

# 5 Materials Science

## 5-1 A New Experimental Technique Using Resonant X-Ray Scattering; Observation of Ferro-Type Orbital Ordering and Elucidation of its Scattering Mechanism

Manganese 3d orbital states in thin films and superlattices have been investigated by a newly developed technique [1,2]. Here "orbital state" means the orbital occupancy of 3d electrons and their spatial arrangements. These artificial materials are expected to demonstrate "orbital-state-mediated phase-control". For the characterization of these materials, accurate examinations of the orbital states are indispensable. The resonant X-ray scattering (RXS) technique has been proved to be a very powerful probe of the orbital states, and now is being applied to a wide range of systems with improved accuracy. The newly developed interference technique has enabled the observation of ferro-type orbital ordering whose signal coincides with fundamental Bragg reflections at  $\Gamma$  points. This method utilizes the interference term between X-rays scattered with RXS and those from Thomson scattering. This term can be extracted from rotation of the polarization. Using the interference technique, we have succeeded in inspecting the orbital states of thin films. Furthermore, we have successfully observed an "orbital superlattice", in which manganese 3d orbital states are periodically modulated on an atomic scale.

Perovskite manganite  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (LSMO) thin films epitaxially grown on three kinds of single crystalline perovskite substrates were investigated. The hetero-

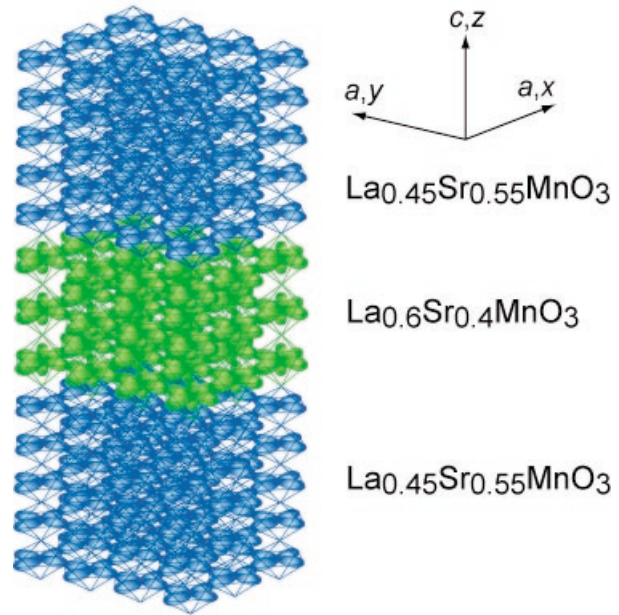


Figure 2 Schematic of  $e_g$  orbital states in the  $[\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3\ 10\text{u.c.}/\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3\ 3\text{u.c.}]_{20}$  "orbital superlattice".  $(x^2-y^2)$ -type orbitals in the  $\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3$  layers and  $(x^2-y^2)/(3z^2-r^2)$  disordered orbitals in the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  layers are presented.

junction between the film and the substrate induces a coherent epitaxial strain in the film whose in-plane lattice parameter is forced to match to that of the substrate. Macroscopic properties such as conductivity and/or magnetization suggest that the orbital states of LSMO films vary with substrate according to the coherent strains present, that is, those on  $\text{SrTiO}_3$  (STO),  $(\text{LaAlO}_3)_{0.3}\text{-}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$  (LSAT) and  $\text{LaAlO}_3$  (LAO) take  $d_{x^2-y^2}$ , unpolarized and  $d_{3z^2-r^2}$  types of  $e_g$  orbitals, respectively [3]. Figure 1 shows the azimuthal angle dependence of the interference term intensity of the (0 1 2) fundamental reflections. The variance among the three films is clearly seen, and the polarization of the  $e_g$  orbitals can be experimentally distinguished by the sign of the interference term. This technique was also applied to the investigation of orbital states in the  $\text{La}_{0.45}\text{Sr}_{0.55}\text{MnO}_3/\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  multilayers [4]. Orbital modulation at the interface of superlattice structure is a completely unexplored subject, and the heterojunction of different orbital states may lead to new physical phenomena. We have successfully observed RXS reflections from the present manganite superlattice by using the interference technique. By analyzing the intensity of the interference term at each reflection, it is clearly demonstrated that the polarization of the  $e_g$  orbitals differs in each layer, presenting an "orbital superlattice". Figure 2 shows the expected  $e_g$  orbital state in this manganite superlattice.

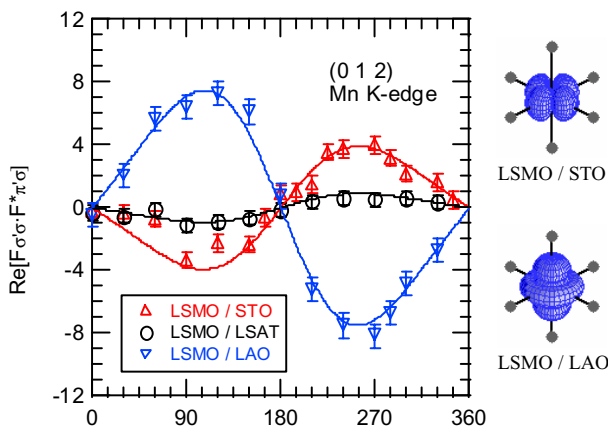


Figure 1 The azimuthal angle dependence of the interference term intensity. Data for the films on STO, LSAT, and LAO are presented as a function of the azimuthal angle  $\Psi$  (left).  $e_g$  orbitals of LSMO/STO and LSMO/LAO samples are shown (right).

The interference technique also brought about important information on the mechanism of RXS. RXS probes the 4p electronic states of Mn atoms by using X-rays tuned to the manganese K-absorption edge. As for the origin of the 4p level splitting, two explanations are possible: one ascribes it to the Coulomb interaction between Mn 3d and 4p states, the other to the hybridization between Mn 4p and O 2p orbitals. These two mechanisms give an opposite sign to the interference term, and the origin of the 4p level splitting is determined by the interference technique. Our results confirm that the origin of the RXS in manganites is mainly attributable to the hybridization between Mn 4p and O 2p orbitals, and not to the Coulomb interaction between the 3d and 4p electronic states.

Thus, the newly developed RXS technique has enabled not only the observation of ferro-type orbital ordering, but also the clarification of the mechanism of RXS.

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## References

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## 5-2 Quantum Phase Transition in DMTTF-QX<sub>4</sub> (X=Cl, Br)

The neutral-ionic phase transition (NIT) in charge-transfer complexes is a novel valence tautomerism, which transforms the states of crystal binding between molecular crystals and ionic crystals in a single organic substance. NIT compounds have also attracted considerable interest as a multi-functional system, as demonstrated by their ferroelectricity, current-induced resistance switching, ultrafast photo-induced phase transformation, and their relaxor behavior with huge dielectric response [1,2]. Using the NIT system, our recent research has developed a new example of quantum phase transition and disclosed their electronic and structural properties.

The charge-transfer complex consisting of DMTTF as the electron donor (D), and QCl<sub>4</sub> as the acceptor (A) (for the chemical structure, see Fig. 3) shows an NIT at 65 K [3]. On the other hand, its fully bromine-substituted analogue, the DMTTF-QBr<sub>4</sub> crystal remains neutral without an NIT at ambient pressure. For DMTTF-QBr<sub>4</sub> we have been able to apply hydrostatic pressure to accurately control the neutral-ionic phase transition temperature from absolute zero to room temperature. In the pres-

sure ranges where the phase transition begins to appear close to absolute zero, quantum paraelectricity was seen as proof that the electric polarization experiences a quantum-fluctuation effect [4]. Moreover, we have been able to achieve almost the same effects as for the above hydrostatic pressure technique by using a molecular size effect (effective pressure). For instance the four Cl atoms on the QCl<sub>4</sub> molecule were substituted one by one with Br atoms. This chemical pressure gives us accurate control to close to the point where the phase transition temperature disappears toward absolute zero (quantum critical point; QCP), as illustrated in Fig. 3. For the 2,6-dibromo-substituted (2,6-QBr<sub>2</sub>Cl<sub>2</sub>) complex in the vicinity of QCP, where the NIT occurs in response to effective-pressure changes at the lowest temperature, we observed quantum paraelectricity as well as molecular charge fluctuation between the neutral-ionic states as evidenced by Raman scattering spectra. The molecular charge (crystal binding) and dielectric polarization simultaneously fluctuate near absolute zero, and these findings represent a new type of quantum phase transition.

To make clear the origin of the anomalous dielectric response at the NIT, the crystal structure of the ionic phase has been determined by using a synchrotron radiation X-ray experiment [5]. A diffraction experiment was performed using an image plate system (Rigaku) installed

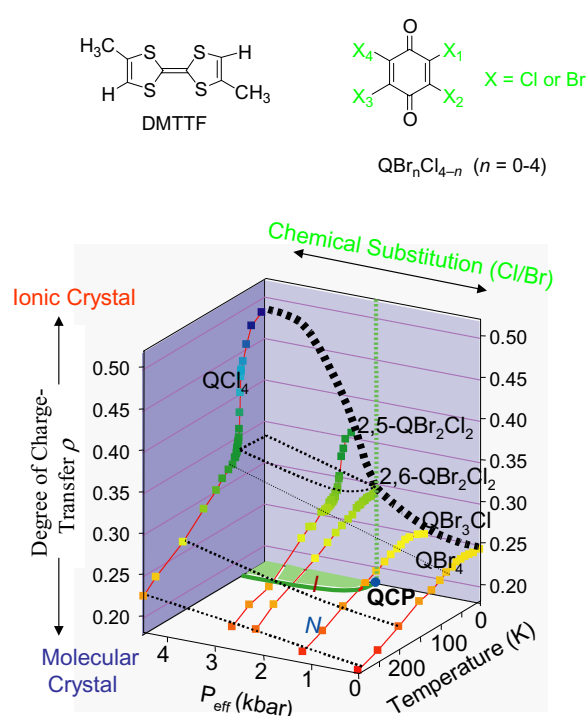


Figure 3 Changes of molecular charge ( $\rho$  for  $D^{+}A^{-}$ ) in DMTTF-QBr<sub>n</sub>Cl<sub>4-n</sub> crystals in response to temperature and effective pressure (QBr<sub>4</sub> used as the standard). Red line: thermal change of  $\rho$  for each complex; black line: variation of  $\rho$  as a function of effective pressure at a fixed temperature. The 2,6-QBr<sub>2</sub>Cl<sub>2</sub> complex is closely located at the point of neutral-ionic transition at absolute zero, that is, on the QCP. The bottom plane represents the neutral-ionic phase boundary.

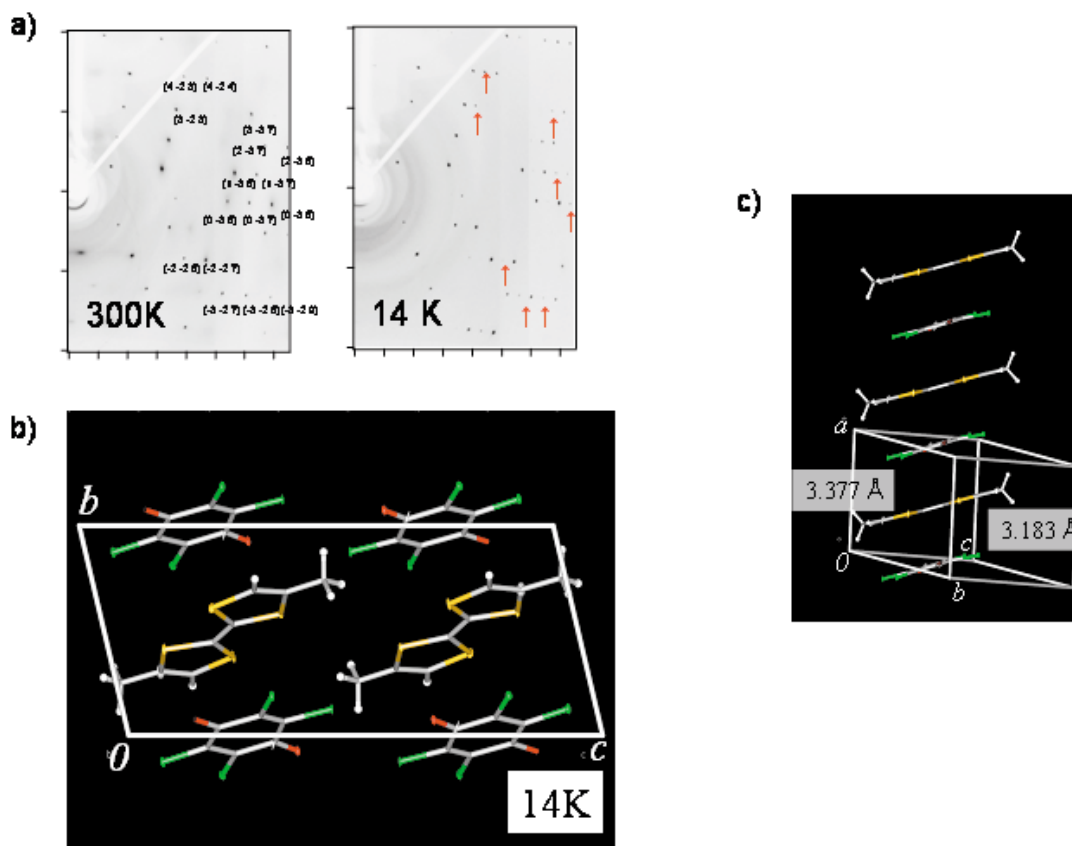


Figure 4  
The crystal structure of DMTTF-QCl<sub>4</sub> in the low temperature phase ( $T = 14$  K). The hydrogen atoms are omitted for clarity. (a) Oscillation photograph taken using the image plate system. Superlattice spots are observed along the  $c^*$ -axis. (b) Unit cell viewed normal to the  $bc$  plane. (c) Molecular stacking in the  $DA$  stack.

in BL-1A. Below  $T_c$ , superlattice spots can be observed at  $(h k l/2)$  showing a cell doubling along  $c$  [Fig. 4(a)]. A crystal structure analysis in the low-temperature phase ( $T = 14$  K) clearly reveals a dimerization in the  $DA$  stack as shown in Fig. 4(c). From the symmetry of the crystal (space group:  $P\bar{1}$ ) one can find that two equivalent  $DA$  dimers in the supercell construct a layer-type antiferroelectric order below  $T_c$ .

We can expect that the accurate control by use of both pressure and chemical modification will be a useful method for the further development of new organic materials with diverse functionality, including non-linear optics and switching using light, electric field, and current.

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- [5] C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>Cl<sub>4</sub>S<sub>4</sub>, Triclinic, space group  $P\bar{1}$ ,  $a = 7.0962(9)$  Å,  $b = 7.556(2)$  Å,  $c = 16.896(4)$  Å,  $\alpha = 95.813(7)^\circ$ ,  $\beta = 104.12(1)^\circ$ ,  $\gamma = 91.08(1)^\circ$ ,  $V = 873.2(3)$  Å<sup>3</sup>,  $R = 0.063$ ,  $R_w = 0.066$ , based on 1387 observed reflections ( $F > 3\sigma(F)$ ,  $2\theta_{\max} = 86.9^\circ$ ) and 237 variable parameters.

## 5-3 Anisotropic Resonant X-Ray Scattering from Antiferromagnet Hematite, Fe<sub>2</sub>O<sub>3</sub>

Anisotropic resonant X-ray scattering is a useful method for studying local electronic states in a crystal. Up until now, however, very little experimental work on this scattering has been reported. The present work is a basic study of resonant X-ray scattering in a magnetic material.

Anisotropic resonant scattering is described by the anisotropic tensor of susceptibility (ATS). In general ATS scattering is very small compared with charge scattering, but it can be measured using a forbidden reflection, since the anisotropic tensors violate the conventional extinction rule for Bragg reflection. Resonant diffraction is sensitive to the X-ray energy and allows us to investigate a specific atom in a crystal. ATS scattering is furthermore dependent on the X-ray polarization and is sensitive to the atomic direction, i.e. the electronic orbital. Using this scattering we can obtain information about the local anisotropy of the unoccupied electronic states.

The electric dipole approximation is usually applied to the resonant (or anomalous) scattering factor. In some samples (Fe<sub>2</sub>O<sub>3</sub>, FeS<sub>2</sub> etc.), however, the quadrupole transition effect has been observed in ATS scattering [1,2]. It is important whether the quadrupole effect is observed

or not in resonant X-ray phenomena. We can obtain more detailed information on the electronic states from the observation of the higher order effect. On the other hand, magnetic X-ray scattering also shows anisotropic properties. Therefore magnetic scattering should be taken into account in the scattering from magnetic materials. In principle we can obtain the spin and orbit magnetization densities from non-resonant magnetic scattering, while resonant magnetic scattering gives us information on the magnetically ordered electronic states.

We have selected as a sample, the antiferromagnet hematite,  $\text{Fe}_2\text{O}_3$ , which has a corundum structure and a magnetic moment almost perpendicular to the three-fold rotation axis (the hexagonal [001] direction) at room temperature. In order to clarify the resonant scattering process in hematite, we have investigated the forbidden reflections near the Fe K-absorption edge. The experiment was carried out with four-circle diffractometers at BL-3A and 4C, where the incident beam was polarized horizontally and the scattering plane was perpendicular to it, i.e.  $\sigma$ -polarized. The integrated intensity was measured for the hexagonal 003 and 009 forbidden reflections at different X-ray energies or azimuthal angles.

We first measured the energy spectra of the 003 and 009 forbidden reflections intensities. These spectra have only one peak (7.105 keV) at the same energy in the pre-edge region and there is a small non-resonant intensity below the edge. Above the edge, however, manifest non-resonant intensity was not observed because of large absorption.

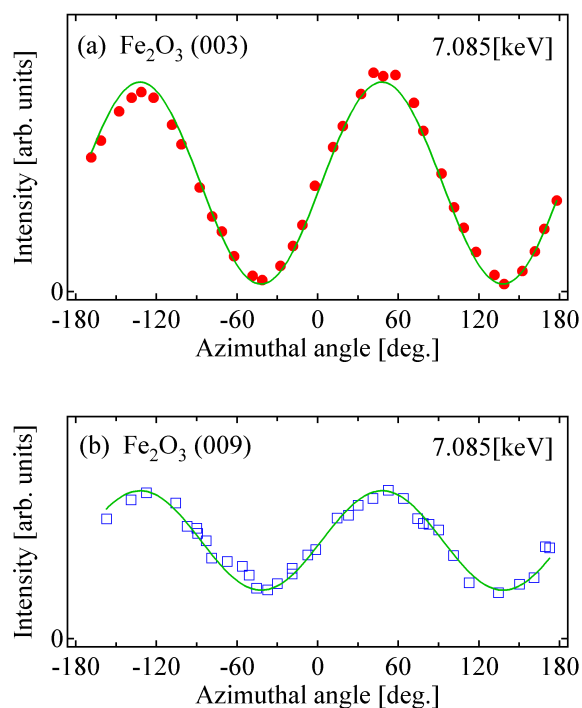


Figure 5  
Azimuthal angle dependence of the 003 and 009 reflections in hematite at a non-resonant energy. The solid lines are calculated based on non-resonant magnetic scattering.

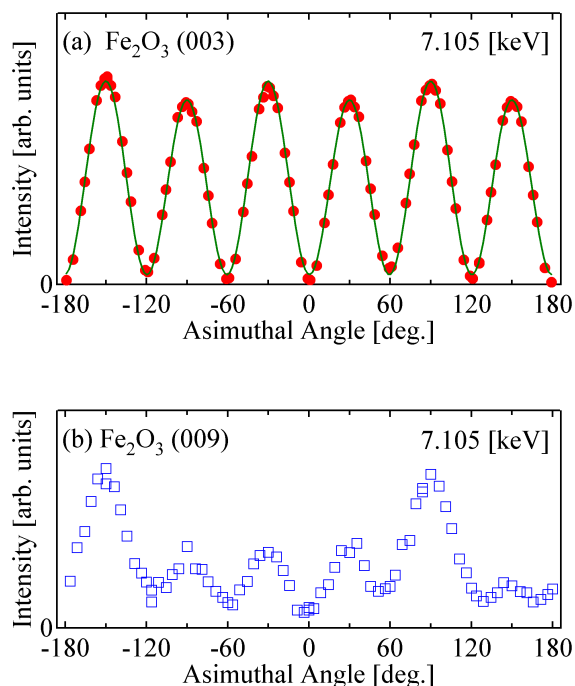


Figure 6  
Azimuthal angle dependence of the 003 and 009 reflections in hematite at the resonant peak energy. The solid line is calculated from electric dipole-quadrupole and quadrupole-quadrupole transition.

The azimuthal angle dependence of the forbidden reflections measured at the non-resonant energy, 7.085 keV, shows a twofold pattern (Fig. 5) in spite of the three-fold rotation axes at the iron sites. This property can be explained by non-resonant magnetic scattering due to the antiferromagnetic moment in the (00/) plane. At the resonant peak energy, on the other hand, the threefold pattern is observed in the 003 reflection, where a local maximum is a little different from the neighboring one as shown in Fig. 6(a). This character is explained by the electric dipole-quadrupole and quadrupole-quadrupole transition as shown in Fig. 6(a). Finally the azimuthal dependence of the 009 reflection at the resonant energy scarcely shows threefold symmetry as shown in Fig. 6(b). This phenomenon cannot be explained by only the electric multipole transition process, which should satisfy the usual point symmetry. The non-resonant magnetic scattering contribution also cannot account for this property because its intensity is smaller than that of the resonant one by about ten times. Therefore we conclude that the resonant 009 reflection may be affected by the resonant magnetic scattering with different scattering process.

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