, and solubilizing agents. Previous surface tension experiments on aqueous solutions of C_{12}E_{n}(n = 10, 20, 30, and 40) showed that the critical micelle concentrations of these surfactants decreased as n increased. This phenomenon is exceptional in the Hydrophile Lipophile Balance concept; thus, it is important to clarify the origin of this unusual phenomenon for colloidal chemistry.

The spiral configurational contribution due to the TGT (Trans-Gauche-Trans) conformation of poly(oxyethylene) chain may change the property of oxyethylene groups as the poly(oxyethylene) chain length becomes extremely long. In the present study, we have performed SAXS measurements to determine the micelle structures of C_{12}E_{n}(n = 10, 20, 30 and 40) to examine the effect of poly(oxyethylene) chain length on micelle formation.

Experiment

C_{12}E_{n}(n = 10, 20, 30 and 40) were supplied by Nihon Surfactant Industry Co. Ltd in Japan. Their purities were checked by surface tension, high performance liquid and super critical fluid chromatographies; these samples have a narrow distribution of poly(oxyethylene) chain lengths. SAXS measurements were performed at 25°C at BL-10C of KEK-PF. The concentrations of the surfactants prepared were 1, 4, 7, 10, 13, 16 and 19% in third distilled water.

Results and Discussion

$I(s)$ vs. $s$ plots of C_{12}E_{20} are shown in Fig. 1. The radius of gyration for $R_g$ of micelles was determined from the Guinier Plot only for the 4% solution since the correlation peak between the micelles appeared in the other solutions. The Guinier plots are shown in Fig. 2. The $R_g$ values are 36.8A (C_{12}E_{10}), 38.1A (C_{12}E_{20}), 38.7A (C_{12}E_{30}), 38.9A (C_{12}E_{40}). The $R_g$ value slightly increased as the poly(oxyethylene) chain length increased. The results were interpreted in such a way that the long poly(oxyethylene) chains form spirals and hence the micellar size does not become large.

References

In a series of papers\(^1\) we have been investigating the crystallization behavior of blends between fully-deuterated high-density polyethylene (DHDPE) and hydrogenous polyethylene with various degree of side chain branching. For the blend of DHDPE with linear low-density PE with ca. 17 ethyl branching per 1000 carbon atoms [LLDPE(2)], the almost perfect cocrystallization occurs even when the sample is cooled slowly from the melt. On the other hand, the blend with high-density PE (HDPE) with no branching or LLDPE(3) with higher degree of branching (41 branching) shows the phase segregation between the lamellae of the D and H species. In this way the phenomenon of cocrystallization and phase segregation depends sensitively on the degree of branching of the H species.

In order to clarify the origin of this curious phenomenon we investigated the various factors including the thermodynamic stability of the blend and so on. One of the most important factors may be a kinetic factor for the crystallization process. Then we have performed the temperature jump experiments, during which the small-angle X-ray scattering (SAXS) was measured as a function of time. The temperature jump cell constructed by ourselves could supply a quite high rate of temperature jump, ca. 600°C/min from 160°C to 110°C for example, followed by very small temperature fluctuation. The SAXS measurement was performed by using an "enzyme diffractometer" installed on the beam line BL10C. The results may be summarized in the following way.

(1) The invariant \(Q\) was evaluated as a function of time. With an increase in the degree of supercooling \(\Delta T\), the crystallization rate was found to increase drastically, where the \(\Delta T\) is defined as the difference between the quasi-statically determined crystallization temperature \(T_c\) and the actual crystallization temperature \(T_c\) used in the experiment (\(\Delta T = T_c^\text{eq} - T_c\)).

(2) The results obtained in the item (1) were compared with the infrared spectral data collected during the isothermal crystallization with almost the same \(\Delta T\). The rate of increment of the infrared band intensity is far higher than that of the SAXS invariant, allowing us to deduce the following crystallization mechanism for the PE samples: at first the trans-zigzag chains are generated in the melt of randomly coiled chains. After a lapse of some time, these trans chains gather together to form a larger crystalline cluster as detected by SAXS measurement. This may be the first experimental proof for the crystallization mechanism of PE viewed from the molecular level.

(3) The crystallization rates measured for the pure components of PE were compared with each other: the crystallization rate is in the order of HDPE >> DHDPE = LLDPE(2) >> LLDPE(3). This indicates that the pair of the components with the similar crystallization rate is considered to show the cocrystallization behavior.

(4) The crystallization rate of the blends was compared with those of the pure component. In cases of the blend systems with phase segregation, the blend crystallizes more slowly than the pure samples. In the case of DHDPE/LLDPE(2), on the other hand, the crystallization rate is rather enhanced for the blend compared with those of the pure samples, i.e., the acceleration effect was found out.

FURTHER ANALYSIS OF ELEMENTAL DISTRIBUTIONS IN A MAMMALIAN CELL USING ELECTRONIC ZOOMING TUBE

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Introduction

Imaging of elemental distribution with high spatial resolution is one of the major applications of soft X-ray microscopy. At tissue level, calcium distribution has been studied using L absorption edge of calcium1,2). For the investigation at subcellular (<1 μm) level, an electronic zooming tube would be one of the most powerful tools because of its high spatial resolution 3,4). Our previous study revealed that using this detector absorption spectra at local areas in a mammalian cell were obtainable in the soft X-ray region (1.5-10 nm)5). In the present study, further analysis was conducted to derive the differences of elemental contents with subcellular resolution.

Materials and Methods

Contact image of a dry human HeLa cell were obtained by illuminating monochromatic X-rays at BL-11A ranging from 1.5 to 8.0 nm. Electromagnetically enlarged picture by the zooming tube was introduced to the image processor, and stored as an image of 256 pixels and 241 pixels. The wavelengths were chosen as either side of the absorption edges: for iron 1.7 and 1.8 nm, for oxygen 2.25 and 2.35 nm, for nitrogen 3.0 and 3.15 nm, for calcium 3.45 and 3.6 nm, and for carbon 4.25 and 4.45 nm. At any local areas in the cell, the elemental contents which were expressed as mass thickness \( \rho x \) (product of density and thickness of specimen) were calculated as follows:

\[
\frac{T_s}{T_b} = \exp(-\left(\mu_s - \mu_b\right)\rho x)
\]

where \( T_s \) and \( T_b \) are the transmission (the ratio of the photon intensity of the area concerned and that of the background) at the shorter (\( T_s \)) and longer (\( T_b \)) side of the absorption edge. \( \mu_s \) and \( \mu_b \) denote the mass absorption coefficients at either side of the absorption edge. In the case of nitrogen and oxygen, transmissions were corrected by carbon absorption. Iron and calcium contents were calculated taking the correction for carbon, nitrogen and oxygen absorption into account.

Results and Discussion

The elemental contents were calculated for the eight intracellular areas chosen from cytoplasm, peripheral parts of cytoplasm and peripheral parts of nucleus. The central parts of nucleus were omitted, since this area had very low transmitted-photon intensity. Table I summarizes the average numbers of elemental contents for each intracellular part. Carbon was the most abundant, followed by nitrogen and oxygen. Trace elements, iron and calcium, were also detected. The relative values of mass thickness of these elements, which were normalized at carbon mass thickness, suggest that the relative content of oxygen seems to depend on the intracellular areas, while that of nitrogen does not. More remarkable variation in the contents of trace elements was observed; calcium and iron seem more abundant in cytoplasmic areas. For further examination of the spatial correlation of these elements, 23 areas of 0.5 μm square, which is around the resolution limit in the present setup, were selected in the cytoplasm. Figure 1 plots the content of carbon against that of iron. While the areas rich in either one of the two elements were noticed, there seems to exist the areas showing significant correlation between iron and calcium content. This result suggests intracellular structures containing both elements. Mitochondria may be a possible candidate. The mapping of these three distinct regions is in progress.

| Table I. Elemental contents in cellular local areas. |
|---|---|---|---|
| Element | Mass thickness (x10^(-3) g/cm^2) |
| Nucleus (periphery) | Cytoplasm | Cytoplasm (periphery) |
| C | 2.76 (1) | 1.70 (1) | 0.58 (1) |
| N | 1.40 (0.51) | 0.711 (0.42) | 0.206 (0.51) |
| O | 2.44 (0.88) | 0.955 (0.56) | 0.26 (0.45) |
| Ca | 0.0406 (0.015) | 0.108 (0.064) | 0.0495 (0.085) |
| Fe | 0.0374 (0.014) | 0.130 (0.076) | 0.119 (0.21) |

Fig.1 Correlation of iron and calcium content for cytoplasmic areas.

References

OXYGEN K-EDGE X-RAY ABSORPTION SPECTRA IN (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_4\)O\(_8\)

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Introduction

PrBa\(_2\)Cu\(_3\)O\(_7\) is unique in being a semiconductor-not a superconductor - having an isostructure with YBa\(_2\)Cu\(_3\)O\(_7\) (Y123), while all the other RBa\(_2\)Cu\(_3\)O\(_7\) (R rare-earth element) is a superconductor with almost the same critical temperature 90 K. The suppression of the superconductivity by Pr in (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_3\)O\(_7\) has been discussed by many researchers. In this paper we study the properties of (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_4\)O\(_8\) and discuss the similarity and the dissimilarity to those of (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_3\)O\(_7\).

Experimentals

The specimens of (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_4\)O\(_8\) were successfully prepared for \(x \leq 0.7\). In order to obtain the informations of the hole states on oxygen, X-ray absorption measurements (XAS) near oxygen K-edge of the (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_4\)O\(_8\) and (Pr\(_x\)Y\(_{1-x}\))Ba\(_2\)Cu\(_3\)O\(_7\) were performed at the BL11 beam line of PF KEK by means of a total-photoemission-yield method. The sample was scraped with a diamond file to generate the fresh clean surfaces. The total resolution was about 1 eV.

Results

Fig 1 (a) and (b) show prepeaks of oxygen K-edge of (a)YBa\(_2\)Cu\(_3\)O\(_7\) and (b)PrBa\(_2\)Cu\(_3\)O\(_7\) respectively. The peaks were successfully decomposed into two gaussian peaks located at 528 (L-peak) and 529 eV (H-peak). For superconductor YBa\(_2\)Cu\(_3\)O\(_7\), two peaks have almost the same intensity, while for PrBa\(_2\)Cu\(_3\)O\(_7\) the L-peak is weaker and the H-peak is stronger. Hence, the reduction of superconducting properties seems to be correlated with the L-peak intensity. Figure 1 (c) and (d) show those prepeaks of (c) YBa\(_2\)Cu\(_4\)O\(_8\) and (d) (Pr\(_{0.6}\)Y\(_{0.4}\))Ba\(_2\)Cu\(_4\)O\(_8\), respectively. Each of the prepeaks was decomposed into two gaussian peaks also. Two peaks are almost of equal intensity independent of the Pr-content in this PrY-124 system. Present study was reported precisely in the Reference[3].

References

LONG-RANGE STABILITY OF MOLYBDENUM/SILICON MULTILAYERS

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Introduction

Mo/Si multilayers have the highest soft-x-ray reflectivity in the wavelength region around 130Å. In order to make them fit for practical use, their stability, heat resistance and radiation tolerance have been investigated by several researchers. We have examined long-range stability of Mo/Si multilayers stored in air.

Experiment

Mo/Si multilayers, with the number of layer pairs of 25 and layer period of 75Å, were deposited by rf magnetron sputtering on silicon wafers. These multilayer samples were stored in a desiccator for 6 months.

Hard-x-ray reflectivity was measured with small-angle x-ray diffractometer using CuKα radiation (1.54Å), and soft-x-ray reflectivity was measured with high-precision reflectometer at the beam line BL-11A using s-polarized radiation. The grating was 2400 lines/mm pitch and beryllium filter was employed to screen the higher order diffraction.

Results

Figure 1 and Fig. 2 show the change of hard-x-ray reflectivity curve of Mo/Si multilayers with Mo on top and Si on top, respectively. Si-on-top multilayers showed no apparent change after 6 months, but on the other hand the reflectivity curve of Mo-on-top multilayers obviously changed after 3 months. This change is in good agreement with the calculated reflectivity curve considering the surface oxidation of Mo top layer. The calculation led to the conclusion that about 10Å of Mo top layer was oxidized.

Figure 3 shows soft-x-ray reflectivity of Mo/Si multilayers stored in air for 6 months. The reflectivity of Mo-on-top multilayers was 58% and that of Si-on-top multilayers was 65% at the wavelength of 130Å. Both Mo-on-top and Si-on-top Mo/Si multilayers as-deposited had the same reflectivity of about 65%. The reflectivity of Si-on-top Mo/Si multilayers did not change. If 10Å of top Mo layer of Mo/Si multilayers was oxidized, calculated reflectivity is reduced about 10%. This reduction is consistent with the discrepancy between the reflectivity of Mo/Si multilayers with Mo on top and that with Si on top stored in air for 6 months. We can conclude that in the case of Si-on-top Mo/Si multilayers surface oxidation has no effect on their reflectivity, and that in the case of Mo-on-top Mo/Si multilayers Mo surface layer is oxidized in air and as the result their soft-x-ray reflectivity is reduced. Although we have a few data at present, we will continue the examination of long-range stability of Mo/Si multilayers.

References

CHARACTERIZATION OF A NEW MULTILAYER SEMICONDUCTOR DETECTOR FOR WIDE-ENERGY-RANGE AND MULTI-ENERGY-RESOLVED X-RAY OBSERVATIONS

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I. Introduction

A newly designed "multilayer" photodiode-type semiconductor detector for wider x-ray-energy-regime observations is proposed. This new-type detector is also applicable to the use of simultaneous observations of "multi-energy resolved" x-ray tomography measurements using the signal from each layer. Monochromatized x rays (BL-15C and BL-11A) are utilized for the detector characterization [1].

II. Specification for the Multilayer Detector

The specifications for the multilayer detector are as follows: Figure 1 shows the schematic drawings of the four-layer detector. Each layer is essentially a p-n junction photodiode; this diode unit has a 300-μm wafer thickness, and a 10×10-mm\(^2\) active area. Each diode-unit layer has its own output wires. For adjoining diode units, the same type of a semiconductor region faces to each other (i.e., p type to p type and n type to n type). A fully depleted operation is employed.

As shown in Fig. 1, we inject x rays from two different directions A and B for the purpose of demonstrating its remarkable high-energy x-ray response and its usefulness as an "multi-energy-resolved" x-ray tomography detector, respectively.

III. Characterization of the Multilayer Detector

When the parallel x-ray injection (the direction A of Fig. 1) along the wafer surfaces is employed, a remarkable feature of a flat response in the 10-20-keV region is achieved. This striking feature will be maintained up to 30 keV, and then decreases slowly with increasing E. Also, a slight decrease in the low-energy side is interpreted by the existence of a 10-μm-thick dead layer. This will be minimized by the improvement of its electrode shape.

As compared with conventional single-crystal detectors, one of the advantages of this multilayer detector is no need of a kV-order bias operation employed for a usual 10-mm-thick single-crystal detector. It is sufficient for the multilayer detector to supply only a few-tens volts.

Furthermore, when we take account of a theoretical prediction using a three-dimensional thermal-diffusion effect, only a few-volt bias for such multilayer detectors will provide similar remarkable high-energy-response characteristics in current-mode operations for intense plasma x-ray observations.

The x-ray response data from each photodiode layer (see the direction B of Fig. 1) agrees well with the theoretical calculation. This result encourages us to utilize this configuration of the multilayer detector as an x-ray-energy resolved detector; that is, for one layer behind some layers, these front layers work as x-ray absorbers. Therefore, the data comparison between these multilayers lead to x-ray energy analyses even if no "red" filters are prepared.

This gives a remarkable advantage for a detector installation in a vacuum chamber without any accesses of changeable filters; such a serious configuration is frequently realized because of narrow detection spaces. Another essential merit is the fact that incident x-ray-energy-resolved data are easily attained at the same time. Therefore, the combination of several units of these multilayer detectors may provide spatially resolved x-ray-tomography data having such an simultaneous energy resolution.

This multilayer detector having such "two-direction" special characteristics are usefully employed for several various research fields.

EXPERIMENTAL VERIFICATION OF A NEW THEORY ON X-RAY SIGNALS FROM SEMICONDUCTOR DETECTORS

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1. Introduction
Recently, we proposed a new theory on the x-ray response of semiconductor detectors. [1] In order to verify this theory, experiments have been carried out using intense x rays (BL15C and BL11A). We designed, fabricated, and prepared the following four semiconductor detectors.

2. Experimental Apparatus
One is a commercially available SSB BO detector having the wafer thickness \(d_{\text{waf}}\) of 215 \(\mu\)m. This is a fully depleted detector in a 100-V bias operation. Another is fabricated as a fully depleted detector (XD5) in a 100-V bias operation having \(d_{\text{waf}} = 300 \mu\text{m}\). The other two detectors (XD19 and XD9) are partially depleted having \(d_{\text{waf}} = 525 \mu\text{m}\). The observed values of the depletion-layer thicknesses \(d_{\text{dep}}\) are 212 \(\mu\text{m}\) and 1 \(\mu\text{m}\), respectively. These are employed for the investigations of the dependence of the thermal-diffusion lengths \(L\) of x-ray-produced minority carriers on their x-ray-energy responses. Using the photoluminescence method, \(L\) for XD19 and XD9 are observed to be 120 \(\mu\text{m}\) and 20 \(\mu\text{m}\), respectively.

3. The Comparison Between the Data and Theories on a Semiconductor X-ray Detector Response
For the x-ray-response normalized by the x-ray energy \(\eta/E\) obtained from the SSB BO and the XD5 detectors (fully depleted detectors), the data points are explained by the conventional theory using each value of \(d_{\text{dep}}\).

On the other hand, the filled and the open circles in Fig. 1 represent the data from XD9 and XD19, respectively. For these partially depleted detectors, neither of the data sets is fitted by the similarly calculated dotted curve (XD9) and dashed curve (XD19) from the conventional theory. As the essential difference in the two groups, the field-free-substrate regions exist only for the detectors in Fig. 1.

A proposal to solve the x-ray response has been made by the MIT group [2]; they employed the total wafer thickness of a detector as the x-ray-sensitive region in place of \(d_{\text{dep}}\). To highlight this viewpoint, \(d_{\text{waf}}\) of each detector in Fig. 1 is designed to be the same value of 525 \(\mu\text{m}\). The dot-dashed curve in Fig. 1 is the calculated result from the above assumption using \(d_{\text{waf}} = 525 \mu\text{m}\) in place of \(d_{\text{dep}}\). Neither of the two-data sets still can be fitted by this MIT prediction. Furthermore, in spite of the use of the same-thickness wafers, each data set shows obviously different x-ray response.

On the other hand, our new theory [1] is physically based on the combination of the x-ray responses contributed both from the depletion layer (as conventionally described) and from the field-free substrate region (a new effect of the three-dimensional diffusion of x-ray-produced charges). In particular, we utilize the exact solution of the diffusion effect in an closed circuit detector operation.

The solid curves in Fig. 1 show the predicted responses of these two detectors from our theory using the detector parameters; the predicted curves using our new theory can fit these data.


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Fig. 1
NEXAFS Study on the Rubbing Strength Dependence of the Surface Structure of Polyimide BPDA-C8

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Introduction

It is well known that a rubbed polymer surface may align a liquid crystal (LC) film, whose optical axis makes a pre-tilt angle from the polymer substrate. As for the mechanism of the alignment, it is widely believed that the mechanically rubbed polymer is subjected to the local structure change, such as realignment of the polymer chain, and hence the elongated chain induces the uniaxial alignment of the LC film. Although many surface analytical techniques have been applied to reveal the mechanisms of the alignment, complete understanding is still lacking.

In this study, we have performed a series of experiments with use of C K-edge NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy for the first time in order to investigate the rubbing strength effect on the polymer surface.

Experimental

We used BPDA (biphenyl-3,3',4,4'-tetracarboxylic dianhydride) type polyimide with octyl chains between BPDA groups (BPDA-C8). C K-edge NEXAFS spectra were taken on the BL-11A at KEK-PF with a Grasshopper monochromator. Measurements were performed in total electron yield mode for 1000Å thick polyimide films on ITO(Indium Oxide) glass plate. Mechanical rubbing was applied on the polymer surface under different pressure condition, denoted as strong(s) and weak(w) rubbing.

Results and Discussion

Figure 1 shows a typical C K-edge NEXAFS spectrum of BPDA-C8(s) polyimide. The peak (a) can be assigned as a transition from C1s to π* (C=C) orbital.

In order to investigate the orientation of the rigid biphenyl parts of the polymers, we have examined the incident angle dependence of the intensity of the peak (a) in Fig. 2. The data was plotted with theoretical fit where we have assumed a Gaussian distribution function and the polarization factor of the incident beam P=1, and θ is defined as the angle between the substrate plane and the incident X-ray beam. The rubbing direction was fixed in the incident plane. As clearly seen from the figure, the biphenyl part of BPDA-C8 tilts from the surface by about 15 degree, and its angle has no connection with rubbing strength. A model structure of the polymer is illustrated in Fig. 3. It is found that the rubbing strength merely affects the FWHM of the distribution function. We can conclude that the tilt angle of the rigid part originates from the conformation of the polymer.

References

Mo/B₄C AND Ru/B₄C MULTILAYER POLARIZERS FOR SOFT X RAYS

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Introduction
Multilayer coatings exhibit remarkable polarizing power at the Brewster angles for soft x-rays (SXR's).¹ We have so far developed them for the studies of polarization of beamline SXR's² and SXR fluorescence.³ We have recently fabricated multilayer polarizers for 180-eV region by Mo/B₄C and Ru/B₄C systems. Using them we optimized and evaluated the polarization of the beamline BL-11A.

Samples and Measurements
Samples of Mo/B₄C and Ru/B₄C, both 199 layers in total, were prepared by a magnetron sputtering system on Si wafers. A dc power of 100 W (1.3 W/cm²) was fed for the metal targets, while an rf power of 400 W (2.3 W/cm²) for the B₄C target. Ar pressure was 2.0 mTorr. The reflectance measurement was carried out on BL-11A using the soft x-ray reflectometer with a 0.5-eV resolution. We used a carbon filter to cut off unwanted higher orders. Prior to the reflectance measurements we evaluated the polarization of the SXR's emergent from the monochromator using a rotating analyzer² mounted with a Ru/B₄C multilayer.

Results and Discussion
Figures 1 and 2 show the reflectance spectra measured for the Mo/B₄C and the Ru/B₄C multilayers for s-polarization, where several incidence angles (θ) are indicated beside the spectra. The Mo/B₄C sample has a 22.8% reflectance at 183 eV (θ = 45°), while the Ru/B₄C sample has 20.0% at 185 eV (θ = 47°). The reflectances are about half and one third the calculated values for the respective samples. The disagreement with the ideal values arises dominantly from the surface and interface roughness. Figure 3 shows the output intensity of the rotating analyzer in logarithmic scale vs its azimuthal angle measured for the emergent beam of 168 eV. The polarization degree was 98.2%. The polarization was finally obtained by optimizing the deflection mirror of the beamline, while measuring the polarization degree. It was also found that the position of the deflection mirror optimized for 168 eV is the same position optimized for 93 eV in the previous study.²

References
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CALIBRATION OF SOFT X-RAY SPECTROMETERS FOR PLASMA DIAGNOSTICS

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Introduction

VUV/soft x-ray measurements are important methods to diagnose impurities in magnetically confined plasmas of the type used in fusion research. These measurements require instruments that provide simultaneous spectral, temporal and spatial resolution of the plasma radiation.

Recently we have constructed the space- and time-resolving flat-field VUV(150-1050 Å)1) and soft x-ray(20-350 Å) spectrographs by using an aberration-corrected concave grating with varied spacing grooves which gives us a wide simultaneous spectral coverage and the efficient detection geometry for an MCP detector.

For quantitative analyses of emission lines, it is important to characterize the efficiency of these spectrograph systems throughout its wavelength range. We have performed calibration experiments for these spectrographs. In this report we describe the experiment for the grazing incidence soft x-ray spectrograph.

Experimental

Experiments have been performed at the beamline 11A. The schematic drawing of the grazing incidence soft x-ray spectrograph is shown in Fig.1. The concave grating used has a radius of curvature of 5649 mm, a nominal groove density of 1200 g/mm and a ruled area 50 mm wide by 30 mm high, which is ruled with varied spacing (Hitachi, P/N001-0266). The incident angle is 87° and the effective braze wavelength is 100 Å. The entrance slit has a 100 μm width and 2 mm height, which gives spatial resolution. An MCP intensified detector having 50x50 mm² active area is set on the flat-field output plane.

Calibration experiments have been carried out by monitoring the incident photon intensity just behind the entrance slit by using an XUV silicon photodiode (IRD, AXUV100) and then measuring the output image. Measurements are repeated for incident wavelength from 50 Å to 140 Å, for several different points of irradiation on the grating along groove direction and for two (S and P) polarization geometry in the spectrograph.

Results

In Fig.2, the relative efficiency is plotted as a function of output wavelength on the spectrograph including second- and third-order light. It is noted that the higher order diffracted light is considerable for this grating. These data are taken for the irradiation position at the center of the grating and for P polarization geometry.

References

NEXAFS Studies on the Temperature Dependence of Surface Structure of Liquid n-C$_{50}$H$_{102}$ (pentacanthe)

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Introduction

The orientation-analysis with NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy has been restricted to the solid sample. However, it would be of great interest if we can apply the surface sensitivity of NEXAFS to the system of liquid and/or liquid crystal meso-phases. In this study, we have carefully selected a liquid sample, whose vapor pressure is low enough under our vacuum condition ($10^{-2}$ Torr), and have found for the first time the pre-transitional ordered structure at the surface of the liquid phase of an n-alkane.

Experiment

C K-edge NEXAFS spectra were taken on the BL-IIA at KEK-PF with a total-electron-yield technique. The sample used in this experiment was pentacanthe film of 2500 Å thickness, (n-C$_{50}$H$_{102}$) evaporated on Cu substrate. In order to investigate the orientation of the molecule at various temperatures, we examined the incident angle dependence measurement of the spectra ranging from 280 to 310 eV, at room temperature and around the melting point.

Results and Discussion

Figure 1 summarizes C K-edge NEXAFS spectra for grazing incidence (GI: $\theta = 20^\circ$) and normal incidence (NI: $\theta = 90^\circ$) at room temperature (RT), just below and just above the bulk melting point (95.5 °C). Peaks (a) (287.80eV) and (b) (293.40eV) have been assigned as $\sigma^*$ (C-H) and $\pi^*$ (C-C) resonances, respectively. At room temperature, the height of the peak (a) for NI is smaller than that for GI. On the contrary, the relative intensity difference of the peak (a) between NI and GI is drastically reversed just below the melting point. In the liquid phase, the spectra for GI and NI arc almost identical.

From the behavior seen in Fig. 1, we can deduce the structural change of the sample with temperature as follows: At room temperature, the molecular long axis is almost parallel to the substrate. As the temperature is increased, the molecular axis starts reorienting and becomes perpendicular to the substrate surface just below the transition point. In the liquid phase, the molecules become random coils, hence the spectra were almost identical.

In order to investigate whether pentacanthe shows a pre-transitional ordered structure even at the liquid surface, we continuously monitored the change of the intensity of the peak around the melting point (Fig.2). In the course of increasing temperature, it is noticeable that the intensity changes a little at the (bulk) melting point (95.5°C) and at 1°C above this temperature the intensity suddenly decreases. On the course of decreasing temperature, the intensity jumped up at around 96.4°C and gradually increased until 94.5°C. We obtained similar behavior at second and third procedures except for the small variation in the transition temperatures. As is clear from the figure, some ordered phase is observed at the range of almost two degrees above the (bulk) melting point. Since the unknown ordered structure was observed not only in the first heating/cooling process but also in the second and third one, the structure corresponds to the thermodynamically stable state. From these results, we can conclude that pentacanthe have the pre-transitional ordered structure at the liquid surface even at almost two degrees above the (bulk) melting point.

References

THE STUDIES ON THE CORE HOLE EFFECT OF AROMATIC HYDROCARBONS IN NEXAFS SPECTROSCOPY

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It has been the subject of interest to obtain the density of unoccupied states (DOUS) for relatively large organic molecules. We have been studying the applicability of the technique of near edge X-ray absorption fine structure (NEXAFS) spectroscopy to this subject, in which electronic excitations from core orbitals (e.g. C1s) to various vacant orbitals are observed. Since the NEXAFS spectrum, however, may be significantly deformed from DOUS due to the excitonic effect caused by the interaction between core-hole and the excited electron[1,2], it is necessary to assess the magnitude of the excitonic effect systematically. Our previous paper has evaluated the variation of the magnitude of the excitonic effect among various delocalized \(\pi\)-conjugated systems, such as fullerenes, naphthacene and p-sexiphenyl[3]. In this work, we extend our study to other \(\pi\)-electron systems, chrysene, perylene and coronene, whose degrees of \(\pi\)-conjugation are estimated to lie between these for fullerenes and naphthacene.

The samples were thin films of 3000\(\AA\) thickness prepared by vacuum evaporation. C K-edge NEXAFS spectra were measured at the beamline 11A of PF and the beamline 2B1 of UVSOR. Analysis of the observed spectra was performed by ab initio MO calculation program GSCF3, coded by one of the authors (N.K.), with use of hole-potential method[4]. While convoluting the delta functions at each transition energy with Gaussian function to obtain NEXAFS spectra, we have taken account of the difference among the C1s binding energies, \(\Delta IP\), for each atom in the molecule. In Fig. 1, we show the C K-edge NEXAFS spectra of chrysene, perylene, and coronene with the results of inverse photoemission spectroscopy (IPES)[5] and the calculated NEXAFS spectra. Since IPES spectrum of chrysene is not available in the literature, we have used the DOUS estimated from ab initio calculation for the ground-state. As is clear from the figures, the resemblance between IPES and NEXAFS spectra are rather poor, as was observed in the case of naphthacene[3].

In order to evaluate how the excitonic effect affects the MO and the NEXAFS spectra, we depict the details of MO calculations for perylene in Fig. 2 as an example. Abscissa represents the number of the excited atom shown in the inset. Orbital maps of the unoccupied MOs of the ground-state are illustrated at the left-hand side. Also shown are the energies of the core excited states. Positions of bars in each column correspond to the energy levels of the unoccupied MOs in the excited states which, in the hole-potential method, correspond to the excitation energy (excitation energy are calibrated by \(\Delta IP\)). The length of each bar gives the excitation intensity. Delta function at each energy level is convoluted and their weighted sum over the C atoms gives the simulated NEXAFS spectrum (right). The first peak (I) consists of the excitations from the C1s orbitals of atoms 1, 2, 3 to the same final MO. The second peak (II), on the other hand, is formed by the contributions from both MO-a and MO-b with the excitation of atoms 5 and 6. Considering the variation of the energy levels of MO for various excited atoms, we can conclude that DOUS information of this size of \(\pi\)-conjugated system is hardly obtainable from NEXAFS spectra.

REFERENCES
Recording of Soft X-Ray Hologram by a Backside Illuminated CCD Camera

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Introduction
Soft x-ray holography has a potential for obtaining high resolution three-dimensional images of biological microstructure. Resolution of Gabor in-line holography is determined by spatial coherence (source size), temporal coherence (monochromaticity), and resolution of a detector. If source size is small enough and a diffraction pattern is enlarged by shadow projection, it is not essential for recording a hologram to use a detector with extremely high resolution, such as a resist. Instead of this, a moderate resolution detector with high quantum efficiency, such as a backside illuminated CCD camera, can be used. Hologram data of the CCD camera can be digitized directly, and an artifact from a readout process can be avoided.

We used a zone plate and a pinhole to make a point source, and recorded holograms by a CCD camera. Some preliminary results of recording x-ray holograms are given in this report.

Experimental
Optical arrangement is shown in Fig. 1. The Grasshopper monochromator installed at BL11A was used. The monochromatic radiation of 3.1–3.3 nm from the monochromator was focused on a pinhole (ø1.0 μm) by a zone plate (diameter: 1.0 mm, outermost zone width: 0.25 μm). A specimen was placed 30.0 mm downstream from the pinhole. Divergent soft x-rays from the pinhole formed a shadow-projection image of the specimen on a CCD camera (Astromed Ltd., CCD: EEV P86000/T, 22 ×22 μm/pixel, 578×385 pixels) which was set 667 mm downstream from the pinhole. The magnification ratio was 22. The image was in-line hologram of the specimen, since the pinhole could be regarded as a partially coherent point source.

Specimens, such as chemical fibers (ø5 μm), tungsten wires (ø5 μm), molybdenum wires (ø13 μm), human red blood cells, crab muscles, were observed. The exposure time was about 30 min under the ring current of ~300 mA.

Results and Discussion
Fig.2 shows a hologram of tungsten wires (ø5 μm), and Fig.3 shows a hologram of human red blood cells. Disappearance of higher order diffraction fringes is due to the lack of the spatial coherence. Computer-aided reconstruction processes of these holograms are currently under way.

Acknowledgements
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![Fig. 1 Schematic of the optical system.](image1)

![Fig. 2 Hologram of ø5μm tungsten wires.](image2)

![Fig. 3 Hologram of red blood cells.](image3)
S K-EDGE SEXAFS ANALYSIS OF HIGHER COORDINATION SHELLS OF c(2x2)S OVERLAYERS ON Ni(100) AND Ni(110)

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Introduction

By virtue of recent developments of theoretical aspects of EXAFS, one can obtain detailed information on local structures beyond the first nearest neighbor (n.n.) shells by using, for instance, the FEFF6 code [1]. In this study, we have analyzed polarization-dependent S K-edge SEXAFS of c(2x2)S overlayers on Ni(100) and Ni(110), and have determined detailed surface structures for the first and second Ni layers.

Experimental

Clean and (1x1)-ordered Ni(100) and Ni(110) crystals were dosed with saturated amounts of H2S at ~600 K. Very clear and sharp c(2x2) LEED patterns were obtained for both surfaces. S K-edge SEXAFS spectra were recorded with the S-K fluorescence yield mode at ~100 K. Polarization dependence was examined at normal (θ=90°) and grazing (θ=15°) x-ray incidence. For Ni(110), azimuthal angle dependence was investigated only in the plane including the [001] axis.

Results and Discussion

In the previous study [2] we already determined the local surface structures up to the second n.n. shells for both surfaces. For S/Ni(100) it has been clarified that the S atom locates at the fourfold hollow site with the S-Ni1 and S-Ni2 (Ni1: surface layer Ni, Ni2: second layer Ni) distances of 2.19 Å and 3.14 Å, respectively. In the present study, we have theoretically evaluated polarization-dependent SEXAFS including multiple-scattering paths for sufficiently large clusters by using FEFF6 [1]. Figure 1 shows Fourier transforms of SEXAFS at θ=20° obtained experimentally and theoretically. Both spectra are well consistent with each other, indicating high reliability of FEFF standards. Although there have been found several intense multiple scattering paths in the higher n.n. shells, some contributions appearing in the Fourier transforms can be described within the single scattering scheme. We have consequently found a buckling of the second layer Ni, as shown in Fig. 2. It is revealed that the second layer Ni locating exactly below the S atom lies deeper by 0.04±0.02 Å than the other second layer Ni atoms. The conclusion is in good agreement with the LEED study [3].

For S/Ni(110), the S atom is known to locate at the twofold hollow site with the S-Ni1 and S-Ni2 distances of 2.28 Å and 2.20 Å, respectively [2]. Note that the second layer Ni2 is placed closer to the S atom than the surface layer Ni1. We have performed similar FEFF simulations and found that there also exists a buckling of the second layer Ni and the magnitude is ~0.05±0.02 Å.

References


Fig. 1. Fourier transforms of S K-edge SEXAFS kχ(k) of c(2x2)S/Ni(100) at x-ray incidence angle of 15°, obtained experimentally and theoretically.

Fig. 2. Schematic side view of surface structure of c(2x2)S /Ni(100).
S K-EDGE SEXAFS ANALYSIS OF HIGHER COORDINATION SHELLS OF \((\sqrt{3}\times\sqrt{3})R30^\circ S/Ni(111)\)

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Introduction

Recent developments of the theory of EXAFS including multiple scattering events allow one to analyze higher coordination shells with high accuracy. In this study, we have analyzed polarization-dependent S K-edge SEXAFS of \((\sqrt{3}\times\sqrt{3})R30^\circ S/Ni(111)\) beyond the first nearest neighbor (n.n.) shell by using theoretical standards given by FEFF6 [1], and have consequently obtained detailed surface structure.

Experimental

A clean and \((1\times1)\)-ordered Ni(111) crystal was dosed with 1 L H\(_2\)S at \(-200\) K. A very clear and sharp \((\sqrt{3}\times\sqrt{3})R30^\circ\) LEED pattern was obtained. S K-edge SEXAFS spectra were recorded with the S-K fluorescence yield mode at a temperature of 95 K and x-ray incidence angles of 90° (normal incidence), 55° and 15°.

Results and Discussion

In the previous study [2] we already determined the local surface structure. It was revealed that the S atom locates at the threefold hollow site with the S-Ni(surface) distance of 2.13 Å. The main purpose of the present work is to clarify which hollow site the S atom favors. As shown in Fig. 1, there are two inequivalent threefold hollow sites on Ni(111); one is so-called hcp site exactly above the second layer Ni (Fig. 1(a)), and another is so-called fcc site above the third layer Ni (Fig. 1(b)). These two sites provides exactly the same features for the first n.n. shell, and one needs the analysis of the higher n.n. shells to distinguish the two geometries. We have performed FEFF6 simulations [1] employing sufficiently large clusters. In these calculations, the S-Ni(surface) distance of 2.13 Å was employed, and no lateral or vertical displacements of substrate Ni layers were assumed. Figure 2 shows Fourier transforms of experimentally and theoretically (for both hcp and fcc sites) obtained SEXAFS functions \(k\chi(k)\). When one compares the features around 3-5 Å, one can conclude that the fcc site is more appropriate. The fcc-site adsorption was also found in the case of \((\sqrt{3}\times\sqrt{3})R30^\circ Cl/Ni(111)\) whose surface structure was determined by the triangulation of back reflection x-ray standing-wave method [3].

The second peak in the experimental Fourier transform appears at \(-3.8\) Å, which is slightly larger than that in the fcc-calculated one by \(-0.1\) Å. From the conventional curve-fitting analysis of the shell, we have found an expansion of the spacing between the first and second Ni layers by \(-9\%\) upon adsorption of the S atoms.

References


Fig. 1. Structure models of \((\sqrt{3}\times\sqrt{3})R30^\circ S/Ni(111)\): (a) hcp and (b) fcc.

Fig. 2. Fourier transforms of S K-edge SEXAFS functions \(k\chi(k)\) obtained experimentally (solid), together with calculated ones (hcp: dotted, fcc: dashed). The fcc site is found to be more probable.
EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDY OF ZnSSe AND ZnMgSSe

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Introduction

ZnSe based II-VI alloys have been considered to be suitable material for application to short wavelength optoelectronic devices. Recently, blue lasers based on a ZnSSe-ZnMgSSe double heterostructure (DH) have been successfully operated under the continuous wave mode at room temperature. However, the atomic disorders of ZnSSe and ZnMgSSe have never been investigated enough, though the randomness in the distribution of each element is strongly connected with electronic and excitonic properties. We present a sulphur K-edge extended x-ray absorption fine structure (EXAFS) study to elucidated the distribution of chalcogen atoms in ZnS_{x}Se_{1-x} (x=0.06) and Zn_{1-x}Mg_{y}S_{x}Se_{1-y} (x=0.18, y=0.2) with zincblende structure.

Experimental

ZnSSe and ZnMgSSe films were grown on GaAs(100) substrates by molecular beam epitaxy (MBE). The film thickness of samples is about 1.5μm. Sulphur K-edge EXAFS (2400-2900 eV) measurements were carried out at BL-11B with a gas-flow proportional counter. The sample temperature was kept at about 100K with liquid-N2 cooling. The EXAFS data are analyzed according to a standard procedure by adopting the parameters calculated with the FEFF 5 program for the backscattering amplitude |f(k)| and the phase shift function δ.

Results and Discussion

Figure 1 shows a sulphur K edge EXAFS spectrum of ZnS_{x}Se_{1-x} (x=0.06). The Fourier transform of the EXAFS function K²g(k) is presented in Fig.2. The EXAFS data of Zn_{1-x}Mg_{y}S_{x}Se_{1-y} (x=0.18, y=0.2) could be obtained similarly. The analytical results of the EXAFS in ZnSSe and ZnMgSSe of the effective coordination number N and the interatomic distance R are summarized in Table I and II. It was found that each interatomic distance in these compounds has almost the same length as that in a binary compound, respectively. Further, the ratio of numbers of sulphur to selenium atoms in the second-neighbours around sulphur atoms are proportional to the respective composition ratio both in ZnSSe and in ZnMgSSe. This result indicates that there is no clustering in ZnSSe and that chalcogen atoms are also randomly distributed in ZnMgSSe.

References

Introduction

There have already been reported the structures of SO₂ on Ag(110) and Pd(100) surfaces, which show that the plane of the SO₂ molecule is nearly perpendicular to the surface. Recently we have studied SO₂ adsorption on clean Ni(100) and Ni(111) surfaces at ~170 K by means of S K-edge XAFS and found that on both surfaces the SO₂ molecule is adsorbed with the molecule plane parallel to the surfaces. These findings are in clear contrast with all the previous studies. In the present study, we have investigated the adsorption behavior of submonolayer SO₂ on Cu(100) by S K-edge XAFS.

Experimental

A Cu(100) single crystal was prepared by mechanical polishing and electrochemical etching. The cleaning was carried out by argon ion bombardment (1 kV) and annealing (930 K) by means of electron bombardment. The surface cleanliness and order were confirmed by XANES and LEED, respectively. The sample was cooled down to 180 K and subsequently dosed by 0.4 L with SO₂ gas in an UHV chamber. Polarization dependant S K-edge XANES, EXAFS and S 1s XPS measurements were carried out at BL-11B.

Results and Discussion

The S 1s binding energy of submonolayer SO₂ on Cu(100) is higher by 5.2 eV than that of atomic S on Cu(100), and is lower by 2.6 eV than that of multilayer SO₂. These results indicate that there exists molecular SO₂ on the surface exclusively, and that the Cu substrate contributes to lower the binding energy by charge transfer to the adsorbed SO₂ and the final state relaxation. Fig. 1 shows the Fourier Transform of the S K-edge EXAFS function kχ(k) of SO₂. The peak A is assigned to an S-O bond, whose distance was determined to be 1.51 Å by the curve-fitting analysis. It is found longer by 0.08 Å than that of solid SO₂, being in agreement with the XPS results. O K-edge SEXAFS study of the same system was carried by Pangher et al.¹, who determined the O-S and O-Cu distances as 1.48 Å and 1.95 Å, respectively. The former is in agreement with our results within experimental error. The peaks B and C come mainly from S-Cu contributions but cannot be explained by a single shell. Some multiple scattering contributions should be taken into account. Although the adsorbed structure has not been determined yet, our results, combined with O K-SEXAFS, imply that the O atoms of SO₂ molecule are directly bound to the Cu substrate with the O-S bond inclined as ~60° from the surface normal.

Fig. 1. Fourier Transform for S K-edge EXAFS of SO₂/Cu(100)

Adsorption of SO₂ on Ni(110) studied by S K-edge XAFS

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INTRODUCTION

Recently, we have investigated the surface structures of SO₂/Ni(111) and SO₂/Ni(100) and found that on both surfaces SO₂ adsorbs with the molecular plane parallel to the surfaces [1]. However, the previous conclusion for Ni(110) by ARUPS [2] seems contradictory with our work. Thus in the present study, we examined the surface structure of SO₂ adsorbed on Ni(110) surface by means of S K-edge NEXAFS and SEXAFS.

EXPERIMENTAL

A clean and (1x1)-ordered Ni(110) crystal was prepared in an UHV chamber and was subsequently dosed with 0.4 L SO₂ at 170 K. Azimuthal-angle dependence of the XAFS spectra was investigated in different runs. In the first run the electric field vector E was kept along the [110] azimuth, and in the second run E was kept along the [001] azimuth. S K-edge NEXAFS and SEXAFS were measured in the fluorescence yield mode at BL-11B at 92 K.

RESULTS and DISCUSSION

The S K-edge NEXAFS spectra of the submonolayer SO₂ on Ni(110) were taken at incident X-ray angles θ of 90°, 55° and 15°. The polar dependence of the spectra was similar to that of SO₂/Ni(111) and Ni(100) [1]. The polar angle dependence of the π* and σ* peaks indicates that SO₂ adsorbs with molecular plane parallel to the surface. From the lower energy shift of the σ* resonance by 1.4 eV compared to the multilayer one, we can deduce the elongation of the S-O bond length. From the intensity of the π* resonance in the 55° incidence spectrum we found that the charge transfer from the substrate to the π* orbital upon SO₂ adsorption on Ni(110). On the contrary, little azimuthal dependence was observed, and this implies that SO₂ molecule is oriented randomly with respect to the azimuthal angle.

Fig. 1 shows the Fourier transforms of the extracted SEXAFS functions \( k^2 \chi(k) \), with the electric field vector E is along the [110] azimuth. The feature appearing at ~1.1 Å can be ascribed to the S-O coordination and the bond length was determined to be 1.49±0.03 Å which is longer than that of multilayer SO₂ (1.43 Å), being in agreement with the NEXAFS remarks. The one at ~1.9 Å is to the S-Ni shell and the distance is found to be 2.20±0.03 Å and the S atoms are found to locate on the long- and short-bridge sites with equal amounts of distribution. A consequent schematic structure is shown in fig. 2.

REFERENCES

Adsorption of SO$_2$ on Ni(111) and Ni(100) studied by S K-edge XAFS

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INTRODUCTION

Since sulfur dioxide SO$_2$ plays a role of a strong $\pi$ acceptor than CO, structure and electronic properties of submonolayer SO$_2$ on metal surfaces are quite interesting. We report on the surface structure and electronic properties of SO$_2$ adsorbed on Ni(111) and Ni(100) studied by S K-edge NEXAFS and SEXAFS.

EXPERIMENTAL

Clean and (1×1)-ordered Ni(111) and Ni(100) crystals were prepared in an UHV chamber and were subsequently dosed with 0.5 L SO$_2$ at 170 K. At this temperature only submonolayer SO$_2$ adsorbs on the surfaces since multilayer desorbs above 120 K. Polarization dependent S K-edge NEXAFS and SEXAFS were measured in the S-K fluorescence yield mode at BL-11B at 92 K.

RESULTS and DISCUSSION

Fig. 1 shows the S K-edge NEXAFS spectra of submonolayer SO$_2$ on Ni(100) taken at incident X-ray angles $\theta$ of 90°, 55° and 15°, together with the spectrum of multilayer SO$_2$. Similar spectra were obtained for Ni(111). Two intense resonances found in the spectra are assigned to the transitions of S1s-to-$\pi^*$ and S1s-to-$\sigma^*(S-O)$, respectively. The $\pi^*$ resonance is most enhanced at grazing X-ray incidence and the $\sigma^*$ resonance is maximized at normal incidence, this implying the flat-lying orientation of the molecular plane. From the curve-fitting analysis, the $\omega$ value (polar angle) is given as 90±10° on both surfaces. The lower energy shifts of the $\sigma^*$ resonances by 1.4 eV on Ni(111) and 1.7 eV on Ni(100) were observed compared to multilayer one, indicating the elongation of the S-O bond lengths. The intensity of the $\pi^*$ resonance in the 55° incidence spectrum (equivalent of polarization-averaged spectrum) is noticeably suppressed compared to the multilayer one. This means that the charge transfer from the substrate to the $\pi^*$ orbital upon SO$_2$ adsorption.

From the SEXAFS analysis, the S-O bond lengths were determined to be 1.48±0.03 Å for SO$_2$/Ni(111) and 1.51±0.03 Å for SO$_2$/Ni(100). The S-O distances are found to be longer than that of multilayer SO$_2$ (1.43 Å), being in agreement with the NEXAFS remarks. The S-Ni distances are estimated to be 2.16±0.03 Å for SO$_2$/Ni(111) and 2.18±0.03 Å for SO$_2$/Ni(100) and the S atoms are found to locate at the bridge site on both surfaces. Consequent schematic structures are shown in fig. 2.

![Fig. 1 S K-edge NEXAFS spectra of submonolayer SO$_2$ on Ni(100), together with that of multilayer SO$_2$.](image)

![Fig. 2 Schematic views of surface structures of submonolayer SO$_2$ on Ni(111) and Ni(100).](image)
Structural and electronic properties of adsorbed C<sub>4</sub>H<sub>4</sub>S on Cu(100) studied by S K-XAFS

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Introduction

Adsorption of aromatic sulfur compounds on metal surfaces has been an important subject for understanding the mechanisms of the hydrodesulfurization process. Recently, we have investigated the surface structures of thiophene on Ni(100) at 43 K by means of S K-edge SEXAFS and NEXAFS, and found that the C<sub>4</sub>H<sub>4</sub>S molecule is adsorbed with the molecular plane parallel to the surface and the S atom locates at the bridge site. In the present work, the adsorption of thiophene on Cu(100) has been studied using S K-edge SEXAFS and NEXAFS spectroscopies in comparison to the previous investigation.

Experimental

A Cu(100) single crystal was mechanically and electro-chemically polished. Cleaning was carried out by argon ion bombardment (600 eV) and annealing (~1000 K) by means of the electron bombardment. The surface cleanliness and order were confirmed by NEXAFS and LEED, respectively. Submonolayer C<sub>4</sub>H<sub>4</sub>S adsorption on the clean Cu(100) was carried out by dosing ~5 L C<sub>4</sub>H<sub>4</sub>S (1 L = 1.0x10<sup>18</sup> Torr·s; 1 Torr = 133 Pa) at ~220±10 K. It was kept at 105 K during the spectroscopic measurements.

Results and Discussion

Fig. 1 shows the NEXAFS spectra of C<sub>4</sub>H<sub>4</sub>S/Cu(100) together with that of multilayer C<sub>4</sub>H<sub>4</sub>S. Comparing with the multilayer C<sub>4</sub>H<sub>4</sub>S spectrum, two features at 2472.3 eV and 2473.5 eV were assigned to the π' and σ'(S-C) transitions, respectively. The σ'(S-C) resonance is most enhanced at normal X-ray incidence and π' resonance is enhanced at grazing incidence. This implies the flat-lying orientation of the molecular plane on the surface. Though polarization dependence is effectively canceled out at 55° incidence for any specific sample orientation, the π' resonance is suppressed comparing to that of multilayer C<sub>4</sub>H<sub>4</sub>S. This comes from the charge transfer from the Cu substrate to π' orbital, then we estimated the amount of charge transfer by comparing the intensity of π' resonance of C<sub>4</sub>H<sub>4</sub>S/Cu(100) with that of multilayer C<sub>4</sub>H<sub>4</sub>S and it was estimated as (1.0±0.2)e. This is smaller than that of C<sub>4</sub>H<sub>4</sub>S/Ni(100) ((1.4±0.2)e).

From the analysis of the EXAFS spectra, the S-C distance and the polar angle of the S-C bond with respect to the surface normal were found to be 1.71±0.05 Å and 90±8° respectively. These results indicate that the distance of S-C bond is as long as that of multilayer (1.71 Å) and the molecular plane of C<sub>4</sub>H<sub>4</sub>S is completely flat on the surface. The S-Cu distance was found to be 2.43±0.02 Å and the adsorption site of S atom was determined to be bridge site. Comparing to the results of C<sub>4</sub>H<sub>4</sub>S/Ni(100), the adsorption site of S and the polar angle of S-C bond are the same as those on Ni(100). However, the distance of the S-C bond is shorter than that on Ni(100) (1.80±0.05 Å) and the distance between S and substrate atom is longer than that on Ni(100) (2.20±0.02 Å).

All the results of SEXAFS and NEXAFS indicate that charge transfer from Cu to C<sub>4</sub>H<sub>4</sub>S is smaller than that from Ni to C<sub>4</sub>H<sub>4</sub>S, and the interaction between Cu and C<sub>4</sub>H<sub>4</sub>S is weaker than that between Ni and C<sub>4</sub>H<sub>4</sub>S. Since the d band of Cu lies deeper than that of Ni, the π' orbital of C<sub>4</sub>H<sub>4</sub>S on Cu has a weaker interaction with the d band of Cu comparing to that of Ni.
Adsorption and Decomposition of Silane on Cu(111)

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Introduction

The study of the metal/silicon interfaces has become a topic of great interest, because of important applications in electronic devices. However, only a few studies have been reported in reverse systems (silicon on metal) so far, which is also important from the standpoint of catalytic reaction mechanism. So, we mainly investigated the growth and the structure of copper silicide by means of Si K-edge XAFS.

Experimental

Details of the ultra high vacuum chamber and experimental procedures have been described elsewhere. Briefly, a Cu(111) crystal was cleaned by cycles of Ar⁺ sputtering and annealing. Silane was deposited on the Cu(111) at 110 K, followed by annealing to 230 K and 600 K.

Result and Discussion

The silane saturated surface at 110 K displayed a clear $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern which is in agreement with the work by Wiegand et. al. As temperature raised, the LEED pattern changed to weak $(1 \times 1)$ at 200 ~ 300 K. At 500 ~ 600 K a clear $(\sqrt{3} \times \sqrt{3})R30°$ pattern appeared again and at 700 K returned to the $(1 \times 1)$ pattern.

Fourier transformation resulted from the SEXAFS spectra of silane saturated sample at 110 K, 230 K and 600 K are shown in Fig. 1. At 110 K, the grazing incidence spectrum has a distinct peak which is assigned to the nearest neighbor Cu, while the normal incidence spectrum has less distinct peak. From the curve-fitting analysis using theoretical parameters by Rehr et. al., we determined that the Si-Cu distance on Cu(111) is 2.45 Å, and the adsorption site is a 3-fold hollow. Moreover, from the theoretical simulation FEFF6, the Si atom might be located on top of the Cu atom in the second layer (hcp site). From the previous studies, the adsorbed species on Cu(111) would be mainly SiH₂ and hydrogen atoms.

At 230 K, both normal and grazing incidence spectra have a distinct peak. At grazing incidence the peak is assigned to a Si-Cu bond, but at normal incidence the peak could be assigned to a Si-Si bond, not a Si-Cu bond by the curve-fitting analysis. The Si-Cu distance is determined to be 2.44 Å, and the Si-Si distance 2.34 Å, which is equal to that of a Si crystal. This result suggests that a few Si atoms are combined with each other, and made an island-like structure.

At 600 K, the polarization dependence is much reduced. From the analysis of the spectra, we concluded that the main peak is assigned to a Si-Cu bond whose distance is determined to be 2.48 Å, and that the surface Cu atom might be replaced by the Si atom. This result suggests that a drastic change occurs in the structure of adsorbed species between 230 K and 600 K.

![Fig. 1](image-url)
Surface Structure Study on \( (\sqrt{17} \times \sqrt{17})R14^\circ \) S/Cu(100) by SEXAFS and STM

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INTRODUCTION

The S/Cu(100) system is known to exhibit two different LEED patterns depending on the S coverage [1]. At the low S coverage near 0.25 ML, a \( p(2 \times 2) \) LEED pattern is observed. Another stable S/Cu(100) phase which shows clear \( (\sqrt{17} \times \sqrt{17})R14^\circ \) LEED pattern is formed after thermal annealing of the saturation coverage of 0.47 ML [1]. The previous structural study on the \( (\sqrt{17} \times \sqrt{17})R14^\circ \) phase by STM has clearly indicated a drastic reconstruction of the surface Cu layer [2]. We have measured S K-edge SEXAFS of the S/Cu(100) system and further observed STM images of the system. From these results we have successfully elucidated the reconstructed surface structure of the \( (\sqrt{17} \times \sqrt{17})R14^\circ \) S/Cu(100) system and proposed a new structure model which is consistent with both the SEXAFS and STM results.

EXPERIMENTAL

A clean Cu(100) crystal was dosed with \( 4.0 \times 10^{-4} \) Pa H\(_2\)S for 300 s (900 L) at \( \sim 800 \) K. A very sharp and intense \( (\sqrt{17} \times \sqrt{17})R14^\circ \) LEED pattern was observed. Polarization dependent S K-edge SEXAFS measurements were carried out in the fluorescent X-ray yield mode at BL-11B. The SEXAFS spectra of this sample were taken at the X-ray incident angles of 90° (normal incidence), 55° and 15°. In order to suppress thermal vibrations, the sample was cooled down to 100 K using liquid N\(_2\). STM images were taken with a sample bias voltage of 25 mV and a constant tunnel current of 2.5 nA using another UHV chamber at ambient temperature.

RESULTS AND DISCUSSION

From the analysis of SEXAFS spectra the first nearest neighbor (n.n) S-Cu bond distance is determined to be 2.29 ± 0.03 Å, which is almost independent of the X-ray incident angle. This implies that all the S-Cu distances are nearly equal to each other even if two or more inequivalent S atoms are present in this system. The averaged S-Cu bond angle with respect to the surface was found to be 30 ± 3°. When the amplitude reduction factor \( s_0^2 \) is assumed to be 0.74, the coordination number \( N \) in this system can be determined as 5.1 ± 0.5.

From the AES study it was clarified that each \( (\sqrt{17} \times \sqrt{17})R14^\circ \) unit mesh contains eight S atoms [2]. It is found from the STM images that there exist two types of S atoms. Half of the eight S atoms \( (S_1) \) are imaged as bright spots in each unit mesh and their interatomic separation is 4.0 ± 0.15 Å. Another half of S atoms \( (S_2) \) are imaged as darker spots in each unit mesh and these atoms are assumed to be embedded in the plane of the surface Cu layer.

Colaianni et al. [2] have already proposed a surface structure model of the \( (\sqrt{17} \times \sqrt{17})R14^\circ \) S/Cu(100) system. However the S-Cu distances and the coordination number in this model does not satisfy the present SEXAFS results. In order to meet the SEXAFS results we propose a new structure model as depicted in fig. 1. The top-layer \( S_1 \) atoms locate at the trapezoid-shaped hollow site composed of four Cu atoms of the first layer. The embedded \( S_2 \) atoms are surrounded by six Cu atoms (two of the first Cu layer and four of the second layer) and locate on the normal four-fold hollow site of the second layer. The \( S_1-Cu \) and \( S_2-Cu \) distances are all equal to 2.29 Å. This model successfully explains both the STM and SEXAFS results.

REFERENCES

DEPTIIE SELECTIVE CHEMICAL STATE ANALYSIS OF FLY ASH USING S K-EDGE NEXAFS

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Sulfur K-edge NEXAFS (Near Edge X-ray Absorption Fine Structure) spectra of fly ash powder samples were measured using both total electron yield (sample current) and sulfur K-X-ray fluorescence yield methods. The total electron yield probes surface less than 100 Å depth and the X-ray fluorescence yield probes deeper than 1000 Å. Therefore we can obtain both the surface and bulk chemical information on powder samples.

The experiment was performed on the beam line BL-11B. InSb(111) double-crystal monochromator was used.

The samples measured were fly ash powders. Australian coals from Newlands and Saxonvale were burned in an industrial furnace at 1700 K and fly ash powders were gathered [1, 2].

The obtained spectra are shown in Fig. 1. Six hours were required to accumulate one set of spectra shown in Fig. 1 because the sulfur concentration was less than 0.3 %. The S$^{6+}$ peak was at 2482 eV and S$^{2-}$ peak 2473 eV. Therefore we could determine the chemical state of sulfur using these NEXAFS spectra.

The surface was S$^{2-}$ chemical state, and the bulk was mixture of S$^{2-}$ and S$^{6+}$ chemical states. We have found that the S$^{2-}$/S$^{6+}$ ratio of bulk was different when the coal origin was different.

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References
INTRODUCTION

SrTiO₃ (cubic perovskite-type crystal structure at room temperature) is a typical insulator with a wide band gap (E₝ − 3.2 eV). This transition metal oxide has no 3d electron formally, namely, the valence band of SrTiO₃ consists of mainly O2p bands in origin[1]. Therefore, it may be considered that its valence band structure can be simply described by one-electron picture. However, there is little experimental evidence which has directly demonstrated whether the electronic structure of SrTiO₃ is described by one-electron picture or not. So, in order to examine the electronic structure of O2p valence bands, we have performed ARP studies of SrTiO₃(110) surface.

EXPERIMENTAL

The ARP experiments were performed at the Photon Factory (BL-11C), using the hemispherical electrostatic analyzer with an acceptance angle of ±1° (VSW). Total instrumental energy resolution was 150-250 meV full width at half maximum, depending on the photon energy in the energy range of 18~32 eV. All ARP spectra were recorded on normal emission with a light incidence angle of θ= 50° and measured at room temperature. The base pressure in the ARP systems was ~3x10⁻¹⁰ Torr.

Polished, (110) oriented single crystals of SrTiO₃, which were reduced by annealing in UHV at 800 °C for several hours, were free from charging effect. Annealing in UHV and O₂ were used to remove contamination. The cleanliness of the sample surfaces was confirmed by Auger electron spectroscopy. The sample geometrical structure was checked using low-energy electron diffraction.

RESULTS AND DISCUSSION

Normal emission spectra of SrTiO₃(110) surface are taken between 18 and 32 eV in the [001] (A|| [001]) azimuth and [110] (A|| [110]) azimuth. Four features in this valence band are observed labeled E, F, G and H for A|| [001] and I, J, K and L for A|| [110]. In the direct transition model, these valence bands in the normal emission spectra should arise from transitions involving initial states with crystal momentum lying Γ-Σ-M of the bulk Brillouin zone for the (110) surface. In order to map the bands, we assume direct transitions into a free-electron-like final state of the form:

E(k||)=(h²k²/2m²)E₀, where m* is the effective mass of the electron, E₀ is the inner potential referred to E₝, and k|| is the component of the wavevector of the outgoing photoelectron normal to the surface. E₀ and m* have been decided as empirical adjusting parameter to obtain initial-state dispersion which is symmetric about the Brillouin zone boundary. Using V₀=12.0 eV and m*=1.10mₑ, where mₑ is the free-electron mass, empirical valence band structures along Σ-line (squares for A|| [001] and triangles for A|| [110]) are shown in fig. 1 together with the band structure calculated by Takegahara(solid lines) using APW method with LDA approximation[2] for comparison. The binding energy of the calculated band structure is referenced to valence band maximum. Although there are some disagreements in fig. 1, our empirical band structure of the O2p valence bands along Σ line in the bulk Brillouin zone was in qualitatively overall agreement with the calculated band structure.

REFERENCES


MAGNETIC CIRCULAR DICHRORISM STUDY OF KBr AND RbBr EXCITONS

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Introduction

Magnetic circular dichroism (MCD) in the exciton region of Alkali Halides provides useful information about their related electronic structures. However, MCD studies in the VUV region have been severely limited because of their experimental difficulties. The pioneering MCD measurements of KI and RbI were performed by Ahrenkiel1) and Onaka2). Although they obtained effective g values (g_{eff}) at fundamental exciton peaks, their results did not agree with each other. We, therefore, decided to measure the MCD of several Alkali Halides in order to settle the g_{eff} values of their exciton peaks. Since we have already reported the results for KI and RbI3), we present here the recently obtained results for KBr and RbBr.

Experiment

We have measured MCD spectra of KBr and RbBr in the energy region 6 ~ 9eV at BL-11C. The measurement was carried out at room temperature as well as at low temperature (30K). A calcium fluoride stress modulator is used for a quarter-wave retarder and linearly polarized synchrotron radiation from Sera-Namioka monochrometer is converted to 50-KHz left and right circularly polarized light. The detector is a sodium salicylate-coated photomultiplier specially designed for use under high magnetic fields. The dc component of an output of the photomultiplier is kept constant by controlling a high voltage applied to the photomultiplier. The ac component, which is proportional to the MCD signal, is detected with a phase-sensitive technique.

Results

Figure 1 displays MCD (in reflection) and reflectance spectra of RbBr taken at 30K in the region below 9.0eV. Spectra of KBr are similar to those in Fig. 1. There are five exciton peaks (1, 2, 3, 4, 5) and two weak structures (3, 7). The MCD signals for each structures is proportional to the logarithmic derivative of reflectance. Similar results are obtained for KBr. This indicates the validity of a rigid shift model, thus allowing a direct derivation of the g_{eff} for each transition without resorting to Kramers-Kronig analyses. The obtained g_{eff} values are tabulated in Table 1.

The assignments of the structures deduced from the present g_{eff} values are consistent with those determined from previous piezoreflectance studies4); 1 and 2 are attributed to spin-orbit split Γ excitons, 3 and 4 to F^- - F^- interband thresholds, 5, 6 to L excitons.

References


Table 1. Effective g-values experimentally obtained at room temperature and at 30K.

<table>
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<tr>
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<th>1</th>
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<td>RbBr(30K)</td>
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<tr>
<td>KBr(30K)</td>
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<td>-0.77</td>
<td>-0.44</td>
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<tr>
<td>KBr(300K)</td>
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<td>-0.54</td>
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FIG. 1 (a) Reflectance spectrum of RbBr at 30K. The spectral features are denoted by arrows. (b) MCD and logarithmic derivative spectra of RbBr, - (ΔR/R)_{MCD} and (1/R)(dR/dE) respectively. The sign of the MCD spectrum is reversed for convenience when making comparison.
PHOTOEMISSION STUDY OF Mn-ZnTe(110) INTERFACE

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Introduction

Diluted magnetic semiconductors Cd_{1-x}Mn_xTe and Zn_{1-x}Mn_xTe, have attracted considerable attentions because of their novel magnetic and magneto-optical properties [1]. Recently, it has been reported that deposition of Mn onto CdTe(110) surfaces yields interdiffusion across the interface and leads to the formation of Cd_{1-x}Mn_xTe surface alloys [2,3]. In this study, we have measured the valence-band photoemission of Mn-ZnTe(110) interface through Mn 3p-3d resonance.

Experimental

Photoemission measurements were performed at BL-11D. Clean ZnTe(110) surface was in situ prepared by cleavage under 3x10^{-10} Torr. Mn was deposited onto the (110) surface. The Mn coverages \( \theta \) were determined with a quartz thickness monitor.

Results and Discussion

Figure 1 shows photoemission spectra of Mn-ZnTe(110) interface as a function of \( \theta \). For each coverage, thick and thin curves indicate the spectra measured just on resonance (hv=50.0 eV) and at antiresonance (hv=47.5 eV), respectively. Binding energy is referred to the Fermi level \( E_F \). Peaks at 10.7 eV originate from Zn 3d core emission. With increasing \( \theta \) from 0 to 1.0 \text{	ext{\AA}}, Mn 3d-related peaks at 4.9 eV grow up in the resonance spectra. For \( \theta >1.0 \text{\AA} \), the emission at \( E_F \) is observed and the spectral feature gradually approaches that of metal Mn [2] with \( \theta \). One notices that the spectra for \( \theta \) below 1.0 \text{\AA} are apparently different from that of metal Mn and close to that of bulk Zn_{1-x}Mn_xTe [4]. Therefore, we assume a formation of Zn_{1-x}Mn_xTe surface alloy as a result of the interaction of Mn atoms with ZnTe(110) surface. In comparison with the spectra of bulk alloys [5], we have evaluated the x-values for surface alloys in parentheses in Fig.1.

Figure 2 shows the Mn 3d partial density of states (DOS) of the Mn-ZnTe(110) interface at \( \theta =1.0 \text{\AA} \) derived from subtracting the antiresonance spectrum from the resonance one. Binding energy is referred to the valence band maximum. It should be noticed again that the Mn 3d partial DOS is similar to that of the bulk alloy [4]. All Mn 3d spectra are almost unchanged for \( \theta \) below 1.0 \text{\AA} and consist of three characteristic features: a main peak at 3.7 eV, valence bands at 0-2.5 eV and a satellite structure around 8 eV [6]. The relative intensities of these structures are almost independent of \( \theta \).

References

HIGH-RESOLUTION VUV PHOTOABSORPTION CROSS SECTION MEASUREMENTS ON CO

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A-X Bands of CO: The Astronomical Situation

Carbon Monoxide (CO) is the second most abundant interstellar molecule after H2. Because the latter is homonuclear and has no dipole moment, it does not readily absorb or emit radiation and is difficult to observe. CO, on the other hand, is easily detected and studied, and therefore is used as a tracer of molecular material in galaxies. Estimates of CO abundances are, however, poorly determined observationally and not well understood theoretically. Incomplete or inconsistent molecular parameters have contributed to many of the difficulties in the past. As a consequence, the acquisition of improved spectroscopic and photoabsorption cross section data for CO at VUV and FUV wavelengths (91 - 140 nm) has been a major focus of our research program using the 6V0PE spectrometer on beam line 12B.

Recently, absorption by interstellar CO was detected by astronomers who used the Goddard High Resolution Spectrograph on the Hubble Space Telescope (HST) to observe the spectrum of the star ζ Ophiuchi. This star is hot and its spectrum is very similar to that of a "blackbody" at about 40,000 K. Other observations have demonstrated that there are a number of interstellar clouds between us and ζ Ophiuchi. These clouds are detected and studied through absorption features in the spectrum of the background star.

Determination of molecular densities in these clouds from the strengths of the observed absorption features requires accurate oscillator strengths (f-values). For the A1Π(v') - X1Σ(0) bands of CO observed on the line of sight to ζ Ophiuchi, the f-values for the higher vibrational level bands (v'=12) are needed. These lines are weaker and therefore less saturated (i.e., the absorption is more proportional to the density integrated along the line of sight) than those of stronger absorption bands at longer wavelengths.

A review by Morton & Noreau (1994) found a number of discrepant oscillator strengths for the A(1ν)-X(0) bands with larger ν'. In particular, f-values measured by Chan et al (1993) disagreed with those of Eddelsberg et al (1992); there were calculated values that supported each set of experimental data. Consequently, the astronomers could not use the literature f-value data to constrain the conclusions from their observations, but instead obtained f-value data from them: In other words, the astronomers used the 1.5B HST to perform measurements that should and could have been done in the laboratory.

A-X Bands of CO: Observations and Results

At approximately the same time as the HST observers were observing absorption by CO, we used the 6V0PE to study absorption by the (11,0) - (14,0) bands of the A-X system of CO at wavelengths between 121 and 127 nm. This unique spectrometer, used in the 4th order of a 1200 grooves/mm grating, allowed us to study the CO absorption spectrum with higher resolution than other groups could use. The methods used were similar to those employed in our previous work (Stark et al 1991, 1993), though we used a new absorption cell, 52 mm long with 2 mm thick MgF2 windows, in order to improve control and measurement of the density of the absorbing gas. Pressures of 0.2 to 3 Torr were measured with a capacitance manometer. Our results (Smith et al 1994) support the experimental values of Chan et al (1993) and the calculated one of Kirby & Cooper (1989).

Intersystem bands of CO

Spin-changing 'intersystem' molecular transitions, which are in principle forbidden by the strict rules for electric dipole radiation, are observed when molecular levels are perturbed. Federman et al (1994) detected absorption by seven intersystem bands of CO, a'(17), a'(14), a'(11), d(12), d(7), e(5), and e(4)-X(0), in limited observations with the GHRS on HST of the line of sight to ζ Ophiuchi. Many more such bands will be detected as HST observations continue and as more wavelengths and sources are observed. Quantitative use of these bands in analyses of interstellar clouds will require correct and complete fundamental spectroscopic data. The intersystem bands are weak and, therefore, more likely than 'allowed' bands to be unsaturated. Federman et al (1994) found that the results of their observations were inconsistent and pointed to the f-values as the most likely cause of the discrepancies.

We made preliminary observations of four of the intersystem bands observed by Federman et al (1994). Other bands were blended with the much stronger A-X bands. Analysis of the data are in progress, as are plans for additional measurements on CO cooled to 77 K, at which temperature the blending should be reduced. The authors thank W. H. Parkinson for his assistance with this project, which was supported by NASA grant NAGW-1596 to Harvard University.

References

EXAFS STUDY OF SELENIUM UNDER PRESSURE

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Introduction

Crystalline Se consists of infinite spiral chains. Each atom is covalently bonded to two nearest neighbors within a chain and has four second nearest neighbor atoms in the adjacent chains. Pressure variation of the structural parameters of Se reflects anisotropic character of the bonding[1]. In order to study pressure dependence of intra- and inter-chain bonding we measure EXAFS of Se under pressure up to 10 GPa at room temperature.

Experimental

EXAFS measurements were performed using MAX90, a cubic-type multianvil apparatus installed in BL-13B2 of the Photon Factory. The sample was powdered and sandwiched between two layers of a Scotch tape. It was inserted in a hole of a Boron-Epoxy cube. The synchrotron radiation was monochromatized by a Si(111) double crystal monochromator. The size of the incident x-ray beam was reduced to 0.5 x 0.5 mm^2. The intensities of the incident and transmitted x-rays were measured by ionization chambers.

Results and discussion

Figure 1 shows the radial distribution function \(|F(r)|\) at various pressures, which were obtained from Fourier transform of \(\chi(k)\) multiplied by \(k\). The first and second peaks correspond to the covalent bond length and interchain distance, respectively. The position of the second peak shifts to lower \(r\) and the intensity of the peak strongly increases with increasing pressure, whereas those of the first peak are almost constant. We carried out Fourier back-transform of \(|F(r)|\) in the corresponding region and fitted filtered spectrum weighted by \(k^2\) using theoretical parameters tabulated in FEFF table[2]. Figure 2(a) shows the first, second and third neighbor distances as a function of pressure. The present values agree with those determined by the high-pressure x-ray diffraction study[1]. Figure 2(b) shows the pressure dependence of mean square displacements \(r^2\) of the first and second peaks. The mean square displacement of the first peak slightly increases with increasing pressure while that of the second peak strongly decreases. These changes are attributed to the weakening of the covalent bond and the strengthening of the interchain interaction.

References


Fig. 1. The magnitude of Fourier transform of \(k\chi(k)\cdot|F(r)|\), for Se at various pressures.

Fig. 2. (a) First(circle), second(square) and third(triangle) neighbor distances for crystalline Se as a function of pressure. Lines indicate results of an x-ray diffraction study[1] (b) Mean square displacements, \(r^2\), for first(circle) and second(square) peak as a function of pressure.
Introduction

Cs2Au1Au11x6 (X=Cl, Br, I) are well known as perovskite-type Au mixed-valence compounds. In these crystals, all the halogens are distorted from the midpoint of the Au ions, and the linear [Au+1Cl2]- and square planar [Au+3Cl4]- complexes are formed alternately. Recently, we have found a pressure-induced tetragonal-to-tetragonal transition in the metallic phase. This structural phase transition is regarded as a band Jahn-Teller transition driven by the Au'+ii-Au'' transition. The purpose of this paper is to investigate the behavior of the Au valence state in Cs2AuCl6 under high pressure from the analysis of the Au L3 near edge structure.

Experimental

The Au L3 near edge structure of Cs2AuCl6 under high pressure was measured by using MAX90, a cubic-type multianvil apparatus, installed in the BL13-B2 station. The anvils used were made of sintered diamonds having an edge length of 3 mm. BN was used as a pressure transmitting medium in a boron-epoxy cube. The incident and the transmitted beams were measured by ionization chambers filled with N2 and Ar gas, respectively.

Results and Discussion

Figure 1 shows the X-ray absorption near edge structure (XANES) of Au L3 in Cs2AuCl6 at 0 and 4.5 GPa. The sharp line (called white line) at the lowest energy side of Au L3 corresponds to the allowed transition from 2p to 5d in Au ions. Therefore, the intensity of the white line is related to the density distribution of the unoccupied 5d states.

In the case of the Au mixed valence compound, Cs2AuCl6, the white line consisting of those of the Au' and Au+11 ions cannot be separated. As shown in Fig. 1, the intensity of the white line at 4.5 GPa is remarkably weaker than that at 0 GPa, which indicates that the sum of the valences of Au' and Au+11 decreases with increasing pressure. This phenomenon is explained as follows.

The charge transfer from Au' to Au+11 through the bridging halogen Cl and the ligand-to-metal σ donation influence the Au valence state. Both of them increase with increasing pressure. Among them, the latter is responsible for the decrease in the intensity of the white line. At ambient pressure, considering only the nearest neighbor Cl ions, the Au' and Au+11 are coordinated by two and four Cl ions, respectively. When the pressure is increased, the bridging Cl ions approach the midpoint of the Au' and Au+11 ions. Consequently, the practical coordination numbers of Au' and Au+11 sites changes from 2 to 6 and from 4 to 6, respectively. The pressure induced σ donation from the Cl ions in [Au+11Cl4]- to Au' and from the Cl ions in [Au+1Cl2]+ to Au+11 is presumably responsible for the remarkable decrease in the intensity of the white line under high pressure.

References

The pressure-induced amorphization of some silicates and germanates is likely to relate to the coordination change of Si or Ge atoms. Generally, fourfold coordinated Si or Ge atoms are stable at ambient pressure. The coordination change often occurs from fourfold to sixfold under high pressure. Andrault et al. (1992) conducted in-situ XAFS measurements under high pressure at room temperature by using a diamond anvil cell (DAC) and found that the coordination change of Ge atoms occurs on CaGeO$_3$-wollastonite from 7 GPa to 12 GPa. They suggested that the coordination change could lead to the pressure-induced amorphization. On the other hand, Nagai (1995) indicated that CaGeO$_3$-wollastonite is transformed into the rhodonite-form at about 6 GPa and that the X-ray diffraction pattern of the rhodonite-form is maintained up to 15 GPa without showing the amorphization. The wollastonite-rhodonite transition progresses up to 673 K under high pressure. However, the Ge atoms of CaGeO$_3$-rhodonite are not sixfold but fourfold coordinated. This inconsistency between the diffraction data and the XAFS data is a controversial problem. It is difficult to obtain high resolution XAFS data using a DAC, because the Bragg reflections of diamond anvils interfere with the XAFS signals. Therefore, we are performing supplementary XAFS experiments under high pressure at room temperature using a cubic anvil type apparatus (MAX90) installed at BL-13B2 using sintered diamond anvils, in order to avoid the Bragg reflections and further conducting the preliminary XAFS measurements under high pressure and moderate temperature (from 293 K to 873 K).

The powder mixture of the sample and BN filled in the half volume of sample chamber and the other half was filled with the powder mixture of Ge and BN. Cell parameters were calculated by the first neighbor distance of Ge-Ge in order to estimate the pressure values. Intensities of the monochromatized incident X-ray beam and those of the transmitted X-ray were measured by ionization chambers.

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**Experimental**

Sintered diamond anvils truncated 3x3 mm square were used and the pressure mediums (6x6x6 mm$^3$) were made of the amorphous boron/epoxy resin. Carbon disks were used as heaters and the sample temperature was monitored with an almele-chromel thermocouple.

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**References**

SITE-SPECIFIC PHOTOCHEMICAL REACTION OF PMMA AND RELATED POLYMERS NEAR OXYGEN K-EDGE

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Introduction

In the previous work,1,2) we found that photon stimulated ion desorption (PSID) from poly(methylmethacrylate) (PMMA) thin films was highly dependent on the photon energy (hν) near carbon and oxygen K absorption edges. The photon energy dependence of CH3+ ion yield showed a remarkable difference from the absorption spectrum, indicating a clear evidence of site-specific photochemical reaction in PMMA. There are two methyl groups in PMMA: one is bonded to the main chain and the other one is to the end of side chains. Therefore, it was difficult to distinguish experimentally from which chemical site the observed CH3+ ions originate.

In the present experiment, we measured hν dependencies of CH3+ ion yields near oxygen K-edge for poly(methyl acrylate) (PMA) and poly(methacrylic acid) (PMAA) which, in contrast to PMMA, have a methyl group at the end of side chain and at the main chain, respectively.

Experiment and Results

The experiments were performed at the beam line BL13C at the Photon Factory of The National Laboratory for High Energy Physics. The PSID ions were measured with the previously described time-of-flight (TOF) mass spectrometer using pulsed soft x-ray during single-bunch operation of the storage ring. The thin polymer films (thickness < 100 Å) were prepared by spin-coating onto Au-evaporated Si(100) wafers.

Figure 1 compares hν dependencies of CH3+ ion yields (PIY) from PMMA, PMA and PMAA near oxygen K-edge, where the total electron yield (TEY) spectrum of PMMA is also shown. In the TEY spectrum, there are four absorption features A, B, C and D. The feature A can be ascribed to the electronic transition of 01s(C=O)→π* (C=O), B to 01s(O-CH3)→π* (C=O) and O1s(C=O)→σ* (C-OCH3). C to O1s(O-CH3)→σ* (O-CH3), and D to O1s(O-CH3)→σ*(C-OCH3).2) In the PIY spectra of CH3+, PMMA and PMA show an intense peak at hν corresponding to the absorption feature C, while PMAA gives a faint peak. The results lead to a conclusion that CH3+ observed by the excitation of PMMA with hν=536eV [O1s(O-CH3)→σ* (O-CH3)] originates from the CH3 group bonded to the end of the side chain.

References

XANES STUDY ON THE CARBON NANOTUBES AND RELATED MATERIALS

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Introduction

New types of carbon structures such as carbon nanotubes and fullerenes attract much interest to their electronic properties because of the unique structural features. The band structures of the single-shell nanotubes and fullerene molecules have been calculated, some of the results being compared with measured spectra for unoccupied orbitals. In this study, we present XANES of the carbon nanotubes as compared with those of fullerenes, C_{60} and C_{70}.

Experimental

The preparation procedure of carbon nanotubes and fullerenes used in this study was described elsewhere. The XANES spectra were recorded by monitoring total electron yields at BL13C. The energy resolution (E/ΔE) at the C K-edge was about 1000 with the entrance and exit slit width of 50 μm.

Results and Discussions

Figure 1 shows the XANES spectra of the nanotubes and fullerenes. Each spectrum exhibits different features in the region between 285 eV and 290 eV, which are assigned to 1s-π* transitions. In contrast to the XANES of fullerenes with plural sharp features, the XANES of the nanotubes displays a sharp, intense feature at 284.5 eV with two broad features at 287.7 eV and 288.7 eV. The latter two features cannot be assigned to 1s-π* transition but assigned to interlayer bands with a symmetry by an analogy to HOPG. The nanotubes used in this study were observed as concentric multi-layer tubes consisting of six-membered rings alone, with diameters of a few tens of nanometers and length of a few micrometers by a microscopic technique. The almost infinitely long graphitic structure yields degeneracy of π bands, resulting in an analogous 1s-π* XANES feature to HOPG shown in Fig. 2.

The XANES features of the nanotubes are almost identical with that of the HOPG measured with the incident angle of 30 degree except the interlayer bands. However, taking into account the random orientation of the nanotubes, the spectrum should be compared with that of HOPG measured with the incident angle of 55 degree. The comparatively low intensity of the 1s-π* transition in the XANES of the nanotubes may be attributed to the curvature of the sheets which reduces the interaction among the π orbitals in the nanotubes.

Fig. 1 The XANES spectra of (a)C_{60}, (b)C_{70}, and (c)nanotubes. All the spectra were normalized in the intensity at 310 eV.

Fig. 2 The XANES of HOPG with different incident angles.

References
XPS DEPTH PROFILING BY CHANGING EXCITATION ENERGY

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INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is often used for surface analysis by which lots of chemical information is obtained. However, by use of conventional x-ray sources, such as Mg Kα (1253.8 eV) or Al Kα (1486.6 eV) emissions, high surface sensitivity cannot be achieved in some cases because of large inelastic mean free paths (IMFP). For instance, subshell electrons such as Si2p or Al2p with binding energies at about 100 eV have IMFP larger than 30 Å. The use of low energy x-rays from SR enhances the surface sensitivity by choosing the most appropriate incident energies. Furthermore, SR enables non-destructive depth profiling by changing the incident energy for XPS. The present paper describes preliminary results on depth profiling of around the surface of zeolite particles.

EXPERIMENTAL

All the experiments were carried out at the BL-13C coupled with a multi-purpose analytical chamber with a hemispherical electron analyzer. The zeolite sample used in the present paper was faujasite-type with a Si/Al ratio of 9.6. To minimize the charging, the zeolite powder was dispersed on a stainless steel plate.

RESULTS AND DISCUSSION

Figure 1 shows the XPS spectrum measured with an excitation energy of 184 eV. The spectrum exhibits photoelectron peaks corresponding to the important constituent elements of zeolites. When the incident energy is as low as 200 eV, photoionization cross sections for these subshells are very high. For instance, the cross section for Al 2p at 200 eV-excitation is hundred times higher than that at excitation by conventional Mg Kα x-rays. Thus, highly surface sensitive spectra are obtained without long-time data acquisition.

Figure 2 shows the change of Al/Si ratio with incident x-ray energy. The steep increase of the ratio with incident energy below 400 eV indicates the Al enrichment at the external surface of the zeolite particles. Further analysis is being conducted to obtain the quantitative depth profile.

Fig. 1 XPS spectrum of zeolite at 184 eV excitation

Fig. 2 Change in Al/Si ratio with incident energy

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SR-XPS and XAS study on the surface oxidation of chromium nitride films

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Introduction

Metal nitrides which possess high hardness and corrosion resistance character have been applied to the surface-coating films of many kinds of tools. The surface oxidation of nitride films which affects the properties of the films have been studied by means of x-ray photoelectron spectroscopy\textsuperscript{(1,2)}. However, the surface oxidation mechanisms are not yet clarified.

The purpose of this study is to clarify the surface oxidation behavior of chromium nitride films which have been reported to be superior to TiN films from the viewpoint of the oxidation resistance.

When a conventional AlK\textsubscript{α} x-ray source (h = 1486.6eV) is used, inelastic mean-free-path for N\textsubscript{1}s is approximately 20-30Å which is not suitable for the discussion on the surface oxidation mechanisms at the initial stage. Thus, we have employed SR x-ray source (h = 772eV) by which the inelastic mean-free-path for N\textsubscript{1}s is approximately 10-15Å.

Materials and methods

The CrN films were deposited onto austenite stainless steel by cathode arc ion plating method at 500 °C under 5x10^{-6}Pa\textsuperscript{(3)}. These samples were obtained by oxidizing the films under an ambient atmosphere at 300 °C and 400 °C for an hour. All the XPS and XAS measurements were performed at the BL-13C\textsuperscript{(4,5)}. The excitation energy used for the XPS measurements was 772eV. The XAS spectra were recorded in the total-electron-yield mode.

Results and discussion

Fig. 1 shows the N\textsubscript{1}s XPS spectra of as-received and oxidized CrN films. In the spectrum of the as-received film, a small peak is observed at 398.9eV which may be assigned to nitrogen or nitrogen monoxide, besides the main peak at 396.2eV which is assigned to N\textsuperscript{2+} of CrN. The ratio of the small peak to the N\textsuperscript{2+} peak increased with progress of oxidation. In the spectrum of the sample oxidized at 400 °C, a new peak was observed at a higher binding energy at 402.6eV.

Fig. 2 shows the N K-edge XAS spectra of as-received and oxidized CrN. N\textsubscript{2p}-Cr\textsubscript{3d} and N\textsubscript{2p}-Cr\textsubscript{4s} peaks assigned to chromium nitride were observed in the spectrum of the as-received sample. In the sample oxidized at 300 °C, a sharp peak assigned to 1s-\(\pi^*\) transition was observed at a higher energy than the N\textsubscript{2p}-Cr\textsubscript{3d} peak. The sharp peak indicates that the intermediate is not oxynitride but interstitial nitrogen.

The above results indicate that with replacement of nitrogen in chromium nitride by oxygen the released nitrogen occupies the interstitial position in the chromium oxide matrix as molecular or atomic nitrogen. A part of the interstitial nitrogen in the chromium oxide matrix is evolved from the surface with further progress of oxidation. Oxynitride species, described as CrN\textsubscript{x}O\textsubscript{y}, are not likely formed during the course of the surface oxidation.

References

STRUCTURE STUDIES ON THE PROTEINS THAT CONTAIN ANOMALOUS SCATTERING ATOMS

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Introduction
Anomalous scattering is one of the powerful physical characteristics that utilize the phase information and the choice of a structure and its enantiomorph in the protein crystallography\(^1\). The precise measurements of the diffraction data allow us to use the anomalous scattering in practically. In the natural proteins, many electron transporting proteins have atoms that have anomalous scattering. Among them, ferredoxin from *Sulfolobus acidocaldarius* is one of the most interesting one because the organisms are found in the critical environment which is very low pH and high temperature. The ferredoxin has two iron-sulfur clusters. Using the anomalous scattering, we tried to solve the structure of the ferredoxin.

Experimental
Crystallization of the ferredoxin, Mr 10,908 excluding the clusters, was done by the batch method\(^2\). The tetragonal crystal belongs to the space group P4\(_3\)2\(_1\)2 or P4\(_1\)2\(_1\)2 with the cell dimension of a = b = 50.12Å and c = 69.52Å. The recordings of the diffraction images on the imaging plates were carried out with the oscillation method using BL-14B station in the Photon Factory. The recorded images were digitized by using BAS2000 image processor. The wavelength used are 1.743, 1.740, and 1.500Å. The collected intensities were successfully processed by the Rossmann's programs system\(^3\). The obtained r.m.s.(|ΔF|)/r.m.s.(F) were 0.04, 0.06, and 0.07, respectively, over 10 - 5 Å resolution.

Results
To obtain the phase information, location of the iron-sulfur cluster had been examined by using the Patterson function with using the anomalous scattering effects of the present crystal at 5 Å resolution. The anomalous difference Patterson function that calculated with single wave length indicated that there are several reasonable peaks that corresponding to the iron-sulfur cluster (Fig. 1). The interpretations of those peaks are underway.

Fig. 1. The Harker sections of anomalous difference Patterson map.

References
LOCAL STRUCTURE OF MOLTEN SILVER HALIDE MIXTURES

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Introduction
Silver halides which are classified as ionic bonded compounds actually exhibit the intermediate properties between ionic and fully covalent bonded materials. The results of our neutron diffraction measurements show that the structure factor of molten AgI has a small prepeak around 1 Å⁻¹ and that the prepeak intensity has a maximum value around molten (AgBr)0.5(AgI)0.5[1,2]. These results suggest the existence of a cluster in the molten mixtures. It is interesting to study partial structures in the molten mixtures. In addition, there is a problem that the structure obtained from XAFS spectra of largely disordered systems does not agree with the result of diffraction measurements. In this study, we have measured XAFS spectra of molten Ag halides and those mixtures.

Experimental
XAFS measurements were carried out about Ag- and I-K absorption edges by a transmission method using the spectrometer installed at BL14A. Si(311) and Si(553) double crystal monochrometers were used. The sample thickness in each fused quartz cell was adjusted to the values from 50μm to 180μm which give the edge jump of about 1. The sample was melted under He atmosphere to eliminate bubbles from the melt.

Results and discussion
Figure 1 shows normalized XAFS oscillations around Ag-K edge, χ(k), of molten Ag(Br1-xIx) near the melting temperature. Clear oscillations are observed for molten AgI and the amplitude of oscillations is large in low k region. On the other hand, the amplitude of χ(k) for molten AgBr is small, which suggests large fluctuations in Ag-Br ionic distance. With increasing AgI concentration, the amplitude becomes large.

Figure 2 shows χ(k) around I-K edge of the molten mixtures. Note that the maximum concentration of AgBr is 0.8. The χ(k) around I-K edge for the molten mixtures show similar patterns. However, the first peak of molten Ag(Br0.4I0.6) is slightly shifted towards larger k. This result may be correlated with the maximum of the prepeak intensity obtained from our neutron diffraction measurements.

The nearest neighbor ionic distances obtained from curve fit analysis based on a Gaussian model are about 0.2 Å shorter than those obtained from the neutron diffraction measurements. The first nearest partial coordination numbers are also inconsistent with the result of the neutron diffraction. A further analysis is now in progress to obtain partial structures in the molten mixtures.

References
EXAFS STUDY OF THE $\alpha$-AgI PHASE STABILIZED AT ROOM TEMPERATURE IN A GLASS MATRIX

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I. INTRODUCTION

The superionic $\alpha$-AgI phase of $\beta$-AgI has been recently stabilized at room temperature in a new superionic glassy composite, $80\text{AgI} \cdot 15\text{Ag}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ ($\alpha$-AgI composite) [1]. In this experiment, the local structure around Iodine has been studied by temperature dependent EXAFS measurements at the Iodine K edge in the $\alpha$-AgI composite and, for comparison, in the superionic pure glassy matrix $65.3\text{AgI} \cdot 26\text{Ag}_2\text{O} \cdot 8.7\text{B}_2\text{O}_3$ and in $\beta$-AgI. Data analysis was performed by the cumulant method [2], which allow a model independent characterization of the thermal and static disorder.

II. EXPERIMENTAL

Absorption spectra were recorded in the transmission mode at the beam line 14A. The electron-beam energy was 2.5 GeV and the maximum stored current 380 mA. A Silicon (533) double crystal monochromator was used. The temperature range explored extended from 10K to 300K for the $\beta$-AgI composite and from 10 K to 463 K for the $\beta$-AgI, while the superionic glass was measured only at 10K and 300K.

III. RESULTS AND DISCUSSION

The EXAFS signal was extracted from the absorption coefficient according to the conventional procedure [2]. Figure 1 shows the EXAFS signals, $k\chi(k)$, for the three compounds at 10 K and 300 K. A reasonably good signal to noise ratio was achieved below 11 Å$^{-1}$ for all the spectra at all temperatures. The $k^3\chi(k)$ EXAFS signals were Fourier transformed in the range 2.7-11 Å$^{-1}$ and the first-shell peaks backtransformed to separate the corresponding contributions. The phase and amplitude of the first-shell EXAFS were then separately analyzed by the cumulant method [2], taking the 10K spectrum of $\beta$-AgI as a harmonic reference. By studying the temperature dependence of the cumulants, the thermal and static contributions to disorder have been separated. In all of the systems considered, the thermal disorder shows an analogous temperature dependence, suggesting a similar local vibrational behaviour. However, a large contribution from static disorder is found in pure glass and in the glassy portion of the composite material. For $\beta$-AgI, the values are in good agreement with those previously obtained from the analysis of Ag K and I L3 EXAFS [2]. The present results on the glassy samples essentially confirm previous findings [3]. Work to separately determine the contributions from the $\alpha$-phase and the glassy network in the $\alpha$-AgI composite is in progress.


FIG. 1. EXAFS signals $k\chi(k)$ at 10 K (upper curves) and 300 K (lower curves). (a), $\beta$-AgI in the $\beta$-phase; (b), $\alpha$-AgI composite ($80\text{AgI} \cdot 15\text{Ag}_2\text{O} \cdot 5\text{B}_2\text{O}_3$) and (c), pure glass ($65.3\text{AgI} \cdot 26\text{Ag}_2\text{O} \cdot 8.7\text{B}_2\text{O}_3$).
EXAFS STUDIES ON Pt-Sn/SiO₂ CATALYSTS FOR SELECTIVE UNSATURATED NITRILE SYNTHESIS REACTIONS

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Introduction

The bimetallic Pt-Sn/SiO₂ catalysts prepared by the selective bimetallic CVD reaction of Sn(CH₃)₄ and Pt metal particles on SiO₂ exhibit much higher activity than the monometallic Pt/SiO₂ catalyst for NO dissociation and unsaturated nitrile synthesis from NO and hydrocarbons (nitroxidation).¹ In this work, the structure of Pt-Sn bimetallic ensemble was investigated by EXAFS. We considered the model structure combined with other characterizations and the reason for these promoting effect.

Experimental

A Pt/SiO₂ (1.7 wt%) catalyst was prepared by a conventional impregnation method with aqueous solution of H₂PtCl₆ • 6H₂O, dried at 373 K, calcination at 773 K in air and reduced with H₂ at 673 K. Pt-Sn/SiO₂ catalysts were prepared by the reaction at 423 K between Sn(CH₃)₄ vapor and Pt/SiO₂. 2CH₄ per Sn were evolved during the reaction. No Sn(CH₃)₄ reacted with SiO₂ at this temperature. All residual carbon species were removed as CH₄ by reduction with H₂ at 573 K. The catalysts were reduced again at 673 K in situ before each run. Nitroxidation reactions were carried out in a closed circulating system. EXAFS spectra of these catalysts were measured at BL-14A (Sn-K edge) and BL-10B (Pt-LIII edge) for each reaction step. The EXAFS spectra were analyzed by the program "Rigaku EXAFS". The FEFF code 5.05 was used for curve fitting analysis of Sn-Pt and Sn-Sn bonds.²

Results and Discussion

Figure 1 shows the Fourier transform of k²χ(k) of Sn K-edge EXAFS oscillation for Pt-Sn/SiO₂ catalysts (Sn/Pt = 2.0).

These results leads to the bimetallic ensemble model structure as shown in Figure 2. These distances are shorter than expected from Pt-Sn alloy structure, maybe due to the higher Sn concentration or simple Debye-Waller factor estimation.

Pt-Sn bimetallic ensemble, as shown in Figure 2, seems to stabilize the allylic species derived from alkene dehydrogenation, which play an essential role for selective unsaturated nitrile synthesis. It also works for dissociating NO bond and these nature lead to the selective unsaturated nitrile synthesis.

References

TEMPERATURE DEPENDENCE OF LOCAL STRUCTURE AROUND Cs+ ION IN Rb2CsC60

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Introduction
X-ray diffraction technique revealed that alkali-doped C60 superconductors A2BC60 (A and B indicate alkali metals) have a face-centered-cubic lattice (f.c.c.) at room temperature, where alkali metals occupy the octahedral (1/2,1/2,1/2) and tetrahedral (1/4,1/4,1/4) sites.1 2 It has been generally considered that a metal ion with larger ionic radius occupies the former site, and that with smaller ionic radius the latter site. However, we have found from the Cs K-edge EXAFS spectra of Rb2CsC603 and Na2CsC604 that the Cs+ ion occupies both octahedral and tetrahedral sites; in Rb2CsC60 at 19 K, 17% of Cs+ ion occupies the tetrahedral site.5

In the present work, the temperature dependence of the local structure around the octahedral Cs+ ion in Rb2CsC60 is investigated in order to clarify their behavior around Tc.

Experimental
Preparation of C60 and Rb2CsC60 was previously described in details.3–5 Tc was ascertained to be 31.5 K by SQUID magnetometer (SHE VTS900). The EXAFS measurements were performed using synchrotron radiation of the Photon Factory at the National Laboratory for High-Energy Physics (KEK, Tsukuba).6 Cs K-edge X-ray absorption spectra were collected in transmission mode, using BL-14A with two Si(553) flat crystal monochromators. The sample temperature was regulated using a closed-cycle He refrigerator (Cryomech CP510) equipped with a temperature controller (Tristan Technologies LT10), and was detected on the sample cell with a (Au-0.07% Fe)-chromel thermocouple.

The computer programs "XAFS93" and "MBF93" were employed for EXAFS data analysis.2,8 The magnitude and imaginary part of Fourier transform, |I(k)| and Im[I(k)], were obtained from the EXAFS oscillations k^2 |I(k)|.2 In order to determine the structural parameters, the Fourier filtering technique was employed.6 A non-linear least-squares fitting was applied to the filtered data according to the following theoretical equation.9

Results and Discussion
The two-shell fitting by dividing into the tetrahedral Cs-C and octahedral Cs-C was employed in the parameter fitting. The wp's of Cs+ ion at the tetrahedral and octahedral sites were fixed to 0.1 and 0.9 in all temperatures, respectively; the analysis involving the anharmonic Debye-Waller terms was impossible. The N around Cs+ ion was fixed to the crystallographic values, 24 for the tetrahedral site and 12 for the octahedral site.2,5

The octahedral rCs-C was determined to be 3.78(2) Å at 11 K. The value is rather close to that predicted based on X-ray diffraction data, 3.80 Å.1,2 The temperature dependence of the octahedral rCs-C and α(2) are shown in Fig. 1(a) and (b). The rCs-C increases with decrease in temperature below 100 K and reaches a maximum around 40 K. The behavior is in contrast with that of Rb-C in Rb2CsC60 which exhibits the decrease around $T_c$.

The α(2) increases monotonically above 11 K. No anomalous behavior was found around $T_c$. The solid curve in Fig. 1(b) is fits of α(2) in all temperatures to an Einstein oscillator model, yielding the Einstein temperature $θ_E = 330$ K ($ω_E = 230$ cm⁻¹). The $ω_E$ is 1.5 times higher than that for the tetrahedral Rb-C determined by Rb K-edge EXAFS.5 The wp for the tetrahedral Rb-C shifts lower near implying the softening of lattice. However, such a softening has not been observed around the octahedral Cs+ ion.

The behavior of the tetrahedral rRs-C around $T_c$ suggests the importance of anharmonic moment, α(3). The preparation of a sample with the Cs+ ion occupying only the octahedral site is in progress, in order to perform the analysis taking into account the anharmonic moments.

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EXAFS STUDIES ON THE SOLID-SOLID PHASE TRANSITION (PHASE $\alpha'$ - $\delta$) IN CH$_3$NH$_3$I

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Introduction

Solid methylammonium iodide is known to exist in four different forms named $\alpha'$, $\beta'$, and $\delta$. Phase $\alpha'$ stable at room temperature has a tetragonal structure (P4/nmm). The C-N axis coincides with a four-fold rotation axis in the crystal, and hence the cation is orientationally disordered about this axis. Phase $\delta$ is a metastable one existing below 166 K. The stable phase is obtained by cooling the salt under a high pressure (200 MPa) or by annealing it around 200 K for a long time (5 days - 3 months). Phase $\varepsilon$ is an ionic plastic phase forming the CsCl-type cubic structure.

The $\alpha'$ - $\delta$ transition is reversible for cooling and heating processes at ambient pressure so long as the sample is carefully purified and dried. This transition is of a higher-order nature and interpreted as an order-disorder process of the CH$_3$NH$_3^+$ ion about the C-N axis. The dynamical behavior of the cation was studied by $^1$H NMR and anomalous cationic motion was found from the temperature dependency of $^1$H spin-lattice relaxation time in the $\alpha'$ - $\delta$ transition region from ca. 130 to 170 K. In the present paper, we investigated the temperature dependence of the local structure around I$^-$ ion in Phase $\alpha'$ and $\delta$ in order to further clarify the nature of the $\alpha'$ - $\delta$ phase transition.

Experimental

CH$_3$NH$_3$I was prepared in the same way as that for the $^1$H NMR study. Iodine K-edge X-ray absorption spectra were collected in the transmission mode at BL-14A of the Photon Factory (KEK, Tsukuba) in the temperature range of 30-297 K. The incident beam was monochromatized by Si(553). The sample temperature was regulated using a closed-cycle He refrigerator (Cryomech CP510) equipped with a temperature controller (Tristan Technologies LTC-10). The temperature was observed by a silicon diode sensor. The programs “XAFS93” and “MBF93” were employed for EXAFS data analysis.

Results and Discussion

In Fig. 1, the imaginary parts and magnitudes of the radial structure function, $\Phi(r)$, are shown. Comparing the crystal structure of Phase $\alpha'$ and $\delta$, a pronounced peak around 3 Å was attributable to the C and N neighbors of the I$^-$ ion. The best fitting analysis for the peak was carried out using a 2 shell model and a restricted 4 shell model (the Debye-Waller term $\sigma^2$ is limited to one kind for each C and N scattering atom) in Phase $\alpha'$ and $\delta$, respectively. In the fitting calculation, the parameters $\eta$ and $\Delta\Omega$ were fixed to the values evaluated from the EXAFS spectrum at 30 K and the crystal data of Phase $\delta$. The temperature dependence of $\sigma^2$ is shown in Fig. 2. $\sigma^2$ increased gradually with increasing temperature from 100 K. The sudden decrease in $\sigma^2$ was observed near the transition point. This anomalous behavior is considered to relate to the change of the librational motion of the cation due to the transition.

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Fig. 1. Radial structure function, $\Phi(r)$, for the I K-edge of CH$_3$NH$_3$I at 297 and 30 K.

Fig. 2. Temperature dependence of $\sigma^2$ (O for the N scattering atom and • for the C scattering atom) in Phase $\alpha'$ and $\delta$ of CH$_3$NH$_3$I.
SITE PREFERENCE OF Fe\textsuperscript{2+} IONS IN DIOPSIDE SOLID-SOLUTIONS OF THE SYSTEM CaMgSi\textsubscript{2}O\textsubscript{6}-CaFe\textsuperscript{2+}AlSiO\textsubscript{4}  

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Introduction  
Partitioning of cations between the M(1) and M(2) sites in a pyroxene crystal is supposed to reflect the temperature at which the crystal attained thermal equilibrium. In the present study, the distributions of Fe\textsuperscript{2+} and Mg\textsuperscript{2+} ions over the M(1) and M(2) sites were determined by single-crystal X-ray diffraction on the diopside solid-solution of the system CaMgSi\textsubscript{2}O\textsubscript{6}(Di)-CaFe\textsuperscript{2+}AlSiO\textsubscript{4}(Es), employing the anomalous dispersion technique related to the Fe K absorption edge.

Experimental  
Crystals of diopside solid-solution containing Es components were synthesized from a mixture of reagent grade SiO\textsubscript{2}, MgO, FeO\textsubscript{x}, and Al\textsubscript{2}O\textsubscript{3}, and CaCO\textsubscript{3} for alkali tests in the molar ratio of Di70\% - Es30\%. From the results of EPMA, the composition of the crystal chosen for structure analysis was assessed as Cao.998Mgo.529Feo.387Alo.086 (Al0.45aSi1.54tJo.0). The crystal was confirmed to have a diopside-type structure with the space group C2/c, and a=9.774(6), b=8.865(8), c=5.303(3) Å, β=105.94(4)° and V=440.5(6) Å\textsuperscript{3}. The crystal was shaped into a sphere with the diameter of 60 μm for intensity collection. Intensities were measured on the four-circle diffractometer installed at HL-14A with two wavelength lengths 0.750(1) and 1.745(1) Å, the latter being a little longer than the Fe K absorption edge. Absorption corrections were carried out by utilizing the absorption coefficients given by Sasaki. No corrections were carried out for polarization. In total 3108 and 124 crystallographically independent intensity data, which satisfied the condition |Fo| ≥ 3σ(|Fo|), were obtained with the beams of wavelengths 0.750 and 1.745 Å, respectively. The structure was refined with the least-squares method starting from the atomic parameters given by Tabira et al. for a crystal of diopside solid-solution containing Co. The final R and wR values were 0.028 and 0.035 for the reflection data collected with the 0.750 Å radiation, and 0.037 and 0.049 for the other data. All the dispersion terms were taken from the table given by Sasaki.

Results  
The populations of Fe\textsuperscript{2+} ions obtained from the data of 0.750 Å radiation are 0.365 at the M(1) site and 0.022 at M(2), indicating practically complete localization of Fe\textsuperscript{2+} at M(1). Difference Fourier synthesis was carried out utilizing the differences of the observed structure factors obtained with 1.745 and 0.750 Å radiations for the coefficients. Fig.1 shows the section of the map through the plane z=1/4, on which the M(1) and M(2) sites lie. The deep depression of electron-density observed at M(1) unequivocally indicates the localization of Fe\textsuperscript{2+} at the M(1) sites.

References  
INVESTIGATION OF STRUCTURE OF THE SOL-GEL DERIVED SODIUM GERMANATE GELS BY EXAFS

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Introduction

It has been reported by Ivanov et al.\(^1\) that, in the relation between composition and physical properties such as density and refractive index of alkali germanate glasses, a peak appears when the alkali content is increased, which is now known as "germanate anomaly". The structure of melt-derived germanate glasses is known to be constructed by two types of coordination polyhedron, i.e., GeO\(_4\) and GeO\(_6\). Melt-derived GeO\(_2\) glass consists of four-fold coordinated Ge atoms till alkali content amounts to 20 mol% where the fraction of the six-fold coordinated Ge is 25%. In general, structure with ions or atoms in low coordination state is favorable at high temperatures, and at low temperatures structure with high coordination state is preferred. Therefore, it is expected that Na\(_2\)O-GeO\(_2\) gels prepared by sol-gel method, which enables the low temperature processing of glasses, may contain larger amount of six-fold coordinated Ge atoms than melt-derived one. With such a background, a sodium germanate gels were prepared by sol-gel method, and the coordination state of Ge atoms in the gels was examined by Ge-EXAFS using high luminous X-ray at the Photon Factory.

Experimental

High purity Ge(O-C\(_2\)H\(_5\))\(_n\) (99.999 %) and NaOCH\(_3\) (28wt% in methanol) were used as starting materials. The alkoxide mixture corresponding to the oxide composition of xNa\(_2\)O-(100-x)GeO\(_2\) (x=10,15,20 mol%) were diluted with anhydrous ethanol, and then another solution consisting of water, HCl and ethanol was added dropwise to the former solution while stirred and cooled in the water/ice bath. The molar ratio of water, ethanol and HCl to Ge alkoxide was 2.0, 20 and 0.005, respectively, in the final solutions. The mixed solutions were kept standing in the room for gelation in a tight-sealed container. These solutions set to gels in two days. After aging in the room for one day, these gels were transferred to 60°C oven for drying. The specimens were X-ray amorphous. In the neighborhood of the Ge K-absorption edge (11.1036keV), X-ray absorption measurement of the samples were performed at BL-1A. White X-ray generated by synchrotron was monochromated using Si(311) crystal monochromator. Two ionization chambers were used to detect the incident and transmitted beams. Hexagonal GeO\(_2\) (h-GeO\(_2\)) crystal used as reference of four-fold coordinated Ge\(^{4+}\) ion, and tetragonal GeO\(_2\) (t-GeO\(_2\)) crystal as that of six-fold coordinated one.

Results

Figure 1 shows the RDF curves of xNa\(_2\)O-(100-x)GeO\(_2\) gels, together with those of t-GeO\(_2\) and h-GeO\(_2\) crystal. Since phase shift parameter is not taken into consideration in the radial distribution function (RDF) curves, RDF peaks appear at lower r position than real position. In the figure, each sample except t-GeO\(_2\) crystal has a peak at 1.40Å. The first peak for t-GeO\(_2\) crystal is located at larger distance as 1.55Å, because the Ge-O distance in octahedral GeO\(_2\) is longer than that of tetrahedral GeO\(_4\). The first peak for gels is broader than that of h-GeO\(_2\) crystal, suggesting that two types of coordination states exist in these samples. At the lower side of the second peaks of gels, a small and broad peak appears with increase of Na\(_2\)O content. The phenomenon may be explained in terms of the edge-shared GeO\(_2\) octahedra in those sample. Table 1 shows the coordination number of Ge atom, the corrected inter-atomic distances and Debye-Waller factors, respectively, obtained from non-linear least square fitting of the first RDF peak. The fraction of six-fold coordinated Ge atoms is much more than that of melt-derived glass of the same composition.

References


Table 1. Result of non-linear least square fitting

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<th>xNa(_2)O (mol%)</th>
<th>r(_1) (Å)</th>
<th>σ(_1)</th>
<th>r(_2) (Å)</th>
<th>σ(_2)</th>
<th>(\text{Rc}) (Å)</th>
<th>GeO(_2) content (%)</th>
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<td>0.048</td>
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<td></td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>t-GeO(_2)</td>
<td>-----------</td>
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POLARIZED TOTAL REFLECTION FLUORESCENCE EXAFS ANALYSES FOR THE ANISOTROPIC STRUCTURES OF Mo OXIDE ON TiO2(110) CATALYSTS

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Introduction

Structure of active sites on heterogeneous catalysts are strongly affected by the interaction of the support. It is reported that Mo oxide deposited on TiO2 has a strong interaction with TiO2 surface and MoO3 layer structure is easily formed. Rutile TiO2(110) has an anisotropic structure against [110] and [001]. Such a strong anisotropy is expected to affect the overlay MoO3 and the dynamic structure under reaction conditions might have anisotropic properties. In this study, we adopted PTRFXAFS(Polarized Total Reflection Fluorescence X-ray Absorption Fine Structure) to explore the surface structure of TiO2.

Experimental

TiO2(110)(20 x 40 x 1mm) single crystal was annealed for 5 hr at 823K. The catalysts for 0.5L (1L = MoO3 120mg/100m2) were prepared by a wet impregnation method with (NH4)6Mo7O24•4H2O aqueous solutions. After supporting, the single crystal was calcined for 3 hr at 773K in air. The measurement was performed at BL14A. Four axis goniometer was applied to set the particular orientation of the sample against the polarization direction of the incident X-ray and to achieve the total reflection condition. The X-ray absorption spectra for Mo K-edge were obtained from 3 directions such as s, p polarization for [110] and s one for [001]. The fluorescence was detected by a scintillation counter(Nal).

Results and Discussion

As shown in Fig.1, we observed that the χ(k) for each directions shows no anisotropic characteristics. This indicates that the coordination number and bond distances for the three directions should be very similar. In order to elucidate the structure formed on TiO2(110), we analyzed the spectra with FEFF6.0. At first, we analyzed the spectra with MoO3 and MoO42- spectra calculated from FEFF. But MoO3 shows completely different spectra while MoO42- presents much better results. This result is contradicted to the one for Mo oxide catalyst prepared with TiO2 powder. The research to reveal the discrepancy is in progress.

Fig.1 Mo K-edge EXAFS spectra for molybdenum oxide on TiO2(110).
METAL ATOM ORDERING IN FLUORITE-RELATED COMPOSITE MODULATED
\( \text{Nb}_2\text{Zr}_{x} \text{O}_{2x+1} \) (\( x = 7 - 12 \)) SOLID SOLUTION

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Introduction

Zirconium niobium oxide solid-solution \( \text{Nb}_2\text{Zr}_{x} \text{O}_{2x+1} \) (\( x = 7 - 12 \)) is a high-melting point (~1450°C), colourless crystalline solid. Its structure is related to that of the mineral fluorite (CaF₂). Because there are more oxygen atoms in the formula \( \text{MO}_{2+i/x} \) than can be accommodated by the fluorite-type structure \( \text{MO}_2 \) the structure adapts by packing the oxygens together more closely. What results is a composite modulated structure in which \( x \) metal atoms pack together with \( 2x+1 \) oxygen atoms in one direction. The actual location of the edge was determined by performing EXAFS experiments on \( \text{Zr} \) foil and \( \text{ZrO}_2 \) powder. Once the parent structure unit cell had been determined satellite reflection positions were located to determine the actual modulation wave-vector magnitude, which subsequently proved to be sufficiently close to \( l_{1/2}\text{a}^* + b^* \) that data could be collected in a \( 12x \) \( \text{a}^* \text{b}^* \text{c}^* \) supercell. The need to collect the data on a commensurate reciprocal lattice was due to the constraints imposed by the current software and hardware at Beam Line 14A.

Experiment

The project was allocated six days on Beam Line 14A from 24 May to 30 May 1994. Single crystals of \( \text{Nb}_2\text{Zr}_{x} \text{O}_{2x+1} \) had been grown at various compositions according to the method described previously¹ using hafnia-free zirconia as starting material. During this visit to the Photon Factory a composition close to the Zr-rich end member of the solid-solution \( x = 12 \) was chosen. A crystal of approximate dimensions 25 x 25 x 20 \( \mu \text{m} \) was selected. Data were collected at two wavelengths, \( \lambda = 0.68920 \, \text{Å} \) and \( \lambda = 0.74953 \, \text{Å} \), which is 8 eV below the \( \text{Zr} \) absorption edge, and far below the edge at \( \lambda = 0.74953 \, \text{Å} \).

The actual location of the edge was determined by performing EXAFS experiments on \( \text{Zr} \) foil and \( \text{ZrO}_2 \) powder. Once the parent structure unit cell had been determined satellite reflection positions were located to determine the actual modulation wave-vector magnitude, which subsequently proved to be sufficiently close to \( l_{1/2}\text{a}^* + b^* \) that data could be collected in a \( 12x \) \( \text{a}^* \text{b}^* \text{c}^* \) supercell. The need to collect the data on a commensurate reciprocal lattice was due to the constraints imposed by the current software and hardware at Beam Line 14A.

At \( \lambda = 0.68920 \, \text{Å} \) three shells of data were collected, a full sphere \( ^{1} - ^{30} \, \text{°} \) \( 2\theta \) and hemispheres \( \pm h, \pm k, \pm l \) for \( ^{30} - ^{40} \, \text{°} \) \( 2\theta \), and \( ^{40} - ^{50} \, \text{°} \) \( 2\theta \). A scan rate of 8° min⁻¹ was used. The intensities of reflections were well down on what would normally be expected for a crystal of these dimensions.

The wavelength was then set far below the \( \text{Zr} \) absorption edge at \( \lambda = 0.74953 \, \text{Å} \) in order to collect a second data set where there was effectively no scattering contrast between \( \text{Zr} \) and \( \text{Nb} \). At this wavelength the intensities of reflections increased by a factor of about 10 relative to the first wavelength. Four shells of data were collected, a full sphere \( ^{1.09} - ^{32.70} \, \text{°} \) \( 2\theta \), and hemispheres \( \pm h, \pm k, \pm l \) for \( ^{32.70} - ^{43.67} \, \text{°} \) \( 2\theta \), \( ^{43.67} - ^{54.72} \, \text{°} \) \( 2\theta \), and \( ^{54.72} - ^{65} \, \text{°} \) \( 2\theta \).

Results and Discussion

Data were merged in \( \text{mmm} \). \( R_{\text{merge}} \) for \( \lambda = 0.68920 \, \text{Å} \) and \( \lambda = 0.74953 \, \text{Å} \) data sets, respectively, was 1.86 % and 1.68 % for all data with \( l > 3\sigma(l) \). The structure of \( \text{Nb}_2\text{Zr}_{x} \text{O}_{2x+1} \) \( x = 12 \) was refined as a composite modulated structure using the program JANA² to an overall \( R_w \) of 0.0406 for \( \lambda = 0.68920 \, \text{Å} \) and \( R_w \) of 0.0687 for \( \lambda = 0.74953 \, \text{Å} \).

The dispersive modulation wave amplitudes obtained from these refinements are in remarkable agreement with those obtained from a Fourier decomposition of the previously published, conventional superstructure refinement of the \( x = 8 \) member³. Despite the enhanced scattering contrast between \( \text{Zr} \) and \( \text{Nb} \) for \( \lambda = 0.68920 \, \text{Å} \) data, metal atom ordering was not found to be significant. Comparative refinements as incommensurately and commensurately modulated structures gave distinctly better \( R \)-values for the former case.

Variation in metal ion coordination sphere as a function of \( t = \sum_{i} \frac{q_{ix}}{q_{ix} + q_{ix}} \).

Each curve represents the distance between a specific metal-oxygen pair.

A paper reporting the results of these structure refinements has been accepted for publication in Acta Crystallographica, Section B, to appear in mid-1995⁴.

References

2) V. Petricek. Programs for Modulated and Composite Crystals, Institute of Physics, Praha, Czech Republic (1994).
DIFFRACTION STUDY OF ELECTRON DENSITY IN C-TYPE RARE EARTH OXIDES

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Introduction

The rare-earth (RE) oxides provide a coherent sequence of compounds for studying physical properties by diffraction imaging with synchrotron radiation. Their magnetic interactions are often complex and difficult to elucidate. Many physical properties of those compounds are affected by the partial filling of their f-electron subshells. The f electrons are not involved strongly in chemical bonding, their effect being only of second order for most properties. The number of unpaired electron spins when filling the RE atoms' f orbitals according to Hund's rule spans a wide range. The oxides have correspondingly diverse magnetic properties. Indeed, the lanthanide elements and their compounds were the proving ground for elaborating the simple theory of magnetism. Understanding their magnetic properties requires precise knowledge both of the system without interactions, and of the mechanisms involved in those interactions. Analysis of the deformation electron density, or $\Delta \rho$ map, focussing on the influence of the crystal field and cation-cation interactions on the density near RE atoms may assist our understanding of the magnetic interactions in the RE oxides. The C-type sesquioxides Y$_2$O$_3$, Dy$_2$O$_3$, and Ho$_2$O$_3$ were studied.

Experimental

Single crystals of Y$_2$O$_3$, Dy$_2$O$_3$, and Ho$_2$O$_3$ were prepared by flux growth techniques. Diffraction images of the $\Delta \rho$ density for naturally faced crystals with min/max dimensions 38/102, 46/61 and 36/83 $\mu$m for Y$_2$O$_3$, Dy$_2$O$_3$, and Ho$_2$O$_3$ respectively were measured with focused 0.7 Å synchrotron X-radiation at beam line 14A (1). The vertically polarised beam from the vertical wiggler was monochromated by a double Si (111) crystal monochromator. Intensities for six standard reflection were measured every 100 reflections to monitor the stability of the incident beam. The measured intensities were modified and their variances adjusted for fluctuation of standards. After Lorentz and polarisation corrections, absorption corrections were evaluated analytically. Extinction was corrected as part of the least squares structure refinement.

Results and Discussion

The two crystallographically distinct cation sites in the body centred $/a3$ cubic structure of the C-type sesquioxides can be derived from the ideal cubic 8-fold coordination. There are two empty sites along the body diagonal for metal M1 and two along the face diagonal for M2. The M1 coordination is slightly distorted octahedral. The M2 coordination is strongly distorted, with 2-fold symmetry. The two crystallographically distinct cation sites makes these structures an attractive target for studying the effect of the crystal field. The high $\Delta \rho$ symmetry around M1 cations in RE oxides shown in Fig. 1 becomes progressively more prominent from Y to Dy and Ho, reflecting near 6-fold cation coordination, highlighting the significance of repulsive cation-cation interactions. On the other hand the $\Delta \rho$ symmetry near the M2 cation is lower than that expected from cation-cation interactions alone. The map is strongly influenced by the low symmetry (C2) O-coordination crystal field. The relative strength of the crystal field (CF), $H_c$, and the magnetic exchange interactions, $H_{ex}$, determines the anisotropy, i.e. the magnetic moment direction. The magnetic structure can be complex and non-collinear even for simple magnetic interactions. If the CF symmetry is low enough and the magnetic interactions are smaller than the first excited CF energy-level the magnetic behaviour is dominated by the CF anisotropy. That occurs at the M2 cation sites in the RE oxides, where $H_c>H_{ex}$. The influence of the crystal field (C$_2$) on the $\Delta \rho$ maps is strong compared to that of the repulsive cation-cation interactions. Cation-cation interactions have a more significant effect on the structure, and a dominant effect on the electron density at the M1 octahedral sites where $H_c$ is less strong. This effect, which is significant at distances well beyond normal bond lengths, is spin dependent and may thus determine the nature of magnetic ordering and structural phase transitions.

References


![Fig. 1. $\Delta \rho$ in the plane through the M1 cation site for (a) Y$_2$O$_3$, (b) Dy$_2$O$_3$ and (c) Ho$_2$O$_3$. Contour interval 1.5 eÅ$^{-3}$.](image-url)
Common features of n-type and p-type porous silicon layers studied by X-ray multi-crystal diffractometry

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Introduction

Porous silicon (PS) is a kind of silicon having a pore structure, and exhibits strong visible photoluminescence. However, it doesn’t seem that the correlation between the microstructure and photoluminescence has been well established. In order to elucidate the emission mechanism of visible light from PS layers, it is essential to find common features such as the emitting part and its morphology for both p-type and n-type PS layers. To our knowledge, however, no study has been carried out to compare the structural features of both p-type and n-type PS layers. While the n+ PS layers showed one sharp peak from the Si substrate and a group of peaks from the PS layer depending on the forming current densities, in the p+ PS layers, prepared with large current densities above 200mA/cm², also exhibited similar extended intensity distributions. This extended distribution is well explained by assuming a mosaic structure in the PS layer, which is composed of small and elongated crystallites which were formed as a result of relaxation of constrained stresses in the PS layer. Their spatial extension was four times larger in the direction parallel to the surface than in the direction normal to the surface. From microscopy observations, it was also found that the n+ PS layers are composed of nearly the same crystallites as those in the p PS layers formed above 200mA/cm², and that the n+ PS layers exhibited a lot of nanocrystallites in the vicinity of the external surface of the PS layer. In fact, hydrogen atoms were detected more densely near the surface of PS layer than inside the PS layer.

Common features for both p+ PS and n+ PS layers are as follows: (1) the parts which can emit visible photoluminescence are not amorphous, but crystalline, (2) such parts are composed of nanocrystallites of several nm’s whose orientations are slightly different from the Si substrate, (3) such crystallites absorb much hydrogen atoms near the surface of PS layer, especially for the n+ PS layers with an intense back ground in a wide angular range. In conclusion, visible light emission comes from only the PS layer that has a spongelike structure consisting of a large number of silicon parts of few nm’s in size, and that photoluminescence is probably due to charge carrier confinement in such three dimensional structure. Detailed studies of the crystallite size and the photoluminescence peak position are now in progress.

Experimental Procedure

We used p-type and n-type (100) CZ Si wafers with small resistivities less than 0.02Ωcm. The details of specimen preparation were almost the same as those in our previous studies [1]. The crystallinity of PS layers formed heavily doped substrates was investigated by measuring 400 rocking curves with X-ray multi-crystal diffractometry: X-ray double-crystal diffractometry and X-ray triple-crystal diffractometry; a (111,100,400,100) setting, with the specimen as the third crystal and the analyzer as the fourth (140L). In this study only preliminary verification with the naked eye of visible light emission was carried out by using a He-CD laser.

Experimental Results and Discussion

X-ray rocking curves from n+ PS layers were quite different from those of p+ PS layers: the p+ PS layers showed two separate peaks which are respectively ascribed to the Si substrate and to the PS layer, while the n+ PS layers showed one sharp peak from the Si substrate and a group of peaks which are ascribed to several layered pore-structures formed in the PS layer depending on the forming current density. In this connection, SEM observations revealed that the p+ PS layer exhibits simpler pore structures than the n+ PS layer [2]. A comparison between these results indicates that the n+ PS is inferior to the p+ PS in crystallinity. For the n+ PS layers, besides several peaks, intense diffuse intensity is always seen over a wide angular range. Such diffuse intensity suggests that the n+ PS layer contains a lot of scattering Si nanocrystallites which are distributed over a large angular range, especially near the top surface of PS layer. This is consistent with the results obtained by HRSEM [2].

Two dimensional intensity distribution around the reciprocal lattice point (RLP) in reciprocal space revealed that an intensity distribution elongated along the [100] direction was always seen for all the PS layers, indicating that the lattice spacing of the PS layer is predominantly elongated along the direction normal to the surface of the PS layer than along the in-plane direction of the PS layer. According to our previous results on the p+ PS layers [1], the lattice expansion is mainly ascribed to the hydrogen atoms, although the effect of silicon oxide can contribute secondarily to the lattice expansion. The p+ PS layers, prepared with large current densities above 200mA/cm², also exhibited similar extended intensity distributions. This extended distribution is well explained by assuming a mosaic structure in the PS layer, which is composed of small and elongated crystallites which were formed as a result of relaxation of constrained stresses in the PS layer. Their spatial extension was four times larger in the direction normal to the surface than in the direction parallel to the surface. From microscopy observations, it was also found that the p+ PS layers are composed of nearly the same crystallites as those in the p PS layers formed above 200mA/cm², and that the n+ PS layers exhibited a lot of nanocrystallites in the vicinity of the external surface of the PS layer. In fact, hydrogen atoms were detected more densely near the surface of PS layer than inside the PS layer.

Common features for both p+ PS and n+ PS layers are as follows: (1) the parts which can emit visible photoluminescence are not amorphous, but crystalline, (2) such parts are composed of nanocrystallites of several nm’s whose orientations are slightly different from the Si substrate, (3) such crystallites absorb much hydrogen atoms near the surface of PS layer, especially for the n+ PS layers with an intense back ground in a wide angular range. In conclusion, visible light emission comes from only the PS layer that has a spongelike structure consisting of a large number of silicon parts of few nm’s in size, and that photoluminescence is probably due to charge carrier confinement in such three dimensional structure. Detailed studies of the crystallite size and the photoluminescence peak position are now in progress.

References
SUPPRESSION OF II-POLARIZATION OF 14.4KEV SYNCHROTRON RADIATION BY 840 REFLECTIONS OF A SI CHANNEL-CUT POLARIZER

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Introduction

Electronic scattering vanishes for a 90° scattering in the direction of the incident linear σ-polarization, while there will generally be nuclear resonance scattering. When scattered beams are mixed with σ-polarized electronic scattering and π-polarized nuclear resonance scattering, which can be generated from a GIAR-film of enriched ^57Fe irradiated by σ-polarized incident beam, the resonance scattering can be separated by an analyzer at a scattering angle 2θ_B=90°, where θ_B is the Bragg angle.

The aim of this study is to develop the polarizer and the analyzer for producing pure σ- or π-polarized beams, and then, to detect separately the nuclear resonance scattering.

Experimental

Polarizers of 2θ_B=90.2° for 14.4 KeV radiation are produced using the asymmetric and symmetric 840 reflections from grooved surfaces of a silicon single crystal. The angular width of the 840 reflection measured with a Si(840) analyzer in the (+,+), geometry is about 1°, which is close to the theoretical width 0.36°. The σ- and π-polarized components of the radiations monochromatized and polarized by the double 840 reflections are observed at BL-14B with the Si(840) analyser and a scintillation counter as shown in Figs.1. Energy and current of synchrotron beam were 2.5 GeV and about 300mA, respectively. The analyzer crystal was set on a four-circle goniometer. The rocking curves of the σ-, π-components were measured by step scanning around the horizontal and vertical axes.

Result

Figures 2(a) and (b) show rocking curves of the σ- and π-components, respectively, normalized with the intensity of the beam incident on the analyzer. Counting rates at the peak of the σ- and π-components are 4.2x10^4 cps and 20 cps, respectively. The integrated intensity ratio I_π/I_σ is 2.9x10^-4, which is much larger than calculated one. The disagreement is due to large angular divergence of the incident beam in the plane parallel to the direction of the σ-polarization vector.
SYNCHROTRON RADIATION TIME GATE WITH QUARTZ RESONATOR

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An X-cut quartz resonator fast gate has been developed for synchrotron radiation applications, especially for the nuclear resonant scattering. One of the first experiment observation of the enhancement of X-ray intensity on oscillating quartz crystal was reported by Fox and Carr'. When an electric signal of frequency f is applied to the X(2110)-planes in an X-cut plate, the interplanar spacings of these planes change in a periodic compression and elongation movements according to the crystal resonance frequency. The variation of d-spacing of diffraction planes with time is equivalent to the change of the Bragg angle \( \theta_B \) with time. Therefore, if the alignment is set around the peak position of the rocking curve, the diffraction intensity will oscillate with time.

X-cut 766.95kHz quartz resonator device was prepared from a pure Z synthetic quartz with thickness \( L = 3.7 \) mm. The electrodes are thin films of Au evaporated on both X-plane surfaces, and the crystal is supported by two contact points, in order to allow free oscillations without dampening. Fig. 1 is the schematic representation of the experimental arrangement of crystal optics made at Photon Factory - BL14B. Wavelength \( \lambda = 0.6 \) Å and high indexes back reflection Si 16 8 0 and quartz 16 8 8 0 was used in order to supply an accurate angular resolution. The rocking curves of vibrating (16 8 8 0) quartz profiles were measured. Increasing signal amplitudes applied to the resonator shows an effect of peak intensity decrease, and consequently, an enlargement of profile width, as predicted theoretically. The time modulation profiles of SR intensity by the reflection of vibrating quartz were measured at several angular positions around the Bragg angle. Fig. 2 shows the time modulation at \( \delta = 6.0 \) arcsec, where \( \delta \) is the angular displacement of the diffraction angle from the peak position on the rocking curve. At this position gating time of 400 nsec, rise time of 200 nsec and signal-to-background ratio of 15 % were obtained.

The present results depend on various factors, such as, resonator diffraction planes and the magnitude of applied field. The signal-to-background ratio can be improved by using more perfect dislocation-free and high Q-value crystals. The X-ray topographs of (16 8 8 0) reflection Bragg case images revealed a lot of dislocation lines, and oscillation nodes of vibration. The especial characteristics of the present fast gate is the possibility of changing the diffracted intensity modulation width and the decay time by keeping the frequency constant.

Fig. 1 Experimental setting for the SR time measurement with quartz resonator.

Fig. 2 Time modulation of SR diffracted by a 766.95 Hz resonator at \( \delta = 6.0 \) arcsec. Refer to the text for the definition of \( \delta \).

Reference

1) G. W. Fox and P. H. Carr, Phys. Rev. 37 (1931) 1622

Acknowledgments

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RATIO OF THE Si(100):As 1 x 2 AND 2 x 1 DOMAINS DETERMINED FROM GRAZING-ANGLE X-RAY STANDING-WAVE DATA

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Introduction
A clean Si(100) surface inclined by a few degrees towards the [011] direction reconstructs in a structure with Si–Si dimers parallel to the edges of double-layer-height steps. Adsorption of arsenic on such a surface produces a structure of a 1 x 2 or 2 x 1 single-domain structure depending on the adsorption condition [1]. Our attempt to prepare a single-domain Si (100):As surface resulted, however, in a double-domain structure with coexisting 1x2 and 2x1 As dimers. On such a surface ordered As atoms occupy three positions 0, x and 1–x with respect to the (022) lattice planes, where position 0 is occupied by 2 x 1 As–As dimers with dimer bonds parallel to the step edges, while positions x and 1–x are occupied by perpendicular 1x2 As dimers. We determined the number ratio of As atoms forming the 1 x 2 and 2 x 1 dimers in our sample using grazing-angle X-ray standing waves under ultrahigh vacuum condition.

Experimental
Our silicon substrate had a surface inclined from the (100) plane by 4° along the [011] axis. Arsenic was deposited on the substrate at 650 °C in a molecular-beam-epitaxy chamber (10⁻⁶ Torr). X-ray experiments at BL-14B excited the 022 or 022 Bragg reflection in the grazing-angle geometry with 16.8 keV X-rays. The reciprocal lattice vector h for the 022 reflection is directed out of the surface by 4°, while h for the 022 reflection is parallel to the surface. We recorded As K emission as a function of AO at fixed glancing-angles near the critical angle for total external reflection (1.85 mrad).

Ratio of arsenic atoms located at the 1x2 and 2 x 1 positions
Emission yield is expressed as A+B'η. A is the position-independent component of the standing-wave field strength [3]. B' is associated with the position-dependent component B [3], but does not include position information for fluorescing atoms. An equal number of As atoms occupying positions x and 1–x cancels out phase φ in the sin(2πx+φ) term in the expression for B [3]. η is defined as η_022 = P_2x2 + P_1x2 cos(2πx) for the 022 reflection, and η_022 = P_1x2 + P_2x1 cos(2πx) for the 022 reflection [4]. P_2x2 and P_2x1 are the fractions of As atoms in the 1x2 and 2 x 1 dimers, respectively. Here we assume x = 0.336 obtained from a surface x-ray diffraction experiment [5]. For a perfectly ordered surface, P_2x1 + P_1x2 should be equal to unity. It is to be noted that η does not depend on phase φ of the standing wave, being independent of Δθ. We have evaluated η_022 and η_022 by least-square fits of two emission curves for the 022 and 022 reflections. Substitution of these values gave us the simultaneous equations for P_1x2 and P_2x1, which led to P_1x2 = 61.7% and P_2x1 = 37.5%. This shows that our sample surface is highly ordered with only 0.8% of the As atoms at random positions.

References
HIGH-RESOLUTION ELECTRON DENSITY MAP FOR THE Si(111) 7×7 SURFACE

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Introduction
Proposal 94G140 aims at studying the structures of dimers and atomic steps on Si and GaAs (100) surfaces with X-ray diffraction and scattering techniques at a synchrotron source. These surfaces have simple, basic structures, and are important for epitaxial growth of GaAs on silicon substrates. The proposal involves calculation of electron densities for surfaces from X-ray data. Combined with the design of a vacuum X-ray scattering facility, the geometry of grazing-incidence diffraction limits accessible reciprocal space. Reduced scattering power at high angles further reduces the number of measurable Bragg reflections, leading to low resolution in the electron-density maps calculated with the conventional method. To overcome the difficulty, we have tried the maximum-entropy (ME) method, which has been quite successful [1].

Maximum-entropy method
The ME method does not use Fourier transform to calculate electron densities from observed structure factors $F_{i}^{\text{obs}}$. It does not assume zero amplitudes for missing reflections, which extends the data resolution and improves the sampling of reciprocal space. The power of the ME method has been demonstrated in powder diffraction [2], which suffers from similar problems to surface diffraction. A calculation of electron densities needs a set of phased $F_{i}^{\text{obs}}$ data.

Application to Si(111) 7×7 surface
The 7×7 reconstruction of the Si (111) surface is the most complex one ever discovered, which provides a good test for the ME method. In-plane reflections observed from a clean Si(111) 7×7 surface at a synchrotron source are given phases obtained from a refined model [3], which are used as a constraint in a maximization of Shannon-Jaynes entropy. The calculation assumes the symmetry of plane group $p6mm$. The map obtained from 84 fractional-order reflections with a 1.135 Å resolution clearly resolves all the 102 atoms of Takayanagi's DAS model [4] (see the figure). The figure shows a 7×7 unit cell. This is a first high-resolution electron density map calculated for a two-dimensional surface structure. Electrons are concentrated on the atomic sites showing highest peaks at the ad-atom locations where there is an overlap with the third-layer atoms. The atomic positions determined from the map are in good agreement with those from a least-squares refinement. It was evidenced that the 102 atoms are visible in a map calculated from a reduced data set with 20 strongest reflections.

References
MAXIMUM-ENTROPY ELECTRON-DENSITY MAPS FOR ARSENIC-ADSORBED Si(001) 1X2 SURFACE

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Introduction
The 1X2 structure of arsenic deposited Si (001) surface has been refined by Jedrecy et al. [1] using X-ray diffraction data. The refinement assumed the symmetry of plane group p2mm and used the 17 structure-factor data collected from a double-domain sample at a synchrotron source. The 17 Fobs data included 6 integer reflections, with both h and k indices integer, which are forbidden in bulk silicon of the diamond structure. Two As atoms are found to be located at the center of a 1X2 unit cell, forming a dimer with a 2.55 Å bondlength. The four top-layer Si atoms are shifted by 0.15 Å towards the As dimer (Fig. 1). No shift is found in the positions of the second-layer Si atoms.

Experiment
We attempted surface X-ray diffraction experiments on a single-domain 1X2 Si (001) sample without coexisting 2X1 domains. Our samples were prepared by heating in ultrahigh vacuum clean silicon substrates with the surface tilted from the (001) plane by 4° towards the [110] azimuth; evidences show that double-layer-height steps are energetically favored and silicon dimers are oriented parallel to the step edges on both the upper and lower terraces, thus producing a single-domain 1X2 surface. However, we could only prepare double-domain samples showing fairly strong 2X1 RHEED spots, on which arsenic was deposited in a molecular-beam-epitaxy chamber. No satisfactory data was collected at BL14B using a UHV surface X-ray diffraction facility [2].

Maximum-entropy electron density map
Fig. 2 shows a maximum-entropy electron-density map calculated using Jedrecy's 17 Fobs data with phases assigned from the refined model. In addition to the top-layer As and Si atoms, small peaks are seen at the second-layer atom positions. These peaks are absent in a map calculated using a reduced data set with the 6 integer reflections excluded. Further studies will clarify the contribution of non-spherical electron distributions around unreconstructed Si atoms to these peaks.

Reference
ANOMALOUSLY-ENHANCED ANOMALOUS TRANSMISSION OF X-RAYS
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Introduction

Borrmann and Hartwig\(^1\) showed the multi-beam effect on the anomalous transmission in Ge and the present authors predicted\(^2\) an extreme enhancement can be expected for 6-beam (000, 220, 044, -224, -202) case. Experiments along this line have not been tried until quite recently\(^3\). In this report computations are extended to a Si crystal tilted around the 6-beam position, and corresponding experiments have been conducted at BL-14B.

Theoretical

The dynamical-theoretical computation of the wave field in Si, i.e., 12-dimensional eigenvalue problem, have been performed; absorption coefficients along an intersection keeping 220 Bragg condition satisfied are shown in Fig.1, approaching at large tilting separately to 2-ray effects.

In general azimuths all the curves tend to a single value, that is, the mean absorption. Single effect reduces the absorption to one thirtieth of the mean value and the multi-diffraction at the vertex point enhances the reduction further by twenty.

Experimental

Transmitted intensities around the 6-ray position have been measured at a wavelength 1.22\(\AA\) for a wedge-shaped Si plate; contour maps of the results at a thickness 3.9mm are shown in Fig.2. The strong enhancement of an anomalous transmission due to the multi-ray effect is clearly seen in all intensities 000, 220, 044, though the quantitative comparison needs numerical deconvolution with respect to the instrumental widths.

Reference

1) G.Borrmann and W.Hartwig
2) T.Joko and A.Fukuhara
3) A.Y.Kazimirov, M.V.Kovalchuk, V.G.Kohn, T.Ishikawa and S.Kikuta
MODEL-INDEPENDENT DETERMINATION OF ELECTRON DENSITY PROFILES IN MULTILAYERS USING ANOMALOUS-DISPERSION X-RAY REFLECTOMETRY DATA

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Introduction

In most X-ray reflectometry works on thin-film multilayers, model structures are fit to specular reflection data to determine the layer thickness, densities and r.m.s. roughness at the surface and interfaces. One of the authors and co-workers have developed a technique for ab-initio determination of the one-dimensional electron-density distribution in the overlayer using specular-reflection data collected at X-ray wavelengths close to and away from the absorption edge of the substrate material [1]. The technique is based on an X-ray scattering theory using a distorted-wave Born approximation [2], retrieves the phase information for the reflected wave from anomalous dispersion data like in conventional crystallography, and reconstructs electron-density profiles by Fourier transform.

Simulations

To apply this technique to multilayer studies, we performed simulations on structures with alternate carbon and element E layers on Ge substrates. A unit structure uses a stack of a 70 Å-thick layer of element E on a 30 Å-thick carbon layer. Parratt's formula is used to simulate specular reflections at photon energy close to the Ge K edge and 8.27 keV. Fig. 1 shows reconstructed profiles for a single and triple layer of Al-C (E = Al) where a momentum transfer range of $q_z = 2 \text{ Å}^{-1}$ was Fourier transformed. Similar profiles have been computed for a series of $(E(70\text{Å })C(30\text{Å }))$ layers with $E$ varying from Be to W including Al, Cr, Ni, Ge, Mo and Sn. Reconstructions agree with the model profiles for layers using low-Z Es.

Experiments

In a beam time scheduled in mid March 1995, anomalous-dispersion reflectometry data will be collected from a few multilayers including Al-C on Ge substrates and GaAs-AlAs on GaAs substrates at BL-14B.

This work is supported by the Japan-India Cooperative Scientific Programme, organized by the JSPS and DST.

References


Fig. 1. Model (broken line) and reconstructed (circle) electron-density profiles for a single (left) and a triple (right) Al(70Å )-C(30Å ) layer on germanium substrates.
COMPTON SCATTERING OF 20- TO 40-KEV PHOTONS

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The scattered-energy spectra of monochronized synchrotron-radiation photons toward 90° by C, Al, Fe, Cu, Au and Pb samples were measured using high-purity Ge detectors to obtain incoherent scattering function (S) in the 1.14 < x < 2.28 Å⁻¹ region. The incoherent scattering function (S(x,Z)) is defined as the ratio of the differential Compton-scattering cross sections of bound electrons in one whole atom (\(\frac{d\sigma}{dx}\)bc) and one free electron (\(\frac{d\sigma}{dr}\)fc),

\[ S(x,Z) = \frac{(\frac{d\sigma}{dx})_{bc}}{(\frac{d\sigma}{dx})_{fc}}, \]

where

\[ x = \frac{k_0}{12.399} \sin(\frac{\theta}{2}). \]

Here, k₀ is the incident photon energy in keV, θ is the scattering polar angle and Z is the atomic number of the atoms in the scatterer; x is the momentum transfer in Å⁻¹. The multiple-scattering intensity was evaluated by a Monte-Carlo calculation. Theoretical values of an incoherent-scattering function using the Waller-Hartree theory [1] which is based on form factor approximation (\(S^{WH}\)) is widely used for keV photon-transport calculations. It is also possible to calculate the incoherent scattering function by integrating the double differential Compton-scattering cross section based on an impulse approximation with respect to the scattered photon energy (\(S^{IA}\)) [2].

The number of incident photons were monitored using a free air ionization chamber, which was calibrated with a calorimeter. S was obtained by fitting the measured Compton peak with double differential Compton scattering cross section derived by Ribberfors [2]. In Fig. 1, the measured S of Cu is compared with \(S^{WH}\) and previous measurements [3-5]. The measured S of C, Al, Fe and Cu agreed with that based on the Waller-Hartree theory (\(S^{WH}\)) as well as that based on a relativistic impulse approximation (\(S^{IA}\)) within the experiment error (2.5%). The measured S of high-Z atoms (Au and Pb) is smaller than \(S^{WH}\) by 3 to 6% and agrees with \(S^{IA}\) (Fig. 2).

\[ S^{IA}\] and \(S^{WH}\) agrees for high k₀ while they differ for low k₀ (Fig. 2). Doppler broadening of the scattered photon energy affects this. The details of this measurement appears in the author’s recent publication [6].

QUANTITATIVE ANALYSIS OF GROWN-IN MICRODEFECTS IN A CZ-SILICON CRYSTAL OBSERVED BY HIGH ENERGY X-RAY TOPOGRAPHY


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Introduction

Grown-in microdefects in a Czochralski (CZ) grown silicon crystal have been observed by using high energy synchrotron radiation diffraction topography and analyzed quantitatively. Possible origins of the microdefects are discussed.

Experimental

Synchrotron radiation topography experiments were performed at the vertical wiggler beam line BL-14C, with 60 keV high energy x-rays monochromatized by using a Si (220) monochromator cut asymmetrically. A specimen observed was an as-grown CZ-silicon plate, about 5 mm in thickness, with the [100] surface orientation perpendicular to the growth direction [001], cut from a boule pulled at a growth rate 0.1 mm/min.

Results and Discussion

The density distribution of the microdefects (Fig. 1(a)) was obtained directly from a traverse topograph of 0 0 8 reflection. The size of the microdefects was determined from the height of the defect-images in the topograph by using the kinematical diffraction theory with an assumption that the strain field around the defects was spherical. The radial distribution of the defects size is shown in Fig. 1(b).

It was also determined that the lattice distortion associated with the defects was an extrinsic type (an interstitial type), so that possible sources of the microdefects are ascribable to silicon self-interstitials or oxygen atoms, but not to vacancies. The total number of the point defects, which contributed to the formation of the microdefects, was estimated from the total misfit volume of the defects for the two models of the microdefects: aggregates of self-interstitial atoms and oxygen precipitates (silicon oxide). (see Fig. 1(c)).

Fig. 1. Radial distributions of the density of the microdefects (a), of the size of the microdefects (b), and of the number of the point defects contributed to the microdefects (c).
AORTOGRAPHIC CORONARY ARTERIOGRAPHY WITH SYNCHROTRON RADIATION

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1. Introduction

From 1981, the intravenous K-edge energy subtraction coronary arteriography have been developed. In Japan, a two-dimensional image acquisition system with SR has been developed. The results of animal experiments and human studies have revealed various problems of intravenous CAG with SR, including the overlap of the coronary artery on cardiac chambers and other vessels, and the dilution of contrast material. In this study, we employed two-dimensional SR angiography in combination with the non-selective arterial injection of contrast material in dogs to assess the diagnostic possibility in visualizing the coronary arterial structure.

2. Methods and Materials

The two-dimensional coronary angiographic system (2D-CAG system) with SR is constructed at the vertical wigglar beam line of BL-14C of the Photon Factory in Tsukuba. This system consists of a movable silicon (311) monocrystal, fluorescent plate (FUJI FILM HR-6), avalanche-type pickup tube (HARPICON) camera, x-ray shutter, image acquisition system and workstation. The monochromatic x-ray beam size is a 40 x 70 mm. The energy of the beams is adjusted to 150 eV above the iodine K-edge.

X-ray images were converted to light images with a fluorescent plate, and this light image was detected by the avalanche-type pick-up tube camera. The x-ray TV images were digitized in a 1024 x 1024 pixel matrix with a 12-bit depth using a 12-bit analog-to-digital converter. All images were stored as digitized images in a 144-megabyte frame memory. A workstation (Hewlett Packard 715/33) was used for image processing and control of the image acquisition system.

The acquisition interval of each image was set at 66 msec. The image acquisition time of each frame was set 66 msec because the insufficient x-ray flux and brightness of new TV camera. Dogs were anesthetized with phenobarbital. A 6F catheter was inserted into the aorta. Contrast material (Iomeprol 350, 0.80 ml/kg) was injected by the injector at the rate of 10 ml/sec.

3. Results and discussions

Typical images are shown in Fig 1. The coronary arteries could be imaged clearly, and the image quality was almost the same as that of selective coronary arteriography. The 1.2 mm in diameter of the main coronary artery and about 0.2 mm in diameter of the distal branches of the left anterior descending, circumferential, and right coronary arteries were observed.

Aortographic CAG with SR provides clear images of the coronary arteries probably because the image contrast is markedly improved by the SR angiographic method and the dilution of contrast material is not as marked as that in the intravenous method. This method might produce the new diagnostic approaches of coronary artery with SR.

References
(The HARPICON was jointly developed by NHK (Japan Broadcasting Corporation) and Hitachi, Ltd.)
APPLICATION OF A PROPORTIONAL SCINTILLATION X-RAY IMAGING CHAMBER TO SYNCHROTRON RADIATION EXPERIMENTS

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Introduction

When applied to the x-ray scattering experiments at the third generation synchrotron radiation facilities such as SPring-8, APS, and, ESRF, the gaseous detectors based on electron multiplication processes could occasionally become unstable due to the space charge abundantly generated in their volumes. It is, therefore, an important task for synchrotron radiation science to develop a new type of gaseous detectors that are highly space-charge-resistive. In this respect, the x-ray imaging chamber operated in the proportional scintillation mode is one of the most promising device, since the proportional scintillation takes place under a much lower electric filed strength compared to that needed to initiate the electron multiplication.

Experimental

The incoming x-ray photons to a proportional scintillation x-ray imaging chamber (PSXIC) are first converted into secondary electrons in a drift chamber filled with, for example, Xe (98%) + Triethylamine (2%) gas mixture at 1 atm. Being transported to a parallel plate avalanche chamber, the secondary electrons then induce the proportional scintillation with an electric field of ~lkV/cm. The luminous pattern reproducing the 2D image of the scattered x-ray photons is observed with an image-intensifier-associated CCD camera. The real-time x-ray images thus obtained can be processed with a video digitizer and a personal computer.

Having constructed a prototype of proportional scintillation imaging chamber (PSXIC), we examined its performance at BL-14C of PF/KEK by observing the diffraction patterns of several well-known samples and the monochromatized direct beam images.

Results and Discussion

Figure 1 displays the observed Laue diffraction pattern of β-cyclodextrin powder with integrating 255 video frames. One could see not only the ordinary circular diffraction pattern but the several Laue spots due to the remaining crystal structure in the sample as well. After optimizing the operational conditions, we irradiated the prototype with the monochromatized direct beam (20keV, ~10^8 photons/mm^2/sec) in order to verify its space-charge-resistivity. As shown in Fig.2, the prototype succeeded in stably visualizing the direct beam images without any discharge for longer than 1 hour. These encouraging results obtained in the present study will provide us with a strong support in continuing our PSXIC project.

Fig.1 The observed Laue diffraction pattern of β-cyclodextrin powder

Fig.2 The observed monochromatized direct beam image (1mm × 2mm)

References

Pressure Induced Structure Change of Molten KCl

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Introduction

The molten alkali halide has been considered to transform into dense state under high pressure, which is accompanied by the increase of the coordination number of nearest neighbor ions. Recent numerical simulations showed that this type of pressure induced structure change occurred in the molten KCl. However, the experimental approach is required to elucidate this structure change. This report is the results of high pressure experimental study on the structure of molten alkali halide. In this study, KCl is chosen as a representative alkali halide, because the structure of molten KCl is expected to change at relatively low pressure.

Experiments

Structure of molten KCl under high pressures has been examined by the in situ X-ray diffraction method using synchrotron radiation. Experiments were conducted at the wiggler beamline (BL14C) in PF by the energy dispersive method with white beam (up to 120keV). High pressure was generated by the cubic-type high pressure apparatus, MAX90. Diffraction profiles were collected just above the melting points of KCl up to 4 GPa. (Figure 1). The structure factor, S(Q), for molten KCl was obtained from the acquired diffraction data using the analyzing method proposed by Tsuji et al. (1989).2

Results and Discussion

S(Q) for molten KCl under pressure is shown in Figure 2. There is no abrupt change in peak positions and overall feature of S(Q) up to 4 GPa. However, the first peaks around Q = 2.3 Å⁻¹ becomes sharp and high with pressure. These indicate that the structure of molten KCl gradually changes up to 4 GPa.

In order to clarify the structure of molten KCl corresponding to the observed S(Q), we try to reconstruct S(Q) by the molecular dynamics. As a result of simulation, the observed S(Q) can be explained the following structure change in molten KCl. The distance of nearest K-Cl does not change much with pressure. The coordination number of nearest neighbor ions increases with pressure.

References

DENSITY OF LIQUID SELENIUM AND TELLURIUM UNDER PRESSURE

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Introduction

X-ray diffraction measurements for liquid Se and Te indicated that there was a drastic change in the structure factor under high pressure[1]. Recently, Brazhkin et al. [2] found another transition (L-L' transition) in liquid Te under high pressure. They detected abrupt volume contraction when a sample was being heated at constant pressure. To understand these structural changes, the pressure dependence of the density will provide valuable information. We have developed a new X-ray absorption method for density measurements using MAX80 installed in ARNE5[3]. Since the sample thickness changes with pressure, we need other standard of thickness to calculate the density from measured x-ray absorption. We therefore put a sapphire ball, which is x-ray transparent, in a sample capsule as a calibrant of the thickness, and measured x-ray absorption as a function of sample position. In the previous experiments, however, the data was not good enough to detect the L-L' transition, at which the reported volume change was 1%. Since a major reason of the error was an instability of monochromatized x-ray beam due to frequent injection in AR, we carried out the present experiment at the Photon Factory. The density of liquid Te was measured up to 700°C at 4 GPa.

Experimental

Experiments were carried out using MAX90, a cubic-anvil apparatus installed in the BL14C station. The energy of the x-ray passed through a Si(311) double-crystal monochromator was 59 keV. The intensity of the incident beam (I0) was monitored by fluorescence x-ray from Sn foil on the x-ray path. The intensity of the transmitted beam (I) was measured by a scintillation detector. The size of the incident x-ray beam at sample position was 0.1 x 0.1 mm^2. The specimen was placed in a 2-mm-o.d., 1-mm-i.d. BN capsule together with a sapphire ball 0.5 mm in diameter. By moving press, I was measured at various sample positions without changing the beam position.

Results and discussion

Figure 1 shows the logarithm of I/I0 at 3.7 GPa and 700°C as a function of press height. x. The curvature of the sapphire ball was clearly observed. The solid line in Fig. 1 represents the result of a parameter fitting. The simulation well reproduced the experimental values.

Figure 2 shows the density of Te at around 4 GPa as a function of temperature. The jump of the density at the Tel-Tell transition and that upon melting were clearly observed. The error estimated from a variation of data is ±1.0%, which is two thirds of that of prior experiments. In the present experiment, however, the proposed L-L' transition was not confirmed.

References


Figure 1. Example of log(I/I0) for crystalline Te at 3.7 GPa and at 700°C as a function of press height.

Figure 2. Density of Te at 4 GPa as a function of temperature.
ZrRuP crystallizes in two modifications, the Fe2P-type hexagonal structure (h-ZrRuP) and the Co2P-type orthorhombic one (o-ZrRuP). Both phosphides are layer compounds. Each layer in h-ZrRuP is occupied by either Zr and P atoms or Ru and P atoms (1). The two dimensional triangular clusters of Ru3 are formed and linked with each other through the Ru-P bonds in the basal plane. In contrast, the layers in o-ZrRuP are filled with Zr and Ru atoms and are all equivalent (2). We have studied X-ray diffraction of o-ZrRuP at high temperatures and high pressures.

o-ZrRuP was prepared by reaction of stoichiometric amounts of Zr, Ru and red phosphorus powders at 1000°C and 2 GPa (3). The cubic-anvil type high pressure apparatus was used for the X-ray study at high temperatures and high pressures. The diffraction patterns of ZrRuP were recorded at 20 = 4° with an energy dispersive method.

The cell volume (V0) of o-ZrRuP at atmospheric pressure linearly decreased with increasing pressure at the rate of d(V0-V)/dP = 1.12 Å3/GPa up to 4 GPa. The volume at 4 GPa reduced to about 97.5% of V0. Figure 1 shows temperature dependence of lattice constants and volume at 4 GPa. The lattice constants and volume linearly increased with temperature up to 1000°C. o-ZrRuP transformed to the hexagonal phase at around 1100°C and 3.5 GPa. The density of both structures was 8.172 g/cm³ for o-ZrRuP and 8.148 g/cm³ for h-ZrRuP at room temperature and atmospheric pressure. The density of o-ZrRuP is slightly larger than that of h-ZrRuP. Thus, h-ZrRuP becomes a high temperature phase. However, h-ZrRuP was quenched and very stable at the normal condition.

Fig. 1 Lattice constants and volume of o-ZrRuP at high temperatures and 4 GPa.
Structure Change of Magnetic Body in Hydrogel

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Introduction

Actuation of polymer gel by applying electric field has been investigated as a possible way to a practical artificial muscle.[1] Actuation of polymer gels by magnetic field, however, has not been reported so far. There are many advantage in the magnetic field as a trigger for the gel actuation. We prepared hydrogel of poly(vinyl alcohol) (PVA) containing ferromagnetic body, and investigated as a magnetically active hydrogel.[2] Here, we will report on the structure change of magnetic body immobilized in the hydrogel by magnetic field.

Experimental

Ferro-fluid was prepared by conventional coprecipitation method, using sodium oleate as an emulsifier. The ferro-fluid was immobilized in PVA hydrogel by repetitive freezing-and-thawing method. Thus prepared PVA hydrogel was served for small angle X-ray scattering measurements. The instrument of BL-15A was used. Wavelength of the X-ray, the distance between sample and detector, and the irradiation time were 1.488Å, 2 m, and 300 sec, respectively. Applied magnetic field was 1.4 T, and was in parallel direction to the PSF anode line.

Results and Discussion

In Fig. 1, the effect of magnetic field application on the X-ray scattering profiles was shown. Scattering intensity is mainly attributed to the magnetic body in the gel, since the content of ferro-magnetic particles is much higher than that of PVA. There is a small hump at q= ca.0.08 which can be considered to be attributed at the scattering by the magnetic body in the gel whose size is about 80 Å. The effect of the magnetic field was observed in Fig.1. In Fig. 2, distance distribution function p(r) was shown.

Thermally Induced Structure Change of Polyurethane Elastomer

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Introduction

We have been investigating on polymer gels, and their application as artificial muscle or gel-actuators. The results suggests that the action of the gel actuator induced by electric field depends on the dielectric constant of the solvent or medium which is occluded in the polymer network.[1,2]

For the clarification of the role of the solvent on the actuation, we expected the polymer chain itself takes places the role of solvent when it has enough flexibility, and investigated the effect of flexibility of polymer chain, using polyurethane elastomers which has melting point at ca.50°C.[3,4] In this report, the effect of temperature on the scattering profile of the polyurethane elastomer.

Experimental

Polyurethane elastomer investigated was synthesized by conventional prepolymer method. Materials used were hexamethylene diisocyanate (HDI), polycaprolactone diol (PCL, MW=2000), and 1,4-butane diol. The contents of the polymer was HDI:PCL:BD=10:4:4 in mole ratio.

Scattering experiments were carried out using the small angle X-ray scattering (SAXS) instrument in BL-15A. Sample detector distance was 60 cm. Wavelength of the X-ray was 1.488 Å. Measurements were carried out by varying temperature, keeping the elapsed time constant at 100 sec for each sample.

Results and Discussion

The polyurethane sample shows melting behavior at 40°C. The scattering profile shown in Porod plots changed before and after melting. (Fig.1) Scattering intensity after melting (at 60°C) is smaller than before melting (at 30°C). Porod slope changed from -3.42 for before melting to -2.96 for after melting, suggesting fractal surface changed into rougher by melting. Electrical actuation was not observed in this elastomer, suggesting that crosslinks by allophanate bonds disturbed the mobility of the polymer chain. Persistence length estimated from Kratky plot decreased by melting. These feature in the scattering profile changed drastically by the composition of the elastomer. Particularly in the elastomer rich in soft segment, the scattering intensity decrease by melting was remarkable, and electrically induced anisotropic structure change was confirmed.

Figure 1. Double logarithmic plots of the scattering curves of a polyurethane elastomer.

References
FETAL TENDON DIFFRACTION PATTERNS MIRROR FETUS ACTIVITY

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Introduction

Our studies of the changes in collagen with age using synchrotron radiation and imaging plate detectors, have provided us with exciting new information about the packing changes in human fetal tendon with the time duration of the pregnancy. The diameter distribution of extensor tendon fibrils in the fetal stages is unimodal whereas at birth the distribution is bimodal. The arrangement of the fibrils becomes more ordered as the pregnancy advances. These changes closely correlate with the activity of the fetus.

Experimental

Samples for this research ranged in age from 14 to 20 weeks after conception for both skin and tendon, twelve samples in all. These samples were studied during two separate visits to Tsukuba. For ethical reasons, such specimens cannot be freely chosen, but those available were supplemented by some from fetal sheep. The sheep tendons were obtained at 133 and 140 days, representing a much more advanced stage of fetal development, since the normal gestation period for sheep is 145 days. These samples were stored in physiological saline at -20°C until required. For the X-ray diffraction study samples were placed in specially designed cells to maintain 100% humidity. The samples were slightly stretched during exposure to remove the natural crimp. All samples were examined using the low angle facility, BL15A source at the Photon Factory. Sample to imaging plate distances of 2400 and 600 mm were used for each sample. Exposure times of 5 to 60 seconds enabled us to handle the full dynamic range of intensities in the patterns. Data were recorded on imaging plates and later extracted by electronic scan. Calibration was achieved by exposing moist rat-tail tendon, which is known to have a constant repeat distance of 67 nm.

Data Handling

A high precision analysis of the two dimensional data was carried out using the Smithsonian astronomy computer packages, IRAF(1986) and SAO Image(1991) to display and smooth the image, to remove background and to determine the positions and intensities of the reflections. Equatorial reflections were fitted to cylindrical arrays using a Bessel Function analysis of scattering from cylindrical fibres, similar to the study of embryonic tissue by Eikenberry et al (1982).

Results and Discussion

It is immediately obvious from that the equatorial pattern from fetal tendon, Figure 1, is quite different from post-partum tendon, Fig 2. These patterns are similar to the pattern for skin, in fact, these samples have the best developed collection of "cylindrical peaks" of any samples yet studied. These reflections were all fitted to cylindrical arrays using a Bessel Function analysis of scattering from cylindrical fibres arranged in an hexagonal lattice, similar to that of Eikenberry et al. Cylinder radii varied slightly from sample but was always lower than 40nm for human samples and slightly larger, around 45 nm for sheep These results agree with those of electron microscopy which suggest that mature tendon does not have fibrils of uniform diameter, but other tissues give a range of diameters similar to our results.(Parry et al)

The highly organised lateral regularity of these samples from the early stages of gestation suggest that the fetal tendon material has not as yet acquired the one-dimensional character required in maturity. Such regularity is also a feature of two-dimensional collagenous tissue such as skin but is not exhibited in mature tendon, a collagenous tissue required to act only under tension. The gradual alignment within the tissue does mirror in time the increased movement of the fetus.

References

AN X-RAY DIFFRACTION STUDY
ON A SINGLE FROG SKINNED MUSCLE FIBER
IN THE PRESENCE OF VANADATE
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Introduction

ATP plays a crucial role in muscle contraction. Each ATP molecule is split into an ADP molecule and an inorganic phosphate on a myosin head (M). The phosphate is released prior to the ADP molecule. Vanadate (Vi) binds to a myosin head and forms a stable M-ADP-Vi complex in which vanadate probably occupies the phosphate site. Formation of the complex suppresses contraction of a skinned muscle fiber. Using a technique to record a two-dimensional diffraction pattern from a single skinned muscle fiber on an imaging plate with synchrotron radiation, we studied the arrangement of the M-ADP-Vi complex in a frog skeletal muscle fiber.

Materials and Methods

A single muscle fiber from a sartorius muscle of a bull frog Rana catesbeiana was used. The fiber was isolated in a relaxing solution and treated with 0.5% Triton X-100 for 10 min to make the sarcolemma permeable to solutes. Fibers with a diameter of 100-150 μm were selected.

Experiments were conducted at the beam line 15A. Exposure time was 30 sec. To minimize the variation in the intensity measurements, care was taken to use the same plate in all exposures and to keep constant the interval between the exposure and scanning.

Dantzig and Goldman reported that a stable M-ADP-Vi complex is formed only during active contraction. Following their methods, two procedures were adopted. One involved Ca²⁺-free contraction at a depleting MgATP concentration (50 μM) and the other, ordinary Ca²⁺-activated contraction.

Results and Discussion

Monitoring force development of the fiber, we considered that a stable M-ADP-Vi complex was formed during active contraction in the presence of 1 mM vanadate. The results obtained with two procedures were consistent with each other and could be summarized as follows.

Both in the presence and absence of Ca²⁺, the intensities of the equatorial reflections were similar or close to that of the fresh relaxed muscle. This indicates that most of the heads with ADP and vanadate stay close to the backbone of the thick filament. The first layer line was predominantly the first myosin layer-line located at 43 nm. This also suggests that the heads forms a helix around the shaft of the thick filament. Actin layer-lines were weak, suggesting that the myosin heads were detached from the thin filament.

The results in the present study suggest that the M-ADP-Vi complex has a weak affinity toward actin regardless of the state of the regulatory system on the thin filament. It is clear that the formation of M-ADP-Vi holds the myosin head in the detached state.

References
RECORDING OF X-RAY DIFFRACTION PATTERNS FROM SINGLE MUSCLE FIBERS USING AN X-RAY IMAGE INTENSIFIER AND A COOLED-CCD CAMERA.

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Introduction

A new X-ray detector system based on an X-ray image intensifier and a cooled CCD camera has been developed1). The image intensifier has an aperture of 150 mm² and the CCD camera has 1024 × 1024 pixels. This system has an advantage not only that it is free from count-rate limitation but also that it has a high sensitivity and a low noise. Thus it is suitable for recording a diffraction pattern from a weakly diffracting material. We used this system to record an X-ray diffraction pattern from a single skinned muscle fiber of frog.

Methods

Single muscle fibers with a diameter of 100-150 μm were dissected from a sartorius muscle of bullfrog, and treated by Triton to permealize the cell membrane. An X-ray diffraction pattern was intensified by the X-ray image intensifier was recorded by the cooled CCD. Images were read out through a 12-bit A/D converter to a frame grabber installed in a personal computer. An X-ray exposure was 60 sec. There was no sign of radiation damage after several exposures. The experiments were made at BL15A with a specimen-to-detector distance of 140 cm.

Results

Figure 1 is an X-ray diffraction pattern from a single skinned fiber in a relaxing solution after background subtraction. Although the diffraction from a single fiber is quite weak, the pattern clearly shows the features like the myosin layer-lines. The quality of the pattern is comparable to that recorded on an imaging plate2) showing that the sensitivity and noise of the system are similar to that of an imaging plate. However, there are two kinds of spatial non-uniformity in sensitivity: one is a global effect which reduces the sensitivity in the periphery compared to the center. Another is a local effect which can be noticed by the rather noisy background in the pattern.

Discussion

The present study shows that this detector system can be used in place of an imaging plate. It has an advantage over an imaging plate that the sensitivity is stable and thus the intensities can be compared directly between different exposures. The non-uniform sensitivity over the detector area should be corrected using an appropriate method.

We have used this system to study the effect of MgADP on the structure of rigor muscle fibers. The results will be reported elsewhere.

References

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Figure 1
X–RAY DIFFRACTION OF THE LIVE SQUID RETINA IN THE DARK AND LIGHT

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Introduction

The initial step of the visual process is the absorption of light by the visual pigment. The squid visual pigment is located in microvilli which are cylindrical extensions of the cell membrane, arranged hexagonally within the rhabdomes. Until now, only a few papers have been published on the structural study of invertebrate rhabdomes by x-ray diffraction. In those papers, however, the retina fixed by glutaraldehyde was used, because this tissue disintegrated within 1 hour of dissection. Previously, we have reported that we could succeed in recording the x-ray diffraction pattern from unfixed retina by the use of the synchrotron radiation and a storage phosphor screen, the imaging plate\textsuperscript{1}. Also, we have reported the some change of diffraction pattern induced in response to the light stimulation\textsuperscript{2}. In the last study, we have repeated x-ray experiments with samples in the artificial seawater containing other ionic components than the previously used one, in order to disclose the relation between the light-induced structural changes observed previously and the visual excitation of photoreceptors. Unexpectedly, however, the symmetry of diffraction intensities differed between them: that is, the mirror symmetries on both vertical axis (b-axis) and horizontal axis (a*-axis) which were observed with the retina in the previously used artificial seawater, were lost with the retina in the newly adopted one\textsuperscript{3}. This result suggests that the mirror symmetries of the microvillar cross-section are lost by changing the ionic composition of artificial seawater, but the lattice arrangements of microvilli are kept nevertheless. Thus, we have done the experiment to account for which component of the artificial seawater causes this change.

Experimental

Living, active specimens of the squid, Watasenia scintillans were captured at Toyama Bay of the Japan sea and brought to Tsukuba within several hours. The squids were decapitated and their retinas dissected in dim red light. For the x-ray experiment, a 1-mm thick slice of retina was kept in an artificial seawater chamber with Mylar windows at 4 °C. Schematic diagram of a slice of squid retina was shown in the previous report\textsuperscript{4}. The artificial seawater containing D-glucose was oxygenated and gently circulated through the sample chamber during the experiment. A 100 W halogen lamp in conjunction with an interference filter and a heat filter, was used for light stimulation (about 500 nm in wavelength).

X-ray experiments have been performed with a mirror–monochromator optics (the Muscle Diffractometer) at BL–15A\textsuperscript{1}. The wavelength of the radiation was 0,150 nm. The sample–to–detector distance was 1872 mm. X-ray diffraction intensity was recorded on the imaging plate and stored on magnetic tape after converting to the digital signals with the image reader and the image processor\textsuperscript{5}. X-ray diffraction data were successively taken with the same sample in the dark and light, respectively. The exposure time was 3 minutes and each recording finished within 40 minutes after decapitation.

Results

The x-ray diffraction patterns showed two types; that is, the mirror symmetric and asymmetric ones with respect to both vertical and horizontal axes, by using newly adopted artificial seawater. Therefore, the origin of the asymmetry in diffraction pattern could not be disclosed. In response to the light stimulation, the change of diffraction pattern was also observed with retina in the artificial seawater containing choline ion instead of sodium ion.

References

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KINETICS OF THE CONFORMATIONAL CHANGE OF OVOMACROGLOBULIN

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Introduction
Ovomacroglobulin (OMG) is a homolog of human α2-Macroglobulin (α2M). α2M is a high molecular mass (720 kDa) protein in plasma that inhibits proteases. What is characteristic to this inhibitor is that it can inhibit almost all kind of endo-protease. The mechanism of this inhibitory reaction is called "trap mechanism", which is triggered by the cleavage of so called "bait-region" that is a part of α2M polypeptide chain by protease(12). This cleavage is followed by the conformational change of α2M that engulfs the protease, which physically inhibits protease to access substrates. During this reaction intra-molecular thiolester in α2M molecule is cleaved.

Our plan is to understand this trap mechanism from bio-physical point of view to know the underlying relation between structure and function and to know the potential of protein.

We have already studied the kinetics of the trapping conformational change of human α2M observed with time resolved small angle X-ray scattering (SAXS)(21). This study called the relation of the conformational change and trapping mechanism into question. To get further information we are now comparing the trapping reaction between homologs of α2M in different species and different tissues.

Last year, we observed the kinetics of the conformational change of α2M that had been found in the plasma of horseshoe crab, Limulus polyphemus, reacting with trypsin. Limulus α2M (LAM) was selected because it was thought to be a simple model of α2M. LAM traps one trypsin molecule while human α2M traps two trypsin molecules. The reaction of LAM with proteases shows interesting similarities and differences with the reaction of human α2M. Its value of LAM was estimated to decrease 15% with rate constant 0.59 sec⁻¹ and Rg (radius of gyration) seemed to change from 6.4 nm to 5.6 nm with rate constant 0.62 sec⁻¹. Both rate constants were smaller than that of human α2M reacting with trypsin (0.8 ± 0.2 sec⁻¹) and human α2M dose not change its value significantly but changes only its Rg. The change of its value suggested dissociation during the reaction. Although these results were interesting and gave new information about α2M family, they also showed that the reaction of LAM with protease was more complicated than it had been thought.

This year we selected OMG. OMG is made of four identical subunits as α2M but trap only one trypsin molecule and has no intra-molecular thiolester. These facts encouraged us to investigate OMG, which is likely to be proved to be useful in elucidating essential features of the protein structure and function.

Experimental
X-ray solution scattering experiments were performed at BL-15A small-angle installation. The stopped-flow apparatus and the data accumulating system were renewed this year, which made our experiment easier to accumulate a lot of shots (13). The mixing ratio (vol:vol.) of stopped-flow apparatus was 1:1. The temperature of the apparatus was kept at 15°C. Data of each 100 ms time slice were recorded during 9.4 s. Data of 80 to 150 shots were accumulated. Rgs of each time slice were calculated from Guinier plot.

Results and Discussion
Excess amount of trypsin was reacted with OMG to make a second order reaction to pseudo-first order reaction. Three different trypsin concentrations were used to know the concentration dependency of the observed conformational change. This will show whether the rate limiting step is second order reaction or first order reaction. In the case of human α2M, it was first order reaction. Human α2M was also reacted with trypsin as a standard material to ensure the condition of this experiment. Further temperature dependency of the conformational change of human α2M will be found out because we already have data at 5°C and the temperature is 15°C this time.

As new system for measurement and data processing was introduced to BL-15A this year and the experiment was done in December the data are not completely analyzed yet. The following results are of preliminary analysis.

When OMG reacted with trypsin, as in the case of α2M, the scattering intensity increased in the small angle region due to a decrease of Rg (from 7.9 nm to 6.7 nm) and the scattering intensity decreased in the mid region. The half life of the decrease in Rg seemed to be several times longer than that of α2M.

References
Solution X-ray Scattering Study on Conformational Changes of Transferrin Dependent on Various Bound-Metal Ions.

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INTRODUCTION
A family of metal-binding glycoprotein, the transferrins are found in vertebrate blood plasma (transferrin), avian egg white (ovo-transferrin), mammalian white blood cell and milk, and many body fluids (lactoferrin). The transferrins consist of a single polypeptide having molecular weight ca. 80kDa. Recently, x-ray crystallographic structure of rabbit transferrin, and homologous protein, human lactoferrin were resolved [1]. These proteins were consist of two lobes which were connected with a short connecting peptide. Each lobe is further divided into two dissimilar domains. The metal-binding site is located within the intradomain cleft, and binds some trace metal ions reversely. X-ray crystallographic structures of Fe(III)-free and -bound human lactoferrins show a different topology of four domains [1]. Conformational changes were induced on Fe-binding [2]. It was confirmed by solution X-ray scattering studies that radius of gyration, Rg, and internal structures of transferrin molecule were changed [3].

Ovotransferrin shows positive cooperativity on Fe(III)-bindings, whereas there shows negative cooperativity on Al(III)-binding. And this protein shows non-cooperativity on bindings of some other metal such as Co(II), Cu(II), and Tb(III) etc. For lanthanide(III) complexes of ovotransferrin, the metal release rate from these sites differed markedly in the presence of EDTA. The half-value periods of the release reaction increased with a good correlation to the atomic number on lanthanide.

MATERIALS & METHOD
Metal-binding ovotransferrins were prepared according to previously [2]. Solution X-ray scattering experiments were carried out at BL-15A of Photon Factory, KEK.

RESULTS & DISCUSSION
Radii of gyration, Rg, were calculated from Guinier plots and were shown in Table 1. Metal-bound transferrins and apotransferrin at the same concentration were compared. In metal complexes of transferrin, Rg of metal-transferrin were dependent on the ionic radii of bound-metal ions. Conformational change of transferrin depends on bound-metal ions.

Previously, stabilities of lanthanide-transferrin complexes depend on the ionic radii of bound ions [2]. Conformational change induced by lanthanide ions is in relation to these ionic radii as shown in Fig. 1. These results are in relation to stability of its lanthanide-transferrin complexes.

Table 1 Radii of gyration, Rg, for apotransferrin and Fe-, Tb-, Nd-, Yb-bound transferrins. The concentration of transferrins is 1.5% in 10mM Tris-HCl containing 10mM bicarbonate, pH 8.2.

<table>
<thead>
<tr>
<th>Transferrin</th>
<th>Rg (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apotransferrin</td>
<td>28.23 (+ 0.05)</td>
</tr>
<tr>
<td>Fe-transferrin</td>
<td>27.21 (+ 0.02)</td>
</tr>
<tr>
<td>Nd-transferrin</td>
<td>27.72 (+ 0.04)</td>
</tr>
<tr>
<td>Tb-transferrin</td>
<td>27.54 (+ 0.03)</td>
</tr>
<tr>
<td>Yb-transferrin</td>
<td>27.31 (+ 0.03)</td>
</tr>
</tbody>
</table>

Fig. 1 Relationship between Rg(app) of lanthanide-bound transferrins and ionic radii of lanthanide.

Conformational Changes of the Myosin Head During Hydrolysis of ATP and Upon Binding of Nucleotide Analogs by X-ray Solution Scattering

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Introduction
We have found distinct conformational changes of the myosin head during hydrolysis of MgATP and upon binding of MgADP.Vi by X-ray solution scattering techniques1). The effects of binding of two MgADP-fluoride complexes to S1 were investigated. To clarify the conformational change of S1 in the active state, modeling studies were done using the S1 crystal structure2).

Experimental
Papain-treated chicken skeletal S1 was used immediately after purification by gel filtration. X-ray solution scattering was done at 19°C at BL15A. The experiments on samples with MgADP, MgADP.Vi, MgADP.AIF4 and MgADP.BeF3 were made. The two fluoride complexes are a new class of phosphate analogs. Pair distance distribution functions (p(r)) were calculated from the intensity data of 0.003<Sc0.050Å-1 using a maximum entropy method. Modeling studies have been made using α-carbon coordinates of S1 crystal structure3).

Results and Discussion
The radius of gyration values (Rg) of S1 samples used are depicted in Fig.1, where the data at 6 mg/ml are shown. The Rg of S1 in MgATP solution was about 3Å less than that of free S1 and that of the S1.ADP.Vi complex decreased by ~1.5Å. Both S1-fluoride complexes also decreased to a value close to that of S1.ADP.Vi, suggesting a conformational analogy of these complexes with the S1.ADP.Vi and/or the S1.ADP.Pi.

To analyze the conformational change of S1 in the active state, modeling studies were carried out for free S1 and S1 in MgATP solution. The crystal structure was slightly modified to fit to the scattering data of free S1. To get a model of S1 in MgATP solution3), we applied a rigid-body bending of a residue to the free S1 model. The present best-fit models are shown in Fig.2. The scattering curves from these models gave a fairly good agreement with the observed ones. p(r) functions were also compared to the observed ones in Fig.2. The observed features of the p(r) functions are reproduced and the reduction of Rg and the maximum chord length in the active state could be explained. Better fits to the observed data can be achieved by taking into account some alteration of internal structure. Detailed calculations are in progress.

References

Fig.1 The radii of gyration of various samples at 6mg/ml.

Fig.2 Models and comparisons of p(r) functions for free S1 (left) and for S1 in the active state (right).
X-RAY SOLUTION SCATTERING STUDIES OF THE MYOSIN HEADS FROM SMOOTH MUSCLE

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Introduction

It is well known that phosphorylation of light chain on the heads of myosin molecules is an integral component of the regulatory mechanism of smooth muscle. We started x-ray scattering study on the structural alterations of myosin subfragment-1 (S1) and heavy meromyosin (HMM) from smooth muscle with and without phosphorylation in the absence and presence of MgATP.

Experimental

Smooth muscle S1 and HMM were prepared from turkey gizzard myosin by Staphylococcus protease digestion. Phosphorylation of light chain on them was made by myosin light chain kinase and ATPyS. X-ray solution experiments were done at 19°C with the small-angle diffractometer at BL15A. Scattering data were collected with a 1D-PSD. The protein concentration was varied from 3 to 10 mg/ml.

Results and Discussion

The Guinier plots of scattering data from all samples gave straight lines in the range of 0.0028 < S < 0.0048 Å⁻¹ (S=2sinθ/λ), showing no aggregates in solution. From the slope of straight lines in this plots, the radii of gyration (Rg) were determined from all samples. In the case of HMM, the apparent Rgs were given because the small-angle data enough to determine true values could not be measured. The Rg values at 3mg/ml for HMM and 5mg/ml for S1 are depicted in Fig.1. When HMM was phosphorylated, the Rg value decreased by ~7Å. In the presence of MgATP, further decrease (~8Å) in Rg occurred. Without phosphorylation of light chains, much larger decrease (~14Å decrease) in Rg as well as the change of the scattering profile occurred upon addition of MgATP. When S1 was phosphorylated, the Rg value tended to slightly increase in the absence of MgATP and decrease upon addition of MgATP. The Rg value of S1 without phosphorylation decreased by about 3Å upon addition of MgATP, being similar to the skeletal muscle S11). The effect of MgADP.Vi, which is an analog of the MgADP.Pi, was similar to the skeletal muscle S1, but those of MgADP-fluorosalculuminate and fluoroberyllate, which are the other analogs of the MgADP.Pi, were different from it2).

Fig.2 shows the preliminary modeling studies using the aggregate of 10Å-diameter spheres on the conformational change of the HMM molecule without phosphorylation in the absence and presence of MgATP. Bending down of the two heads around the head-rod junction seems to be caused by binding of MgATP.

References

X-RAY SOLUTION SCATTERING STUDIES ON MONOMERIC ACTIN-MYOSIN HEAD COMPLEX

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Introduction

In order to study the structure of a complex of monomeric actin and myosin head (S1), nonpolymerizable G-actin was prepared by the reaction of G-actin with m-maleimidobenzoic acid N-hydroxysuccinimide ester (MBS) and 5-diazonium tetrazole (DHT). Recently, we succeeded to make an 1:1 complex of monomeric DHT/MBS-G-actin and started an X-ray solution scattering study on the structure of this complex in solution.

Experimental

DHT/MBS-G-actin was chemically crosslinked to the regulatory light chain-deficient S1 through MBS. The crosslinked complex was column-chromatographed and ultracentrifuged to remove unreacted S1, actin, and aggregates. X-ray scattering was performed by using the small-angle diffractometer at BL-15A. Measurements on DHT/MBS-actin-S1 complex were made using a 1D-PSD in an exposure time of 5 min at 18°C. The protein concentration was varied between 2.9 mg/ml and 11.6 mg/ml. The specimen-to-detector was 2351 mm.

Results and Discussion

The Guinier plots of the net scattering data were linear for all specimens in the range of $0.081 \times 10^{-4} < S^2 < 0.150 \times 10^{-4}$ Å$^{-2}$. There was no evidence of upward curvature at lower values of $S^2$, showing no aggregates in solution. Fig. 1 shows the concentration (c) dependence of the radius of gyration ($R_g$). The $R_g$ value, extrapolated to zero protein concentration, was 60.6 Å. The zero-angle intensity $(I(0)/c)$ versus c plot also was linear and extrapolation of this plot to zero concentration yielded a value of 160 kD as an apparent molecular weight, which was determined relatively using the bovine serum albumin (Fig. 2). This estimated value was close to that of the sum of the molecular weights of actin and S1 used. The $R_g$ value of DHT/MBS-G-actin is 23.6 Å and that of this S1 was 40 Å, consistent with the report by Garrigos et al. Using these values and from the parallel axes theorem, the distance between the centers of gravity of two molecules in the complex was estimated to be about 100 Å. This relatively large value suggests that the actin molecule is crosslinked to the proximal end of the S1 molecule.

References


![Fig. 1 The apparent gyration radius ($R_g$) of monomeric actin-S1 complex as a function of protein concentration (c). As a reference, the data of bovine serum albumin are also plotted.](image)

![Fig. 2 The zero-angle intensity $(I(0)/c)$ versus c plot of monomeric actin-S1 complex. As a reference, the data of bovine serum albumin are also plotted.](image)
MEDIUM-ANGLE X-RAY DIFFRACTION STUDIES OF LIVE FROG SKELETAL MUSCLE DURING ISOMETRIC CONTRACTION

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Introduction

We have been analyzing the structural change of the thin actin filaments in live frog skeletal muscle during isometric contraction using the atomic structures of constituent proteins. To obtain high-angle data, we extended to record the medium-angle X-ray diffraction patterns up to ~1 nm axially. We describe some features of the diffraction pattern in the medium-angle region during contraction.

Experimental

X-ray diffraction patterns from the sartorius muscles of the bullfrog were recorded on a 18x18 cm² imaging plate at BL-15A in the resting state and during contraction at full filament overlap at 15°C. The fiber axis was tilted by ~ 3° to bring the second meridional actin reflection at 1/1.35 nm⁻¹ onto the sphere of reflection. The electric pulse stimulation was applied to the muscle for 1.3 s and this was repeated 20 times at resting intervals of 0.5 min. Diffraction pattern was recorded for 1 s during the plateau phase of isometric tension and summed on the sample plate during repetitive stimulations. The last tension was just less than 80% of the initial tension. Before stimulation, the resting patterns were recorded for the same exposure time. The specimen-to-detector distance was 0.75 m.

Results and Discussion

Fig.1 shows the comparison of the paired X-ray diffraction patterns from the resting and contracting muscle, where the patterns were filtered and the Gaussian background was subtracted to see weaker layer-line reflections in the medium-angle region. During contraction, the thin filament-based reflections are intensified with preserving their distribution along the layer line, similarly to the low-angle layer lines. In the low-angle region, the intensity reversal of the second and third thin filament-based layer lines was clearly seen during contraction at this camera length, as was suggested in earlier experiments. This change has been attributed to the tropomyosin movement in the actin filament on activation. Distinct intensification was also observed at several places on the low lines around the radial distances of 1/4 nm⁻¹, 1/2.3 nm⁻¹ and 1/2 nm⁻¹. These relatively broad reflections are belonging to their principal layer lines. The shift of the second actin meridional reflection at 1/1.35 nm⁻¹ toward the equator is much clearly seen during contraction. About 0.3% increase of this spacing corresponding to the filament elongation was consistent with the shift of the first actin meridional reflection reported in our previous result. Changes in thick filament-based reflections are seen: among the meridional reflections with the 3n orders of the basic 43 nm repeat, the intensities of the 15th and 24th reflections increased, while those of the 18th, 21th and 27th ones decreased during contraction. Their spacing increase was as large as 1-1.5%.

References


Fig.1 Diffraction patterns from a frog skeletal muscle in the resting (a) and during contraction (b).
THE EFFECT OF STRETCH ON THE STRUCTURE OF RIGOR FROG SKELETAL MUSCLES: AN X-RAY DIFFRACTION STUDY

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Introduction

We studied the effects of stretch on the structure of frog skeletal muscles in the rigor state. We found that small but distinct changes of the thin filament structure firmly attached by the myosin heads were caused by stretching, which have not been shown previously. Main results are described below.

Experimental

Sartorius muscles of the bullfrog were rigorized at full filament overlap with iodoacetate treatment for more than 24 hrs at room temperature. The rigor muscle was set in the X-ray chamber and stretched for 5 s by the force of nearly half the maximum active tension with a moving coil-driver. X-ray diffraction patterns from muscles were recorded before stretch and during stretch each for 4.5 s on an imaging plate at BL15A. This was repeated three times and the diffraction patterns were summed on the same plate. The specimen-to-detector distance of 1.55 m was used to cover the first actin meridional reflection.

Results and Discussion

Fig. 1 shows a comparison of the paired X-ray diffraction patterns from the muscle before stretch and during stretch. At first glance, both patterns are quite similar to each other. However, careful inspection indicated that there were several distinct changes which were caused by stretching. The actin meridional reflections at 1/2.7 nm\(^{-1}\) (Fig.2) and the two layer lines at 1/5.1 nm\(^{-1}\) and 1/5.9 nm\(^{-1}\) shifted toward the equator, showing their spacing increase of 0.25% on average with preserving their integrated intensities. The center of gravity of the 5.9 nm layer-line profile moved slightly to the high-radius side but that of the 5.1 nm layer-line profile did not move. The intensity profile of the 2.7 nm meridional reflection changed little. The meridional reflections such as 1/4.8 nm\(^{-1}\), 1/7.2 nm\(^{-1}\) and 1/14.4 nm\(^{-1}\) which originally arise from the myosin filament repeat shifted toward the equator; their spacing increase was 0.18% on average. The integrated intensity of the 14.4 nm reflection increased by about 25%, while those of the other two reflections less increased, in contrast with the change taking place in the active muscle during stretch. Thus, stretching the rigor muscle causes the elongation of the thin and thick filaments by similar amount to that observed in the active muscle. There is relatively large intensity increase of the 14.4 nm meridional reflection, which indicates that the conformational change of the attached myosin heads may be caused by stretching.

References

It is well-known that GroEL from E. coli belongs to the heat shock-protein Hsp60 family. This GroEL functions with GroES in an ATP-dependent manner during the folding and assembly of protein substrates in vivo. The GroEL chaperones the refolding of a number of denatured enzymes with or without ATP in vitro. The GroEL consists of 14 equal subunits, whose molecular weight is $57.3 \times 10^3$ as calculated from the amino acid sequence.

The molecular architecture of native GroEL has been studied by solution X-ray scattering\(^1\). The radius of gyration for the native molecule was estimated to be 66.0 Å in 50mM Tris-HCl, 100mM KCl at pH 7.5 and 25°C. The maximum dimension was estimated to be 170 Å, based on the pair distance distribution function. Results of the model analysis using small sphere model ($r = 6$ Å) show that the shape of GroEL is like a cylinder of which radius and height are 68 Å and 150.7 Å, respectively. The whole structure of GroEL is similar to a crystal structure ($\Phi = 137$ Å, $h = 146$ Å) shown by K. Braig et al \(^2\). However, the central penetrating hole through GroEL was not confirmed in the best-fit structure by small sphere model. In stead of a penetrating hole, there were two caves on both end of the heptamers. The radius of the cave was one third (23 Å) of the cylinder radius and the depth was one sixth (25 Å) of the cylinder height.

We monitored a static solution X-ray scattering of GroEL, binding to ATP analog (AMP-PNP) in 50mM Tris-HCl, 20mM Mg\(^{2+}\), 100mM KCl at pH 7.5 and 25°C. The $R_g$ of GroEL in the presence of the ATP analog decreased about 6% in its absence. One can expect that this change would be due to an alternation in the inside structure of GroEL. However, the scattering patterns of the small sphere model that diminished the central cave were not coincident with the measured pattern. Thus, the external shape of GroEL model should be changed. When ATP was bound to GroEL, the radius of the cylinder was smaller than that of GroEL without ATP, while the height of GroEL remained constant with and without ATP.

The kinetics of 20mM Mg\(^{2+}\)-ATP binding to 4.5 µM GroEL oligomer was analyzed by using stopped flow X-ray scattering in 50mM Tris-HCl, 100mM KCl at pH 7.5 and 25°C. The time course of this structure change is shown in the Figure. The ordinate displays integral values of scattering intensity from 260th to 300th channel. The decrease in integral values of scattering intensity indicates that the structure of GroEL would change in some part in Guinier region. The rate of the structure change was estimated to be about 0.02 s\(^{-1}\).
PHASE TRANSITION BEHAVIOR OF SELF-ASSEMBLED GLYCEROPHOSPHOLIPID MIXTURE STUDIED BY X-RAY DIFFRACTION

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Introduction

Only when some special glycerophospholipid is dispersed in pure water, self assembling occurs, and only one gigantic aggregate is produced. Besides, when the self assembled lipid is mixed with other non-assembled lipid, all the lipids present self-assemble together, and only one gigantic aggregate is produced. When these two types of aggregates are studied by differential scanning calorimetry (DSC), it is impossible to distinguish them, in spite of much difference of molecular composition. In this paper, how to distinguish them by X-ray diffractometry will be reported.

Experimental

Self assembled sample is put into a small quartz vessel, and the vessel is sealed in an aluminum pan with holes on both bottom and top, and the pan is set in a DSC apparatus with holes, in which X-ray beam can pass through via the sample to a detector. Temperature dependent phase transition behavior is studied by DSC and X-ray diffractometry at the same time by using the beam line 15A of the Photon Factory, KEK Japan.

Results and Discussion

In Fig. 1, results of the mixture of DPPA and DPPC (molar ratio of 0.01:0.99) are shown: where DPPA (dipalmitoylphosphatidic acid) is a self assembling lipid, and DPPC (dipamitoylphosphatidylcholine) is a non assembling lipid. In this case, only one molecule of DPPA controls one-sidedly all the other 99 molecules of DPPC to build only one gigantic aggregate. DSC curve and temperature dependences of three outer X-ray diffraction lines, all of them reflect main phase transition of the sample, shows exactly the same manner as that of pure DPPA. However, the innermost X-ray diffraction line changes independent of main phase transition, which implies that alkyl chains of the aggregate exhibit more complicated movement with temperature.
AN X-RAY DIFFRACTION STUDY ON UTERINE MUSCLE OF PREGNANT RATS

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Introduction

Uterus is a characteristic organ which undergoes reversible and extensive changes during pregnancy. Hormonal environment and mechanical stimuli from growing fetuses are considered to cause these changes. In the previous (91-225) and present proposal, using imaging plates, we have succeeded to record two-dimensional X-ray diffraction patterns from intact smooth muscles at physiological conditions. The patterns from taenia coli of guinea pigs and anococcygeus of rats showed dynamic structural changes in its contractile elements with contraction. It is suggested that number of myosin filaments may increase during contraction of rat anococcygeus muscle but not guinea pig taenia coli. In the present study we tried to elucidate the structure of rat uterine muscle.

Materials and Methods

Female rats of Wistar-Imamichi strain (180-250 g) were used. The day 0 of pregnancy was determined when sperm is observed in the smear of vaginal contents after mating. In almost all pregnant rats, delivery occurs on the 21st day of pregnancy. On the 21st day of pregnancy before the beginning of delivery, a 15x30-mm sheet of uterine tissue was excised from corpus uteri. In vivo extension was kept by splinting the tissue with a 30-mm square silicone-rubber sheet. As soon as excised, the tissue was soaked in a 37°C physiological saline bath equilibrated with bubbles of 95% O₂ + 5% CO₂. In the bath, endometrium and cricoid muscle were stripped off on the silicone-rubber splint. Remaining tissue is a sheet of longitudinal muscle cells aligned well on a serous membrane. The sheet is about 200 μm thick. In the preliminary experiment of the present study, we found that the longitudinal muscle sheet isolated from cricoid muscle develops tension of 1.4-3.4 N/cm², which is somewhat smaller than that developed by an intact uterine tissue (4.6-5.7 N/cm² longitudinal muscle sheet).

The muscle sheet with the silicone-rubber splint was set vertically on the X-ray beam of BL-15A. The 37°C physiological saline was constantly pouring over the muscle. A 5-mm square hole at the center of the splint allowed the beam to pass through the muscle sheet. Diffraction patterns were recorded on Fuji imaging plates with 60 s exposure.

Results and Discussion

The diffraction pattern showed the 3rd, 5th and higher orders of reflections from collagen. The 4th order reflection was also clearly observed. These reflections were observed as wide arcs across the meridian. The width of the arc narrowed with a longitudinal stretch of the muscle sheet. The 5.9-nm actin layer-line was observed. Its intensity distribution seemed to be less dependent on stretching of the specimen. On the equator, a broad peak probably due to arrays of thin filaments was observed. No reflection or layer line from myosin filament was resolved.

These results indicated that in the present specimen, aligned myosin filaments with regular arrangement of myosin projections are not considerable in density.

References

THE EFFECT OF SUCCESSIVE STIMULATION OF THE MUSCLE ON THE TIME LAG BETWEEN X-RAY INTENSITY CHANGE AND TENSION DEVELOPMENT.

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Introduction

On contraction of the muscles, marked changes in X-ray reflections are observed, suggesting that conformational changes of contractile molecules and the movement of myosin heads during muscle contraction. However, time resolved X-ray diffraction studies have been shown that these intensity changes reach their maximums before the peak of tension. The time lag between the intensity changes and the peak tension may give us the information about conformational changes of actin and myosin filaments to develop tension.

Materials and Methods

The experiment was done at the beam line 15A, using a small-angle X-ray diffractometer. Sartorius muscles of the bullfrog were continuously perfused with the Ringer solution (115 mM NaCl, 2.5 mM KCl, 1.8 mM CaCl₂, pH 7.2 at 13°C), and were stimulated by 5 successive stimuli at an interval of 80 ms during which the following twitches started while tension was still being exerted by the muscles. Contractions were repeated 10 times for each muscle at a 20 s interval.

Results & Discussion

The time needed to the peak tension after the onset of stimulation (Ti) and the amount of peak tension (Fi) depend on the number of twitch cycle. As the number of twitch cycle increases, Ti decreases and Fi increases. But both Ti and Fi become constant at the twitch cycles more than three times under the present experimental condition. The maximum effects of successive twitches on Ti and Fi are seen at the 3rd twitch.

The intensity of the 14.3 and 21.5 nm reflections measured with a 5 ms time resolution are shown in Fig.1, together with the isometric tension record. The time needed to peaks of the 14.3 nm intensity change after the onset of stimulation (Ti) also becomes shorter by successive twitches as in the case of Ti. On the other hand, the 21.5 nm intensity starts to decrease at the 1st twitch and remains low without appreciable recovery of the intensity while contractions continue, suggesting that the myosin heads once moved from their resting positions at the 1st twitch never return to their initial positions during successive twitches.

Both Ti and Ti decrease, but the difference, Ti-Ti is fairly constant at any twitch cycle, suggesting that the time for movement of myosin heads from thick to thin filaments is negligibly small.

Fig.1 The 1st stimulus is given at t=0, and the times when the muscle is stimulated are shown by the vertical lines. Both intensity and tension are expressed relative to the peak value of each change. Each data point represents a mean value of 6 different muscles. (): 14.3 nm. (): 21.5 nm intensity.
X-RAY DIFFRACTION STUDIES OF THE GLYCERINATED SINGLE SKELETAL MUSCLE FIBRES IMMEDIATELY AFTER THE HYDROLYSIS OF A NEAR STOICHIOMETRIC AMOUNT OF PHOTO-RELEASED ATP

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When a stoichiometric amount of ATP is photo-produced in muscle fibre, the unloaded fiber shortens about 10 nm per half sarcomere, the distance which is comparable to the tilting of myosin head [1]. Our previous studies indicated that the crossbridge configurations of the fibres thus shortened were different from those of rigor fibres [2]. In the present study we investigated in more detail the crossbridge configuration of the muscle fibres similarly treated by use of two dimensional X-ray diffraction technique.

The photolysis of caged ATP was made by a light flash produced with a Xe-lamp (Eagle co.). X-ray diffraction of muscle fibres was obtained by use of an X-ray beam emitted from a synchrotron (Photon Factory, Tsukuba) and recorded on imaging plates. A bundle of about ten single glycerinated fibres prepared from rabbit psoas muscle was mounted by connecting each fibre end to the extension of a force transducer and a servomotor with T-clips. The sarcomere length of fibres was set at 2.5 μm. The preparation originally in relaxed state was put in a rigor solution. After rigor tension was fully developed it was transferred to a caged ATP solution. Then the preparation was put in air and light-flashed. The fibers produced tension (about 1/3 P₀) following the photogeneration of about 110 μM ATP. At 250 ms after the light flash, X-ray exposure was started and stopped at 3 s later. Then immediately the preparation was put in relaxing solution. This cycle was repeated 20 times and all the data accumulated to improve the resolution of the diffraction patterns.

The equatorial diffractions of the fibres following the photogeneration of 110 μM ATP showed only small changes indicating almost all the crossbridges are attached with thin filament and disordering of the filament lattice is minimal [3]. On the other hand their meridional diffraction patterns showed significant changes from those of the rigor fibres; i.e., compared with the diffraction pattern of rigor fibres the 5.9 nm actin layer line became weak and shifted away from the center (Fig. 1), the 14.3 nm and 21.5 nm myosin layer lines became weak.

The crossbridges in the fibres photoactivated as above are not cycling but may be frozen in force producing states. The above results indicate that these myosin crossbridges remain attached with thin filaments but are in configurations different from those of rigor states.

References

Fig. 1. The intensity distributions along the 5.9 nm actin layer line. Solid circles and open triangles respectively represent the data points before and after the caged-ATP flash.
TIME-RESOLVED SAXS STUDIES OF BLOCK COPOLYMERS UNDER LARGE OSCILLATORY SHEAR DEFORMATION

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Introduction

Rheo-optical studies are conducted on a sphere-forming block copolymer. Small-angle X-ray scattering (SAXS) is detected with a stage-mounted Imaging Plate (IP) detector recently developed at the Photon Factory. X-ray data are simultaneously obtained with stress measurements on large-amplitude oscillatory shear deformation, with the purpose to elucidate a relationship between macroscopic properties of the systems and their mesoscopic structure as revealed by SAXS.

Experimental

Figure 1 shows the schematic diagram of the optical system of SAXS apparatus with an Imaging Plate (IP) X-ray detector mounted on a Y-Z stage and a hydraulic sample deformation device\textsuperscript{1}) that are controlled by a computer. The direction of the oscillatory shear deformation is the Oy axis. The X-ray beam is irradiated along the Ox axis. It is also irradiated along Oz axis by rotating the sample by 90° around the Oy axis. There is a 100mm x 100mm square aperture for the scattered X-rays in front of the IP stage. The size of the IP is 400mm x 200mm, which is used by dividing into eight sections. Each section is moved to the position of the aperture in turn as shown in the figure and the X-ray pattern is recorded. The IP stage and the magnet shutter move synchronously at any phase of the strain and are controlled by a computer. The X-ray data are detected simultaneously with the analog data such as stress and strain. The studied sample is a polystyrene-block-poly(ethylene-alt-propylene) copolymer (number-average molecular weight $M_n=3.4 \times 10^4$, heterogeneity index $M_w/M_n=1.3$ where $M_w$ is weight-average molecular weight, and the PS volume fraction in the copolymer is 0.103) having spherical micro domains composed of polystyrene block chains (PS) in a matrix of poly(ethylene-alt-propylene) block chains (PEP). The amplitude of the strain is 50% and the frequency is 0.0944 rad/s.

Results and Discussion

The results indicate that the spheres are packed in a body-centered-cubic (bcc) lattice and that the shear deformation induces a preferential orientation of (110) lattice planes parallel to Oxy plane. Figure 2 shows the deformed bcc lattice (a) and SAXS pattern (b) at a maximum strain at tenth cycle. The angle of peak position $\psi$ is defined as shown in figure 2(b). Figure 2(c) shows the change of $\psi$ (solid circle) obtained by exposing for 1 sec at eight phases of a half cycle, and the result of fitting (solid line) these data by a sinusoidal curve. In this figure the stress and the strain are also shown. The dynamic lattice deformation is in-phase with the macroscopic strain, but lags behind the macroscopic stress.

Reference

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DECOMPOSITION STRUCTURE OF Al-Li ALLOYS IN THE EARLY STAGE STUDIED BY SR-SAXS/100 SCATTERING PROFILE ANALYSIS

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Introduction
The decomposition process of Al-Li alloys is of particular interest because the decomposition path has not been yet fully understood. According to several researches, the system should order homogeneously first, and then the secondary spinodal decomposition occurs. But naturally, there arises a question whether one can imagine a 'homogeneously ordered' state for an off-stoichiometric sample.

The interesting point is whether the domain size of initial ordering stage is smaller or larger than the spinodal wavelength in the secondary spinodal decomposition. For this purpose, we modelled the 100 profile in the similar formulation as used in SAS, and discussed the effect of sublattice correlation among the neighboring precipitates.

Formulation of the SAS/100 intensity
After the compositional modulation occurs to form precipitates, the system can be described in terms of the particle systems consisting of ordered precipitates dispersed in the disordered matrix. If the long-range ordered state is achieved in the initial stage of ordering, one can expect an interference effect in 100 profile. We formulated the 100 intensity by two-phase model. The SAS intensity can be written as:

\[ I(\mathbf{k}) = A \rho \beta^2 (kR) \left[ 1 - \int (1 - P(r)) \sin(\mathbf{k} \cdot r) dr \right] \]

The 100 scattering intensity can be written as:

\[ I(\mathbf{k}) = S \rho \beta^2 (kR) \left[ 1 + \int P(r) \phi(r) \sin(\mathbf{k} \cdot r) dr \right] \]

where the scattering vector, \( \mathbf{k} \), is the sum of the vector to the 100 reciprocal point, \( \mathbf{k}_0 \), and the deviation from the point, \( \mathbf{k}' \). \( \mathbf{k}' \) corresponds to the scattering vector \( \mathbf{k} \) for SAS. \( \phi(1), \rho, \beta \) are the form factor, LRO of the precipitates, pair distribution function of the particles, and the sublattice correlation function of the precipitates respectively. When we take the correlation length for \( \phi(1) \), \( g \), larger than the interparticle distance, remarkable increase in the intensity at 100 is observed due to the large coherent 100 domain. On the contrary, the 100 profile is just the sum of the individual particle scattering if \( g \) is less than the interparticle distance.

Results and Discussions
The scattering intensities obtained for Al-11.8Li aged at 393K are shown in Fig. 1. It is clearly seen that no interference effect is observed in the very early stage of phase decomposition. It has been observed that the Guinier radius for 100 is slightly larger than that for SAS, but not so large as the interparticle distance. This results agrees with the simulation results, which suggest no LRO state prior to the phase separation.

References

Fig. 1 100 scattering profile for Al-11.8Li
USE OF XENON-GAS PSPC FOR THE IMPROVEMENT OF SIGNAL-TO-NOISE RATIO IN STOPPED-FLOW X-RAY SOLUTION SCATTERING

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We have reported the application of synchrotron small-angle X-ray scattering (SAXS) to the study of protein folding to investigate a globularization process during the folding [1,2]. It has been shown that this process occurs mainly at an early step within a subsecond time interval during the folding in bovine carbonic anhydrase and phosphoglycerate kinase. However, the main difficulty in the use of the SAXS stopped-flow technique for monitoring the fast protein globularization was the low signal-to-noise ratio. This circumstance strongly limits the analysis of the kinetic curves to obtain the amplitudes and rate constants of the kinetic processes. To overcome the difficulty, one has to make a large number of accumulations, which demands a lot of protein sample.

In this study, we show the remarkable improvement in the signal-to-noise ratio in the SAXS stopped-flow experiments attained by exchange of the gas in the PSPC detector from argon to xenon. The gas exchange increases the sensitivity of the detector more than three times [3], so that the signal-to-noise ratio increases remarkably in the same experimental condition. Figure 1 shows the globularization process during refolding of bovine carbonic anhydrase induced by concentration jump of urea from 8.5 M to 4 M at pH 8.0 and 15°C, and monitored by the SAXS stopped-flow technique with (A) argon- and (B) xenon-gas PSPC detector in the same experimental condition. One can see that the xenon-gas PSPC detector allows us to obtain a good resolution of two fast kinetic processes with quite different amplitudes during the first 0.5 s of refolding, while the resolutions is much poorer when we use the argon-gas detector. Thus, the use of the xenon-gas PSPC strongly stimulates the application of the SAXS stopped-flow technique to monitoring very fast protein folding processes in a millisecond time interval.


Fig.1. Refolding kinetics of bovine carbonic anhydrase monitored by the SAXS stopped-flow technique with (A) argon- and (B) xenon-gas PSPC detector. Concentration of the protein was 7 mg/ml, and the number of accumulation was 60.
INTENSITIES OF EQUATORIAL X-RAY REFLECTIONS FROM SHORTENING MUSCLE FIBERS AT VARIED ACTIVATION LEVELS

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Introduction

The intensity ratio of the two equatorial X-ray reflections of skeletal muscle \(I_{1,0}/I_{1,1}\) is believed to reflect the number of myosin head attached to or in the vicinity of the thin filament. It is known that this intensity ratio decreases as the muscle is activated by increasing intracellular calcium\(^1\), but does not increase during shortening of fully activated muscle until the load is reduced to less than 20% of isometric tension \(P_0\)^2,3). To test whether the intensity ratio \(I_{1,0}/I_{1,1}\) is also insensitive to shortening velocity at a submaximal activation level, we made a time-resolved measurement of the equatorial reflection intensities of skinned rabbit skeletal muscle fibers shortening at a submaximal concentration of activating calcium.

Materials and Methods

Bundles of skinned rabbit psoas fibers were mounted on the experimental apparatus. They were activated by raising the calcium concentration to \(pCa \approx 4\) (fully activated) or \(pCa \approx 6\) (submaximally activated) at \(\sim5^\circ C\). When isometric tension reached a plateau, the fibers were allowed to shorten under a load of 0.5 \(P_0\) or 0.1 \(P_0\). The time resolution of the X-ray recording was 20 ms.

Results and Discussion

The intensity ratios \(I_{1,0}/I_{1,1}\) measured for the four combinations of the experimental conditions (activation level and load) are summarized in Table 1. Upon full activation, the intensity ratio decreased by \(\sim40\%\), as has been reported earlier\(^1\). After the start of shortening at 0.1 \(P_0\), the intensity ratio increased by \(\sim16\%\), and this accounted for \(\sim23\%\) of the total change upon activation (transition from resting to isometric contraction). Shortening at 0.5 \(P_0\) did not affect much the intensity ratio. In submaximally activated fibers, shortening at 0.1 \(P_0\) increased the intensity ratio by \(\sim12\%\). This value accounted for \(\sim27\%\) of the total change upon activation, since the intensity ratio decreased only \(\sim25\%\) upon submaximal activation. The intensity ratio was again insensitive to shortening at 0.5 \(P_0\). The present results confirms the previous report\(^3\) that the intensity ratio changes toward its resting value during shortening at light loads. Further, the present results raise a possibility that shortening affects the activation level of contracting fibers, especially at submaximal calcium concentrations.

References


Table 1 Equatorial intensity ratio \(I_{1,0}/I_{1,1}\) under various conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>resting</th>
<th>isometric</th>
<th>shortening</th>
</tr>
</thead>
<tbody>
<tr>
<td>full active 0.1(P_0)</td>
<td>1.05</td>
<td>0.62</td>
<td>0.72</td>
</tr>
<tr>
<td>full active 0.5(P_0)</td>
<td>0.92</td>
<td>0.62</td>
<td>0.65</td>
</tr>
<tr>
<td>submaximal 0.1(P_0)</td>
<td>1.18</td>
<td>0.89</td>
<td>0.97</td>
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<tr>
<td>submaximal 0.5(P_0)</td>
<td>1.25</td>
<td>0.99</td>
<td>1.02</td>
</tr>
</tbody>
</table>
SMALL-ANGLE X-RAY DIFFRACTION STUDIES OF A MOLLUSCAN SMOOTH MUSCLE USING A LONG CAMERA LENGTH

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In a previous work, X-ray diffraction patterns from the anterior byssus retractor muscle (ABRM) of Mytilus edulis were recorded with a short camera length of 60 cm in order to observe layer line reflections in both small- and medium-angle regions, from the equator to the 6.9 Å layer line, using an imaging plate of dimensions 200x200 mm. From changes in the axial period of strong meridional reflections in the medium angle region, elongations of the thin and thick filaments were estimated to be 0.48, and 0.33%, respectively, in the ABRM that isometrically held a tension of 12.2 kglm⁻². However, it was difficult to measure changes in the axial period of the off-meridional 59, and 51 Å layer lines accurately in the X-ray patterns recorded at 60 cm from the specimen. Changes in the axial distance of those layer lines were smaller than one pixel step, 0.1 mm, at which the intensity data were read from the imaging plate. Moreover, overlap between the very strong 59 Å, and the weak 51 Å layer line reflections makes it difficult to locate the centre of the latter reflection.

In this work, the specimen was set away from the focusing point of the X-ray beam to the utmost limit, 220 cm, in the point-focusing camera at BL-15A in order to effect separation between layer line reflections. For activating the thin filaments almost over the total length, the specimen was fixed at a natural length at which the thin filaments fully overlapped the thick filaments, and stimulated by a strong acetylcholine solution (10⁻² M). Small angle patterns were taken from the same part of a muscle bundle in the contracting, resting, and catch states using a fixed camera length, and 15 s X-ray exposure.

X-ray patterns from a specimen in the resting, and contracting states are compared in Fig. 1. The specimen maintained a tension of 12.2 kglm⁻² during the X-ray exposure in the contracting state. The 59, and 51 Å layer lines move toward the equator during contraction by 3.0, and 2.6 pixel steps, respectively, satisfactorily long distances that can be measured accurately. Elongations of the pitch of the left-handed (59 Å in the pitch), and right-handed (51 Å in the pitch) helices are estimated from those axial movements of the layer lines to be 0.54, and 0.42%, respectively. The inequality in those changes of the pitch indicates an unwinding of the left-handed helix. Increase in the axial period of actin, and decrease in the azimuthal angle between adjacent actins on the left-handed helix are calculated at 0.47%, and 6.7 min from the increases in the pitch of the two helices. The former agrees well with the measured value, 0.48%.


Fig. 1.
NEW RIPPLE PHASE APPEARING IN DIMYRISTOYLPHOSPHATIDYLCHOLINE–CHOLESTEROL MULTIBILAYER VESICLES.

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Introduction
In fully hydrated Phosphatidylcholine multibilayers it has been reported the phase sequence of $L_c$, $L_d$, $P_{d'}$, and $L_a$ from low to high temperature. In the $P_{d'}$ phase undulated bilayer structure with periodicity of 12–14 nm has been observed. In our recent study using synchrotron X-ray diffraction, we characterized the new liquid crystalline phase appearing between the $P_{d'}$ phase and the $L_a$ phase in dilaurylphosphatidylcholine (DLPC). In this study we report new ripple phase in dimyristoylphosphatidylcholine (DMPC) with cholesterol between the $P_{d'}$ phase and the $L_a$ phase.

Experimental
Fully hydrated multibilayers of DMPC with and without cholesterol were prepared by the conventional methods. DMPC and cholesterol were obtained from Avanti Polar Lipid Inc. (Birmingham, AL, USA) and Sigma chemical Co. (St. Louis, MO), respectively. X-ray diffraction measurements were carried out at the BL-15A station. Time resolved diffraction profiles were recorded with a PSPC (Rigaku Denki).

Results and Discussion
Figure 1 displays temperature change of the X-ray diffraction profile of fully hydrated DMPC with 2.0 mol% cholesterol during heating run. These were successively recorded during slow temperature scanning at the rate of 0.05°C/min. Below the main transition temperature ($T_m$) of 23.9°C, the (01) peak due to the ripple periodicity appears in the range of 0.04–0.08 nm$^{-1}$ of $2 \sin \theta / \lambda$. The ripple periodicity observed just below the main transition temperature is above 20 nm (0.05 nm$^{-1}$) which is larger than that in the $P_{d'}$ phase. To present temperature change of the (01) peak, contour–line–plot of intensity in ($2 \sin \theta / \lambda$)–temperature space is drawn in figure 2. Below 23.54°C the (01) peak due to the normal ripple structure with periodicity of 13.6 nm is observed. This (01) peak intensity decreases from 23.3°C to 23.54°C indicating disappearance of the normal ripple structure ($P_{d'}$). Instead of this (01) peak, another peak is produced at smaller angle region. This peak is due to the another ripple structure with long periodicity. Intensity of this peak is higher than that in the normal ripple structure and its ripple periodicity has strong temperature dependence. (17.5 nm at 23.46°C and 22.5 nm at 23.64°C). This long ripple structure is observed in the narrow temperature range of 0.25°C.

In DSC experiment there observed a shoulder at 0.3°C lower than the main transition peak. This corresponds to the transition between the normal ripple structure ($P_{d'}$) and the long ripple structure. Thus, we considered this long ripple structure as the new ripple phase named $P_{d'}$ (long). DSC experiments suggest that the hydrocarbon chain partially melts in the $P_{d'}$ to the $P_{d'}$ (long) phase transition. This is similar to the case of the $L_x$ phase which takes place between $P_{d'}$ and $L_a$ in fully hydrated DLPC. Because hydrocarbon chain melting is hindered in the $L_x$ phase. These facts suggest that order–disorder phase transition of phosphatidylcholine proceeds stepwise.

References

Fig. 1 X-ray diffraction profiles of DMPC with 2.0 mol% cholesterol in heating through the main transition.

Fig. 2 Contour–line–plot of the intensities of DMPC with 2.0 mol% cholesterol in heating through the main transition.
COMPLEX FORMATION BETWEEN PHOSPHATIDYLCHOLINE AND DIACYLGLYCEROL

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Introduction
The phase diagram of fully hydrated binary mixtures of dipalmitoylphosphatidylcholine (DPPC) with 1,2-dipalmitoylglycerol (DPG) identifies regions where stoichiometric complexes of 1:1 and 1:2 DPPC:DPG, respectively, are formed. The structural parameters of the 1:1 complex in the presence of pure DPPC have been determined by synchrotron low-angle and static X-ray diffraction methods. Structural changes upon transitions through phase boundaries were correlated with enthalpy changes observed by differential scanning calorimetry (DSC) in mixtures of DPPC with 5, 7.5, 10 and 20 mol% DPG dispersed in excess water.

Results
Phase separation of a complex in gel phase could be detected by calorimetry in the mixture containing 5 mol% DPG but was not detectable by synchrotron low-angle X-ray diffraction. Static X-ray measurements provide evidence of phase separation particularly in the reflections indexing chain packing. In the mixture containing 7.5 mol% DPG, two distinct lamellar repeat spacings could be seen in the temperature range from 25°C to 34°C. A lamellar spacing of about 6.6 nm was assigned to pure gel phase DPPC since the change in the spacing corresponds with thermal transition of the pure phospholipid and a longer repeat spacing of about 7.2 nm was assigned to domains of the 1:1 complex of DPPC:DPG. In the temperature range from 34°C to 42°C, i.e., in the region of coexistence of the ripple phase of DPPC and the gel phase of the complex a single rather broad lamellar reflection appears due to superposition of two reflections of DPPC and the complex; the lamellar spacing of DPPC in the ripple phase is similar to that of the gel phase of complex. In the coexistence region of the liquid-crystalline phase of DPPC and the gel phase of complex (42 ~ 48°C), the lamellar reflections of the both phases are present. The fluidus boundary lies between the coexistence region and the fluid region. In the fluid region (48 ~55°C), the gel state of complex persists up to the fluidus boundary whereupon the liquid-crystalline state of complex replaces the gel state of the complex. This indicates that the complex is also immiscible with DPPC even above the fluidus boundary at least in the temperature range close to the phase boundary. For mixtures comprising 10 and 20 mol% DPG in DPPC, complex formation is clearly detectable in both the gel region and the coexistence region by X-ray diffraction. A comparison of the electron density profiles reconstructed from the lamellar reflections of DPPC and the 1:1 complex of DPPC:DPG is shown in Fig. 1. This indicates that the thickness of both the bilayer and the water layer of the gel phase complex are greater than those of the respective thickness of gel phase DPPC.

Fig. 1. Electron density distributions in gel phase DPPC:DPG and DPPC

References
Image Distortion of TV-type X-ray Detector and Imaging Plate

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Introduction

We have developed a TV-type X-ray detector which is intended for real-time measurements and for time-resolved measurements (in a few tens of millisecond time resolution) of X-ray diffraction patterns. This detector consists of a 9-inch Be-windowed image intensifier, an optical lens, a charge coupled device (CCD) and a data acquisition system. The main role of the image intensifier is to obtain the sufficient signal gain and thereby high signal-to-noise ratio of the X-ray image when the X-ray image (220 mm\(^2\)) is demagnified into the small format of the CCD (12 mm \(\times\) 12.2 mm). However, the image intensifier has drawbacks regarding an image distortion and non-uniformity of response: A convex detection surface of the image intensifier leads to the spatial distortion, and the electrostatic field of the image intensifier is susceptible to the small change of the surrounding magnetic field. Therefore, software for the correction of the spatial distortion and the non-uniformity of response is required when this detector is applied to X-ray diffraction experiments. Prior to the development of the software, the image distortion of the detector was quantitatively measured and compared to that of the IP.

Experimental and Analysis

A brass grid mask which has holes of 0.5 mm\(^2\), 4 mm apart from each other was attached in front of the TV-type X-ray detector and the IP. The brass grid mask was made by numerically controlled machine. The error of the hole spacing was less than 0.02 mm. An radioisotope \(^{241}\)Am (11.1 GBq) was placed 0.6 m from the detectors. The exposed IP was read by BAS2000 system with an 100 pm \(\times\) 100 pm pixel size.

The peak positions of the holes in the image were determined by calculating the center of gravity of the peaks. Then, the distances between two neighboring peaks were calculated and histogramed.

Results and Discussion

Fig. 1 shows the grid mask patterns which were recorded by the TV-type X-ray detector. Fig. 2(a) shows the histogram of the distances between two neighboring peaks in different concentric regions in the image by the TV-type X-ray detector. In the case of the IP, the histograms (Fig. 2(b)) were made along the X (laser scanning direction) and Y (IP scanning direction) axis, separately. It can be seen that going from the central to the peripheral region of the TV-type X-ray detector, the pixel size decreases and its variation increases gradually. In the case of the IP, the pixel size was 100.2 \(\mu\)m and 99.2 \(\mu\)m, along the X and Y direction, respectively. The pixel non-squareness was about 1.0 %.

Figure 1: The grid mask pattern which was obtained by TV-type X-ray detector.

Figure 2: The histograms of the distances between two neighboring peaks.
ANALYSIS OF THE FOLDING INTERMEDIATE OF ASPERGILLUS NIGER ACID PROTEINASE A USING pH JUMP METHOD

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Introduction

Proteinase A [EC 3.4.23.19] secreted by the fungus Aspergillus niger var. macrosporus is a non-pepsin-type acid proteinase.1) It is distinctly different from ordinary pepsin-type aspartic proteinases in primary structure, substrate specificity, and reactivity to inhibitors. The enzyme consists of two polypeptide chains, a light chain of 39 residues and a heavy chain of 173 residues.2) They are bound non-covalently to each other. Three-dimensional structure of proteinase A are not known. From the pH–titration analyses by NMR, CD, and HPLC (gel filtration) measurements, it was found that the enzyme was unfolded around neutral pH with the concomitant dissociation of the two chains. The midpoint pH of unfolding were 6.1 for CD and HPLC, and 6.5 for NMR and enzymatic activity assay. The difference between these midpoint values were independent of sample concentration, and can be explained by supposing an intermediate form during the unfolding.

In order to elucidate the unfolding profiles of proteinase A in more detail, the conformation and molecular shape of the enzyme were studied at various pHs using small angle X-ray scattering (SAXS).

Experimental

Proteinase A was purified by column chromatography from the culture filtrate of A. niger. The sample was prepared by dissolving in 50 mM buffer, 100 mM NaCl at the concentration of 5 mg/ml. The buffers used were Na acetate (pH 4.1), Na MES (pH 6.2, 6.5, 6.75), and Na HEPES (pH 7.0). X-ray solution scattering static measurements were performed at BL15A small-angle installation. The temperature of the apparatus was kept at 35°C. The conformation of proteinase A was analyzed from Kratky plot. Rs (radius of gyration) at each pH were calculated from Guinier plot.

Results and Discussion

Kratky plot of SAXS data at pH 4.1 showed that the enzyme had native conformation, and the plots at pH 6.4 and above showed that the enzyme was in the unfolded state. This is consistent with the results by NMR and CD measurements. The Kratky plot at pH 6.0 and 6.25 showed intermediate pattern between the curves in the native state and in the unfolded state, and was quite similar to the pattern in the molten-globule state.3) The Guinier plot at each pH showed that the Rs values increased along with the pH values. These Rs values were almost in agreement with those obtained by P(r)s (pair distance distribution function).

From the previous study of pH–titration analyses, apparent Hill coefficient of the unfolding was about 4, which indicated the possibility that simultaneous deprotonation of carboxyl group and the consequent electrostatic repulsion in the molecule might cause the dissociation of the two polypeptide chains. The results that the Rs increased after unfolding confirmed this hypothesis.

It had been suggested that the dissociation of two chains and the unfolding of each chain had occurred subsequently. In order to elucidate the intermediate process of unfolding more precisely, pH-jump stopped flow kinetics experiments are in progress.

We thank Dr. Kazumoto Kimura and Dr. Kaoru Ichimura at Dokkyo University School of Medicine for their help to analyse SAXS data.

References

Characteristics in the Static and Kinetic SAXS Spectra of the Calmodulin-Mellitin-Ca\(^{2+}\) and Calmodulin-TNS-Ca\(^{2+}\) Systems

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Introduction
Calmodulin (CaM) is one of the typical Ca\(^{2+}\)-binding proteins, which regulates enzyme activity in many intracellular Ca\(^{2+}\)-dependent processes. Small polypeptide of melittin (ME) has been shown to inhibit CaM binding to target enzymes in a Ca\(^{2+}\)-dependent manner. The hydrophobic dye, TNS, widely used as a probe of hydrophobic interactions of proteins, also exhibits the calcium dependent interaction with calmodulin. We have performed the stopped-flow experiments on the Ca\(^{2+}\)-dependent interaction of CaM with ME and TNS with detections of fluorescence and CD changes of UV light and clarified that the binding mechanisms of calmodulin are quite different against ME and TNS. In the present studies, the characteristics of the static and kinetic small angle X-ray scattering (SAXS) spectra for the CaM-ME-Ca\(^{2+}\) and CaM-TNS-Ca\(^{2+}\) systems were examined.

Experimental
The static and kinetic experiments of SAXS were carried out at BL-15A. CaM was purified from fresh bovine brain according to the procedure using the hydrophobic interaction gel chromatography. ME was purchased from Sigma and purified by gel chromatography before use. TNS, recrystallized twice in ethanol, was used.

Results and Discussion
The pair distance distribution functions, P(r) for the CaM-ME and CaM-TNS complexes shown in Fig.1 mean that the CaM-ME complex formed rather spherical structure, while the CaM-TNS complex remains as a dumbbell structure as that of CaM alone. Fig.2 shows the time domains of the square of radius of gyration, \(R_g\), for the dissociation process of the CaM-ME (a) and CaM-TNS (b) complexes, respectively. From the present works and our previous works using CD and fluorescence detections, the details of the complex formation mechanism for the CaM-ME system, in which both of N and C-terminal domains of CaM participated, was able to be discussed and it was clarified to be rather complicated than those CaM-TNS systems, where only N terminal of CaM was participated in the complex formation.
The Structural Study of the GroEL Bound the Denatured Rhodanese

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**Introduction**

The chaperonin GroEL from *E. Coli* is one of the molecular chaperones. It has shown to facilitate *in vitro* folding of the rhodanese (Rho), a monomeric bovine liver enzyme whose molecular weight is 33kDa.\(^\text{1)}\) In this folding process, it has been known that the GroEL arrests denatured rhodanese (dRho), suppresses the formation of insoluble aggregates and releases the dRho very slowly in the ATP-dependent manner. To clarify the molecular mechanism of GroEL-mediated folding process, we have done solution small angle X-ray scattering experiments of GroEL-dRho system. In this report, we show the Rg and the structural change between dRho bound and unbound GroELs.

**Experimental**

The experiments were done at BL-15A, using the small angle X-ray scattering technique. The GroEL overproducing strain pKY206/AD21 was kindly supplied from Professor K. Ito, Institute for Virus Research, Kyoto University. The GroEL was purified according to the procedure of Mizobata et al.\(^\text{2)}\) The Rho was purified according to the procedure of Horowitz with some modification\(^\text{3)}\), and denatured with 5M GdnCl. The concentration of the GroEL and the dRho was 2.11 mM and 1.5 mM, respectively.

**Results and Discussion**

Fig.1 shows the scattering curves of the GroEL and the GroEL-dRho complex. The scattering curves displayed two minima at h=0.06, 0.105 Å\(^{-1}\), a faint minimum at h=0.15 Å\(^{-1}\), and one major maximum at h=0.07 Å\(^{-1}\). These peak and valleys corresponded to those of the spectrum that had been observed by Igarashi\(^\text{4)}\), and the minimum or the maximum peaks didn’t change so largely between GroEL and GroEL-dRho complex. It is said that such spectrum reflects the native GroEL shape, that is, two heptamer rings that consist of seven 33kDa subunits are stacked on top of each other, and the little change of the peak and valleys of the spectra may suggest that little shape change has occurred on the GroEL molecule when the dRho had bound to it. In other words, the GroEL kept a native shape when the dRho had bound to it. Fig. 2 shows the change of the radius of gyration (Rg) between the GroEL and the GroEL-dRho complex. The Rg values were estimated from Guinier plots of normalized scattering curves in a region of hRg≈1 or hRg<1. The estimated Rg value of the GroEL was 69±3 Å, while that of the GroEL-dRho complex was 71±4 Å. When the dRho has bound to the GroEL, the Rg value increased by 2 Å. This may suggest that the dRho bound to the surface of the GroEL molecule, not to the inside of the central cavity of it. Furthermore, thinking of little change of scattering curves between the GroEL and the GroEL-dRho complex, we thought that the dRho bound in a rather expanded shape. From now on, we are going to determine the equilibrium constant of the GroEL-dRho complex, and are going to do kinetic experiments.

**References**

ASSESSMENT OF PERFECTION OF MELT-GROWN 2-METHYL-4-NITROANILINE (MNA) SINGLE CRYSTALS

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Recently considerable interest has developed for organic materials with extremely high optical nonlinearities. In particular, MNA is one of the most promising materials for nonlinear optical devices. The growth of MNA single crystals of large size and high quality is prerequisite for accurate characterization and technical applications of their materials.

MNA crystallizes in the monoclinic structure with space group $I a$ (equivalent to $Cc$), lattice parameters of $a=8.22\,\text{Å}$, $b=11.62\,\text{Å}$, $c=7.58\,\text{Å}$, $\beta=94.08^\circ$ and four molecules per unit cell at room temperature. The melting point of MNA crystals is about 133°C. So far, solution, vapor or melt growth have been applied for the growth of MNA single crystals. However reports on the assessment of structural perfection of the grown crystals have been limited in number.

In this work, MNA single crystals were grown from melt by Bridgman method. The structural perfection of grown crystals was examined by synchrotron X-ray topography, which have been successfully applied for characterization of defects in some organic molecular crystals such as urea and benzophenone.

MNA single crystals were grown in the pyrex tube 5 mm in an inner diameter from melt by Bridgman method. The growth direction was normal to (102). In cooling process after crystal growth, some cracks were introduced in the direction of about 73° to the growth direction, so their planes are expected to be (112). For X-ray topographic experiments, the cylindrical grown crystals were cleaved along cleavage plane (010) into thin specimens of ~0.3 mm in thickness.

The synchrotron X-ray topography yielded the well-defined topographic images with no intrinsic asterism for the specimens, as shown in Fig. 1. Large volumes of the specimen are dislocation free, except for upper and lower regions as shown in Fig. 1. The volumes at A are missing from the image, since they are of a different crystallographic orientation to the rest. The dark regions at B show high defect density. These upper and lower regions had adhered to the tube, where considerable strain will have been induced by the difference between the expansivities of the crystal and tube during growth and subsequent cooling. The strain can yield mechanical deformation of the crystals with the introduction of defects. This is one of major problems for crystal growth with Bridgman method.

These results suggested that the crystals of high quality can be grown from melt by Czochralski method.

![Fig. 1 X-ray topograph of (010) section, which is obtained by cleaving and polishing the MNA crystal grown from melt by Bridgman method. The topograph was taken in the 112 reflection. Some cracks at C and D are observed, which were introduced during the cooling process after crystal growth and handling of specimen, respectively.](image)

References

GLIDE MOTION OF DISLOCATION IN ICE CRYSTAL CLOSE TO THE MELTING TEMPERATURE

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Introduction
In-situ observations of dislocations in ice crystals were carried out by x-ray topography in a temperature range between 254.7K and 272.7K under shear stress of 0.060MPa. A steep increase of dislocation velocity was found as a temperature approaches the melting point.

We have already reported this phenomenon that dislocation velocity in ice crystals increased steeply just below the melting point$^1$, however, could not yet realize the mechanism of it because of not sufficient number of measurements. In this study we took notice of the change in the shape of dislocation lines by the difference of temperature, in addition to the accurate measurement of dislocation velocity itself.

Experimental
Specimens were prepared from single crystals of ice I$_h$ (ordinary ice) grown by the Czochralski's technique. The dimensions of the specimens were 2.8X5.8X30mm$^3$.

A small deformation apparatus was mounted on a goniometer, and uniaxial compressive load was applied to the specimen as described in the previous report$^1$. Temperature fluctuation was suppressed as low as ±0.05K by blowing temperature controlled nitrogen gas. Temperature difference between the top and the bottom of the specimen chamber was smaller than 0.09K.

Motion of the dislocations were observed intermittently by the x-ray TV topography camera, and the images were recorded on a videotape. Displacement of dislocations was measured by comparing two images recorded at different times.

Results and Discussion
Fig.1 shows the temperature dependence of dislocation velocity measured between 272.7K and 254.7K, at an effective shear stress of 0.060MPa. The data below 269.7K fitted on the solid line give an activation energy of 0.63eV using Arrhenius' equation. This value agreed well with those reported so far. On the other hand the data above 269.7K show a steep increase, which yield about 50% larger velocity at 272.7K than the extrapolated value from lower temperatures.

These velocities plotted in this figure are the average values of several tens of dislocations in a same condition, for the velocities are distributed over somewhat a wider range as reported in previous report$^1$. This distribution may be caused by the characteristics of individual dislocations and by low shear stress. That is the velocities of different shapes of dislocations may differ each other even if they are in a same condition.

It was also found that the curvature of the migrating dislocation lines critically depends on the temperature as shown in Fig.2. The curvature radii above 269.7K are significantly larger than those below the temperature. This suggests that the cause of steep increase of dislocation velocity is related to the change in shape of dislocation line. Theoretical consideration will be given in a separate paper.

Acknowledgment
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RELATION BETWEEN MINUTE LATTICE STRAIN AND ANOMALOUS OXYGEN PRECIPITATION IN A CZOCHRALSKI-GROWN SILICON CRYSTAL

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Introduction

Analysis of minute lattice strain fields using double-crystal x-ray topography with higher order reflections is effective for studying the degree of lattice perfection. In this work, this technique is applied to quantitatively determine the strain fields in an as-grown CZ Si wafer which shows ring-shaped region of densely distributed oxidation-induced stacking faults (OSFs) after oxidation thermal treatment. The resulting variation profile of the lattice dilation shows a small valley in the ring-shaped region, while also showing a peak just outside the ring-shaped region. Furthermore, the sign of the inclination angle reverses in the just outside the ring-shaped region.

Experimental

Double-crystal reflection topographs were taken for a fan-shaped as-grown sample which shows ring-shaped region of densely distributed OSFs after oxidation thermal treatment. The experimental arrangement was set up on beam line 15C. Two sets of topographs were taken with Ilford L4 nuclear emulsion plates at four offset angles from the exact Bragg condition. In one case (case A), incident x rays were impinged from the wafer edge side, and in the other case (case B), from the wafer center. Exposure times were 30 seconds while the storage ring was operated at an energy of 2.5 GeV with an average positron beam current of 330 mA. Photographic densities were digitalized by a microdensitometer.

Results

In double-crystal reflection topography, the image contrast can be approximated very well by assuming a linear relation between the Bragg angle deviation and local intensity change, given by Bonse as

\[ \Delta I = k \delta \omega = k \left( \frac{\Delta d/d}{d} \tan \theta_p - \hat{n}_g \cdot \Delta \theta \right), \]

where \( \Delta I \) is the local intensity change, \( \delta \omega \) the local Bragg angle deviation in radian units, \( \theta_p \) the exact Bragg angle, \( \Delta d/d \) the local variation in the lattice spacing, \( \Delta \theta \) the angle of local inclination from the exact plane, \( \hat{n}_g \) and \( \hat{n}_t \) the unit vectors parallel to the goniometer axis and the lattice tilt axis, respectively, and \( k \) the slope of the diffraction profile. Equation (1) shows that local variations in both lattice spacing and inclination contribute to \( \Delta I \). Kikuta et al. reported a way to isolate these two contributions. Their method uses the fact that the sign of \( \hat{n}_g \cdot \hat{n}_t \), in eq. (1) is inverted after a 180 degree rotation about the diffraction plane normal to the sample. When the intensity changes in cases A and B are denoted by \( \Delta I_A \) and \( \Delta I_B \), respectively, we obtain the expressions,

\[ \Delta I_A + \Delta I_B = -2k \frac{\Delta d}{d} \tan \theta_p, \]  

and

\[ \Delta I_A - \Delta I_B = -2k \hat{n}_g \cdot \hat{n}_t \Delta \theta, \]

which give separately \( \Delta d/d \) and \( \Delta \theta \), respectively.

The isolated \( \Delta \theta \) and \( \Delta d/d \), obtained from two sets of topographs using eqs. (2) and (3), are shown in Figs. 1(a) and 1(b), respectively. Comparing Figs. 1(a) and 1(b) shows that \( \Delta d/d \) contributes to the topographic contrast much more than \( \Delta \theta \). The two broken lines show the boundaries of the ring-shaped region. In this region, we find that the variation profile of the lattice spacing shows a small valley in the ring-shaped region, while it shows a peak in the area just outside the ring-shaped region. In addition, the sign of the inclination angle changes in the exterior region.

References

Performance of Imaging Plate as an X-Ray Area Detector Used for Plane-Wave X-Ray Topography

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Introduction

Plane-wave x-ray topography (PWT) combined with synchrotron radiation (SR) is sensitive enough to detect minute strain fields caused by microdefects and impurity inhomogeneity in as-grown silicon crystals. Striation contrast recorded on imaging plates (IPs) enabled us to analyze local lattice distortion in silicon\textsuperscript{1-3}. We have developed a system for characterizing lattice distortion\textsuperscript{4}, utilizing an IP-processing system for transmission electron microscopy, JEOL PIXsysTEM\textsuperscript{5}. Since the characteristics of IPs affect the results of distortion analysis, the dynamic range, spatial resolution and granularity of IPs have been investigated using the PWT optics.

Experimental

The exposure of IPs to an SR x-ray was performed at the beamline BL-15C of the Photon Factory. The wavelength of the x-ray was tuned to 0.112 nm by a Si-111 double-crystal monochromator. The x-ray beam was incident at a glancing angle of 0.8° on a 100-mm diameter Si crystal used as the 800 asymmetric-reflection collimator. The x-ray beam diffracted from the collimator was limited by a slit of 50 X 3 mm\textsuperscript{2} and was recorded on the IP. During the exposure, the IP was traversed back and forth at a constant speed perpendicular to the diffracted beam in the scattering plane in order to record a uniform image.

In measurements of the dynamic range and the granularity, the x-ray dose was changed by using several Al plates with different thicknesses as absorbers. In measurements of the spatial resolution, an x-ray test chart made of a 30 μm-thick Pb film was positioned in front of the IP. The test chart was used as a metal mask to produce a square-wave input pattern with spatial frequencies from 2.0 to 20 lp/mm. The type of IPs used in this experiment, Fuji DL-UR IE, provided higher spatial resolution than other types of IPs. After the exposure, the IPs were processed to produce digitized images using the PIXsysTEM.

Results

The intensity of IP images was linear to the x-ray dose over 4 orders of magnitude of intensity. This result was obtained in both the high sensitivity (HS) mode and the high resolution (HR) mode, and was consistent with the result obtained by electron exposure\textsuperscript{6}.

To evaluate the spatial resolution of the IP images from square-wave input patterns, the contrast transfer function (CTF) was plotted against a function of spatial frequency, as shown in Fig. 1. At a spatial frequency where the CTF response is higher than 0.9, the output pattern reproduces the input pattern. In this case, the input pattern recorded on IP can be completely read out at lower spatial frequency than 4 lp/mm and 2.5 lp/mm in the HR and HS modes, respectively.

The fluctuation of the intensity of the IP images was characterized by the root mean square (RMS) granularity. Figure 2 shows RMS profiles obtained from IP images. In a low-dose region from 10\textsuperscript{3} to 10\textsuperscript{8} photons/mm\textsuperscript{2}, RMS exceeds 10 and rapidly decreases with an increase in the x-ray dose, since the granularity is mainly caused by a quantum mottle. In the high-dose region from 10\textsuperscript{8} to 10\textsuperscript{10} photons/mm\textsuperscript{2}, RMS slowly decreases and approaches 1 with an increase in the x-ray dose, since a structure mottle due to the IP and its processing system is dominant.

References

Skew diffraction measurement of silicon surface deformation induced by As$^+$ ion-implantation

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Introduction

The fabrication of shallow junction has become one of the important subjects in semiconductor technology for very large scale integration circuits. Recent development on ion-implantation techniques made the shallow dopant injection possible, and the rapid thermal annealing technique was also developed to activate dopant atoms after ion-implantation.

To apply these techniques to semiconductor fabrication processes, recovery of the silicon lattice must be estimated. X-ray diffraction provides a useful method for the estimation of lattice deformation. In the asymmetric reflection, it is difficult to reduce the extinction distance to less than 1 μm. However, the extinction distance becomes very short when the total reflection occurs.

In this study, the skew geometry with grazing-incidence conditions has been applied to the estimation of surface lattice deformation in As$^+$ ion-implanted silicon.

Experimental

The samples used in this experiment were 8 inch, n-type CZ silicon wafers with a resistivity of ~1 Ω·cm, and As$^+$ ion-implantation was performed with an energy of 70 keV and a dose of $10^{15}$ atoms/cm$^2$.

After the ion implantation, the wafers were provided for X-ray rocking curve measurements without thermal annealing, together with an unprocessed wafer as reference. The X-ray optics was set up at the BL-15C. The incident X-ray beam was monochromatized by the 111 silicon double-crystal monochromator at a wavelength of 0.653Å, and the 448 skew reflection was selected to measure the rocking curve of the sample.

The critical angle ($θ_c$) for the total reflection was 1.67 mrad. The measurement was carried out by inclining the sample to the incident X-ray beam by an angle of $θ$ (about $θ_c$) and by rotating the sample around the surface normal without changing the grazing angle $θ$.

Results and Discussion

Figures 1 and 2 show the rocking curves of the reference wafer and an As$^+$ ion-implanted wafer. In Fig.2 we find that the diffraction intensity is enhanced on the lower angle side of the rocking curve.

The extinction distance at a grazing angle of $θ_c$ was calculated according to Kishino's theory and was found to be 0.222 μm. Therefore, the asymmetry of the rocking curve in Fig.2 is considered to be caused by the surface deformation due to the ion-implantation.

The skew geometry has the advantage that the setting of the grazing-incidence conditions is easy, and many reflection planes are available without changing the grazing angle; therefore detailed information about the anisotropy of lattice deformation will be investigated.

Reference

Measurement of Faraday effect in Co K-edge by tunable X-ray polarimeter

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Introduction

We have constructed a tunable X-ray polarimeter in order to measure an optical activity with X-rays. The polarimeter can analyze a rotation angle and a degree of ellipticity of the polarization of X-rays transmitted by a specimen. It consists of a polarizer and an analyzer in an arrangement similar to that used in visible-light optics, i.e., crossed Polaroid. The polarizer and the analyzer are monolithic silicon 422 channel-cut crystals providing four consecutive Bragg reflections. The channel-cut crystal operates as a high-extinction polarizer in an energy range around \( \theta_B = 45^\circ \) by intentionally introducing a small offset angle between the two sides of the channel.

In order to evaluate the performance of the polarimeter, we have measured the Faraday rotation spectra with a Co foil near K-absorption edge. The Faraday rotation is related with the X-ray magnetic circular dichroism (XMCD) through the Kramers-Kronig transformation. The results were compared with those of XMCD after they were transformed by Kramers-Kronig relation.

Experiment and results

The Faraday rotation spectra were measured in an energy range of about 70 eV around the Co K-absorption edge. The magnetic field of 1 T was applied to the specimen in parallel and anti-parallel to the beam direction. The absorption spectra were simultaneously measured by using two sets of ion chambers which were placed upstream and downstream of the specimen. The experiment was carried out at BL-4A and BL-15C. Transmission XMCD spectra were measured at AR NE-1 in which elliptically polarized X-rays were provided from the insertion device. The applied magnetic field was about 0.6 T. Figure 1(a) shows the Faraday rotation spectra and the absorption spectra of the pure Co foil (4 µm thick) near the Co K-edge. The error of the measured rotation was within 10 µrad. The Faraday rotation spectra were reversed when the magnetic field was reversed. The difference of the Faraday rotation spectra between parallel and anti-parallel magnetic field were transformed according to the Kramers-Kronig relation. The results are shown in Figure 1(b) along with the XMCD spectra. Good agreement has been obtained between the transformed Faraday rotation spectra and the XMCD spectra.

Figure 1
Polarization Tunable X-ray Optics for Synchrotron Radiation
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Introduction
Circularly polarized x-rays (CPX) plays an essential role in studies of magnetic materials through magnetic Compton scattering, magnetic Bragg diffraction and magnetic circular x-ray dichroism. To date, many kinds of x-ray optics have been developed using an x-ray phase retarder (XPR) to transform linearly polarized synchrotron radiation to circular polarization. Because most of these optics were complicated and inefficient, they have not been used so much at synchrotron radiation facilities. However, recent development of transmission x-ray phase retarders (TXPR's) opened up new possibilities to construct simple and efficient polarization-tunable x-ray optics [1,2]. We have developed new polarization-tunable x-ray optics at the Photon Factory.

Experimental
Figure 1 is a drawing of our polarization-tunable x-ray optics. The optics consists of a double-crystal monochromator and a TXPR. The three crystals are arranged in (+, −, +) setting. The scattering plane of the optics is inclined by 45° with respect to the horizontal plane to equally excite σ and π polarization components in the TXPR. After the monochromatization and collimation of the incident beam at the double-crystal, the TXPR makes polarization transformation. Since the phase shift, δ, produced between σ and π components in the TXPR is tunable through the offset from the Bragg condition, Δθ, the polarization of the outgoing beam is easily controlled through Δθ. For example, CPX is produced when δ is (n+1/2)π rad (n:integer) and vertical polarization when δ is (2n+1)π rad.

We checked this optics at BL-15C (bending magnet beamline). The wavelength was selected at 1.026 Å with Si(220) double-crystal monochromator. For the TXPR, we used a 1.09 mm thick diamond (001) plate near the asymmetric Laue 111 diffraction condition. To measure the polarization of the outgoing beam we mounted a Si(642) analyzer crystal (θB=45°) on a four-circle goniometer and measured reflected integrated intensities for various χ-angles. We measured polarization states for Δθ=+150°, +20° and +10°.

Results and Discussion
Figure 2 shows results of polarization measurements. At each Δθ of +150°, +20° and +10°, horizontal, circular and vertical polarizations were produced respectively. The transmission ratio at the TXPR was as high as 70%. This confirms us that the quite simple optics in Fig.1 is very effective for polarization-tunable transformation of synchrotron radiation. If this optics is used at planar undulator or wiggle beamlines, brilliant and arbitrary-polarized x-rays will be obtained.

References
Introduction
Dynamic theory of x-ray diffraction leads to anisotropy of refractive index near the Bragg condition (diffractive birefringence). To date several kinds of x-ray phase retarders (XPRs) have been developed based on this principle. Among them transmission x-ray phase retarders (TXPRs) which make use of transmitted (forwardly diffracted) beam have remarkable features as follows [1]: 1) phase shift is tunable through the offset from the Bragg angle, 2) sign of the phase shift reverses between opposite side of the Bragg peak, 3) high efficiency of polarization transformation and 4) position and direction of the outgoing beam is kept unchanged from the incoming beam. Due to these advantages the TXPRs have been used at many synchrotron radiation facilities for control of polarization.

So far, we have used nearly perfect crystals such as silicon, diamond and germanium for TXPRs. Since TXPRs are usually operated away from the Bragg condition, the phase shift is not so sensitive to imperfections in TXPRs. This suggests us new possibilities to make TXPRs of mosaic crystals. To show that mosaic crystals are available for TXPRs, we tested LiF crystals at BL-15C.

Experimental
Figure 1 is a drawing of the experimental setup. The horizontally-polarized white radiation from the bending magnet is monochromatized at 1.57 Å by a Si(111) double-crystal A. Slits B and D limit the beam size to 1mm×1mm and collimate the beam to 9.6° in vertical and 7.6° in horizontal. Between the slits is an ionization chamber C for an intensity monitor. The horizontally-polarized and monochromatic x-rays is incident on a 0.75 mm thick LiF(O01) plate E adjusted near the 002 Laue diffraction condition. The scattering plane of E is inclined by 45° with respect to the horizontal plane to excite σ and π components with equal amplitude. The mosaicity of the LiF crystal was estimated to be 35° from the rocking curve measurement. A Si(422) crystal F is mounted on a four-circle diffractometer to measure the polarization of the transmitted beam. At several offset angles of -50°, -25°, -17°, -125°, -85°, and -65°, we measured χ-angle dependence of the reflected integrated intensities.

Results
Figure 2 shows results of polarization measurements. Clear change of polarization is observed with the offset angle of the LiF crystal. In particular, at the offset of -125° reflected integrated intensities are almost constant with respect to χ-angle, which indicates production of circularly polarized x-rays. Transmission ratio at the LiF crystal (i.e. efficiency of polarization transformation) was about 10 %. This confirms us that even mosaic crystals are available for TXPRs under proper operating conditions.

References
X-ray Polarization Imaging to Study Birefringent Materials
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Introduction
In the visible light wavelength region, polarization imaging, e.g., polarizing microscopy, is one of the most popular methods to investigate optical properties of birefringent (double refractive) materials such as fibers, minerals and crystals. In the x-ray energy region, polarization imaging technique has not been developed so far because birefringence does not appear when x-rays pass through materials. However recent researches on diffractive birefringence [1], which appears during dynamic diffraction of x-rays at perfect and mosaic crystals, opened up new possibilities to expand this technique to x-rays. We have developed x-ray polarization imaging technique based on the diffractive birefringence.

Experimental and Results
In the typical polarizing microscopy, a sample is placed between polarizer and analyzer. Linear polarization produced by the polarizer suffers polarization transformation at the sample. The analyzer visualizes the polarization state to give information about the optical properties of the sample. Figure 1 is a simple expansion of this scheme to x-ray synchrotron radiation. The optics consists of a double-crystal monochromator A, a sample B and an analyzer C. Reflected beam by the analyzer C is recorded on an x-ray film or on an imaging plate D. Polarizer is not necessary because horizontal polarization of synchrotron radiation is used in Fig.1.

Preliminary tests for polarization imaging were performed at BL-15C using the optics in Fig.1. Wavelength was selected at 1.5Å with the Si(111) double-crystal A. The double-crystal consists of an asymmetrically-cut first crystal (α=10°) and a symmetrically-cut second crystal. The vertically expanded beam by the asymmetric reflection was incident on a LiF(002) sample crystal B adjusted around the 002 Laue diffraction condition. The scattering plane of the LiF crystal was inclined by 45° with respect to the horizontal plane to excite both σ and π components. Polarization of the transmitted beam was projected on an x-ray film D by a Si(333) analyzer C (θb=45°). Photograph 1 is the image recorded on the x-ray film. Exposure time was about 5 minutes under single bunch operation of the storage ring.

Photograph 1 clearly shows polarization-dependent contrast caused by birefringent properties of the sample. This preliminary result convinces us that polarization imaging technique is available for characterization of birefringent materials even in x-ray energy region. For example, surfaces, interfaces and films would be studied with this technique under grazing incidence diffraction condition. Further it would be applied to characterize polarization-tunable insertion devices such as elliptic multipole wigglers and asymmetric wigglers.

References

Fig.1 Optics for x-ray polarization imaging.
A: double-crystal monochromator, B: sample crystal, C: analyzer crystal, D: x-ray film

Photo.1 Polarization-dependent image recorded on the x-ray film D. (visual range is 6mm×8mm)
STRUCTURAL CHANGE OF SURFACE GOLD LAYER
BY ADSORPTION OF ALKANETHIOL MONOLAYER
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Introduction
Grazing incident surface X-ray diffraction (GISXRD) has been used for in situ structural studies of electrode/electrolyte interfaces by employing the synchrotron orbital radiation (SOR) source (1,2).
Recently, many investigations on gold electrodes modified with self-assembled monolayer of thiol molecules have been carried out. However, the only limited information on the structure of these monolayers and the structural change of the electrode surface is available.

In this report, we compared the diffraction patterns from the gold electrodes with and without adsorbed monolayers and discussed the structural change of gold surface layer as a result of the adsorption of ferrocenylalkane thiol monolayer.

Experimental
Gold substrates were prepared on glass by vacuum deposition (ULVAC, EBH-6) at 300 °C. Ferrocenylundecane thiol used as a modifier molecule was synthesized (3). Surface modification of gold was carried out by dipping the substrate in hexane solution containing ferrocenylundecane thiol. The GISXRD experiments were performed on the 53-pole permanent magnet wiggler beamline 16A at Photon Factory. The X-ray beam is monochromated at a wavelength of 1.488 Å. The glancing angle of the X-ray beam on the surface of the gold electrode is made to be 0.126°. A specially designed electrochemical cell is mounted on the 0-axis of a two-circle diffractometer. The diffracted intensity was measured by one dimensional gas proportional counter, in front of which a Soller collimator is placed, as a function of a diffraction angle, 2θ, and a vertical component of the momentum transfer, Qz.

Results and Discussion
Figure 1 shows the equal intensity contours of X-rays as a function of 2θ and Qz measured at the gold surface before and after adsorption of ferrocenylundecane thiol at open circuit voltage in 0.1 M HClO4. Although only one sharp peak around 2θ=35° corresponding to (111) surface atomic structure was observed at the gold surface before adsorption, several peaks distributed like as a fan-shape were observed at the modified gold electrode. Such peak distribution suggests some surface domains with (111) structure existed on the gold surface and that the plane of them were not parallel each other. Thus, the adsorption of ferrocenylundecane thiol leads to a change of the surface structure of gold. S.-Huethorst et al., reported by STM measurements that gold surface atom dissolved in the thiol solution with the formation of a gold thiolate complex, when gold substrate was dipped in the organic solution containing thiol molecules (4).
Thus, the present structural change of surface gold layer was also suggested to be due to the adsorption of thiol molecules.

References

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NON-CENTROSYMMETRIC ALIGNMENT OF OPTICALLY NONLINEAR MATERIALS
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Introduction

Langmuir-Blodgett (LB) films may allow designer control of molecular level packing^ to produce non-centrosymmetric films suitable for second-harmonic generation (SHG)^2^-^4. C22H4

These dye materials (see above structure) comprise of a hydrophilic head with a hydrophobic alkyl tail which may be aligned at the air-water interface prior to deposition, but when transferred to a solid substrate the layers frequently invert to form centrosymmetric bilayer arrangements (^Y-type). Unless interleaved by compatible spacer layers, 2^-3 very few single-legged dyes form non-centrosymmetric multilayers in which molecules pack in a parallel manner (Z-type). However, with the addition of a second hydrophobic group at the opposite end to the hydrophilic chromophore helps Z-type deposition, 4 but there is only a narrow range of alkyl chain lengths which allows the films to be non-centrosymmetric. Z-type deposition and associated nonlinear optical properties of cationic dyes may be improved by the addition of a third alkyl chain and the use of an amphiphilic anion. The SHG from one of these dyes has been shown to increase quadratically with the number of LB layers to a thickness of ca. 0.6)im, this being the thickest Z-type structure obtained to date.

Grazing incidence synchrotron X-ray diffraction studies were performed on a ten layer LB film of the heptadecyl homologue of dye I using wiggler BL16 at the Photon Factory. 5 The data from measurements in the plane of the film (Qx scans) and out of the plane (Qz scans) are shown in Figure 1. The plots have been attributed to an hexagonal lattice with vertical alignment of the hydrophobic chains. The single diffraction peak at Qx = 1.520 Å^-1 corresponds to a d-spacing of 4.133 Å (d10 = 2π/Qx) and to an area of 19.72 Å^2 from the ordered domains and is smaller than the Langmuir isotherms which are averaged over the entire film. The areas at collapse of the different alkyl homologues range from 23 to 29 Å^2 molecule^-1; the values approximate to the cross-sectional area and indicate that the molecules adopt a "stretched" rather than a "U-shaped" configuration. Thus, the alkyl chains point in opposite directions and the molecules must align at the air-water interface with one of the hydrophobic chains adjacent to the water surface.

![Figure 1a X-ray diffraction data for an LB film of dye I (n = 17) at λ = 1.488 Å: Qx resolved scan. The solid line is a Lorentzian fit to the experimental data.](image1a)

![Figure 1b. A slice through the maximum at Qx = 1.520 Å^-1.](image1b)

References

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PHOTOEMISSION STUDY OF Cs OVERLAYER ON NbC(111)

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1 Introduction

Alkali metal adsorption on solid surfaces has for a long time been a subject as a fundamental chemisorption system, which leads to various interesting phenomena such as a work function decrease, an activation of a surface toward gas adsorption, etc.

In this short report, we present the result of the study on the Cs/NbC(111) system using the photoemission (PE) spectroscopy.

2 Experiment

The PE experiments were performed on BL-16U. The clean NbC(111) surface was obtained by repeated flashings to around 1500 °C. Cesium was deposited on the surface at room temperature using a well-degassed SAES dispenser.

The base pressure was less than 2x10^-8 Pa.

3 Result and Discussion

Fig.1 shows both the photoemission peak intensity ratio Cs 4d/Nb 4p and the work function change ΔΦ as a function of Cs deposition time. The curve of the PE intensity ratio consists of two linear segments with a kink at around 2 min. deposition. This shows that the Cs monolayer completes on the NbC(111) surface at ~ 2 min. deposition. The ΔΦ falls into the minimum value of ~3.8 eV in coincidence with the monolayer completion.

Fig.2(A) shows the Cs 4d core region PE spectra of (a) 30 sec. and (b) 2 min. Cs depositions. In addition to the spin–orbit doublet of 4d peaks, the three distinct Cs N\textsubscript{4} 5\textsubscript{5}O\textsubscript{2} 6\textsubscript{2}O\textsubscript{3} Auger peaks (indicated with bars) are seen. Both the Auger and the photoemission peaks shift to the lower binding energy side as a function of Cs coverage by ~ 1.9 eV and ~ 0.5 eV, respectively (fig.2(B)). The possible core level shift arising from the initial state effect could be cancelled when we only consider the difference between Auger and PE shifts. The free atom to metal shift in the Auger and PE peaks are mainly caused by the “extra-atomic” relaxation due to the screening of the final two- and one-hole states with valence electrons, respectively [1]. The similar effect could be expected in the Cs/NbC(111) system because the coverage dependent adsorption of Cs proceeds from the isolated to the metallic state with increasing coverage. The larger shift in the Auger peaks exhibits that the two-hole screening increases remarkably in the metallic region of Cs layer compared with the one-hole screening.

References

XAFS STUDY ON IMPLANTED ARSENIC IN SINGLE- AND POLY-CRYSTALLINE SILICON

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Introduction

Ion implantation is one of the most commonly used processes of fabricating LSI devices. Locations of implanted impurities and lattice distortions are significant factors to decide electrical property. The local environment around implanted As into single-crystalline Si\textsuperscript{1,2} and poly-crystalline Si\textsuperscript{3} has already been reported. They proposed the existence of SiAs precipitate, vacancy complex defects (As\textsubscript{v}V) as well as substitutional As after annealing. The aim of this study is to compare the local structure around implanted As into single-crystal with poly-crystal.

Experimental

Single-crystalline samples were implanted with 70 keV, 1 \times 10^{16} As/cm\textsuperscript{2} and poly-crystalline ones were implanted with 40 keV, 1 \times 10^{16} As/cm\textsuperscript{2}, respectively. After implantation, samples were annealed at 800°C or 1000°C.

The XAFS measurements were carried out on the beam line 17A of Photon Factory (PF). The wavelength of incident X-ray is set with a Si (111) double crystal monochromator and the fluorescence X-ray was detected by Ge solid state detector.

Results and Discussion

After implantation, before any annealing, all the samples were amorphous and the only nearest neighbor (NN) shell is observed. Next NN (NNN) shell is visible after annealing. XAFS results of this work are shown in Table I. In comparison with annealing temperature, the atomic distance (R) of NN is almost the same but one of NNN is smaller at lower temperature annealing for single-crystalline sample. This R of NN (R\textsubscript{NN}) is larger and the R of NNN (R\textsubscript{NNN}) is smaller than that of Si (R\textsubscript{NN} 2.35 Å and R\textsubscript{NNN} 3.84 Å), respectively. The changes of R\textsubscript{NN} and R\textsubscript{NNN} indicate that the lattice distortion is localized around the As atom. The coordination number (N) of NN and NNN increased forward to 4 and 12 at higher temperature annealing. It means progress of substitution of As atoms and recovery of Si crystallinity during annealing.

For poly-crystalline sample, though R\textsubscript{NN}, N\textsubscript{NN} and N\textsubscript{NNN} show the same tendency as single-crystalline sample, R\textsubscript{NNN} is longer than one for single-crystalline sample and also Si. Therefore, the lattice distortion around the implanted As expands in poly-crystal more than in single-crystal. We consider this difference of lattice expansion is caused by the mechanism of re-growth from amorphous between single- and poly-crystal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R\textsubscript{NN}</th>
<th>N\textsubscript{NN}</th>
<th>R\textsubscript{NNN}</th>
<th>N\textsubscript{NNN}</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-implanted</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800°C 30 min.</td>
<td>2.38</td>
<td>2.55</td>
<td>3.81</td>
<td>5.22</td>
</tr>
<tr>
<td>1000°C 30 min.</td>
<td>2.40</td>
<td>2.83</td>
<td>3.85</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Table I. XAFS results of As into Si

(a) Implanted into single-crystalline Si
(b) Implanted into poly-crystalline Si

References

XAFS STUDY ON THERMAL STABILITY OF TiSi₂

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Introduction

TiSi₂ is of interest for use in contacts and interconnects in VLSI applications because of its low resistivity and high temperature stability. Two different structures of TiSi₂ have been known after annealing.¹⁻³ These are TiSi₂ of C₄₉ and C₅₄ phases. The C₄₉ phase is a metastable and high resistivity phase. In comparison, the C₅₄ is a stable and low resistivity phase. Fabricated conditions, for example film thickness and annealing temperature and time, decide which phase is presented. We have already investigated this material by grazing incident X-ray diffraction.⁴ Now we try to analyze these structures by XAFS.

Experimental

Three specimens were prepared for this experiment. Ti was deposited on (100) p-type Si wafer. The initial thickness was 30 nm. Two of them were annealed at the temperature 675°C and 800°C for 30 second, respectively. It was already proved that the sample after 675°C annealing was formed the C₄₉ and one after 800°C annealing was the C₅₄.⁴

The XAFS measurements were carried out at BL-17A of Photon Factory (PF). The wavelength of incident X-ray is set with a Si (111) double crystal monochromator. The measurements were done on the Ti K edge at room temperature. Fluorescence X-ray was detected by Ge solid state detector (SSD).

Results

Figure 1 shows normalized XANES spectra of three samples. The XANES spectrum of as-deposited Ti sample has a sharp pre-edge peak and it indicates the presence of metallic Ti. After annealing, the Ti pre-edge disappears. It means Ti did not show metallic character and some silicide was formed. The spectra of the 675°C and 800°C samples have some of the same. Aldrich et al.² reported the annealing temperature dependence of XANES spectra. They showed the same tendency with our results, that is, the XANES spectrum of the C₄₉ phase is resemble to that of the C₅₄. It might be difficult to decide the structure of TiSi₂ by only XANES measurement. The reason is the resemblance of their local structure around Ti atom; though crystalline structure is different between the C₄₉ and the C₅₄, Ti atom in the C₄₉ is surrounded by 10 Si atoms and that of the C₅₄ is the same.⁵ The atomic distance and coordination number are obtained by EXAFS analysis. EXAFS analysis is now in progress.

References

SYNCHROTRON RADIATION ASSISTED ETCHING OF SILICON DIOXIDE FILMS USING ANHYDROUS HYDROGEN FLUORIDE
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Introduction
Decreasing the feature size and film thickness in the integrated circuits, the high-selective, damageless, and clean etching technique is required for the fabrication processes. In this study, we tried vacuum-ultra-violet light assisted etching of silicon dioxide films with AHF (anhydrous hydrogen fluoride) gas.

Experimental procedure
Thermally oxidized single-crystalline silicon substrates were used as the samples. The typical thickness of the oxide film was 125 nm. The experiments were carried out in the beam line BL-17B of the Photon Factory facility. In this line, the peak of the light intensity appears at the wavelength of about 10 nm.

Figure 1 shows the schematic diagram of the experimental system. The sample was introduced into the reaction chamber in high-vacuum. Then, AHF gas was introduced into the reaction chamber. Moreover, argon gas was introduced into the gas inlet between the reaction chamber and the differential pumping chamber in order to prevent a back flow of the corrosive gas to the light source. The total pressure in the reaction chamber was maintained to 0.1 Torr by evacuation, where the partial pressure of AHF was 0.01 Torr. The sample surface was irradiate with synchrotron radiation light through the patterned mask made of nickel. The distance between the mask and the sample surface was 0.5 mm. The etching time is defined as the irradiated duration.

Experimental Results and Discussion
First, the dependence of the etch rate on the light intensity was examined, where the light intensity is proportional to the electron beam current in the storage ring. The etch rate is found to be proportional to the light intensity as shown in Fig.2.

Figures 3 shows an optical micrograph of the etched surface. The etching was observed only in the irradiated region. The etched pattern agrees with that of the mask in the accuracy of a micron at least. These results indicate that the etching reaction is the surface excited reaction.

In all experimental conditions, the etching of silicon substrates was not observed. Considering the measurement error, the selectivity of etch rate of SiO2 respect to Si is more than 100.

Fig.1 Schematic diagram of etchining system
Fig.2 Etch rate as a function of light intensity
Fig.3 Optical micrograph of the etched surface
GIXD STUDY ON EFFECT OF IMPLANTED BF₂ AND LINE WIDTH ON TITANIUM SILICIDATION
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Introduction

TiSi₂ is one of the most important low resistivity contacts for ULSI fabrication. The TiSi₂ has two phases of high resistivity C49-TiSi₂ formed at 600 °C - 700 °C and low resistivity C54-TiSi₂ formed at 700 °C - 850 °C. Although the latter phase is useful, the resistivity often rises for narrow lines and highly doping of As or P due to residual C49-TiSi₂ even after high temperature annealing. However, it was reported BF₂ implantation did not affect rise of resistivity. In this paper, we will report quantitative characterization of the phases in a function of line width and BF₂ dosage by the glancing incident x-ray diffraction (GIXD).

Experiments

Silicides were formed on unimplanted or BF₂ implanted Si(001) at dosages of 2×10¹⁵ or 5×10¹⁵ /cm², and/or line pattern at 0.8 or 0.5 μm with a standard rapid thermal annealing (RTA) process. The 1st and 2nd RTA conditions were 700 °C, 30 sec and 800 °C, 30 sec, respectively. Sputtered Ti was 30 nm in thick. By GIXD apparatus with 0.13 nm x-ray, we measured x-ray diffraction from lattice planes perpendicular to the surface. Incident angle was set near the total reflection in order to be sensitive to thin silicide films. We observed the (060) and (131) for C49-TiSi₂ and the (131), (311), (040), and (022) for C54-TiSi₂, and evaluated the fraction of the phases from integrated intensities of their peaks.

Result and Discussion

After 1st RTA, we observed only the C49-TiSi₂ on all of implanted film and unimplanted line samples, but both the phases with 15% of the C54 in unimplanted film sample. Furthermore, the integrated intensity from the C49 decreases as increasing of BF₂ dosage. Therefore, both BF₂ doping and fabrication of lines suppress silicidation from Ti/Si during thermal annealing. The figure shows the fraction of the C54 after 2nd RTA in a function of BF₂ dosage and line width. In film samples, the C49 after 1st RTA for unimplanted and low dose samples all transforms to the C54 after 2nd RTA, but that for high dose one remains 50% of the C49. This tendency becomes remarkable for line samples, and the phase transition is perfectly interrupted for implanted line samples. Therefore, BF₂ implantation and line fabrication suppress the phase transition from the C49 to C54, each other.

Furthermore, we observed the epitaxial C49 in high implanted film sample after 1st and 2nd RTA oriented to the Si(001) substrate from rocking curve measurements. Our results indicate that the suppression of the phase transition originates in the epitaxial C49.

![Figure 1: the dependence of C54 fraction in TiSi2 on BF2 dosage and line width](image)

Circle, square, and triangle represent not-patterned, 0.8 μm line width, and 0.5 μm line width, respectively. More dosage or narrower line width decreases fraction of the C54 in the samples.

References

HIGH ACCURACY X-RAY REFLECTIVITY STUDY
OF THIN SiO₂ ON Si

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Introduction
The structural characterization of oxide films is crucial for the understanding of their reliability in a metal-oxide-semiconductor (MOS) system. Glancing incidence X-ray reflectometry is a powerful technique to prove their density, thickness and microroughness of silicon-oxide interface and oxide surface that have intimate relation to the reliability of ultra thin gate oxide.

Experimental
HCl/O₂, dry oxygen and ozone grown oxide under several growth conditions are evaluated by X-ray reflectometry. Measurements were carried out at Photon Factory beamline-17C. Highly parallel, intense photon flux provides more than seven decades of reflectivity at wave length 1.3Å, results in high precision data. We applied the optimization program based on the Vidal and Vincent formalism[1] with modified Marquardt minimization procedure to the data. The charge to breakdown Qbd characteristics and surface state densities D sitcom on a 1×10⁻¹⁵cm⁻² area under stress of 0.1A/cm² are also measured for 7nm thick oxides grown in above conditions.

Results and Discussion
Fig.1 shows the typical reflectivity data. Fig.2 show the growth temperature dependence of oxide density grown by different method for 7nm thick oxides. We can see a distinct dependence of densities on growth method. The ozone grown oxides are tend to more dense compared to oxygen grown oxides and much dense to HCl grown oxides. The measured microroughness is tend to decrease with the increasing temperature for HCl grown oxides. A measured Qbd and D sitcom are summarized in table. The ozone grown oxide improves the Qbd by a factor of 2.2 compared to the oxygen grown oxide and a factor of 1.3 compared to HCl oxidation. The D sitcom for ozone grown oxide is lower than that of oxygen grown oxide and a half of HCl grown oxide.

HCl oxides with less dense have an enlarged amorphous network due to the catalytic effect of Cl with Si-H, Si-OH and Si-Cl bonds that can easily create a physically weak spot or local trap sites by the hot carrier. Dry oxygen grown oxides have a dense structure free from impurities but their oxygen vacancies gives poor Qbd. In the ozone grown oxides, some ozone molecules dissolve and provide oxygen radicals that effectively prevent the generation or the termination of Si dangling bonds during the growth that leads to dense, highly reliable SiO₂ film.

<table>
<thead>
<tr>
<th>Growth condition</th>
<th>Density (g/cm³)</th>
<th>D sitcom (eV⁻¹cm²)</th>
<th>Qbd (C/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry O₂ 900°C</td>
<td>2.28</td>
<td>0.9E12</td>
<td>20</td>
</tr>
<tr>
<td>Dry O₂ 900°C</td>
<td>2.27</td>
<td>1.0E12</td>
<td>9</td>
</tr>
<tr>
<td>HCl 1000°C</td>
<td>2.13</td>
<td>2.0E12</td>
<td>15</td>
</tr>
</tbody>
</table>

References
HIGH-RESOLUTION 4d-4f RESONANT PHOTOEMISSION OF CeB$_6$


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Recently, a considerable improvement of the experimental energy resolution in the photoelectron spectroscopy enables us to study the low-energy excitations in the Ce compounds.$^1$ The validity of the so-called Kondo resonance peak has been intensively investigated by means of the high-resolution photoemission spectroscopy.$^2-^4$ Since the Kondo temperature of Ce compounds investigated by means of the high-resolution photoemission spectra, are much smaller than the experimental energy resolution (c.a. 15 meV), the evidence of the Kondo peak has been suggested by comparing the spectra with the one predicted based on the single impurity Anderson model.$^1$

Figure 1(a) and (b) show the high-resolution photoemission spectra of CeB$_6$ measured at excitation energy of 121.0 eV and 114.0 eV, respectively. In Fig. 1(a), the spectral profiles consist of a broad peak at the binding energy of 2.4 eV and two sharp peaks near the Fermi level. Since the photoelectron intensity of the off-resonance spectrum measured at 114.0 eV is negligibly small compared with the on-resonance spectrum at 121.0 eV, the most part of the on-resonance spectrum is considered to be originated from the Ce 4f states. The broad peak at 2.4 eV corresponds to the photoexcited 4f hole state. The two peaks near the Fermi level correspond to the spin orbit split 4f$^{5/2}$ and 4f$^{7/2}$ states. The spin orbit split energy was estimated to be 260 meV from the figure. Since the experimental energy resolution in the present study (78 meV) is larger than the crystal field excitation energy, we could not clearly observe the spectral features manifesting the crystal field excitation in the 4f$^{5/2}$ spectra even in an expanded scale. To investigate the low energy excitation at the Fermi level, we should further improve the experimental energy resolution. In addition, we should clarify some uncertainties which exist in the photoemission experiments.

The photoemission spectra are surface sensitive and it is not easy to estimate properly the surface sensitivity which is included inevitably into the valence band spectra. It has been reported that the Ce atoms tends to trivalent at surfaces because of small coordination number.$^5$ To obtained reliable photoemission spectra which could be held in precise investigations of the low energy excitations in Ce compounds, not only the 4d-4f resonant photoemission spectra with further improved energy resolution but also photoemission spectra on a well defined surfaces such as single crystal surfaces are awaited.

References
PHOTOEMISSION STUDY OF Ce/Ni(110) SYSTEM

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1 Synchrotron Radiation Laboratory, Institute for Solid State Physics, University of Tokyo, Tokyo 106

The electronic structures of the Ce compounds have been investigated by numerous photoemission experiments. In most cases the experimental results have been analyzed successfully by the Anderson impurity (AI) model. However, there remain some questions under debate. Generally, surface electronic structures are different from bulk electronic structures. Therefore, it is indispensable to scrutinize the contribution of surface effects in the argument over the electronic structure of solid state on the basis of photoemission spectra. Some experiments showed that this is really the case in Ce metal and some Ce compounds. In such photoemission experiments, it is important to prepare a well-defined surface. One possible method to prepare a well-defined surface is to construct Ce overlayers on a certain substrate in an ultrahigh vacuum. The investigation of Ce overlayers deposited on metal or semiconductor surfaces is quite interesting regarding the elucidation of surface properties of the Ce metal and its compounds.

We have studied the electronic structures of Ce/Ni(110) system by the 4d-4f resonant photoemission using synchrotron radiation and the Ce 3d core level X-ray photoemission. The results are interpreted in conjunction with the inter-diffusion of Ce and Ni atoms through the interface. The annealing after the deposition of Ce causes active diffusion of Ce atoms into the Ni substrate and Ni atoms into the Ce layers and brings about a well-ordered surface. Both the Ce 3d core level and valence band spectra show remarkable changes depending on the degree of inter-diffusion between Ce and Ni at the interface. It is revealed that a close relation exists between the Ce concentration and strength of the 4f-conduction states hybridization in the surface layer.

It is remarked in Fig. 1 that spectral features for the Ce coverage of less than 4Å are different from those for the Ce coverage of more than 12Å. The Ce 3d spectra for the coverage of more than 10Å resemble to those of Ce-Ni intermetallic compounds rather than that of pure Ce metal. This shows that a pure Ce film is not formed but inter-diffusion of atoms between the Ce adsorbate and the Ni substrate takes place. Since intermetallic compounds are formed as a result of this diffusion, the hybridization between the Ce 4f states and Ni 3d states is enhanced.

References
SURFACE ELECTRONIC STRUCTURE OF SINGLE-DOMAIN Si(001)2x2-Al;
AN ANGLE-RESOLVED PHOTOELECTRON SPECTROSCOPY STUDY USING
SYNCHROTRON RADIATION

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Takashi Simatani*, Yuji Mori*, Akito Kakizaki* and Shozo Kono*

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Though overlayers of group-III metals on Si(001) surface have attracted much attention due to interesting growth mode and adsorbate structure, there are very few reports on the surface electronic structures [1,2],

We report the first angle-resolved photoelectron spectroscopy (ARPES) result on a single-domain Si(001)2x2-Al surface. The ARPES measurements were done on BL-18A PF KEK. ARPES spectra were measured along seven mirror lines of the surface Brillouin zone (SBZ, see Fig. 1a) such as [110], [1T0], [100], τ11τ11, τ8, τ11τ11, τ0, τ11τ11 and τ0 τ0 for complete determination of the dispersions of surface states (SS's). To map out the dispersions of SS's, we used the "grey-scale E, k diagram" where the brightness is roughly proportional to I/W ; I is the intensity of a peak and W is the width of the peak as shown in Fig. 2 [3]. As shown in Fig. 2, we have deduced that there exist five SS's, S1, S2, S3, S4, and S5. Fig. 3 summarizes the experimental results. All the five SS's were found to have the expected 2x2 periodicity of SBZ suggesting that they are the intrinsic SS's.

From the structure model (see Fig. 1b) and the details of the characteristics of dispersions, it may be plausible to assign the state S1 to the Al-Al dimer-bond state and S2 (S3') and S3 (S4') to the Al-Si back-bond states [3].

References

Fig. 1 (a) SBZ of Si(001)2x2-Al surface. (b) A schematic diagram for the structure of surface unit cell and bonds between constituents.

Fig. 2 Part of grey-scale E, k diagram for Si(001)2x2-Al surface. The white (black) broken lines are the edges of bulk bands projected to 1x1 SBZ (the assigned dispersions of the surface states).

Fig. 3. Summary of measured surface state dispersions. The squares (circles) are the previous results for Si(001)2x2-Ga (-In) taken from ref. 1 (2).
X-RAY CRYSTAL ANALYSIS OF F1-ATPASE FROM A THERMOPHILIC BACTERIUM

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Introduction

F1-ATPase (F1) is the soluble and catalytic portion of ATP synthase (Fo-F1 complex); ATP synthase catalyses the conversion of the proton gradient across membranes into ATP, thus playing a crucial role in oxidative phosphorylation.

F1 from a thermophilic bacterium PS3 (TF1) is a very stable molecule and has a molecular weight of 385,000, with a subunit composition of α₃β₃γδε(α, 55,000; β, 52,000; γ, 32,000; δ, 20,000; ε, 14,000). The primary structures of all the subunits of TF1 were determined from the DNA sequence, and an overproducing system for the α, β and γ subunits was established.

Recently, a core part of F1, αβγδε complex was successfully reconstituted using over-expressed subunit preparations. The αβγδε complex show 20% of the ATPase activity of TF1, with similar kinetics features. However its ATPase activity lacks sensitivity to metal ions and azide.

We have crystallized TF1, but at the moment, crystals give low resolution (ca 9 Å) diffraction pattern(1). In contrast, the αβγδε complex gave diffraction patterns to 4 Å resolution using sealed tube x-ray source. In the experiment described here, we dealt with the crystals of the αβγδε complex.

Crystallization

Crystals of the αβγδε complex were grown by hanging drop method. The 10μl drop contained 10-15 mg αβγδε complex /ml (120 mM sodium sulfate, 50 mM Tris-HCl (pH 8.0)) and 11-15 % polyethylene glycol 20,000. The 4 ml reservoir contained PEG 20,000, with concentration higher by 2 % than the concentration in the drop, and was set at 15°C. Plate crystals with multiple faces and with typical dimensions 0.5 mm x 0.5 mm x 0.3 mm grew in 2 weeks. The crystals are cubic, with cell dimensions a=160 Å.

Data collection at Photon Factory

The modified crystallization conditions described above lessened the transport problem of the crystals to PF.

Native data sets to 3.0 Å resolution were collected at BL18B and using Sakabe camera with 430 mm film cassette. Data were collected in a usual oscillation mode, because the cell was too large for Weissenberg mode.

Data Analysis

In addition to the program WEIS for analysis of Weissenberg data(2), the program DENZO was introduced to our analysis system this year. The conversion rule of mis-setting angles obtained by AUTO was established for the program DENZO. Unmerged data set obtained by either WEIS or DENZO was transferred by a program ROTAPREP to CCP4 program system (3) for further analysis. The scaling and merging of the data were done by SCALA and AGROVATA(3), and F values were obtained by TRUNCATE. A comparison of performances of WEIS and DENZO is described in proposal No 94G03 in this issue.

The collected native data showed that the spacegroup of the crystal is P2₁3, which was previously difficult to know from precession photography due to multiple faces and crowdedness of diffraction spots. Assuming a third of αβγδε complex is contained in an asymmetric unit, a value of Vm=3.2 Å³ / dalton is obtained, which is consistent with values for other protein crystals. This means that the three α subunits have equivalent conformation in this crystal form and the same is true for the three β subunits.

References

X-RAY CRYSTAL ANALYSIS OF RAT DNA POLYMERASE β AND E.coli PHOB PROTEIN
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Introduction
Both prokaryotes and eukaryotes have multiple species of DNA polymerases. Among eukaryotic enzymes, DNA polymerase β works for DNA repair.

DNA polymerase β is the smallest DNA polymerase consisting of a single polypeptide chain with molecular weight of about 39,000. From simplicity in molecular architecture and reaction mechanism, the enzyme is suited for mechanistic study of nucleotidyltransferase reaction in DNA synthesis.

Recombinant DNA polymerase β was over-produced in E.coli, and was extensively purified in an active form. Rat DNA polymerase β consists of two protease-resistant segments, a small N-terminal domain (1-87, 8k domain) and a large C-terminal domain (88-335, 31k domain). The 8k fragment retains single-strand DNA binding property while the 31k fragment doesn’t bind to DNA. Site-directed mutagenesis study has demonstrated that the residues contained in 31k fragment are involved in primer recognition.

Our extensive search of crystallization conditions of the intact DNA polymerase β was only partially successful. However, the 31k C-terminal fragment formed X-ray grade crystals. In the experiment described here, we dealt with the crystals of the 31k fragment of the DNA polymerase β.

Crystallization & derivatization
Crystals of the 31k protein were grown by microdialysis. The crystals are orthorhombic, space group P212121, with cell dimensions a=120.3 Å, b= 64.2 Å, c= 39.4 Å. Assuming one 31k fragment in an asymmetric unit, a value of Vm= 2.37 Å³/dalton is obtained, which is consistent with values for other protein crystals. The crystals were transferred to a synthetic mother liquor with the same contents as the reservoir solution except an elevated PEG concentration to 7%. Heavy atom derivative solutions were prepared by including appropriate concentration of the reagent in the above synthetic mother liquor. The immersion period was usually 2 days except 2 weeks for K2PtCl4.

Data collection at Photon Factory
Native data sets to 2.0 Å resolution were collected at BL18B using Sakabe camera with 430 mm film cassette. Derivative data sets were collected to a slightly lower resolution of 2.8 Å for the four candidates (pHMB, methylmercury chloride, Ethylmercury chloride, K2PtCl4). Data were collected utilizing feature of Sakabe camera when the crystal was mounted along c-axis, otherwise data were collected in a usual oscillation mode.

Data Analysis
In addition to the program WEIS for analysis of Weissenberg data(2), the program DENZO was introduced to our analysis system this year. The conversion rule of mis-setting angles obtained by AUTO was established for the program DENZO. Unmerged data set obtained by either WEIS or DENZO was transferred by a program ROTAPREP to CCP4 program system (3) for further analysis. The scaling and merging of the data were done by SCALA and AGROVATA(3), and F values were obtained by TRUNCATE. A comparison of performances of WEIS and DENZO was made in other crystals(described in proposal No 94G03 in this issue).

Using this system, the native data was found to extend to 2.0 Å resolution with Rmerge=6.5%. The K2PtCl4 derivative data showed clearly the positions of bound Pt in the Harker sections.

Reference
CRYSTAL STRUCTURE ANALYSIS OF H2-PROTEINASE FROM HABU VENOM

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Introduction
In the local hemorrhagic process to which crotalid and viperid venoms lead, metalloproteinases play the role of the disruption of the pericellular basement membrane protein of vessel wall. These enzymes share the zinc chelating sequence HEXXHXXGXXHD and the methionine containing turn sequence CIM. H2-proteinase [EC 3.4.24.53] is a major metalloproteinase in the venom of Trimeresurus flavoviridis (Japanese habu snake). It is a member of the lowest molecular weight class of snake venom proteinase family and consists of 201 amino acid residues (1). It is confirmed that this enzyme digests the oxidized insulin B chain, the fibrinogen Act-chain and some synthetic peptides. The enzyme preferably hydrolyzes the peptides which have five or more residues and a bulky hydrophobic P1' residue, which is the carboxyl side of the digested peptide bond. Although H2-proteinase is free from the hemorrhagic activity and its function is unclear, it is homologous to hemorrhagic proteinases. We are determining the crystal structure of this protein to examine the structural characteristics of the substrate recognition of these snake venom proteinases.

Experimental
Crystals were obtained from an ammonium sulfate solution by means of hanging drop vapor diffusion method. The crystal has a shape of truncated bipyramid and belongs to the space group P4_2_2 with cell dimensions a = 77.8 and c = 82.3 Å. Diffraction data for MIR phasing were collected using a Rigaku R-AxisIIIC imaging plate detector with a rotating anode generator, and the initial phase from 3 derivatives (KAu(CN)4, EMTS, Er2(SO4)3) had been obtained at 2.5 Å resolution.

In Photon Factory, we collected higher resolution data (up to 2.2 Å) and anomalous diffraction data for the zinc atom on screenless Weissenberg cameras at the BL6A and the BL18B stations (2). These data were processed using the program WEIS (3). A Bijvoet difference Patterson map shows peaks corresponding to the zinc and its position was determined. Then, the data were added to the MIR phasing as a 4-th derivative and an electron density map was recalculated.

An initial model was built using the program TURBO-FRODO and refined using the program X-PLOR. Current model has an R-factor of 0.176 for 10,587 reflections (F > 2σ) between 8.0 to 2.2 Å resolution.

Results
The H2-proteinase molecule has dimensions 50 x 45 x 30 Å with a cleft dividing into 2 domains (Figure). The N-terminal domain (upper) is composed of approximately 150 residues with 5 β strands and 4 α helices, and the irregularly folded C-terminal domain has only 1 helix.

The catalytic zinc-ion is located at the center of the cleft and binds in a distorted tetrahedral manner to 4 ligands — His143, His146, His150 in the consensus binding sequence and the putative catalytic water. The wall of the S1' pocket, which recognizes the hydrophobic bulky P1' residue, consists of Phe134, Val138, Ile169, Pro173.

This enzyme has 2 disulfide bridges in the C-terminal domain: one connects Cys161 and Cys164 near the Met-turn, another bond occurs between Cys158 on a loop area and Cys180 in a helix. These features are different to 2 snake venom proteinases — adamalysin II (4) and atrolysin C (5), and may related to substrate recognition.

Figure. Schematic drawing of H2-proteinase.

References
STRUCTURAL STUDIES ON HYDROXYLAMINE OXIDOREDUCTASE

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Introduction
Hydroxylamine oxidoreductase (HAO), isolated from \textit{Nitrosomonas europaea}, is a multi-heme enzyme that catalyzes the oxidation of hydroxylamine to nitrite\textsuperscript{1}. This is a trimeric enzyme of identical 63 kDa subunits, each containing seven c-hemes and heme P460\textsuperscript{2}. We have carried out crystallographic studies to elucidate the three dimensional structure and the functional properties of HAO.

Experimental
Crystallization of HAO was performed by the vapor diffusion method using ammonium sulfate as precipitant. The space group is \textit{P6}_3 with cell dimensions $a = b = 96.2\text{Å}$, $c = 265.6\text{Å}$ and with two subunits per asymmetric unit. Two heavy atom derivatives was prepared by soaking in 1mM $\text{K}_2\text{PtCl}_4$ and 10mM $\text{UO}_2\text{Ac}_2$. We have tried to couple the anomalous dispersive effect of heavy atom with the MIR phasing.

The diffraction data collection was carried out with a screenless Weissenberg camera for macro molecule\textsuperscript{3} with a Fuji imaging plate at the BL-18B station in Photon Factory. The Pt-derivative Bijvoet data was collected using 1.07Å wavelength near the absorption edge of Pt atom. The twenty-one images were independently processed by the WEIS program system\textsuperscript{4} to assign indices and integrate intensities. Then, intensity data were merged and scaled by the CCP4 program suit. After these process, the merged R-factor was 0.048 with completeness of 95.1% at 4.0Å resolution.

Result
The position of the Pt-binding site was located by the isomorphous difference Patterson map (Fig. 1). Anomalous effect was evaluated between each Bijvoet pairs and supplied to calculate difference Patterson map. The same peak could be found on the Bijvoet difference Patterson map (Fig. 2). This shows that the anomalous signal of Pt atom introduced to HAO could be detected. Now, more suitable derivative preparation and the phasing by MIRAS method is in progress.

References
LAUE DIFFRACTION OF *ARTHROMYCES RAMOSUS* PEROXIDASE CRYSTALS

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**Introduction**

Peroxidase purified from *Arthromyces ramosus* (ARP) is a fungal peroxidase capable of catalyzing the oxidation of a variety of compounds using hydrogen peroxide.\(^1\) ARP consists of 344 amino acid residues and one iron protoporphyrin IX, and contains 5% of carbohydrate and 2 calcium ions. The crystal structure of ARP has been determined at 1.9 Å resolution.\(^2\) The first step of the enzyme reaction, compound I formation, occurs at the distal side of the heme, where histidine and arginine residues play an important role. This step involves formation of enzyme-H₂O₂ complex followed by cleavage of H₂O₂, producing the compound I and a water molecule. We have found that upon formation of a complex with triiodide the conformation of His56 changes but that of Arg53 does not. In order to shed light on the reaction mechanism, we have attempted to determine the structure of a metastable intermediate, the compound I. As the first step of this study, we have evaluated Laue diffraction of ARP crystals.

**Experimental and Results**

The crystals belong to space group *P*₂₁₂₁ with *a*=74.6 Å, and *c*=117.5 Å, and have one molecule per asymmetric unit.\(^3\) Laue diffraction data were collected at the BL18B using Laue camera.\(^4\) The distance from the crystal to the imaging plate (40x20 cm) was 388 mm. The exposure time of each shot was 10 msec. In total, four Laue diffraction patterns were recorded on the imaging plates, and read out by BAS-2000. One of the diffraction patterns is shown in Fig. 1. The intensity data were processed using the PF version of the program system modified by Higashi. The data from 7.0 to 2.5 Å resolution were collected. These were merged and scaled with PROTEIN system to yield 5,395 independent reflections. The *R*_merge and completeness were 18% and 50%, respectively.

ARP crystal gave sharp diffraction spots and was suitable for structural analysis by Laue method. The electron density map, calculated with the present data and the phases derived from the previous 1.9 Å resolution structure, could be interpretable but was rather noisy.

We tried to prepare the crystal of the compound I by soaking the native ARP crystal in the solution containing H₂O₂. Unexpectedly such treatment did not lead to the color characteristic of the compound I, although the color of ARP solution changed immediately when hydrogen peroxide solution was added to it.

References

Glycinin, the major storage protein of soybean seeds, shares many structural characteristics with other 11S globulins distributed in many legume and nonlegume seeds. It is initially synthesized as a single polypeptide precursor consisting of covalently linked acidic and basic polypeptide. After the signal sequence is removed cotranslationally in the endoplasmic reticulum, the resultant proglycinine subunits assemble into trimers of about 8 S. The trimers move into the protein bodies and are then cleaved to form acidic and basic polypeptides linked by a disulfide bridge. We have studied the improvement of food functions of glycinin by protein engineering and have developed new proglycinins with better nutritional and functional properties than the native glycinin. In order to clarify the relationship between glycinin structure and functional properties at the molecular level, the protein structural analysis is inevitable. As the crystallization of glycinin has not yet been attained due to the polymorphism of its primary structure and heterogeneity of the molecular species, we tried to elucidate the structure of proglycinin expressed in Escherichia coli.

Experimental and Results

The proglycinin (AlbBlb-3, lacking the N-terminal 3 amino acids and having the initiation methionine) expressed in Escherichia coli. JM105 transformed with plasmid pKGA1bBlb-3 was extracted from the cells and purified by using a Hiload 26/10 Q-Sepharose as described previously. Crystallization of the proglycinin was performed by the dialysis equilibrium method. The proglycinin solution (6.6 mg/ml) was dialyzed against 0.1 M Tris-HCl (pH 7.6), containing 1.5 mM phenylmethylsulfonyl fluoride, 1 mM EDTA, 0.02% sodium azide and 10 mM 2-mercaptoethanol at 4°C. Crystallization usually commenced within 49 hours and the crystals grew to more than 1.0 mm in length within one week. The crystals mounted in quartz capillaries were subjected to X-ray diffraction experiments using a Nonius precession camera with Ni-filtered CuKa radiation generated by a Rigaku X-ray generator. The crystals diffracted X-rays to a resolution limit at least 2.9 Å on still photographs. The precession photographs indicate that the crystals belong to tetragonal system, spacegroup P4₁ or P4₃, with unit cell dimens-ions of a=b=115.2 and c=147.1 Å. The density of the crystals, as measured in a Ficoll density gradient, was found 1.16 g/cm³ at 25°C. Using a partial specific volume of 0.722 cm³/g as estimated from the amino acid composition of the proglycinin, the number of protomers/asymmetric unit is calculated to be 3.17. Assuming three molecules of proglycinin per asymmetric unit, the solvent volume fraction, Vsol, is 58.4%.

Heavy atom derivatives were prepared by soaking the native crystals to the mother liqud containing 1.0 mM methyl mercury (CH₃HG), 1.0 mM p-chloromercurybenzene sulfonate (PCMB), 5.0 mM gold chloride (KAuCl₄) for 15-20 hours at 20°C. The low resolution (6 Å) diffraction data of the native proglycinin and the heavy atom derivative crystals were collected by a Siemens X-1000 area detector at Research Institute for Protein Chemistry, Osaka University. These data were processed and scaled by using Xengen and Phases software package. The heavy atom sites determined from the isomorphous difference Paterson maps were refined by Phasit of Phases software package. The overall mean figure of merit wasa 0.607 for 4,348 diffractions. The solvent flattening technique was applied on the isomorphous replacement phases to improve the overall mean figure of merit to 0.85. The resulted map clearly distinguishes the protein region from that of solvent. The protein region indicates the boundaries of the proglycinin molecule composed of three protomers related by a three-fold axis symmetry. This three-fold symmetry axis in the asymmetric unit was refined, and the protein density was averaged by Phases software package. The data collection and refinement at more than 3 Å resolution is now under way.

References

CRYSTALLIZATION AND PRELIMINARY X-RAY ANALYSIS OF COPPER AMINE OXIDASE FROM ESCHERICHIA COLI

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Introduction
Monoamine oxidase (MAO) catalyzes the oxidative deamination of a monoamine to the corresponding aldehyde, hydrogen peroxide, and ammonia. MAOs have been found in animals, plants, and microorganisms. Though it is thought to be involved in the metabolism of biogenic amines, its physiological role remains controversial. Copper-amine oxidases comprise two identical subunits and contain an organic cofactor as well as a copper atom in each subunit. 6-hydroxydopa quinone, also known as topa quinone (TPQ), was shown to be the cofactor of copper-amine oxidases of animals, plants, and microorganisms¹. Recently, it was found that TPQ was produced through posttranslational modification of a tyrosine residue, and that cofactor site peptide sequences containing this tyrosine residue, which are converted to TPQ, were highly homologous.

E. coli MAO contains copper and topa quinone as cofactors. Therefore, crystal structure analyses of copper/TPQ-amine oxidase are required to determine the structure of the enzyme active site, the interaction between the Cu atom and the TPQ, and the interaction between a substrate and the enzyme.

Results and Discussions
MAO overproduced by means of cloning was purified to homogeneity by preparation of a periplasmic fraction, DEAE-cellulose column chromatography, and crystallization.³

The purified MAO has been crystallized by means of the hanging drop technique using sodium citrate as a precipitant. The systematic absence of reflections in the h00 and h0l zones of precession photographs indicates that the crystals belong to the orthorhombic system, space group P2₁2₁2₁, with unit cell dimensions of a = 136.1 Å, b = 168.4 Å, and c = 81.6 Å. The unit cell volume was 1.87 x 10⁶ Å³. The density of the crystals, as measured in a Ficoll density gradient, was found to be 1.15 g/cm³ at 25 °C. Using the partial specific volume of proteins, 0.735 cm³/g, as estimated from the amino acid composition of the MAO, the number of protomers/unit cell was calculated to be 7.96.

Assuming two subunits of MAO (Mr = 162,000 Da as a dimer) / asymmetric unit, the solvent volume fraction, Vsol, is 58 %, and the ratio of cell volume to unit protein mass, Vm, is 2.88 Å³ / Da. The number of subunits in an asymmetric unit is agreement with the fact that the enzyme consists of two homodimers in solution². A search for heavy atom derivatives and data collection for determination of the three-dimensional structure of the MAO are in progress.

References
The structure of the photosynthetic reaction centre (RC) from *Rhodopseudomonas viridis* is known to high resolution. It contains a firmly bound tetraheme cytochrome from which electrons are donated back to a special pair (P) of bacteriochlorophylls, which is photooxidized upon absorption of light. Tyrosine at position 162 of the L-subunit of the reaction centre (L162Y) is a highly conserved residue positioned halfway between P and proximal heme group (c-559) of the cytochrome. By specific mutagenesis this residue was exchanged against seven kinds of aminoacids. This time we could obtained good crystals from the two mutants (Y->F and Y->T) and could determine the structures using the X-ray data collected at Photon Factory and at our institute.

The X-ray data collection for the mutant Y->F was carried out at the BL18B station in the Photon Factory ($\lambda=1.00$ Å). The intensity data were obtained using a Weissenberg camera for macromolecular crystallography and an imaging plate as a detector. The imaging plates were digitized with a BA100 Bio-image Analyzer and the intensities were integrated and scaled with the program, WEIS. The X-ray data for the mutant Y->T were obtained with a MAR-Research imaging plate detector using Ni-filtered CuKα radiation. Table 1 contains a summary of the data collection statistics.

The crystal structures of mutant reaction centres were determined using the wild type structure. Positional and temperature factor refinements were performed with the program XPLOR. The refinement converged at crystallographic R-factors of 19.1% (10-2.5 Å) for the Y->F mutant and 18.7% (6-3.2Å) for the Y->T mutant. Table 1 contains a summary of refinement statistics.

Apart from the mutation site, the overall structures of the mutants are nearly unchanged to the wild type. The r.m.s. deviations of Ca positions of Y->F and Y->T mutants from the wild

<table>
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<th>Mutant</th>
<th>Y-&gt;F</th>
<th>Y-&gt;T</th>
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X-RAY CRYSTAL ANALYSIS OF $\alpha_3\beta_3$ COMPLEX OF F1-ATPASE FROM A THERMOPHILIC BACTERIUM
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2)Research Lab. of Resource Utilization, Tokyo Institute of Technology, Nagatsuda, Yokohama 227

Introduction

F1-ATPase (F1) is the soluble and catalytic portion of ATP synthase (Fo-F1 complex). ATP synthase catalyses the conversion of the proton gradient across membranes into ATP. The ATP synthase is universally found in energy transducing membranes.

F1 from various sources share common properties such as subunit stoichiometry, and molecular weight values for the subunits and for the whole molecule. F1 from a thermophilic bacterium PS3 (TF1) has a molecular weight of 385,000, with a subunit composition of $\alpha_3\beta_3\gamma_6\delta\epsilon$, where $\alpha$ (55,000); $\beta$, 52,000; $\gamma$, 32,000; $\delta$, 20,000; $\epsilon$, 14,000). An overproducing system and purification methods for the subunits was established (1).

The $\alpha_3\beta_3$ complex of TF1 has been found recently (2), using the recombinant proteins. The complex has ATPase activity, one third of the ATPase activity of F1, but lacks in sensitivity to metals and azide which F1 has got. Therefore it is assumed the complex can be assumed to be a core complex for ATPase activity.

In this report, we describe an x-ray analysis of the crystals of the $\alpha_3\beta_3$ complex.

Crystallization

Crystals of the $\alpha_3\beta_3$ complex were grown by a modified method from the previous one (3). The new conditions allowed easy transport of the crystals to the PF. The crystals are cubic, with cell dimensions $a=159.5\,\text{Å}$. Estimation of the mass included in an asymmetric unit indicates that three $\alpha$ subunits and three $\beta$ subunits in the complex have the same conformations, respectively.

Data collection at Photon Factory

Native data sets to 3.2Å resolution were collected at BL18B and using Sakabe camera with 430 mm film cassette. In the typical data collection, one exposure had 3 degree rotation (with no translation) and 2 minutes exposure time. Crystals were stable enough for a total 60 degree rotation where a complete set of reflections was obtained.

Data Analysis

Both DENZO and our version of WEIS were used for analysis of the Weissenberg data. The modification of WEIS was described previously (3). The collected intensity by either program was evaluated using rotaprep, scala, agrovata in CCP4 program package (4). The results are summarized in the following table.

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<th>DENZO</th>
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<table>
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These statistics may show that DENZO performs better than WEIS in data collection. The structure solution by molecular replacement is in progress.

References

X-RAY CRYSTAL STRUCTURE ANALYSIS OF OLIGO-1,6-GLUCOSIDASE COMPLEXED WITH AN INHIBITOR /\-NITROPHENOL

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Introduction

Oligo-1,6-glucosidase is a unique enzyme which hydrolyzes the non-reducing terminal \( \alpha-1,6 \)-glucosidic bonds of isomaltosaccharides, panose and \( \alpha \)-limit dextrans, but which does not act on \( \alpha-1,4 \)-glucosidic bonds of maltosaccharides. On the basis of the results from extensive studies on Bacillus oligo-1,6-glucosidases, the proline theory for protein thermostabilization has been proposed (1, 2). This theory suggests that a protein would be thermostabilized with increases in the frequency of proline occurrence at \( \beta \)-turns and the total number of hydrophobic residues in the protein. For elucidation of the structure-function relationship as well as dissection of the proline theory, X-ray crystallographic works of the enzyme has been carried out by our group. The crystal structure of an oligo-1,6-glucosidase from the mesophile, Bacillus cereus ATCC7064 has already been solved by 3.0 \( \AA \) X-ray analysis (3), and refined at 2.0 \( \AA \) Resolution. In order to explain the function in more detail from a structural viewpoint, we have analyzed the structure of oligo-1,6-glucosidase complexed with an inhibitor, \( \beta \)-nitrophenol by X-ray crystal analysis.

Experimental

Crystals of the complex were prepared, as described in the previous work of the enzyme (4), by a hanging drop vapor equilibration of a solution containing 4% protein and 2mM \( \beta \)-nitrophenol against 52% saturated ammonium sulphate (pH 7.0). The crystals isomorphous with the native ones were obtained in two weeks. Diffraction data were collected on BL-18B station of PF, KEK, using a screenless Weissenberg camera with a crystal-to-IP distance of 429.7 mm and a X-ray wavelength of 1.00 \( \AA \). A diffraction pattern was recorded on an image plate by rotating the crystal by 4.5° around the hexagonal c-axis, with the coupling constant of 1.5°/\( \text{mm} \), rotation speed of 2°/sec and 12 oscillations. The rotation angle was overlapped by 0.5° between the adjacent exposures. Sixteen imaging plates of diffraction patterns were digitized on a Fuji BAS2000 photoscanner. The resulting raw data were processed with a program WEIS to 39,805 observed reflection data at 2.5 \( \AA \) resolution. These observations were scaled and merged into the data set of 18,068 unique reflections for the complex crystal with Rmerge of 0.096. The set of the native data used in the previous work of native enzyme structure was again applied to the present analysis of the complex structure. The ratio of intensity change between the native and the complex data sets was 0.057 at 2.5 \( \AA \) resolution.

Results and Discussion

The structure analysis of the binary complex was carried out by difference Fourier method. The initial phase angles for the complex were calculated from the coordinates of native enzyme structure refined at 2.0 \( \AA \) resolution. The quality of diffraction data for the complex crystal was not so good because of the poor crystallinity. However, the \( \text{IFo-Fc} \) difference Fourier maps revealed two large peaks of electron density which were located in the cleft containing the active site of the enzyme. Both peaks were assigned to \( \beta \)-nitrophenol molecules.

The previous X-ray study of oligo-1,6-glucosidase revealed that the molecule consists of three structural domains including the N-terminal (\( \alpha/\beta \)barrel) domain. From some analogies in primary and tertiary structures among proteins functionally related to the present enzyme, the active site of the enzyme is predicted to lie on the C-terminal edge of the parallel \( \beta \)-sheet in the N-terminal domain. The possible candidates for the catalytic residues of the enzyme are Asp199, Glu255, Asp329 which are located on the C-terminal ends of the \( \beta \)-strands, \( \beta \)4, \( \beta \)5 and \( \beta \)7, respectively. One of the two \( \beta \)-nitrophenol molecules found on the difference Fourier maps existed in the vicinity of these putative catalytic residues, with the other \( \beta \)-nitrophenol molecule next to itself. The former \( \beta \)-nitrophenol may act as an inhibitor against the enzyme by blocking the active site for the substrate through strong binding to the catalytic residues. The latter may bind to one of the substrate-binding sites. The more detailed crystallographic analysis of the complex structure is now underway.

References


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N-Domain

Subdomain

C-Domain

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Introduction
We have recently solved the crystal structure of serrata protease, which is a zinc metalloproteinase with several binding Ca\(^{2+}\) ions, by use of anomalous dispersion of Zn\(^{2+}\) ion at 2.0 Å resolution\(^1\). Seven Ca\(^{2+}\) ions were then found from a native difference Fourier map calculated using the data from a wavelength of 1.000 Å, based on their geometry. We have investigated that accurate identification and location of their Ca\(^{2+}\) ions is possible by use of small anomalous dispersion of the Ca\(^{2+}\) ion.

Experimental
X-ray diffraction data of Bijvoet pair reflections were collected using at beam line BL6A2 and BL18B using Weissenberg camera\(^2\) (Table 1). Two kinds of wavelengths used were 1.283 Å at BL6A2 and 1.500 Å at BL18B, respectively. The contributions of f and f" for Ca\(^{2+}\) ion are 0.356 and 0.924 at 1.283 Å and 0.348 and 1.227 at 1.500 Å, respectively. The diffraction intensities were recorded on the imaging plate (20X40 cm), and read out by Fuji BA100 and BAS2000. The intensities from 1.283 Å were evaluated using WEIS program system\(^3\), but the evaluation of the data from 1.500 Å is in progress. For data from 1.283 Å, R\(_{merge}\), R\(_{sym}\)(obs), and R\(_{sym}\)(calc) were 0.0359, 0.0315 and 0.0145, respectively.

Results
An anomalous difference Fourier calculation at 3.5 Å resolution was carried out to locate Ca\(^{2+}\) binding sites (Fig. 1). The phases of each reflections in the calculation were derived from the crystal structure analysis at 2.0 Å resolution whose R-factor was 0.184. Four positions with significantly prominent peaks (Ca1, Ca2, Ca3, Ca4 and Ca5) were similar to those of five Ca\(^{2+}\) ions among seven Ca\(^{2+}\) ions identified from native Fourier map at the wavelength of 1.000 Å. At the two positions of Ca6 and Ca7, there did not show any peak in the map.

<table>
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<th>Beam line</th>
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<th>BL18B</th>
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<tbody>
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</tr>
<tr>
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<tr>
<td>Coupling const (deg./mm)</td>
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<td>Δω (deg.)</td>
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<td>Number of oscillations</td>
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</table>

References
X-ray Structure Analysis of Prolyl endopeptidase

Chong Khoon Tee, Satoshi Murakami, Takashi Tomizaki, Takao Sato, Yukio Morimoto and Tomitake Tsukihara

Department of Biological Science and Technology, Faculty of Engineering, University of Tokushima, Tokushima 770

Introduction

Prolyl endopeptidase [EC3.4.21.26] from Flavobacterium meningosepticum over-expressed in E. coli for the purposes of crystallographic studies. The protein is a monomer protein with 78K containing of 705 amino acids. The recombinant enzyme (25mg/mL) has been crystallized by the batch method from solutions of 21 - 25% (w/v) polyethylene glycol (PEG1.5K) and 50mM Sodium phosphate buffer at pH 7.5. Crystals were grown within one or two weeks at 25°C upto dimensions of about 1.5mm x 0.8mm x 0.5mm.

Crystals were monoclinic ( space group P 21, a = 89.26Å, b = 144.26Å, c = 59.41Å, β = 97.35° , Vm = 2.4 Å³/Da, Vprot = 51%, Z = 4) with two molecules in the asymmetric unit related by a noncrystallographic diad.

Experimental and Results

Fresh crystals were chosen for data collection. Diffractions of SR were collected by using a macromolecular Weissenberg Camera installed at BL-18B, the Photon Factory. Measurement conditions are shown with Table 1. Diffraction image data were processed with the program package DENZO and scaled with SCALEPACK ( Z.Otwinowski ).

A total of 46,804 observations of 12,454 unique reflections [ I > 3σ ( I ) ] were measured from a single crystal with an Rsym of 9.07% and 65.8% completeness to 3.5 Å resolution.

This data set was used to calculated with Self-rotation functions search by the POLARRFN (in the CCP4 suite). This results suggested that there were two protein molecules related by one non-crystallographic 2-fold axis in the asymmetric unit, which is perpendicular to the b*(h)-axis direction.

Table 1. Summary of Data Collection

<table>
<thead>
<tr>
<th>λ (Å)</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oscillation range (° /frame)</td>
<td>5.5</td>
</tr>
<tr>
<td>Overlap (° )</td>
<td>0.5</td>
</tr>
<tr>
<td>No. of Frame</td>
<td>37</td>
</tr>
<tr>
<td>Total oscillation range (° )</td>
<td>185</td>
</tr>
<tr>
<td>Exposure time (sec/frame)</td>
<td>66</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>46,804</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>12,454</td>
</tr>
<tr>
<td>Completeness (%)</td>
<td>65.8</td>
</tr>
<tr>
<td>Rmerge (%)</td>
<td>9.07</td>
</tr>
</tbody>
</table>

The structure will be soluted by the method of multiple isomorphous replacement (MIR). Several heavy atom derivatives preparation are in progress and two heavy atom derivatives used in structure solution. Eight Hg sites were located using Patterson search techniques and used in difference Fourier calculations which revealed the heavy atom positions in another derivative. Four sites were found in the Pt derivative. The refinement of all heavy atom positions and calculation of phases were carried out using MLPHARE (CCP4). The overall figure of merit was 0.54 for 6226 reflections of 10 to 5 Å resolution. The electron density maps calculated from the MIR phases revealed approximately molecular boundary and identified nearly the corresponding 2-fold axis to the resulting noncrystallographic symmetry of self-rotation function search described above. This map suggested to be the existence of the disulfide bond between two cystain residues in C-terminal domain which expected from the amino acid sequence of this enzyme.
proposal No 94G064

X-ray Crystallographic Analysis of Yeast Lipoamide Dehydrogenase

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Introduction

The pyruvate dehydrogenase complex is a well-organized multienzyme system consisting of multiple copies of three component enzymes, pyruvate dehydrogenase(E1), dihydrolipoyl acetyltransferase(E2), and lipoamide dehydrogenase(E3), which catalyses the serial reactions specifically and efficiently. The complexes are classified into two types of the central core structures composed of E2s with different symmetries depending on organisms. One has the 432 symmetry in Gram negative bacteria and the other the 532 symmetry in Gram positive bacteria and in eukaryotes. To elucidate the reaction mechanism and relationship between core structural symmetry and function, we are analyzing the crystal structure of E3 from yeast.

Experimental

The E3 from yeast in the latter type was crystallized by a desalting method. Newly obtained crystals have a different form from the previous ones analysed already at 4.5Å resolution as they have the same space group, but slightly different in cell parameters (a=97.1, b=158.6, c=68.0Å). Diffraction data were collected up to 2.98Å (max. 2.49Å, 65% completeness) by a Weissenberg camera for macro molecular crystallography using synchorotron radiation. The Rsym was 5.3 - 6.3% and Rmerge was 6.4%.

Results and discussion

The crystal structure was solved by the molecular replacement method with glutathione reductase. Three programs(X-PLOR, MERLOT, MOLREP) gave a significant unique solution with reasonable crystal packing, as shown in Fig.1. The initial phases were improved by averaging and flattening of electron density map(DENAF). The atomic coordinates of the molecular model constructed by FRODO were refined by XPLOR with a constrain of non-crystallographic 2-fold symmetry. The present R-factor is 22.6% at 2.49Å resolution.

Although the molecular packing is different, the molecular structure is almost the same as the previous one. As for the complexes with 432 symmetry, the X-ray structures of E3s from Azotobacter vinelandii and Pseudomonas fluorescens have been proposed by Hol et. al. Thus it is revealed that the tertiary structures of E3s are essentially the same even in the different architecture between the two types. Such a strong conservation of the structure may be the functional restrain by the enzyme, although the E3s are assembled into the different core structures on complex formation. The structural difference between the two types and the effect on the reaction are important knowledge for understanding the organization of this multienzyme system, and for modifying it or for designing new systems. Further refinements of the structure are in progress.

Fig. 1. A packing diagram of model molecules in the unit cell, viewed down the c axis

Reference

X-RAY ANALYSIS OF 3-ISOPROPYLMALATE DEHYDROGENASE FROM FACULTATIVE THERMOPHILE, BACILLUS COAGULANS

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Introduction

3-IsopropyImalate dehydrogenase (IPMDH; EC 1.1.1.85) catalyzes a third reaction on leucine biosynthesis pathway. The enzyme of facultative thermophile Bacillus coagulans is composed of two identical subunits [Mw=39,808 (366 amino acid residues)]. Although the crystal structures of IPMDH from extreme thermophile Thermus thermophilus and its chimeric enzyme with Bacillus subtilis were reported, the reaction mechanism is not yet established. Several IPMDHs of various organisms living at different temperature have been identified. The optimum temperature of B. coagulans IPMDH is around 60 °C, which is lower than that of T. thermophilus IPMDH (around 75 °C). To learn the thermostability rationally, it is necessary to compare the three-dimensional structures between them. We have been engaged in an x-ray analysis of B. coagulans IPMDH.

Experimental and Result

The gene coding for the B. coagulans IPMDH has been cloned and expressed in Escherichia coli. After sonication, heat treatment and polyethylene glycol fraction, the enzyme was highly purified with column chromatography in the order of Q-sepharose, hydroxylapatite and phenyl-5PW.

Several crystalline forms were obtained from surveying various conditions using hanging drop vapor diffusion method (Table 1). Among them, the form I, which grew to a maximum size of 1.0 × 0.7 × 0.7 mm³ during 6 months, was suitable for x-ray analysis, as the asymmetric unit contained one dimeric molecule. The other forms, II and III, were estimated to have 3 or 4 dimeric molecules in their asymmetric unit from the reasonable value of V_m.

The x-ray diffraction data of the form I were collected on imaging plates by the weissenberg method at the BL-18B beam line of the photon factory (wavelength 1.00 Å). 25 frames of diffraction patterns were independently processed by the program WEIS to assign indices and integrate intensities. The intensity data then were scaled and merged by several programs in CCP4 suite. 50,159 reflections were observed, of which the 18,442 independent reflections were numbered with R-merge of 0.073 and the completeness of 61.9 % within 3.0 Å resolution.

Molecular replacement (program AMoRe) was applied to solve the structure using the data of 30 to 3.5 Å resolution (completeness 77.9 %). The unique solution was obtained by using dimeric polyalanine structure constructed from T. thermophilus IPMDH as a probe molecule. Closer examination by using a monomeric polyalanine gave more precise orientation and position which are essentially the same as but slightly different from those of dimeric probe. The initial structure of IPMDH thus obtained was refined to an R-factor of 0.419 by rigid-body approximation.

Table 1. Crystallization and crystal data

<table>
<thead>
<tr>
<th>[Crystallization]</th>
<th>Form I</th>
<th>Form II</th>
<th>Form III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein conc.</td>
<td>10mg/ml</td>
<td>10mg/ml</td>
<td>12.5mg/ml</td>
</tr>
<tr>
<td>Buffer</td>
<td>50mM Tris/HCl</td>
<td>50mM Tris/HCl</td>
<td>20mM K-phosphate</td>
</tr>
<tr>
<td>Precipitant</td>
<td>1.0M AS</td>
<td>2.0M AS</td>
<td>1.8M AS</td>
</tr>
<tr>
<td>Additives</td>
<td>12% PEG</td>
<td>4% MPD</td>
<td>6.5</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>8</td>
<td>25 °C</td>
</tr>
<tr>
<td>Temperature</td>
<td>25 °C</td>
<td>20, 25 °C</td>
<td>4, 25 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Crystal data]</th>
<th>Form I</th>
<th>Form II</th>
<th>Form III</th>
</tr>
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<tr>
<td>Space Group</td>
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<td>P212121</td>
<td>P21212</td>
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<td>a = 114.5 (Å)</td>
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<tr>
<td></td>
<td>b = 114.5 (Å)</td>
<td>b = 241 (Å)</td>
<td>b = 241 (Å)</td>
</tr>
<tr>
<td></td>
<td>c = 194.4 (Å)</td>
<td>c = 115 (Å)</td>
<td>c = 122 (Å)</td>
</tr>
</tbody>
</table>

AS : ammonium sulfate, PEG : polyethylene glycol 4000, MPD : 2-methyl-2,4-pentanediol

References

Bragg Reflections from the Crystalline Phase in Thermally Oxidized SiO₂ Thin Films on Si(111) and Si(110) Surfaces

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Introduction

Recently, Iida et al. [1] reported that very weak peaks were observed in the X-ray diffraction from the thermally oxidized thin film on a Si(001) surface. They claimed that these peaks were Bragg peaks originated from small crystallites which coexisted with the amorphous phase having some epitaxial relationship with the Si substrate. A pseudo-cristobalite structure was proposed as a possible model, in which the atomic arrangement is similar to that of the cristobalite structure, while the unit cell is tetragonal so as to match the lateral lattice spacing with that of the Si substrate. Takahashi et al. [2] extended this study more precisely in order to obtain definite information about the structure of the crystalline phase. The result is that the crystallites locate not only at the interface between the Si substrate and the amorphous layer, but also widely in the amorphous layer, preserving the epitaxial relation with the substrate. The volume fraction of such crystallites was estimated to be a few percent of the whole volume of the amorphous layer.

In this report we show that similar Bragg peaks were observed from the oxide layers on Si(111) and Si(110) surfaces, indicating the existence of crystallites having epitaxial relationship with the Si substrate.

Experiment

The samples were prepared by oxidizing Si wafers at 950°C in a dry oxygen atmosphere. The surface of the Si(111) wafer was 4° tilted from the (111) towards the (112). The thicknesses of the oxide layers were 860Å and 760Å for the Si(111) and Si(110) wafers, respectively. The oscillation photographs were taken using the Weissenberg camera and Imaging plate detectors at BL-18B in Photon Factory, KEK [3].

Results and Discussion

The diffraction patterns from the SiO₂/Si(111) and SiO₂/Si(110) samples are shown in Fig.1 and Fig.2, respectively. The needle-shaped scatterings emanating from the 111 Bragg points are crystal truncation rod (CTR) scatterings, due to the abrupt truncation of the crystal surfaces. In both figures spot-like scatterings, denoted by 'extra peak', are observed at the lower angle side of the CTR scatterings. The positions of these extra peaks are 0.42 0.42 0.51 and 0.45 0.45 1 of the reciprocal space in Fig.1 and Fig.2, respectively. It was also found that the extra peaks disappeared when the oxide layers were removed by HF treatments. These features resemble very well to the observations of the SiO₂/Si(001) samples, indicating that the crystallites exist also in the oxide layers on the Si(111) and Si(110) surfaces.

The authors thank to Prof. N.Sakabe of Tsukuba University and Dr. N.Watanabe of Photon factory for their kind help and to Prof. J.Harada of The University of Electo-communications for discussions and encouragement.

References


Fig.1 Oscillation photograph around the 000 and 111 points in the reciprocal space for the SiO₂/Si(111) sample.

Fig.2 Oscillation photograph around the 000 and 111 points in the reciprocal space for the SiO₂/Si(110) sample.
ELECTRONIC STRUCTURES OF ITINERANT FERRIMAGNETS
Fe₇X₈ (X=S and Se)
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Takehisa KONISHI, Tomohiko SAIHO, Atsushi FUJIMORI
Kanta ONO, Akito KAKIZAKI, and Takehiko ISHII
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Introduction
Transition metal chalcogenides have been studied extensively for their various magnetic structures and physical properties. To clarify the electronic states is important for the essential understanding of these compounds. The spin-polarized photoemission spectroscopy (SPPES) enables us to study spin states of the magnetic materials directly. In the present paper, we will report results on Fe₇S₈ and Fe₇Se₈ studied by SPPES. Both compounds are itinerant ferrimagnets with crystal structures of the metal deficient NiAs-type [1]. The compounds attract interest for their magnetism intermediate between itinerant-electron and local-moment types.

Experimental
The SPPES measurements have been performed at the "Revolver" undulator beamline BL-19A of the Photon Factory, National Laboratory for High Energy Physics. The spin analyses were made with a 100 keV Mott-detector. During the SPPES measurements, we magnetized the sample with an external pulse magnetic field of ~1 T, which is enough for the saturation magnetization. The residual magnetization was ~20 % of the saturation magnetization according to SQUID measurements. The sample was mounted on a He cryostat and cooled down to 35 K during the measurements. The clean surface was obtained by scraping in situ with a diamond file. The vacuum of the analyzer chamber was better than 3x10⁻¹⁰ Torr.

Results and Discussion
Figure 1 shows the spin-polarization spectra near the Fermi level with statistical errors. At the photon energy of hv=65 eV, the cross section of the Fe 3d bands are more than 10 times larger than the S 3p and Se 4p bands. The figure shows negative spin polarization near the Fermi level in both compounds. Negative spin polarization indicates the contribution from the Fe 3d minority band. For Fe₇Se₈, the binding energy at which the spin-polarization becomes negative (Eₜ=0.2 eV) is close to the Fermi level compared with Fe₇S₈ (Eₜ=0.5 eV). It suggests the difference in the exchange splitting in the Fe 3d bands related with larger electronegativity of sulfur than that of selenium. If we compare the spin polarization spectrum with the band-structure calculation [2] for Fe₇Se₈, we can see the narrowing of Fe 3d band as in Ni metal. Although an itinerant model is appropriate for Fe₇Se₈ [2], electron correlation effects play an important role for the electronic states of the compounds.

References

Fig. 1 Spin-polarization spectra with spin integrated spectra (solid curves). The length of the bar in the spin polarization spectrum indicates the statistical error. Dashed lines represent smoothed spin polarization.
COINCIDENCE MEASUREMENTS OF THE DISSOCIATIVE PHOTOIONIZATION EXCITATION OF N\textsubscript{2}

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\textsuperscript{2}Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305
\textsuperscript{3}Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305

Introduction

Photoionization of a molecule at which an electron is emitted from an inner-valence orbital has been one of the important subjects of experimental and theoretical studies concerning electron correlation. Photoionization of N\textsubscript{2} has been studied to substantiate the electronic and vibrational structures or the potential energy curves of N\textsubscript{2}\textsuperscript{+} lying lower than ca. 25 eV originated from outer valence orbitals. However, those of N\textsubscript{2}\textsuperscript{+} lying higher than ca. 25 eV originated from orbitals including inner-valence ones have not not been fully understood. Since the dominant relaxation pathways of highly-lying correlation states of ions may be their bond dissociation, dissociation fragments can provide a sensitive probe in the spectroscopy of these highly-lying states.

Here we present a new experiment of measuring the excitation function of highly-lying ionic states of N\textsubscript{2}.\textsuperscript{1} This has been performed by the combined measurement of "a dissociation probe" with "a fluorescence probe" for observing the following dissociative photoionization excitation (DIE) process

\[
N_2 + h\nu \rightarrow N_2^* + e^- \rightarrow N^* + N^+ + e^- \rightarrow N + h\nu,
\]

as a result of the dissociation of highly-lying ions. A coincidence technique is employed to discriminate the fluorescence from neutral dissociation fragments.

Experiment

The experimental apparatus is consisted of a fluorescence photon detector and a time-of-flight (TOF) mass spectrometer to detect photoions. Nitrogen was fed through an effusive nozzle and intersected at the right angle with dispersed SR in the extreme-uv region from a 3 m normal incidence monochromator at the beam line BL-20A. A fluorescence photon in the region of the wavelength of 105-180 nm emitted from N\textsuperscript{*} was detected by a microchannel plate (MCP) coated with CsI behind a LiF window of 1 mm in thickness. A fragment ion N\textsuperscript{+} traveling through the drift tube of a TOF spectrometer was detected by an MCP in coincidence with a fluorescence-photon signal.

Results and Discussion

Each of the fluorescence photon - photoion coincidence spectra obtained at the the photon energies of 36.5 - 44.3 eV showed a broad spectrum with two sharp peaks. The excitation spectrum of a coincidence yield obtained in the present experiment is shown in figure 1. Figure 1 shows the onset at the photon energy about 35 eV and increases gradually with increasing the photon energy. Langhoff et al.\textsuperscript{2} calculated the partial photoionization cross section into highly-lying ionic states of N\textsubscript{2}, i.e., C \textsuperscript{2}Σ\textsubscript{u}+, F \textsuperscript{2}Σ\textsubscript{g}+, G \textsuperscript{2}Σ\textsubscript{g}+, and 2\textsuperscript{2}Σ\textsubscript{g}+. The present excitation spectrum of a coincidence yield in figure 1 shows similar behavior and the threshold energy to the calculated partial-channel photoionization cross section for 2\textsuperscript{2}Σ\textsubscript{g}+. This implies that the major origin of the sharp peaks as shown in figure 1 is the 2\textsuperscript{2}Σ\textsubscript{g}+ state.

References


Figure 1: The excitation spectrum of a coincidence yield. Theoretical photoionization cross sections for the 2\textsuperscript{2}Σ\textsubscript{g}+ state are shown together; \ldots, polarization CI calculation and \ldots, single-excitation CI calculation.
**DISASSOCIATIVE PHOTOIONIZATION OF H\textsubscript{2} AT 26-42 eV**

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**INTRODUCTION**

Dissociative ionization process in H\textsubscript{2} has been extensively studied both experimentally and theoretically. In the energy region below the double ionization of H\textsubscript{2} (threshold of H\textsubscript{2}\textsuperscript{++}: 45 eV), three H\textsubscript{2}\textsuperscript{++} \(2\Sigma_g^+(1s\sigma_g), 2\Sigma_u^+(2p\sigma_u)\) and \(2\Pi_u(2p\pi_u)\) are well known as the ionic states which produce H\textsuperscript{+} through the direct ionization.

**EXPERIMENTAL**

The measurements were carried out at the BL20A equipped with a 3-m normal incidence monochromator. Molecular hydrogen beam was perpendicularly crossed with SR beam, and produced ions were detected at 0\textdegree{} and 90\textdegree{} with respect to the direction of SR polarization. The kinetic energy of protons was analyzed with a parallel-plate type electrostatic analyzer.

**RESULTS AND DISCUSSION**

Below the threshold for direct ionization to H\textsubscript{2}\textsuperscript{++} \(2p\sigma_u\) (=29 eV), autoionization via the Q\textsubscript{1} \(1\Sigma_u^+\) doubly excited state \([1-3]\) is the only process producing fast protons. The kinetic energy spectra in this region were observed to be strongly enhanced at 0\textdegree{}, demonstrating that this process can be explained in terms of the axial recoil approximation. The kinetic energy spectra of protons are shown for the incident photon energy 32-40 eV in Figure 1 for the observation angle of 0\textdegree{} and 90\textdegree{}. With increasing photon energy, the spectra are dominated by direct ionization to the H\textsubscript{2}\textsuperscript{++} \(2p\sigma_u\) and \(2p\pi_u\) states and show a strong dependence on angle \([4]\) that reflects the angular distribution of the photoelectrons. Above 30 eV, the contribution of autoionization via the Q\textsubscript{1} and Q\textsubscript{2} states can be seen mostly in the spectra registered at 90\textdegree{}.

The autoionizing states appearing above 30 eV are the doubly excited states of \(1\Pi_u\) symmetry.

Dissociative Photoionization of O₂ as Studied by Photoion Kinetic Energy Spectroscopy

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Introduction
Molecular ionization in the vuv region is under a strong control of resonance effect via superexcited states. The resonanced assisted ionization is one of the most distinguished interests. It is understood that studies on dissociative photoionization can provide the information on the partial photoionization cross section as well as the potential structure of ionic states. Previously we presented the partial photoionization cross section of O₂⁺ (B²Σg⁺) by the analysis of released kinetic energy of O⁺ produced via

O₂⁺ hν → O₂⁺ (B²Σg⁺) + e⁻

which enabled to study the photoionization in the vicinity of threshold for an upper ionic states. Based on this approach we further examine the dissociative photoionization of O₂ in the region of ionization photon wavelength λ of 45-62nm or the photon energy 20-27.5eV.

Experiment
The experiment was performed using synchrotron radiation (SR) from a 3m normal incidence monochromator equipped at BL-20A. The monochromatic SR beam was transmitted through O₂ gas in a cell. The ions emitted from the gas cell were dispersed using a hemispherical energy analyser. A dispersed image of the spectrum at the exit position of the analyzer was obtained using a continuous resistive-anode type position sensitive detector behind a microchannel plate. The analyzer system was set at a pseudo magic angle relative to the longer axis of eliptically polarized SR to remove the photoionization anisotropy.

Results and discussion
Figure 1 shows a gray scale plot of the ion yield spectrum as a function of both ion kinetic energy (KE) in 0-3 eV and X for 62< X <45nm (photon energy 20-27.5eV). In the region of X >61.1nm a vertical structure at KE ~ OeV is observed which corresponds to the parent ionization onto O₂⁺ (X²Πg⁻, A²Πg⁻, a²Πg⁻, and b²Σg⁻) and the dissociation of O₂⁺ (b²Σg⁻, v ≤ 4). Energetic ions due to the dissociation of O₂⁺ (B²Σg⁺, v') into O⁺ (c²Σg⁻) + O⁺ (¹Σg⁻) show up at the ionization thresholds of O₂⁺ (B²Σg⁺, v'). Although, because of the overlapping thermal distribution, the well defined vibrational structure is not obtained in Fig. 1, yet the greater KE ions are noticed by the expansion of the KE spectral region at the vibronic thresholds of O₂⁺ (B²Σg⁺, v).

Depressed yields are obtained for smaller KE component (i.e., lower vibrational levels) around the window resonance due to O₂⁺ (c²Σg⁻, 3σ, v=0, 1) superexcited states, which gives rise to an "island" on 2D surface.

Two intense vertical structures in the region of λ for X < 50.5nm are ascribed to the dissociation of O₂⁺ (c²Σg⁻, v=0 and 1) into the O⁺ (X²Σg⁻) + O (¹Σg⁻) and the second limit of O₂⁺ (c²Σg⁻) + O (¹Σg⁻) releasing KE=1.9eV and 2.9eV respectively. It should be noticed the clear enhancement of KE ~ 1.9eV peak (identical energy for c²Σg⁻, v=1 and 2nd limit) at the SR photon energy for O₂⁺ (c²Σg⁻, v=1). Nothing is obtained at KE ~ 2.9eV (c²Σg⁻, v=1 and 1st limit). This is the evidence of the autoionization of O₂⁺ (c²Σg⁻, 3σ, v=1) in outgoing dissociating motion.

References
Dissociative Excitation of N₂O in Superexcited States

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Introduction

Neutral dissociation (ND) in competition with autoionization plays an important role among various decay channels of molecular superexcited states.¹ Observations of ND by measuring undispersed vuv fluorescence excitation spectra (FES) of neutral fragments have recently been reported.²⁻⁴ To obtain more detailed information on the ND of superexcited states, we have measured the yield spectra of dispersed vuv fluorescences from excited fragments as a function of both excitation wavelength (λₑ) and fluorescence wavelength (λᵢ). The spectra are presented as two-dimensional fluorescence excitation spectrum (2D-FES). This experiment is an extension of our previous ones on simple diatomic molecules.⁵

Experiment

Synchrotron radiation from a 3m normal incidence monochromator at BL-20A was intersected with N₂O gas in a cell and fluorescences from the gas were dispersed with a secondary monochromator equipped with a 1200lines/mm grating with a curvature radius of 20cm at 64°. A dispersed image of a fluorescence spectrum was obtained using a continuous resistive-anode type position-sensitive detector behind a microchannel plate coated with CsI.

Results and Discussion

Figure 1 shows an obtained 2D-FES. An undispersed FES is also presented. Ionization potentials for some one-electron ionic states are indicated in the FES. Diagonal structures in the 2D-FES are due to scattered primary light, which appear as higher components of the secondary monochromator. Each vertical line structure corresponds to the partial fluorescence yield of an excited O or N atom produced by dissociative excitation of N₂O. A broad structure in the region of 67nm<λₑ<85nm and 140nm<λᵢ<200nm is due to the emission of N₂(a^3Πₗ→X^1Σ₀⁺). The simultaneous enhancement of fluorescence lines at certain discrete λₑ indicates the multistep predissociation of well-defined vibrational N₂O**(spin-allowed dissociation). Weaker fluorescence intensities due to the spin-forbidden dissociation indicate the importance of the spin-orbit interaction in predissociation. In the region of λₑ<60nm, broad structures in each dispersed FES are due to multiply excited neutral states converging onto ionic satellites.⁶

References

HIGH-RESOLUTION MAPPING OF TWO-DIMENSIONAL STRAIN IN ION-IMPLANTED CRYSTALS FROM TRIPLE-CRYSTAL X-RAY DIFFRACTION DATA

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The results reported here are from the first high-resolution triple-crystal diffraction experiments performed at the Australian National Beamline Facility. At the center of the ANBF is a multi-purpose high-resolution two-axis vacuum X-ray diffractometer. The Si (111) sample studied has been implanted with B+ ions of 100 keV energy through a one-dimensional SiO2 strip pattern with a 5.83 μm period and 4 μm open region, to produce a sample with a periodic superstructure in the lateral direction. The triple-crystal data were collected in the form of two-dimensional intensity maps in the vicinity of the 111 Bragg peak. Results collected both in air and vacuum are compared, and a comparison is made between results with and without the oxide layer. The data collected in vacuum indicate that it is possible to measure lattice distortions perpendicular to the surface with a 50 Å depth resolution at the ANBF [1]. The periodic superstructure produced well-resolved 11 satellite reflections on both sides of the Bragg peak from the oxide-removed sample, each associated with a crystal truncation rod. The CTR data were analyzed using the Petrashen-Chukhovskii algorithm which retrieved phase information for the Bragg wave. The solutions were Fourier synthesized to map out 2D lattice distortions in a near-surface layer of the sample with spatial resolutions of 0.016 and 0.265 μm in the depth and lateral directions respectively. The 2D distributions of deposited B+ ions are clearly displayed. Equally plausible maps have been obtained for this sample by determining the relative phases of the satellites with the sequential trial method and the minimum-energy method [2].

References

CTR intensity distributions (left) and reconstructed 2D strain map (right). The periodic oxide mask pattern was removed before X-ray data collection. Thick black lines on the surface indicate the locations and size of the removed oxide strips.
INITIAL EVALUATION OF BIGDIFF FOR MATERIALS CHARACTERISATION

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Introduction

The experiment evaluated the performance of BIGDIFF as a materials processing research tool when used with capillary samples and imaging plate detection. Measurement of the instrument angular resolution function with a NIST-660 LaB₆ powder, using a Si(111) channel cut monochromator and wavelength close to that of CuKα, has shown that the performance is excellent for data collection times in the vicinity of 5-15 minutes. BIGDIFF data were also collected for an alumina-matrix ceramic material to compare instrument performance with that achieved using a laboratory x-ray Bragg-Brentano diffractometer. This comparison has indicated the excellent definition obtained for low concentration phases with BIGDIFF.

Experimental

The BIGDIFF instrument has been described by Foran et al (1994). Data for this experiment were collected as follows- wavelength 1.5378 Å, Debye-Scherrer geometry, capillary diameter = 0.3mm, Fuji BAS 2000 imaging plates scanned for a strip 8 mm wide centred on the equatorial plane of the instrument, recording time 15 minutes.

Results and Discussion

A plot of FWHM versus 2θ for the LaB₆ data, using the pseudo-Voigt approximation for peak shape (Fig. 1.) was described reasonably well with the function proposed by Cox et al (1988).

\[ FWHM(°) = \left[ \phi_v^2 (2 \tan \theta / \tan \theta_m - 1)^2 + \delta^2 \right]^{1/2} \]

where \( \phi_v \) (vertical divergence of incident beam) = 0.0036° and \( \delta \) (diffracted beam divergence) = 0.040°. The FWHM values are excellent in terms of characterising low concentration phases.

An evaluation was conducted with an alumina-matrix ceramic processed by reaction-sintering a mix of 88% zircon (ZrSiO₄), 10% alumina (α-Al₂O₃) and 2% MgO which is of particular interest in view of the complexity of prospective phases which may develop in the material. The material was readily characterised by SR which indicated the phases α-Al₂O₃, t- and m-ZrO₂ and MgO.Al₂O₃ (spinel) whereas the results from laboratory x-rays were equivocal.

Fig. 1. Angular resolution of BIGDIFF measured with NIST LaB₆ capillary specimen. Continuous line is the FWHM function described in the text.

References

DIFFRACTION ANOMALOUS FINE STRUCTURE STUDY OF BASIC ZINC SULPHATE AND BASIC ZINC TOLUENE SULPHONATE

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Introduction

The techniques of XAFS and XANES have been widely used to probe the local environment of absorbing atoms in materials. Interpretation of the absorption data (which is related to \( \Gamma'' \)) can yield information about the environment surrounding the absorbing atoms [1]. Similar information can also be obtained by measuring the intensity of fluorescent radiation emitted by the specimen.

Creagh [2,3] has shown that the variations in \( \Gamma'' \) due to XAFS are carried through to the real part \( \Gamma' \), and therefore into the structure factor \( F_{hkl} \). The measured intensities contain information concerning the local environments of the absorbing atom. Moreover, because different atomic sites may appear in the expression for \( F_{hkl} \) with different weightings it is possible to determine the environments for each site [4].

In our experiment the basic zinc sulphate (bzs) has a known structure, in which the zinc atoms have different local environments, whereas the structure and the environments for the zinc atoms in zinc toluene sulphonate (bzt) are not known. We have used the DAFS technique to determine the zinc environments and to solve the structure for both bzs and bzt.

Experiment

The diffractometer (BIGDIFF) at BL20B was used to undertake the DAFS experiments. BIGDIFF is essentially a Debye-Scherrer camera using imaging plates to record the scattered intensities. A Weissenberg screen, fitted in front of the imaging plates, is scanned across the plates in synchronism with the rotation of the primary beamline monochromator. Thus the position of a line on the screen is related to the incident photon energy and \( F_{hkl} \). As well, the intensities of the Bragg-scattered lines are modulated differently from the background, which is caused by Fluorescent XAFS. The imaging plate carries both DAFS and conventional Fluorescent XAFS data.

Results and Discussion

Figure 1 shows an xrd pattern recorded on an imaging plate in one hour during single bunch mode. The top trace was taken with fixed photon energy, 40 eV below the zinc K-edge. The cassette was then moved, and the photon energy was scanned from -40 to +300 eV relative to the edge. The variation in intensity of the background due to Fluorescent XAFS. From the line positions the crystal structure can be determined using conventional powder diffraction techniques. By finding the variation of integrated intensities of different diffraction lines it is possible to deduce the site symmetry around the zinc atoms. This is not possible using conventional XAFS techniques.

Preliminary analysis for bzs confirms that its structure is triclinic (\( a = 8.351; b = 8.350; c = 11.003; \alpha = 94.40; \beta = 83.01; \gamma = 119.96 \)) and there are two distinct Zn sites. For bzt the structure has not yet been determined but the DAFS data seems to indicate that the environments of the zinc atoms in the structure are similar.

The ability of BIGDIFF to be used for DAFS experiments has been confirmed.

Figure 1

References

NON-SPECULAR X-RAY REFLECTIONS FROM POLISHED SILICON SURFACES AND IN-PLANE MICROSTRUCTURES

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Introduction
We demonstrated in the previous report [1] that the r.m.s. roughness of the 3 - 20 Å range can be evaluated for polished silicon surfaces from X-ray specular reflection data collected at a synchrotron source. The samples investigated, A, B, C and D, were prepared on Si(100) wafers using similar but different mechanochemical polish procedures. Reflection profiles with markedly different decay features were observed from the samples, which were well fit by Parratt's formula including a damping factor exp\((-q^2\sigma^2)\)

where \(\sigma\) is the r.m.s. roughness, \(\sigma\) represents the average deviation of local surface heights from a mean surface characterizing the vertical roughness. To provide information on the in-plane structure of the roughness, non-specular X-ray reflections are investigated here.

Experimental
The experiments used evacuated "BIGDIFF" at the BL20B station to reduce air scatter [2]. Each sample was \(\omega\)-scanned for fixed positions of a slit mounted on the \(2\theta\) arm to define the angular resolution of the set-up at 0.3 mrad for 1.54 Å X-rays. The scans varied \(q_y\) for constant \(q_z\) values in reciprocal space. Data were collected for scattering angles \(2\theta/2\theta_c = 7.7 \sim 17.9\) where \(\theta_c\) is the critical angle for total external reflection of silicon crystal (= 3.9 mrad). Samples A, B, C and D showed quite different levels of diffuse intensities between the specular peak at \(q_y = 0\) and Yoneda wings at the both ends of the profiles (Fig. 1). Samples C and D with highly finished surfaces, hence the smallest \(\sigma\) values, produced very weak diffuse scattering with sharp, resolution-limited specular peaks.

In-plane roughness structures
Our data analysis uses a scattering theory based on the Born approximation for self-affine surfaces [3]. The height-height correlation is assumed to be described by

\[ C(x, y) = \sigma^2 \exp\left(-\frac{r^2}{\xi^2}\right) \]

where \(r = (x^2 + y^2)^{1/2}\), \(\xi\) is the correlation length and \(h\) the fractal index. Fits of diffuse profiles in a few sets of data collected at different \(2\theta\) values consistently produced \(\xi = 1.5 \sim 1.7\ \mu\text{m}\ and \(h = 0.5\) for sample A, and \(\xi = 1.5 \sim 1.8\ \mu\text{m}\ and \(h = 0.3\) for sample B. The much greater \(\xi\) values (6.0 and 6.7 \(\mu\text{m}\ for A and B) obtained from 1-mm scan traces of a stylus profilometer show long-range surface waviness to which X-ray scattering may be insensitive. Data analysis is under way for samples C and D.

References

Fig. 1. \(\omega\)-scan profile from sample A at \(2\theta/2\theta_c = 9.4\). A specular peak is at the center and Yoneda wings are on the edges.
Introduction

Biological Auger Effects have been found in cells with Br-DNA when they are exposed to soft X-rays with energies above and below the K-absorption edge of Br.\(^{1,2}\) The biological Auger effects were sometimes correlated to enhanced DNA damage such as single- or double-strand break. Free radicals induced in DNA are regarded as precursors of base damage and strand breaks.\(^2\) Therefore, it is of interest to examine whether the Auger Effects are also reflected in the yield of free radicals in Br-substituted DNA when they are exposed to soft X-rays with energy corresponding to the K-absorption edge of Br. In the present study 5-bromo-2'-deoxyuridine and 2'-deoxy-thymidine complexes (BrdU*dThd) were employed as Br-substituted DNA models, and the yields of free radicals were measured by ESR after irradiating them in the solid state with soft X-rays having energies above and below the K-absorption edge of Br.

Materials and methods

Solid complexes between BrdU and dThd were prepared by dissolving them in aqueous solutions with adequate weight ratios (BrdU/BrdU*dThd; 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) and dehydrating by centrifugal evaporation. About 50 mg of powder was enclosed in polyethylene tube suitable for the beam size of X-rays from the synchrotron under 1 atmospheric pressure of Ar and exposed to soft X-rays.

Synchrotron radiation at the Photon Factory of the National Laboratory for High Energy Physics was used as a source of soft X-rays. Monochromatic X-rays at 13.45 and 13.52 keVs corresponding to below and above the K-absorption edge, respectively, were obtained using a channel-cut silicon crystal. The exposure dose was measured by a free-ionizing chamber.

The absolute numbers of free radicals induced in the complexes by irradiation were measured by ESR spectrometry.

Photon mass attenuation (\(\mu/\rho\)) and energy absorption (\(\mu_{\text{en}}/\rho\)) coefficients of BrdU and dThd for soft X-rays at 13.45 and 13.52 keVs corresponding to below and above the K-absorption edge, respectively, were obtained using a channel-cut silicon crystal. The exposure dose was measured by a free-ionizing chamber.

The absolute numbers of free radicals induced in the complexes by irradiation were measured by ESR spectrometry.

Photon mass attenuation (\(\mu/\rho\)) and energy absorption (\(\mu_{\text{en}}/\rho\)) coefficients of BrdU and dThd for soft X-rays at 13.45 and 13.52 keVs were first determined by these values of elements (H,C, N, O and Br) according to the data of Hubbell\(^{1}\) and calculated by adding the coefficients of elements in each compound with suitable weighting.

Photon fluxes per roentgen (photons/cm\(^2\)R) and energy fluences per roentgen (erg/cm\(^2\)R) were obtained by 86.9/(\(\mu/\rho\))\(_{\text{air}}\)/1.6\times10\(^{-6}\)/hv(MeV) and 86.9/(\(\mu_{\text{en}}/\rho\))\(_{\text{air}}\), respectively.

Yields of free radicals per photon fluence was obtained by assuming that free radicals induced in the powder within the mean free path (1/\(\mu\)) of photons contributed to actual ESR signal intensities and converting them to the number of free radicals induced per gram, roentgen and photon fluence. Yields of free radicals per energy absorption was obtained by assuming that photon fluence exponential decreased with increasing powder depth and, therefore, calculating total energy absorbed by integrating the photon fluence over the whole powder and multiplying it by the photon energy and energy absorption coefficients. Finally, ESR signal intensities were converted to the number of radicals induced per gram, roentgen and absorbed energy.

Results and discussion

Figs.1 shows the plots of number of free radicals per photon fluence at 13.45, 13.52 (soft X-rays) and 1250 keVs (\(\gamma\)-ray) against BrdU content in BrdU*dThd complex. The higher the content of BrdU the more radicals were produced at 13.45 and 13.52 keVs. The values obtained from 80% BrdU were 25-50 times those of pure dThd at both energies. The value at 13.52 keV was 3 times that at 13.45 keV in the 80% complex. Fig.2 shows the plots of number of free radicals per absorbed energy at 13.45, 13.52 and 1250 keVs. The values obtained from 80% BrdU were 5-14 times those of pure dThd at both energies. The yield of the 80% complex at 13.52 keV was twice that at 13.45 keV. The presence of Br resulted in a marked increase of radical yields compared with those in the absence of Br at the energy above K-edge and a more gentle increase was observed at the energy below K-edge. A negligible increase due to Br was observed in the case of \(\gamma\) irradiation. The results suggested that Br enhanced the efficiency of radical formation at both energies near K-edge, probably due to Auger effects. However, Auger processes seemed to participate in the radical formation with higher efficiency at 13.52 keV than at 13.45 keV. The difference in the yields between 13.45 and 13.52 keVs was small in the complexes with less than 40%, indicating that substitution of BrdU with relatively high level was required for the actual DNA.


Materials and methods

Solid complexes between BrdU and dThd were prepared by dissolving them in aqueous solutions with adequate weight ratios (BrdU/BrdU*dThd; 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) and dehydrating by centrifugal evaporation. About 50 mg of powder was enclosed in polyethylene tube suitable for the beam size of X-rays from the synchrotron under 1 atmospheric pressure of Ar and exposed to soft X-rays.

Synchrotron radiation at the Photon Factory of the National Laboratory for High Energy Physics was used as a source of soft X-rays. Monochromatic X-rays at 13.45 and 13.52 keVs corresponding to below and above the K-absorption edge, respectively, were obtained using a channel-cut silicon crystal. The exposure dose was measured by a free-ionizing chamber.

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Figs.1 shows the plots of number of free radicals per photon fluence at 13.45, 13.52 (soft X-rays) and 1250 keVs (\(\gamma\)-ray) against BrdU content in BrdU*dThd complex. The higher the content of BrdU the more radicals were produced at 13.45 and 13.52 keVs. The values obtained from 80% BrdU were 25-50 times those of pure dThd at both energies. The value at 13.52 keV was 3 times that at 13.45 keV in the 80% complex. Fig.2 shows the plots of number of free radicals per absorbed energy at 13.45, 13.52 and 1250 keVs. The values obtained from 80% BrdU were 5-14 times those of pure dThd at both energies. The yield of the 80% complex at 13.52 keV was twice that at 13.45 keV. The presence of Br resulted in a marked increase of radical yields compared with those in the absence of Br at the energy above K-edge and a more gentle increase was observed at the energy below K-edge. A negligible increase due to Br was observed in the case of \(\gamma\) irradiation. The results suggested that Br enhanced the efficiency of radical formation at both energies near K-edge, probably due to Auger effects. However, Auger processes seemed to participate in the radical formation with higher efficiency at 13.52 keV than at 13.45 keV. The difference in the yields between 13.45 and 13.52 keVs was small in the complexes with less than 40%, indicating that substitution of BrdU with relatively high level was required for the actual DNA.
ESR-DETECTION OF ACTIVE OXYGEN SPECIES IN VARIOUS SOLUTIONS IRRADIATED BY MONOCHROMATIC X-RAY
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Introduction
A thymidine analogue of bromodeoxyuridine (BrdU) had been used as a radiosensitizer. The mechanisms of radiosensitization in BrdU-substituted cells were reported by Webb, et al.¹ and Ling, et al.² But, these data did not support the hypothesis that a component of the enhanced radiosensitivity of BrdU-substituted cells results from greater interaction between hydroxyl radicals (from H_2O_2) and BrdU-substituted DNA. The process of the DNA damages from an hydrated electron is unclear. Then, we examined the detection of the active oxygen species using a spin trapping agent by ESR measurement in aqueous solution contained a cationic surfactant, cetyltrimethyl ammonium bromide (CTAB), BrdU or a human melanoma cultivated (HMF) cells.

Experimental and Methods
(1) Human melanoma (HMF) cells were treated with 10μg/ml of BrdU for 6 hr before harvesting. (2) HMF cells were washed with medium RPMI1640 and were added a spin trapping agents (TMP=2,2,6,6-tetramethyl piperidine hydrochloride: DMPO=5,5-dimethyl-1-pyrroline N-oxide) before irradiation with different wavelength (0.918A, 0.922A). (3) 10 and 0.1 mM CTAB aqueous solutions contained with spin trapping agents were irradiated with different wavelength (Dose=30kR). (4) The irradiated samples were stoked at 77K and were measured by ESR (JEOL, RE3XR type) after thawing of the samples.

Results
(1) In HMF cell suspension (Figs.1,2), the radiosensitization of BrdU by X-ray (0.918A, 30kR) was observed as a presence of DMPO-C signal (.) besides DMPO-OH signal (x). This C-center radical should be produced from the membrane lipid free radicals of the HMF cells.

(2) In the CTAB micellar aqueous solutions (Figs.3-5), TMP-NO signal (º) and DMPO-OH signal (x) were observed separately. The main products of DMPO-OH was not dependent on the presence of BrdU, because CTAB was contained of Br-ion.

In conclusion, center carbon radical was observed in melanoma cell suspension by the BrdU-radiosensitization with monochromatic X-rays (0.918A).

References
CASCADE AUGER TRANSITIONS OF RESONANTLY-EXCITED S 1s and Cl 1s HOLES

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Introduction
Decay processes of the resonantly-excited states is very important not only for unraveling the mechanism of photodissociation or photon-induced desorption of gaseous molecules. Recent investigations showed that deep core holes mostly decay via the spectator Auger transitions. In this work we focus our attention on the cascade Auger transitions in MoS2 and SiCl4 followed by those processes.

Experimental
Molybdenite foil of 10 mm in diameter was used for MoS2 sample. For SiCl4 sample, high-purity solution was degassed and adsorbed on Cu(110) clean surface at 90 K through a microchannel-plate gas doser. The number of layers of the multi-layered sample was estimated to be about 1200. The electron spectra were taken by the use of a hemispherical electron energy analyzer. The total energy (photon + electron analyzer) resolution for the most spectra was estimated to be better than 1.3 eV for the S(KL2,3L2,3) Auger electrons (~2115 eV) and 1.5 eV for the Cl(KL2,3L2,3) Auger electrons (~2380 eV), respectively.

Results and discussion
Strengths of the decay channels to various Auger transitions determined are displayed in Fig. 1 as a function of the photon energy. It is clearly seen that both the L2,3VV(1) and L2,3VV(2) Auger lines are greatly enhanced at the Si 1s absorption edge. Figures 2 and 3 show spectral evolutions of the S(L2,3VV) Auger energy region of MoS2 and the Cl(L2,3VV) Auger energy region of SiCl4, respectively. Origin of the high energy satellite like the L2,3VV(2) Auger lines has been extensively discussed and attributed to the double ionization.1) The signals of the higher energy side in the present work are well-resolved than those in the previous works and are assigned as the double ionization satellites originating from the cascade Auger transitions such as KLL2,3 -> (L1L2,3VV)L2,3 and KL2,3L2,3 -> (L2,3VV)L2,3.

The satellite intensity was analyzed for the S(L2,3VV) Auger line in MoS2. The observed satellite was found to be one third as intense as that expected. The satellite intensity was analyzed for the S(L2,3VV) Auger line in MoS2. The observed satellite was found to be one third as intense as that expected. The discrepancy between the calculated and experimental ratios is probably due to very fast relaxation of the double core-hole states in condensed phase.

Reference

Fig. 1 Decay channels to various Auger transitions at the Si 1s absorption edge.

Fig. 2 Evolutions of the S(L2,3VV) Auger electron spectra for MoS2 and the Cl(L2,3VV) Auger electron spectra for SiCl4.
SPECTATOR AUGER DECAY OF S 1s HOLE STATES IN IONIC SULFUR COMPOUNDS

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Introduction
The decay process of the resonantly-excited deep core holes has not been completely understood, though much attention has been directed to the Auger decay of the outer core holes. Recently we have reported that the spectator Auger lines in silicon compounds, niobium compounds and molybdenum compounds are separated and shift towards the higher electron energies almost in proportion to the exciting photon energies. In this work, Auger decays after the resonant S 1s → 3p* excitation were studied for sulfur containing compounds.

Experimental
The electron spectra were taken by the use of a hemispherical electron-energy analyzer based on the Au 4f7/2 line of metallic Au at 84.0 eV. In order to minimize the effects of charging on the peak width and spectral drift, the surfaces of the insulating samples were exposed to very low-energy electrons. Other details are given elsewhere.

Results and discussions
Figure 1 shows the XANES spectra around the S 1s absorption edge. Figures 2 shows the photon energy (hv) dependences of the KL2,3L2,3 Auger electron spectra of Li2SO4 where the spectator Auger structure slowly disappears when hv is beyond the peak maximum of the XANES spectra. The spectator Auger line shifts with increasing hv almost in the entire energy region of the XANES peak. Furthermore the peak splitting between the spectator and normal Auger lines becomes clearer. Splitting into the spectator and normal Auger lines in Li2SO4 suggests that the resonantly excited 3p* deeply merges into the continuum. A similar general trend was observed for S, KSCN, and Na2SO3 as well.

The spectator shift energies observed are summarized in Table 1. From this table two interesting features are drawn. First, the amount of the energy is independent of the element itself but dependent on the substance containing it. Secondly, the energies for the insulators are larger than those for the semimetallic samples. The phenomena are interpreted in terms of the Auger resonant Raman scattering and bandlike structures of the unoccupied states in the insulating solids.

Reference

Table 1. Threshold energies for the normal Auger transitions and spectator Auger shift energies.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Eth (eV)</th>
<th>Shift energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>2473</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>MoS2</td>
<td>2472</td>
<td>4.5</td>
</tr>
<tr>
<td>PbS</td>
<td>2472</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>S</td>
<td>2472</td>
<td>12</td>
</tr>
<tr>
<td>KSCN</td>
<td>2473</td>
<td>6.5</td>
</tr>
<tr>
<td>Na2SO3</td>
<td>2478</td>
<td>10</td>
</tr>
<tr>
<td>Li2SO4</td>
<td>2482</td>
<td>9.5</td>
</tr>
</tbody>
</table>

Fig. 1 XANES spectra at the S 1s absorption edge.

Fig. 2 KL2,3L2,3 Auger electron spectra for Li2SO4.
Introduction

The escape depth of photoelectron is depended on the kinetic energy of electron. In the present study, SR-X-ray beam (1.9-4.6 keV) was irradiated to the SiO₂ thin film on the Si or the O₂⁻-ion implanted Si surface, in order to obtain the Si₁s photoelectron which has various kinetic energy. From the relationship between the kinetic energy of photoelectron and the Si/SiO₂ ratio, which is observed from the Si₁s XPS spectra, the thickness of the oxide film has been estimated.

Experimental

The experiments were performed at the BL-27A station. The sample used was 99.9999 at.% Si(100) single crystal. It was oxidized in the air at 300°C for 15 min and 700°C for 30 min. O₂⁻-ion irradiated sample (10 keV, 3.6 x 10¹⁷ ions/cm²) was also used. The XPS spectra were measured with a VSW Class-100 employing a hemispherical electron energy analyzer fitted in ARIES-50 spectrometer.

Results and discussion

Fig. 1 shows the sequential change of the Si₁s XPS spectra for the 30 min oxidized specimen as a function of the photon energy. In a spectrum taken at 1915.68 eV photon energy, only one peak is observed, which can be assigned as the SiO₂. On the other hand, the peak of elemental Si is appeared in the spectrum at 2195.44 eV. The peak intensity of elemental Si increased gradually with the photon energy.

Fig. 2 shows the Si/SiO₂ ratio which is obtained from the peak intensity of XPS, as a function of the kinetic energy of Si₁s photoelectron. The ratio increased monotonically with the kinetic energy of photoelectron. This result shows that the Si substrate is observed since the escape depth of photoelectron becomes larger with the increase of its kinetic energy. From the relationship between the kinetic energy and escape depth, the thickness of the oxide film can be estimated as 3.2 nm for the 700°C, 30 min oxidized specimen.

References

Molecular Orientations of Condensed Si(CH₃)ₙCl₄₋ₙ (0≤n≤4) Probed by Near Edge X-ray Absorption Fine Structure

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Introduction
Polarization of synchrotron radiation is widely used for the determination of geometrical structure of adsorbed molecules. The method referred to as near-edge X-ray absorption fine structure (NEXAFS) is mainly based on the variation of absorption intensity from core to valence unoccupied orbital by changing the angle between electric vector of synchrotron beam and solid surface. Therefore, most of the NEXAFS work to date has dealt with adsorbed molecules having p-derived unoccupied orbitals in different directions, i.e. σ* and π* orbitals. In this report, we present examples in which we can simultaneously determine the orientations of two different molecular axes in a molecule which has only σ bonds.

Experimental
The experiments were performed at the BL-27A station. The high-purity solution of Si(CH₃)ₙCl₄₋ₙ (0≤n≤4) molecules were degassed and dosed on the Cu(110) substrate at 90 K. The thickness of the layer was determined to be 600 L by the temperature-programmed desorption (TPD) measurement. The NEXAFS was measured by the partial electron yield (PEY) mode. The kinetic energies of the electron were centered around 1500 eV for Si K-edge and 2040 eV for Cl K-edge, both of which are slightly lower than those of the respective KLL Auger electrons.

Results and discussion
Fig.1 shows the partial electron yields around the Si K-edge as a function of photon energy (NEXAFS spectra) for five kinds of Si(CH₃)ₙCl₄₋ₙ molecule. For SiCl₄ or Si(CH₃)₄, only one resonance peak corresponding to the resonant excitation from SiIs to σ*(tg) orbital is observed below the ionization threshold. For compounds containing both chlorine and methyl groups (n=1,2,3), two resonance peaks are seen. The lower-energy peaks (peaks A) are attributed to the excitation from SiIs to σ*(tg) orbital around the Si-Cl bond, while the higher-energy peaks (peaks B) are assigned to that around the Si-C bond.

The polarization dependence of the NEXAFS spectra for Si(CH₃)₃Cl is displayed in fig.2. Peak A almost disappears for the 1° incidence in which the electric vector is nearly perpendicular to the surface. At this incidence angle, the electrons from the Si Is orbital cannot be excited into the σ* orbital which is parallel to the surface. This suggests that the Si-Cl axis of the Si(CH₃)₃Cl molecule is nearly parallel to the surface. Comparison with the theoretical relation between relative peak intensity and 3cos²(θ-1) value revealed that the average polar angle of the Si-Cl and Si-C bonds are 90±5° and 43±5°, respectively. For Si(CH₃)Cl₃ and Si(CH₃)₂Cl₂, polarization dependences of the resonance peak intensities are not clear, which suggests that these molecules are randomly oriented in condensed layer.

References

Fig. 1
Si K-edge NEXAFS spectra for a Si(CH₃)ₙCl₄₋ₙ multilayer.

Fig. 2
Polarization dependence of Si K-edge NEXAFS spectra for a Si(CH₃)₃Cl multilayer. The θ-value for each spectrum represents the angle between incident photon beam and surface viewed from the top.
PHOTON STIMULATED DESORPTION BY DEEP-CORE EXCITATION; ION DESORPTION FROM CONDENSED SiCl₄ FOLLOWING RESONANT EXCITATION

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Introduction
Desorption of specific species from adsorbed molecules after photostimulation is one of the fascinating topics in the surface science. In order to desorb specific species composed of plural atoms, core excitation is superior to the valence excitation, because the energy of the core orbital is inherent to the atom and we can excite the specific atom by tuning the energy of the synchrotron beam. Most of the work about photon stimulated desorption (PSD) by core excitation has employed photons in VUV region (<1 keV). We consider that deep-core excitation using photons in X-ray region (>1 keV) is in some case suitable for the selective excitation because the energy separation of the core orbital becomes larger in deep core region. Here we report the photon stimulated ion desorption from condensed layer of SiCl₄ following the deep-core excitation (Si and Cl K-edges).

Experimental
The experiments were performed at the BL-27A station. The high-purity solution of SiCl₄ was degassed and dosed on the Pt(111) substrate at 85 K. The thickness of the layer was determined to be 600 L by the temperature-programmed desorption (TPD) measurement. The XANES was measured by both total electron yield (TEY) and partial electron yield (PEY) modes. The desorbed ions were measured by a quadrupole mass spectrometer without energy filter operating in pulse-counting mode. The incident angle between photon beam and the surface was 7° and the takeoff angle of the desorbed ions was 83°.

Results and discussion
Figs. 1(a) and 1(b) show the mass spectra of desorbed ions from condensed SiCl₄ after Si 1s→σ* and Cl 1s→σ* resonance excitations. For the Si 1s excitation, not only molecular ions (SiCl⁵⁺, SiCl⁴⁺) but atomic ions (Si⁺, Cl⁺) are observed almost in comparable intensities, while more than 80% of the desorbed species are Cl⁺ ions for the Cl 1s excitation.

It has been revealed that the Cl 3p* component in 8a₁ orbital is higher than that in 9t₂ orbital. Considering that the bonding orbitals of the Si-Cl bond are mostly composed of the Cl 3p orbital, the existence of an electron in anti-bonding Cl 3p* orbital would reduce the binding energy of the Si-Cl bond. This fact makes the fragmentation of the Si-Cl bond easy compared with the Cl 1s→σ*(9t₂).


Fig. 1 Mass spectra of desorbed ions from condensed layer of SiCl₄ after Si 1s→σ* (upper spectrum) and Cl 1s→σ*(8a₁) (lower spectrum) excitations.

Fig. 2 Total electron yield and Cl⁺ desorption yield from condensed layer of SiCl₄ as a function of the incident photon energy.
**P(KLL) SPECTATOR AUGER DECAY IN PHOSPHORUS COMPOUNDS**

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**Introduction**

It is well known that the Auger decay processes following an inner-shell resonant excitation are different from those after an ionization, because of the excited electron remaining in unoccupied orbitals. Very recently we have reported that in several kinds of compounds the spectator Auger lines are separated from the normal Auger ones and shift linearly with incident photon energies [1]. In the present work, we studied the P(KLL) spectator Auger processes in several solid phosphorus compounds.

**Experimental**

The experiments were carried out at BL-27A station. The electron spectra were measured by the use of a VSW hemispherical electron-energy analyzer based on the assumption that the binding energy of Au4f7/2 line of metallic Au is 84.0 eV. To avoid the peak shift caused by surface charge, very low energy electrons were flooded on the samples during the measurements. Other details were given elsewhere [1].

**Results and discussion**

Figure 1 shows P(KL2,3L2,3) resonant Auger spectra of Na2HPO4 near the PIs absorption edge. It is clearly seen that the KL2,3L2,3 Auger peaks are split into the peaks A and B. The spectator Auger peak A shifts with increasing incident photon energy (hv), while the kinetic energy (Ek) of the normal Auger peak B is almost constant. The peak splitting suggests that localized component of unoccupied orbitals merges deeply into the continuum. Figure 2 shows the Ek's of the spectator and the normal Auger peaks as functions of incident photon energies. Both the peak splitting and the linear Ek shift of the spectator peak are easily noticed. Similar results were obtained for insulating Na2HPO4 and Ca3(PO4)2.

Figure 3 shows the same plot for semiconducting GaP as Fig. 2. At a glance, it is seen that in this case the Auger peak splitting does not happen, whereas the spectator Auger peak shifts linearly with hv.

The Auger peak splitting which have been observed for both insulating and semiconducting substances are interpreted in terms of the Auger resonant Raman effect. Furthermore the Auger peak splitting which have been observed only for insulators can be explained in connection with the formation of core exciton because of very weak core-hole screening by conduction electrons.

**References**

Proposal No 93-G316

SPECTATOR AUGER DECAY AND IONIC FRAGMENTATION FOLLOWING 1SRESONANT EXCITATION

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Introduction

It is important to investigate the details of the Auger decay processes following an inner-shell resonant excitation from the viewpoint both revealing not only the nature of decay processes but also the mechanisms of photodissociation and photoinduced desorption. The purpose of this work is to study the S(KLL) resonant Auger decay and the photodesorption of ionic fragments following 1S excitations for multi- and mono-layered S-containing molecules.

Experimental

The experiments were carried out at BL-27A station. Research grade CS₂ and n-C₃H₇SH were degassed and dosed on Cu(100) substrate, cleaned by Ar⁺ sputtering and 500K annealing. The number of the layers of the multi-layered molecules was estimated to be 500. To prepare the mono-layer, the substrate on which 3 layers of CS₂ adsorbed was heated to 125K. The thickness of the adsorbed molecules was determined by TPD (Temperature Programmed Desorption) measurements. Desorbed fragment ions were counted by the use of a quadrupole mass analyzer.

Results and discussion

Following results were obtained.

1) From the analysis of XANES (X-ray Absorption Near Edge Structure) spectra, the average polar angle of the S-C bond direction of the multi-layered CS₂ is 62° and almost all of the mono-layered CS₂ molecularly adsorb on Cu(100).

2) S(KLL) spectator Auger processes
   (a) Multi-layered CS₂ and n-C₃H₇SH
      In the vicinity of 1S edges, S(KL₂,3L₂,3) Auger peak split into normal and spectator Auger peaks and the latter shift almost linearly with incident photon energy (hν) (Fig.1 and 2).
   (b) Mono-layered CS₂
      S(KL₂,3L₂,3) Auger peak shift almost linearly with hν. However, the Auger peak splitting is not observed (Fig.2).

   The results (a) and (b) can be explained in terms both of the Auger resonant Raman effect and of the core-hole screening by conduction electrons of the Cu substrate.

3) Desorption of fragment ions

   For the multi-layered CS₂, fragments are detected only when hν is adjusted at σ* resonance, whereas the intensity of the σ* absorption is much weaker than that of π* absorption (Fig.3).
Some studies have referred that DNA formed Ca-DNA complex in aqueous solutions involving calcium (Ca) ions, bonding of Ca ions to phosphate moiety first then secondarily to base moiety in DNA. In several years we have studied strand breaks in DNA induced through an atomic target of calcium. The aim of this study was to observe the enhancement effect on strand breaks in DNA induced by the K-shell ionization of Ca atom.

Col E1 plasmid DNA purchased from Takara Co.Ltd. was irradiated in buffered aqueous solution with appropriate concentration of Ca ions. The buffered solution (pH 8.0) was consisted of 10 mmol/dm³ tris-hydroxy methyl-aminomethane and 1 mmol/dm³ EDTA. The DNA concentration was 0.94 mg/ml finally and calcium chloride was added to become an appropriate concentration in irradiated solution. The energy selected for irradiation were 4.030 keV and 4.071 keV, which were corresponded to slightly below and above the K-shell absorption edge of calcium. The numbers of double-strand breaks (DSB) and single-strand breaks (SSB) per one molecule of Col E1 DNA were obtained by the calculation with Povirk’s equation after electrophoretic separation of three forms of plasmid DNA. The detection of the amount of the three forms was done with C4880 CCD camera.

Figure 1 shows the electrophoretic patterns of Col E1 DNA when the DNA solutions were irradiated with 4.071 keV X-rays at various exposures. In Figure 1 a), the patterns of Col E1 DNA irradiated in the solution with 6 mmol/l Ca ions and in Figure 1 b), the patterns of that without Ca ions were shown. The increase of form III with increasing of exposure means the increase of DSB with increasing of exposure. The comparison of Fig.1 a) and b) shows clearly that the yield of DSB in DNA irradiated in the presence of Ca ions is much higher than that in the absence of Ca ions. The number of DSB per one molecule of Col E1 DNA calculated by Povirk’s equation was plotted as a function of exposure in Fig. 2. About 70 % enhancement of the yield of DSB was obtained under the irradiation in the presence of 6 mmol/l Ca ions in comparison with that in the absence of Ca ions.
Co/Pt multilayer is one of the most attractive candidates for next-generation high-density magneto-optical recording media. With decreasing Co layer (i.e. ferromagnetic layer) thickness, the direction of the easy axis of magnetization changes from in-plane to out-of-plane. This change might be attributed to the influence of interfaces of the artificial layered structure on the magnetic properties. Core-level Magnetic circular dichroism (MCD) measurement would be a suitable technique for studies of this system, since it has great advantages of element specificity and site selectivity.

We report here a core-level MCD study of Co/Pt multilayers with varying Co layer thicknesses with almost the same Pt layer thickness.

Six Co/Pt layered samples were prepared on a glass substrate by an rf sputtering method. The top layer was a Pt one in order to avoid oxidation. The Co layer thickness of each sample, determined from both low- and high-angle X-ray diffraction methods, was 3Å, 4Å, 6Å, 9.3Å, 11Å and 14.1Å. The MCD experiments were made using directly characterized circularly polarized undulator radiation on BL-28A. Since the degree of circular polarization of the undulator radiation depends strongly on energy, the spectra were taken separately for the energy regions around the Co M2,3 (and Pt O3) and Pt N⁵-(and Pt O2) edges. The measurements were done with a bulk-sensitive reflection method in a Faraday configuration. The dichroic signals in reflectivity were recorded for two opposite directions of the external magnetic field. The field strength was 2T and was sufficient for saturation of sample magnetization.

Figure 1 shows the reflection MCD spectra in the region around Co M2,3 and Pt O3 edges. A negative peak observed at 61eV grows as Co layer thickness increase, except the Co(14Å)/Pt(15.6Å) sample. This is mainly because of an increase of the Co concentration in the whole system. For samples with thinner Co layer thicknesses (<6Å), the low energy side of the negative peak is sharp as compared with that for the samples with thicker Co layer (>9.3Å) (denoted by †). These features strongly reflect the electronic structure of Co at or around the Co/Pt interfaces which is different from that of bulk. It was confirmed that the samples with thinner Co layer thicknesses (<6Å) had perpendicular magnetic anisotropy and a Co(14Å)/Pt(15.6Å) sample with the thickest Co layer had in-plane magnetic anisotropy. Therefore we can see the systematic variation of the electronic state of Co/Pt interfaces with the change in the magnetic anisotropy.

The role of non-magnetic layers cannot be ignored. Figure 2 shows the reflection MCD spectra taken around the Pt N6,7 edge. Except a Co(14Å)/Pt(15.6Å) multilayer, no appreciable difference is observed. Pt atoms only at the Co/Pt interfaces would have the magnetic moment and are responsible for the MCD signals.

From the results at the Co M2,3 edge combined with the result at the Pt N6,7 edges, we can conclude that the perpendicular magnetic anisotropy mainly depends on the electronic structure of Co at Co/Pt interfaces and that Pt atoms at the interfaces play a partial role in the magnetic anisotropy.

Recently, we have measured the reflectivity spectra of these samples down to 4eV at BL-11C. More detailed discussion will be presented elsewhere on the basis of the dielectric tensors obtained from Kramers-Kronig analysis.

Figure 1 Reflection MCD spectra around the Co M2,3 edge. Co layer thickness (Å)/Pt layer thickness (Å) are presented. The sharp spectral features are denoted by †.

Fig. 1

Fig. 2 Reflection MCD spectra around the Pt N6,7 edge.

Fig. 2
Magnetic Circular Dichroism at the Co M2,3 Edge in CoS2

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Introduction

CoS2 has the pyrite structure and is a metallic ferromagnet whose Curie temperature, \(T_c\), is about 120 K. The total magnetic moment is 0.84 \(\mu_B\) per Co atom. The ions form an fcc array of the NaCl structure; the Co ions occupy the Na sites while the S2 molecules the Cl sites. The strong cubic crystalline field splits the d-band to the lower t2g and upper eg bands, and the Fermi level lies in the middle of the upper eg band.1) We have measured magnetic circular dichroism (MCD) in the Co 3p (M2,3) core-level absorption spectra for obtaining the electronic structure information of the unoccupied state.

Experiment

The MCD experiment was performed on CoS2 single crystal at 62 K in the region around Co M2,3 edge using directly characterized circularly polarized undulator radiation on beamline BL-28A. The measurements were made with a bulk-sensitive reflection method in a Faraday configuration using an ultrahigh-vacuum-compatible superconducting magnet. The photon helicity was fixed and the direction of the 2-T magnetic field direction was switched. The sample chamber was kept at a pressure of \(-1 \times 10^{-9}\) Torr during the measurements. In order to obtain the off-diagonal element of the complex dielectric tensor from the reflection MCD (RMCD) data through a Kramers-Kronig analysis, we measured reflectivity in lower energies from 4 to 50 eV.

Results and Discussion

The absorption coefficients for two opposite magnetization directions, \(\mu^+\) and \(\mu^-\), were obtained by the Kramers-Kronig analysis of the RMCD and reflectance spectra. Here, \(\mu^+\) and \(\mu^-\) represent the absorption coefficients involving transition with \(\Delta Iz=+1(n+)\) and \(\Delta Iz=-1(n-)\) with the z axis taken in the direction opposite to the sample magnetization. The difference, \(\mu^+-\mu^-\), i.e., the MCD spectrum around the Co M2,3 core edge is displayed in Fig.1. The MCD spectrum was found to exhibit a strong negative peak in the low energy side of the M2,3 edge, followed by a strong positive and a weak negative peak in the high energy side of the M2,3 edge with increasing energy.

According to recently discovered MCD sum rules,2,3) the ratio of the orbital to spin magnetic moments can be determined from the MCD spectrum by the following equation, by neglecting the expectation value of the magnetic dipole operator, \(\langle Tz^2 \rangle\),

\[
\frac{m_{orb}}{m_{spin}} = \frac{3}{2} \left( \frac{1}{M_{2,3}} \right) \int_{-1}^{1} (\mu^+-\mu^-)dz
\]

(1)

Fig.1 MCD spectrum of CoS2 around the Co M2,3 edge.

Configuration interaction is so strong at the Co M2,3 edge that the Co M2,3 edge cannot be separated. However, we assume that the equation (1) can be applied to the obtained MCD if the notation M2,3, \(z\) represents the energy region of the strong negative MCD signal, and the notation M2,3, \(\nu\) stands for the region of the strong positive and the weak negative MCD signal. Then we obtain a value of \(m_{orb}/m_{spin}=0.17\). The value is in good agreement with a value of \(m_{orb}/m_{spin}=0.16\) determined from a neutron diffraction experiment.4) We have applied the same modified MCD sum rule to the Co M2,3 MCD for Co single crystal. We obtained a value of \(m_{orb}/m_{spin}=0.095\). The value is in good agreement with a value of \(m_{orb}/m_{spin}=0.095\) obtained from the Co L2,3 MCD by the transmission method5) and a value of \(m_{orb}/m_{spin}=0.097\) determined from the Einstein-de Haas effect.6)

We consider the weak negative peak at the M2,3 edge. The negative weak peak is 2.6 eV higher in energy than the strong positive peak. An electronic structure calculation1) shows that the antibonding S2 p\(\pi^*\)-state molecular orbital, weakly hybridizing with the exchange-split d states, is about 2 eV higher in energy than the Fermi level. Therefore we attribute this weak negative MCD peak to the S2 p\(\pi^*\)-state.

References

STRUCTURAL STUDY OF BIOLOGICAL SUBSTANCES BY CIRCULAR DICHROISM

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Introduction

Chiral objects show a preferential absorption for right or left circularly polarized light. The phenomenon of circular dichroism (CD) has been very useful in characterizing any chiral molecules such as proteins, nucleic acids and their complexes. Non-synchrotron sources have been used to measure CD in the wavelength region from about 135 nm in the vacuum ultra-violet to 10 μm in the infrared. To extend the wavelength range to 100 nm (12.4 eV) or shorter wavelength, the use of synchrotron radiation is required.

The CD bands at wavelengths shorter than 180 nm involve the transitions from the bonds in the backbone of polypeptide. Since σ-σ* transition moments are directed along the bond, the spectral range below 180 nm may provide a fruitful region to explore polypeptide secondary structure. In the wavelength range shorter than 135 nm, no measurement of CD spectrum has been done with biological molecules. Our present interest is concerned with the feasibility for the observation of CD spectrum below 135 nm and the determination of secondary structure of proteins and polypeptide by it.

Experimental

CD experiments were performed on the helical undulator beam line BL28A. The measurement of CD spectrum was carried out by a transmission method in the region of wavelengths from 28 nm (45eV) to 50 nm (25eV) and 50 mA ring current (single bunch mode). The specimen was made by dropping a small amount of aqueous solution of bovine myoglobin or purple membrane of Halobacterium halobium onto a polycarbonate sheet supported by a Ni-mesh, and drying it in a desiccator.

Results and Discussions

The spectra of transmitted beam were measured on a bovine myoglobin sample or a purple membrane one for the right and left circularly polarized lights, respectively. CD spectra calculated from these data were different in sign and amplitude from sample to sample. The present result indicates that the obtained CD data are not significant and suggests some problems which should be considered in the following study. The improvement of the signal-to-noise ratio is needed by increasing incident beam intensity and also, lowering the higher harmonics of incident beam. To confirm the significance of CD spectrum, it is helpful to extend measurements to the region of longer wavelength and connect with the spectrum observed until now. Since the position of specimen may not be precisely the same between the measurement with the right circularly polarized light and the left one, it is necessary to get a specimen with even thickness everywhere, though it is not an easy task due to the hydrophobic property of polycarbonate.

References

Magnetic Circular X-Ray Dichroism at K-Edge in Transition-Metals and Alloys

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INTRODUCTION

Magnetic circular X-ray dichroism (MCXD) has been observed at the K-edge in the various ferromagnetic transition metals and alloys. Since the K-edge is originated in the 1s→4p dipolar transitions, it was not easy to understand the correlation between 4p and 3d orbitals from the observed spectrum. Igarashi and Hirai[1] have recently calculated the K-edge MCXD spectrum in Fe and Ni on the basis of the tight-binding model including the spin-orbit interaction. They have shown that the 3d-orbital moment on the neighboring sites induces the 4p-orbital moment on the core-hole site through the p-d hybridization. They also obtained the sum rule for orbital angular momentum. In this report, we compare the MCXD integrated intensity with the orbital magnetic moments in Fe, Co, and Ni.

EXPERIMENTAL

The MCXD spectrum was measured on the beamline 28B using the transmission method. Thin foils of the ferromagnetic Fe (2µm in thickness), Co (4µm, fcc), and Ni (5µm) pure metals were prepared. The crystal structure was confirmed as bcc (Fe) and fcc (Co and Ni) by X-ray diffraction.

RESULTS AND DISCUSSION

Figure 1 shows the K-edge MCXD spectrum in Fe, Co, and Ni. It demonstrates the difference spectrum (Δμt) to the normalized XANES spectrum. Edge energy E₀ is defined as the photon energy at the first inflection point of the XANES spectrum. The MCXD in Fe is characterized by the positive and negative peaks located at about 0 and 6 eV. On the other hand, the spectra in Co and Ni yield the negative and broaden peak at about 5 eV in the vicinity of the edge. The spectrum in Co has the largest effect among these metals. The overall shape of these spectra has been well reproduced by the calculations.[1] According to the calculations, the spin-orbital interaction of the 3d-states plays a dominant role in generating the spectrum. One can comprehend that the 4p-states on the core-hole site correlate with the 3d-states on the neighboring sites through the p-d hybridization. This indicates that the MCXD spectrum has a sensitivity to local magnetic structure, especially local symmetry.

Igarashi and Hirai have also proposed the sum rule for the orbital angular momentum.[1] It is represented as follows:

\[
\frac{\int \Delta \mu_t \, d\omega}{\int \mu_t \, d\omega} = \frac{3 <L_z>}{2 N_A},
\]

where \( <L_z> \) is the expectation value of orbital angular momentum, \( N_A \) the hole population of 4p-states per atom. Although we applied the MCXD data to eq.(1), it was difficult to estimate precisely the orbital moment because of the ambiguity of the denominator in eq.(1). In fig.2, we thus compare the MCXD integrated intensity with the orbital magnetic moments in the literature.[2] It may indicate that a linear relation possibly holds between these quantities.

References


Fig.1. MCXD spectrum at the K-edge in Fe, Co, and Ni metals.

Fig.2. A comparison between the MCXD integrated intensity and the orbital magnetic moments.[2]
Introduction

The magnetic ordering of RE-TM systems are mainly ruled by 3d(TM)-4f(RE) interaction. Because 4f-state of RE atoms is highly localized, this interaction is indirect through the agency of conduction electrons and very complicated. X-ray MCD (Magnetic Circular Dichroism) with core level excitation is powerful tools to investigate the unoccupied conduction states.

The MCD in Co-RE (RE = La, Pr, Nd, Sm, Gd, Tb, Dy) amorphous thin films was measured at Co K-edge. The MCD spectra at Co K-edge correspond with orbital polarization of 4p(TM) unoccupied conduction states of Co sites. The information about contribution of orbital moments of 3d(TM)- and 4f(RE)-electrons to 4p(TM) conduction states was analyzed from the MCD spectra.

Experimental

Co-RE amorphous thin films were deposited about 2μm-thick on polyimide films by RF magnetron sputtering method. The measurements of MCD were carried out at the beam line PF-BL28B with circularly polarized X-ray. MCD were measured at room temperature using the transmission geometry with two ion chambers in front and behind of the sample. The zero point at energy scale of MCD spectra were chosen as the first inflection point of XANES (X-ray Absorption Near Edge Structure).

Results and discussion

Fig. 1 shows the MCD spectra of Co-RE amorphous thin films at Co K-edge. The spectra of Co-LRE (La, Pr, Nd, Sm) are negative between 0(eV) and 10(eV), on the other hand, those of Co-HRE (Gd, Tb, Dy) have positive and negative peaks at the same energy range. The spectra of both systems seems to consist of two peaks at 3(eV) and 8(eV) denoted by arrows (A) and (B) for Co-LRE, and (C) and (D) for Co-HRE, respectively. Peaks (D) on MCD spectra in Co66Tb34 and Co66Dy34 disappear in Co67Gd33, indicating that (D) is originated from orbital moments of 4f(RE)-electrons which is equal to zero in the case of Gd atoms.

Fig.2 shows the schematic diagram illustrating a series of couplings between orbital moments and magnetic ones. Co-LRE systems are ferromagnetic and Co-HRE systems are ferrimagnetic. As for all the samples, the direction of magnetic moments on RE atoms are parallel to total ones. The direction of orbital moments of 4f(RE)-electrons on RE atoms in Co-LRE systems are parallel to that in Co-HRE systems. This coincide with the fact that the peak (B) in Co-LRE systems didn't change the sign for the peak (D) at the case of Co-HRE systems. The direction of orbital moments of 4f(RE)-electrons (L.μ) are parallel to that of 3d(TM) one (L.μ) in Co-LRE and are antiparallel in Co-HRE when L.μ isn't frozen completely. This relationship of directions between L.μ and L.μ coincides with that of signs of peaks between (A) and (B) in Co-LRE systems and between (C) and (D) in Co-HRE systems. Therefore, the peaks (A) and (C) is strongly affected from orbital moments of 3d(TM)-electrons though L.μ is very small. The structure about 15(eV) on MCD spectra in all samples is considered as the part of oscillation of Magnetic EXAFS because the wave length of electron whose energy is about 15(eV) corresponds to the distance between the absorption atom and its nearest neighbor. This is supported by resemblance of shapes between XANES and MCD spectra in many pure metals and alloys.

In summary, we classified the origins of each peaks on MCD spectra at Co K-edge in Co-RE amorphous alloys. The MCD spectra at Co K-edge reveals the degree of orbital polarization of the 4p(TM) state of Co atoms, and they are strongly affected by 3d(TM)- and 4f(RE)-electrons.

![MCD spectra of Co-RE amorphous thin films at Co K-edge. The compositions of samples were Co70La30, Co70Pr30, Co70Nd30, Co70Sm30, Co66Tb34, and Co66Dy34.](image)

![Schematic diagram illustrating the coupling between the orbital moments and magnetic moments of the RE and TM. (a), (b) indicates the cases of Co-LRE and Co-HRE, respectively.](image)
Local Magnetic Study in Fe/Ho Multilayered Films

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Introduction
Circular Magnetic X-ray Dichroism (CMXD) is a powerful method to study local magnetism of ferro(i)-magnetic materials. Recently a variety of the CMXD measurement at K-, L-edge in metallic compounds, alloy, and multilayered films has been performed. We have already reported the CMXD results of some Fe(40Å)/Ho(1Å) multilayered films and discussed that the interface of Ho layers is magnetized to the extent of as much as 8Å even at room temperature by the influence of neighboring Fe layers.

In this paper, we report the CMXD spectra at the Fe K-edge and Ho L\textsubscript{2,3}-edge in Fe(XÅ)/Ho(XÅ) (X=2.5~80) multilayered films and discuss the magnetic properties which depend on the layer thickness(X) in the Fe/Ho multilayered films.

Experimental
Fe/Ho multilayered films were prepared by an alternative rf sputtering method onto 15μm aluminum foils. The thickness of each layer was controlled by the deposition time and confirmed by X-ray analysis. The ratio of Fe layer thickness to Ho layer thickness was kept to 1:1 and total film thickness was 1μm. The magnetization was measured with a vibrating sample magnetometer.

The CMXD spectra at the Fe K-edge and Ho L\textsubscript{2,3}-edge were measured by using circularly polarized X-rays emitted from the elliptical multipole wiggler at BL-28B station. The measurements were carried out with a transmission method at room temperature and at low temperature(23K). The magnetic field of 6kOe was applied parallel to the sample plane.

Results and Discussion
Figure 1 shows the CMXD spectra (Δμ/μ) at (a) the Fe K-edge and (b) the Ho L\textsubscript{2,3}-edge in Fe(XÅ)/Ho(XÅ) multilayered films at room temperature. For comparison, the CMXD spectra in pure Fe at room temperature, pure Ho, HoFe\textsubscript{2} and Fe(10Å)/Ho(10Å) at 23K are shown together. The Fe K-edge spectra in the multilayers with larger layer thickness(≥30) are almost the same as that in pure Fe, while the Ho L\textsubscript{2,3}-edge spectra are just opposite in sign to that in pure Ho. This means that Fe/Ho moments in multilayers(X>30Å) are aligned parallel to the magnetic field at room temperature. The spectra at Ho L\textsubscript{2}-edge in multilayers(X≥30) are similar to that in HoFe\textsubscript{2} alloy rather than that in pure Ho. This means that Ho atoms near the interface are magnetized like HoFe\textsubscript{2} alloy.

The spectrum at Fe K-edge in Fe(10Å)/Ho(10Å) multilayer at 23K looks like that in HoFe\textsubscript{2} rather than that in pure Fe, while the spectra at Ho L\textsubscript{2,3}-edges are similar to those in pure Ho. This means Fe atoms in Fe(10Å)/Ho(10Å) are similar to those in HoFe\textsubscript{2} alloy and Ho moments are aligned parallel to the magnetic field in contrast to the case of X≥30Å.

However, the spectrum at Ho L\textsubscript{2}-edge in Fe(10Å)/Ho(10Å) is not exactly the same to that in pure Ho. This implies that Fe and Ho atoms in Fe(10Å)/Ho(10Å) influence each other and there does exit some concentration modulation through the interface.

References

Fig.1 The CMXD spectra in Fe(XÅ)/Ho(XÅ) multilayered films, together with those of pure Fe, Ho and HoFe\textsubscript{2}.
Magnetic Circular X-Ray Dichroism at Fe K-Edge in Ferrimagnetic Fe-Oxides

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INTRODUCTION

Magnetic circular X-ray dichroism (MCXD) has been observed at the Fe K-edge in the various ferrimagnetic Fe-oxides. In particular, the dichroic signal located in the so-called pre-peak region, which is interpreted as the 1s→3d dipole-allowed transitions[1-3], has attracted interest in connection with the electronic states of ferric (Fe³⁺) and ferrous (Fe²⁺) ions lying at tetrahedral (Td) or octahedral (Od) environment. Since the Fe ions rule the ferrimagnetism in Fe-oxides, the information about the electronic states is indispensable to understand the magnetic ordering and the local symmetry. In this report, the observed MCXD spectrum is compared with the spectrum calculated on the basis of a cluster model[4]. The observed features can be qualitatively reproduced by the calculations.

EXPERIMENTAL

The MCXD spectrum was measured on the beamline 28B using the transmission method of powder sample. The following ferrimagnetic Fe-oxides were prepared: YIG and Ho-IG with garnet structure (a notation of Fe ion configuration is [3Fe³⁺]_3[2Fe²⁺]_9O₁₂), magnetite ([Fe³⁺]_6[Fe²⁺]_4O₁₂) and Li-ferrite ([Fe²⁺]_6[1.5Fe³⁺]_9O₁₂) with inverse spinel structure, maghemite ([Fe²⁺]_6[5/3Fe³⁺]_10O₁₂) with spinel structure, and Ba-ferrite (BaO•6Fe₂O₃) with magneto-plumbite structure.

RESULTS AND DISCUSSION

Figure 1 shows the MCXD (Δ μ t) and XANES (μ t) spectra in YIG. Dispersion-type MCXD is observed at both the pre-peak and main absorption regions. The sign changes from negative to positive, as the photon energy is increased around the pre-peak region; on the other hand, around the main absorption, the spectrum shows only a subtle signal.

From a comparison between garnet and inverse spinel about Fe-ion configuration and magnetic ordering, we conclude that the pre-peak structure is originated in the Fe³⁺ ion lying at the T₃-sites, and the main absorption is mainly ascribed to the Fe²⁺ and/or Fe³⁺ ion lying at the O₅-sites. The sign of MCXD spectrum reflects the direction of the major local moment contributed to the net magnetization.

Figure 2 shows the MCXD spectrum calculated on the basis of a cluster model[4], assuming that the 1s→3d dipole transitions are allowed at the T₃-sites by the mixing between Fe 3d-4p orbitals through the hybridization with O 2p orbitals. This calculation has reproduced not only the dispersion-type spectrum but also the sign alternation. It also predicts that the MCXD spectrum at the O₅-sites shows the opposite sign by taking into account the next neighboring Fe-ions. It is a critical condition for the O₅-sites, because this polyhedral environment holds centro-symmetry. According to the experimental result, the MCXD at the O₅-sites reflects the distortion from the inversion symmetry.

References

Fig.1. MCXD and XANES spectra in YIG.

Fig.2. The calculated MCXD spectrum at the Fe K-edge in YIG.

- Fig.2. The calculated MCXD spectrum (a) at T₃-sites, and (b) at O₅-sites.[4]
MAGNETIC COMPTON PROFILE OF UTe

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Introduction

Uranium monotelluride (UTe) has NaCl type crystal structure with ferromagnetic ordering temperature $T_c$ of 104K. It is also known to be a high $T_c$ dense Kondo material.

The magnetic Compton profile (MCP) has characteristic feature that the MCP gives only "spin moment" in the momentum space. This feature gives us an opportunity of separating spin and orbital contribution. In this paper we report the MCP of UTe and try to determine orbital magnetization and spin magnetization from a combination of the MCP and magnetization experiments.

Experimental

A UTe single crystal sample was made by the Bridgmann method at Oarai Branch of Tohoku University and brought to the KEK. The single crystal was cleaved to get (100) plane and shaped into a rectangle of size of 8mmx5mmx1mm. A special caution has been paid for treating nuclear fuel substance (U); The sample was held in a copper disk and sealed with 12.5μm Kapton foil under He atmosphere to avoid the leakage of U. The whole disk was set on a cryogenic refrigerator and the magnetic field of 5kOe was applied along <100> direction by the electromagnet. The sample temperature was kept at 80K during measurements in order to achieve magnetic single domain within 5kOe. The incident energy of X-ray was 59.38keV and the scattering angle was 160°.

Results and Discussion

Fig. 1 shows that the MCP of UTe has the negative sign. This is clear indication that the magnetic spin moments are aligned antiparallel to the magnetic field. This also indicates that the orbital magnetization of UTe compound is dominant and parallel to the magnetic field. The least squares fitting of the MCP to U5f momentum distribution shows that the MCP can be well decomposed into U5f components and conduction electron-like components (7s, 7p, 6d). Thus obtained values are $-1.21\mu_B$ for 5f electrons and $-0.36\mu_B$ for conduction electron-like electrons, respectively. The later is very close to the value of $-0.34\mu_B$ estimated from the neutron experiment. The orbital magnetization $\mu_L$ is also estimated using the total magnetization $\mu_{tot}$ and listed in Table 1, which is qualitatively in agreement with the recent Land structure calculation by Brooks et al.

References


Table 1 Magnetic moments of UTe.

<table>
<thead>
<tr>
<th>MCP ($\mu_B$)</th>
<th>Neutron ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_L$ (5f)</td>
<td>$-1.21$</td>
</tr>
<tr>
<td>$\mu_O$ (s,p,d)</td>
<td>$0.36$</td>
</tr>
<tr>
<td>$\mu_O$ (tot.)</td>
<td>$1.57$</td>
</tr>
<tr>
<td>$\mu_L$ (tot)</td>
<td>$2.27$</td>
</tr>
<tr>
<td>$\mu_L$ (tot. 1)</td>
<td>$1.91$</td>
</tr>
</tbody>
</table>

Fig. 1 MCP of UTe.
5d-Electronic States in Pt Alloys Probed by Magnetic Circular X-Ray Dichroism

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INTRODUCTION

Magnetic circular X-ray dichroism (MCXD) provides detailed information about electronic states in magnetic materials. In particular, the possibility of direct separation of orbital ($M_o$) and spin ($M_s$) magnetic moments using the magneto-optical sum rules[1] stimulates various applications to magnetism. This technique is useful for studying magnetic local environment effect of Pt atom in 3d-transition metals. In this report, we present a systematic variation of Pt 5d-magnetic states in the ferromagnetic or ferrimagnetic intermetallic compounds of transition metal (TM) and Pt.

EXPERIMENTAL

The TM-Pt (TM=Cr, Mn, Fe and Co) alloys were prepared by arc-melting method under an Ar atmosphere. The Cu$_4$Au-ordered phase was realized by a suitable thermal treatment. The MnPt$_3$, Fe$_5$Pt and CoPt$_5$ compounds are ferromagnetic, and the CrPt$_5$ is ferrimagnetic. The MCXD measurements were made on the beamline AR-NE1A2 by the transmission method with powder sample.

RESULTS AND DISCUSSION

In order to apply the MCXD data to the sum rules, it is necessary to calculate the following quantities:[1]

$$\rho = \frac{\int_{L_2} (\Delta \mu_L) d\omega + \int_{L_2} (\Delta \mu_S) d\omega}{\int_{L_1-L_2} (3\mu_I) d\omega},$$

$$\delta = \frac{\int_{L_2} (\Delta \mu_L) d\omega - 2 \int_{L_2} (\Delta \mu_S) d\omega}{\int_{L_1-L_2} (3\mu_I) d\omega},$$

where the integration is over the $L_2$ and $L_2$-edges taking into account a rescaling factor. The sum rules give us the ground-state expectation value of orbital $<L_z>$ and spin $<S>$ angular momenta on the basis of atomic model. The magnetic dipole term[1] was approximately replaced with a Lorentz local field. In the case of Pt L-edges, the sum rules are consequently expressed as follows: $\rho = (1/2)<L_z>$ and $\delta = (13/9)<S>$. For the analysis, we adopted the standard procedure composed of the following three steps: Rescaling of XANES spectra, an estimation of white-line intensity, and an integration of MCXD spectrum.

Figure 1 shows the derived orbital $M_o$, spin $M_s$ and total $M_t$ magnetic moments per Pt atom. The value of $M_o$ takes a negative value in TM=Cr and almost collapses in TM=Mn and turns to a positive sign in TM=Fe and Co. On the other hand, the value of $M_s$ increases monotonically from a small positive one in TM=Cr to the order of 0.3 $\mu_B$ in TM=Fe and Co. The dependence of $M_t$ on TM-element is as a whole in good agreement with the data obtained from neutron scattering[2] and band calculations[3]. It is clearly shown that the ferrimagnetism is realized in the CrPt$_5$. It should be emphasized that, in the case of TM=Mn, the spin character dominantly contributes to the Pt moment; whereas the Pt moment in TM=Cr is ascribed to the orbital character. The nature of correlation between Pt 5d- and TM 3d-electrons is still an open question.

References


Fig.1 The derived orbital $M_o$ (circle), spin $M_s$ (square) and total $M_t$ (open-diamond) magnetic moments per Pt atom in this series. The closed-diamond shows the data in the literature.
Pt 5d Orbital and Spin Magnetic Moments in Ferrimagnetic CrPt₃ Compound

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INTRODUCTION

Magnetic circular X-ray dichroism (MCXD) is a powerful technique for studying magnetic local environment effect because of the element selectivity and the angular momentum sensitivity. In transition metal (TM) and Pt alloy with the Cu₃Au-type superstructure, some ferromagnets (e.g., Fe₃Pt) are suitable for this study and the MCXD spectrum at the Pt L-edges has been systematically measured. However, ferrimagnets (e.g., CrPt₃) in this system are not yet studied. In this report, we present for the first time the MCXD spectra in the ferrimagnetic CrPt₃ compound. The orbital and spin magnetic moments of Pt atom are derived from the magneto-optical sum rules [1].

EXPERIMENTAL

The samples used in this study were made by arc-melting method. The Cu₃Au-ordered phase was realized by a suitable thermal treatment and verified by X-ray powder diffraction. Ferrimagnetic CrPt₃ (T_c=481K) and ferromagnetic MnPt₃ (T_c=395K) and pseudo-binary (CrMn)Pt₃ were prepared. The MCXD spectrum was measured on the beamline AR-NE1A2 by using the transmission method with powder sample.

RESULTS AND DISCUSSION

Figure 1 shows the rescaled MCXD and normalized XANES spectra at the Pt L₂ and L₃ edges in CrPt₃. The MCXD spectrum shows a positive sign at both the L₂ and L₃ edges, although ferromagnet ordinarily exhibits a positive (negative) sign at the L₂-edge (L₃-edge). These spectra can be interpreted by the following features: (1) Pt 5d-moments are antiferromagnetically coupled with Cr 3d-moments, (2) the Pt 5d-moments originate in orbital component due to a large spin-orbit coupling, but (3) spin has little contribution to the moment. The orbital and spin angular momenta were estimated by the sum rules on the assumption of initial electronic configuration. The derived orbital (Mₜ), spin (Mₙ), and total magnetic moments are consistent with the neutron scattering data [2]. The values of Mₜ and Mₙ are of the order of -0.1 μₜ and nearly zero, respectively.

To verify the interpretation, the MCXD spectra were recorded from MnPt₃ and (CrMn)Pt₃ as shown in Fig.2. In MnPt₃, the dichroic signal exhibits the ordinary sign on ferromagnet and a nearly equal magnitude at the L₂- and L₃-edges. This leads to the conclusion that an orbital moment almost vanishes in the Pt 5d-states and the moments originate in spin. This feature is in contrast with the results of CrPt₃. In (CrMn)Pt₃, the dispersion-type MCXD spectrum has first been observed at the L₃-edge. This profile can be resolved into the positive peak came from CrPt₃ and the negative one of MnPt₃. It is found that the Pt 5d-magnetic states sensitively depend on the neighboring TM-atoms.

References

CONSTRUCTION OF $\gamma$-e\g SPECTROMETER BY MEANS OF TOF METHOD

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Introduction

The triple-cross section referring to photons and electrons is connected to three dimensional electron momentum density (EMD) $\rho(p)$ as follows,

$$d^3\sigma = \frac{\alpha^2}{2} \frac{dE'd\Omega}{E} \frac{d\Omega}{\omega} \frac{d\Omega}{\omega'} X(\omega,E,E',\theta) \rho(p).$$

where $\alpha$ is the fine structure constant, and $\omega$ and $\omega'$ are the incident and scattered photon energy, $p$ and $p'$ are the initial and the recoil electron momentum, and $E$ and $E'$ the initial and the recoil electron energy. A momentum conservation, $p = p' - K$, holds, where $K$ is the scattering vector. $X$ is the cross section function which includes $\omega, E, E'$ and the photon scattering angle $\theta$.

The possibility of determining experimentally 3D-EMD by the coincidence measurement of scattered photons and recoil electrons was for the first time demonstrated by Rollason et al. However, only 2D-EMD informations have been observed due to the low counting rates and the limited energy resolution. High energy resolution is needed to get 3D-EMD. In this paper, we propose a new spectrometer using a time of flight (TOF) method as the electron detector.

Experimental

Figure 1 shows schematically present spectrometer. The scattered photons are detected by solid state detector (SSD). The recoil electrons are detected by multichannel plate (MCP), measuring the TOF for recoil electrons to travel from the sample to the MCP. This is by virtue of the fact that the Accumulation Ring at KEK is operated in a single bunch mode with a repetition time of 1.28 $\mu$s. The energy resolution of electrons in this system depends upon the sample-detector distance (L) and the bunch width of electrons.

Results and Discussion

Figure 2 shows a preliminary result of the TOF spectrum of recoil electrons from aluminum foil (1 $\mu$m thickness) obtained without the coincidence with scattered photons. The experimental conditions are $\omega = 60$ keV, $\theta = 150^\circ$, $L = 1.75$m, and the emission angle of recoil electrons relative to the incident photons is 15$^\circ$. The peaks at t=6,12 and 30 ns in Fig.2 come from incident photons(60 keV), elastic photoelectrons and recoil electrons, respectively. The bunch width of electrons was estimated from the FWHM of the first peak to be 230 ps, which corresponds to about 0.2 a.u. in the momentum space. The third peak, the Compton profile of recoil electrons, is much distorted due to the multiple scattering of recoil electrons inside the sample.

A Monte Carlo simulation has been performed for the same conditions as the experiment. The result of simulation adopting 100,000 photons are shown in lower part of Fig.2. A qualitative agreement is seen between experiment and simulation, which means the multiple scattering is important.

Magnetic Compton Profiles of Amorphous Gd\(_{60}\)Fe\(_{20}\)Al\(_{20}\)

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Introduction

Magnetic Compton profiles (MCP) give the direct information of momentum distributions of magnetic electrons in ferromagnetic materials. MCP can be further analyzed into individual momentum distributions of spin polarized 3d, 4f and s,p-like band electrons, and these spin magnetic moments can be estimated. Temperature dependence of MCP of a-Gd\(_{60}\)Fe\(_{20}\) had already been reported\(^3\): The temperature dependence of the magnetic moment of Gd-4f electrons is larger than that of Fe-3d electrons.

In this paper, we report on the temperature dependence of MCPs of a-Gd\(_{60}\)Fe\(_{20}\)Al\(_{20}\) and estimate spin magnetic moments of the Fe-3d, Gd-4f and s,p-like electrons.

Experimental

The amorphous alloy was prepared by arc melting followed by hammer and anvil quenching in an atmosphere of purified argon. The sample was confirmed by X-ray diffraction to be amorphous. Its thickness was about 62\(\mu\)m.

The MCP of a-Gd\(_{60}\)Fe\(_{20}\)Al\(_{20}\) was measured on the beam line AR-NE1 using circularly polarized X-rays of 48 keV, which were obtained from the elliptical multipole wiggler\(^2\). A 13-segmented Ge solid state detector was used and the scattering angle was 160\(^\circ\). The momentum resolution was 0.96 a.u. The measurements of the MCP were carried out at temperatures 10K, 50K, 100K and 150K. Magnetization measurement of a-Gd\(_{60}\)Fe\(_{20}\)Al\(_{20}\) was also performed at corresponding temperatures.

Results and Discussion

Figure 1 shows MCPs, each of which is normalized by the corresponding bulk magnetic moment. The difference between MCPs cannot be observed. Table 1 shows spin magnetic moments of the Fe-3d, Gd-4f and s,p-like electrons at each temperature. The temperature dependence of magnetic moments of the Fe-3d and Gd-4f are identical within the experimental error ±0.4\(\mu\)/chemical formula. The negative value of the Fe-3d magnetic moment suggests that the spin magnetic moments of the Fe-3d are antiferromagnetically coupled with that of the Gd-4f.

![Figure 1](image)

Table 1 Evaluated spin magnetic moments (\(\mu\)/chemical formula) of the Fe-3d, Gd-4f, s,p-like electrons.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>s,p-like</th>
<th>Fe-3d</th>
<th>Gd-4f</th>
<th>bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>10K</td>
<td>1.08</td>
<td>-2.42</td>
<td>19.2</td>
<td>17.9</td>
</tr>
<tr>
<td>50K</td>
<td>0.87</td>
<td>-1.95</td>
<td>17.7</td>
<td>16.6</td>
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<tr>
<td>100K</td>
<td>0.83</td>
<td>-2.24</td>
<td>15.0</td>
<td>13.6</td>
</tr>
<tr>
<td>150K</td>
<td>0.56</td>
<td>-1.48</td>
<td>10.1</td>
<td>9.19</td>
</tr>
</tbody>
</table>

References

PROGRESS OF THE IMAGING ZONE PLATE SOFT X-RAY MICROSCOPE

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2 Center for X-ray Optics, LBL
3 Tokyo Metropolitan Institute of Medical Science

Introduction

An imaging soft x-ray microscope using a zone plate with a 50 nm outermost zone width is in operation at the beamline AR-NEIB and its first experimental results have been reported elsewhere.1 During last year the microscope has been improved by introducing a visible pre-focus unit. Some quite good x-ray images have been obtained.

Visible light pre-focus unit

The object distance of a high resolution zone plate is very close to its focal length which is usually shorter than 1 mm and its focal depth is only several microns. In our microscope, the focal length and the focal depth of the OZP are about 0.84 mm and ±2.1 μm, respectively. Therefore, it is very difficult to align the OZP without any auxiliary implement. Based on the above consideration, a visible light pre-focus unit has been developed and introduced into the x-ray microscope as shown in Fig. 1. The unit consists of two objectives (a coarse and a fine) and common eyepieces. The coarse adjustment objective is used to monitor the adjustment of the x-ray optical system in its view field (~ 0.1 mm). The fine adjustment objective with a 0.2 mm central hole to make x rays pass through is used to measure an object distance of the OZP. Its focal depth is designed to be about ±1.5 μm. Since that is less than the focal depth of the OZP, the object distance can be measured and adjusted precisely.

Experimental results

A finer zone plate with a 45 nm outermost zone width as a test pattern is imaged by the microscope.2 The small width of zones down to 55 nm are successfully resolved. According to Rayleigh’s criterion, the spatial resolution of a zone plate microscope is comparable to the width of the outermost zone. Since that width of the OZP is 50 nm, we would believe that the resolution of our microscope has almost reached its diffraction limit.

Some dry biological specimens, diatoms, have been clearly observed at a high resolution as shown in Fig. 2. It has been confirmed that our microscope is applicable to biology.

Reference

1 J.-D. Wang, Y. Kagoshima at al., PHOTON FACTORY ACTIVITY REPORT #11, 422 (1993).

Fig. 1. Schematic of the visible light pre-focus unit.

(a) Outermost region of a fine zone plate test pattern.
(b) Dry diatoms.
Magnetic Circular Dichroism at L\textsubscript{\alpha\beta}-Edges in Transition Metal Platinum Compounds


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INTRODUCTION

Magnetic circular dichroism (MCD) has been widely used for studying local magnetic states of magnetic atom. The transition metal (TM)-platinum intermetallics with the CuAu-type structure have been received interest in local magnetic environment effect because of the variety of magnetic ordering. Although the MCD study of the Pt 5d-states has been already made,[1] it is indispensable to investigate the 3d-states at the TM-sites to understand the magnetism in this system. In this report, we present the MCD spectrum at the TM L\textsubscript{\alpha\beta}-edges in the ferromagnetic Fe\textsubscript{3}Pt and CoPt\textsubscript{3} intermetallics. The MCD data are applied to the sum rules[2] to separate the 3d-magnetic moments into the spin and orbital characters.

EXPERIMENTAL

The samples used in this study were made by arc-melting method. The CuAu-ordered phase was realized by a suitable thermal treatment and verified by X-ray powder diffraction. The ferromagnetic Fe\textsubscript{3}Pt, CoPt\textsubscript{3}, pure Fe and pure Co were prepared. The MCD spectrum was recorded on the beamline NE1B in AR using the total photoelectron yield method. We measured the MCD signal at the L\textsubscript{\alpha\beta}-edges (2p→3d) of Fe and Co.

RESULTS AND DISCUSSION

Figure 1 shows the MCD and XAS spectra, (a) at the Fe L\textsubscript{\alpha\beta}-edges in Fe\textsubscript{3}Pt, and (b) at the Co L\textsubscript{\alpha\beta}-edges in CoPt\textsubscript{3}. The MCD spectrum has a negative (positive) sign at the L\textsubscript{\alpha\beta}-edge (L\textsubscript{\alpha\beta}-edge) in both the intermetallics. These spectra are very similar to that of pure Fe or Co; however, the integrated intensity decreases. These observations indicate that Pt atom gives no considerable influence on the magnetic states of TM atom but possibly induces some modifications in the spin-orbit coupling in this series.

To separate the magnetic moments into the spin and orbital characters, the MCD and XAS data were applied to the sum rules.[2] We assumed that the initial electronic configuration was 3d\textsuperscript{5} in Fe and 3d\textsuperscript{6} in Co. The derived orbital (\(M_\sigma\)), spin (\(M_\pi\)), and total (\(M_\mu\)) magnetic moments are shown in Table I in comparison with the data in the literature.[3] The agreement is generally poor. For the reason, the following items are possibly considered: (1) The mixing between the L\textsubscript{\alpha\beta} and L\textsubscript{\alpha\beta} edges is not avoidable, thus the integrated intensity of XAS yields the serious ambiguity, (2) some secondary processes in the photoabsorption are superimposed on the spectrum, (3) it is difficult to estimate the contribution of the 2p→ns dipolar transitions, (4) the magnetic states of surface are different from that of bulk. Moreover, the uncertainty of hole population is the serious problem. As the results, the applicability of the sum rules to the MCD spectra is restricted.

Table I. Magnetic moments (\(\mu_\mu\)) of Fe and Co in this system.

<table>
<thead>
<tr>
<th>Material</th>
<th>(M_\sigma)</th>
<th>(M_\pi)</th>
<th>(M_\mu)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe in Fe\textsubscript{3}Pt</td>
<td>0.05</td>
<td>1.30</td>
<td>1.35</td>
<td>2.03[3]</td>
</tr>
<tr>
<td>pure Fe</td>
<td>0.02</td>
<td>0.98</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.06</td>
<td>2.21</td>
<td>2.27</td>
<td></td>
</tr>
<tr>
<td>Co in CoPt\textsubscript{3}</td>
<td>0.10</td>
<td>1.09</td>
<td>1.19</td>
<td>1.64[3]</td>
</tr>
<tr>
<td>pure Co</td>
<td>0.12</td>
<td>0.98</td>
<td>1.10</td>
<td></td>
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<tr>
<td>Co</td>
<td>0.14</td>
<td>1.57</td>
<td>1.71</td>
<td>[4]</td>
</tr>
</tbody>
</table>

Fig.1. MCD (upper) and XAS (lower) spectra, (a) at the Fe L\textsubscript{\alpha\beta}-edges in Fe\textsubscript{3}Pt, and (b) at the Co L\textsubscript{\alpha\beta}-edges in CoPt\textsubscript{3}.
Search for Extremely Weakly Interacting Neutral Bosons Using the Undulator Light Source
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The possible existence of extremely weakly interacting neutral bosons (denoted here as $X^0$) is conceivable under many recent particle physics theories that extend the Standard Model. Although stringent limits exist on $X^0$ bosons due to astrophysical and cosmological considerations, such limits depend on models of stellar evolution, supernovae, the early Universe, etc.

In order to perform a direct search for the electron-coupling $X^0$ bosons, we have devised an entirely new experimental method, i.e., a synchrotron light source is used as the $X^0$ source: electrons moving in a magnetic field should emit $X^0$ bosons as well as $\gamma$-quanta. We employed the undulator-NE3 since it has the largest brilliance in the world. This novel method has enabled us to search for $X^0$ bosons with a sensitivity thus far unreached.

Figure 1 shows a simple diagram of the experimental setup. The $\gamma$-quanta are stopped in the shield, while the $X^0$ bosons pass through it. Some of the $X^0$ bosons can be detected with the Ge detector by a process similar to the photoelectric effect [1]. This photoelectric-like effect is enhanced at low energies for high-$Z$ materials, e.g., Ge ($Z = 32$), because its cross section is proportional to $Z^5$ and $E_{X}^{-3.5}$ where $E_{X}$ is the energy of the $X^0$ bosons.

We used a low-background Ge detector which was shielded by lead and oxygen-free copper. Data acquisition is triggered by an energy deposition in the Ge detector greater than 0.6 keV. One output is fed into a peak-hold ADC to precisely measure the energy. Another is used for recording the pulse shape via a Flash ADC at a recording rate of 100 megasamples/s.

To exclude electronic noise events, various cuts are applied on the event’s pulse shape, e.g., an event whose maximum pulse height is below the average noise amplitude is rejected. The efficiency of these cuts is estimated to be greater than 80% above 1.0 keV based on Compton scattering data of 22.2-keV $\gamma$-quanta from $^{109}$Cd.

Events which synchronize with the $e^-$ beams are denoted as “on” and those which do not are denoted as “off.” Since $X^0$ events are included in only the on events, good time resolution is required. Using the pulse shape information, a time resolution of 134 ns FWHM is achieved at energies as low as 1.3 keV. Subtracting the off spectrum from the on spectrum gives the “observed” $X^0$ spectrum in which background events cancel out.

The “observed” $X^0$ spectrum is fitted with the expected one by freely varying the electron-coupling constant of the $X^0$ bosons $\alpha_{Xee}$, which is found to be statistically consistent with zero. The resultant upper limit on $\alpha_{Xee}$ at the 90%-confidence level is shown in Fig. 2(a) as a function of the mass of $X^0$ bosons $m_{X}$, where the results clearly rule out the existence of light bosons with $\alpha_{Xee}$ larger than $9.2 \times 10^{-18}$. We note that our upper limit is 10000 times more stringent than the previous upper limits from direct searches [2]. This experiment also can set limits on new forces, mediated by scalar or vector bosons, coexisting with electromagnetism, as shown in Fig. 2(b). The potential energy of such a force is given by $V(r) = \frac{3}{5} \beta r e^{-r/\lambda}$ where $\beta = \alpha_{Xee}/a$ and $\lambda = \hbar c/m_{X}$. We note that this experiment excludes regions where previous limits are poor, $\lambda > 10^{-3}$, $10^{-3} > \lambda > 10^{-6}$ m [3].

MONOCHROMATIC X-RAY COMPUTED TOMOGRAPHY WITH SYNCHROTRON RADIATION


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Introduction

Conventional x-ray computed tomography (CT) is widely used to diagnose many kinds of disease in clinical practice. Whereas, synchrotron radiation (SR) x-ray CT is presently used in scientific research to analyze the fine structure of materials, because of its monochromatic characteristics as sufficient x-ray flux, non-beam hardening effects, and energy spectrum tunability [1].

Since 1991, we have been constructing a preliminary biomedical CT system with SR to visualize the fine structure in living animals and to detect contrast materials for quantitative functional evaluation, such as in the assessment of the regional blood flow and metabolism of organs in correspondence with their anatomical structures[2, 3].

This report describes a new monochromatic x-ray SR-CT system which was designed and constructed to detect very low concentration (a few µg/ml) of contrast materials.

Materials and Methods

The SR-CT system is constructed at the beam line NE-5A of the Tristan Accumulation Ring in Tsukuba (6.5 GeV, 20-30 mA, 1 T bending magnet). This system consists of a rotating x-ray shutter, a silicon (111) and silicon (511) double monochromator, an x-ray slit system, a rotating object table, 768ch CCD line detector, and a computer (Fig. 1 & Table. 1). By using the monochromator, the x-ray energy can be changed from 30 to 52 keV without high order x-ray energy contamination. The x-ray detector consists of BGO scintillators, a silicon photo-diode array and signal processing units. The dynamic range of the detector is 6000:1, and detectable width is about 150mm, with 200 µm spatial resolution. Projection data are digitized by a 16 bit A/D converter and entered into the computer. The CT images are reconstructed by filtered back projection methods.

Discussion

A new monochromatic x-ray SR-CT is under development in an effort to obtain clear images and to detect very low concentration of contrast materials by using advantages of the properties of SR. In a preliminary experiment with an imaging plate, we noted that it was necessary to decrease the x-ray scatter and to prepare a detector with wide dynamic range and high spatial resolution. In the new monochromatic x-ray SR-CT system, the new CCD detector with wide dynamic range and the double monochromator to eliminate high order x-ray contamination is being constructed to apply animal experiments.

Acknowledgment

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References
2. Takeda T, et. al. Proc. of the Workshop on Medical Applications Using synchrotron Radiation, impress

Fig.1 Schematic diagram of the monochromatic x-ray SR-CT system

Table.1 The monochromatic x-ray SR-CT system specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Object size</td>
<td>150 mm width</td>
</tr>
<tr>
<td>Spatial resolution</td>
<td>&lt; 0.5 mm</td>
</tr>
<tr>
<td>Slice thickness</td>
<td>0.1 - 3.2 mm</td>
</tr>
<tr>
<td>Scan time</td>
<td>&gt; 3 msec/projection</td>
</tr>
<tr>
<td>Scan angle</td>
<td>360°</td>
</tr>
<tr>
<td>Beam energy</td>
<td>30 - 52 keV</td>
</tr>
</tbody>
</table>
INTRODUCTION

The analysis using fluorescent x-ray is used to reveal very low concentration of elements at the order of picogram. But these measurement requires thin specimens slices that are scanned at perpendicular to the surface. A new fluorescent scanning (FS) x-ray computed tomography with monochromatic x-ray from synchrotron radiation (SR) is being developed to detect non-radioactive contrast materials in living object like radionuclide examinations with single photon emission computed tomography (SPECT) [1-2]. The study was done by a first-generation CT configuration. The results of this FS x-ray computed tomographic experiment with a phantom are reported.

METHOD

FS x-ray computed tomography consists of a silicon (111) channel-cut monochromator, an x-ray shutter, an x-ray slit system, a scanning table for the target organ and an x-ray detector with highly purified germanium which detects fluorescent x-ray excited by synchrotron monochromatic x-ray. The experiment was carried out at the bending magnet beam line of BLNE-5A of the Tristan accumulation ring (6.5 GeV, 30 mA) in Tsukuba, Japan. The energy of the monochromatic x-ray beam was adjusted to 33.37 keV.

The monochromatic x-ray beam was collimated into 1 x 2 mm² (horizontal and vertical) using an x-ray slit system. In the detecting portion, excited fluorescent x-ray was also collimated to 1 x 2 mm². Data acquisition time was 60 s in each scanning point. Data analysis was performed only with a Kq, line correcting for object absorption. FS x-ray CT image was obtained by point scanning. A box-shaped phantom with cross ditch filled by iodine contrast material, was scanned. Scanning step size was set to 1 mm in both x-y directions.

RESULTS and DISCUSSIONS

The Kq1, Kβ1, and Kβ2 of fluorescent x-ray and the Compton scattering for emitted monochromatic x-ray were observed at excited iodine content of 4 microgram. The minimal detectable dose of 50 µg/ml iodine in this experiment means the excitation dose of iodine is 100 ng. The image of the phantom filled with 2 mg/ml iodine solution is shown in Fig.1. The corrected image for x-ray absorption by the object shows homogenous distribution of iodine contrast material, whereas the image without correction of x-ray absorption showed inhomogeneous distribution. The correction of x-ray absorption by the object is indispensable to demonstrate the regional distribution of contrast element and to perform quantitative analysis.

FS x-ray tomography can be available to detect a low concentration of contrast material and to reveal its distribution clearly.

Acknowledgment

This research was partially supported by a Grant-in-aid for Science Research #06507002 from the Ministry of Education, Science and Culture.

References


Fig. 1 The image obtained by fluorescent scanning x-ray tomography using a phantom
Compression of Gold up to 10 GPa

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Introduction

Sodium chloride has been widely used as an internal pressure standard in high-P and high-T x-ray diffraction experiments using the multi-anvil apparatus. The phase transition of NaCl into CsCl structure and the recrystallization of NaCl restricts the P-T range of experiments below 25 GPa and 1000°C. On the other hand, a recent progress of multi-anvil device extends the experimental P-T range over 30 GPa and 2000°C. Thus we need establish another pressure scale.

Among many candidates, gold is the most plausible pressure scale, because it is chemically inert and structurally stable in wide P-T range. However the proposed gold pressure scales1,2 show some deviation from the NaCl pressure scale. This difference between two pressure-scales results from the lack of the good quality compression data of gold. The purpose of this study is to determine the equation of state for gold based on NaCl pressure scale.

Experiments

X-ray diffraction experiments were carried out using the cubic type high pressure apparatus MAX80 installed at AR-NE5 by the energy dispersive method. The diffraction angle is fixed at 8° or 10°. Five or more diffraction lines of gold are observed. The number of peaks used for the calculation of unit cell volume of gold are at least four. In order to minimize the effect of deviatoric stress on the volume data, two types of sample cell assembly are used. One is a liquid cell for the room temperature compression experiments, and the other is a solid cell for high temperature experiments. In the former cell, hydrostatic pressure is assured until the freezing of liquid (up to 10 GPa). The latter solid cell is used up to 17 GPa and 1000°C, in which the deviatoric stress is released by the high temperature annealing.

Results and Discussion

Isothermal compression curve of gold is shown in Figure 1. Calculated isotherm by Anderson et al2 is also shown in Figure 1. At the low pressure, equation of state proposed by Anderson et al2 shows a good agreement with the present experimental data. However, the disagreement between calculation and observation becomes large with increasing pressure at room temperature. Pressure calculated by Anderson's EOS is the slightly lower than that of NaCl pressure scale above 6 GPa.

In order to determine the new equation of state of gold, we have to perform further experiments above 10 GPa and high temperature.

Fig. 1. Isothermal compression curves of gold at 25°C and 400°C. Solid circles show the results of liquid cell experiments. Open symbols are the data points obtained by solid cell experiments. Solid lines are calculated isotherms by Anderson et al2.

References

VISCOSITY MEASUREMENT OF SILICATE MELT AT HIGH PRESSURE

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Introduction
Viscosity of silicate melt at high pressure is a fundamental key to understand the behavior of magma migration in the earth. In situ falling sphere method using X-ray shadowgraph enables us to measure silicate viscosities as low as 10^9 Pa s at pressures up to several GPa (Kanzaki et al., 1987). This method has, however, some problems such as a reaction between a specimen and volatiles released from the pressure medium in a practical use. In this study, we tried to measure the viscosity of jadeitic liquid at high pressure precisely, and we made several improvements in the sample assembly in order to reduce the uncertainty caused by unexpected reactions of a specimen with the pressure medium.

Experiment
Synthesized glass with jadeite composition was used as a starting material. This starting material was finely grounded and loaded in a graphite container. Pyrophyllite pressure medium and thermal insulator made of ZrO2 are adopted in the present study instead of boron-epoxy pressure medium in order to prevent the specimen from reacting with boron oxide derived from boron-epoxy during high temperature runs. In situ viscosity measurements with shadowgraph on falling spheres at high pressures, 2-4GPa, were performed using synchrotron radiation at BL-13 MAX90 and AR-NE8 MAX80 stations. Experimental procedure is essentially identical to the previous study (Kanzaki et al., 1987).

After the run, quenched charges were examined for H2O content using Fourier-transform infrared spectroscopy (FTIR). The measurements were made on doubly polished cross sections of the quenched glass, with thickness of 130μm. FTIR spectra were collected using a JASCO model 300 FTIR spectrometer equipped with a JASCO Micro-20 microscope and a MCT detector installed at Earthquake Research Institute, University of Tokyo. Spectra were recorded from 1400-7900cm^-1, with a resolution of 4cm^-1, using 10x10μm² aperture to limit the area from which the spectrum was taken. 64 scans were averaged for each spectrum, and the height above the background of the absorption band at 3530cm^-1 was measured from a plot of spectrum. This absorption peak is attribute to the fundamental OH-stretching vibration (e.g., Stolper, 1982). Absorbances were converted to wt% H2O using the absorption coefficient 67 liter/(mol cm) (Stolper, 1982). The density of the glass is assumed to be 2400g/liter.

Result and discussion
Figure 1 shows the viscosity of jadeite determined in the present study. The results of previous studies are also shown. Measured viscosity at 1400±20°C and 3GPa is 2.15±0.1 in log poise. This value is about an order of magnitude lower than the value predicted by Persikov et al. (1989). This discrepancy is possibly ascribed to the dissolved water in the jadeitic melt. Water contents were 0.44wt% at the center and 0.56wt% at the edge of the recovered charge. Quantitative evaluation of the effect of water on the viscosity of silicate melt is necessary as a future study.

References
SIMULATION OF SCATTERING X-RAYS FOR IMPROVING IMAGE QUALITY IN SR CORONARY ANGIOGRAPHY

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Introduction
In a study of coronary angiography, a two-dimensional imaging system was selected in Japan. That employs monochromatized SR[1]. Such system is very useful for diagnosis of the heart. However, there exists a problem: harmful scattering x-rays generated when passing through a patient's body may come into an x-ray detector. They may deteriorate the image contrast and visibility. Therefore, we need computer simulation for scattering x-rays in order to investigate the behavior of the scattering x-rays; a simulation program for that purpose is under development.

Simulation and Experiment
The simulation program uses the Monte-Carlo method. In the program, an x-ray photon is injected repeatedly into an acrylic phantom whose thickness is 200mm, corresponding to the thickness of a patient's body. Thomson scattering, Compton scattering and photoelectric process were taken into consideration in a photon energy range from 10keV to 100keV. This program gives photon position on the detector, photon energy and the total photon number.

We have performed an experiment in order to verify the simulation program, using 33.17keV monochromatic x-rays at NES5A beamline of AR. A result showing a ratio of the number of scattering x-ray photons against the number of direct x-ray photons, both in the simulation and the experiment, is shown in Fig.1. The simulation agrees well the experimental data; this shows that the simulation program reflects well x-ray scattering behavior.

X-ray Grid Effect
We have applied our simulation program to a system with an x-ray grid. We have found as follows; by using an x-ray grid, the direct photons are attenuated to 34.5%, while the scattering photons are to 9.9%, at the x-ray energy of 33.17keV which corresponds to the above K-edge energy of Iodine. The thickness of the grid is 1.5mm, while that an aluminum and a lead foil is both 0.25mm. This result shows that an x-ray grid works effectively for eliminating scattering x-rays going into the detector.

Discussion
The simulation program will be used in order to find the best method to suppress only scattering x-rays without significant loss of direct x-rays, and further to find the necessary photon density of x-rays from SR source. We will be able to improve the design of a compact SR source dedicated to medical applications, as proposed by the present authors[2] using the results.

References
Introduction

Barium disilicide (BaSi$_2$) has one stable phase with an orthorhombic structure$^{(1)}$ and two metastable phases at ambient condition. One of the metastable phase has a cubic structure$^{(2)}$ and the other has a trigonal structure$^{(3)}$. These metastable phases are synthesized under high-temperature and high-pressure conditions. These conditions indicate the structural phase transition occurs under pressure in the sequence: orthorhombic $\rightarrow$ cubic $\rightarrow$ trigonal. The structure of cubic and trigonal BaSi$_2$ are similar to the crystal structure of period earlier alkaline-earth metal disilicides: cubic BaSi$_2$ has same structure as one period earlier disilicide, SrSi$_2$; trigonal BaSi$_2$ has almost the same structure as two periods earlier disilicide, CaSi$_2$. Thus, the structural sequence of BaSi$_2$ under pressure resembles to that alkaline-earth disilicides changes to the disilicides of the earlier elements in group 2A like Ba $\rightarrow$ Sr $\rightarrow$ Ca. This relationship in structural sequence of alkaline-earth disilicides is opposite to that of pure elements; the structure changes into that of the latter element in the same group with increasing pressure. It is interesting study why the structural sequence of alkaline-earth disilicides is different from that of elements. However, the structural sequence among three phases of BaSi$_2$ is not well known. To date, the crystal structures were determined for quenched samples. Therefore, we carried out in-situ X-ray measurements for BaSi$_2$ at pressures up to 7.1 GPa and temperatures up to 1000°C.

Experimental

X-ray diffraction measurements were carried out by a transmitting energy-dispersive method with synchrotron radiation in AR-NE5. Powdered sample and NaCl pressure marker were compressed in solid pressure transmitting medium with a multi-anvil type high-pressure apparatus, MAX80. Pressure was evaluated from a lattice constant of NaCl.

Results and Discussion

The starting material is orthorhombic BaSi$_2$. The sample shows no phase transitions when compressed up to 7.1 GPa at room temperature. Figure 1 shows X-ray diffraction patterns in heating process at 2.9 GPa. On heating at 2.9 GPa, phase transition from the orthorhombic phase to the trigonal phase occurs about 450°C. On further heating, peaks of the cubic phase appear about 550°C. At 750°C, a large part of the sample transforms into the trigonal phase. However, peaks of the trigonal phase are still observed above 750°C. Thus, it is found that the trigonal and the cubic phases coexist in a wide temperature range at 2.9 GPa. The same experiments were carried out at 7.1 GPa. With increasing temperature, orthorhombic BaSi$_2$ changes into trigonal BaSi$_2$ in the same way that at 2.9 GPa. Further heating up to 800°C results in a new phase, which is different from the known cubic phase. The cubic phase does not appear in this case. The structure of new phase is now under investigation.

References


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Fig.1 X-ray diffraction patterns in heating process at 2.9 GPa. The symbols, o, c, t and B represent diffraction peaks from orthorhombic BaSi$_2$, cubic BaSi$_2$, trigonal BaSi$_2$ and BN pressure capsule, respectively.
A TOPOLOGICAL PHASE TRANSITION OF AgCl UNDER HIGH PRESSURE
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Introduction
AgCl with the B1 structure was reported to transform to a high pressure phase, of which X-ray data could not be explained by the B2 structure. The X-ray data were too poor to determine the true structure.

The aim of the present work is to obtain using precise diffraction data using synchrotron radiations. The final goal of this work is to reconsider the mechanism of the B1-B2 transition on the basis of the pressure behavior of AgCl.

Experiments
High pressure experiments were carried out using a DIA type cubic anvil apparatus "MAX80" installed at AR-NE5 in KEK. Chemical reagents of dry AgCl (5N) and a mixture of NaCl (5N) and BN (4N) were separately encased in a boron-epoxy cubic pressure medium. X-ray diffraction patterns under high pressure were taken by an energy dispersive method.

Results
Three high pressure phases (HPPs) were observed in the pressure and temperature range up to 17.5 GPa and 500°C, as shown in Fig. 1.

The B1 structure was stable up to about 8 GPa. The HPP1 was observed between 8 and 13 GPa and is suggested to have the KOH structure (space group; P21). The HPPII with the TII structure (Cmcm) was stable between 13 and 17 GPa. The HPPIII with the B2 structure (Pm3m) was found at 17.5 GPa and 500°C.

Discussion
We demonstrate that these four structures can be described systematically using a common monoclinic cell, and the cell parameters change continuously from the B1 to B2 structures. A topological mechanism by a simple deformation is proposed to explain these transformations, in which the [110] and [110] directions of the B1 structure correspond to the [100] and [011] of the B2 structure respectively.

Fig. 1 Crystal structures of a) the B1 type, b) the KOH type, c) the TII, d) the B2 type. Small and large circles show Ag+ and Cl−, respectively. Broken lines show the common subcell.
MONOCHROMATIC X-RAY CT USING FLUORESCENT X-RAYS GENERATED BY SYNCHROTRON RADIATION

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Introduction

In medical imaging using synchrotron radiation, such as K-edge subtraction angiography and monochromatic X-ray CT, it is necessary to use high intensity monochromatic X-rays with different energies.

The fluorescent X-rays, generated by irradiating the target materials with a white X-ray, offer a large beam size due to its divergent characteristics. The purpose of this study is to develop an X-ray CT system using fluorescent X-rays, to investigate its fundamental characteristics, and to obtain quantitative CT images.

Experiments

Fluorescent X-rays which range from about 20 keV to 70 keV are generated by irradiating several target materials with a white X-ray from a 6.5 GeV SR-ring in Tsukuba as shown in Fig. 1. The intensity of fluorescent X-rays are 6.2 x 10^4 ~ 3.0 x 10^5 photons / mm^2 / sec x mA at 30 cm from the focal spot on the target. The purity of the X-rays are improved to better than 95% by using K absorption filters.

Cylindrical phantoms filled with iodine contrast media with different concentrations are used for quantitative imaging objects. A total of 120 projections covering 360 degrees are obtained by rotating the object using a 64 channel CdTe array detector (2 x 2 mm x 0.5 mm /channel) operated in photon counting mode.

Results and Discussion

Fig. 2 shows examples of monochromatic X-ray CT images of cylindrical phantoms filled with iodine of various concentrations ranging from 0.1 mg/ml to 80 mg/ml. The measured CT numbers calculated from the central ROI of each image and theoretical CT numbers for low concentration region are plotted in Fig. 3. The magnitude of the measured CT numbers are about 30% less than the theoretical values, which are calculated from the attenuation coefficients. This discrepancy suggests the effects of scattering radiation. However, the linearity is fairly good and quantitative CT images without beam hardening effect may be obtained using CT number normalization.

The fluorescent X-ray source using an SR may be useful for quantitative, element selective imaging.

Reference

In-situ X-ray Study of Mullite at High Pressure and High Temperature

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Introduction

Chemical decomposition of mullite $3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ under high pressure and high temperature is studied using synchrotron x-ray diffraction measurement. This report presents some results for extended pressure and temperature ranges.

Experimental

The pressure was applied to the samples using the cubic anvil high pressure apparatus (MAX080) at AR-NE5C. The truncation size of the anvil top is 6mm and the pressure medium is a pyrophyllite cube with an edge length of 8mm. High purity mullite powder and sodium chloride, which is used as a pressure marker, were embedded in the BN lined graphite furnace separately. Sample temperature was monitored by a B-type thermocouple and was increased stepwise under fixed pressure. X-ray diffraction pattern was collected at every constant temperature and pressure condition.

Results

At 3.8GPa, 4.5GPa, and 5.7GPa, the chemical decomposition of mullite was observed at around 1240 °C. At 6.5GPa, on the contrary, peaks of kyanite appeared at 1100 °C. The decomposition of mullite is represented as

$$3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \rightarrow 2(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2) + \text{Al}_2\text{O}_3$$

Figure 1 is the x-ray diffraction patterns obtained at 1240 °C and 5.7GPa. The solid line represents the initial pattern at the P-T condition. The dotted line is a pattern collected after 13 minutes. The decomposition of mullite or the formation of allumina was observed dynamically. Figure 2 shows a P-T diagram concerning the stability of mullite. At pressure above 6GPa, the decomposition may take place at lower temperature than that at lower pressure.
STRUCTURAL MODIFICATIONS OF CaGeO₃-WOLLASTONITE UNDER HIGH PRESSURE AND MODERATE TEMPERATURE

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Introduction
There are possibilities that some elementary processes of a transformation can be observed under high pressure and at low temperature where a phase transition to a high pressure stable phase can not occur kinetically. CaGeO₃-wollastonite belongs to pyroxenoid group. The arrangement of oxygen atoms approximates close packing in a rude way and octahedrally coordinated Ca atoms alternate with tetrahedrally coordinated Ge atoms between the oxygen layers. Andrault et al. (1992) suggested that the coordination change of Ge atoms occurs in CaGeO₃-wollastonite under high pressure and at room temperature and that the coordination change may lead to a pressure-induced amorphization. However, Nagai (1995) indicated that CaGeO₃-wollastonite is transformed into the rhodonite structure at about 6 GPa and then a perovskite polymorph appears at about 15 GPa without showing the amorphization, on the basis of the X-ray diffraction measurements under high pressure by using a diamond anvil cell. The rhodonite-form of CaGeO₃ has never reported before, therefore, the stability of the CaGeO₃-rhodonite was investigated in this study.

Experimental

In-situ X-ray diffraction measurements were performed under high pressure and moderate temperature by using a cubic anvil type apparatus (MAX80) which is installed at the beamline AR-NE5C. In the present study sintered diamond anvils truncated 4x4 mm square and 7x7x7 mm pressure medium made from the amorphous boron/epoxy resin were used. Carbon disks were used as heaters and sample temperature was monitored with an almel-chromel thermocouple. A sample chamber was filled with CaGeO₃ powders and powder mixture of NaCl and BN. Incident white X-ray beam cut by slits (0.2x0.2 mm²) was led into the sample and diffracted X-ray through a vertical collimator and slits (0.2x0.2 mm²) were detected by a pure Ge-SSD. In consideration of energy range of photons and energy dependence of counting efficiency of Ge-SSD, 2θ-angle was fixed at 3.8°. Pressure values were estimated on the basis of the Decker's equation of state for NaCl (Decker, 1971).

Results and Discussion

Diffraction profiles were obtained at about 6.8, 8.8 and 12.2 GPa with increasing temperature up to 600°C. The intensities of reflections of the rhodonite-form became stronger in comparison with those of the wollastonite-form from room temperature to 400°C. After the garnet-form appears in a run at 6.8 GPa and the perovskite-form is detected both in a 8.8 GPa-run and a 12.2 GPa-run above 450°C, the intensities of reflections of the rhodonite-form were suddenly weakened. The garnet-form and the perovskite-form are thermodynamically stable phase reported before. This result suggests that the CaGeO₃-rhodonite is a 'kinetically metastable' phase under high pressure. The wollastonite-rhodonite transition progresses metastably at low temperature where a phase transition to a high pressure stable phase can not take place kinetically.

References

Phase relations and the mechanism of phase transitions in metal hydrides under high H2 pressures have been investigated by in situ x-ray diffraction using MAX80 installed at the Accumulation Ring of KEK.

By a specially designed sample cell, accommodating an internal hydrogen source LiAlH4, which supplies H2 on thermal decomposition, and a NaCl capsule impermeable to hydrogen, measuring conditions up to ca. 1200°C and H2 pressure of 7 GPa were attained, and the process of hydrogenation of a metal sample was studied by pursuing temporal variations of the crystal structure and the lattice parameter of the hydride phase.

One of the most important discoveries in the last few years is the formation of superabundant vacancies in metal hydrides, which takes place after prolonged heat treatment (5–10 h) at high temperatures (~800°C) and high H2 pressures (~5 GPa). This manifests itself as a gradual decrease of the lattice parameter (by ~1%) during the heat treatment, as shown in Fig. 1 for Pd hydride. This lattice contraction was retained after cooling and being brought to ambient conditions, and even after degassing of hydrogen in vacuum.

Similar lattice contraction has been observed in a fairly large number of metals (Ni, Mn, Pd-Rh and Pd-Pt alloys, TiH2 and ZrH2) and appears to be quite general.

In some cases, a vacancy-ordered structure was formed, as revealed by the appearance of superlattice reflections. Figure 2 shows a diffraction pattern observed with a PdH sample at 500°C after the prolonged heat treatment at 800°C. In addition to diffraction lines from the ordinary (vacancy-free) fcc PdH, superlattice lines having simple-cubic indices arising from a lattice-contracted (vacancy-ordered) phase of Cu3Au structure can be clearly seen. The vacancy concentration was estimated from the relative intensity of the superlattice lines to be 17 at. % which agrees well with 18 at. % obtained from density measurements.

In Pd-Rh alloys, the phase separation process was found to be dramatically accelerated under high hydrogen pressures. This indicates that the diffusivity of Rh and Pd atoms is enhanced by at least 5 orders of magnitude as a consequence of superabundant vacancy formation.

The phenomenon of superabundant vacancy formation in hydrides promises to open a new perspective of research in the wide area of metal science and is therefore believed to be worthy of further investigations.

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STRUCTURE OF LIQUID ALKALI METALS UNDER PRESSURE

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Introduction

X-ray diffraction for liquid Rb has been measured under pressure up to 4 GPa. Synchrotron radiation with high brightness, high energy and small divergence was used [1-3]. Volume dependences of static structure factor \( S(Q) \) and pair distribution function \( g(R) \) were obtained in the volume range \( (V/V_0) = 1 \sim 0.6 \) to investigate the effect of the electronic change on the ion-ion pair potential and the structure of liquid metals.

Experimental

The experiments were carried out using a cubic-type high-pressure apparatus, MAX80, installed on AR-NE5C. To obtain \( S(Q) \), measurements at diffraction angles \( 2\theta = 2, 2.5, 3, 3.5, 4, 5, 6, 8, 11 \) and 15° were carried out for each experimental point. Details of the experiments and data analysis are given elsewhere[1].

Results and discussion

Obtained \( S(Q) \) for liquid Rb at several pressures are shown in Fig. 1. With increasing pressure, the peak position shifts towards higher \( Q \) and the height of the first peak increases. In Fig. 2, the first-peak position of \( S(Q) \), \( Q_1 \), is shown as a function of the \((v/v_0)^{-1/3}\), where \( v_0 \) is the volume at atmospheric pressure. \( Q_1 \) shows different pressure dependences below and above 3 GPa. Below 3 GPa it varies as expected from a uniform compression model: \( Q_1 \) changes proportionally to \( v^{-1/3} \). Above 3 GPa \( Q_1 \) changes slightly less than the expectation. Packing fraction \( \eta \) was estimated from the obtained \( S(Q) \). It varies as \( v^{-0.3} \) below 3 GPa. Above 3 GPa it shows a larger change with \( v \).

References

STORAGE OF PULSED SLOW POSITRON BEAM
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Introduction

In order to achieve high intensity single bunch of slow positrons for the studies of positron plasma, polyelectron \( (e^+/e^-) \) systems, elementary particle studies, and so on, we are constructing an efficient positron storage and extraction system.

The points are:
1) how may number of positrons can be accumulated to obtain maximum intensity of bunch of positrons
2) how to extract the accumulated positrons by bunching in time and focusing in space

How Many Positrons can be Accumulated?

A simple way of positron storage is to use a Penning trap. According to our experience, slow positrons can be stored in a Penning trap of \( 10^{-6} \) Torr for 300 \( \mu \)s in a region of 10 m. This implies that 30 sec of storage becomes possible at \( 10^{-11} \) Torr. The storage time becomes longer if allowed for a larger confinement space. Typical positron intensity presently available is: \( 10^4 \) (RI source) \( \sim 10^5 \) \( e^+/s \) (electron Linac of about 1kW beam power). Using the latter value we expect accumulation of \( 10^{10} \) positrons.

How to store the positrons

The idea of our trap is illustrated in the figure. It is composed of two sections: section 1 for trapping and condensing the positrons, and section 2 for storage. The pulse of the PF Slow Positron Source has the time profile of 1 \( \mu \)s and their energy is around 400 eV. The energy of 400 eV is high for the storage, but is suitable for trapping. If the energy were several 10's eV, the geometrical length of the positron beam becomes several tens of meters while running through the 30 meters of the solenoid flight tube. This means that the Penning trap must be as long. If the energy is 400±5 eV (the energy width is just a guess at present) the pulse length is about 40 cm.

In order to cope with the high energy of 400 eV, the Penning trap is held at a potential of 390 eV and the positrons enter the trap after decelerated. After thus trapping the positrons in section 1 the potential in section 1 is gradually raised from upstream so that the positrons are compressed into a small volume, and finally all the positrons are sent to section 2. This cycle of trapping \( \rightarrow \) compressing \( \rightarrow \) storing is repeated synchronous with the repetition of the electron Linac operation of 20~50 pps.

How to Extract the Positrons

The stored positrons are extracted downstream. In order to increase the positron density both in space and time, it is necessary to give focusing and bunching. For this purpose the extracted bunch of positron enter into the field of an acceleration region where a static harmonic oscillator potential is applied. The performance of the harmonic oscillator potential is to give a time bunching, but by utilizing the discrete nature of the electrodes it is possible to attain lense effects, too.

Achievement during October 1993 - September 1994

Up to September 1994 designing of the section 1 and 2 has been carried out, and the set-up and a test run will be performed within the fiscal year of 1994.

Conceptual design of the storage and extraction of one-shot positron bunch

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