From Fe$_3$O$_4$/NiO bilayers to NiFe$_2$O$_4$-like thin films through Ni interdiffusion


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From Fe₃O₄/NiO bilayers to NiFe₂O₄-like thin films through Ni interdiffusion

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Ferrites with (inverse) spinel structure display a large variety of electronic and magnetic properties making some of them interesting for potential applications in spintronics. We investigate the thermally induced interdiffusion of Ni²⁺ ions out of NiO into Fe₃O₄ ultrathin films resulting in off-stoichiometric nickel ferrite-like thin layers. We synthesized epitaxial Fe₃O₄/NiO bilayers on Nb-doped SrTiO₃(001) substrates by means of reactive molecular beam epitaxy. Subsequently, we performed an annealing cycle comprising three steps at temperatures of 400 °C, 600 °C, and 800 °C under an oxygen background atmosphere. We studied the changes of the chemical and electronic properties as result of each annealing step with help of hard x-ray photoelectron spectroscopy and found a rather homogenous distribution of Ni and Fe cations throughout the entire film after the overall annealing cycle. For one sample we observed a cationic distribution close to that of the spinel ferrite NiFe₂O₄. Further evidence comes from low energy electron diffraction patterns indicating a spinel type structure at the surface after annealing. Site and element specific hysteresis loops performed by x-ray magnetic circular dichroism uncovered the antiferromagnetic alignment between the octahedral coordinated Ni²⁺ and Fe³⁺ ions and the Fe³⁺ in tetrahedral coordination. We find a quite low coercive field of 0.02 T, indicating a rather low defect concentration within the thin ferrite films.

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I. INTRODUCTION

Iron oxides are of special interest due to a number of astonishing properties in dependence of the Fe valence state and the underlying crystallographic and electronic structure. Magnetite (Fe₃O₄) is among the most studied ferrites due to its ferrimagnetic ordered ground state with a saturation moment of 4.07 µB per formula unit and a high Curie temperature of 860 K for bulk material.¹,² This magnetic ground state is accompanied by half metallicity, i.e. only one spin orientation is present at the Fermi energy,³ making this material a potential candidate for future spintronic devices with 100% spin polarization.⁴,⁵ Magnetite crystallizes in the cubic inverse spinel structure (equal distribution of Fe³⁺ on A and B sites and Fe²⁺ exclusively on B sites) with lattice constant a = 0.8396 nm (space group Fd3m). The oxygen anions form an fcc anion sublattice.

Often, Fe₃O₄ thin films are grown on cubic MgO(001) substrates by various deposition techniques,⁶–¹¹ since the lattice mismatch between Fe₃O₄ and MgO(001) (a = 0.42117 nm) is only 0.3%, comparing the oxygen sublattices. A severe limit of epitaxial thin film growth on MgO substrates is Mg²⁺ segregation into the Fe₃O₄ film if the substrate temperature is above 250°C.¹² Mg rich interfaces¹³ and Mg interdiffusion have been studied in detail,¹⁴ having significant influence on interface roughness or anti phase boundaries. Thus, the underlying electronic and magnetic structure influences the properties of the magnetite thin film in question or the tunnel magnetoresistance in magnetic tunnel junctions with magnetite electrodes.¹⁵–¹⁸

Potential approach to minimize or suppress Mg segregation, besides rather low substrate temperatures during magnetite growth, is an additional buffer layer, e.g. metallic iron¹⁹ or NiO²⁰ between the Fe₃O₄ and the substrate. This approach is also of interest with respect to the possibility for building a full oxidic spin valve making use of the exchange bias between the ferrimagnetic magnetite and the antiferromagnetic nickel oxide.²⁰–²²

The usage of other substrates like SrTiO₃ could also prevent Mg interdiffusion. Despite the large lattice mismatch of -7.5% between the doubled SrTiO₃ bulk lattice constant (0.3905 nm) and magnetite it is possible to grow epitaxial Fe₃O₄ films on the SrTiO₃(001) surface.²³,²⁴ In particular, concerning coupled Fe₃O₄/NiO bilayers grown on SrTiO₃, so far only Pilard et al. have reported on the magnetic properties of the Fe₃O₄/NiO interface.²⁵ On the other hand, NiFe₂O₄ thin films are of huge interest nowadays, since they are magnetic insulators or semiconductors. Therefore, they can be used as spin filters²⁶ or for thermal induction of spin currents via the spin Seebeck effect.²⁷,²⁸ Furthermore, electrical charge transport and spin currents can be manipulated by the spin Hall magnetoresistance using NiFe₂O₄ thin films adjacent to nonmagnetic material.²⁹
Therefore, we study here the possibility to form nickel ferrite starting with a distinct Fe$_3$O$_4$/NiO bilayer grown on Nb-doped SrTiO$_3$(001). Knowledge about the modification of the underlying crystallographic, electronic and magnetic structure by Ni interdiffusion is indispensable for potential applications. We also want to investigate fundamental aspects especially of Ni$^{2+}$ diffusion from a NiO buffer layer into a Fe$_3$O$_4$ top layer as well as NiO surface segregation through the Fe$_3$O$_4$ film, since knowledge of diffusion processes in oxides appear to be still quite rudimentary for many systems.

We perform a systematic three step annealing cycle of Fe$_3$O$_4$/NiO bilayers after synthesis and simultaneously investigating surface crystallographic and ‘bulk’ electronic structure changes by means of low energy electron diffraction (LEED) and hard x-ray photoelectron spectroscopy (HAXPES). Furthermore, we carry out structural analysis before and after the overall annealing cycle employing x-ray reflectivity (XRR) and synchrotron radiation based x-ray diffraction (SR-XRD), as well as element and site specific x-ray magnetic circular dichroism (XMCD) after the overall annealing cycle to analyze the resulting magnetic properties in detail.

II. EXPERIMENTAL DETAILS

Two samples with Fe$_3$O$_4$/NiO ultra thin film bilayers on conductive 0.05 wt. % Nb-doped SrTiO$_3$(001) substrates have been prepared, using the technique of reactive molecular beam epitaxy (RMBE). The substrates have been supplied with a polished surface and were annealed once at 400 °C for one hour in an oxygen atmosphere of 1 $\times$ 10$^{-4}$ mbar prior to deposition. Afterwards the chemical cleanness and composition was proven by XPS, while the crystalinity of the surface was checked by LEED. Oxide films have been deposited by thermal evaporation from pure metal rods in low oxygen atmosphere. During film growth, the substrate was heated to 250 °C, 600 °C, 800 °C for 20 to 30 minutes in an oxygen atmosphere of 5 $\times$ 10$^{-6}$ mbar to avoid reduction or further oxidation of the sample. Prior to and after the annealing studies XRR measurements at 2.5 keV photon energy were performed to determine the film thickness. After each annealing step, the films were studied in-situ by soft x-ray photoemission and HAXPES to clarify the chemical composition in the surface near region and in the bulk region, respectively. In addition, LEED measurements were performed to check the crystallinity of the individual layers of the NiO/Fe$_3$O$_4$ bilayer.

For HAXPES an energy of $\hbar\nu = 5934$ eV was used, creating photoelectrons with high kinetic energy, which allows a higher probing depth compared to soft x-ray photoemission ($\hbar\nu = 1000$ eV).

The information depth, from which 95% of the photoelectrons originate, is defined as

$$ID(95) = -\lambda \cos \varphi \ln(1 - 95/100),$$

with the inelastic mean free path $\lambda$ and the off-normal emission angle $\varphi$. The maximum information depth for the Fe 2p core level for HAXPES and soft x-ray photoemission measurements is 22 nm and 2.5 nm, respectively, estimating $\lambda$ by the TPP-2M formula. As the beamline features a 2D photoelectron detector, which can be operated in an angular mode, photoelectron spectra at different emission angles were acquired, each with an acceptance angle of $\sim 7^\circ$.

Subsequently, structural analysis of the annealed films was performed using SR-XRD, while the resulting film thickness and layer structure of these films were determined by means of lab based XRR using Cu K$_\alpha$ radiation. SR-XRD experiments have been carried out ex-situ at PETRA III beamline P08 (DESY, Germany) using a photon energy of 15 keV. In both cases the measurements were performed in $\theta - 2\theta$ diffraction geometry. For the analysis of all XRR experiments an in-house developed fitting tool based on the Parratt algorithm and Nêvo-Croce roughness model was used. The SR-XRD measurements were analyzed by calculating the crystall truncation rod (CTR) intensity within the full kinematic diffraction theory to fit the experimental diffraction data.

XMCD spectroscopy was performed at the Fe L$_{2,3}$ and Ni L$_{2,3}$ edges with the samples at room temperature at beamline 6.3.1 of the Advanced Light Source, Lawrence Berkeley Laboratory. We have utilized total electron yield (TEY) as detection mode. The external magnetic field of 1.5 T has been aligned parallel to the x-ray beam and been switched for each energy. The angle between sample surface and x-ray beam has been chosen 30°. The resolving power of the beamline has been set to $E/\Delta E \sim 2000$, the degree of circular polarization has been about 55%. For the analysis of the Fe L$_{2,3}$ XMCD spectra, we have performed corresponding model calculations within the atomic multiplet and crystal field theory including charge transfer using the program CTM4XAS.
III. RESULTS

A. Surface characterization

In Figs. 1(a)-(c) the LEED pattern of the cleaned substrate and the as prepared NiO and Fe$_3$O$_4$ films are presented exemplarily for sample A. Figs. 1(d) and (e) show the LEED images recorded after the last annealing step of 800 °C for sample A and sample B, respectively.

After cleaning of the SrTiO$_3$ substrates the LEED pattern shows very sharp diffraction spots of a (1×1) surface with square structure and negligible background intensity (cf. Fig. 1(a)), indicating a clean (001) oriented surface with long range structural order. Additionally, XPS measurements show chemically clean substrates without carbon contamination (not shown here).

![LEED patterns for sample A](image)

**FIG. 1:** LEED patterns for sample A recorded directly after a) preparation of SrTiO$_3$ substrate, b) deposition of NiO, c) deposition of Fe$_3$O$_4$, d) the last annealing step of 800 °C. For comparison, (e) shows the LEED pattern for sample B after the final annealing step. Marked with red squares are the respective (1×1) surface unit cells in reciprocal space. The blue square indicates the ($\sqrt{2} \times \sqrt{2}$)R45° superstructure typical for magnetite.

The LEED image recorded directly after RMBE of NiO also exhibits a quadratic (1×1) structure (cf. Fig. 1(b)) as expected for the NiO(001) surface unit cell. However, the pattern is rotated by 45° and $\sim \sqrt{2}$ times larger than the pattern of the SrTiO$_3$(001) substrate. The broadening of the diffraction spots is most likely caused by defects due to relaxation processes induced by the high lattice misfit of $\sim$6.9% for NiO(001) compared to SrTiO$_3$(001).

The LEED pattern of the as prepared Fe$_3$O$_4$ film (cf. Fig. 1(c)) reveals a quadratic (1×1) surface structure with almost doubled periodicity compared to NiO, as the real space lattice constant of the magnetite inverse spinel structure is about twice as large, giving a lattice misfit of only 0.7% for Fe$_3$O$_4$(001) on NiO(001). Furthermore, additional diffraction spots of a ($\sqrt{2} \times \sqrt{2}$)R45° superstructure can be seen, which is characteristic for well-ordered Fe$_3$O$_4$(001) surfaces.$^{37-39}$

![Soft XPS spectra](image)

**FIG. 2:** Soft XPS spectra of a) Fe 2p, b) Ni 2p region of sample A and c) Fe 2p, d) Ni 2p region of sample B after each annealing step. For sample A the spectra of the untreated sample are shown exemplarily.

LEED results indicate a cube-on-cube growth for both, NiO and Fe$_3$O$_4$ films. Additionally, the Ni 2p and Fe 2p XPS spectra recorded directly after preparation of each film (not shown here) exhibit a characteristic shape for a Ni$^{2+}$ and a mixed Fe$^{3+}$/Fe$^{2+}$ valence state, respectively. Thus, combining the results from XPS and LEED, we can conclude that the as-prepared films are consisting of stoichiometric Fe$_3$O$_4$/NiO bilayers.

Fig. 2 shows the Fe 2p and Ni 2p core-level spectra of both samples after transport to DLS under ambient conditions (sample A) and after each annealing step using soft XPS. After the first annealing step at 400 °C, the Fe 2p peak shape is similar to the untreated sample (cf. Fig. 2(a)). No charge transfer satellites are visible indicating a Fe$_3$O$_4$ stoichiometry and the presence of mixed oxidation state.$^{40,41}$ For both samples, Fe 2$p_{3/2}$ and Fe 2$p_{1/2}$ peaks are located at binding energies of 710.4 ($\pm$0.2) eV and 723.8 ($\pm$0.2) eV, respectively, corresponding to the values for magnetite known from literature.$^{40}$ Furthermore, no Ni 2p signal is visible for both samples due to the small information depth demonstrating that neither Ni diffused into the Fe$_3$O$_4$ film nor that the Fe$_3$O$_4$ film was deconstructed (cf. Fig. 2(b), (d)). Consequently, the first annealing step at 400 °C only removed surface contaminations from the transport, without effecting the initial layer structure of the sample.

After the annealing step at 600 °C, a distinctive satellite typical for trivalent iron becomes visible between the
Fe 2p\(_{1/2}\) and Fe 2p\(_{3/2}\) peaks for sample A and sample B (cf. Fig. 2(a), (c)). Further, Fe 2p\(_{1/2}\) and Fe 2p\(_{3/2}\) are shifted to a binding energy of 710.9 (\(\pm 0.2\)) eV and 724.4 (\(\pm 0.2\)) eV, respectively. The shift to higher binding energies and the satellite at \(\sim 8\) eV above the main peak confirm the presence of Fe\(^{3+}\) and a deficiency of divalent iron.

In contrast to lower annealing temperature, Ni 2p peaks becomes visible after the 600°C annealing step. Both samples show an intense Ni 2p signal consisting of two main peaks accompanied by satellite peaks at \(\sim 7\) eV above their binding energies. The shape of the spectra and in particular the absence of a shoulder at the high energy side of Ni 2p\(_{3/2}\) displays that no NiO cluster have been formed at the surface of both samples. The occurrence of such a shoulder \(\sim 1.5\) eV above the 2p\(_{3/2}\) peak is reported to be characteristic for NiO. The binding energy of 855.2 (\(\pm 0.2\)) eV of the Ni 2p\(_{3/2}\) peak also confirms the origin of NiFe\(_2\)O\(_4\) and not of NiO. Thus both, iron and nickel spectra obtained after annealing at 600°C point to a formation of NiFe\(_2\)O\(_4\) at the surface near region of both samples as a result of intermixing.

The last annealing step at 800°C influences the peak shape of neither the Fe 2p nor the Ni 2p spectra of sample B (cf. Fig. 2(c), (d)) indicating a complete intermixing of the two layers already after the annealing at 600°C. However, for sample A a NiO specific shoulder at the high energy side of Ni 2p\(_{3/2}\) appears (cf. Fig. 2(b)). Further, a shift to lower binding energies takes place resulting in a binding energy of 854.5 (\(\pm 0.2\)) eV for Ni 2p\(_{3/2}\), indicating the presence of NiO at the surface. Since there is no change in the Fe 2p spectra for sample A, we conclude that NiO clusters are formed at the surface of a NiFe\(_2\)O\(_4\) like film.

LEED pattern recorded from samples A and B after the final annealing step are presented in Figs. 1(d) and (e). The diffraction pattern can be attributed to the (001)-(1x1) surface of nickel ferrite which shows a lattice constant similar to magnetite (cf. Figs. 1(c))). However, the \(\sqrt{2} \times \sqrt{2}\)R45° superstructure indicative for magnetite is not observed after the final annealing step. Therefore, this result underpins the formation of nickel ferrite as concluded before from XPS where Fe\(^{3+}\) is primarily observed. Furthermore, the LEED spots of sample A are sharper than the spots of sample B. We attribute this finding to the formation of a stoichiometric NiFe\(_2\)O\(_4\) film for sample A while the ferrite film is less ordered for sample B where the Ni content of the film is too low (see below). The formation of NiO islands concluded from our detailed XRR analysis cannot clearly be concluded from the LEED experiments since the diffraction peaks of the NiO film coincide with diffraction peaks from the nickel ferrite film due to the coincidence between the nickel ferrite lattice constant and the doubled NiO lattice constant.

B. XRR

Fig. 3 shows the measured and calculated XRR intensities obtained at DLS prior to the annealing experiments for both samples. The XRR intensity obtained from sample A clearly shows the beating of two layers with almost identical thickness while the intensity obtained from sample B points to two layers with very different thickness. In addition, the data show well defined intensity oscillations for both samples pointing to a double layer structure and flat homogeneous interfaces and films. For the calculation of the intensity distributions and the exact layer structure a basic model was used, consisting of a two layer model with identical thickness while the intensity obtained from sample A clearly shows the beating of two layers with almost identical thickness. In Table I the fit parameters, e.g. dispersion \(\delta\) and rms-roughness \(\sigma\), are shown. Here, the obtained values for the dispersion of the as prepared samples are within 1% of corresponding literature values.

The measured and calculated XRR intensities of the annealed samples as well as the used model are also presented in Fig. 3. For both samples the XRR shows clear intensity oscillations with a changed periodicity compared to the as prepared films. Taking into account the electron densities and layer structures obtained from XRR this effect can be attributed to an intermixing of the two initial oxide layers. In case of sample A a three layer model was necessary to describe the data after annealing (cf. Fig. 3(a)). As concluded from the obtained dispersion \(\delta\) the first layer on top of the substrate is a thin nickel oxide layer while the second layer is a 8.2 nm thick nickel ferrite film on top of a NiO layer on a SrTiO\(_3\) substrate (insets of Fig. 3). In Table I the fit parameters, e.g. dispersion \(\delta\) and rms-roughness \(\sigma\), are shown. Here, the obtained values for the dispersion of the as prepared samples are within 1% of corresponding literature values.
TABLE I: Model parameters used for the XRR intensity calculations, with dispersion δ, surface roughness σ and film thickness d.

<table>
<thead>
<tr>
<th>sample A</th>
<th>substrate</th>
<th>layer 1</th>
<th>layer 2</th>
<th>layer 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>as prepared*</td>
<td>δ = 1.48 × 10⁻⁴, σ = 2.4 Å, d = 5.6 nm</td>
<td>δ = 1.65 × 10⁻⁴, σ = 3.9 Å, d = 5.5 nm</td>
<td>δ = 3.4 × 10⁻⁴, σ = 3.0 Å, d = 1.9 nm</td>
<td></td>
</tr>
<tr>
<td>annealed*</td>
<td>δ = 1.50 × 10⁻⁴, σ = 0.1 Å, d = 6.0 nm</td>
<td>δ = 1.58 × 10⁻⁴, σ = 2.0 Å, d = 8.2 nm</td>
<td>δ = 1.58 × 10⁻⁴, σ = 3.0 Å, d = 1.9 nm</td>
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</table>

<table>
<thead>
<tr>
<th>sample B</th>
<th>substrate</th>
<th>layer 1</th>
<th>layer 2</th>
<th>layer 3</th>
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</thead>
<tbody>
<tr>
<td>as prepared*</td>
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<td>δ = 1.65 × 10⁻⁴, σ = 3.2 Å, d = 5.5 nm</td>
<td>δ = 3.4 × 10⁻⁴, σ = 3.0 Å, d = 1.9 nm</td>
<td></td>
</tr>
<tr>
<td>annealed*</td>
<td>δ = 1.50 × 10⁻⁴, σ = 0.1 Å, d = 1.0 Å</td>
<td>δ = 1.58 × 10⁻⁴, σ = 7.1 Å</td>
<td>δ = 1.58 × 10⁻⁴, σ = 3.0 Å, d = 1.9 nm</td>
<td></td>
</tr>
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</table>

* measured at photon energy of 2500 eV

Fig. 5 shows the photoelectron spectra for the Ni 2p₁/₂ and Ni 2p₃/₂ core level of both samples. After the annealing step at 400 °C the main Ni 2p₃/₂ peak is located at binding energy of 854.5 (± 0.2) eV indicating NiO stoichiometry. Further, for both samples, a shoulder on the high binding energy side of the Ni 2p₃/₂ peak is visible, which is also typical for NiO. This shoulder almost completely disappears after annealing at 600 °C of both samples. Biesinger et al. identified such a peak shape without a shoulder for the spinel type material NiFe₂O₄. Besides, the Ni 2p₃/₂ peak is shifted to a higher binding energy of 855.0 (± 0.2) eV, which is comparable to binding energy reported for Ni in a NiFe₂O₄ stoichiometry. The small mismatch between the measured value and literature is due to an overlap of intensities originating from several layers with slightly different stoichiometries. In summary, similar to the soft XPS results, an exchange of Fe²⁺ ions with Ni²⁺ ions in the Fe₂O₄ spinel structure through interdiffusion seems to be likely.

For sample B, the peak shape does not change with the next annealing step at 800 °C (cf. Fig. 5(b)). However, for sample A the shoulder on the high binding energy side re-appears as observed for the initial bilayer system (cf. Fig. 5(a)). Additional, the Ni 2p₃/₂ peak is shifted to a lower binding energy, suggesting the formation of NiO like structures, which is consistent with the NiO formation at the surface seen in the XRR and soft XPS measurements.

Furthermore, a quantitative analysis of the photoelectron spectra was performed to prove the formation of nickel ferrite. After subtracting a Shirley background, the intensities \( I_{\text{Fe}} \) and \( I_{\text{Ni}} \) of the Fe 2p peaks and the Ni 2p₁/₂ peak (due to the overlap with the Fe 2s, the Ni 2p₃/₂ peak has not been considered) have been numerically integrated. From these results, the relative photoelectron yield

\[
y_{\text{Ni}} = \frac{I_{\text{Ni}}}{I_{\text{Ni}}/\sigma_{\text{Ni}} + I_{\text{Fe}}/\sigma_{\text{Fe}}} = \frac{N_{\text{Ni}}}{N_{\text{Ni}} + N_{\text{Fe}} \cdot C(\varphi)}
\]

of Ni has been calculated, using the differential photoionization cross sections \( \sigma \) reported by Trzhaskovskaya et al. Newberg et al. derived, that this yield is equal to the atomic ratios, but modified with a factor \( C(\varphi) \), that depends on the angle of photoemission (neglecting...
photoelectron diffraction effects). The resulting yields from different detection angles are plotted in Fig. 6. The curves from the data of the first annealing steps show for both samples a decreasing yield for higher emission angles as indicated by the blue dashed lines. This behavior points to an intact stack of oxide films due to a longer pathway of the photoelectrons for higher emission angles. The lines are calculated for a stack of two separated Fe$_3$O$_4$/NiO films using the thicknesses obtained from XRR analysis. With the successive annealing steps, the photoelectron yield from Ni increases, which indicates that there is diffusion of Ni into the Fe$_3$O$_4$ film and/or Fe into the NiO film.

Since there is no evidence of NiO in the Ni 2p HAXPES spectra after annealing at 600 °C, a model consisting of a stoichiometric 8.2 nm thick NiFe$_2$O$_4$ on top of a 3.4 nm thick NiO layer was used for sample A (green dashed line Fig. 6(a)).

With further annealing at 800 °C the intensity ratios (Fig. 6(a)) show a continuous increase of the nickel intensity. This indicates, that more Ni atoms are diffusing/transported through the nickel ferrite layer to the very surface forming NiO as detected by XRR and soft XPS measurements. The photoelectron yield for this annealing step (dashed red line) was calculated using the layer structure and thicknesses obtained from the XRR analysis (cf. inset Fig. 3(a)). This model is based on a stoichiometric 8.2 nm thick Ni$_x$Fe$_3-x$O$_4$ film with $x = 1$ between two NiO films. The supposed segregation behavior of Ni and the formation of NiO at the surface could be explained by its lower surface energy of 0.863 J/m$^2$ compared to the surface energy of 1.235 J/m$^2$ for NiFe$_2$O$_4$(001). Thus, one would expect an inversion of the initial bilayer ordering with NiO under magnetite. However, during the diffusion process Ni is partly incorporated in the initial magnetite film and stoichiometric NiFe$_2$O$_4$ is formed. After saturation of the nickel ferrite the residual Ni starts to form NiO at the surface. In our case, however, this process is obviously not completed due kinetic effects and residual NiO is still underneath the nickel ferrite.

In case of sample B one can conclude that a single homogeneous film was formed by the interdiffusion process already after the second annealing step. Its stoichiometry does not change from the second to the third annealing step (cf. Fig. 6(b)). The ratio of Ni and Fe, assuming a complete intermixing, can be determined from equation (2), as then the angular factor $C(\phi) \equiv 1$. The amount of nickel and iron does not match the ratio of 1 : 2 for stoichiometric nickel ferrite, but is 1 : 2.6 for the sample B indicating an excess of Fe atoms. The experimental data are in good agreement with the calculated behavior (dashed red line) for a homogeneously mixed single layer which is also consistent with the model obtained from XRR. Thus, the resulting stoichiometry of the sample B is Ni$_x$Fe$_3-x$O$_4$ with $x = 0.83$.

The used simulation of the photoelectron yield do not describe the measured data in full detail but give an idea
of the possible course. One limitation is that a model consisting of a stack of separated homogenous layers was used. Thus, potential concentration gradients or clusters are not implemented in the simulation. Further, effects caused by x-ray photoelectron diffraction (XPD) are not considered. Nevertheless, the general trend is described well.

FIG. 6: Relative photoelectron yield at different off-normal emission angles a) for sample A and b) for sample B. The dashed lines show the calculated intensities using the models obtained from XRR analysis.

D. SR - XRD

Fig. 7 shows SR-XRD measurements and calculated CTR intensity along (00L) direction close to the perovskite SrTiO$_3$(002)$_P$ and spinel (004)$_S$ Bragg peak for both samples after annealing. Here, $L$ denotes the vertical scattering vector in reciprocal lattice units (r.l.u.) with respect to the lattice constant of the SrTiO$_3$(001) substrate. Indices $P$ and $S$ indicate the bulk notation for perovskite type and spinel type unit cells, respectively. For both samples a clear peak from the SrTiO$_3$(001) substrate at $L=2$ and a broad Bragg peak originating from the oxide film around $L \approx 1.87$ is observed. The structural parameters, e.g. vertical layer distances, are determined by analyzing the CTRs applying full kinematic diffraction theory. The structural models obtained from the XRD analysis coincide with the layer models used in the calculation. The model is similar to that obtained from the analysis of the XRR (cf. inset of Fig. 3).

For sample A the model consists of a NiFe$_2$O$_4$ layer between two thin NiO films (cf. inset of Fig. 7). The distinct oscillations close to the Bragg peak of the oxide film (Laue fringes) can be clearly attributed to the nickel ferrite layer indicating a well ordered homogeneous film of high crystalline quality. The diffracted intensity originating from the NiO results in a broad peak underneath the Bragg reflection of the nickel ferrite due to the small film thicknesses of the NiO films which cannot directly be seen by the bare eye in the experimental data. Furthermore, the vertical lattice constants obtained from curve fitting are $a_{NiO} = 0.4177$ nm for the NiO films and $c_{NiFeO} = 0.8334$ nm for the NiFe$_2$O$_4$ layer. These results are in good agreement with the bulk values of $a_{bulk}^{NiO} = 0.4176$ nm and $c_{bulk}^{NiFeO} = 0.8339$ nm, respectively.

For sample B the Laue oscillations completely vanish, pointing to inhomogeneities within the film (cf. Fig. 7(b)). This effect is possibly caused by the excess of Fe atoms in the film as observed by HAXPES. However, the peak width is in accordance with the NiFe$_2$O$_4$ thickness of 7.1 nm. In addition, the vertical lattice constant $c_{NiFeO} = 0.8304$ nm obtained from the calculations confirms the presence of a strongly distorted structure of the annealed film, since it is notably lower than the value of bulk NiFe$_2$O$_4$.

E. XMCD

XMCD has been employed after the overall annealing cycle to analyze the resulting magnetic properties element specifically after annealing at 800 °C. Fig. 8 depicts the XMCD spectra of samples A and B performed at the Fe L$_{2,3}$ and Ni L$_{2,3}$ edges, respectively. Both samples show a strong Ni dichroic signal (cf. Fig. 7(a)), and in order to extract the spin magnetic moments we use the spin sum rule developed by Chen et al. The number of holes are determined from the charge transfer multiplet simulations for each sample. We also account for the core
hole interactions which mix the character of the L3 and L2 edges\textsuperscript{55,56} by considering the spin sum rule correction factors obtained by Teramura \textit{et al.}\textsuperscript{55} We find a Ni spin moment of 0.51 $\mu_B$/Ni atom and an orbital contribution of 0.053 $\mu_B$/Ni atom summing up to a total Ni moment of 0.56 $\mu_B$ for sample A. In case of sample B we derive $m_{\text{spin}} = 0.91$ $\mu_B$/Ni atom, $m_{\text{orb}} = 0.122$ $\mu_B$/Ni atom, and hence a total Ni moment of 1.03 $\mu_B$/formula unit (f.u.). The latter value is rather close to that recently found by Klewe \textit{et al.}\textsuperscript{57} on a stoichiometric NiFe$_2$O$_4$ thin film.

Turning to the Fe moments we find strong indications that our heat and diffusion experiments lead to a Ni$_2$Fe$_{3-x}$O$_4$ layer or cluster formation in both samples. Since we obtain $m_{\text{spin}} = -0.028$ (+0.11) $\mu_B$/Fe atom and $m_{\text{orb}} = +0.015$ (+0.007) $\mu_B$/Fe atom at the Fe sites of sample A (sample B) we find very small net contributions to the overall magnetic moments. In comparison Klewe \textit{et al.}\textsuperscript{57} found an iron spin moment of around 0.1 $\mu_B$/Fe atom and a further orbital contribution of around 10-15% of that value. This indicates an (almost complete) structural inversion of the prior bilayer system, i.e. the iron ions occupy in equal parts octahedral and tetrahedral positions within the crystal. Since the moments of these octahedrally and tetrahedrally coordinated cations are aligned antiparallel the moments cancel each other nearly out in a perfect inverse spinel structure.

Fig. 8(c) presents the charge transfer multiplet calculations for the single iron cations in octahedral and tetrahedral coordination as well as the best fits to the experimental Fe L\textsubscript{2,3}-XMCD spectra of sample A and B with (red) and without (blue) consideration of Fe\textsuperscript{2+}$\text{_{oct}}$ ions. The resulting lattice site occupancies are 16.3% Fe\textsuperscript{2+}$\text{_{oct}}$, 32.2% Fe\textsuperscript{3+}$\text{_{oct}}$, 51.5% Fe\textsuperscript{3+}$\text{_{tet}}$ (42.6% Fe\textsuperscript{2+}$\text{_{oct}}$, 57.4% Fe\textsuperscript{3+}$\text{_{tet}}$) for sample A, and 24.0% Fe\textsuperscript{3+}$\text{_{oct}}$, 31.5% Fe\textsuperscript{3+}$\text{_{oct}}$, 44.5% Fe\textsuperscript{3+}$\text{_{tet}}$ (55.6% Fe\textsuperscript{3+}$\text{_{oct}}$, 44.4% Fe\textsuperscript{3+}$\text{_{ tet}}$) for sample B including (not including) Fe\textsuperscript{2+}$\text{_{oct}}$ ions into the respective fit. The result that for sample A over 50% are in Fe\textsuperscript{3+}$\text{_{oct}}$ coordination as to the calculations also corresponds with the small negative spin moment determined by the spin sum rule.

From the overall multiplet fits (Fig. 8(c)) one can clearly see that feature \textit{i} (Fig. 8(b)) is very small if Fe\textsuperscript{2+}$\text{_{oct}}$ cations are not explicitly considered in the respective simulations. The origin of this feature in ferrites with inverse spinel structure other than magnetite is still not entirely understood.\textsuperscript{44,57,58} In both Fe L\textsubscript{2,3}-XMCD spectra of samples A and B peak \textit{i} is significantly smaller than results obtained very recently on NiFe$_2$O$_4$ thin films grown by pulsed laser deposition (PLD),\textsuperscript{44} but somewhat more intense than it is in the result of Klewe \textit{et al.}\textsuperscript{57} Also their corresponding multiplet simulation resembles our approach (not considering the Fe\textsuperscript{2+}$\text{_{oct}}$ sites) rather well.

The presence of peak \textit{i} in the Fe L\textsubscript{2,3}-XMCD of sample B can at least partly be explained by the lack of Ni\textsuperscript{3+}$\text{_{oct}}$ ions as to the HAXPES measurements. Since peak \textit{i} also occurs in XMCD experiments on bulk material\textsuperscript{58} one can think about several additional reasons about the presence of some Fe\textsuperscript{2+}$\text{_{oct}}$ ions. For instance, a small fraction of the Ni ions might be present in form of Ni\textsuperscript{3+} or coordinated on tetrahedral sites as result of the interdiffusion process. Despite the fact that Ni\textsuperscript{2+} prefers octahedral coordination, even measurements on NiFe$_2$O$_4$ bulk crystals indicate a few of the Ni ions to be on tetrahedral sites.\textsuperscript{58} Furthermore, oxidation or reduction of a fraction of the Fe at the very surface of the thin films can not be entirely excluded as the probing depth of the total electron yield is only around 2 nm at the Fe L\textsubscript{2,3} and Ni L\textsubscript{2,3} resonances.
of oxides.\textsuperscript{58,59}

For sample B we also recorded element specific hysteresis loops at the Ni L\textsubscript{3} edge and the site specific loops at Fe L\textsubscript{3} resonances for peaks \textit{i} – \textit{iii} (cf. Fig. 8(b)). Fig. 9 displays the resulting magnetization loops. One can see the ferrimagnetic ordering between the Fe\textsuperscript{3+} cations and the other Fe and Ni cations. For all octahedrally coordinated cations we probe a in-plane open magnetization curve, whereas the Fe\textsuperscript{3+} cations exhibit a closed, paramagnetic magnetization curve. In out-of plane configuration we only probed the Ni sites (see insets in Fig. 9). Whereas recently reported values of the coercive field are in the order of \( H_c = 0.1 \) T or more for NiFe\textsubscript{2}O\textsubscript{4} thin films,\textsuperscript{44,57,60} we find significantly lower values for hysteresis loops of the octahedrally coordinated cations (cf. Fig. 9(b)), despite it is difficult to obtain exact values for \( H_c \) as the magnetization curves are pretty flat. We want to point out rather flat magnetization curves appear to be typical also for NiFe\textsubscript{2}O\textsubscript{4} epitaxial thin films\textsuperscript{61} and nanoparticles.\textsuperscript{62} A number of reasons might be responsible for the observed discrepancy, a strongly increased \( H_c \) might be caused by exchange coupled grains\textsuperscript{60} or a high defect density.\textsuperscript{57} for instance. On the other hand, similar values for the coercive field measured here have been found on polycrystalline as well as epitaxial Ni\textsubscript{2}Fe\textsubscript{1−\textit{x}}O\textsubscript{4} thin films.\textsuperscript{61} The bulk value of NiFe\textsubscript{2}O\textsubscript{4} has been reported to be 0.01 T\textsuperscript{62} which is closer to the values obtained here.

\textbf{IV. SUMMARY AND CONCLUSIONS}

We investigated the modification of the crystallographic, electronic, and magnetic properties of Fe\textsubscript{3}O\textsubscript{4}/NiO - bilayers due to thermally induced interdiffusion of Ni ions out of the NiO layer into the magnetite film. We annealed two bilayers, sample A (B) comprising initially 5.6 nm (1.5 nm) NiO and 5.5 nm (5.4 nm) Fe\textsubscript{3}O\textsubscript{4} in three steps at 20 - 30 minutes in an oxygen atmosphere of 5 \( \times \) 10\textsuperscript{-9} mbar. LEED demonstrates the extinction of the magnetite specific \((\sqrt{2} \times \sqrt{2})R45^\circ\) superstructure, however, a spinel like \((1 \times 1)\) surface structure occurs after the overall annealing cycle.

Structural analysis reveals that the annealing cycles lead to homogenous layers of Ni\textsubscript{2}Fe\textsubscript{1−\textit{x}}O\textsubscript{4}. In case of sample A consideration of additional NiO layer on the surface and interface leads to the best agreement between calculated and experimentally observed XRR and SR-XRD results. For sample B SR-XRD indicates a strongly distorted structure with a vertical lattice constant of \( c = 0.8304 \) nm whereas the vertical lattice constant \( c = 0.8334 \) nm of sample A is close to that of bulk NiFe\textsubscript{2}O\textsubscript{4} (\( d_{NiFeO}^{bulk} = 0.8339 \) nm).

These findings are supported by the soft XPS and HAXPES experiments. Firstly, the formation of Fe\textsuperscript{3+} upon annealing at 600 °C is confirmed by the shape and binding energy positions of the Fe 2p core level spectra. Further annealing at 800 °C do not cause any changes in the Fe 2p spectra. Secondly, for sample B the shape and binding energy of the Ni 2p spectra indicate the formation of an inverse spinel ferrite, whereas in case of sample A NiO characteristic features first diminish after annealing at 600 °C and re-appear after the entire annealing cycle at 800 °C. Due to surface sensitivity soft XPS analysis clearly reveals an occurrence of Ni\textsuperscript{3+} in NiO stoichiometry at the surface near region after the last annealing step. Further, HAXPES analysis shows also an increasing amount of Ni\textsuperscript{3+} ions. This may be associated with the much thicker initial NiO layer of sample A leading to Ni diffusion to the sample surface. We assume that NiFe\textsubscript{2}O\textsubscript{4} was formed on top of the residual NiO film after the annealing step. Further, HAXPES analysis shows also an increased amount of Ni\textsuperscript{2+} ions. This process, however, is not completed in our case, probably due to kinetic effects.
Furthermore, we determined a Ni:Fe ratio of 1:2.6 for sample B and thus, a resulting stoichiometry of Ni$_{0.83}$Fe$_{2.17}$O$_4$. This is in accordance with the weak crystalline quality of sample B seen in the XRD measurements.

We employed XMCD to study the internal magnetic properties of the thin films resulting from the Ni interdiffusion process. In excellent agreement to complementary charge transfer multiplet simulations we find a strong increase of Fe$^{3+}$-O$_4$-coordinated cation fraction (around 50%) compared to stoichiometric Fe$_3$O$_4$, resulting in very small Fe net magnetic moments as determined from the experimental XMCD data by applying the sum rules. The magnetic properties after the annealing cycle are in both samples dominated by the contribution of the Ni$^{2+}$ ions, which exhibit magnetic moments of 0.56 $\mu_B$/f.u. (sample A) and 1.03 $\mu_B$/f.u. (sample B). The latter value corresponds quite well to the value very recently reported for a stoichiometric NiFe$_2$O$_4$ thin film. The lower value found for sample A can be explained by the formation of (antiferromagnetic) NiO-rich islands or clusters at the surface of the sample which contribute to the Ni L$_{2,3}$-XAS signal but not to the corresponding XMCD. Finally, performed element specific hysteresis loops on sample B find a rather small in-plane coercive field. This is a further indication for the formation a magnetically well ordered NiFe$_2$O$_4$-like thin film by means of thermal interdiffusion of Ni$^{2+}$ ions into magnetite from Fe$_3$O$_4$/NiO bilayers.

In conclusion we presented a comprehensive study of epitaxially grown Fe$_3$O$_4$/NiO heterostructures and its structural evolution due to Ni interdiffusion as consequence of three distinct thermal annealing steps. A multi-technique approach tackling the structural, chemical, electronic and magnetic properties leads to a rather complete and conclusive picture, which is also in good agreement with corresponding model calculations. We have demonstrated that it is possible to synthesize Ni$_{3-x}$Fe$_{3-x}$O$_4$ thin films, also with compositions close to stoichiometric NiFe$_2$O$_4$ with high crystalline quality by thermally induced intermixing of distinct Fe$_3$O$_4$/NiO bilayers grown on Nb-doped SrTiO$_3$(001). If the initial Fe$_3$O$_4$ and NiO thin film thicknesses can be controlled precisely one may obtain Ni$_3$Fe$_{3-x}$O$_4$ thin films with tunable band gap employing this approach, which might be of interest for several applications, e.g. in the field of spintronics (spin valves), or for experiments concerning the spin Hall magnetoresistance and the spin Seebeck effect. Thus, additional transport effects based on either charge or spin currents can be amplified or suppressed depending on the bad gap properties of the NiFe$_2$O$_4$-like material.

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