Magnetic Anisotropy in Thin Layers of (Mn,Zn)Fe₂O₄ on SrTiO₃ (001)

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Herein, a ferrimagnetic manganese zinc ferrite (Mn₀.₅Zn₀.₅Fe₂O₄) film with a thickness of 200 nm is prepared without a buffer layer on strontium titanate (001) (SrTiO₃) using pulsed laser deposition. Its magnetic properties are investigated using superconducting quantum interference device (SQUID), X-ray absorption spectroscopy with subsequent X-ray magnetic circular dichroism (XMCD) and magneto-optic Kerr effect (MOKE). Hysteresis loops derived from SQUID exhibits bulk-like properties. This can further be confirmed by bulk-like XMCD spectra. In remanent magnetization, an in-plane magnetization with basically no out-of-plane component is found. The magnetic moments derived by the sum rule formalism from the XMCD data are in good agreement to the magnetization observed by SQUID and MOKE. XMCD as well as MOKE reveal an in-plane angular fourfold magnetic anisotropy with the easy direction along [110] for (Mn₀.₅Zn₀.₅)Fe₂O₄ on SrTiO₃. The element-specific magnetic moments from XMCD show a stronger contribution of Fe to the anisotropy than of Mn and distinct contributions of the orbital moments.

1. Introduction

(Mn,Zn)Fe₂O₄ (MZFO) ferrites are very important soft magnetic materials because of their remarkable magnetic, electrical, and optical properties. MZFO ferrites are well known for high initial magnetic permeability, saturation magnetization, electrical resistivity, and low power losses.

With the advent of nanotechnology, there is particular interest in nanostructured ferrites, where the finite size effect can be used to tailor structural, magnetic, and electrical properties of the ferrites. Compared with their bulk counterparts, nanoparticles, thin films, and nanocrystalline ceramics are often more favorable for practical applications due to their low eddy current and hysteresis losses, and single magnetic domain structure.

Recently, considerable research activities have been focused on studying nanocrystalline MZFO structures. The crystallite size and the nature of grain boundaries among crystallites are just two of many factors that affect the nature of the magnetic coupling in the nanoparticles and polycrystalline films.

From a more fundamental perspective, epitaxial ferrite films have served as a model system in which, for example, the effects of modified super-exchange interactions and cation redistribution have been observed.

Many groups have used a variety of thin-film growth techniques, including pulsed laser deposition (PLD), sputtering, and electron beam reactive evaporation to synthesize spinel ferrites. A detailed review about thin ferrite films was presented by Suzuki et al. in 2001.

For ferrite films grown on SrTiO₃, it has been claimed that good crystallinity along with good magnetic properties can only be achieved using buffer layers such as CoCr₂O₄, NiMn₂O₄, or MgAl₂O₄. The intention of these buffer layers is to prevent the diffusion of titanium into the layer and to accommodate the lattice mismatch between substrate and layer which can be up to 10%. For CoFe₂O₄ thin films, a strong correlation between Ti interdiffusion and the magnetic properties of the film was observed. Detailed studies about the growth with and without buffer layers were also related to the strain-induced magnetic switching of the
magnetic anisotropy.\textsuperscript{[19]} This led to a discussion that such ferrite films without buffer layers show magnetic properties, which makes them interesting candidates for various applications.\textsuperscript{[12–16,20–24]}

It is not surprising that structural disorder, ranging from cation disorder to grain boundaries, has a significant effect on the electronic and magnetic properties of ferrites. The mixed ferrite MZFO is between the antiferromagnetic ZnFe\textsubscript{2}O\textsubscript{4}, which exhibits no net magnetization in its ideal normal spinel structure, and the ferrimagnetic MnFe\textsubscript{2}O\textsubscript{4} with a very low coercive field.\textsuperscript{[2]} The properties of MZFO can effectively be tuned by adjusting the ratio of Zn and Mn cations in the unit cell. Therefore, this mixed ferrite is an ideal system for investigating the cation interaction in spinel ferrites and the influence of cation distribution on their magnetic properties.

Figure 1 shows the ideal cubic spinel structure with composition AB\textsubscript{2}O\textsubscript{4}, where A is a divalent ion (A\textsuperscript{2+}) and B a trivalent ion (B\textsuperscript{3+}), respectively. The oxygen atoms make up an fcc lattice, where in case of normal spinel structure one-eighth of the octahedral (O\textsubscript{h}) sites are occupied by A\textsuperscript{2+} ions and half of the octahedral (O\textsubscript{h}) sites by B\textsuperscript{3+} ions. The cation distribution in general can be described as (A\textsuperscript{2+}\textsuperscript{x} B\textsuperscript{3+}\textsuperscript{1−x})\textsubscript{1/2} A\textsuperscript{2+}\textsubscript{1/2} O\textsubscript{4}, where the brackets ( ) and [ ] denote tetrahedral and octahedral sites, respectively. The inversion parameter x is between 0 (normal spinel) and 1 (inverse spinel). The exchange interaction between ions on tetrahedral and octahedral sites is negative and stronger in comparison with the exchange interaction between atoms occupying same sites. Therefore, the spin alignment of atoms is opposite between T\textsubscript{d} and O\textsubscript{h} sites.

Investigations regarding both the ion distribution and magnetic properties of ferrites with a composition of Mn\textsubscript{1−x}Zn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} have been published already, where among others X-ray magnetic circular dichroism (XMCD) has been applied to get information about the magnetic anisotropy of the sample. X-ray absorption measurements in combination with X-ray magnetic dichroism allow the discussion of magnetic properties on a microscopic, atomic level. Therefore, we have applied sum rules to get both the spin and orbital magnetic moments of Fe and Mn ions.\textsuperscript{[35,36]}

2. XMCD Data Analysis by Sum Rules

The XMCD sum rules have been introduced by Thole et al.\textsuperscript{[17]} and Carra et al.\textsuperscript{[38]} For the L\textsubscript{2,3}-edge spectra of transition metals, the XMCD difference intensity is directly proportional to the atomic magnetic moment of the excited atom or ion. The orbital and spin sum rules link the averaged dichroism intensities with ground-state expectation values of orbital (⟨L\textsubscript{z}⟩) and spin moment (⟨S\textsubscript{z}⟩) according to

\[
⟨L\textsubscript{z}⟩ = \frac{4}{3} n_\text{h} \frac{\Delta A_{L\textsubscript{z}} + \Delta A_{S\textsubscript{z}}}{A_{L\textsubscript{z}} + A_{S\textsubscript{z}}} 
\]

and

\[
⟨S\textsubscript{z}⟩ = n_\text{h} \frac{\Delta A_{L\textsubscript{z}} - 2 \Delta A_{S\textsubscript{z}}}{A_{L\textsubscript{z}} + A_{S\textsubscript{z}}} 
\]

with \( ⟨S\textsubscript{z}⟩ = ⟨S\textsubscript{z}⟩ + \frac{2}{3} ⟨T\textsubscript{z}⟩ \). \( n_\text{h} \) is the number of d core holes. The operator T represents the intra-atomic magnetic dipole operator. The quantities A and ΔA stand for \( A = \int dE \frac{\mu^+}{E} (E) + \mu^- (E) \) and \( ΔA = \int dE \left[ \frac{\mu^+}{E} (E) - \frac{\mu^-}{E} (E) \right] \), respectively. Indices mark the respective edges (L\textsubscript{z} and L\textsubscript{z}). The magnetic moments follow in the usual way.

There are several complications to get atomic orbital (m\textsubscript{o}) and spin (m\textsubscript{s}) magnetic moments applying XMCD sum rules. Obtaining the spin moment requires the separate integration over each of the spin-orbit split core levels. However, the 2p–3d Coulomb interaction can lead to mixing of the j = 3/2 and j = 1/2 manifolds, so that an accurate separation is difficult. For the current analysis, however, no strong influence is anticipated. A further complication is the contribution from the magnetic dipole term (T) to the spin sum rule, which is neglected here. Finally, the number of d-holes \( n_\text{h} \) has to be known. Background and edge-step subtraction requires a data evaluation with high accuracy. For the light 3d TM elements, an error of 5–20\% is discussed for the spin moments.\textsuperscript{[39,40]}
3. Results and Discussion

3.1. Structure

In our previous study,

we have presented a detailed analysis of the structure and cation distribution of the 200 nm MZFO film on SrTiO$_3$ (001) (STO). The structure has been characterized with state-of-the-art methods such as X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), atomic force microscopy (AFM), and X-ray diffraction (XRD).

Here, we present a short summary about the main points. XPS yielded a stoichiometry of Mn$_{0.41}$Zn$_{0.53}$Fe$_{1.5}$O$_4$ (using oxygen for normalization). Within the uncertainties of the method, this agrees well with the targeted stoichiometry. However, both oxygen and/or cation vacancies are possible. The LEED diffraction pattern of the MZFO layer exhibits a weak fourfold symmetry and indicates epitaxial growth with a (001) surface orientation.

From XRD, we get the epitaxial in-plane relation [001]$_{[\text{Mn, Zn}]_2\text{Fe}_2\text{O}_4}$$/[001]_{\text{SrTiO}_3}$. By optimizing the growth conditions, epitaxial growth, very good crystallinity and the intended composition could be obtained without a buffer layer contrary to previous claims.

In addition, we have shown how X-ray absorption spectroscopy (XAS) and XMCD measurements may be used to answer detailed structural questions. Therefore, spectra were calculated for ions with different valencies occupying Td and/or Oh sites using the computer code CTM4XAS. The spectra were weighted and compared with the experimental one. This method allows direct conclusions regarding the cation distribution in the sample.

The focus of our previous study was the interpretation of XAS and XMCD of the Fe $L_{1,2}$ edges, where we got an excellent agreement between experimental and theoretical data. The prepared layer could be described by a configuration with about 75% Fe$^{3+}$ in Oh, 18% Fe$^{3+}$ in Td, and a small amount (about 7%) of Fe$^{2+}$ ions on octahedral site (approximated quite generously in the previous study by 10% Fe$^{2+}$ in Oh and 90% Fe$^{3+}$ distributed among Oh and Td in a 3:1 ratio). Reifining the analysis for Mn now in addition, results in Mn$^{2+}$ occupying mainly Td sites but also with 20–40% of Mn$^{2+}$ on Oh sites.

3.2. Superconducting Quantum Interference Device

SQUID in-plane magnetization loops with the sample at 5 and 300 K are shown in Figure 2. The characteristic magnetic properties (coercive field [$H_c$], remanent magnetization [$M_r$], and saturation magnetization at 7 T [$M_s$]) are summarized in Table 1. For these measurements, the magnetic field was applied in-plane along the [100] direction (compare Figure 1). As pointed out later, this direction is a magnetically harder direction. Considering the uncertainties in the values for thickness and density of the layer, an error of at least 10% is introduced in the determination of the magnetic moments in units of $\mu_B$ per MZFO unit.

The coercive fields are 60 Oe at 5 K and 30 Oe at 300 K, typical values for the soft magnetic Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ for thin layers and bulk material. For example, Suzuki et al. obtained $H_c = 50$ Oe and Alaen et al. determined $H_c = 30$ Oe for MZFO films at room temperature.

After normalization of the measured mass magnetization to the amount of atoms in a MZFO unit (by taking the geometric size of the sample and the molar mass of MZFO into account), a remanent magnetization of 3.5 $\mu_B$ and a saturation magnetization of 5.8 $\mu_B$ per formula unit (f.u.) have been derived for 5 K. At room temperature, there is a decrease to 2.1 and 3.1 $\mu_B$ per f.u., respectively. For comparison with literature, the saturation magnetization in units of emu/cm$^3$ has been used: $\approx 140$ emu g$^{-1}$ (T = 5 K) and $\approx 72$ emu g$^{-1}$ (T = 300 K). Assuming a mass density of 5 g cm$^{-3}$, these values agree very well with published values of Suzuki et al. (350 emu cm$^{-3}$ at T = 300 K) and of Alaen et al. (700 emu cm$^{-3}$ at T = 10 K).

The deviation of the hysteresis loops in Figure 2 from a square shape may result from disordered regions. However, the loops correspond quite well to the loop from a thin layer of MZFO on a buffered substrate. Clearly, the same quality of structural order with respect to the magnetic properties has been achieved on an unbuffered substrate.

3.3. Magneto-Optical Kerr Effect

Angle-dependent MOKE measurements of the 200 nm thick Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ film have been performed. Complete in-plane hysteresis loops have been measured every 5° of azimuthal angle to study possible crystalline anisotropy effects. Therefore, the Kerr rotation of the sample has been measured in the range of the magnetic field between $-500$ and $+500$ Oe. After measuring the hysteresis loops with NanoMOKE, the coercive fields displayed a fourfold symmetry as shown in Figure 3. As the SrTiO$_3$ substrate has been aligned with its [100] orientation to 0°, the
easy axes of the MZFO film are found along the [110] direction of both STO and MZFO.

A similar symmetry is also found when analyzing the remanent magnetization. As their absolute values are difficult to obtain, normalization to the saturation magnetization in the respective angle needs to be performed. Even then the uncertainty level is higher as in the case of determination of the coercive field. Therefore, the data are not shown here. The general behavior could be explained by the Stoner–Wohlfarth model. What is measured in remanence and also reflected in the coercive field is the component of the magnetization along the measured azimuthal angle. If the initial magnetization is not along an easy axis, the magnetization will switch toward this axis once the external field is switched off. If the angle to the easy axis exceeds $45^\circ$, the magnetization will jump to the next easy direction. In addition to the easy axis being rotated to the [110] direction, additional but much smaller maxima in coercive field are observed along the [100] direction. They are not observed in the remanent magnetization values.

Reviewing the single hysteresis loops that are used to obtain the values of the coercive fields, one observes certain changes. As shown in Figure 4, the shape of the loops for the easy axis (panel a; at $45^\circ$) and close to the expected hard axis (panel b; at $5^\circ$; data for $0^\circ$ show a similar shape) changes. These shapes again reflect Stoner–Wohlfarth behavior. If external magnetic field and easy axis are parallel, a square-like hysteresis loop is expected, as the magnetization stays in the easy direction as long as the external field does not switch it over. If the angle between easy axis and external magnetic field increases, rotation of the magnetization toward the easy axis gradually sets in, rounding the hysteresis loop more and more. As in our case, a fourfold anisotropy is observed; the magnetization starts switching toward the next easy axis if the angle to the magnetization is above $45^\circ$. Even stronger changes can be observed for the loops measured at $15^\circ$ (panel c). In this particular angle, the magnetization reversal process seems to be different, signaling a second reversal process with partial out-of-plane magnetization signal, possibly resulting from a transverse magnetization component detected in longitudinal Kerr geometry. It has to be mentioned that no out-of-plane MOKE hysteresis loop could be obtained applying magnetic fields of up to 0.12 T, indicating a canted orientation of the magnetization during reversal.

Figure 3. Polar plot of the coercive field (red dots) along with a guide-to-the-eye fit (blue line) of the 200 nm MZFO film on STO(001) obtained by hysteresis loops measured with NanoMOKE.

Figure 4. In-plane MOKE hysteresis loops obtained at azimuthal angles of a) $45^\circ$, b) $5^\circ$, and c) $15^\circ$ relative to the [100] direction.
3.4. X-Ray Absorption Spectroscopy and X-Ray Magnetic Circular Dichroism

XAS and XMCD measurements of the Fe $L_{3,2}$ edge and Mn $L_{3,2}$ edge were considered to investigate the origin of the magnetization. In Figure 5a,b, the absorption spectra dependence on light polarization and the respective XMCD are shown for the in-plane geometry (easy axis—azimuthal angle 45°) for both the Mn and Fe $L_{3,2}$ edges.

In our previous study, we have shown first for the same data set that XAS and XMCD spectra also provide information about the cation distribution in our sample.\[34\]

The magnetic properties of the film are in the focus of this work. The measurement of the in-plane XMCD covered four azimuthal angles—nominally 0°, 15°, 30°, and 45°. The spectral shape of the XMCD dependent on the azimuthal angle is shown in Figure 5c for Fe and Mn. Small changes in the XMCD difference signals are observed. To derive quantitative magnetic information, the sum rules have been applied.

In Table 2, the calculated spin and orbital magnetic moments are summarized. For these calculations, the number of d-holes is a critical parameter with respect to the absolute values. In this work, a value of 4.31 was used. This resulted from the average of the values determined by Crocombette et al. for the various lattice sites of Fe in magnetite.\[45\] Considering the distribution of cations as proposed in ref.\[34\] (with 10% Fe$^{2+}$ in Oh sites and Fe$^{3+}$ distributed in a 3:1 ratio between Oh and Td sites), this value would change to ≈4.5. Thus, all magnetic moments would be larger by 4% which, however, is within the error bars of about 10–20%. For Mn, the number of d-holes was taken to be 5, as no other estimate was available. However, we expect some deviation, which adds moderately to the overall uncertainty.

First, it is clear that the magnetic moments of Mn and Fe are oriented antiparallel to each other, which was already clear from Figure 5. In addition, orbital moments reach relatively large values. Considering possible error bars ranging to 10–20% due to the shortcomings of the sum rules for nonmetallic materials, the uncertainty in the number of d-holes (which can only be estimated), and the strong dependence on data quality, a clear angle dependence of the magnetic moments is obvious. Using the nominal stoichiometry, total magnetic moments can be calculated for each angle. The total magnetic moments per MZFO unit scale between 1.6 and 2.5 $\mu_B$ are thus in the same range as the results from SQUID measurements (2.1 $\mu_B$, which have been obtained along a [100] direction corresponding to the 0° angle here). Assuming the fourfold symmetry already observed in MOKE, the four data points can be mirrored to obtain a full 360° picture again. Under this assumption, a very similar anisotropy as the one in MOKE can be seen in Figure 6.

In Figure 6, polar plots of the calculated magnetic moments are shown after application of the symmetry operation obtained by MOKE for a) Mn, b) Fe, and c) the total moments. It appears that there is a bigger anisotropic effect for iron compared with the manganese. In addition, within the borders of the validity of the sum rules, the orbital moments show a stronger variation with angle, however, on a smaller absolute level. This is particularly true for the increased moments at 45° with regard to the easy axis (here, e.g., 0°). Also increased coercive field values have been obtained at these angles in the MOKE data. Although the anisotropy observed in both MOKE and XMCD could in general be related to a higher-order magneto-crystalline order, a clear explanation is still missing.
Measurements have also been performed in out-of-plane geometry (magnetization and light incidence perpendicular to the surface). The sample exhibited only a very small XMCD signal that was mainly limited to the $L_3$ edge. With regard to XMCD difference values, they are less than 10% of those for in-plane measurements and, therefore, no sum rule analysis was applied. The sign of the XMCD possibly suggests a parallel alignment of Fe and Mn moments. Nevertheless, compared with the in-plane geometry, the out-of-plane magnetization is very small.

### 4. Conclusion

Using SQUID, MOKE, and XMCD, it has been possible to examine the magnetic structure of the 200 nm thick Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ layer in great detail. Out-of-plane as well as in-plane measurements at different azimuthal angles revealed the structure of the magnetic anisotropy. Both, SQUID and MOKE, provided hysteresis loops. As these methods are integral methods, no element-specific information could be obtained there. Therefore, XMCD measurements have been used to get information about the element-specific origin of the anisotropy.

The magnetic moments of the layer could be calculated using SQUID data for one in-plane orientation (45$^\circ$ away from the easy axes) and exhibited values comparable with those of bulk and film Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ [12,20,33,42,43]. The resulting remanent in-plane magnetization at room temperature had a value of 2.1 $\mu_B$. This value could also be confirmed using the sum rule analysis in XMCD within the uncertainty.

In general, the loops obtained in SQUID and MOKE measurements have the same shape. Nevertheless, there are some in-plane azimuthal angles where the shape of the hysteresis loop changed in MOKE. This change arose from some cross-talk of out-of-plane components in the measurement process during the magnetization reversal. Other than that cross-talk in out-of-plane direction within this reversal process, only a very small out-of-plane magnetization could be measured using XMCD. In MOKE, no out-of-plane hysteresis loop could be obtained.

Using the in-plane azimuthal rotation in the MOKE experiment made it possible to get information about the magnetic anisotropy of the layer, which was found to be fourfold with the easy axes along the [110] directions. At the angle of the expected hard axes, a particular increase in the coercive field could be observed in MOKE. A slight increase is also found in the XMCD data. Interestingly, this increased magnetization seems to result mainly from orbital moments as derived from

| Angle | Element | $m_s$ [$\mu_B$] | $m_o$ [$\mu_B$] | $m_{tot}$ [$\mu_B$] | $M_{MZOFO}$ [$\mu_B$] |
|-------|---------|----------------|----------------|--------------------|----------------------|
| 0$^\circ$ | Mn | 1.17 | 0.07 | 1.24 | -1.62 |
|       | Fe | -0.73 | -0.39 | -1.12 | |
| 15$^\circ$ | Mn | 1.38 | 0.27 | 1.65 | -1.48 |
|       | Fe | -0.91 | -0.24 | -1.15 | |
| 30$^\circ$ | Mn | 1.19 | 0.51 | 1.70 | -1.73 |
|       | Fe | -1.01 | -0.28 | -1.29 | |
| 45$^\circ$ | Mn | 1.37 | 0.37 | 1.74 | -2.55 |
|       | Fe | -1.06 | -0.65 | -1.71 | |

Figure 6. Polar plot of magnetic moments derived from sum rule analysis of XMCD data measured in remanence for a) Mn, b) Fe, and c) MZFO. In the latter, red points mark the four measured angles and black points result from symmetry operation.
XMCD sum rule analysis. To date, no final answer can be given for that unexpected behavior. It is proposed that interface or surface effects could be the origin.

As a result of these comparisons, it can be stated that the three methods are mostly in good agreement with each other. The prepared MZFO layer exhibited general magnetic properties that are comparable to previously published results. However, in the current investigation, no buffer layer is used. Nevertheless, magnetic moments resulting from different techniques reach bulk values. It is clear that the shape anisotropy prefers the in-plane magnetization over the out-of-plane direction. Interestingly, for the in-plane magnetization, a clear fourfold azimuthal anisotropy has been obtained. This is in agreement with the overall cubic structure of both STO substrate and MZFO layer. The orientation of the easy magnetization axis along the [110] direction might have been obtained. This is in agreement with the overall cubic structure of both STO substrate and MZFO layer. The orientation of the easy magnetization axis along the [110] direction might correspond to the expected orientation of the respective orbitals. This is emphasized by the strong azimuthal variation of the orbital moments as compared with the spin moments.

In the next step, a detailed magnetic anisotropy could be utilized to study the electromagnetic interaction using ferroelectric BaTiO$_3$ as substrate. Changes in the ferroelectric polarization state could change the size and/or shape of the azimuthal magnetic anisotropy.

5. Experimental Section

A 200 nm thick film of the nominal composition Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ was prepared on a SrTiO$_3$ (001) substrate (SurfaceNet GmbH) using PLD. The MZFO target was prepared by pressing and sintering of a defined mixture of Fe$_2$O$_3$, MnO, and ZnO powders (purity better than 99.9%). A Kr excimer laser ($\lambda = 248$ nm) was used, supplying pulses of 600 mJ with a pulse frequency of 30 Hz. During deposition, the crystal was heated to 1000 K in a $6 \times 10^{-4}$ mbar O$_2$ atmosphere.

The resulting layer was characterized in situ LEED and XPS as well as AFM and XRD. The results have been published previously[14] and are summarized in Section 3.

The magnetic properties of the film were investigated by SQUID, MOKE, and XMCD. Although in SQUID investigations only in-plane magnetic properties were probed, MOKE and XMCD were performed both in in-plane and out-of-plane geometry.

SQUID magnetization loops were recorded at 5 and 300 K to probe the temperature dependence. A Quantum Design MPMS-7 magnetometer was used that can apply magnetic fields ($H$) ranging from +7 to 7 T.

X-ray absorption spectra with circularly polarized synchrotron radiation for XMCD were recorded at the beamline U65/2-PC1 at BESSY II. The polarization direction of light was changed from left to right circular polarized while keeping the magnetization constant. Measurements were done at 30° grazing incidence with a degree of circular polarization of 95%. Spectra were recorded for a set of azimuthal angles ($\phi = 0^\circ$, $15^\circ$, $30^\circ$, and $45^\circ$) with respect to the crystallographic orientation by rotating the sample. Magnetization was performed in this particular azimuthal orientation applying five pulses of a 50 mT field. XAS spectra were recorded in remanent magnetization.

MOKE was used to probe the symmetry of magnetization in more detail through a complete azimuthal rotation of 360° in steps of 5°. Magnetic hysteresis loops were measured with a Durham Magneto Optics NanoMOKE3 at the MPI Stuttgart at each azimuthal angle. Data were taken at a fixed position. All measurements were performed using a class 3R red solid-state laser diode with a wavelength of 660 nm, linearly p-polarized. To reduce noise, multiple averages of the hysteresis loops were taken at room temperature in a maximal range of the magnetic field ($\mu_0H$) from $-0.12$ to $0.12$ T.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

magnetic anisotropy, magneto-optical Kerr effect, manganese zinc ferrite, sum rules, superconducting quantum interference device, thin films, X-ray magnetic circular dichroism

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