Structural and magnetic investigation of the interfaces of Fe$_3$O$_4$/MgO(001) with and without NiO interlayer

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We present an investigation on the structural and magnetic properties of the interfaces of Fe$_3$O$_4$/MgO(001) and Fe$_3$O$_4$/NiO/MgO(001) by extracting cation-selective magnetooptical depth profiles by means of x-ray magnetic reflectivity (XRMR) in combination with charge-transfer multiplet simulations of x-ray magnetic circular dichroism (XMCD) data. For Fe$_3$O$_4$/MgO(001), the magnetooptical depth profiles at the Fe$^{3+}_{\text{oct}}$ and the Fe$^{3+}_{\text{tet}}$ resonant energies follow exactly the structural profile, while the magnetooptical depth profile at the Fe$^{3+}_{\text{tet}}$ resonance is offset by 3.2 ± 1.3 Å from the interface, consistent with a B-site interface termination of Fe$_3$O$_4$ with fully intact magnetic order. In contrast, for Fe$_3$O$_4$/NiO(001), the magnetooptical depth profiles at the Fe$^{3+}_{\text{oct}}$ and the Ni$^{2+}$ resonances agree with the structural profile, but the interface positions of the magnetooptical depth profiles at the Fe$^{3+}_{\text{oct}}$ and the Fe$^{3+}_{\text{tet}}$ resonances are laterally shifted by 3.3 ± 1.4 Å and 2.7 ± 0.9 Å, respectively, not consistent with a magnetically ordered stoichiometric interface. This may be related to an intermixed (Ni,Fe)O layer at the interface. The magnetooptical depth profiles at the Ni L$_3$ edge reveal uncompensated magnetic moments throughout the NiO film.

INTRODUCTION

Magnetite (Fe$_3$O$_4$) is a half-metallic ferrimagnet in the inverse spinel structure. This structure consists of a cubic close-packed oxygen lattice whose interstitial sites are populated by three different iron species: 1/2 of the octahedral B-sites are occupied randomly by divalent Fe$^{2+}_{\text{oct}}$ and trivalent Fe$^{3+}_{\text{oct}}$ cations, and 1/8 of the tetrahedral A-sites are occupied by trivalent Fe$^{3+}_{\text{tet}}$ cations. The two octahedrally coordinated species Fe$^{2+}_{\text{oct}}$ and Fe$^{3+}_{\text{oct}}$ are ferromagnetically coupled by double exchange, while the Fe$^{3+}_{\text{oct}}$ and Fe$^{3+}_{\text{tet}}$ cations couple antiferromagnetically via superexchange. Therefore, the magnetic moments of the Fe$^{3+}$ cations compensate each other and the resulting macroscopic moment of Fe$_3$O$_4$ of 4.07 $\mu_\text{B}$/f.u. is determined by the magnetic moments of the Fe$^{3+}_{\text{oct}}$ cations [1].

Due to these magnetic properties, magnetite is a long-standing candidate to contribute to all-oxide thin-film spintronic devices, as a source for spin-polarized currents [2][7]. These kinds of devices utilize the fact that many metal oxides with varying electronic and magnetic properties grow in spinel or rock-salt structures, such as the conducting ferrimagnets Fe$_3$O$_4$ and γ-Fe$_2$O$_3$, the insulating ferrimagnets NiFe$_2$O$_4$ and CoFe$_2$O$_4$, the insulating antiferromagnets NiO, CoO and FeO, or the insulating diamagnets MgO and MgAl$_2$O$_4$, which all share a cubic close-packed oxygen lattice with very similar lattice constants [2]. This allows epitaxial growth of film stacks with a large variety of spin electronic functionality but with little strain and thus supposedly well-matching interfaces.

However, a drawback of this concept is that the structural similarity of these metal oxides also means that undesired modifications at their interfaces are difficult to detect, such as interdiffusion of Mg [8], Ni [9, 10] or Co [11] into Fe$_3$O$_4$ films, or the transformation of the different iron oxides into each other [12, 13]. All-oxide spintronic devices with Fe$_3$O$_4$ electrodes did indeed not prove to be very successful yet; their shortcomings were speculated to stem from magnetic dead layers at the substrate interface [14, 15] or other interface effects [7].

Of particular interest have been the interfaces between Fe$_3$O$_4$ films and the tunnel barrier material MgO [7, 13, 19], as well as the interface between Fe$_3$O$_4$ and antiferromagnetic films, e.g. NiO, exhibiting exchange bias [17, 20]. This effect can cause a shift of the coercive fields of the ferrimagnetic Fe$_3$O$_4$ film and be used to pin its magnetization state.

In this study, we investigate the structural and magnetic properties of the Fe$_3$O$_4$/NiO and Fe$_3$O$_4$/MgO interfaces. We grow Fe$_3$O$_4$ single layers and Fe$_3$O$_4$/NiO bilayers on MgO(001) by reactive molecular beam epitaxy (RMBE) and investigate the distribution and magnetic order of the three cations Fe$^{2+}_{\text{oct}}$, Fe$^{3+}_{\text{oct}}$ and Fe$^{3+}_{\text{tet}}$ of Fe$_3$O$_4$ and of the Ni$^{2+}$ cations of NiO by x-ray resonant magnetic reflectivity (XRMR) combined with charge-transfer multiplet analysis of x-ray magnetic circular dichroism (XMCD) spectra. We find that the magnetic structure of Fe$_3$O$_4$ on MgO is intact down to the interface, while on the Fe$_3$O$_4$/NiO interface the data indicates a disturbed magnetic order. XRMR data on the Ni L$_3$ edge indicate
uncompensated magnetic moments in the antiferromagnet NiO.

**EXPERIMENTAL DETAILS**

The deposition and characterization methods of the samples followed the ones presented in Refs. [10, 20]. We prepared Fe$_3$O$_4$/MgO(001) and Fe$_3$O$_4$/NiO/MgO(001) samples in a multichamber ultra-high-vacuum system with a base pressure of $p_0 < 1 \times 10^{-8}$ mbar. Before deposition, the MgO(001) substrates were annealed at 400°C in an oxygen atmosphere of $1 \times 10^{-4}$ mbar for 1 hour. Our films were grown by RMBE. For the NiO, we deposited nickel in an oxygen pressure of $1 \times 10^{-5}$ mbar, and for the Fe$_3$O$_4$, we deposited iron in an oxygen pressure of $5 \times 10^{-9}$ mbar. We limited the substrate temperature to 250°C in order to avoid interdiffusion of Mg into the films [8]. After growth, the electronic structure of the samples was characterized in situ by x-ray photoelectron spectroscopy (XPS) using a Phoibos HSA 150 hemispherical analyzer and an Al Kα anode, and their surface structure by low-energy electron diffraction (LEED). The Fe 2p XPS spectra show the Fe$^{2+}$ and the Fe$^{3+}$ features typical for Fe$_3$O$_4$, and the LEED patterns confirm the characteristic $(\sqrt{2} \times \sqrt{2})$R45° surface structure of Fe$_3$O$_4$ [21, 22] (both not shown here).

Fe$_3$O$_4$/MgO(001) and Fe$_3$O$_4$/NiO/MgO(001) samples were transported under ambient conditions to BESSY II for x-ray absorption spectroscopy (XAS), XMCD, x-ray reflectivity (XRR) and XRMR on the XUV diffractometer at beamline UE46.PGM-1 [23]. The samples were placed between two permanent magnets in a magnetic field of 200 mT at room temperature. The x-rays had a degree of 90% circular polarization.

All XAS and XMCD spectra were recorded in total electron yield (TEY) mode with an incident glancing angle of 30°. XRR and XRMR curves were obtained by $\theta$-2$\theta$ scans in the range $2\theta = 0° - 140°$ at selected resonant photon energies with both right and left circularly polarized x-rays. The structural properties of the samples (thickness $d$, roughness $\sigma$) obtained by XRR at an off-resonant energy (1000 eV, cf. Fig. 1) are summarized in Tab. 1.

In order to obtain magnetic information with higher depth sensitivity, we measured XAS and XMCD in total fluorescence yield mode (TFY) and reflection mode on a different Fe$_3$O$_4$/NiO/MgO sample at Diamond Light Source (DLS), on the RASOR diffractometer of beamline I10. The sample was placed in a similar magnet setup, again in a magnetic field of 200 mT and at room temperature. Here, the x-rays had a degree of circular polarization of 99%. The structural properties of this sample can be found in Tab. 1 too.

| $d_{Fe_3O_4}$ | $d_{NiO}$ | $d_{MgO}$ |
|---------------|-----------|-----------|
| 25.2 ± 0.3 nm | 9.3 ± 0.1 nm | 17.6 ± 0.1 nm |
| 27.3 ± 0.2 nm |

| $\sigma_{Fe_3O_4}$ | $\sigma_{NiO}$ | $\sigma_{MgO}$ |
|-------------------|----------------|----------------|
| 3.3 ± 0.5 Å       | 3.2 ± 0.5 Å    | 2.0 ± 0.6 Å    |
| 3.0 ± 0.2 Å       | 4.2 ± 0.8 Å    |
| 2.7 ± 0.5 Å       | 2.5 ± 0.3 Å    |

**TABLE I.** Film thicknesses $d$, and rms roughnesses $\sigma$, of the three investigated samples, obtained from off-resonant XRR measurements recorded at 1000 eV. Corresponding data and fits for the UE46.PGM-1 samples are shown in Fig. 1.

![Figure 1](image1.png)

**FIG. 1.** XRR measurements of the two samples recorded at the three resonant energies of the Fe L$_3$ XMCD spectrum of Fe$_3$O$_4$ (708.4 eV, 709.5 eV, 710.2 eV), the energy of the Ni L$_3$ maximum (853.6 eV) and at an off-resonant energy (1000 eV). 

**DATA ANALYSIS**

**XMCD**

To obtain cation- and lattice-site-selective magneto-optical depth profiles, first the XMCD spectra have to be analyzed. Figures 2(a) and (b) show exemplarily XAS and XMCD spectra, respectively, of the Fe L$_{2,3}$ edges of the Fe$_3$O$_4$/NiO/MgO sample. Charge-transfer multiplet calculations of the three Fe cations of Fe$_3$O$_4$ using the Thole code [24] with assistance of CTM4XAS [25, 26] provide the three individual XAS and XMCD spectra shown below the data. For these calculations, we used Ref. [20] as a starting point: we assumed the three-cation model with crystal field energies of $10D_{q,oct} = 1.0$ eV in octahedral and $10D_{q,tet} = -0.6$ eV in tetrahedral coordination. The splittings between the initial and final charge-transfer states were chosen as $\Delta_{init} = 6$ eV and $\Delta_{final} = 9$ eV, and for the exchange splitting, $g \cdot \mu_B = 12 \pm 1$ meV was used. The multiplet...
states resulting from these calculations were compared to the experimental data by assuming a Gaussian instrumental broadening of 0.25 eV and a Lorentzian lifetime broadening of 0.3 eV at \( L_3 \) and 0.6 eV at \( L_2 \). Adding the three individual cation spectra with a 1:1:1 ratio, as expected for \( \text{Fe}_3\text{O}_4 \), results in a total XAS and a total XMCD spectrum (orange lines in Figs. 2(a),(b), respectively), which fit both the XAS and the XMCD data well. The multiplet analysis reveals that at those energies for which the XMCD spectrum has its extrema (708.4 eV, 709.5 eV, 710.2 eV), most of the XMCD signal originates from one dominant cation species [27]. The individual contributions of each cation species to the XMCD spectrum at these three energies can be found in Tab. II. Therefore, XRMR measurements on those energies are mostly sensitive to one specific cation species. This allows to disentangle the contributions of the individual cations to the magnetooptical depth profiles.

Since the TEY mode has a probing depth of about 3 nm in \( \text{Fe}_3\text{O}_4 \) [28], the TEY signal from the buried NiO film was strongly attenuated at the Ni \( L_3 \) edge. For a clearer signal, we brought a 18 nm \( \text{Fe}_3\text{O}_4 / 27 \) nm NiO/MgO sample to beamline I10 of DLS, and measured XAS and XMCD in TFY mode at a fixed incident angle of 30° parallel to beamline I10 of DLS, and measured XAS and signal, we brought a 18 nm Fe was strongly attenuated at the Ni \( L_3 \) edge. Since the TEY mode has a probing depth of about 3 nm, \( \text{Fe}_3\text{O}_4 (a) \),,(b), respectively), which fit both the XAS and the XMCD data well.

The XRMR data were recorded by measuring XRR curves at resonant photon energies \( E_i \) with extrema in the XMCD signal (maximum at 708.4 eV, minimum at 709.5 eV, maximum at 710.2 eV, see Fig. 2(b)) with both left and right circularly polarized x-rays. Resonant ‘non-dichroic’ XRR curves were obtained by averaging the signals \( I \) from both helicities (\( \sigma = \text{right/left} \))

\[
I = (I_{\text{right}} + I_{\text{left}})/2
\]

and the XRMR asymmetry ratios by subtracting and normalizing them:

\[
\Delta I = \frac{I_{\text{right}} - I_{\text{left}}}{I_{\text{right}} + I_{\text{left}}}
\]

These curves were then fitted with the Zak matrix formalism using the software ReMagX [30] to determine the depth profiles of the complex refractive index \( n(z) \)

\[
n(z) = 1 - \delta(z) + i\beta(z)
\]

along the film height \( z \). The optical dispersion \( \delta \) and the optical absorption \( \beta \) can be split into non-magnetic components \( \delta_0, \beta_0 \) and magnetooptical components \( \Delta \delta, \Delta \beta \). In the case of an in-plane magnetic field longitudinal to the x-ray beam as applied here, they can be written as [30]

\[
\delta(z) = \delta_0(z) \mp \Delta \delta(z) \cdot \cos(\theta)
\]

\[
\beta(z) = \beta_0(z) \pm \Delta \beta(z) \cdot \cos(\theta)
\]

for which the magnetooptical contributions depend on the x-ray incidence glancing angle \( \theta \) and sign on the helicity of the x-rays. The optical absorption \( \beta_0 \) is proportional to the XAS signal, while the magnetooptical absorption \( \Delta \beta \) is proportional to the XMCD signal. Thus, \( \Delta \beta(z) \) is a measure of the magnetization along the film depth. A detailed review of the XRMR method and the software is given in Ref. [30], and a conclusive recipe for fitting XRMR data can be found in Refs. [31][32].

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**TABLE II.** Contributions of the three cation species to the extrema in the XMCD spectrum in Fig. 2(b) as obtained by the multiplet analysis.

| Energy (eV) | \( \text{Fe}^{2+}_{\text{oct}} \) | \( \text{Fe}^{3+}_{\text{oct}} \) | \( \text{Fe}^{3+}_{\text{tet}} \) |
|------------|-----------------|-----------------|-----------------|
| 708.4 eV   | 70 ± 5%         | -8 ± 3%         | 22 ± 5%         |
| 709.5 eV   | 19 ± 3%         | -63 ± 3%        | 18 ± 3%         |
| 710.2 eV   | 4 ± 2%          | -25 ± 8%        | 71 ± 10%        |

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RESULTS

Figure 3(a) shows the XAS spectra at the Ni L₃ edge of the 18 nm Fe₃O₄/27 nm NiO/MgO sample recorded with left and right circularly polarized x-rays in TFY mode, and Fig. 3(b) shows their difference. The XMCD signal is about 3% of the XAS maximum. In reflection, the reflected intensity ranges up to about 8% demonstrating a strong magnetooptical signal from NiO. This energy is observed at 709.5 eV, the magnetooptically induced change of the intensity (arb. units)

\[
\begin{align*}
\text{(a) XAS and (b) XMCD spectra in TFY mode at the Ni L₃ edge for a 18 nm Fe₃O₄/27 nm NiO/MgO sample.} \\
\text{(c) Energy scans of the reflected intensity for left and right circularly polarized x-rays.} \\
\text{(d) Difference of the curves in (c).} \\
The green circles indicate the energy at which the XRMR asymmetry ratios.
\end{align*}
\]

The data and fits of the resonant XRR measurements can be found in Fig. 4(b), alongside with the off-resonant XRR curves recorded with 1 keV photons. Figures 4(a) and (b) show the XRMR data for the Fe₃O₄/MgO and the Fe₃O₄/NiO/MgO samples at the three Fe L₃ resonant energies 708.4 eV, 709.5 eV and 710.2 eV, and the Ni L₃ resonant energy 853.6 eV, together with their respective fits, which describe the data very well. The fits in Fig. 4(b) were obtained from the magnetooptical depth profile models which are displayed in Fig. 5(a) for all four resonant energies of the Fe₃O₄/NiO/MgO sample. The grey line represents the optical absorption \(\beta_{\text{off-res}}\) obtained from the off-resonant XRR measurement, and it is interesting to note that it occurs on the Fe₃O₄/MgO(001) and the Fe₃O₄/NiO/MgO(001) samples. This is likely related to a modification of the cation stoichiometry at the Fe₃O₄(001) surface. This effect is discussed in detail in Ref. [27] for Fe₃O₄/MgO(001), and it is not the subject of the current study, which focuses on the Fe₃O₄/MgO and Fe₃O₄/NiO interfaces.

Therefore, Fig. 5(b) focuses upon the interface region of the magnetooptical depth profiles of the Fe₃O₄/MgO sample, according to the fits in Fig. 4(a). Both the interfaces of the magnetooptical depth profile at 708.4 eV (green) and of the one at 710.2 eV (blue) are colocated...
with the structural interface (grey line) at \( z = 0 \) Å. However, the interface of the magnetooptical depth profile at 709.5 eV (red) is shifted by a distance \( \Delta z_{709.5\,\text{eV}} = 3.2 \pm 1.3 \) Å away from the interface into the Fe\(_3\)O\(_4\) film.

The roughnesses of magnetooptical depth profiles at both Fe\(^{3+}\) resonances follow the structural depth profile. In contrast, the roughness of the magnetooptical depth profile recorded at the Fe\(^{2+}\)\(_{\text{oct}}\) energy, \( \sigma_{708.4\,\text{eV}} = 4.4 \pm 0.2 \) Å, is slightly larger than the structural roughness \( \sigma_{\text{substrate}} = 3.5 \pm 0.5 \) Å.

For the Fe\(_3\)O\(_4\)/NiO/MgO film, the results are slightly different. Figure 5(c) shows the Fe\(_3\)O\(_4\)/NiO interface region of the Fe\(_3\)O\(_4\)/NiO/MgO sample. The XRMR data at the Ni \( L_3 \) edge can be well fitted with a homogeneous magnetization profile throughout the NiO film. The interfaces of the magnetooptical depth profiles at the Ni \( L_3 \) edge and at the Fe\(^{2+}\)\(_{\text{oct}}\)-related resonance at 708.4 eV are collocated with the structural interface, indicating intact structural and magnetic order for both species. Notably, both their roughnesses are slightly higher, \( \sigma_{708.4\,\text{eV}} = 6.3 \pm 0.7 \) Å, \( \sigma_{708.4\,\text{eV}} = 5.0 \pm 0.7 \) Å, compared to the structural roughness \( \sigma_{\text{Fe}_3\text{O}_4/\text{NiO}} = 3.0 \pm 0.2 \) Å.

In contrast to the magnetooptical depth profile at 708.4 eV, which directly follows the structural profile, the profiles at 709.5 eV and 710.2 eV are rising with shifts of \( \Delta z_{709.5\,\text{eV}} = 2.6 \pm 0.9 \) Å and \( \Delta z_{710.2\,\text{eV}} = 3.3 \pm 1.4 \) Å, respectively, apart from the interface, pointing to a lack of magnetooptical absorption at resonant energies of both Fe\(^{3+}\)\(_{\text{oct}}\) and Fe\(^{3+}\)\(_{\text{tet}}\) at the interface.

**DISCUSSION**

For the Fe\(_3\)O\(_4\)/MgO sample, it is shown in Fig. 6(b) that the magnetooptical depth profile recorded at a photon energy of 709.5 eV is displaced from the interface
into the Fe₃O₄ film by a shift Δz_{709.5 eV}. From the quality of the fits, we can determine this shift to the range Δz_{709.5 eV} = 3.2 ± 1.3 Å. Since this resonance is governed by the tetrahedrally coordinated Fe ions, this result is consistent with a B-terminated interface having octahedrally coordinated Fe^{2+} and Fe^{3+} cations in the Fe₃O₄ interface layer. Figure 6(a) shows the ideal stacking order at a B-terminated Fe₃O₄/MgO(001) interface. The oxygen lattice of the substrate continues as the oxygen lattice of the film. In [001] direction, Fe₃O₄ can be described as a stack of subsequent B layers consisting of O^{2−} anions as well as Fe^{3+}_{oct} and Fe^{4+}_{oct} cations, and A layers containing Fe^{3+}_{tet} cations with a distance of 1.05 Å between them. The stacking of B- and A-layers is depicted as blue and red shaded areas, respectively, in Fig. 6(a) with the interface layer being a B layer (B-termination). Simulated cation depth profiles following this model are shown in Fig. 6(b). The atomically sharp distributions are smeared out using an interface roughness of σ = 3.5 Å corresponding to the experimentally determined roughness of the Fe₃O₄/MgO interface. The rising edge of the Fe^{3+}_{tet} depth profile is shifted by Δz_{tet} = 1.05 Å from the interfaces of the Fe^{3+}_{oct} and Fe^{4+}_{oct} profiles into the Fe₃O₄ film. Because of the overlap of the individual cation spectra (cf. Fig. 2(b)), the expected magnetooptical depth profiles at the different resonant energies do not follow this behavior exactly.

Taking into account the magnetooptical contributions

![Simulated magnetooptical depth profiles for three models of the Fe₃O₄/MgO interface](image)

**FIG. 7.** Simulated magnetooptical depth profiles for three models of the Fe₃O₄/MgO interface. (a),(d),(g) Illustrations of the stacking orders of Fe₃O₄/MgO interfaces (a) with a single non-magnetic Fe₁₋₄O interlayer, (d) with a single magnetic Fe₁₋₄O interlayer, (g) with an additional Fe^{3+}_{oct} cation in the interface layer, following the model of Chang et al. The atomically sharp distributions corresponding to the experimentally determined roughness of the Fe₃O₄/MgO interface. The rising edge of the magnetooptical profiles from the structural interface can be found in Tab. III.

| Δz_{708.4 eV} (Å) | Fe₃O₄/MgO | Fe₃O₄/NiO/MgO | B-term. Fe₁₋₄ (NM) | Fe₁₋₄ (FM) | Chang |
|-------------------|-----------|---------------|-------------------|------------|-------|
| 3.2 ± 1.3         | 0         | 2.6 ± 0.9     | 2.5               | 4.1        | 5.5   |
| 3 ± 1.4           | 0         | 3 ± 1.4       | 0.5               | 1.1        | -0.5  |

**TABLE III.** Distances of the rising edges of the magnetooptical profiles from the structural interface at the three resonant energies. Considered here are the results from the two investigated samples as well as the discussed interface models: the B-terminated model (cf. Fig. 6), the non-magnetic (NM) Fe₁₋₄ interface layer (cf. Figs. 6(a)-(c)), the ferromagnetic (FM) Fe₁₋₄ interface layer (cf. Figs. 6(d)-(f)) and the model proposed by Chang et al. (cf. Figs. 6(g)-(i)).
as derived from the multiplet calculations of each cation at each of the three energies, the expected magnetooptical depth profiles of a B-terminated Fe$_3$O$_4$/MgO(001) interface can be calculated. They are shown in Fig. 6(c). The expected shift of the magnetooptical depth profile at 709.5 eV is $\Delta \delta_{709.5\text{eV}} = 2.5$ Å, consistent with the experimental result of $\Delta \delta_{709.5\text{eV}} = 3.2 \pm 1.3$ Å. Therefore, the magnetooptical depth profiles indicate a B-terminated Fe$_3$O$_4$/MgO(001) interface with no interlayer, and evidently, also no magnetic dead layer.

In this scenario, the magnetic order of all three sublattices has bulk properties down to the interface. The simulations of the B-terminated interface also predict that the apparent roughness $\sigma_{708.4\text{eV}}$ of the magnetooptical depth profiles at 708.4 eV appears to be about 0.5 Å larger than the structural profile $\sigma_{\text{substrate}}$. This offers an explanation for the slight mismatch of these two roughnesses observed in the experiment. However, while the discrepancy between the model distance and the experimental distance is well within the error range, it is still substantial enough to make a discussion of alternative models worthwhile.

Both the Fe$_3$O$_4$/MgO and the Fe$_3$O$_4$/NiO interfaces have been studied by various methods. Spintronic devices require interfaces that are structurally, but especially also magnetically sharp. Therefore, focus has been laid on the possible presence of interlayers and intermixing at the interfaces. In the case of Fe$_3$O$_4$ directly grown on a substrate, the formation of FeO interlayers has been reported on both metal and oxide substrates 33–37, and particularly on MgO(001) for films deposited at room temperature 13. The possibility of a single atomic Fe$_{1-x}$O interlayer is discussed in the following. The corresponding magnetooptical depth profiles are calculated in Figs. 7(a)-(f) for two scenarios.

Therefore, the first reasonable scenario is that the Fe$_{1-x}$O interlayer forms a magnetic dead layer at the interface, presented in Figs. 7(a)-(c). Figure 7(a) shows an illustration of the stacking order, Fig. 7(b) the cation depth profiles simulated with a roughness of $\sigma = 3.5$ Å, and Fig. 7(c) the resulting magnetooptical depth profiles. Fe$_{1-x}$O is paramagnetic at room temperature. Due to the magnetically dead Fe$_{1-x}$O layer, the rising edges of the magnetooptical depth profiles at both 708.4 eV and 710.2 eV are shifted about 2 Å into the Fe$_3$O$_4$ film compared to the structural interface (cf. Tab. III), not consistent with the observed profiles in Fig. 6(b).

The second scenario assumes that the very thin FeO layer magnetically couples to Fe$_3$O$_4$ and the magnetic order of its Fe$_{2\text{oct}}^{3+}$ sublattice is extended into the FeO layer. The resulting magnetooptical depth profiles show non-monotonic behavior and differ even more from the observed ones (cf. Figs. 7(d)-(f) and Tab. III).

Our data therefore do not indicate any magnetically dead layers, which had been considered to be the cause of the magnetization reduction in Fe$_3$O$_4$ ultrathin films 14, 28, 34, 38, nor interlayers of ferromagnetic FeO. Since it has already been shown that the magnetooptical depth profiles can be explained without an interlayer, it is unlikely that a FeO interlayer of more than a single atomic layer is present.

Another interesting model, which was proposed by Chang et al. for the growth dynamics of Fe$_3$O$_4$ 34, shall also briefly be mentioned here. This model suggests the first interface B-layer to contain one additional Fe$_{2\text{oct}}^{3+}$ cation per unit formula [(Fe$_{2\text{oct}}^{3+}$)$_2$(Fe$_{2\text{oct}}^{3+}$)$_2$O$_3$] instead of (Fe$_{2\text{oct}}^{3+}$)$_2$(Fe$_{2\text{oct}}^{3+}$)$_2$O$_5$. An illustration can be seen in Fig. 7(g). Both the cation depth profiles and the simulated magnetooptical depth profiles resulting from this model, presented in Figs. 7(h),(i), hardly differ from the B-terminated interface shown in Figs. 6(b),(c). Although XRM would in principle be an ideal method to test this model, the lacking spatial resolution in our experiments can neither confirm nor reject a faint phenomenon like an additional Fe$_{2\text{oct}}^{3+}$ cation in the interface layer.

For the Fe$_3$O$_4$/NiO/MgO(001) sample, a noteworthy finding is the dichroic signal of the NiO film. Bulk NiO is an antiferromagnet at room temperature and should not show any circular dichroism. However, as demonstrated in Fig. 8 we clearly observe magnetooptical effects in both TFY mode and in reflection at the Ni $L_3$ edge. Interestingly, we can exclude the XMCD signal to stem from uncompensated surface spins, since the magnetooptical depth profiles clearly show a homogeneous magnetization of the entire film. Size-effects of the magnetic properties of NiO, including ferromagnetic behaviour at room temperature, have been frequently reported before, mostly for NiO nanoparticles 39, 40. For Fe$_3$O$_4$/NiO ultrathin films, a spin-flop coupling of NiO to the Fe$_3$O$_4$(001) interface has been reported 19. In that case, the antiferromagnetic order of NiO aligns perpendicular to the magnetization of Fe$_3$O$_4$, but with a small canting of the Ni$^{2+}$ moments, resulting in a magnetization component parallel to the ferrimagnet. This reaction of NiO to outer magnetic fields has also been confirmed by spin Hall magnetoresistance measurements 44, 45, and can explain the presence of the observed XMCD signal.

The interface of Fe$_3$O$_4$/NiO has mostly been discussed regarding the presence of a NiFe$_2$O$_4$ interlayer. In reports by Gatel et al. 18 and Pilard et al. 46, high-resolution transmission electron microscopy (HRTEM) images show generally sharp interfaces between the rock salt structure of NiO and the spinel structure of Fe$_3$O$_4$. However, this only partly solves the question, because the lack of chemical and magnetic contrast cannot exclude, for instance, the formation of a rock salt (Fe–Ni)O phase or a spinel NiFe$_2$O$_4$ phase. Gatel et al. addressed this issue by performing both HRTEM and electron energy loss spectroscopy (EELS) 18. For a NiO/Fe$_3$O$_4$/MgO(001) sample, for which the NiO film was deposited at a substrate temperature of 700°C, indeed an intermediate NiFe$_2$O$_4$
phase was observed. For a Fe$_3$O$_4$/NiO/MgO(001) stack, which had the Fe$_3$O$_4$ film deposited at 400°C, the interface appeared to be chemically sharp with at most minor interdiffusion [18]. The NiFe$_2$O$_4$ phase they observe in the NiO/Fe$_3$O$_4$/MgO(001) stack is likely caused by thermal interdiffusion due to the high deposition temperature [10].

A formation of a well-ordered NiFe$_2$O$_4$ interlayer does not match our observations. NiFe$_2$O$_4$ crystallizes in the same inverse spinel structure as Fe$_3$O$_4$, but with Ni$_{oct}^{2+}$ cations instead of Fe$_{oct}^{3+}$ sharing the B-sites with Fe$_{tet}^{3+}$. Analogous to Fe$_3$O$_4$, the magnetic moments of the Ni$_{oct}^{2+}$ and Fe$_{oct}^{3+}$ cations on the B-sites align antiferromagnetically to the magnetic moments of the Fe$_{tet}^{3+}$ cations on the A-sites. For the magnetooptical depth profiles, this would imply a decrease of Fe$_{oct}^{2+}$ cations close to the interface and thus of the magnetooptical absorption at 708.4 eV, while the magnetooptical absorption depth profiles for 709.5 eV and 710.2 eV should stay constant in a NiFe$_2$O$_4$ layer. Instead, we observe a reduction of the magnetooptical absorption at 709.5 eV and 710.2 eV as compared to the case of the Fe$_3$O$_4$/MgO interface. This behavior, together with the increased roughnesses of the magnetooptical depth profiles at the Fe$_{oct}^{2+}$ and the Ni$^{2+}$ energies, might indicate a slight interdiffusion of Fe$_{oct}^{2+}$ into the rock salt structure of NiO. However, this effect may not extend farther than a single atomic layer. Notably, the ferromagnetic coupling between the Fe$_{oct}^{2+}$ cations is retained down to the interface regardless of the intermixing.

**CONCLUSION**

We have prepared ultrathin Fe$_3$O$_4$/MgO(001) and Fe$_3$O$_4$/NiO/MgO(001) films by RMBE and performed XMCD and XMR measurements to extract magnetooptical depth profiles for the individual cation species Fe$_{oct}^{2+}$, Fe$_{tet}^{3+}$ and Fe$_{tet}^{3+}$ as well as for Ni$_{oct}^{2+}$. These magnetooptical depth profiles show that for Fe$_3$O$_4$/MgO(001), the magnetic order of all three cation species is stable for the entire film with no interlayer or magnetic dead layer at the interface. For Fe$_3$O$_4$/NiO films, we observe a magnetooptical absorption at the Ni L$_3$ edge in the NiO film corresponding to uncompensated magnetic moments throughout the entire NiO film. The magnetooptical profiles of the iron cations reveal an intact magnetic order for the Fe$_{oct}^{2+}$ cation species down to the interface, while the magnetooptical depth profiles at the Fe$_{tet}^{3+}$ and the Fe$_{tet}^{3+}$ resonances are shifted about 3 Å into the Fe$_3$O$_4$ film, possibly indicating a single intermixed layer containing both Fe$^{2+}$ and Ni$^{2+}$ cations.

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