Anisotropic spin-density distribution and magnetic anisotropy of strained La$_{1-x}$Sr$_x$MnO$_3$ thin films: angle-dependent x-ray magnetic circular dichroism

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Magnetic anisotropies of ferromagnetic thin films are induced by epitaxial strain from the substrate via strain-induced anisotropy in the orbital magnetic moment and that in the spatial distribution of spin-polarized electrons. However, the preferential orbital occupation in ferromagnetic metallic La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) thin films studied by x-ray linear dichroism (XLD) has always been found out-of-plane for both tensile and compressive epitaxial strain and hence irrespective of the magnetic anisotropy. In order to resolve this mystery, we directly probed the preferential orbital occupation of spin-polarized electrons in LSMO thin films under strain by angle-dependent x-ray magnetic circular dichroism (XMCD). Anisotropy of the spin-density distribution was found to be in-plane for the tensile strain and out-of-plane for the compressive strain, consistent with the observed magnetic anisotropy. The ubiquitous out-of-plane preferential orbital occupation seen by XLD is attributed to the occupation of both spin-up and spin-down out-of-plane orbitals in the surface magnetic dead layer.

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INTRODUCTION

Magnetic anisotropy is one of the most important properties of ferromagnets and its external control has been a major challenge both from the fundamental and applied science points of view. From the application point of view, enhancement of the magnetic field, which can be utilized as high-density energy-storage magnets. From the scientific point of view, elucidating the microscopic origin of magnetic anisotropy has been an important issue because it is generally governed by the complex interplay between spin-orbit interaction and microscopic electronic states such as spin and orbital magnetic moments, band structures, and anisotropy of charge/spin densities. Especially, the magnetic anisotropy of ferromagnetic (FM) thin films is of great interest and importance because it can be controlled, e.g., by changing epitaxial strain and film thickness.

As for oxide materials, the perovskite-type manganese oxide La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) has been the most extensively studied ferromagnet due to its intriguing physical properties such as colossal magnetoresistance and half-metallicity. The physical properties of LSMO can be controlled in various ways, e.g., by changing hole concentration $x$, temperature $T$, and external magnetic field $H$ (ref. 2). In the case of thin films, their properties are also strongly affected by epitaxial strain which originates from the lattice mismatch between the film and the substrate. For example, Konishi et al. have shown that FM metallic LSMO ($x=0.3$–0.5) thin films enter the A-type antiferromagnetic (AFM) metallic phase under tensile strain from a SrTiO$_3$ (STO) (001) substrate and the C-type AFM insulating phase under compressive strain from a LaAlO$_3$ (LAO) (001) substrate. The magnetic anisotropy of the LSMO thin films also depends on the epitaxial strain: the magnetic easy axes are in-plane when grown on the STO substrate and out-of-plane when grown on the LAO substrate. First-principles calculations have predicted that the $d_{x^2−y^2}$ orbital is preferentially occupied under the tensile strain and that the $d_{3z^2−r^2}$ orbital is preferentially occupied under the compressive strain. However, previous x-ray linear dichroism (XLD) experiments have shown that the $d_{3z^2−r^2}$ orbital is preferentially occupied for both STO and LAO substrates. This apparent discrepancy with theory has been ascribed to the different orbital occupation between the surface and the bulk, that is, the spatial symmetry breaking at the surface leads to the preferential occupation of the $d_{3z^2−r^2}$ orbital. Thus, the microscopic electronic and magnetic states of LSMO thin films and their relationship with the macroscopic magnetic properties have remained elusive so far.

In the present work, we have employed a method which directly probes the orbital occupation of spin-polarized electrons using angle-dependent x-ray magnetic circular dichroism (XMCD) in core-level x-ray absorption spectroscopy (XAS). In the XMCD spin sum rule, in addition to the well-known term which represents the spin magnetic moment $M_{p,m}$ there is an additional

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 Angular dependence of XMCD spectra and TXMCD

RESULTS

Angular dependence of XMCD spectra and TXMCD

Figure 1a shows a schematic drawing of the experimental setup for angle-dependent XMCD. One can change the direction of the external magnetic field using two sets of superconducting magnets orthogonally arranged. The experimental geometry is schematically shown in Fig. 1b with the definition of the angles of incident x-rays (θ_{inc}), applied magnetic field (θ_H), and magnetization (θ_M). Note that in general θ_M is not equal to θ_H unless the applied magnetic field is large enough to fully align all the electron spins along the magnetic field direction. According to the XMCD sum rules, 13 the “effective” spin magnetic moment $P \cdot M_{spin}$ is proportional to $\Delta I$, where $P$ is a unit vector along the x-ray incident direction, and $\Delta I$ is the integral of the XMCD spectra over the Mn L\_2,3-edge (2p → 3d) absorption edges, respectively. Under the assumption that the orbital magnetic moment $M_{orb}$ and the magnetic dipole moment $M_L$ are small enough compared to $M_{spin}$, the applied magnetic field ($M_H$) is a unit vector along the x-ray incident direction, and $\Delta I$ are the integrals of the XMCD spectra over the Mn L\_2,3-edge absorption edges, respectively.

We have grown LSMO ($x=0.3$) thin films on the Nb-doped STO (tensile strain) and LAO (compressive strain) substrates by the laser molecular beam epitaxy method (See Methods) for the detail of sample preparation, and Supplementary Figs. 2–4 and Supplementary Note 2 for sample characterization. Figure 2a, b show the Mn L\_2,3-edge (2p → 3d) XAS spectra of the LSMO thin films grown on the STO and LAO substrates, respectively. The spectral line shape of XAS for $\theta_H=45^\circ$ (where the magnetic field is applied parallel to the incident x-rays). Since the spectral line shape of XAS is almost independent of $\theta_M$ (See Supplementary Fig. 5), only the XAS spectra for $\theta_H=45^\circ$ are shown here. The spectral line shape of XAS is similar to those obtained in previous XMCD studies of bulk and thin-film samples, and absorption signals of extrinsic Mn\_2$^+$ (ref. 23) are hardly observed. Figure 2c, d show the Mn L\_2,3-edge XMCD spectra of both the substrates for various $\theta_H$’s. Systematic changes in the XMCD integrals at the Mn L\_3 edge (approximately proportional to $P \cdot M_{spin}$) can be seen which arise from the change in the magnetization direction $\theta_M$ under varying $\theta_H$. The XMCD integrals at the Mn L\_3 edge reverse in sign around $\theta_H=-15^\circ$ to $-20^\circ$ for the LSMO/STO film and around $\theta_H=-50^\circ$ to $-55^\circ$ for the LSMO/LAO film. This means that the magnetization is directed nearly perpendicular to the incident x-rays ($P \cdot M_{spin} \sim P \cdot M = 0$) around these $\theta_H$’s, namely, the TXMCD geometry is expected to exist around these angles.

The orange and green curves in Fig. 3a show the expanded XMCD spectra for LSMO/STO at $\theta_H=20^\circ$ and for LSMO/LAO at $\theta_H=50^\circ$, respectively. (We note that we have chosen these angles to be antiparallel to the wavevector of x-rays $k$.)
**Supplementary Table 1.** Panel compressive strain using the Mn$^{3+}$O$_6$ cluster model with TXMCD, we have calculated the TXMCD spectra under tensile or compressive strain, as shown in Fig. 3b. The light red and light blue curves are the absorption spectra for the positive ($\sigma+$) and negative ($\sigma-$) helicity photons, respectively, and the green curves are the absorption spectra averaged over both the helicities. The spectra have been normalized so that the height of the averaged XAS spectra is equal to unity. **c, d** XMCD spectra of the LSMO/STO (**c**) and LSMO/LAO (**d**) thin films with varying $\theta_H$. See Fig. 1 for the experimental geometry.

**Fig. 2** X-ray absorption spectroscopy (XAS) and angle-dependent XMCD spectra of the La$_{1-x}$Sr$_x$MnO$_3$ (LSMO, $x = 0.3$) thin films at the Mn$^{2+}$ absorption edges. **a, b** XAS spectra of the LSMO thin films grown on the Nb-doped SrTiO$_3$ (STO) (**a**) and LaAlO$_3$ (LAO) (**b**) substrates. The light red and light blue curves are the absorption spectra for the positive ($\sigma+$) and negative ($\sigma-$) helicity photons, respectively, and the green curves are the absorption spectra averaged over both the helicities. The spectra have been normalized so that the height of the averaged XAS spectra is equal to unity.

| Photon energy (eV) | XAS (arb. units) | TXMCD intensity (arb. units) |
|-------------------|-----------------|----------------------------|
| 640               | -0.16           | -0.16                      |
| 645               | -0.08           | -0.08                      |
| 650               | -0.01           | -0.01                      |
| 655               | 0.01            | 0.01                       |
| 660               | 0.16            | 0.16                       |

In order to show that the obtained spectra arise from genuine TXMCD, we have calculated the TXMCD spectra under tensile or compressive strain using the Mn$^{3+}$O$_6$ cluster model with $D_{4h}$ symmetry (see ‘Method’ section for details). Here, only the Mn$^{3+}$ ($d^4$) valence state has been considered since the anisotropy of the charge/spin density is negligible for the Mn$^{4+}$ ($d^3$) valence state, where the $t_{2g}$ levels are fully occupied and the $e_{g}$ levels are empty. Using the parameter values listed in Supplementary Table 1, we have calculated the TXMCD spectra corresponding to both tensile and compressive strain, as shown in Fig. 3b. The calculated TXMCD spectra well reproduce the experimental ones, suggesting that the experimentally obtained spectra at $\theta_H = -20^\circ$ for LSMO/STO and at $\theta_H = -50^\circ$ for LSMO/LAO are the genuine TXMCD spectra.
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Fig. 4 Angular dependence of the projected magnetic moment. (a) LSMO/STO (b) LSMO/LAO, deduced from the experimental data using the spin XMCD sum rule (circle) and its simulations. a and b are the data for the LSMO/STO and LSMO/LAO thin films, respectively. The black dashed curve describes the case where there is no magnetic anisotropy, and the blue solid curve describes the case where the shape magnetic anisotropy and magnetocrystalline anisotropy (MCA) are taken into account. Insets show the $\theta_H$ vs. $\theta_d$ relations deduced from the simulation. The strength of the applied magnetic field was 0.7 T for the LSMO/STO film and 0.5 T for the LSMO/LAO film. See Fig. 1 for the experimental geometry.

| Table 1. Best-fit parameters for the simulated curves in Fig. 4a, b |
|-------------------|-----------------|-----------------|-----------------|
|                   | $M_{sat}$ (µμ/Mn) | $K_u$ (kJ/m$^3$) | $(7/2)Q_{zz}$ |
| Substrate         |                |                 |                |
| STO               | 1.255 ± 0.007  | $-37.2 ± 0.8$   | $+0.05 ± 0.01$ |
| LAO               | 1.206 ± 0.014  | $+40.4 ± 2.4$   | $-0.12 ± 0.02$ |

Errors have been estimated using the least squares method. Note that $K_u$ represents the MCA energy excluding shape magnetic anisotropy.

Quantitative estimate of magnetic anisotropy energy and anisotropic spin-density distribution

We have seen in Fig. 2c, d that the sign change of $P \cdot M_{spin}$ occurs around $\theta_H \sim -20^\circ$ for the LSMO/STO film and $\theta_H \sim -50^\circ$ for the LSMO/LAO film. If there were no magnetic anisotropy, $\theta_H$ should be equal to $\theta_d$ and the sign change should occur around $\theta_H = -45^\circ$, where the incident x-ray beam is perpendicular to the magnetic field. The deviation of the sign change angle from $\theta_H = -45^\circ$ in the present experiment indicates that $\theta_H$ is not equal to $\theta_d$ due to finite magnetic anisotropy. This offers the possibility to deduce the sign and magnitude of the magnetic anisotropy by fitting the measured angular dependence of the XMCD intensity to the theoretical one which incorporates the effect of magnetic anisotropy.

Figure 4a, b show the $\theta_d$ dependence of the projected effective spin magnetic moment $P \cdot M_{eff} = P \cdot M_{spin} = (7/2)M_1$ (LSMO/STO) and $(7/2)M_1$ (LSMO/LAO) obtained by applying the sum rule to the XMCD spectra in Fig. 2c (STO substrate) and 2d (LAO substrate), respectively. The obtained angular dependencies are different from the ones which assume $\theta_H = \theta_d$ (black dashed curves), indicating that the effect of magnetic anisotropy has to be taken into account. We have, therefore, simulated the obtained angular dependence of $P \cdot M_{eff}$ based on the Stoner–Wohlfarth model. In this model, a single magnetic domain with uniaxial magnetic anisotropy of the lowest order is assumed. The magnetic energy per volume $E$ is given by an expression which contains $\theta_H$. By minimizing $E$ with respect to $\theta_H$, for each $\theta_d$ one can deduce $\theta_m$ as a function of $\theta_d$ and can calculate the projected magnetic moment $P \cdot M_{eff} = P \cdot M_{spin} = (7/2)M_1$ using the deduced $\theta_m$. It is also possible to deduce the uniaxial magnetocrystalline anisotropy (MCA) constant $K_u$ the saturation magnetization $M_{sat}$ and the electric quadrupole moment $(Q_{zz}) \equiv (1 - 3z^2)$ by taking these variables as parameters and fitting the simulated angular dependence to the experimental one (see the ‘Method’ section for more details). The results of the simulations are shown in Fig. 4a, b by blue solid curves, showing good agreement with the experiment. The best-fit parameter values are listed in Table 1.

DISCUSSION

The deduced anisotropic spin distribution in the LSMO thin films ($x^2-\gamma y^2$-like in the case of the STO substrate and $3z^2-\gamma r^2$-like in the case of the LAO substrate) is consistent with the preferential orbital occupation expected from the strain from the substrate. It is also consistent with the preferential orbital occupation which signals which reflect the anisotropic spin density on the Mn atom. Comparing the signs of the experimental XMCD spectra with the calculated ones, it is clearly demonstrated that the spin-density distribution of the Mn 3d electrons in the LSMO/STO (LSMO/LAO) thin film is more $d_{x^2-y^2}$-like ($d_{2z^2-r^2}$)-like, consistent with the expectation for the tensile and compressive epitaxial strain from the substrates.

The deduced anisotropic spin distribution in the LSMO thin film can be used to determine the anisotropy of the magnetic moments. This offers the possibility to estimate the magnetic anisotropy from the XMCD intensity.
has been suggested by the transport and magnetic measurements and the density-functional calculation. On the other hand, the results of XLD measurements show that the $d_{3z^2}$ orbital is more preferentially occupied than the $d_{xy}$ orbital even in the case of tensile strain (STO substrate), which has been attributed to the symmetry breaking at the surface and interface. The reason why the preferential orbital occupation seen by XMCD is consistent with that expected from the strain, in spite of its surface sensitivity comparable to XLD, may become apparent if one notices that XMCD is sensitive only to the spin-polarized electrons while XLD is sensitive to all the $d$ electrons. If the majority part of the surface Mn atoms occupies the $d_{xy}$ orbital due to the symmetry-breaking effect but are not spin-polarized, the $3z^2-r^2$-like charge-density distribution at the surface and interface should be observed in the XLD measurements, while the $x^2-y^2$-like spin-density distribution from underneath layers should be observed in the XMCD measurements. Indeed, there have been several reports which suggest the presence of magnetic dead layers at the surface or the interface of the FM LSMO thin films.

METHODS

Sample preparation

LSMO ($x=0.3$) thin films were grown on Nb-doped STO (001) and undoped LAO (001) (in the pseudo-cubic notation) substrates by laser molecular beam epitaxy. Since the lattice constant of bulk LSMO is smaller (larger) than that of STO (LAO), the film is supposed to be under tensile (compressive) strain from the STO (LAO) substrate. The thickness of the thin films was around 100 unit cells (~40 nm) for both the samples. The growth rate was estimated from the intensity oscillation of the specular spot in reflection high-energy electron diffraction during the growth. The LSMO films were deposited at the temperature of 1050°C on the STO substrate and 650°C on the LAO substrate, under the oxygen pressure of $1 \times 10^{-6}$ Torr. Since the LSMO/LAO film tends to be fully relaxed at higher growth temperatures and be fully strained to become an antiferromagnetic insulator at lower growth temperatures, we have adjusted the temperature so that the film is partially strained while the ferromagnetic metallicity of LSMO is maintained. After the growth of the films, both the samples were annealed at 400°C for 45 min under 1 atm of O$_2$ to fill oxygen vacancies. The lattice constants of the films were evaluated by four-circle synchrotron x-ray diffraction (XRD) measurements at BL-7C of Photon Factory, High Energy Accelerator Research Organization (KEK-PF), and laboratory-based XRD measurements using the Cu Ka line. The magnetization measurements were performed using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The temperature dependence of the resistivity was measured by the standard four-probe method. The results of the XRD, magnetization, and resistivity measurements are summarized in Supplementary Figs. 2–4 and Supplementary Note 2.

XMCD measurements

The XAS and XMCD measurements were performed using a vector-magnet XMCD apparatus with circularly polarized soft x-rays at the helical undulator beam line BL-16A2 of KEK-PF. The measurement temperature $T$ for the LSMO/LAO film was 30 K, while it was set to 270 K for the LSMO/STO film. A lower $T$ was chosen for the LSMO/LAO film because the saturation magnetization at room temperature was low, while a higher $T$ was chosen for the LSMO/STO film because the magnetic anisotropy at low temperatures was too large to saturate the magnetization along the magnetic hard axis (out-of-plane direction). The strength of the applied magnetic field was 0.7 T for the LSMO/STO film and 0.5 T for the LSMO/LAO film. The spectra were taken in the total electron-yield mode, which is a relatively surface-sensitive measurement mode (with a probing depth $\lambda$ of ~3 nm). When the magnetic field is applied nearly parallel to the film surface, photo-ejected electrons are absorbed back to the sample due to the Lorentz force and the photocurrent drops to almost zero. In order to avoid this, we applied a negative bias voltage of ~200 V to the sample holder to help the photo-ejected electrons escape from the samples. The measurements were performed at a pressure of ~1 $\times$ 10$^{-7}$ Torr. The intensity of the incident x-rays was monitored by a photocurrent from the post-focusing mirror.

Cluster-model calculation

The cluster-model calculation was performed based on the method described in ref. 29, using the ‘Xts’ code (version 8.5) developed by Arata Tanaka. A distorted Mn$^{3+}$O$_6$ octahedral cluster with $D_{3h}$ symmetry (elongated or shrunk along the [001] direction) was used (Fig. 3c). The energy levels of the Mn 3d orbitals under this symmetry are schematically drawn in Fig. 3d. The Mn 3d, Mn 2p core, and O 2p orbitals were taken as basis functions. Charge transfer from the ligand O 2p to the Mn 3d orbitals was taken into account, and we considered three electron configurations for both the initial and final states: $2p^3$,$3d^3$,$2p^3$,$3d^4$,$2p^3$,$3d^5$ for the initial state, and $2p^3$,$3d^3$,$2p^3$,$3d^4$,$2p^3$,$3d^5$ for the final state. We adjusted the following parameters to reproduce the experimental TXMCD spectra: $U_{O2}$ (Mn 3d-3d Coulomb energy), $U_{O3}$ (Mn 3d-2p Coulomb energy), $\Delta$ (charge-transfer energy from O 2p to Mn 3d), $\beta$ (Slater-Koster parameter between Mn 3d and O 2p), and $2\pi \xi_0$ (crystal-field splitting between the Mn $e_g$ and $t_{2g}$ levels). The magnitude of the $D_{3h}$ crystal-field splitting 8$\xi_0$ (splitting between the $x^2$ and $y^2$ and $3z^2-r^2$ levels) was fixed to 0.08 eV and only its sign was varied, because varying the magnitude of 8$\xi_0$ only changed the magnitude of XMCD and did not change the spectral line shape. We neglected the anisotropy of transfer integrals due to the $D_{3h}$ symmetry of the MnO$_6$ cluster and transfer integrals between the O 2p orbitals, in order to reduce the number of adjustable parameters. The x-ray incident angle was chosen to be in the [101] direction. In order to fully align the spins perpendicular to the incident x-rays, a molecular field (an effective magnetic field corresponding to the exchange interaction) of 0.01 eV along the [010] direction was added. We noted that this molecular field is strong enough to saturate the magnetization of the Mn ions.

Simulation of angular dependence of $P \cdot M_{\text{spin}}$ based on the Stoner–Wohlfarth model

We have adopted the Stoner–Wohlfarth model in order to simulate the angular dependence of the projected effective spin magnetic moment $P \cdot M_{\text{spin}}$ (see $P \cdot M_{\text{spin}}$ in Fig. 4a, b). By assuming that the film has only a single magnetic domain and that the magnetic anisotropy has only the uniaxial component of the lowest order, the magnetic energy (per volume) $E$ can be expressed as

$$E = -\mu_{M_{\text{sat}}} H \cos(\theta_{M}\cdot\theta_{H})$$

$$+ \frac{\mu_{M_{\text{sat}}}^{2}}{2} \cos^{2} \theta_{M} - K_{u} \cos^{2} \theta_{M}$$

where $H$ is the magnitude of the external magnetic field, $M_{\text{sat}}$ is the saturation magnetization, and $K_{u}$ is the uniaxial anisotropy constant for MCA ($K_{u} > 0$ for out-of-plane easy axis). The three terms in Eq. (1) represent the Zeeman energy due to the applied magnetic field, the shape magnetic anisotropy which originates from the demagnetization field in the film, and the MCA which originates from a combined effect of microscopic electron occupation and spin-orbit interaction. By minimizing $E$ with respect to $\theta_{M}$, we deduced $\theta_{M}$ as a function of $\theta_{H}$, $H$, $K_{u}$, and $M_{\text{sat}}$. Then, the projection of the effective spin magnetic moment $P \cdot M_{\text{eff}} = P \cdot (M_{\text{spin}} + (7/2) M_{\text{sat}})$ was calculated using the deduced $\theta_{M}$ by the following equation:

$$P \cdot M_{\text{spin}} + (7/2) P \cdot M_{\text{sat}} = M_{\text{sat}} \cos(\theta_{M} - \theta_{H})$$

$$+ (7/4) Q_{zz} M_{\text{sat}}(2 \cos^{2} \theta_{M} \cos^{2} \theta_{H} - \sin^{2} \theta_{M} \sin^{2} \theta_{H})$$

where $(Q_{zz}) = (1 - 3z^2)$ is the electric quadrupole moment (For the derivation of Eq. 2, see Supplementary Note 1). This gives the $\theta_{H}$ dependence of the projected moment $P \cdot M_{\text{proj}}$, for a set of parameters ($K_{u}$, $M_{\text{sat}}$, and $(Q_{zz})$). The obtained $\theta_{H}$ dependence was fitted to the
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The data supporting the findings of this study are available from the corresponding authors on reasonable request.

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AUTHOR CONTRIBUTIONS
G.S., K.Y., T.Kadono, Kishigami, T.H., Y.T., S.S., Y.N., Kikeda, and Z.C. performed XMCD measurements with the assistance of T.Koide and A.F. M.K., M.M., and K.Y. grew and measured films with the assistance of H.K. M.F., M.O., S.Fuchino, A.U., and J.-i. F. developed the type-vector superconducting magnet. J.-I.F., A.U., K.W., H.F., K. Ishigami, T.H., Y.N., T.Kadono, Y.T., S.S., Kikeda, Z.C., and G.S. were involved in the design, construction, and improvement of the XMCD measurement chamber, with assistance of S.Fujihara, T.Koide, and A.F. G.S. analyzed the XMCD data and performed the cluster-model calculation. A.T. developed the code for the cluster-model calculation (Xts version 8.5). G.S. and A.F. wrote the manuscript with suggestions by M.K., M.M., K.Y., and T.Koide, and all the other coauthors. A.F. was responsible for overall project direction and planning.

ADDITIONAL INFORMATION
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