1 Hybridized Orbital Ordering Project

– Orbital hybridization ordering study in strongly correlated electron systems and the external field effect

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1-1 Introduction

Various interesting physical properties have been discovered in strongly correlated electron systems (SCES), in which the strong correlations among orbital, charge, and spin degrees of freedom play important roles. Therefore, it is important to study these electronic ordering states for understanding the phenomena microscopically. Resonant X-ray scattering (RXS) at the *K*-edge is a powerful tool for observing the spatial ordering of charge and orbital degrees of freedom in *3d* transition metal oxides. The RXS signal at the *K*-edge (*1s* → *4p* transition energy) reflects the *4p* electronic state. On the other hand, the RXS signal at the $L_{2,3}$-edge (*2p* → *3d* transition energy) can probe the *3d* electronic state directly, and the signal of resonant magnetic scattering is strongly observed at the $L_{2,3}$-edge of the *d* electron system. Moreover, *K*-edges of O, S, and P ions, which play a key role for the itinerancy through the orbital hybridization with the metal ion, are also observable by using soft X-rays. Hence, resonant soft X-ray scattering (RSXS) is a key technique to elucidate the origin of physical properties in SCES. To perform RSXS measurements, we have developed diffractometers depending on the experimental conditions [1], and have investigated various subjects in SCES by the complementary use of hard and soft X-rays. Here we report recent studies of a peculiar surface orbital ordering state in $LaCoO_3$ thin film [2], and the X-ray photo-excitation effects in a multiferroic perovskite manganite [3].

1-2 Surface ordering and bulk disordering of orbital order in $LaCoO_3$/LSAT(110) thin film [2]

The surface of condensed matter, accompanied by translational and inversion symmetry breaking, occasionally triggers emergent phenomena, and thus has attracted much attention for a long time. It has been known that phase transition at the surface sometimes occurs at a different temperature from that in the bulk. The surface melting of orbital order, where the transition temperature at the surface is lower than in the bulk, has been actually observed for the orbital order in layered manganite [4]. Conversely, we discovered unprecedented surface

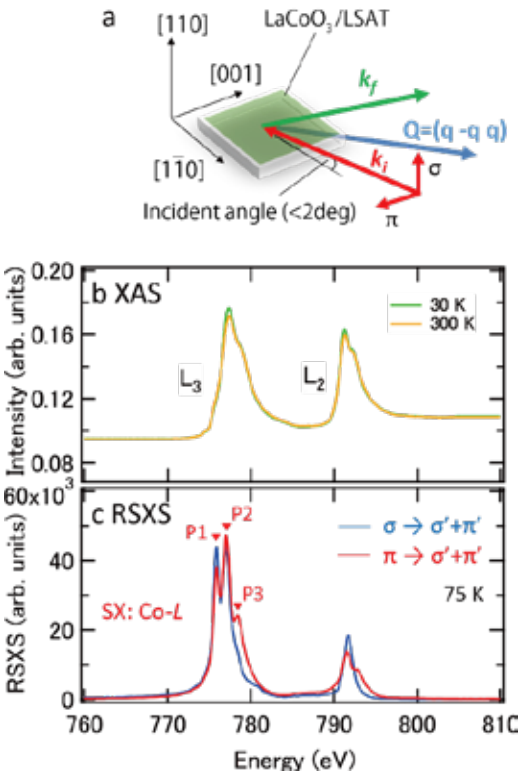

Fig. 1: Schematic drawing of the grazing-incident resonant soft X-ray scattering (GI-RSXS). The diffracted soft X-rays (k_f) were observed with the incident soft X-rays (k_i) in the grazing angle condition. The scattering plane was tuned nearly parallel to the sample surface. XAS and RSXS spectra at the Co $L_{2,3}$-edge of $LaCoO_3$/LSAT(110) thin film.

freezing and bulk melting of electronic order in a tensile-strained epitaxial perovskite-type $LaCoO_3$ thin film grown on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ (LSAT) substrate.

Perovskite-type cobalt oxide $LaCoO_3$, containing Co^{3+} ion with six 3*d* electrons ($3d^6$), is known to show the spin-state transition or spin-crossover by variation of temperature or application of a magnetic field, and has attracted intense interest in recent decades. At the lowest temperature, $LaCoO_3$ is a non-magnetic insulator with the low-spin (LS, $t_{2g}^6e_g^0$, S = 0) state of Co^{3+}. As the temperature increases, it undergoes an insulator-to-metal transition at about 500 K concomitantly with the spin-crossover transition to the high-spin (HS, $t_{2g}^4e_g^2$, S = 2) state. In the intermediate temperature region, the spin-state of Co^{3+}, either the mixed state of HS and LS, or the intermediate-spin (IS, $t_{2g}^5e_g^1$, S = 1), has been highly controversial. The spin state of Co^{3+} ion is sensitive to the distortion and size of the CoO_6 octahedron. Indeed, the thin film of $LaCoO_3$, where the lattice constants increase compared to the bulk crystal, exhibits the non-LS state of Co^{3+} ion even at the lowest temperature, giving rise to ferromagnetism. For example, $LaCoO_3$/LSAT(110) thin film shows a spontaneous magnetization below T_S = 95 K. Recently, we have determined that the spin-state and orbital order of Co^{3+} ion show up with modulation vector $\boldsymbol{q_o} = (q_o, -q_o, q_o)$ with q_o = 1/4 below T_O = 115 K; therefore the magnetic moment arises from ferrimagnetic order [5].

We have investigated the surface state of electronic orders, i.e. spin-state, orbital, and spin, by surface sensitive grazing-incident resonant soft X-ray diffraction (GI-RSXS) in $LaCoO_3$/LSAT(110) thin film [Fig. 1a]. The technique makes it possible to probe the super-lattice of electronic order at the depth of a few nm beneath the surface. Figure 1b shows an X-ray absorption spectrum (XAS) measured by partial fluorescence yield at the reflection condition. The absorption peaks at around 777 eV and 791 eV are assigned to the L_3- and L_2-edge, respectively. Figure 1c shows the resonant scattering spectra at (*q*, *q*, *q*) with $q \sim$ 1/4. Hereafter, we call the three peaks at the Co L_3-edge as P1, P2 and P3 in increasing order of energy.

Figure 2b shows the temperature dependence of the GI-RSXS peak intensities for P1 and P3 in comparison with that of magnetization and the intensity of orbital order observed by resonant

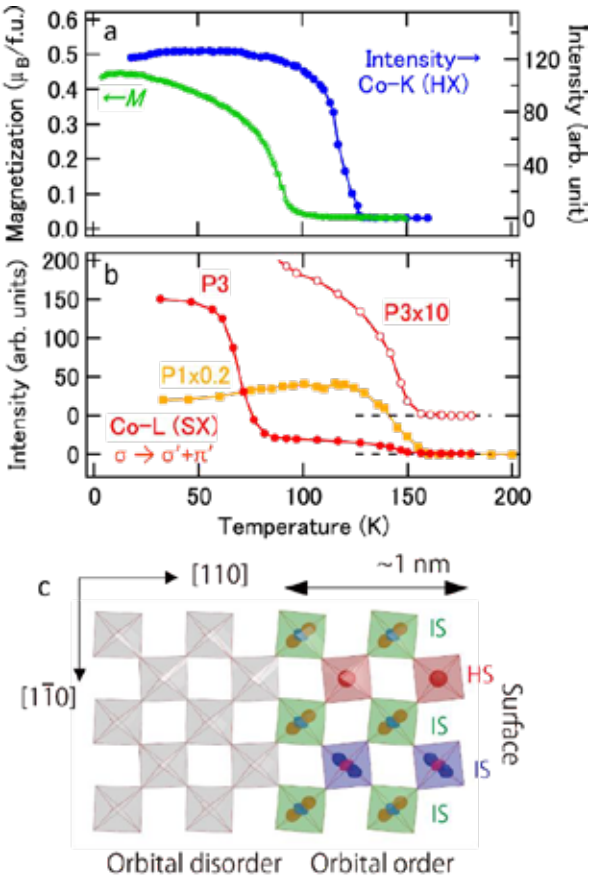

Fig. 2: Temperature dependence of (**a**) magnetization (M) and intensity of super-lattice peaks at (2 + *q*, 2 – *q*, *q*) with *q* = 1/4 measured by hard X-ray diffraction (HX), (**b**) intensities of super-lattice peaks at (*q*, –*q*, *q*) for P1 and P3 of GIRSXS (SX). (**c**) Schematic picture of the surface freezing and bulk melting of orbital order.

X-ray scattering at the Co-K edge (HX) in Fig. 2a. The phase transition temperature of orbital order observed by the GI-RSXS method was revealed to be 155 K (P1 and P3), which was 30 K higher than that in the bulk determined by bulk-sensitive hard X-ray diffraction (HX). The results suggest the coexistence of orbital order phases with different transition temperatures in the present thin film. Taking into account the probing depth, it is reasonable that the resonant peaks of GI-RSXS come from the electronically ordered states emerging at the surface, where the transition temperature becomes higher than that in the bulk; that is, the surface freezing and the bulk melting of orbital order [Fig. 2c] [3].

The origin of the observed surface freezing of orbital order is elucidated by considering the reconstruction of electronic order at the surface with broken symmetries. If the lattice reconstruction at the surface occurred so as to stabilize the Jahn-Teller distortion, it could stabilize the orbitally-active intermediate-spin state of Co^{3+} ion and then

the orbital order at the surface.

1-2 X-ray-induced persistent and bidirectional phase transition in a multiferroic perovskite manganite [3]

Multiferroics, in which the ferroelectric and magnetic order can coexist, have been extensively investigated in recent years because of the possible strong magnetoelectric coupling and related spintronics functions. We investigated the X-ray photo-excitation effects on cycloidal magnetic order in a multiferroic perovskite-type manganite $Gd_{0.5}Tb_{0.5}MnO_3$. The material exhibits competition between the *PIIa* ferroelectric state with commensurate (C) *ab*-plane cycloidal spin structure and the *PIIc* ferroelectric state with incommensurate (IC) *bc*-plane cycloidal spin structure [Fig. 3a]. The phase transition between these two ferroelectric phases can be induced by the application of a magnetic field, and accompanies the IC-C transition. We found that X-ray irradiation can induce the bidirectional and persistent phase transition between IC and C phases. In exposing the sample to X-rays at 10 K,

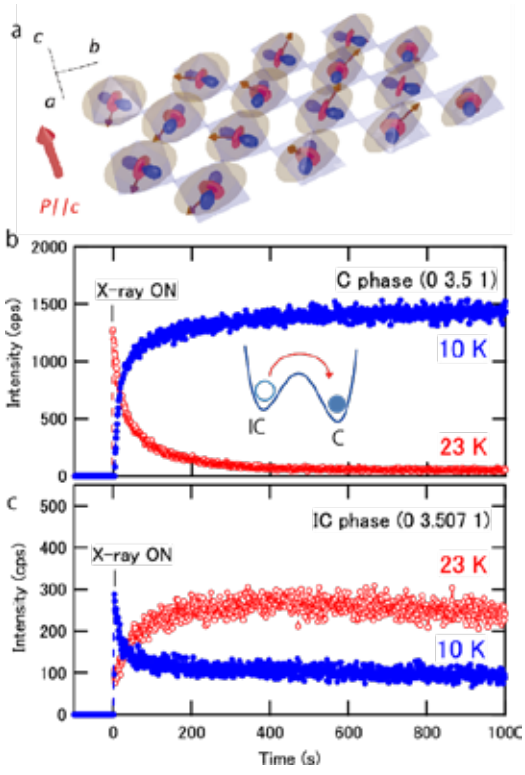

Fig. 3: (**a**) Magnetic structure of Mn spins in the *bc*-cycloidal incommensurate phase of $Gd_{0.5}Tb_{0.5}MnO_3$. X-ray irradiation time dependence of super-lattice diffraction intensities for (**b**) the commensurate (C) (0, 3.5, 1) reflections and for (**c**) the incommensurate (IC) (0 3.507 1) reflections.

the diffraction intensity of the C phase increases, whereas that of the IC phase decreases [Fig. 3b]. This behavior indicates that the majority domains are initially in the IC phase and that X-ray irradiation can wholly change the magnetic order from the IC to the C phase. In contrast, when the magnetic ordering is fully converted to the C phase by X-ray excitation at 10 K and then the temperature is elevated without X-ray irradiation up to 23 K, the X-ray-induced phase transition is observed in the counter direction, i.e. from the C to the IC phase [Fig. 3c].

To determine the magnetic ordering structure in the X-ray-induced phases, we have measured non-resonant X-ray magnetic scattering. The X-ray susceptibility of magnetic moment has to be treated as a tensor, therefore the direction of magnetic moment can be estimated by polarization analysis of the scattering process [Fig. 4a]. The polarization of incident X-ray is parameterized as $P_L = \cos\delta$, where δ is the phase of the light wave and appears in the Jones vector of X-ray as $(E_\sigma, E_\pi) = \frac{1}{2}(1+e^{i\delta}, 1-e^{i\delta})$.

Figures 4b and 4c show the non-resonant X-ray magnetic diffraction profiles for $(0,4-q_m, 3)$ reflection, measured at 18 K and 23 K, where the fully X-ray-induced phase is the C phase and the IC phase, respectively. The magnetic diffraction was measured with the polarization parameter $P_L = \pm 0.75$. To determine the spin cycloidal plane, the diffraction intensity ratio was analyzed as a function of spin ellipticity η, which is defined as $\eta = m_a/m_b$ (m_c/m_b) in the *ab* (*bc*) cycloidal magnetic structure. As shown in Fig. 4d, the intensity ratio increases (decreases) with increasing η for the *ab* (*bc*) cycloidal phase. The experimental results measured at the IC (23 K) and C (18 K) phases are also plotted in Fig. 4d, which show good agreement with the calculated value for the *bc*-cycloidal magnetic structure. This indicates that the X-ray-induced C and IC phases are both the *bc*-cycloidal magnetic structure, and thus the X-ray-induced IC-C phase transition is not accompanied by the flop of the cycloidal plane.

We revealed that the X-ray-induced C phase is the hidden multiferroic phase in the $Gd_{1-x}Tb_xMnO_3$ system, which does not show up with the application of any static field [Fig. 4e]. The origin of the observed persistent and reversible X-ray photo-induced phase transition was elucidated by considering the two (meta-)stable magnetic structures separated by a potential barrier and the alternation of the most

stable state with varying temperature.

References

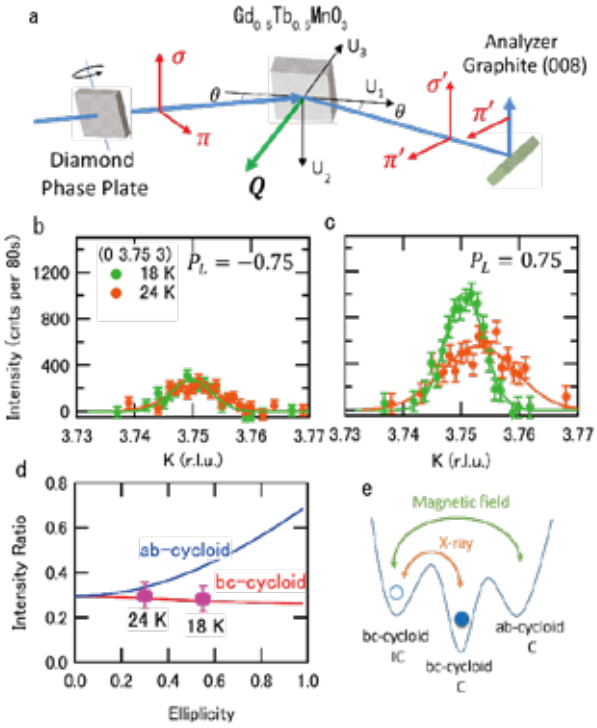

Fig. 4: (**a**) Schematic figure of the experimental setup for the non-resonant X-ray diffraction with tuning the incident X-ray polarization by a phase plate and analyzing the diffracted X-ray polarization by a graphite single crystal. Non-resonant X-ray magnetic diffraction measured at 18 K and 24 K for (**b**) P_L = –0.75 and for (**c**) P_L = 0.75. Here, P_L stands for the presentation of incident X-ray polarization; see the text for the definition. (**d**) The simulated results for the ab-plane and bc-plane cycloidal magnetic ordering in comparison with the ratio of the measured intensity I(P_L = –0.75)/I(P_L = 0.75) with the change of the parameter of the spin cycloid ellipticity. (**e**) Schematic free energy diagrams for the S-ray induced and magnetic field induced phase transition.

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