Orbital Ordering in La$_{0.5}$Sr$_{1.5}$MnO$_4$ Studied by Soft X-Ray Linear Dichroism

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Orbital ordering, which manifests itself in the spatial distribution of the outermost valence electrons, is an important topic in current research of transition-metal oxides, as the magnetic and transport properties are closely related to the orbital and charge degrees of freedom [1]. In particular, charge-orbital ordering of half-doped manganites has attracted much attention [2–8]. The mechanism of charge-orbital ordering is being hotly debated [9–15]. To observe orbital ordering directly is a difficult task. Experimental results of resonant x-ray scattering (RXS) at the Mn $K$ edge in La$_{0.5}$Sr$_{1.5}$MnO$_4$ and LaMnO$_3$ show removal of degeneracy between 4$p_x$ and 4$p_y$; these observations have been argued to be direct evidence of orbital ordering [16,17]. However, the origin 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) [18,19] and multiple scattering theory [20] indicate that RXS measurements pertain mainly to Jahn-Teller distortion, instead of directly observing 3$d$ orbital ordering. Multiplet calculations have shown that one can use linear dichroism (LD) in soft x-ray absorption spectroscopy (XAS) to identify the orbital character of 3$d$ states in orbital-ordered manganites [21].

Half-doped manganites such as La$_{0.5}$Sr$_{1.5}$MnO$_4$ exhibit CE-type [3] antiferromagnetic (AFM) ordering and charge-orbital ordering [16,22,23]. 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. Below the charge-ordering (CO) temperature $T_{CO} = 217$ K, the valence of La$_{0.5}$Sr$_{1.5}$MnO$_4$ orders in an alternating pattern with two distinct sites identified as Mn$^{3+}$ and Mn$^{4+}$ [22,23]. The $e_g$ electrons on the nominal Mn$^{3+}$ sites of La$_{0.5}$Sr$_{1.5}$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 [7]. However, $d_{3x^2 - r^2}$ and $d_{3y^2 - r^2}$ orbitals might be mixed, because orbitals of these two types have the same spatial symmetry with respect to the MnO$_2$ plane. To clarify the nature of orbital ordering in La$_{0.5}$Sr$_{1.5}$MnO$_4$ is essential to reveal the origin of orbital-ordering in half-doped manganites.

In this Letter, we present measurements of LD in Mn 2$p$-edge XAS of La$_{1-x}$Sr$_{1+x}$MnO$_4$. The LD measurements are compared with multiplet calculations to unravel the orbital character of $e_g$ electrons in La$_{0.5}$Sr$_{1.5}$MnO$_4$. We performed also LDA + U calculations to study the orbital ordering of this compound.

Single-crystalline samples of La$_{1-x}$Sr$_{1+x}$MnO$_4$ were grown by the floating zone method [22]. Measurements of x-ray diffraction at room temperature show that our samples are of single phase. The major crystallographic difference between crystals with different $x$ is the $c$-axis length; this decreases significantly from 13.04 Å for $x = 0$ to 12.43 Å for $x = 0.5$, whereas the $a$-axis length shows only a weak $x$ dependence (3.81 Å for $x = 0$ and 3.86 Å for $x = 0.5$). This difference of the $c$-axis length is attributed to a significantly decreased out-of-plane Mn-O bond length with increasing Sr content.

XAS measurements on La$_{1-x}$Sr$_{1+x}$MnO$_4$ 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. Crystals were freshly cleaved in an ultrahigh vacuum at 90 K; the incident angle was 60° from the sample surface normal, and the photon energy resolution was 0.2 eV. 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 [24,25].

Multiplet calculations have shown that one can use LD in L-edge XAS to characterize the 3d orbital character [21]. 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. To verify experimentally such a capability of LD, we measured the LD in Mn \( L_{2,3}\)-edge XAS of LaSrMnO\(_4\), which is expected to exhibit \( 3z^2 - r^2 \) “ferro-orbital” ordering. Figure 1(a) shows our measurements of polarization-dependent XAS and LD on LaSrMnO\(_4\). Most features in the measured LD at Mn \( L \) edge are reproduced by multiplet calculations for Mn\(^{3+}\) ions with occupied \( d_{x^2-r^2} \) orbitals, as shown in Fig. 1(b) [21,26], 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.

We measured also the LD in XAS on La\(_{1-x}\)Sr\(_{1+x}\)MnO\(_4\) with varied doping to clarify further the origin of the LD signal, as shown in Fig. 2(a). Because the Jahn-Teller effect on the Mn\(^{4+}\) ions is insignificant [14,15], 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; the LD magnitude of doped La\(_{1-x}\)Sr\(_{1+x}\)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 La\(_{0.5}\)Sr\(_{1.5}\)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 [27], we calculated LD spectra of Mn\(^{3+}\) with \( d_{z^2-r^2}/d_{x^2-r^2} \) and \( d_{x^2-r^2}/d_{y^2-r^2} \) orbitals occupied, as shown in Fig. 2(b) [28]. Overall the calculated LD of occupied in-plane orbitals such as \( d_{x^2-r^2} \) and \( d_{y^2-r^2} \) is with sign reversed to that of out-of-plane orbitals such as \( d_{x^2-y^2} \) 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 La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\). One might suspect this inconsistency could result from anisotropic \( e_g \) charge distribution on the Mn\(^{4+}\) sites. If so, only \( e_g \) charge with \( d_{x^2-r^2} \) or \( d_{y^2-z^2}/d_{z^2-r^2} \) polarization transferred from Mn\(^{3+}\) to Mn\(^{4+}\) could give rise to a LD similar to the measurement. However, even in the most unfavorable case, that is, even if the transferred \( e_g \) charge on the Mn\(^{4+}\) sites is maximum (leading to equal charges on both Mn sites) and fully \( (3z^2 - r^2) \) polarized, only half of the observed LD could be accounted for. As shown later (see the lower panel of Fig. 3), such transferred \( e_g \) charges, indeed, have a small in-plane polarization. This anisotropy gives opposite contributions to LD with respect to the measurement; the inconsistency cannot be reconciled even if the anisotropic charge distribution of Mn\(^{4+}\) is taken into account.

Furthermore, the line shape of the measured LD spectrum for \( x = 0.5 \) is similar to those from calculations for

![FIG. 1.](image1.png) (a) LD and polarization-dependent XAS taken with E \( \perp c \) (solid line) and E \( \parallel c \) (broken line) of LaSrMnO\(_4\). (b) Calculated LD spectrum of Mn\(^{3+}\) ions with occupied \( d_{x^2-r^2} \) orbitals. The calculated LD is plotted on the same scale as the measured one.

![FIG. 2.](image2.png) (a) LD in Mn \( L_{2,3}\)-edge XAS of La\(_{1-x}\)Sr\(_{1+x}\)MnO\(_4\) with varied doping. Linear-dichroism spectra were derived from XAS normalized to the same peak intensity at Mn \( L_3 \) edge and measured at 300 K for \( x = 0.35 \) and 150 K for \( x = 0.5 \). (b) Calculated LD spectra of Mn\(^{3+}\) ions with \( d_{x^2-r^2}/d_{y^2-z^2} \) and \( d_{x^2-r^2}/d_{y^2-z^2} \) orbitals occupied.
Mn$^{3+}$ with occupied $d_{3z^2-r^2}$ or $d_{z^2-r^2}/d_{x^2-y^2}$ orbitals, implying that La$_{0.5}$Sr$_{1.5}$MnO$_4$ has an orbital polarization of strong $z$ character, e.g., $d_{3z^2-r^2}$ or $d_{z^2-r^2}/d_{x^2-y^2}$. If La$_{0.5}$Sr$_{1.5}$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 La$_{0.5}$Sr$_{1.5}$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 $d_{z^2-r^2}$. In other words, only half of the Mn$^{3+}$ sites contribute to LD; one quarter of the 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 La$_{0.5}$Sr$_{1.5}$MnO$_4$ is dominated by $x^2 - z^2 / y^2 - z^2$ type.

To further study orbital ordering in La$_{0.5}$Sr$_{1.5}$MnO$_4$, we performed LDA + U calculations using the full-potential linearized augmented-plane-wave method on La$_{0.5}$Sr$_{1.5}$MnO$_4$ in CE-type AFM structure with $U$ and $J$ equal to 8 and 0.88 eV for Mn 3$d$ electrons, respectively [18]. Details of the calculations will be described elsewhere [29]. Mahadevan et al. [14] found that the breathing-type Jahn-Teller distortion of La$_{0.5}$Sr$_{1.5}$MnO$_4$ suggested by Sternlieb et al. [23] is not energetically favorable, and proposed a shear-type Jahn-Teller distortion in which the Mn-O length is elongated alternately along the $x$ and $y$ directions. Measurements of x-ray scattering also indicate a shear-type distortion on Mn-O octahedra [30], rather than a breathing-type distortion. Consistent with previous band-structure calculations [14], our LDA + U calculations show also that La$_{0.5}$Sr$_{1.5}$MnO$_4$ without Jahn-Teller distortion is unstable against a shear-type Jahn-Teller distortion. With a shear-type Jahn-Teller distortion of 0.08 Å in-plane O displacement [31], LDA + U calculations give rise to an orbital ordering dominated by $x^2 - z^2 / y^2 - z^2$ on the Mn$^{3+}$ sites of La$_{0.5}$Sr$_{1.5}$MnO$_4$, as shown in Fig. 3, which displays charge-density contours corresponding to the $e_g$ dominated valence bands. Interestingly, we found also that La$_{0.5}$Sr$_{1.5}$MnO$_4$ would exhibit $3x^2 - r^2 / 3y^2 - r^2$ orbital ordering if the on-site Coulomb interactions were not explicitly included, in agreement with previous LDA calculations [14]. Our results suggest that charge and orbital ordering can be well described if the on-site Coulomb interactions of 3$d$ electrons are properly taken into account, as in the LDA + U or Hartree-Fock calculations. Such a cross-type orbital ordering results from a combined effect of AFM structure, Jahn-Teller distortion, and the on-site Coulomb interactions of 3$d$ electrons.

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 $y$ ($y^2$) direction; $y^2 - z^2$ orbitals are occupied if the Mn-O length is contracted along the $x$ ($x^2$ and $z^2$) direction, as shown in Fig. 4. For example, in CE-type charge-orthogonal ordered half-doped manganites of cubic perovskite such as La$_{0.5}$Ca$_{0.5}$MnO$_3$, the Mn$^{3+}$ site exhibits a large Jahn-Teller distortion, in which the Mn-O length is elongated alternately along the $x$ and $y$ directions (two long bonds of 2.06 Å along the zigzag chain and four short bonds of 1.92 Å) [32], producing $3y^2 - r^2 / 3y^2 - r^2$ orbital ordering. As for La$_{0.5}$Sr$_{1.5}$MnO$_4$, the shear-type distortion leads effectively to alternate contractions along the $x$ and $y$ directions in La$_{0.5}$Sr$_{1.5}$MnO$_4$, 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

![FIG. 3. Charge-density contours corresponding to the $e_g$ valence bands of La$_{0.5}$Sr$_{1.5}$MnO$_4$. Upper panel: Charge-density contours in the $ab$ plane. Lower panel: Charge-density contours in the $ac$ plane along the $[100]$ direction.](image)

![FIG. 4. View of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals on the Mn$^{3+}$ sites with different Jahn-Teller distortions. (a),(b) The Mn-O length elongated along the $y$ direction and contracted along the $x$ direction, respectively. Filled circles denote O atoms in which 2$p$ orbitals are omitted for clarity.](image)
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 \(3x^2 - r^2/3y^2 - r^2\). Note that small tetragonal distortions with \(c/a = 0.98\) and \(c/a = 1.04\) in strained thin films of \(La_{0.5}Sr_0.5MnO_3\) can result in ferro-orbital ordering of \(x^2 - y^2\) and \(3z^2 - r^2\), respectively [33,34].

In addition, measurements of temperature-dependent LD of \(La_{0.5}Sr_{1.5}MnO_4\) about \(T_{CO}\) provide us with further evidence that LD in \(La_{0.5}Sr_{1.5}MnO_3\) reflects the nature of orbital ordering. LD measurements with photon energy of 645 eV show that the LD decreases greatly as the temperature crosses \(T_{CO}\), as shown in Fig. 5, indicating that orbital ordering of \(La_{0.5}Sr_{1.5}MnO_4\) follows a similar temperature-dependent trend of charge ordering [23] and Jahn-Teller distortion [16]. To confirm this, more detailed temperature-dependent studies are necessary.

To conclude, we demonstrate that LD in Mn 2\(p\) XAS is a powerful method to test the validity of models for orbital ordering in transition-metal oxides. With LD measurements, we inferred that orbital ordering of the Mn \(e_g\) electrons in \(La_{0.5}Sr_{1.5}MnO_3\) is dominated by \(x^2 - z^2/y^2 - z^2\) type, as corroborated by our LDA + U calculations. Orbital ordering of Mn \(e_g\) electrons in \(La_{0.5}Sr_{1.5}MnO_4\) results from a combined effect of antiferromagnetic structure, Jahn-Teller distortion, and on-site Coulomb interactions. In principle, one can directly observe both orbital ordering and Jahn-Teller ordering in manganites by using resonant x-ray scattering at Mn \(L_{2,3}\) edges [35].

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[24] XAS intensity \(I_q\) for \(E/|c|\) is deduced from \(I_\perp = \frac{1}{2}(I_1 - I_2)\), in which \(I_\perp\) and \(I\) are XAS intensities measured with \(E \perp c\) and with \(E\) in the plane defined by the \(c\) axis and the direction of incident radiation, respectively.
[25] W. B. Wu et al. (to be published).
[26] We used 10\(D_q\) = 2.2 eV, \(\Delta_1 = 0.1\) eV, and \(\Delta_2 = 0.5\) eV. Other parameters are the same as those in Ref. [21].
[28] We used \(U = 8.0\) eV, 10\(D_q\) = 2.0 eV, charge-transfer energy \(\Delta = 2.1\) eV, and \(pd\sigma = 2.1\) eV.
[31] The longer and shorter in-plane Mn-O lengths are, respectively, 2.00 and 1.84 Å, while the out-of-plane Mn-O length is 1.98 Å.