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Magnetic and orbital anisotropy of ferromagnetic $La_{0.6}Sr_{0.4}MnO_3$ thin films studied by angle-dependent x-ray magnetic circular and linear dichroism

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Introduction

Understanding the microscopic origin of magnetic anisotropy and controlling them in magnetic materials has been one of the ultimate goals in the studies of magnetism. In magnetic thin films and multilayers, the emergence of perpendicular magnetic anisotropy and external control of magnetic anisotropy by thickness and epitaxial strain have been reported [1-3]. In order to understand the origin of such magnetic anisotropies and to find ways to control them, it is essential to clarify the spin and orbital states and their mutual coupling. X-ray magnetic circular dichroism (XMCD) in core-level x-ray absorption spectroscopy (XAS) is an ideal tool for this purpose, since one can estimate the spin and orbital magnetic moments separately in an element-specific way. Recently, we have developed an XMCD apparatus equipped with a vector magnet which consists of two sets of superconducting magnets, thereby making it possible to apply a magnetic field in arbitrary direction within the two-dimensional plane [4]. In this report, we present the results of angle-dependent XMCD and x-ray magnetic linear dichroism (XMLD) studies of a thin film of ferromagnetic metallic oxide $La_{0.6}Sr_{0.4}MnO_3$ (LSMO), where both the spin and orbital degrees of freedom affect its electric and magnetic properties [5].

Experiments

We have studied an LSMO thin film grown on a $SrTiO_3$ (STO) substrate using the vector-magnet XMCD apparatus [4] by the following methods: (1) angle-dependent XMCD, (2) transverse XMCD (TXMCD) [6], and (3) XMLD in the normal-incidence configuration. In the angle-dependent XMCD experiment, the sample angle (θ_{sample}) was fixed and only the magnetic-field angle (θ_H) was varied, as shown in the inset of Fig. 2(a).

In TXMCD [6], θ_H is adjusted so that the spin magnetic moments are aligned perpendicular to the incident x-rays [Inset of Fig. 3(a)]. In this way, one can suppress the contribution of spin magnetic moment to XMCD and extract the expectation value of the 'magnetic dipole operator' $\boldsymbol{T}$ defined by $\boldsymbol{T} \equiv \boldsymbol{S} - 3(\boldsymbol{S}\cdot\boldsymbol{r})\boldsymbol{r}/r^2$, where $\boldsymbol{S}$ is the spin angular momentum operator and $\boldsymbol{r}$ is the position operator of the electron. $\boldsymbol{T}$ appears in the XMCD sum rule [7] and represents the anisotropic spin-density distribution [8] (Fig. 1). An intuitive picture of $\boldsymbol{T}$ is given as follows: If we regard $\boldsymbol{T}$, $\boldsymbol{S}$, and $\boldsymbol{r}$ as classical vectors instead of quantum-mechanical operators, $\boldsymbol{T}$ can be rewritten as $\boldsymbol{T} \equiv \boldsymbol{S}^{\perp} - 2\boldsymbol{S}^{//}$, where $\boldsymbol{S}^{\perp}$ and $\boldsymbol{S}^{//}$ are the parallel and perpendicular components of $\boldsymbol{S}$ with respect to $\boldsymbol{r}$, respectively. This expression indicates that $\boldsymbol{T}$ and $\boldsymbol{S}$ have the same (opposite) signs if the electron orbital is perpendicular (parallel) to $\boldsymbol{S}$. Thus information about the orbital polarization can be deduced.

In normal-incident XMLD, the light is incident on the sample surface perpendicular to it and the magnetic field $\boldsymbol{H}$ is applied parallel to one of the in-plane axes, as shown in the inset of Fig. 4(a). Then the difference of the XAS spectra between horizontal (H) and vertical (V) polarizations is measured. Although the STO (001) substrate has equivalent a and b axes and in-plane orbital

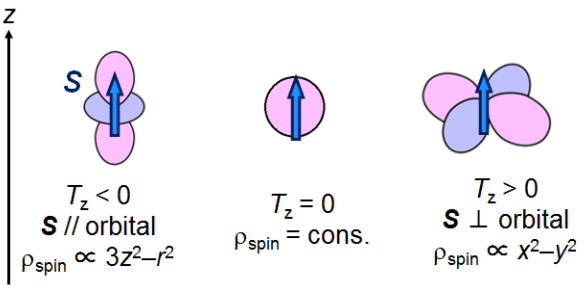

Fig. 1: Relationship between the sign of T_z, the direction of the orbital elongation relative to $\boldsymbol{S}$, and the anisotropy of the spin density distribution, in the case of $S_z > 0$.

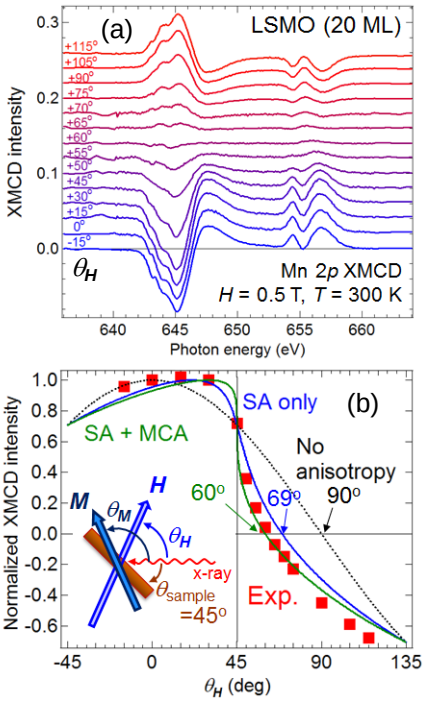

Fig. 2: Angle-dependent XMCD of the LSMO thin film at the Mn 2*p* absorption edge. (a) Magnetic-field-angle (θ_H) dependence of the XMCD spectra. (b) θ_H dependence of the XMCD intensity. Inset shows the experimental setup and the definitions of θ_H, the angle of the magnetization vector (θ_M), and the sample angle (θ_{sample}, fixed at 45°) which are measured from the direction of the incident x-rays.

anisotropy is not expected in the absence of magnetization, when the sample is magnetized along the *b* axis, the external magnetic field and resulting spin polarization may induce the in-plane orbital anisotropy through spin-orbit interaction.

The LSMO thin film was grown on the STO (001) substrate by the laser molecular beam epitaxy. The thickness of the thin film was fixed to 20 monolayers. Details of the sample fabrication and characterization are given in Ref. [9].

The XAS and XMCD measurements were performed at BL-16 of Photon Factory. The XAS spectra were taken in the total electron yield mode. All the measurements were performed at room temperature.

Results and discussion

Figure 2(a) shows the θ_H dependence of the Mn 2*p*-3*d* XMCD spectra of the LSMO film at a fixed sample angle θ_{sample}=45°. Here, both θ_H and θ_{sample} are measured from the direction of the incident x-rays. As the direction of the magnetic field was rotated, the intensity of the XMCD spectra systematically changed and a reversal of the sign was observed around θ_H = 60°. In Fig. 2(b) the XMCD intensity is plotted as a function of θ_H. We note that, due to magnetic anisotropy, the sample magnetization ***M*** is in general not parallel to the magnetic field ***H***. If they were parallel, namely, if $\theta_H = \theta_M$, where θ_M is the angle between ***M*** and the incident x-rays [inset in Fig. 2(b)], the observed XMCD intensity would be proportional to $\cos\theta_H$, as shown by a black dashed curve in Fig. 2(b). However, this does not agree with the measured θ_H dependence, showing that ***M*** and ***H*** are generally not parallel, and that effects of magnetic anisotropy have to be considered.

In order to explain the θ_H dependence of the XMCD intensity, we have performed simulations by taking into account the effects of magnetic anisotropy. There are two major contributions to the magnetic anisotropy: One is the shape anisotropy (SA), which originates from the macroscopic dipole-dipole interaction, and favors in-plane magnetization in the case of thin films. The other is the magnetocrystalline anisotropy (MCA), which originates from the interplay between the anisotropy of electron orbitals and spin-orbit interaction. Assuming that the film has only a single magnetic domain and that the MCA has only the uniaxial component of second order, the magnetostatic energy per volume of the thin film *E* is given by,

$$E = -\mu_0 MH\cos(\theta_M - \theta_H) + (\mu_0/2)M^2\sin^2(\theta_M + \theta_{sample}) + K\sin^2(\theta_M + \theta_{sample}), \quad (1)$$

where *K* is the anisotropy constant for MCA. The three terms in Eq. (1) represent the magnetic energy due to external magnetic field, the SA, and the MCA, respectively. By minimizing *E* with respect to *M* and θ_M, one obtains the θ_H dependence of *M* and θ_M, and thereby the XMCD intensity can be predicted. We first consider the case in which the MCA is absent and only the SA exists. The result is shown in Fig. 2(b) by a blue solid curve. Although the calculation agrees with experiment to some extent, there still remains a deviation from the experimental data, especially in that the reversal of the XMCD occurs at θ_H = 69°, and not at θ_H = 60° as experimentally observed. Next, we take into account for the effect of MCA by regarding *K* as a fitting parameter. The best-fit result is shown in Fig. 2(b) by a green solid curve. Good agreement with the experimental data has been obtained with the MCA constant of $K = +2.0\times10^4\,[\mathrm{J/m^3}]$, in that the XMCD changes its sign at θ_H = 60°. The positive *K* value shows that the LSMO thin film has magnetic easy axes in the plane not only due to the SA but also due to the MCA. The origin of the MCA may be ascribed to the tensile strain from the STO substrate, which is caused by the different lattice constants of bulk LSMO (*a* = 0.387 nm) and STO (*a* = 0.3905 nm).

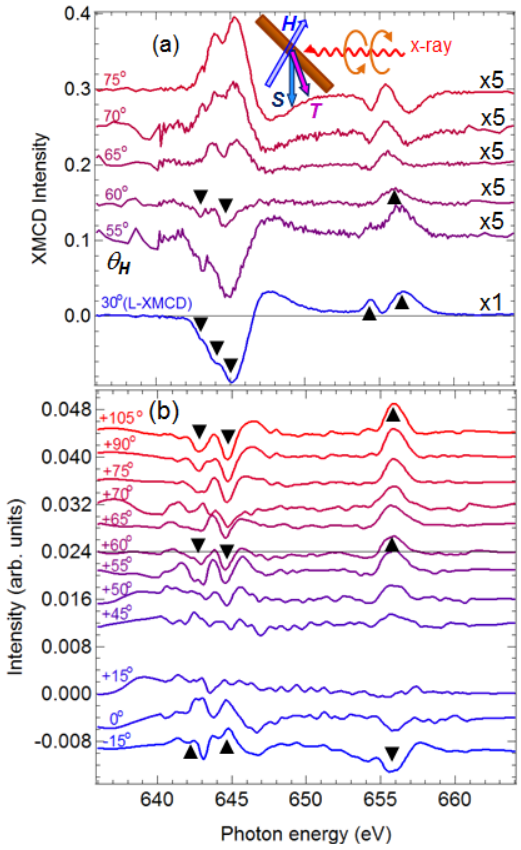

Fig. 3: Transverse XMCD (TXMCD) of the LSMO thin film. (a) Expanded spectra of Fig. 2(a) around θ_H = 60°, where ***S*** is nearly perpendicular to the incident x-rays. The spectral line shape is different from that of the conventional XMCD (longitudinal XMCD, LXMCD). Inset shows the experimental setup. (b) θ_H dependence of the spectral line shape of the TXMCD component extracted from the angle-dependent XMCD spectra in Fig. 2(a). The spectra have been smoothed. Black triangles indicate the positions and the signs of the peaks.

The angle dependence of the XMCD intensity shows that the spin moment becomes perpendicular to the incident light around θ_H = 60°, that is, the configuration of TXMCD [inset in Fig. 3(a)] is realized around θ_H = 60°. (In LSMO, the contribution of orbital magnetic moment is negligibly small due to the weak spin-orbit interaction of the Mn 3*d* orbitals [10]). Indeed, if we expand the XMCD spectra around θ_H = 60°, as shown in Fig. 3(a), it becomes clear that the spectral line shape is quite different from that at θ_H = 30° (longitudinal XMCD, LXMCD). In order to obtain information about the magnetic dipole operator ***T***, we have extracted the TXMCD component from the original XMCD spectra for every θ_H by subtracting the LXMCD spectrum. The extracted TXMCD spectra are shown in Fig. 3(b). TXMCD changes sign at θ_H = 30°: The spectra are negative (positive) at the $2p_{3/2}$ edge and positive (negative) at the $2p_{1/2}$ edge when θ_H > 30° (θ_H < 30°). Comparing the signs of the spectra between TXMCD and LXMCD, they have the opposite sign when θ_H < 30° and

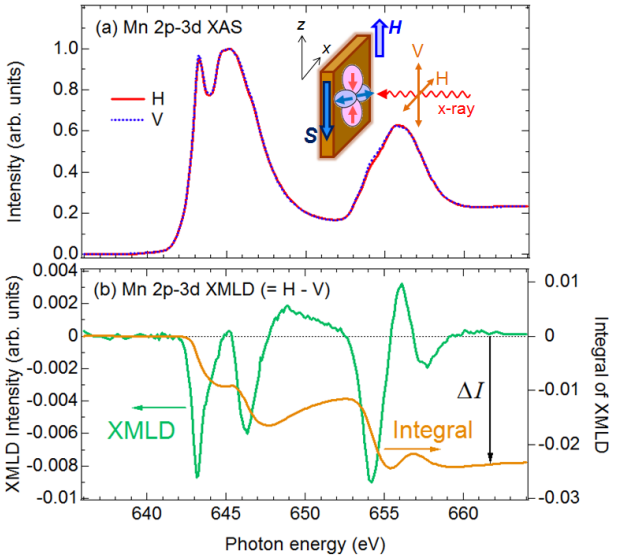

Fig. 4: Normal-incident XMLD of the LSMO thin film. (a) XAS spectra for horizontal (H) and vertical (V) polarizations. Inset shows the experimental geometry. (b) XMLD and its integrated spectra. XMLD is defined as $I_H - I_V$, where I_H and I_V denote the absorption intensities for the H and V polarizations, respectively.

θ_H > 60°, and the same signs when 30° < θ_H < 60°. From the XMCD spin sum rule [7], it follows that the directions of ***T*** and ***S*** are opposite in the former case and the same in the latter case. As already mentioned previously, if ***T*** and ***S*** are in the opposite (same) directions, the electron orbital is elongated parallel (perpendicular) to ***S***. Since ***S*** is directed nearly parallel to the film when θ_H < 30° and θ_H > 60° and perpendicular to it when 30° < θ_H < 60°, it is concluded that the orbital is elongated in the plane in both cases. This indicates that in the LSMO thin film, the $x^2 - y^2$ spin-up orbital is more preferentially occupied than the $3z^2 - r^2$ spin-up orbital, probably due to the tensile strain from the STO substrate. We note that from TXMCD one can extract information about the orbital polarization of spin-polarized electrons. This is in contrast to conventional x-ray linear dichroism (XLD), which is sensitive to the orbital polarization of electrons of both spins.

Finally, we show from the results of XMLD that the shape of the Mn 3*d* orbital is distorted by the application of external magnetic field. Figure 4 shows the XMLD spectrum of the LSMO thin film taken with the geometry described in the inset of Fig. 4. We take the *z* axis along the vertical (V) direction, and the *x* axis along the horizontal (H) direction. The magnetic field ***H*** is applied parallel to the *z* axis. In this coordinate system, the in-plane orbital of the Mn 3*d* e_g level is denoted by $z^2 - x^2$. According to the XLD sum rule [11], the integral of the XLD spectra over the entire absorption edge, $I_H - I_V$, is proportional to the charge quadrupolar moment $Q_{zz} = (3\boldsymbol{L}^2 - L_z^2)/2$, where ***L*** and L_z are the orbital angular momentum and its *z* component, respectively. Since the

integral of the experimental XMLD spectrum is negative as shown in Fig. 4, it follows that $Q_{zz} < 0$, indicating the preferential occupation of the $x^2 - y^2$ ($|L_z| = 2$) orbital compared to the $3z^2 - r^2$ ($|L_z| = 0$) orbital. This suggests that the original in-plane ($z^2 - x^2$) orbital before applying the magnetic field is distorted by the spin polarization, and is more elongated along the x axis than the z axis. It should be noted that this orbital distortion is induced solely by the spin polarization through the spin-orbit interaction.

In summary, we have investigated the magnetic and orbital anisotropies of the LSMO thin film by several spectroscopic methods, which have become possible by our newly-developed vector-magnet XMCD apparatus. From the angle-dependent XMCD experiments, we find that the LSMO thin film grown on the STO (001) substrate shows in-plane magnetic easy axes due to both the SA and the MCA. The MCA constant has been estimated to be $K = +2.0 \times 10^4\,[\mathrm{J/m^3}]$. The TXMCD component has been extracted from the angle-dependent XMCD spectra, and from the dependences of $<T_z>$ and $<S_z>$ on θ_H, we find the preferential occupation of the $x^2 - y^2$ orbital in the ferromagnetic state. From XMLD, it has been found that the $x^2 - y^2$ orbital is elongated perpendicular to the spin magnetic moment through the spin-orbit interaction. These new spectroscopic methods will shed new light on the spin and orbital states of magnetic materials, and will help us to understand the magnetic and orbital anisotropies of the magnetic materials.

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