Cation- and lattice-site-selective magnetic depth profiles of ultrathin Fe$_3$O$_4$(001) films

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A detailed understanding of ultrathin film surface properties is crucial for the proper interpretation of spectroscopic, catalytic, and spin-transport data. We present x-ray magnetic circular dichroism (XMCD) and x-ray resonant magnetic reflectivity (XRMR) measurements on ultrathin Fe$_3$O$_4$ films to obtain magnetic depth profiles for the three resonant energies corresponding to the different cation species Fe$_{3\text{oct}}^{2+}$, Fe$_{3\text{tet}}^{3+}$, and Fe$_{3\text{oct}}^{3+}$ located on octahedral and tetrahedral sites of the inverse spinel structure of Fe$_3$O$_4$. By analyzing the XMCD spectrum of Fe$_3$O$_4$ using multiplet calculations, the resonance energy of each cation species can be isolated. Performing XRMR on these three resonant energies yields magnetic depth profiles that each correspond to one specific cation species. The depth profiles of both kinds of Fe$^{3+}$ cations reveal a $(3.9 \pm 1.0)$-Å-thick surface layer of enhanced magnetization, which is likely due to an excess of these ions at the expense of the Fe$^{2+}$ species in the surface region. The magnetically enhanced Fe$^{3+}_{\text{oct}}$ layer is additionally shifted about $2.9 \pm 0.4$ Å farther from the surface than the Fe$^{3+}_{\text{tet}}$ layer.

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I. INTRODUCTION

Magnetite, Fe$_3$O$_4$, is one of the most frequently investigated transition-metal oxides, since it is a key material in spintronics, spin caloritronics, and material chemistry. Fe$_3$O$_4$ thin films were considered highly suitable for spintronics, spin caloritronics, and material chemistry, since it is a key material in spintronics and spin caloritronics. However, the promise was never quite met, to their predicted half-metallic behavior with 100% spin polarization. Magnetite requires caution, because the bulk material is semiconducting ZnO(0001), lattice-site-selective depth profiles for the three cation species Fe$^{3+}$ and Fe$^{3+}$ located on octahedral and tetrahedral sites of the inverse spinel structure of Fe$_3$O$_4$. By analyzing the XMCD spectrum of Fe$_3$O$_4$ using multiplet calculations, the resonance energy of each cation species can be isolated. Performing XRMR on these three resonant energies yields magnetic depth profiles that each correspond to one specific cation species. The depth profiles of both kinds of Fe$^{3+}$ cations reveal a $(3.9 \pm 1.0)$-Å-thick surface layer of enhanced magnetization, which is likely due to an excess of these ions at the expense of the Fe$^{2+}$ species in the surface region. The magnetically enhanced Fe$^{3+}_{\text{oct}}$ layer is additionally shifted about $2.9 \pm 0.4$ Å farther from the surface than the Fe$^{3+}_{\text{tet}}$ layer.

In particular, drawing conclusions about the cation distribution of magnetite requires caution, because the bulk material of the inverse spinel Fe$_3$O$_4$ should contain divalent Fe$^{2+}$, as well as trivalent ions in both octahedral and tetrahedral coordination, Fe$^{3+}_{\text{oct}}$ and Fe$^{3+}_{\text{tet}}$. In contrast, the DFT+$U$ calculations of the SCV structure predict the first four atomic layers to only contain Fe$^{3+}$ ions and to have a formal stoichiometry of Fe$_{11}$O$_{16}$, in agreement with earlier reports on an excess of Fe$^{3+}$ at the (001) surface. But while the SCV model has been very successful in explaining low-energy electron diffraction (LEED) and adsorption data, a spatial depth resolution has yet to be achieved. It also remains unclear what happens to the Fe$_3$O$_4$(001) surface when it is exposed to air and loses the characteristic for the SCV structure. In this Rapid Communication, we report an investigation of the magnetic surface properties of ultrathin Fe$_3$O$_4$(001) films, in contrast to the bulk, by recording magneto-optical depth profiles of the three cation species in Fe$_3$O$_4$. The $L_z$ x-ray magnetic circular dichroism (XMCD) spectrum of...
magnetite exhibits three extrema at energies characteristic for the Fe$_{\text{oct}}^{3+}$, Fe$_{\text{tet}}^{3+}$, and Fe$_{\text{oct}}^{2+}$ cations. We employ XRMR at those characteristic energies to determine the magneto-optical depth profiles of ultrathin Fe$_3$O$_4$/MgO(001) films for each individual cation species. We find an $\approx 3.9$ Å layer of enhanced magneto-optical absorption at the surface at the resonant energies of both Fe$^{3+}$ species but not for Fe$^{2+}$, suggesting an Fe$^{3+}$-rich surface.

II. EXPERIMENTAL AND THEORETICAL DETAILS

We prepared a 25-nm Fe$_3$O$_4$ film on MgO(001) in a multichamber ultrahigh-vacuum system using reactive molecular beam epitaxy (RMBE). Iron was deposited in an oxygen atmosphere of $5 \times 10^{-6}$ mbar onto MgO(001) at 250 °C. Its chemical composition and ($\sqrt{2} \times \sqrt{2}$)R45° superstructure was confirmed by in situ XPS and LEED, respectively. For details on the deposition and characterization methods, please see Refs. [17,18]. Additionally, two other films of 13 and 50 nm Fe$_3$O$_4$ were deposited on MgO(001). The complementary results obtained from these films are presented in the Supplemental Material [19] (Sec. A).

For the XAS and XMCD study, the sample was transferred from our laboratory under ambient conditions to the Superconducting Vector Magnet Endstation at beamline 4.0.2 of the Advanced Light Source (ALS). It was measured at room temperature in a magnetic field of 4 T along the x-ray beam. The incidence angle of the x-rays was 30° from the [100] direction of Fe$_3$O$_4$, and the degree of circular polarization was 90%. The XAS and XMCD spectra were measured across the Fe $L_{2,3}$ absorption edges (690–750 eV). All XAS spectra were measured in the TEY mode, which has a probing depth in magnetite of about 3 nm [20].

The XAS and XMCD data were analyzed by applying the sum rules [21–23] and charge-transfer multiplet calculations using the Thole code [24] with the assistance of CTM4XAS [25,26]. For the sum rules, we took into account a correction factor of 1.142 derived by Teramura et al. for Fe$^{2+}$ [23] and assumed $14_{\text{holes}}^{\text{Fe}^{2+}}$. For the multiplet calculations, we assumed the three-cation model, using crystal field and charge-transfer parameters as described in Ref. [17]. The parameters and more details regarding the multiplet calculations can also be found in the Supplemental Material [19] (Sec. B, including Refs. [27,28]).

The sample was transferred to BESSY II under ambient conditions and x-ray reflectivity (XRR) and XRMR were performed in the XUV diffractometer at beamline UE46_PGM-1 [29]. It was placed between two permanent magnets in a magnetic field of 200 mT longitudinal in regard to the x-ray beam, at room temperature. The x-rays had a degree of circular polarization of 90%. First, we characterized the structural properties (thickness $d$, roughness $\sigma$) by XRR at off-resonant energies (680 eV, 1000 eV). Second, XAS and XMCD were measured in order to select suitable energies for XRMR. Finally, $\theta$=2θ scans in the range 2θ = 0°–140° at resonant energies $E_i$ with extrema in the XMCD signal [maximum at 708.4 eV, minimum at 709.5 eV, maximum at 710.2 eV, cf. Fig. 1(b)] were performed with both right and left circularly polarized x-rays, to obtain the averaged resonant “nondichroic” XRR curve, $I(z) = (I_{\text{right}} + I_{\text{left}})/2$, and the XRMR asymmetry ratios

$$\Delta I = \frac{I_{\text{right}} - I_{\text{left}}}{I_{\text{right}} + I_{\text{left}}}. \quad (1)$$

These curves were then fitted with the Zak matrix formalism using the software REMAGX to determine the depth profiles of the complex refractive index $n(z)$ [30]. Assuming an in-plane magnetization longitudinal to the x-ray beam, it can be written as

$$n(z) = 1 - \delta(z) + i\beta(z) \pm [\Delta \delta(z) - i\Delta \beta(z)]\cos(\theta), \quad (2)$$

with the magneto-optical absorption $\Delta \beta(z)$ and dispersion $\Delta \delta(z)$ along the film height $z$. The optical absorption $\beta$ is proportional to the XAS signal, while the magneto-optical absorption $\Delta \beta$ is proportional to the XMCD signal [30]. Thus, $\Delta \beta(z)$ is a measure of the magnetization along the film depth. $\delta(E)$ and $\beta(E)$, as well as $\Delta \delta(E)$ and $\Delta \beta(E)$, are coupled by the Kramers-Kronig relations, which for symmetric extrema dictate $\Delta \delta(E_0) = 0$ if $\Delta \beta(E)$ has a maximum at $E_0$ [31]. For this reason, we set $\Delta \delta(z) = 0$ for all models [32]. A detailed review of the XRMR method and the software is given in Ref. [30], and conclusive recipes for fitting XMCD data can be found in Refs. [33–35].

III. RESULTS

The model to fit the off-resonant XRR data consists of a Fe$_3$O$_4$ film of 25.2 ± 0.3 nm thickness and an interface roughness $\sigma_{\text{int}} = 3.5 ± 0.5$ Å and a surface roughness of $\sigma_{\text{surf}} = 3.3 ± 0.5$ Å. An optically thin surface layer of 12 Å had to be included, likely stemming from adatoms settling on the surface upon the exposure to air. However, this layer does
FIG. 2. XRMR data (open circles) and corresponding fits (solid lines) from the Fe₃O₄ film, recorded at the three resonant energies of the XMCD L₃ edge, using the modeled magneto-optical depth profiles of Fig. 3(a). Data were recorded with a magnetic field of 200 mT along the Fe₃O₄[001] direction at room temperature.

not contribute to the magnetic signal. The resulting density profile can be seen as a black line in Fig. 3(a). The XRR curves of the 25-nm sample can be found in the Supplemental Material [19] (Sec. C).

Figure 1 shows the XAS and XMCD spectra of the Fe₃O₄ film, recorded at ALS. Corresponding data measured at BESSY II, under the same conditions in which the XRMR was performed, can be found in the Supplemental Material [19] (Sec. B). The spin and orbital moments obtained from the sum rules are \( \mu_{\text{spin}} = 3.5 \pm 0.3 \mu_B/\text{f.u.} \) and \( \mu_{\text{orb}} = 0.09 \pm 0.02 \mu_B/\text{f.u.} \). Their sum is slightly reduced compared to the bulk value of magnetite of \( \mu = \mu_{\text{spin}} + \mu_{\text{orb}} = 4.07 \mu_B \) [36]. This behavior of magnetite films has been observed previously [17], and can be explained by a higher density of antiphase boundaries (APBs) for thin films due to the antiferromagnetic coupling across APBs reducing the average magnetic moment of the film [37–39]. Additionally, multiplet simulations are fitted to the XMCD data [cf. Fig. 1(b)]. By weighting the individual spectra with respect to the cation stoichiometry given in Fig. 1(c), the XAS and XMCD data can be described well by our model (cf. violet lines). Thus, the cation distribution on different sites almost follows the ideal stoichiometry of 1:1:1, with a slight excess of Fe³⁺.

One feature of this kind of modeling is the fact that each of the three extrema observed in the XMCD spectrum can mainly be attributed to one cation spectrum. Table I shows the contributions \( r_{\text{cation}}(E_i) \) of each cation spectrum at the resonant energies \( E_i \) in the XMCD spectrum, according to

\[
    r_{\text{cation}}(E_i) = \frac{I_{\text{cation}}(E_i)}{|I_{\text{Fe}^{Fe^{+}}(E_i)}| + |I_{\text{Fe}^{Fe^{3+}}(E_i)}| + |I_{\text{Fe}^{Fe^{3+}}(E_i)}|}, \tag{3}
\]

with \( I_{\text{cation}}(E_i) \) being the XMCD signal of the corresponding cation spectrum in Fig. 1(b) at energies \( E_i = 708.4, 709.5, 710.2 \) eV. While there still is a considerable mixing, at least 64% of each extremum can be attributed to its dominant cation.

Accordingly, the strategy to obtain cationic depth profiles is to pick the three corresponding XMCD resonant energies and perform XRMR measurements at these resonances. Figure 2 shows the asymmetry ratios \( \Delta I \) and their fits at the three XMCD resonant energies for the Fe₃O₄ film. The near-surface region of the magneto-optical depth profiles \( \Delta \beta(z) \) that generate the fits are shown in Fig. 3(a), together with the density depth profile obtained from off-resonant XRR (black line). The most striking feature is the behavior at the surface: at the Fe³⁺ resonance energy (708.4 eV, green), the magneto-optical depth profile in fact appears to just follow the density profile. However, at both the Fe²⁺ and the Fe⁵⁺ resonance energies, there are noticeable changes to the \( \Delta \beta \) depth profiles. In order to fit their asymmetry ratios, we must include a thin surface layer of enhanced magneto-optical absorption. The obvious choice of magneto-optical depth profiles which are simply homogeneous through the entire film did not provide satisfactory fits to the data. This necessity is discussed in more detail in the Supplemental Material [19] (Sec. C). The edge of the magneto-optical depth profile of the Fe²⁺ resonance

| Energy     | \( \text{Fe}^{\text{Fe}^{2+}} \) | \( \text{Fe}^{\text{Fe}^{3+}} \) | \( \text{Fe}^{\text{Fe}^{3+}} \) |
|------------|-----------------|-----------------|-----------------|
| 708.4 eV   | 73 ± 5%         | −8 ± 3%         | 19 ± 5%         |
| 709.5 eV   | 18 ± 3%         | −64 ± 3%        | 18 ± 3%         |
| 710.2 eV   | 4 ± 3%          | −16 ± 8%        | 80 ± 10%        |

FIG. 3. (a) Close-up of the surface magneto-optical depth profile of the Fe₃O₄ film, together with the optical density obtained from off-resonant XRR fits (black line). (b) (Fe oct-O-terminated) model of the magnetite unit cell, in scale with Fig. 3(a). Comparison with the model in (b) illustrates the sizes of the enhanced regions being roughly half a unit cell of magnetite (four cation layers).

TABLE I. Contributions of the three cation species to the extrema in the XMCD spectrum in Fig. 1(b), as obtained by the multiplet analysis using Eq. (3).
roughly matches the location of the magnetically enhanced Fe\textsuperscript{3+} layer. The thickness of the magnetically enhanced layer is about $d$\textsubscript{enh} = 3.5 Å for both Fe\textsuperscript{3+} species. This corresponds to slightly less than half a bulk unit cell of magnetite (a/2 = 4.2 Å), as illustrated by Fig. 3(b). Furthermore, the magnetically enhanced layers are not colocated at the same depth: the magnetically enhanced Fe\textsuperscript{3+} layer is shifted about $\Delta z$\textsubscript{enh} = 3.4 Å deeper into the film than the magnetically enhanced Fe\textsuperscript{3+}O\textsubscript{2-} layer. We performed the same experiment on two other samples of different thicknesses, 13 and 50 nm. The above results are robust among these three samples with some variation in the values for $d$\textsubscript{enh} and $\Delta z$\textsubscript{enh}. From this variation, we estimate $d$\textsubscript{enh} = 3.9 ± 1.0 Å and $\Delta z$\textsubscript{enh} = 2.9 ± 0.4 Å. More details on the results of the two other samples can be found in the Supplemental Material [19] (Sec. A).

IV. DISCUSSION

The magneto-optical depth profiles are not identical with the depth distribution of the cations: As quantified in Table I, the signal on each resonance is a mixture of contributions from all three cations. For the magneto-optical depth profile at 710.2 eV approximately 80% of the signal originates from the Fe\textsuperscript{3+}O\textsubscript{2-} and is therefore strongly dominated by this species. And since the position of the layer of enhanced magnetization at 709.5 eV does not match the position of the 710.2 eV layer, we can conclude it to be a distinct physical feature, stemming from the Fe\textsuperscript{3+} species.

There are two possible explanations for the enhanced magnetization layer: either the magnetic scattering factors of the Fe\textsuperscript{3+} cations at the surface are enhanced, or the surface stoichiometry is changed. However, an increase in the magnetic scattering factor large enough to explain the observation would require an increase of the magnetic moment of the surface Fe\textsuperscript{3+} cations at the surface are enhanced, or the surface stoichiometry is changed. However, an increase in the magnetic scattering factor large enough to explain the observation would require an increase of the magnetic moment of the individual cations, which in Fe\textsubscript{3}O\textsubscript{4} are already in the high-spin state with $5\mu_B$. This explanation is therefore implausible.

One ansatz is to take into account rearranged cation distributions due to the reconstructed Fe\textsubscript{3}O\textsubscript{4}(001) surface as proposed by the SCV model [13,14], although in our films no reconstruction is visible in LEED anymore when the XRMR measurements are performed. The SCV model predicts that, in order to achieve polarity compensation, the first unit cell contains only Fe\textsuperscript{3+} species, with the first Fe\textsubscript{3+} layer lying about 1 Å deeper than the Fe\textsubscript{3+}O\textsubscript{2-}. This model matches surprisingly well some aspects of our findings. The first Fe\textsubscript{oct}-O layer remains stoichiometric, but the Fe\textsubscript{oct}\textsuperscript{2+} changes valency to Fe\textsubscript{oct}\textsuperscript{3+} effectively doubling the Fe\textsubscript{oct}\textsuperscript{3+} density. In the second layer, an additional Fe\textsubscript{oct}\textsuperscript{3+} ion is added, increasing the Fe\textsubscript{oct}\textsuperscript{3+} density by 50%. However, we do not observe the depletion of Fe\textsubscript{oct}\textsuperscript{2+} cations in the first 8 Å and the enhancements of Fe\textsubscript{3+} and Fe\textsubscript{oct}\textsuperscript{3+} are less than expected from the SCV model. Also, the Fe\textsubscript{3+} cations still exist in the surface layer to some amount while the SCV model predicts their complete conversion to Fe\textsubscript{oct}\textsuperscript{3+}. This agreement is surprising because it is known that Fe\textsubscript{3}O\textsubscript{4} surfaces hydroxylate on ambient conditions and do not show the \((\sqrt{2} \times \sqrt{2})R45^\circ\) LEED pattern, but instead a \((1 \times 1)\) pattern [14]. This may be attributed to disorder at the surface with loss of long-range order while the local order of vacancies and interstitials is kept. Since our samples were exposed to air before the XRMR measurements, they are in this seemingly unreconstructed state, but the magneto-optical depth profiles are consistent with an intermediate stoichiometry between bulk termination and the SCV surface. Our results now suggest that even in that case, at least the Fe\textsuperscript{3+} enrichment of the surface remains intact. A more detailed comparison of the SCV model to our findings can be found in the Supplemental Material [19] (Sec. D).

An excess of Fe\textsuperscript{3+} cations on the surface can warp the interpretation of surface-sensitive techniques. Figure 4 shows multiplet simulations of the XMCD spectra collected in TEY mode for (a) a Fe\textsubscript{oct}-O-terminated Fe\textsubscript{3}O\textsubscript{4}(001) surface, (b) the surface found in this work, and (c) an ideal SCV surface. (d)-(f) Cation profiles for each model, with a simulated roughness of 2.5 Å. The dashed lines indicate the sensitivity of the TEY signal on the sample depth $d_{FeOz} = z$, which exponentially decays with the electron escape depth $\lambda_e = 30$ Å.

FIG. 4. Multiplet simulations of XMCD spectra collected in TEY mode for (a) a Fe\textsubscript{oct}-O-terminated Fe\textsubscript{3}O\textsubscript{4}(001) surface, (b) the surface found in this work, and (c) an ideal SCV surface. (d)-(f) Cation profiles for each model, with a simulated roughness of 2.5 Å. The dashed lines indicate the sensitivity of the TEY signal on the sample depth $d_{FeOz} = z$, which exponentially decays with the electron escape depth $\lambda_e = 30$ Å.
larization found in SR-XPS on Fe$_3$O$_4$(001) surfaces [9–11]. A comparison of Figs. 4(b) and 4(c) reveals that for samples exposed to air, this effect is weakened compared to what is expected for a pure SCV surface.

V. SUMMARY

In conclusion, we fabricated a Fe$_3$O$_4$/MgO(001) ultrathin film by RMBE. We recorded XAS/XMCD at ALS beamline 4.0.2 as well as XAS/XMCD and XRMR measurements at BESSY II beamline UE46_PGM-1, in order to obtain magneto-optical depth profiles. By fitting multiplet calculations to the XMCD data, we determine the cation contributions at the three resonant energies of the XMCD spectrum, and use XRMR at those energies in order to resolve the magneto-optical depth profiles of the three iron species in Fe$_3$O$_4$. We find that both Fe$^{3+}$ species show an enhanced signal in the near-surface region in an $\approx$(3.9 ± 1.0)-Å-thick layer, with the Fe$^{3+}$ layer located about 2.9 ± 0.4 Å underneath the Fe$^{3+}$ layer. We attribute this to the first unit cell from the surface containing an excess of Fe$^{3+}$ cations. This result needs to be considered in the interpretation of surface-sensitive spectroscopic techniques.

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