

Orbital polarization of LaSrMnO₄ studied by soft X-ray linear dichroism

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Abstract

With polarization-dependent soft X-ray absorption, we determined the orbital character of occupied and the lowest unoccupied e_g orbitals of prototype single-layered perovskite LaSrMnO₄. Our measurements indicate that LaSrMnO₄ exhibits strong orbital polarization in the e_g states of Mn³⁺ sites, leading us to conclude that LaSrMnO₄ has a “ferro-orbital” ordering of $3z^2-r^2$. We found that linear dichroism in soft X-ray absorption is an effective experimental method to identify the nature of orbital ordering in transition-metal oxides such as manganites. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Orbital ordering is one of the important subjects in current research of transition metal compounds [1]. In some compounds, there is a real space ordering of the charge carrier in certain orbitals, i.e., orbital ordering, resulting from superexchange interaction, lattice distortion, and Coulomb correlation of electrons. Orbital ordering manifests itself in the site dependent orientation of the quadrupole moment as a result of the spatial distribution of the outermost valence d electrons. Orbital ordering gives rise to the anisotropy of the electron-transfer interaction. As the magnetic and transport properties are closely correlated to the orbital and charge degrees of freedom, there have been many efforts to clarify the microscopic mechanisms giving rise to such exotic phenomena. For example, a fundamental issue in the physics of the manganites concerns the mechanism of the charge-orbital ordering and charge stripe formation. The mechanism of charge-orbital ordering is being extensively discussed [2–9].

Measurements of resonant X-ray scattering (RXS) at the Mn 1s the threshold have been argued for the evidence of 3d orbital ordering of manganites [10,11]. In one of the interpretations of RXS measurements, a Mn 1s electron is first excited to the unoccupied Mn 4p state by absorbing the incident photon and then a photon is emitted resulting from the 4p → 1s de-excitation. Consequently, the ordering of 4p orbitals, e.g., the alternately arrangement of 4p_x and 4p_y orbitals of Mn in LaMnO₃, is directly observed. Through intra-atomic 3d-4p multipole interaction, ordering of Mn 3d orbitals is indirectly observed. However, such an interpretation of RXS at Mn K-edge is controversial. Orbital ordering in transition-metal oxides is typically accompanied by Jahn–Teller lattice distortion. Calculations based on a local-density approximation including on-site Coulomb interactions (LDA + U) [12,13] and multiple scattering theory [14] indicate that RXS measurements pertain mainly to Jahn–Teller distortion, instead of directly observing 3d orbital ordering. To identify the orbital character of 3d states in orbital-ordered manganites is an important subject.

Polarization-dependent soft X-ray absorption (XAS), particularly linear dichroism, provides us with a powerful means to identify spin and orbital occupation of transition-metal oxides. For example, linear dichroism (LD) in XAS measurements on V₂O₃ enabled important

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observations on its electronic structure, identifying the orbital occupation of V 3d² ions in various phases, defining that they are in a high-spin state, i.e., $S = 1$ [15].

Calculations based on a single-ion model which includes the 3d-3d and 3d-2p multipole interactions and a crystal field have recently shown that the linear dichroism in Mn L_{2,3} absorption exhibits multiplet structure and strongly reflect 3d orbital polarization, but insensitive to the Jahn–Teller distortion of the crystal [16,17]. Linear dichroism therefore is expected to be a promising method to identify the orbital character of 3d electrons of orbital ordered compounds.

LaSrMnO₄, a mother compound of single-layered manganites La_{1-x}Sr_{1+x}MnO₄, has the K₂NiF₄ structure and is an antiferromagnetic insulator. In the single-layered perovskite structure of LaSrMnO₄, there exhibits a strong Jahn–Teller lattice distortion in which the Mn–O bond length along the z -axis is significantly larger than that in the ab plane, i.e., the MnO₂ plane. Consequently, the e_g band of Mn is preferentially occupied by the $d_{3z^2-r^2}$ orbital as a result of the bigger bond length of Mn–O along the z -axis; the lowest unoccupied e_g orbital is $d_{x^2-y^2}$. Figure 1 displays the Mn 3d partial density of states of LaSrMnO₄ in the vicinity of the Fermi level obtained from band structure calculations in the scheme LDA + U [18], showing that LaSrMnO₄ exhibits strong orbital polarization in the e_g band. Because of its large Jahn–Teller splitting, LaSrMnO₄ is a good system for examining whether LD measurements can provide us with information on the orbital character of 3d electrons.

In this paper, we present measurements and multiplet calculations of linear dichroism in Mn 2p-edge XAS to identify the 3d orbital character of the e_g electrons in LaSrMnO₄. Our results clearly demonstrate that linear dichroism in soft X-ray absorption is a powerful experiment tool in determining the nature of orbital ordering in 3d transition metal oxides.

The rest of this paper is organized as follows. In the next section, we briefly describe the experimental details

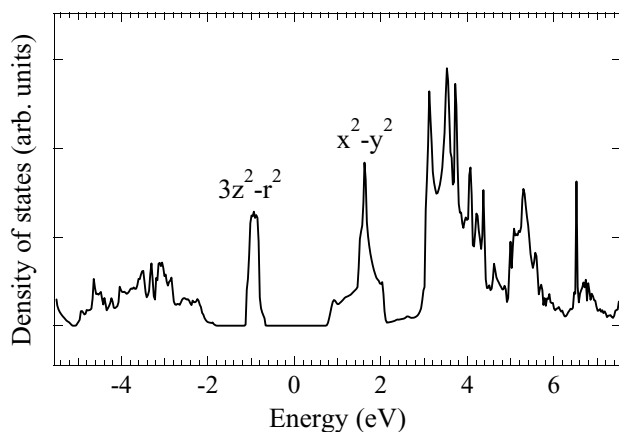


Fig. 1. Partial density of states of Mn 3d in LaSrMnO₄ obtained from LDA + U calculations with $U = 8$ eV. The Fermi level is the zero of energy.

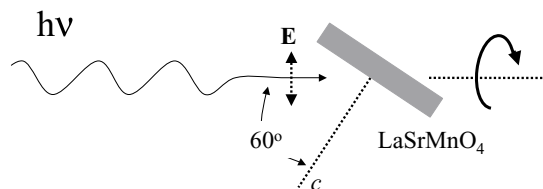


Fig. 2. Schematic illustration of sample rotation for LD measurements. The sample was rotated about the direction of incident photons to obtain two sets of XAS spectra with $E \perp c$ and with E in the plane defined by the c -axis and the direction of incident radiation. Polarization-dependent XAS was deduced as described in the text.

including growth and characterizations of LaSrMnO₄ single crystal, and measurements of linear dichroism. Methods of multiplet are briefly summarized in Section 3. Results and discussion are presented in Section 4, followed by conclusions.

2. Experimental

Single-crystalline samples of LaSrMnO₄ were grown by the floating zone method, as described elsewhere [19]. Measurements of X-ray diffraction at room temperature show that our samples are of single phase and have the $I4/mmm$ tetragonal structure with lattice constants $c = 13.04$ Å and $a = 3.81$ Å. The crystal also exhibits large Jahn–Teller distortion, i.e., the Mn–O bond length of 2.29 Å along the c -axis and 1.90 Å along the a -axis and b -axis.

XAS measurements on LaSrMnO₄ single crystals at various temperatures were performed at the Dragon beamline of the National Synchrotron Radiation Research Center in Taiwan. We recorded XAS spectra by collecting the sample drain current at 300 K. Crystals were in situ cleaved in an ultra-high vacuum at 90 K; the incident angle was 60° from the sample surface normal and the photon energy resolution was 0.2 eV. As shown in Fig. 2, we rotated the sample about the direction of incident photons to obtain LD spectra from which experimental artifacts related to the difference in the optical path and to the probing area have been eliminated. All measured XAS spectra referred to the E vector parallel to the c -axis are shown with a correction for the geometry effect. A geometry effect in XAS measurements is corrected as follows: $I_{\parallel} = 4/3(I - (1/4)I_{\perp})$, in which I_{\perp} and I are measured XAS intensities with $E \perp c$ and with E in the plane defined by the c -axis and the direction of incident radiation, respectively; I_{\parallel} is the deduced XAS intensity for $E \parallel c$.

3. Multiplet calculations

We used a cluster model based on a configuration interaction (CI) approach to calculate XAS and linear dichroism spectra of LaSrMnO₄ [20,21]. In the calculation, octahedral

MnO_4^{5-} clusters were used. Because of strong Mn 3d-O 2p hybridization, the electronic state of the Mn^{3+} ions is described as a linear combination of the $3d^4$, $3d^5\bar{\underline{L}}$, $3d^6\bar{\underline{L}}^2$, where $\bar{\underline{L}}$ denotes a hole on oxygen 2p orbital. We calculated the spectra by exactly diagonalizing the single-ion Hamiltonian under the crystal field where multipole interactions between the 3d-3d and 3d-2p core are described by the Slater integrals and the spin-orbit interactions. The “non multiplet” Hamiltonian describing valence and core states and the effective interaction between electrons are expressed in terms of the 3d-3d and 3d-2p Coulomb interactions (U_{dd} and U_{dc} , respectively), and the hybridization strength between Mn 3d and O 2p. In addition, the charge fluctuation between the ligand 2p and cation 3d is also taken into account with charge-transfer energy Δ defined as $(E_{3d^5\bar{\underline{L}}} - E_{3d^4})$, where $E_{3d^5\bar{\underline{L}}}$ and E_{3d^4} are the average energies of $3d^5\bar{\underline{L}}$ and $3d^4$ configurations, respectively.

The Hatree-Fock values were adopted for the coupling constants of the 2p-core and 3d spin-orbit interactions and 80% of the values were used for the Slater integrals, which describe the 3d-3d and 3d-2p multiplet interactions in the Hamiltonian [22,23]. The values of charge-transfer energy Δ , on-site Coulomb energies U_{dd} and U_{dc} , and hopping integrals ($V(t_{2g})$ and $V(e_g)$) between 3d and oxygen 2p molecular orbitals were included to reproduce the experimental spectra. In addition, we also used octahedral crystal field parameter $10Dq = \varepsilon_d(e_g) - \varepsilon_d(t_{2g})$, and hybridization strength between the O 2p orbitals $2T_{pp} = \varepsilon_L(e_g) - \varepsilon_L(t_{2g})$ as the calculation parameters. To reduce the number of the free parameters, the empirical relation between Slater-Koster hopping integrals $p\sigma \approx -4/\sqrt{3}p\pi$ was assumed.

4. Results and discussion

To experimentally confirm the strong 3d orbital polarization of LaSrMnO_4 concluded from LDA + U band structure calculations, we performed O 1s XAS. Absorption at the oxygen K-edge is a dipole allowed transition in which an O 1s electron is excited to unoccupied O 2p orbitals. The pre-edge structure, i.e., the structure at the absorption threshold, is determined by the hybridization between O 2p and Mn 3d bands. In addition, at slightly higher energies, the XAS structure is determined unoccupied orbitals corresponding to the hybridization between the oxygen and the La 4f/5d and Sr 3d orbitals. In configuration approach, the strength of O 1s \rightarrow 2p transition of LaSrMnO_4 is determined by the weight of $3d^5\bar{\underline{L}}$ character in the ground state. Polarization-dependent O 1s XAS therefore reflects the symmetry of unoccupied Mn 3d orbitals. Fig. 3 depicts O 1s XAS spectra of LaSrMnO_4 with the \mathbf{E} vector of photons perpendicular and parallel to the crystal c -axis. Our measurements reveal that the lowest unoccupied O 2p bands have a strong in-plane character, consistent with the conclusion obtained from LDA + U calculations, indicating that LaSrMnO_4 exhibits x^2-y^2 orbital character in its unoccupied e_g band. It

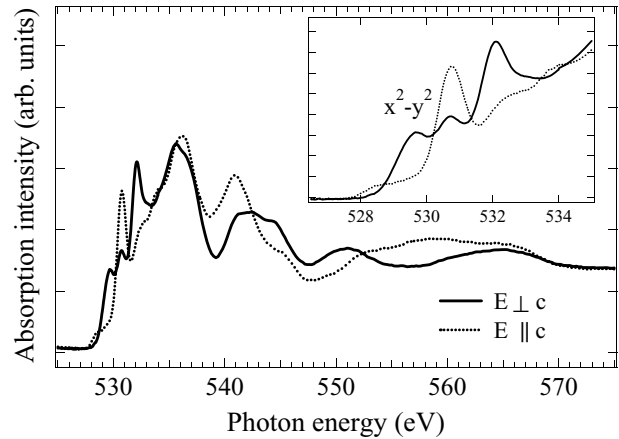


Fig. 3. Polarization-dependent XAS of LaSrMnO_4 single crystal. The solid and dashed lines show the spectra taken with the \mathbf{E} vector of photons perpendicular and parallel to the crystal c -axis.

is interesting to note that the pre-edge results of our O 1s measurements are nearly identical to those of previous measurements with in situ cleaved samples [24], but in contrast to those of specially cut samples with annealing under Ar atmosphere [25].

After establishing the $3z^2-r^2$ orbital character in the occupied e_g band of LaSrMnO_4 , we now present LD measurements in the Mn L-edge absorption. Fig. 4 shows the polarization-dependent XAS spectra of LaSrMnO_4 taken with the \mathbf{E} vector of photons perpendicular ($\mathbf{E} \perp c$) and parallel ($\mathbf{E} \parallel c$) to the crystal c -axis. Since the unoccupied e_g band has a strong orbital anisotropy, the cross section of Mn 2p \rightarrow 3d absorption excited by photons with in-plane polarization ($\mathbf{E} \perp c$) is larger than that with out-of-plane polarization ($\mathbf{E} \parallel c$), if the multiplet effect resulting from 3d-3d and 2p-3d multipole interactions is neglected. In L_3 region,

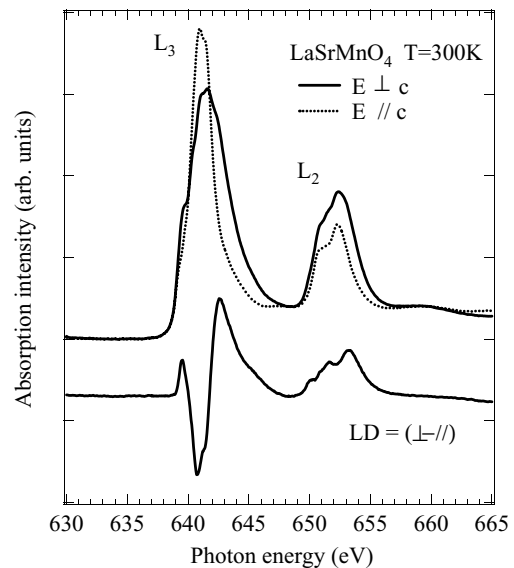


Fig. 4. Measured LD and polarization-dependent XAS taken with $\mathbf{E} \perp c$ (solid line) and $\mathbf{E} \parallel c$ (dashed line) of LaSrMnO_4 .

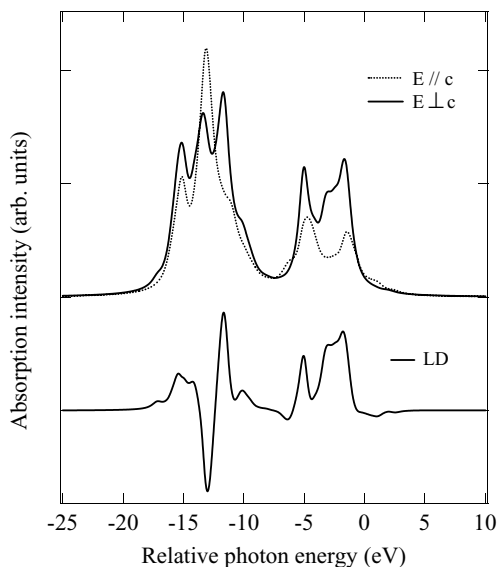


Fig. 5. Calculated LD and polarization-dependent XAS of Mn^{3+} with $3d_{3z^2-r^2}$ orbital occupied. The descriptions for the figure correspond to those of Fig. 4.

the four core 2p states contribute to 3d-2p multipole interaction and multiplet structures, while the two states in L_2 region. The difference in XAS between the two linear polarizations is therefore remarkable in L_3 region compared with L_2 region. By an inspection of 2p-3d multipole interaction described by the Gaunt coefficient, the XAS spectral width for E perpendicular to c is found to be larger than that for E parallel to c both in L_3 and L_2 , if $3z^2-r^2$ is occupied. This causes the basic LD feature especially in L_3 , although less prominent in L_2 . Our measurements of linear dichroism indeed show that the integrated intensity of XAS taken with in-plane polarization is larger than that with out-of-plane polarization, consistent with the above argument.

To further understand the LD spectrum of LaSrMnO_4 , we performed multiplet calculations to obtain polarization dependent XAS. In our calculations, we assumed $10Dq = 2.2$ eV. Other parameters are the same as those used in Ref. [16]. We used parameters Δ_i and Δ_f to represent the energy difference between $3d_{3z^2-r^2}$ and $3d_{x^2-y^2}$ orbitals in the initial and the final states of XAS, respectively; we assumed that $3d_{3z^2-r^2}$ has lower energy than $3d_{x^2-y^2}$ for Δ_i and Δ_f positive. Δ_i and Δ_f result from the contribution of the molecular field and the Jahn–Teller distortion; the former is ~ 0.1 eV at temperature below the transition, while the latter can be several tenth of an eV. By comparing the LD spectra of different values of Δ_i and Δ_f , we found that the LD spectrum is weakly dependent on Δ_f and the basic feature of LD spectrum is determined by 3d electron distribution in the initial state. In other words, LD is insensitive to the Jahn–Teller distortion of the MnO_6 cluster [16]. With $\Delta_i = 0.1$ eV, and $\Delta_f = 0.5$ eV, Fig. 5 shows calculated LD and polarization-dependent XAS of Mn^{3+} with $3d_{3z^2-r^2}$ orbital occupied; the spectra taken with $E \perp c$ and $E \parallel c$ are plotted by solid and dashed lines, respectively.

Most of the features in the measured LD at Mn L-edge are reproduced by multiplet calculations for Mn^{3+} ions with occupied $d_{3z^2-r^2}$ orbitals, revealing that LD in L-edge XAS is an effective means to examine the orbital character of 3d electronic states in an orbital-ordered compound.

The comparison of measurements of polarization-dependent XAS with multiplet calculations leads us to suggest that one can use LD in L-edge X-ray absorption to identify the nature of orbital ordering in transition metal compounds such as the orbital nature of half-doped single-layered manganites which exhibit CE-type antiferromagnetic ordering and charge-orbital ordering [10,19,26,27]. Below a charge ordering temperature $T_{\text{CO}} = 217$ K, the valence of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ orders in an alternating pattern with two distinct sites identified as Mn^{3+} and Mn^{4+} [19,27]. Electron-lattice coupling and Coulomb correlations give rise to alternating orbital ordering. In contrast to the $3z^2-r^2$ “ferro-orbital” ordering in LaSrMnO_4 , e_g electrons of the Mn^{3+} sites in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ are believed to exhibit an orbital ordering of $3x^2-r^2/3y^2-r^2$, in which occupied $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ orbitals are alternately arranged at two sublattices in the ab plane. However, $d_{3x^2-r^2}$ and $d_{x^2-z^2}$ ($d_{3y^2-r^2}$ and $d_{y^2-z^2}$) orbitals might be mixed, because orbitals of these two types have the same spatial symmetry in the MnO_2 plane. One thus can apply the technique of LD in soft X-ray absorption to clarify the orbital character of 3d electrons in the Mn e_g band of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. Furthermore, in principle, one could directly observe both orbital ordering and Jahn–Teller ordering in manganites by using LD in resonant X-ray scattering at Mn $L_{2,3}$ -edges.

5. Conclusions

We have studied the orbital polarization of 3d electrons in the Mn e_g band of LaSrMnO_4 . The results demonstrate that LD in Mn 2p XAS is a powerful method to test the validity of models for orbital ordering in transition-metal oxides. This technique would open up a new avenue for determining the orbital character of 3d electrons in transition metal oxides, and possibly examining the mechanism of orbital ordering.

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