9 Element Strategy Initiative to Form Core Research Center for Electron Materials

– Multi probe study using X-ray and neutrons

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9-1 Introduction

The national "Element Strategy Project" was started in 2012. We are aiming to develop entirely new materials that do not use rare elements. In the Tokyo Institute of Technology for element strategy, we are developing materials based on successful experience far away from development policy, and are pioneering electronic materials to create new guidelines for material design using harmless elements to open up new fields of material science. In the KEK sub-stronghold, we are researching the crystal, electronic, and magnetic structures of light elements such as hydrogen and oxygen in materials synthesized by the Material Creation Group by using synchrotron radiation, muon and neutron sources.

9-2 Bipartite magnetic parent phases in the iron-oxypnictide superconductor

A new class of high-*Tc* iron-based superconductors has been extensively studied since the discovery of the iron-oxypnictide LaFeAsO. An advanced doping method using a hydrogen anion instead of fluorine in LaFeAsO has recently surpassed the doping limit of fluorine, and uncovered a hidden second superconducting phase. In order to investigate a certain hidden phase beyond the second superconducting phase, we have performed a multi-probe study using neutron, muon, and X-ray beams.

Magnetic Bragg peaks by means of neutron powder-diffractions at J-PARC (SuperHRPD and NOVA) were observed with the propagation vector of **q** = (1/2, 1/2, 0) below the magnetic transition temperature T_N = 89 K at x = 0.51. The Fe spin arrangement is described by a stripe type of an antiferromagnetic collinear structure. The magnetic moment at x = 0.51 at 10 K is estimated at 1.2 μ_B per iron atom. Magnetic volume fractions estimated by muon spin relaxation spectra at J-PARC and PSI

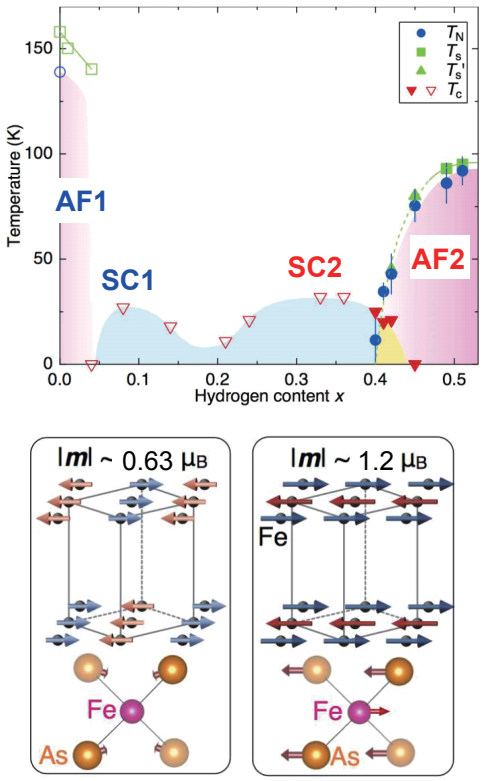

Fig. 1: Magnetic, structural and superconducting phase diagram of $LaFeAsO_{1-x}H_x$ (upper). First and second superconducting phases (SC1 and SC2) are generated by starting from the original and advanced antiferromagnetic phases (AF1 and AF2), respectively. The magnetic structures of AF1 (lower left) and AF2 (lower right) are illustrated with their magnetic moments. The displacements of the Fe and As atoms across the structural transitions are schematically described by the arrows on the $FeAs_4$ tetrahedra.

show the coexistence of the antiferromagnetic static order and superconductivity in the range 0.40 ≤ x ≤ 0.45. Tetragonal to orthorhombic structural transition was observed below 95 K at x = 0.51 from synchrotron X-ray diffraction measurements at KEK-PF (BL-8A/8B). Crystal structural analysis indicates the *Aem*2 space group without inversion symmetry in the antiferromagnetic phase.

Figure 1 illustrates the phase diagram of $LaFeAsO_{1-x}H_x$. The two-dome SC phases are regarded as generated by the carrier doping, starting from the left- and right-hand parent compounds towards the intermediate region of the phase diagram: that is, the substitution to H^- at the O^{2-} sites leads to the SC1 phase, while the substitution to O^{2-} at the H^- sites leads to the SC2 phase.

9-3 Material design strategy for the interface with a step-like potential in the oxide quantum well structure

In designing devices with an oxide quantum well structure, the step-like potential of electrons at the interface, where the electrons are confined entirely within the quantum potential, is required. The $SrVO_3/SrTiO_3$ quantum well structure has a potential architecture in order to obtain the guide to the new material design for controlling the physical properties in oxide devices. Angle-resolved photoemission spectroscopy in the $SrTiO_3/SrVO_3/SrTiO_3$ and the vacuum/$SrVO_3/SrTiO_3$ quantum well structures was performed. We have successfully observed the ideal quantum confinement in the $SrVO_3/SrTiO_3$ interface. This experimental finding originates in the band lineup of the $SrVO_3$ and $SrTiO_3$, and high permittivity of SrTiO3 [1].

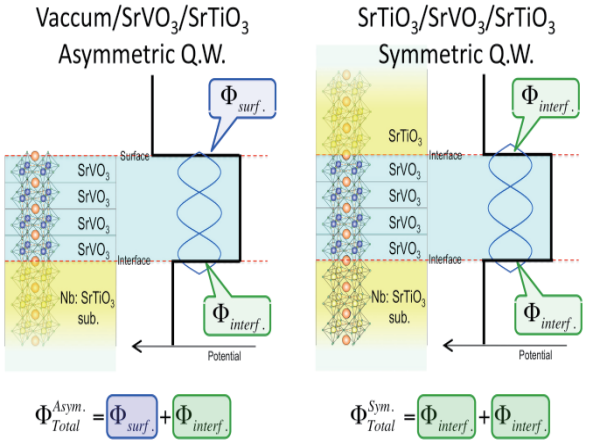

Fig. 2: $SrTiO_3/SrVO_3/SrTiO_3$ "symmetric" and vacuum/$SrVO_3/SrTiO_3$ "asymmetric" quantum well interface structures.

9-4 New thermoelectric candidate "layered clathrate" $BaIr_2Ge_7$

Clathrate is a substance consisting of a rigid cage "host" and a "guest" atom weakly bound to the cage, leading to highly-efficient thermoelectric materials because of low thermal conductivity. A "layered clathrate" $BaIr_2Ge_7$ was newly synthesized and its crystal structure was determined. The guest ion Ba with localized low-lying energy "rattling" mode is confined in the host cage of Ir-Ge, introducing the Einstein type specific heat. The obtained "layered" type structure is exceptional in other rattling materials: clathrate, skutterudite, and β-pyrochlore oxide, having isotropic crystal structures with cubic lattice symmetries.

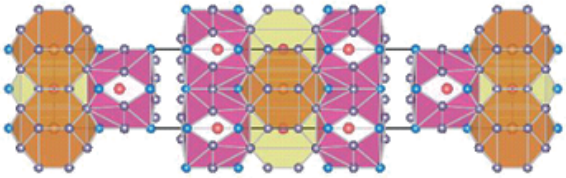

Fig. 3: Crystal structure of new layered clathrate $BaIr_2Ge_7$. The three different types of Ir-Ge cages are described by red, orange, yellow colors.

9-5 New photo emission beamline construction for the element strategy project

We constructed the new beamline BL-2 "Musashi" at KEK-PF to promote research for the element strategy project. High flux and high energy resolution beams over a wide energy range of 30–2,000 eV are realized by the dual lines with vacuum ultraviolet (30–300 eV) and soft X-ray (250–2000 eV). In the beamline, X-ray absorption spectroscopy of all elements can be measured. Additionally, we are able to determine the band structure by angle-resolved photoemission spectroscopy, and to evaluate the chemical bonding state by inner shell photoelectron spectroscopy.

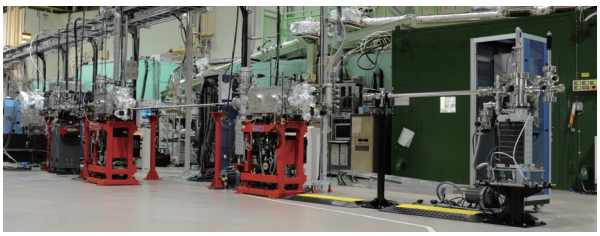

Fig. 4: New "tandem" beamline BL-02 "Musashi" in KEK-PF.

9-6 New muon beamline construction for the element strategy project

We constructed the new beamline “S-line” at J-PARC to promote research for the element strategy project. A muon spin relaxation spectrometer with a 4 kG magnet and a positron counter is being produced and will be installed in the new beamline. A highly efficient and compact new positron counter developed in KEK has been established. The spectrometer will start to be used for measuring new materials in 2014.

9-7 In-situ measurement system for X-ray absorption fine structure

X-ray absorption fine structure (XAFS) is a probe used to determine element-selective local structures in order to clarify the structural and physical properties of new materials. In-situ experiments of XAFS offer many advantages for researching the reaction processes in catalysts and gas sensors. A new in-situ measurement system with fluorescence yield was built under the control of gas atmospheres available in many XAFS beamlines.

References

[1] K. Yoshimatsu et al.,“Determination of the surface and interface phase shifts in metallic quantum well structures of perovskite oxides”, Phys. Rev. B 88, 115308 (2013).

[2] J. Guo et al., “Superconductivity in $Ba_{n+2}Ir_{4n}Ge_{12n+4}$ (n = 1, 2) with Cage Structure and Softening of Low-lying Localized Mode”, Phys. Rev. B 88, 140507(R) (2013).