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, such as colossal magnetoresistance effect and magnetoelectric effect, were discovered in strongly correlated electron systems (SCES). There 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-ray. Hence, resonant soft X-ray scattering (RSXS) is a key technique to elucidate the origin of physical properties in the SCES. To perform RSXS measurements, we have developed new diffractometers depending on the experimental conditions [1]. Here we report recent RSXS studies, antiferromagnetic order with a large orbital angular momentum in $La_{1.5}Ca_{0.5}CoO_3$ [2], and magnetic and electronic structures in manganese thin film [3].

1-2 Antiferromagnetic order of high spin state of Co^{2+} with large orbital angular momentum in $La_{1.5}Ca_{0.5}CoO_3$ [2]

Transition-metal oxides exhibit several distinctive physical properties owing to the close interplay among the charge, spin, and orbital degrees of freedom. In cobalt oxides, the spin-state degree of freedom such as low-spin (LS), high-spin (HS), and intermediate-spin (IS) states emerges additionally from the competition between the Hund coupling and the crystal field effect (CEF). Therefore, a wide variety of physical properties associated with the spin states is expected to be realized. Hence, it is important to study the Co spin state for elucidating the physical properties of Co oxides. In addition to the spin-state degree of freedom, the orbital moment is also a key parameter for the physical properties of Co oxides owing to the orbital degree of freedom in t_{2g} orbitals of Co ions and the relatively strong spin-orbit coupling among *3d* transition metal oxides. Thus, studies of the orbital moment in Co oxides are necessary.

In the $La_{2-x}Ca_xCoO_4$ system, the magnetic and electronic phases have been shown to systematically change depending on the hole concentration *x*. The average Co valence varies from 2+ to 3+ as *x* increases from 0 to 1. Neutron magnetic scattering measurements indicated that the magnetic structure changes at about $x = 0.5$ from an antiferromagnetic structure with a magnetic modulation vector $q = (1/2, 0, 1/2)$ to that with $q = (1/2, 0, 1)$ with increasing *x*. Therefore, the study of the electronic structures related to the magnetism is expected to yield information about the Co valence and spin state. In this research, we have investigated the valence, spin state, and spin angular momentum of Co ions associated with the antiferromagnetic structure by resonant soft X-ray magnetic scattering (RXMS) and X-ray absorption spectroscopy (XAS) measurements near the Co $L_{2,3}$-edge [2].

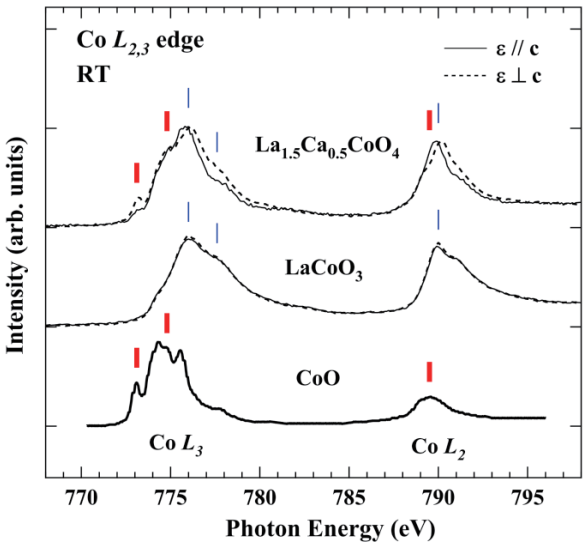

Fig. 1: XAS spectra at the Co $L_{2,3}$-edge of $La_{1.5}Ca_{1.5}CoO_4$, $LaCoO_3$, and CoO [5]. Red (blue) bars indicate the characteristic peak energies in the Co^{2+} (Co^{3+}) XAS spectra.

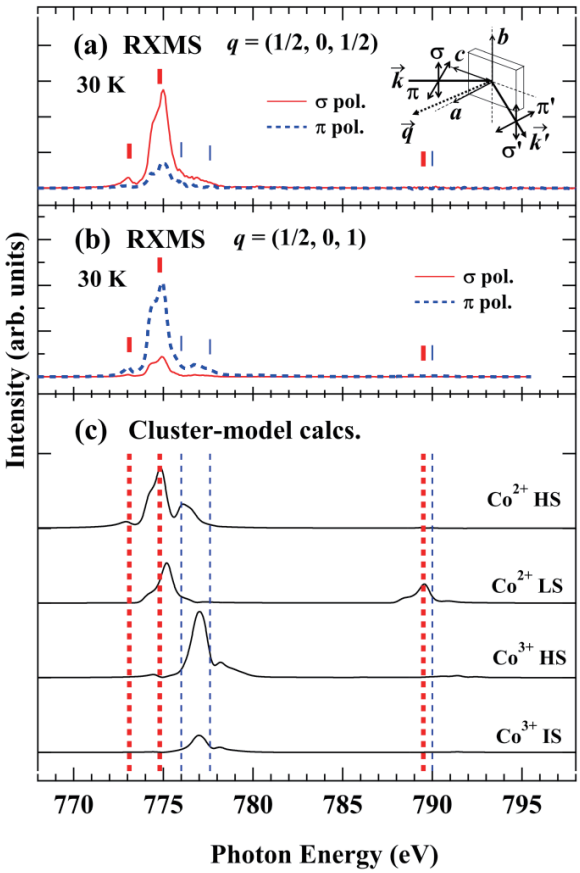

Fig. 2: RXMS spectra at (a) q = (1/2, 0, 1) and at (b) q = (1/2, 0, 1/2) with σ and π polarizations at 30 K. (c) Calculated RXMS spectra using a CoO_6 cluster model of various spin states of Co^{2+} and Co^{3+}. Red (blue) bars and dotted lines correspond to the Co^{2+} (Co^{3+}) XAS structures.

To estimate the valence of the Co electronic structures of $La_{1.5}Ca_{0.5}CoO_4$, XAS spectra were observed near the Co $L_{2,3}$-edge as shown in Fig. 1. The red and blue bars can be assigned to Co^{2+} and Co^{3+} respectively, by comparison with the reference samples, $LaCoO_3$ (Co^{3+}) and CoO (Co^{2+}). Thus, the spectrum has the characteristics of both Co^{2+} and Co^{3+} XAS with a similar intensity ratio. This is consistent with the checkerboard-type charge ordering of Co^{2+} and Co^{3+} [4].

In order to reveal the electronic states of the Co ions associated with the antiferromagnetic order, RXMS measurements were performed near the Co $L_{2,3}$-edge. Resonating signals were clearly observed near the Co $L_{2,3}$-edge below T_N at q = (1/2, 0, 1/2) and q = (1/2, 0, 1) with σ and π polarizations [Fig. 2(a) and (b)]. The observed correlation lengths are consistent with that in neutron scattering. Finally, it was confirmed that these signals are the RXMS at the Co $L_{2,3}$-edge reflecting the antiferromagnetic order. Next the observed RXMS spectra are compared with the spectra calculated for various spin states of Co^{2+} and Co^{3+} under the D_{4h} symmetry crystal field as shown in Fig. 2(c). The model calculation with the Co^{2+} HS state reproduces the experimental spectra well. Thus we have directly determined by RXMS measurements for the first time that the Co^{2+} HS state forms magnetic ordered structures at q = (1/2, 0, 1/2) and q = (1/2, 0, 1). Moreover the ***S*** and ***L*** of the calculated Co^{2+} HS state have been estimated. The estimated ***L***/***S*** is 0.9±0.2, which is significantly large in the *3d* transition metal oxide system. The origin of the large orbital angular momentum was discussed in ref. [2]. This study clearly revealed that RSXS is a powerful technique for determining not only the magnetic structure, but also the electronic states, valence, spin state, and orbital/spin angular momentum.

1-3 Magnetic structure in manganite thin films [3]

The perovskite manganites show various interesting physical phenomena including colossal magnetoresistance (CMR) due to close interplay among charge, orbital, spin, and lattice degrees of freedom. The superlattices $(LaMnO_3)_m(SrMnO_3)_m$ are fabricated as a stage to control the Mn valence artificially. The films are composed of the same number of $LaMnO_3$ and $SrMnO_3$ layers and the average Mn valence is kept at 3.5+. Therefore the Mn valence can be controlled by the stacking of these layers. The Mn valence distributions were

evaluated by the resonant X-ray scattering technique [6]. The result clarified that the Mn valence becomes 3+ (4+) in the $LaMnO_3$ ($SrMnO_3$) layer, and the valence has an intermediate value between 3+ and 4+ only at the interface between the $LaMnO_3$ and $SrMnO_3$ layers. Namely, a rectangular-wave Mn valence distribution is realized in the superlattices. The valence distribution is well controlled by the stacking sequence of the $LaMnO_3$/$SrMnO_3$ layer. Moreover, a new CMR effect was reported in this superlattice system for $m = 2$, which can never be realized in a bulk compound (La,Sr)MnO_3, in which the La and Sr atoms are randomly substituted for each other [7]. This topic is attracting great interest in thin film systems. To elucidate the physical properties in the manganite thin film, it is important to understand not only the valence state but also the magnetic state of Mn ion. Especially, the magnetic structure is important to discuss the origin of the CMR effect. Here we investigated the magnetic structure in the $(LaMnO_3)_5(SrMnO_3)_5$ (L5S5) superlattice by the RXMS technique.

The RXMS was measured near the Mn $L_{2,3}$-edge to determine the magnetic structure. Several magnetic peaks were observable owing to the long periodicity of the L5S5. The temperature dependence of the energy spectra were observed at (0 0 1) as shown in Fig. 3(a). The spectra drastically change, reflecting the magnetic ordering. The integrated intensities increase with decreasing temperature below *Tc* (Fig. 3(b)). Namely, RXMS signals reflecting the ferromagnetism in L5S5 could be detected. The temperature dependence of the energy spectra at (0 0 2) and (0 0 3) was also observed as shown in Fig. 2(c). The RXMS signals were strongly observed at (0 0 1) and (0 0 3), while the signal at (0 0 2) was weak. To analyze the energy spectra, anomalous scattering factors (ASF) of Mn^{3+} and Mn^{4+} were determined by using the XAS of $LaMnO_3$ and $SrMnO_3$. The magnetic component of ASF was also calculated on the basis of the MCD spectrum [8]. The model calculation of the energy spectra was performed by utilizing these AFSs. Finally, we succeeded in determining the valence distribution at Mn sites and the ferromagnetic structure.

As explained, RXMS is an effective technique for determining magnetic structure. However, the observable *Q* region is limited, since the photon energy is in the soft X-ray region. Hence, neutron magnetic scattering is still a fascinating technique,

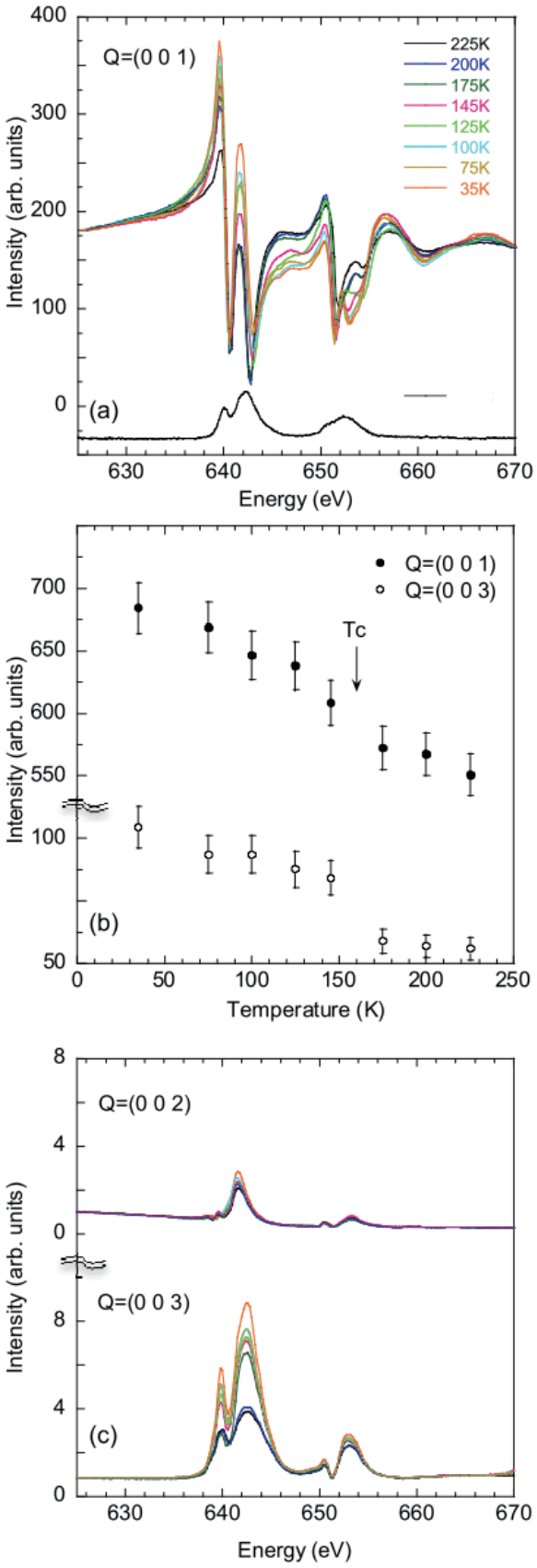

Fig. 3: (a) Temperature dependence of energy spectra at (0 0 1) and XAS near the Mn $L_{2,3}$-edge. (b) Temperature dependence of the intensities at (0 0 1) and (0 0 3) integrated between 638.5 and 642.5 eV. (c) Temperature dependence of energy spectra at (0 0 2) and (0 0 3).

although the sample volume of thin film is limited. We have tried to perform neutron magnetic scattering studies on $SrMnO_3$ film as a first step of studying the magnetism in the film system [9], and have succeeded in detecting a magnetic signal corresponding to the G-type antiferromagnetic order. This is the first observation of the neutron magnetic scattering of $SrMnO_3$, and indicates that the complementary use of RSXS and neutron magnetic scattering is effective for studying magnetism in thin film systems.

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