

1 Hybridized Orbital Ordering Project -Orbital hybridization ordering study in strongly correlated electron system and the external field effect-

Project Leader: Hironori Nakao

1-1 Introduction

The strongly correlated electron system (SCES) shows various intriguing physical properties such as high T_C superconductivity and colossal magnetoresistance effects near the metal-insulator transition, where itinerancy and localization of electrons compete with each other. For example, superconductors discovered in the SCES generally exist in the vicinity of a quantum critical point. Hence, study of the electronic state where itinerancy and localization of electrons compete is important to elucidate the origin of these physical properties. In this project, not only the localized electrons, d -electron in transition metal and f -electron in rare earth metal, but also the itinerant electrons, $O2p$, $P3p$, and so on, are being investigated by the complementary use of photons at the Photon Factory and neutrons and muons at J-PARC. Especially, resonant X-ray scattering utilizing the hard and soft X-ray region is a useful technique to clarify these electronic states and the orbital hybridized states between localized and itinerant electrons. The external field effect on orbital hybridized states is also an important subject in this project.

New diffractometers for resonant soft X-ray scattering experiments are now under construction for the project. One is the world's first diffractometer with a superconducting magnet (< 7.5 T), which is expected to lead to new discoveries under its magnetic field. The other diffractometer is specially designed for small angle diffraction to detect magnetic textures (skyrmion, etc.) and domain structures. We are also using conventional diffractometers in the project. Our research encompasses various subjects such as transition metal oxides, rare earth metal compounds, and organic conductors, which are typical systems in the SCES, and is being performed in collaboration with many external researchers. The cobalt system is a particularly interesting compound having spin-state degrees of freedom in SCES. Here, we report two interesting aspects of cobalt oxides, and also a study of electron-doped manganite, which shows critical-state Jahn-Teller polarons.

1-2 Mystery of Intermediate-Spin State in Cobalt Oxides [1]

The existence of the intermediate-spin (IS) state in cobalt oxides has long attracted controversy. Recent

resonant X-ray scattering experiments clearly elucidated $Co^{3+} e_g$ orbital ordering in $Sr_3YCo_4O_{10.5}$, which has the highest ferromagnetic transition temperature among perovskite Co oxides. This result provides not only a clue to understanding the magnetism but also the first clear evidence of the existence of the IS state of Co^{3+} . This discovery is expected to open up a new field of materials physics, which will combine the IS state concept with many interesting magnetic and electric properties.

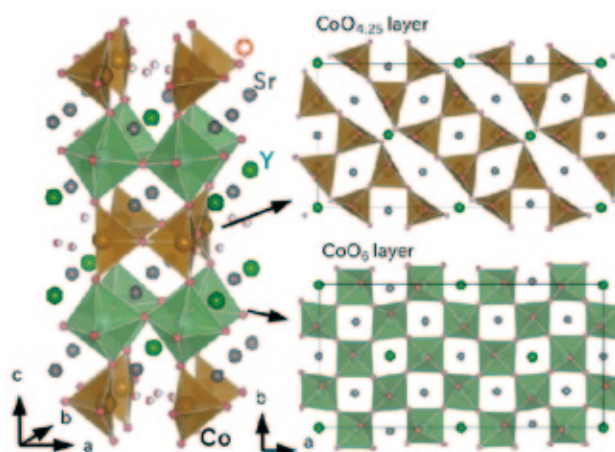


Fig. 1 Crystal structure of $Sr_3YCo_4O_{10.5}$.

The strongly correlated electron system shows various intriguing physical properties due to the close interplay among the charge, spin, and orbital degrees of freedom. In cobalt oxides, spin-state degrees of freedom such as low-spin (LS), high-spin (HS), and the IS state additionally emerge, and a wide variety of physical properties associated with the spin state are expected. Especially, the existence of the IS state is controversial, because in ligand field theory the IS state never becomes the ground state, and yet signs of the existence of the IS state have been reported experimentally, although not unambiguously.

$Sr_{4-x}R_xCo_4O_{10.5}$ ($R = Y$ and lanthanide, $0.8 < x < 1.0$) was recently discovered as a room-temperature ferromagnet with $T_C \sim 370$ K, which is the highest T_C among perovskite-type cobalt oxides. This material typically has the crystal structure shown in Fig. 1: the Sr and Y ions are ordered, and the CoO_6 octahedral layers and oxygen vacant $CoO_{4.25}$ layers are alternately stacked in the direction of the c -axis, while an ideal perovskite structure is composed of a three-dimensional framework of corner-sharing CoO_6 octahedra. As the origin of the ferromagnetism, the importance of spin-state degrees of freedom of Co^{3+} ($3d^6$), namely HS ($t_{2g}^4 e_g^2$), LS (t_{2g}^6), and IS ($t_{2g}^5 e_g^1$), was proposed on the basis of recent powder X-ray diffraction experiments. Here, the wave functions of $3d$ -electrons pointing toward O^{2-} ions, $d_{x^2-z^2}$ and $d_{3y^2-r^2}$, are called e_g orbitals, while those pointing between

them are called t_{2g} orbitals. Therefore, not only the existence of the IS state of Co^{3+} but also the e_g orbital ordering of the IS state were investigated by a resonant X-ray scattering (RXS) experiment near the Co K absorption edge energy, which is a unique technique for combining diffraction with spectroscopy. This experiment was performed at BL-4C and 3A of the Photon Factory in KEK.

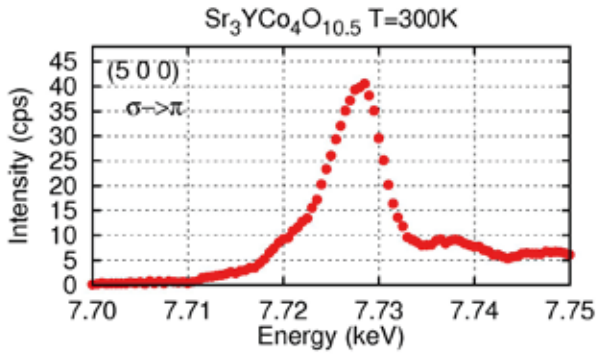


Fig. 2 Energy dependence of the scattering intensity at (500), measured in the ferromagnetic phase at 300 K.

To clarify the orbital ordering in the ferromagnetic phase, the energy dependence of the scattering intensity was measured at several reciprocal lattice points. Signals resonating near the Co K -edge energy were found at $(h00)$: $h = 4n \pm 1$ reflection. The energy dependence of scattering intensity at (500) : $h = 5$ is shown in Fig. 2. Moreover, the RXS signals show a large h dependence of the scattering intensity. The polarization and azimuthal angle dependence of the RXS signal were also measured at 7.727 keV corresponding to the $1s \rightarrow 4p$ transition energy. These results clearly indicate the existence of anisotropic

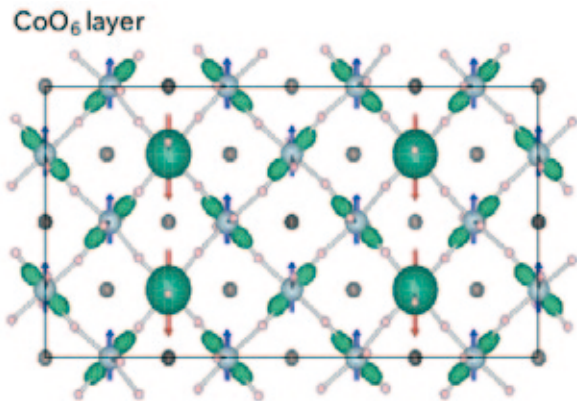


Fig. 3 Determined orbital ordering and proposed magnetic structure in the CoO_6 layer. Anisotropic Co sites (x^2-z^2 / y^2-z^2 type e_g orbital) of the intermediate-spin state and isotropic Co sites of the high spin state are shown.

Co-site ordering as shown in Fig. 3. However, it was difficult to distinguish between the e_g and t_{2g} orbital ordering of Co^{3+} , since the signal contains information of the Co $4p$ state.

In order to clarify the existence of the e_g orbital ordering of the IS state, the RXS signal at the pre-edge region ($1s \rightarrow 3d$ transition energy) was examined, and the RXS signal was discovered at the $1s \rightarrow e_g$ transition energy, which is stronger than that at the $1s \rightarrow t_{2g}$ transition energy. This is direct evidence of not only e_g orbital ordering but also the presence of the IS state, because the signal at the $1s \rightarrow e_g$ transition energy reflects the anisotropy of the e_g orbital, and only the IS state of Co^{3+} ion has the e_g orbital degrees of freedom.

A peculiar spin-state ordering (HS/IS states) and a ferrimagnetic structure based on the determined orbital structure (Fig. 3) are also proposed. To understand the interesting orbital and spin-state ordering, further studies are needed. Neutron scattering experiments to determine the magnetic structure and resonant soft X-ray scattering experiments to elucidate the Co electric state directly are now in progress at the Photon Factory and J-PARC.

1-3 Magnetic structures of $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ studied by resonant soft X-ray magnetic scattering [2]

In the $\text{La}_{2-x}\text{Ca}_x\text{CoO}_4$ system, it is suspected that the spin states of Co^{3+} ions change across $x = 0.5$ from Ca doping x -dependence of the effective magnetic moment. Magnetic structures in this system also show a change across $x = 0.5$.

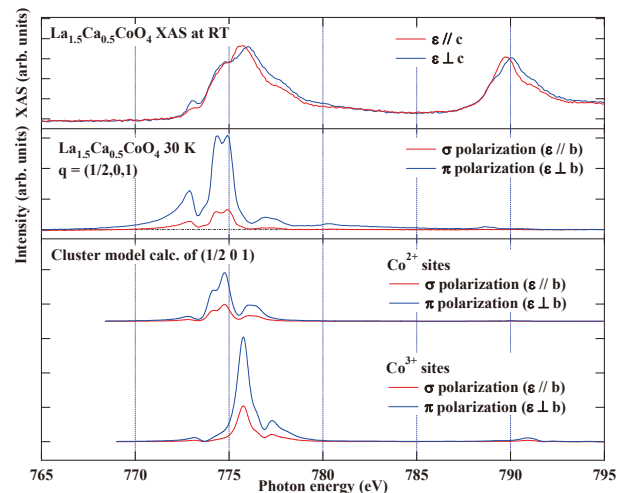


Fig. 4 $\text{Co}2p$ XAS spectra (top), energy scans of resonant soft X-ray magnetic scattering with $q = (1/2, 0, 1)$ (middle), and cluster-model calculations of $(1/2, 0, 1)$ -energy scans with Co^{2+} high spin states and Co^{3+} high spin states (bottom).

Therefore, study of the electronic structures related to the magnetism is expected to yield information about the Co valence and spin state which produces the peculiar magnetism in this system. In this research, we conducted Co $L_{2,3}$ -edge resonant soft X-ray magnetic scattering (RSXS) studies on two magnetic structures, Type I and II, in $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ to study the underlying Co electronic structures precisely[2]. This experiment was performed at BL-16A of the Photon Factory in KEK.

$\text{La}_{2-x}\text{Ca}_x\text{CoO}_4$ takes two kinds of magnetic structure below the Neel temperature ($T_N \sim 50$ K); for $x \leq 0.5$, Type I with $q = (1/2, 0, 1/2)$ and for $x \geq 0.5$, Type II with $(1/2, 0, 1)$. From the x -dependence of the effective magnetic moment, it is expected that Co^{2+} always takes high-spin states but Co^{3+} takes the high-spin state for $x < 0.5$, intermediate-spin state for $x > 0.7$, and mixed state for $0.5 < x < 0.7$. Therefore, it is important to reveal the relationship of these two magnetic structures with the Co-site valence and spin state. We conducted Co $L_{2,3}$ -edge RSXS and XAS measurements in $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$ to study these two magnetic structures precisely as shown in Fig. 4. XAS structures at Co $L_{2,3}$ absorption edges are consistent with the mixed spectra of the Co^{2+} and Co^{3+} electronic states. By comparing the structures in the $\text{Co}2p$ XAS spectra and the RSXS energy scans, contributions from Co^{2+} sites are very important in the RSXS energy scans of both Type I and II. We reproduced the RSXS energy scans of the magnetic orderings by using cluster-model calculations, considering CoO_6 octahedra. Most of the parts are mainly reproduced by the calculations of Co^{2+} sites with high-spin states and not by those of Co^{3+} sites with high-spin states. This means that below the Neel temperature, Co^{2+} sites are magnetically ordered at $q = (1/2, 0, 1)$ and $(1/2, 0, 1/2)$. The lack of observation of magnetism for the Co^{3+} sites is still not understood.

1-4 Critical-state Jahn-Teller polarons in electron-doped cubic SrMnO_3 : isotropic metal versus chain-like ordering [3]

The double-exchange (DE) model has long been discussed as one of the most fundamental theories on the colossal magnetoresistance phenomena in hole-doped perovskite manganites. Due to the competition between ferromagnetic DE interaction induced by doped carriers and antiferromagnetic superexchange interaction among localized spins, there is still controversy over the theory of the ground state, especially in the electron doping regime: a canted-antiferromagnetic metal, phase-separated state consisting of a ferromagnetic metal and an

antiferromagnetic insulator, and anisotropic chain-like magnetic ordering. In this study, by utilizing a high-pressure (5–6 GPa) synthesis apparatus, we successfully synthesized single crystals of cubic perovskite SrMnO_3 with controlled electron concentration, which can realize the most ideal (orbital-degenerate) DE system. We attempted to experimentally elucidate its true electronic and lattice structures by performing systematic transport, magnetic, and synchrotron X-ray diffraction measurements on these crystals.

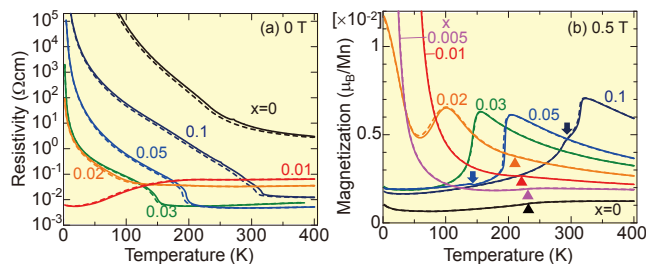


Fig. 5 Temperature profiles of (a) resistivity at 0 T and (b) magnetization at 0.5 T for $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ ($0 \leq x \leq 0.1$) single crystals. The closed triangles and arrows denote the G-type and C-type AFM transitions, respectively.

Figures 5(a) and (b) display the temperature profiles of resistivity at 0 T and magnetization at 0.5 T for $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ ($0 \leq x \leq 0.1$) single crystals, respectively. The undoped SrMnO_3 is a G-type antiferromagnetic (AFM) Mott insulator. Ce substitution for Sr by only 0.5–1% (1–2% electron doping), however, makes the system metallic over the whole temperature range. For these compounds, the antiferromagnetic spins slightly cant at low temperatures. As x further increases to 0.02, the metallic ground state is replaced by the insulating one. For $x = 0.03$ –0.1, a distinct metal-insulator transition shows up, accompanied by a sharp drop in magnetization. The crystal structure simultaneously changes from cubic to tetragonal with elongation of the

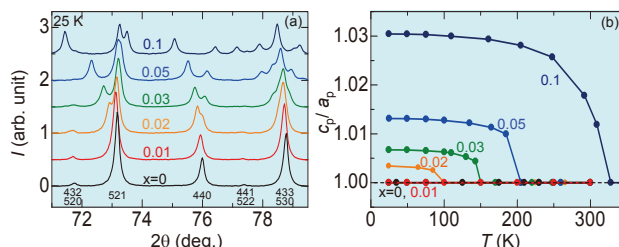


Fig. 6 (a) Synchrotron x-ray powder-diffraction profiles for $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ ($0 \leq x \leq 0.1$) at 25 K. The indices are based on the cubic setting $Pm3m$ and a_p monotonously increases with increasing x (b) Temperature profiles of tetragonality c_p/a_p in warming runs.

c axis [Fig. 6(b)], indicating the $3z^2-r^2$ -type orbital order (with C-type AFM).

Figure 6(a) shows the synchrotron powder X-ray diffraction patterns at 25 K, measured at Beamline 8A at the Photon Factory in KEK. For $x \leq 0.01$, the profiles are nicely indexed with the cubic structure $Pm3m$. On the other hand, those for $x \geq 0.02$ show peak splitting, reflecting the structural change into the tetragonal phase. As shown in Fig. 6(b), the tetragonality c_p/a_p rapidly increases just below T_{OO} and then saturates toward the lowest temperature. Its value almost linearly increases with increasing x up to $x = 0.1$.

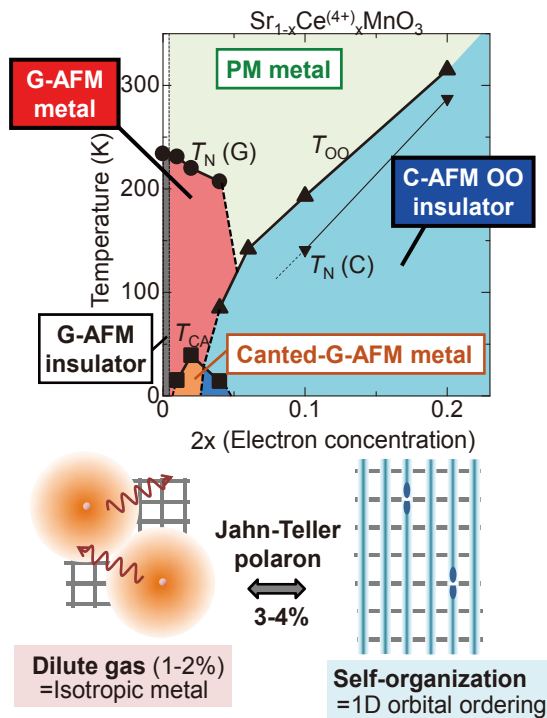


Fig. 7 (Upper) Electronic phase diagram as a function of $2x$ (electron concentration). $T_N(G)$, T_{CA} and $T_N(C)$ indicate the G-type, canted G-type, and C-type AFM transition temperatures, respectively. (Lower) A conceptual diagram of the polaronic states.

Figure 7 summarizes an electronic phase diagram for $Sr_{1-x}Ce_xMnO_3$ ($0 \leq x \leq 0.1$), where a G-type AFM metal and a C-type AFM orbital-ordered insulator critically compete. Note that only $\sim 4\%$ electrons lead to the anisotropic orbital-ordered ground state; the remaining electrons lead to the isotropic (cubic) metal. This is probably due to the strong Jahn-Teller effect inherent in the degenerate e_g orbitals in the cubic system. In fact, detailed transport measurements revealed significantly renormalized electron mass (~ 15 times heavier than band mass) for the adjacent metallic phase, indicating substantial electron-phonon coupling. Thus, the dichotomous electronic/lattice phases in the

lightly-doped DE system can be attributed to the keen competition between the self-organization and itinerancy of the Jahn-Teller polarons.

[1] H. Nakao et al., J. Phys. Soc. Jpn. **80** (2011) 023711.
 [2] J. Okamoto et al., J. Electron Spectrosc. Relat. Phenom. **184** (2011) 224.
 [3] H. Sakai et al., Phys. Rev. B **82** (2010) 180409.