

Orbital Ordering of Manganites Studied by Soft X-ray Linear Dichroism

Correlated-electron materials such as transition-metal oxides have attracted enormous interest because of their interesting physical properties, including superconductivity and colossal magnetoresistance. An electron in a correlated electron material has three attributes: charge, spin, and orbital. The orbital represents the shape of the electron distribution, and the orbital degree of freedom plays an important role in novel properties of correlated-electron materials through strong coupling with charge, spin, and lattice dynamics. From measurements of linear dichroism in Mn 2p-edge x-ray absorption, we found that single-layered manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ exhibits predominantly cross-type orbital ordering, in sharp contrast to the previous understanding of rod-type orbital ordering. Band-structure calculations also reveal that such a cross-type orbital ordering results from a combined effect of antiferromagnetic structure, Jahn-Teller distortion, and on-site Coulomb interactions.

Considering a transition-metal atom in a crystal with the perovskite structure in which the transition-metal is surrounded by six oxygen ions, as shown in Fig. 1, the surrounding oxygen ions introduce the crystal field splitting of the 3d orbitals. Energies of electrons with wave functions of pointing toward O^{2-} ions are higher than those pointing between them. The former wave functions, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, are called e_g orbitals, whereas the latter, d_{xy} , d_{yz} , and d_{zx} , are called t_{2g} orbitals. If there is a lattice distortion e.g., an elongation of the oxygen-metal bond-length along the z direction known as the Jahn-Teller distortion, the $d_{x^2-y^2}$ and d_{xy} orbitals would have energies higher than those of other orbitals in e_g and t_{2g} manifolds, respectively.

The orbital character of 3d electrons is intimately associated with low-energy excitations and spectacular properties of transition-metal oxides. In some compounds, there is a real space ordering of the charge carrier in certain orbitals, called orbital ordering, resulting from 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 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.

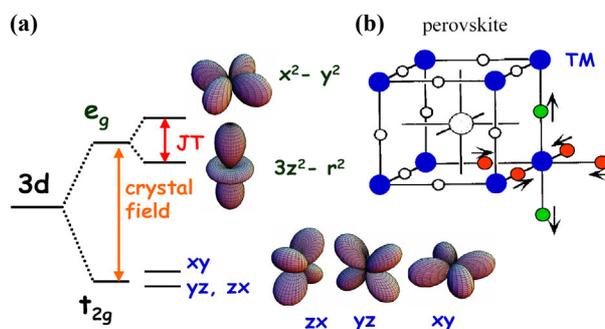


Fig. 1: Electronic structure of transition-metal oxides with a perovskite structure. (a): Schematic energy levels of five 3d orbitals of transition metals in the cubic crystal field and the lift of the fivefold degeneracy to two e_g orbitals and three t_{2g} orbitals. The e_g doublet is split further by an energy JT resulting from a Jahn-Teller distortion of the surrounding O_6 octahedron. (b): The basic perovskite structure with a Jahn-Teller distortion indicated by arrows.

Here we discuss measurements of linear dichroism in Mn 2p-edge X-ray absorption to identify the 3d orbital character of the e_g electrons in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. Our results clearly demonstrate that linear dichroism in soft x-ray absorption is a powerful experimental tool in determining the nature of orbital ordering in 3d transition-metal oxides.

Polarization-dependent soft x-ray absorption spectroscopy (XAS) 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 V_2O_3 enabled important observations on its electronic structure, identifying that V $3d^2$ ions are in a high-spin state. LD in XAS is defined as the difference between

XAS spectra taken with the E vector of photons perpendicular and parallel to the crystal c -axis. One can use LD in L-edge XAS to characterize the $3d$ orbital character of orbital-ordered compounds. To verify experimentally such a capability of LD, we first measured the LD in Mn $L_{2,3}$ -edge XAS of LaSrMnO_4 .

LaSrMnO_4 , a mother compound of single-layered manganites $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$, has the K_2NiF_4 structure and is an antiferromagnetic insulator. In the single-layered perovskite structure of LaSrMnO_4 , there exhibits a strong Jahn-Teller lattice distortion in which the MnO bond length along the z -axis is significantly larger than that in the ab plane, i.e., the MnO_2 plane. Consequently the e_g band of Mn is preferentially occupied by the $d_{3z^2-r^2}$ orbital; the lowest unoccupied e_g orbital is $d_{x^2-y^2}$. Band-structure calculations in the scheme of local-density approximation including on-site Coulomb interaction (LDA+U) show that LaSrMnO_4 exhibits a strong orbital polarization in the e_g band. Because of its large Jahn-Teller splitting, LaSrMnO_4 is a good system for examining whether LD measurements can provide us with information on the orbital character of $3d$ electrons.

Figure 2 shows the polarization-dependent XAS spectra of LaSrMnO_4 taken with the E vector of photons perpendicular ($E \perp c$) and parallel ($E // c$) 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 ($E \perp c$) is larger than that with out-of-plane polarization ($E // c$), if the multiplet effect resulting from $3d$ - $3d$ and $2p$ - $3d$ multipole interactions is neglected. 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 simple symmetry argument.

Half-doped manganites such as $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ exhibit antiferromagnetic (AFM) ordering and charge-orbital ordering. They have a zigzag magnetic structure in which the magnetic moments of Mn on the chain form a ferromagnetic coupling, but AFM coupling between the zigzag chains, as shown in Fig. 3. Below the charge-ordering (CO) 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+} . 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, as demonstrated in Fig. 3(a). 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. $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ might exhibit an orbital ordering of x^2-z^2/y^2-z^2 , as illustrated in Fig. 3(b). One 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 $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$.

Now we present the LD in XAS on $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ with varied doping in Fig. 4(a) to clarify the origin of the LD signal. Because the Jahn-Teller effect on the Mn^{4+} ions is insignificant, the contribution of $3d$ orbitals of these ions to LD is much smaller than that of Mn^{3+} ions. With increasing doping, the proportion of Mn^{3+} ions decreases;

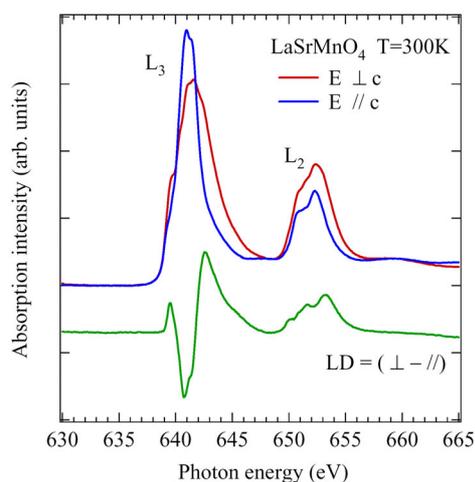


Fig. 2: Measured LD and polarization-dependent XAS taken with $E \perp c$ (red) and $E // c$ (blue) of LaSrMnO_4 .

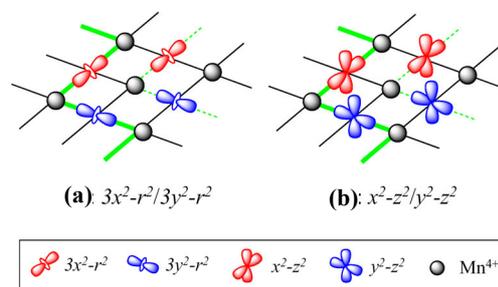


Fig. 3: Illustration of orbital ordering patterns in the MnO_2 plane of half-doped $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. (a) and (b) show the angular distribution of the e_g electrons with $3x^2-r^2/3y^2-r^2$ and x^2-z^2/y^2-z^2 orbital ordering, respectively. Thick and dashed lines indicate ferromagnetic zigzag chains with opposite spins. Orbitals of oxygen $2p$ are omitted for clarity.

the LD magnitude of doped $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ diminishes. Note that the magnitude of LD decreases more rapidly than that from a simple picture of Mn^{3+} - Mn^{4+} dilution. In particular, the LD magnitude of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is $\sim 1/4$ that observed for LaSrMnO_4 ; its sign at the L_2 -edge is the same as that of LaSrMnO_4 . To identify the orbital character of the occupied e_g states, by using a model of MnO_6 cluster based on configuration interaction, we calculated LD spectra of Mn^{3+} with $d_{x^2-z^2}/d_{y^2-z^2}$ and $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbitals occupied, as plotted in Fig. 4(b). Overall the calculated LD of occupied in-plane orbitals such as $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ is with sign reversed to that of out-of-plane orbitals such as $d_{3z^2-r^2}$, $d_{x^2-z^2}$, and $d_{y^2-z^2}$. Surprisingly the conventional orbital ordering model of $3x^2-r^2/3y^2-r^2$ type is incompatible with LD measurements. The calculated LD of $3x^2-r^2/3y^2-r^2$ -type orbital ordering is with sign reversed to that of measured LD from $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. Furthermore, the lineshape of the measured LD spectrum for $x = 0.5$ is similar to those from calculations for Mn^{3+} with occupied $d_{3z^2-r^2}$ or $d_{x^2-z^2}/d_{y^2-z^2}$ orbitals, implying that $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ has an orbital polarization of strong z character, e.g., $d_{3z^2-r^2}$ or $d_{x^2-z^2}/d_{y^2-z^2}$. If $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ exhibited $3z^2-r^2$ orbital ordering, all Mn^{3+} sites, i.e., half of all Mn atoms, would contribute to LD and its magnitude at Mn L_2 -edge would be half of that observed in LaSrMnO_4 , in contrast to the measurements. If $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ exhibits x^2-z^2/y^2-z^2 orbital ordering, by choosing LD as the difference in XAS spectra taken with the E vector parallel to x and z axes, we observe essentially linear dichroism resulting only from the sublattice with occupied $d_{y^2-z^2}$. In other words, only half of Mn^{3+} sites contribute to LD; one quarter of Mn atoms contribute to LD, consistent with the measurements. Our LD measurements thus suggest that orbital ordering of the e_g states on the Mn site in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is dominated by x^2-z^2/y^2-z^2 type.

The existence of orbital ordering of cross-type x^2-z^2/y^2-z^2 can be understood within the framework of crystal field effect with lattice distortion taken into account. On the Mn^{3+} sites of a cubic perovskite, e_g orbitals of $3y^2-r^2$ ($3x^2-r^2$) symmetry are preferentially occupied if the Mn-O length is elongated along the y (x) direction; y^2-z^2 (x^2-z^2) orbitals are occupied if the Mn-O length is contracted along the x (y) direction, as illustrated in Fig. 5. The shear-type distortion of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ leads effectively to alternate contractions of along the x and y directions in, because the longer in-plane Mn-O length (2.00 Å) is close to the out-of-plane

Mn-O length (1.98 Å), while the shorter in-plane Mn-O length is 1.84 Å. Orbital ordering of x^2-z^2/y^2-z^2 is expected to be energetically more favorable than that of $3x^2-r^2/3y^2-r^2$.

In conclusion, 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

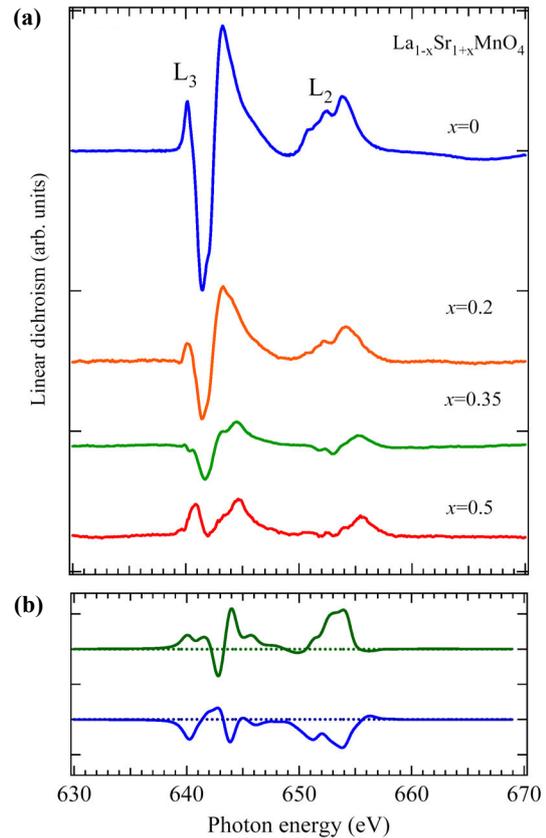


Fig. 4: (a) LD in Mn L-edge XAS of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_4$ with varied doping. Spectra of linear dichroism were derived from XAS normalized to the same peak intensity at Mn L_3 -edge and measured at 300 K for $x \leq 0.35$ and 150 K for $x = 0.5$. (b) Calculated LD spectra of Mn^{3+} ions with $d_{x^2-z^2}/d_{y^2-z^2}$ and $d_{3x^2-r^2}/d_{3y^2-r^2}$ orbitals occupied.

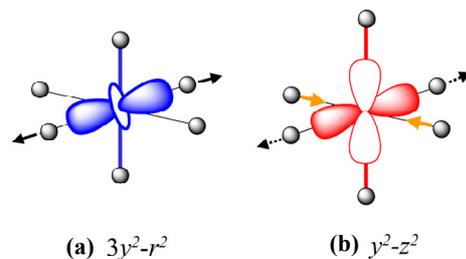


Fig. 5: View of $d_{3y^2-r^2}$ and $d_{y^2-z^2}$ orbitals on the Mn^{3+} sites with different Jahn-Teller distortions. (a) and (b) show the Mn-O length elongated and contracted along the y direction, respectively. Filled circles denote O atoms in which 2p orbitals are omitted for clarity.

$2p$ 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. With LD measurements, we found that orbital ordering of the Mn e_g electrons in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is dominated by x^2-z^2/y^2-z^2 type. Orbital ordering of Mn e_g electrons in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is derived from a combined effect of antiferromagnetic structure, Jahn-Teller distortion, and on-site Coulomb interactions.

BEAMLINE

11A Dragon beamline

EXPERIMENTAL STATION

XAS end station

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PUBLICATIONS

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