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## Condensed Matter Research Center

## 3-1 Overview

The Condensed Matter Research Center (CMRC) was established on April 1, 2009, at the Institute of Materials Structure Science (IMSS) with the aim of pursuing cutting-edge research on condensed matter science through the comprehensive use of multi-probes supplied by the IMSS, such as synchrotron radiation, neutrons, muons, and slow positrons. The CMRC has four research groups: the Correlated Electron Matter Group, the Surface/Interface Group, the Matter Under Extreme Conditions Group, and the Soft Matter Group. Through collaboration among these four groups, the CMRC has been promoting six bottom-up projects: the hybridized orbital ordering project, geometrical correlation project, molecular crystal project, surface/interface project, extreme condition project, and soft matter project (Fig. 1). In the hybridized orbital ordering project, the charge/spin/orbital orderings with hybridized orbitals have been studied under high pressure or a strong magnetic field. In the geometrical correlation project, we have determined the characteristic correlation time for fluctuation in itinerant systems with strong electron correlation under the influence of geometrical frustration using muons, neutrons, and synchrotron X-rays, which have different probing-time scales. In the molecular crystal project, electronic correlation in molecular crystal systems has been investigated to elucidate novel phenomena such as superconductivity, magnetism, ferroelectricity, and charge ordering. In the surface/interface project, crystal structures and electronic structures at the surface and interface of magnetic thin films and multilayers have been studied through depth-resolved magnetic circular dichroism (MCD)/X-ray absorption spectroscopy (XAS), resonant X-ray scattering (RXS), and neutron reflectivity. In the extreme condition project, we have studied changes in the crystal structures, electronic structures,



Figure 1  
Project leaders of CMRC:  
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spin states, valence states, and chemical bonding of important compounds in geophysics to understand changes in their density and elastic, geological, transport, and chemical properties. In the soft matter project, we have investigated spontaneous motion under non-equilibrium conditions, the hierarchical structure of a soft matter complex resulting from self-organization, and functional soft matter interfaces for industrial applications. Some highlights of the CMRC projects are reported in the following sections.

### 3-2 Hybridized Orbital Ordering Project -Orbital Hybridization Ordering Study in Strongly Correlated Electron System and the External Field Effect-

The ordered states of the electronic degrees of freedom (charge, spin, and orbital) play very important roles in strongly correlated electron systems. In particular, the hybridization effect of the electronic orbitals has been a central issue in this field for a long time. In this project, both the hybridized orbital ordering between localized and itinerant electrons and the charge/spin/orbital orderings are studied under high pressure or a strong magnetic field. Resonant hard/soft X-ray scattering and inelastic neutron scattering techniques are used complementarily.

#### ***Doping Variation of Hole Orbital States in $Nd_{2-x}Sr_xNiO_4$ Studied by Polarization-Dependent Soft-X-Ray Absorption Spectroscopy [1]***

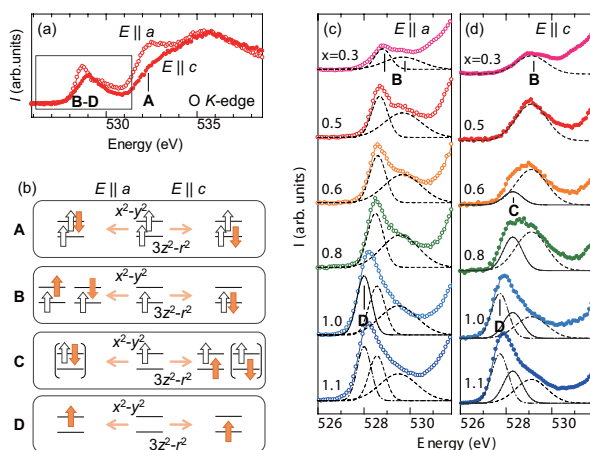
X-ray absorption spectroscopy (XAS) is a strong probe for determining the local electronic structure such as the valence as well as the orbital states. In the case of superconducting layered cuprates, for example, a couple of pre-edge peaks have been clearly observed in the O *K*-edge spectra and the relationship between the orbital character and superconductivity has been intensively studied. While XAS experiments were performed also for layered nickelates for comparison with the superconducting cuprates, previous works on single crystals were limited to the low-doping region below about  $x = 0.5$ . We therefore investigate the orbital state variation toward the metallic region by systematically measuring the polarization-dependent O *K*-edge spectra up to  $x = 1.1$ .

Single-crystal samples of  $Nd_{2-x}Sr_xNiO_4$  ( $x = 0.3-1.1$ ) were grown by a high-oxygen-pressure floating-zone method. XAS experiments were carried out at undulator beamline BL-16A. The O *K*-edge data were taken in

the fluorescence-yield mode with a typical attenuation length of about 30 nm. The XAS spectra for E||a and E||c were measured using vertically and horizontally polarized X-rays in nearly-grazing incidence geometry to the *ab*-plane, respectively, for comparing and analyzing the polarized spectra more accurately. The incidence angle relative to the surface was set to 10 degrees. The measurements were performed in a high vacuum of  $10^{-8}$  Torr, at 50 K.

Figure 2 (a) shows the polarization-dependent O *K*-edge spectra at  $x = 0.5$  for E||a and E||c. Aside from the main peak at about 536 eV, a couple of pre-edge peaks are clearly observed in the lower energy region (three peaks for E||a and two peaks for E||c), labeled with letters A–D. Considering all the possible transition processes as shown in Fig. 2 (b), these pre-edge peaks at about 532 and 529 eV for  $x = 0.5$  are ascribable to processes A and B, as assigned also in the previous work. This simply indicates that the holes are mainly doped into the  $x^2-y^2$  orbital below  $x = 0.5$ . Figures 2 (c) and 2 (d) show the doping variation of the magnified spectra in the pre-edge region. Focusing on the variation below and above  $x = 0.5$  for E||c, an additional peak assigned to process C is clearly discerned above  $x = 0.6$ , directly indicating the existence of  $\text{Ni}^{3+}$  sites with unoccupied  $3z^2-r^2$  orbital. Above  $x = 1.0$ , in addition, the positions of all peaks largely shift to lower energy both for E||a and E||c. This might arise from the appearance of an additional peak assigned to process D, indicating the existence of  $\text{Ni}^{4+}$  sites as the ground state.

Eventually, doping variation of the site occupancy of the respective valence and orbital states can be roughly estimated by fitting and quantifying the pre-edge peaks B–D for E||c; the numbers of  $\text{Ni}^{3+}$  sites with occupied  $3z^2-r^2$  and  $x^2-y^2$  orbitals increase nearly linearly at about  $x = 0-0.5$  and  $x = 0.5-1.0$ , respectively. This indicates



**Figure 2**  
(a) Polarization-dependent O *K*-edge XAS spectra. (b) Schematic of the transition processes A–D corresponding to the pre-edge peaks. Filled arrows represent the transition electrons from the O 1s state to the ground Ni 3d  $e_g$  orbital state shown in the middle. Doping variation of the magnified O *K*-pre-edge spectra for (c) E||a and (d) E||c. Fittings for the peaks corresponding to the transition processes (B, C, and D) as labeled in (b) are indicated by dashed, solid, and chain curves, respectively.

that the excess holes above  $x = 0.5$  are mainly doped into the  $3z^2-r^2$  orbital and thus the  $x^2-y^2$ -based checkerboard-type charge ordering or correlation can strongly persist up to the high-doping metallic region due to the multi-orbital nature.

### 3-3 Geometrical Correlation Project

Geometrical frustration often produces novel phenomena in strongly correlated electron systems, such as the heavy fermion state in which anomalous mass enhancement occurs. The objective of this project is to determine a characteristic correlation time for fluctuation in itinerant systems with strong electron correlation under the influence of geometrical frustration using muons, neutrons, and synchrotron X-ray, which have different probing-time scales.

#### *Quasi-One-Dimensional Spin Dynamics in $\text{LiV}_2\text{O}_4$ : One-to-Three-Dimensional Crossover as a Possible Origin of Heavy Fermion State* [2]

The heavy fermion behavior observed in a cubic vanadium spinel,  $\text{LiV}_2\text{O}_4$ , has drawn much interest, since it is one of the remarkable examples in which only *d*-orbital electrons are relevant to the electronic property. We are revisiting spin fluctuation in  $\text{LiV}_2\text{O}_4$  by examining the earlier results of muon spin rotation/relaxation measurement. Instead of the relationship for the localized electron limit, we used that between muon depolarization rate and spin fluctuation rate ( $\nu_D$ ) for itinerant electron systems to reanalyze the data, revealing that  $\nu_D$  varies linearly with temperature ( $\nu_D / T$ ) over the range of  $10^8-10^{12} \text{ s}^{-1}$  for  $0.02 < T < 10^2 \text{ K}$ . Such a linear *T* behavior as well as the magnitude of  $\nu_D$  is fully consistent with the behavior of magnetic relaxation rate previously observed by inelastic neutron scattering (INS), demonstrating that  $\mu\text{SR}$  and INS have a common time window over a fluctuation spectrum. The linear dependence of  $\nu_D$  on *T* is understood to be a specific feature predicted by a Hubbard model for intersecting one-dimensional (1D) chains. This quasi-1D character, which is coexistent with enhanced uniform susceptibility at low temperatures, supports the scenario of 1D-to-3D crossover for the microscopic origin of heavy-fermion behavior in  $\text{LiV}_2\text{O}_4$ .

### 3-4 Molecular Crystal Project

In this project, electronic correlation in molecular crystal systems will be investigated to elucidate novel phenomena such as superconductivity, magnetism, ferroelectricity and charge ordering. We will analyze the crystal structure under high pressure using a pressure cell developed specifically for molecular crystals to elucidate the mechanism of superconductivity. The charge ordering state of molecular crystal systems is sometimes destroyed under an electric field. The transient

behavior from charge ordered to disordered state will be investigated using structural analysis by synchrotron X-ray.

**Molecular Crystal Project: Electronic Ferroelectricity in a Molecular Crystal with Large Polarization Directing Antiparallel to Ionic Displacement** [3]

The organic charge-transfer complex TTF-CA, comprising an electron donor, tetrathiafulvalene (TTF), and an acceptor, *p*-chloranil (CA) (Fig. 3 (c)), has been attracting considerable attention because of a novel ferroelectric neutral-to-ionic phase transition that occurs in it. Recently, in contrast to the conventional point-charge scenario, the first-principles calculations invoked a significantly larger spontaneous polarization (3–10  $\mu\text{Ccm}^{-2}$  along the *a*-direction) with two contrasting candidate electronic states. The total polarization is predicted to be directed either parallel or antiparallel to the ionic polarization, depending on the antiferromagnetic or nonmagnetic state. This prediction motivated us to experimentally determine both the magnitude and the direction of spontaneous polarization.

The TTF-CA crystal comprises *DA* alternating stacks along the *a*-axis, and the one-dimensional nature of this chain brings about the Peierls- or spin-Peierls-type structural instability, displacing pairwise the ionized *D* and *A* molecules (Fig. 3 (d)). Ferroelectricity emerges when the chain can invert its polarity, i.e., ...*DA DA*...  $\leftrightarrow$  ...*AD AD*..., where the underlines represent dimerized *DA* pairs. The crystal structure is symmetry-broken to a polar space group of *Pn* upon neutral-ionic transition (NIT) as determined by neutron and high-resolution X-ray diffraction experiments.

The symmetry-breaking of the TTF-CA crystal structure under an electric field was probed by the intensity difference between the Bijvoet pair (*hkl* versus  $\bar{h}\bar{k}\bar{l}$ ) reflections; this difference arises from the anomalous X-

ray scattering effect. The simulation based on the crystal structures at *T* = 15 and 40 K predicts that the Bijvoet pair reflections 101 and  $\bar{1}0\bar{1}$  have sufficient intensities and are the most susceptible to the anomalous X-ray scattering for the X-ray wavelength  $\lambda = 1.55 \text{ \AA}$  that is used. The temperature dependence of their normalized integrated intensity  $I_+ \equiv I(101)/\{I(101) + I(\bar{1}0\bar{1})\}$  and  $I_- \equiv I(\bar{1}0\bar{1})/\{I(101) + I(\bar{1}0\bar{1})\}$  was observed. Immediately below *T<sub>c</sub>*, the observed  $I_+$  and  $I_-$  readily approach the values 0.705 or 0.295, which correspond to full polarization into either polarity according to the simulation. Therefore, the poling field of 4  $\text{kVcm}^{-1}$  is regarded as sufficient for developing a single-domain state. By comparing the observed intensity of the Bijvoet pair ( $I_+$  and  $I_-$ ) with the simulation, we found that the positively charged TTF molecules shift toward the positive electrode and that the negatively charged CA shifts toward the negative electrode (Fig. 3 (b)). These experimental observations confirmed the recent first-principles calculations predicting an extreme contribution from electronic polarization that is directed antiparallel to the ionic displacement and governs the magnitude of polarization. The electronic ferroelectricity itself is currently one of the key issues for multiferroelectrics. The electronic response with lower energetic cost of lattice deformations promises both high-performance and high-frequency operations as well as new functionalities.

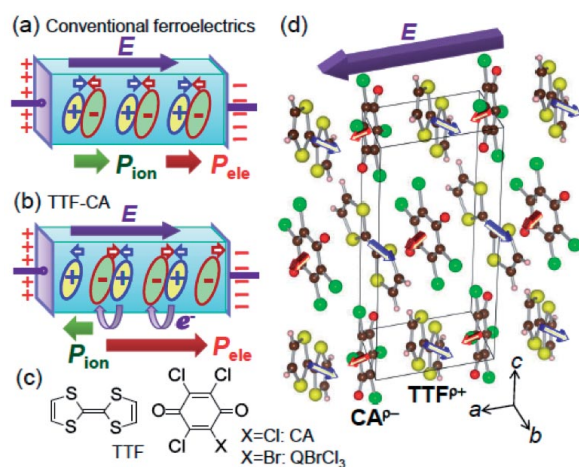
### 3-5 Surface/Interface Project -Crystalline, Magnetic and Electronic Structures at the Surface and Interface of Magnetic Thin Films and Multilayers-

The surface and interface of magnetic thin films play essential roles in the appearance of extraordinary magnetic properties such as perpendicular magnetic anisotropy and the giant magnetoresistance effect. We are investigating the crystalline, magnetic and electronic structures at the surface and interface of magnetic thin films and multilayers, in order to reveal the origin of the fascinating magnetic properties, which cannot be realized in bulk materials. For example, we have studied the magnetic anisotropy of Fe/Ni multilayers, magnetism at the interface between MgO and Heusler alloy, effects of ion irradiation on ultrathin films, and magnetic depth profile of Gd/Cr multilayers, mainly by means of the X-ray magnetic circular dichroism (XMCD) technique. Moreover, neutron reflectivity experiments have started at BL-17 in J-PARC. We also plan to perform muon spin rotation experiments using an ultra-slow muon source.

#### Origin of Ion Irradiation-Induced Perpendicular Magnetization

 [4]

We are investigating Ga<sup>+</sup> irradiation-induced chang-



**Figure 3**  
Schematic illustrations of the electric polarization (solid arrows) and displacement direction (small open arrows) of ions in conventional displacive-type ferroelectrics (a) and TTF-CA crystal (b). (c) Molecular structures of TTF, CA, and QBrCl<sub>3</sub>. (d) Crystal structure of TTF-CA and molecular displacement directions under an electric field.

es in magnetic anisotropy and the crystalline structure of a Pt/Co/Pt ultrathin film by means of X-ray magnetic circular dichroism (XMCD) and extended X-ray absorption fine structure (EXAFS) techniques. XMCD analysis shows a large orbital moment difference between out-of-plane and in-plane directions, which corresponds to perpendicular magnetic anisotropy (PMA), at moderate Ga<sup>+</sup> fluences, while larger fluences reduce the orbital moment difference, resulting in in-plane magnetization. From the EXAFS analysis, enhancement of PMA is directly related to an in-plane lattice expansion caused by ion irradiation and Co-Pt intermixing, which results in a large lattice distortion. Thus, the origin of the ion irradiation-induced changes in magnetic anisotropy is successfully explained.

### 3-6 Extreme Conditions Project

The targets of this project are compounds in the Earth's core/mantle as well as light element minerals. We are studying changes in the crystal structures, electronic structures, spin states, valence states, and chemical bonding of these compounds to understand changes in density and in elastic, geological, transport, and chemical properties. We will use diffraction and spectroscopy techniques employing synchrotron X-rays and neutrons.

### 3-7 Soft Matter Project

Soft matter is a subfield of condensed matter comprising a variety of physical states that are easily deformed by thermal stresses or thermal fluctuations.

They include liquids, colloids, polymers, liquid crystals, amphiphilic molecules, and a number of biological materials. These materials often self-organize into mesoscopic physical structures that are much larger than the microscopic scale (the arrangement of atoms and molecules), and yet are much smaller than the macroscopic scale of the material. The properties and interactions of these mesoscopic structures may determine the macroscopic behavior of the material. In spite of the various forms of these materials, many of their properties have common physicochemical origins, such as a large number of internal degrees of freedom, weak interactions between structural elements, and a delicate balance between entropic and enthalpic contributions to the free energy. These properties lead to large thermal fluctuations, a wide variety of forms, sensitivity of equilibrium structures to external conditions, macroscopic softness, and metastable states. Accordingly, we are investigating structural properties of soft matter such as liquids and amphiphilic molecules; structures formed under far-from-equilibrium conditions are particularly interesting. These investigations will yield basic knowledge to help solve the mystery of life.

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