Sign dependence of the x-ray magnetic linear dichroism on the antiferromagnetic spin axis in LaFeO_3 thin films

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Photoemission electron microscopy has been used to determine the orientation of individual antiferromagnetic domains in LaFeO_3 thin films. We found the antiferromagnetic axes are tilted by 20° out of the surface plane and have a different sign of the x-ray magnetic linear dichroism compared to previous reports on LaFeO_3 . Using multiplet calculations, we show that this sign depends on the orientation of the magnetization with respect to the crystalline axes. This has important bearings on the correct analysis of the coupling between ferromagnetic and antiferromagnetic films in exchange bias systems.

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The recently increased interest in magnetic thin film multilayers is driven by their importance for both a fundamental understanding and technological applications in magnetic devices.^{1,2} An important class of magnetic multilayers contains antiferromagnetic (AFM) thin films, which are used for pinning the magnetization direction of a ferromagnetic (FM) layer. This effect is known as exchange bias, discovered five decades ago.³ Various models have been developed; however, despite active research, the exchange bias effect is still poorly understood.^{4,5} An important missing piece of information is the spin structure of the AFM at the interface. Recent developments of synchrotron radiation-based techniques have enabled the study of this interface region.^{6–8} It has been shown, for example, that the AFM structure in thin films can differ from that of the bulk,⁹ and that the deposition of a ferromagnetic layer can lead to a change of the AFM structure.^{10,11} In addition, studies of the AFM structure at the surface region have been carried out for several materials, such as NiO ,^{12–15} Fe_2O_3 ,^{16,17} LaFeO_3 ,^{8,9} and Cr .¹⁸

Here we report a different approach to determine the spin orientation of individual domains, based on combining spatially resolved x-ray magnetic linear dichroism (XMLD) images with rotating the orientation of the linear polarization. This enables us to determine the magnetic orientation without the need to know the absolute size and sign of the XMLD. Using a photoemission electron microscope (PEEM) we found that the antiferromagnetic axes of LaFeO_3 thin films are tilted 20° out of the surface plane. Comparing our results with the literature and using multiplet calculations we show that XMLD is sensitive to the magnetocrystalline anisotropy and can even change its sign. A change of the XMLD sign has been theoretically predicted^{19,20} for ferromagnetic metals but so far not confirmed by measurements. Here, we report measurements that establish this effect for antiferromagnets.

Thin films of LaFeO_3 with a thickness of 25 nm were grown on SrTiO_3 (STO) (001) substrates using pulsed laser deposition (PLD).²¹ The samples were deposited at temperatures around 1000 K with a partial oxygen pressure of 10^{-4} mbar. Nitrous oxide was pulsed synchronously with the laser pulse, which also produced a partial pressure of

10^{-4} mbar. For all films, x-ray diffraction (XRD) and reflection high-energy electron diffraction (RHEED) indicated epitaxial growth. In order to reduce charging problems associated with PEEM measurements, the low conducting LaFeO_3 films were capped with 1 nm Pt using magnetron sputtering.

Measurements were performed with an Elmitec PEEM (Ref. 22) at the SIM beamline²³ at the Swiss Light Source. The absorption coefficient was measured in electron-yield mode with a typical spatial resolution of about 50 nm. The manipulator allowed a sample rotation about the surface normal (the z -axis) as is shown in Fig. 1(a). The 100% linearly polarized x-rays impinged on the sample at a grazing angle of 16° and the polarization axis could be rotated continuously from 0° to 90° , i.e., between in plane and out of plane.

The AFM domains in LaFeO_3 were imaged using the XMLD effect associated with the multiplet structure at the

FIG. 1. (Color online) (a) Experimental geometry and definition of the coordinate system. (b) Spatially resolved XAS recorded from a bright and dark area, together with the corresponding difference signal (black dots) and calculated spectrum (solid line) (Ref. 25). The inset shows an XMLD image of LaFeO_3 film taken with the E -vector oriented in the plane of the sample.

FIG. 2. XMLD images taken with the E -vector oriented in plane. The XMLD contrast is strongly reduced at 550 K (middle) compared with the contrast at 300 K (left), and is completely recovered upon cooling to room temperature (right).

Fe L_3 and L_2 absorption edges.⁸ The XMLD image was obtained by recording absorption images at photon energies corresponding to the A and B peaks of either the Fe L_3 or L_2 absorption edge [see Fig. 1(b)] and mapping the intensity ratio A/B [see inset of Fig. 1(b)]. Two types of contrast (bright and dark) can be seen. The magnetic origin of this contrast is revealed by local x-ray absorption spectroscopy taken for a bright and dark region [see Fig. 1(b)]. The XMLD spectrum is in good agreement with the spectra for α -Fe₂O₃ (hematite),¹⁶ for which the Fe³⁺, as in LaFeO₃, has a high-spin $3d^5$ ground state in an almost octahedral environment. In addition, the temperature dependence of the XMLD contrast was measured (see Fig. 2). The contrast decreases when approaching the Néel temperature, which in the bulk is 740 K.²⁴ The contrast is completely recovered upon cooling to room temperature, which indicates that, as for α -Fe₂O₃, it is of magnetic origin.

Determination of the orientation of the AFM axis was performed in two steps: first, the in-plane components was measured and second, the out-of-plane component. The intensity at the Fe L absorption edge is given by¹²

$$I = I_0 + I_2 \cos^2 \alpha, \quad (1)$$

where the I_0 is a constant and I_2 is the XMLD signal, whose contribution depends on the angle α between the linear polarization vector (i.e., the E vector) of incident x-rays and the AFM axis. We probe the XMLD signal by first changing the sample angle γ about the z -axis, and then changing the angle ω of the E -vector [see Fig. 1(a)]. The x -axis is parallel to the in-plane component of the x-rays.

For the determination of the in-plane component of the AFM axis, different XMLD images with the E -vector in plane were taken for γ rotated from 0° to 90° in 15° steps. This revealed a fourfold symmetry of the in-plane components, seen as a maximal contrast reversal between the XMLD images shown in Figs. 3(a) and 3(d). It follows that for the sample angles γ of 0° and 90° the in-plane components of the AFM axes are either parallel or perpendicular to the x -axis.

In order to determine the out-of-plane component of the AFM axis, XMLD images with different orientations of the E -vector were taken for both 0° and 90° sample angles. The E -vector was rotated in $\Delta\omega = 5^\circ$ steps from in plane to out of plane with respect to the sample surface.²⁶ Figure 3 illustrates the change in the XMLD images for the two in-plane sample angles $\gamma = 0^\circ$ and 90° (top and bottom row, respectively) and E -vector angle $\omega = 0^\circ, 45^\circ$, and 90° (left, middle, and right columns, respectively). Comparing the domains $P1$ and $P2$ in Fig. 3, one observes that they have the same orientation of the in-plane component, e.g., the same contrast in

FIG. 3. (Color online) XMLD images for the two in-plane sample angles $\gamma = 0^\circ$ and 90° (top and bottom row, respectively) and E -vector angle $\omega = 0^\circ, 45^\circ$, and 90° (left, middle, and right columns, respectively). Comparison of the domains $P1$ and $P2$ shows that they have the same in-plane components, i.e., the same contrast in (d), but a different out-of-plane component, i.e., different contrast in (e). The same holds for $Q3$ and $Q4$. Note that for ease of comparison, the images have been rotated.

Fig. 3(d), but a different out-of-plane component, e.g., a different contrast in Fig. 3(e). This is also the case for $Q3$ and $Q4$.

For a quantitative analysis, the ratio A/B , which we will refer to as the XMLD intensity, was studied as a function of polarization angle for 70 domains from three different sample regions. They can be divided into four characteristic groups of domains, e.g., $P1, P2, Q3$, and $Q4$ in Fig. 3. For clarity, we took the average intensity of domains showing the same behavior. Results for sample angles γ of 0° and 90° are shown in Figs. 4(a) and 4(b), respectively.

In order to determine the orientation of the out-of-plane component, it is sufficient to find the extremes in the XMLD

FIG. 4. (Color online) Averaged signal from individual domains as a function of polarization angle. Results for sample angles (a) 0° and (b) 90° are shown. The data were fitted using Eq. (1), and the fits are represented by solid lines. Our analysis has shown that the AFM axis of all domains is canted by $20 \pm 3^\circ$ from the sample surface.

intensity as a function of the E -vector angle ω . As given by Eq. (1), the XMLD intensity varies with $\cos^2 \alpha$ and hence all possible values are obtained in the range of α from 0° to 180° . By rotating the E -vector, we probe the AFM-axis components in the rotation plane. Therefore, for each AFM orientation with nonzero components in the rotation plane, we expect to see extremes at a specific E -vector angle ω . In addition, we need to know whether either a maximum or a minimum of the XMLD intensity corresponds to a parallel alignment of the E -vector with the AFM axis. This can be derived from Fig. 4. Domains that have their in-plane component of the AFM axis in the direction of the x -axis will always have their XMLD extremes at an E -vector angle of $\omega=0^\circ$ and 90° , independent of how much the AFM axis is canted. Only domains with an in-plane component of the AFM axis perpendicular to the x -axis can have extremes different from 0° and 90° . In Fig. 4(a), two pairs of angle dependences of the XMLD intensity for different domains are shown: one pair ($P1, P2$) with extremes at $\omega=20^\circ$, and 70° and a second pair ($Q3, Q4$) with nearly linear dependence or extremes at 0 and 90° . Following the above arguments and considering the observed fourfold symmetry, the first pair is oriented perpendicular and the second parallel to the x -axis. Hence, from Fig. 4(a) for an E -vector angle 0° we find that an alignment of the E -vector perpendicular to the AFM axis ($Q3$ and $Q4$) corresponds to a low XMLD intensity. After rotating the sample by 90° we find a consistent, reversed behavior for $P1, P2, Q3$, and $Q4$ [see Fig. 4(b)]. The data shown in Fig. 4 were fitted using Eq. (1), and the fits are represented by the solid lines. Our analysis shows that the AFM axis of all domains is canted by $20 \pm 3^\circ$ from the sample surface.

The existence of four domain orientations can be explained by considering the crystallographic structure of the films. LaFeO_3 is orthorhombic and grows with the c -axis in the surface plane and parallel to the STO $\langle 100 \rangle$ axes. Our RHEED measurements showed that the epitaxial films are crystallographically twinned, resulting in the fourfold symmetry. This is in agreement with the studies of Scholl *et al.*⁸ and Lüning *et al.*⁹ of LaFeO_3 grown by molecular beam epitaxy (MBE) on STO(001), where the crystallographic structure was determined with transmission electron microscopy. In their sample, the AFM axis is canted 45° out of the sample surface. We attribute these different orientations (45° vs 20°) to the growth methods and strain effects.^{27,28} Since the reported magnetic moments are not aligned along easy crystallographic axes, there appears to be a delicate balance that is sensitive to small changes in the environment.

Interestingly, the observed XMLD has the opposite sign than expected. It has been shown for $\alpha\text{-Fe}_2\text{O}_3$ that the peak B of the L_3 and L_2 edges is maximal when the E -vector is parallel to the magnetic axis ($E \parallel M$).¹⁶ The same is true for LaFeO_3 grown by MBE onto STO(001) mentioned above. This intensity behavior is in contrast to Fig. 1(b), where the spectra of a bright and dark domain are compared. We have shown that the dark domain is perpendicular to the E -vector, yet the B peak is maximal. This can also be seen in Fig. 4, where the intensity A/B is plotted.

Since the crystal field also can contribute to the linear dichroism, it is in principle possible that a quadrupole mo-

ment in the ground state, induced by a noncubic crystal field, gives rise to an additional, or even opposite, linear dichroism. Indeed, Haverkort *et al.*²⁹ showed, using multiplet calculations, that for NiO on Ag the linear dichroism of magnetic and crystal field origin have opposite signs. However, since our measured XMLD is strongly temperature dependent (see Fig. 2), it is dominated by the magnetic component. We confirmed this by multiplet calculations,²⁵ which showed that for a half-filled d shell with high spin, the small tetragonal distortion can be ignored, as it does not affect the magnetic ground state. Therefore it is sufficient for the calculation to use cubic symmetry for the crystal field, and indeed from here on we adopt the crystallographic coordinates of the STO(001) substrate to describe the AFM axis of the film.

The sign reversal between the XMLD in our study and those of Scholl *et al.*⁸ and Kuiper *et al.*¹⁶ must therefore have a different origin than a purely crystal field. Our multiplet calculations in the presence of a cubic crystal field revealed indeed a reversal of the XMLD [see Fig. 1(b)]. The dichroism depends on the magnetic orientation; it changes sign when the antiferromagnetic axis rotates from the $\langle 100 \rangle$ to either the $\langle 111 \rangle$ or the $\langle 110 \rangle$ directions, with the reversal occurring around 30° . The absolute sign can be retrieved from Ref. 25. The spectra for $\text{Fe } d^5$ in an octahedral field of $\Delta=2$ eV are very similar to those for the isoelectronic $\text{Mn } d^5$ in Fig. 1(e) of Ref. 25. It shows that for an alignment of the E -vector parallel to the magnetic orientation (in this case along the tetragonal axis, i.e., $E \parallel M \parallel [001]$) the peak B is lower than for $E \perp M$. This also remains true if M is at a moderate angle ($<30^\circ$) with one of the $\langle 100 \rangle$ axes. However, if the magnetization direction is near the $\langle 110 \rangle$ or $\langle 111 \rangle$ direction, then the situation is reversed, so that peak B is higher for $E \parallel M$. This is exactly the case for the studies of Scholl *et al.*⁸ and Kuiper *et al.*¹⁶ In the study of Scholl *et al.*, the magnetic axis is at 45° with respect to the $[001]$, while for our case it is 20° . In hematite ($\alpha\text{-Fe}_2\text{O}_3$) the spin axis is trigonal,¹⁶ i.e., along the $[111]$. A similar sign reversal between $[001]$ and $[111]$ for Fe metal was also reported by Kunešs and Oppeneer.¹⁹ However, their investigation was more restrictive since the magnetization was taken only along the crystallographic axes. Using multiplet calculations we verified the sign reversal for the magnetization and incident light in arbitrary directions.

In conclusion, we have shown that PEEM combined with the XMLD effect can be used to determine the orientation of individual antiferromagnetic domains. In LaFeO_3 thin films grown using PLD, four domain orientations were detected with a fourfold symmetry in the plane of the surface, each having their antiferromagnetic axis canted 20° out of the sample surface. This is in contrast to previous literature studies for LaFeO_3 grown with MBE, and we attribute this discrepancy to different strains in the films. Comparing our results with the literature, we observed that the XMLD can change its sign. We showed using multiplet calculations that this is due to the fact that the sign depends on the orientation of the magnetization with respect to the crystalline axes. We would like to emphasize here that the reversal of the XMLD sign has significant implications for the interpretation of XMLD spectra. It is therefore essential that either the relative

orientation of the AFM axis with respect to the crystalline axes is known or, as reported here, that a technique is employed that allows the determination of the XMLD sign. This information is particularly important for the analysis of the coupling between ferromagnetic and antiferromagnetic films in exchange bias systems.

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