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# From $\text{Fe}_3\text{O}_4/\text{NiO}$ bilayers to $\text{NiFe}_2\text{O}_4$ -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  $\text{Ni}^{2+}$  ions out of NiO into  $\text{Fe}_3\text{O}_4$  ultrathin films resulting in off-stoichiometric nickel ferrite-like thin layers. We synthesized epitaxial  $\text{Fe}_3\text{O}_4/\text{NiO}$  bilayers on Nb-doped  $\text{SrTiO}_3(001)$  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  $\text{NiFe}_2\text{O}_4$ . 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  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  ions and the  $\text{Fe}^{3+}$  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 ( $\text{Fe}_3\text{O}_4$ ) is among the most studied ferrites due to its ferrimagnetic ordered ground state with a saturation moment of  $4.07 \mu_B$  per formula unit and a high Curie temperature of 860 K for bulk material.<sup>1,2</sup> This magnetic ground state is accompanied by half metallicity, i.e. only one spin orientation is present at the Fermi energy,<sup>3</sup> making this material a potential candidate for future spintronic devices with 100% spin polarization.<sup>4,5</sup> Magnetite crystallizes in the cubic inverse spinel structure (equal distribution of  $\text{Fe}^{3+}$  on A and B sites and  $\text{Fe}^{2+}$  exclusively on B sites) with lattice constant  $a = 0.8396 \text{ nm}$  (space group  $\text{Fd}\bar{3}m$ ). The oxygen anions form an fcc anion sublattice.

Often,  $\text{Fe}_3\text{O}_4$  thin films are grown on cubic  $\text{MgO}(001)$  substrates by various deposition techniques<sup>6–11</sup>, since the lattice mismatch between  $\text{Fe}_3\text{O}_4$  and  $\text{MgO}(001)$  ( $a = 0.42117 \text{ nm}$ ) is only 0.3%, comparing the oxygen sublattices. A severe limit of epitaxial thin film growth on  $\text{MgO}$  substrates is  $\text{Mg}^{2+}$  segregation into the  $\text{Fe}_3\text{O}_4$  film if the substrate temperature is above 250 °C.<sup>12</sup> Mg rich interfaces<sup>13</sup> and Mg interdiffusion have been studied in detail,<sup>14</sup> having significant influence on interface roughness or anti phase boundaries. Thus, the underlying elec-

tronic and magnetic structure influences the properties of the magnetite thin film in question or the tunnel magneto resistance in magnetic tunnel junctions with magnetite electrodes.<sup>15–18</sup>

Potential approach to minimize or suppress Mg segregation, besides rather low substrate temperatures during magnetite growth, is an additional buffer layer, e.g. metallic iron<sup>19</sup> or NiO<sup>20</sup> between the  $\text{Fe}_3\text{O}_4$  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.<sup>20–22</sup>

The usage of other substrates like  $\text{SrTiO}_3$  could also prevent Mg interdiffusion. Despite the large lattice mismatch of -7.5% between the doubled  $\text{SrTiO}_3$  bulk lattice constant (0.3905 nm) and magnetite it is possible to grow epitaxial  $\text{Fe}_3\text{O}_4$  films on the  $\text{SrTiO}_3(001)$  surface.<sup>23,24</sup> In particular, concerning coupled  $\text{Fe}_3\text{O}_4/\text{NiO}$  bilayers grown on  $\text{SrTiO}_3$ , so far only Pilard *et al.* have reported on the magnetic properties of the  $\text{Fe}_3\text{O}_4/\text{NiO}$  interface.<sup>25</sup> On the other hand,  $\text{NiFe}_2\text{O}_4$  thin films are of huge interest nowadays, since they are magnetic insulators or semiconductors. Therefore, they can be used as spin filters<sup>26</sup> or for thermal induction of spin currents via the spin Seebeck effect.<sup>27,28</sup> Furthermore, electrical charge transport and spin currents can be manipulated by the spin Hall magnetoresistance using  $\text{NiFe}_2\text{O}_4$  thin films adjacent to nonmagnetic material.<sup>29</sup>

Therefore, we study here the possibility to form nickel ferrite starting with a distinct  $\text{Fe}_3\text{O}_4/\text{NiO}$  bilayer grown on Nb-doped  $\text{SrTiO}_3(001)$ . 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  $\text{Ni}^{2+}$  diffusion from a NiO buffer layer into a  $\text{Fe}_3\text{O}_4$  top layer as well as NiO surface segregation through the  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{NiO}$  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  $\text{Fe}_3\text{O}_4/\text{NiO}$  ultra thin film bilayers on conductive 0.05 wt. % Nb-doped  $\text{SrTiO}_3(001)$  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  $400^\circ\text{C}$  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 crystallinity 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  $250^\circ\text{C}$ , while the oxygen pressure was kept at  $1 \times 10^{-5}$  mbar for NiO and  $5 \times 10^{-6}$  mbar for  $\text{Fe}_3\text{O}_4$  to guarantee optimal oxidation condition. A deposition rate of 0.85 nm/min and 4.6 nm/min was used for the growth of NiO and  $\text{Fe}_3\text{O}_4$  films, respectively, which was controlled by a quartz micro-balance adjacent to the source. One sample has been created with a 5.6 nm NiO film (sample A) and the other with a 1.5 nm NiO film (sample B). Thereafter, 5.5 nm thick  $\text{Fe}_3\text{O}_4$  films were deposited on the NiO films. Film stoichiometry and surface structure have been monitored *in-situ* by x-ray photoelectron spectroscopy (XPS) using Al  $\text{K}_\alpha$  radiation and LEED, respectively.

The samples were transported under ambient conditions to the Diamond Light Source (DLS) synchrotron, where the effects of annealing on the bilayer system were studied at beamline I09 by heating the samples in three steps at  $400^\circ\text{C}$ ,  $600^\circ\text{C}$ , and  $800^\circ\text{C}$  for 20 to 30 minutes in an oxygen atmosphere of  $5 \times 10^{-6}$  mbar to avoid reduction or further oxidation of the sample.<sup>30</sup> 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  $\text{NiO}/\text{Fe}_3\text{O}_4$  bilayer.

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

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

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

with the inelastic mean free path  $\lambda$  and the off-normal emission angle  $\varphi$ .<sup>31</sup> 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.<sup>32</sup> 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  $\text{K}_\alpha$  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<sup>33</sup> and Névot-Croce roughness model<sup>34</sup> was used. The SR-XRD measurements were analyzed by calculating the crystal truncation rod (CTR) intensity within the full kinematic diffraction theory to fit the experimental diffraction data.

XMCD spectroscopy was performed at the Fe  $\text{L}_{2,3}$  and Ni  $\text{L}_{2,3}$  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  $30^\circ$ . 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  $\text{L}_{2,3}$  XMCD spectra, we have performed corresponding model calculations within the atomic multiplet and crystal field theory including charge transfer using the program CTM4XAS.<sup>35,36</sup>

### III. RESULTS

#### A. Surface characterization

In Figs. 1(a)-(c) the LEED pattern of the cleaned substrate and the as prepared NiO and Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub> 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).

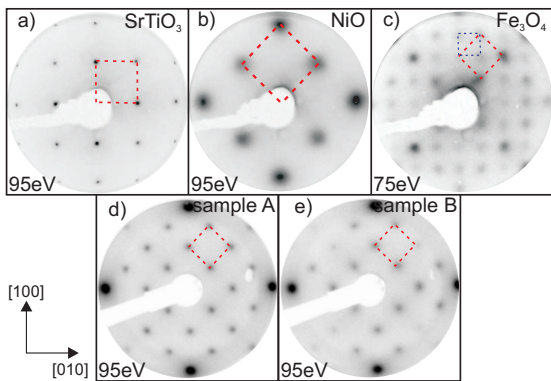


FIG. 1: LEED patterns for sample A recorded directly after a) preparation of SrTiO<sub>3</sub> substrate, b) deposition of NiO, c) deposition of Fe<sub>3</sub>O<sub>4</sub>, d) the last annealing step of 800 °C. For comparison, (e) shows the LEED pattern for sample B after the final annealing step.

Marked with red squares are the respective (1 × 1) surface unit cells in reciprocal space. The blue square indicates the  $(\sqrt{2} \times \sqrt{2})R45^\circ$  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<sub>3</sub>(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 -6.9% for NiO(001) compared to SrTiO<sub>3</sub>(001).

The LEED pattern of the as prepared Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub>(001) on NiO(001). Furthermore, additional diffraction spots of a  $(\sqrt{2} \times \sqrt{2})R45^\circ$  superstructure can be seen, which is characteristic for well-ordered Fe<sub>3</sub>O<sub>4</sub>(001) surfaces.<sup>37-39</sup>

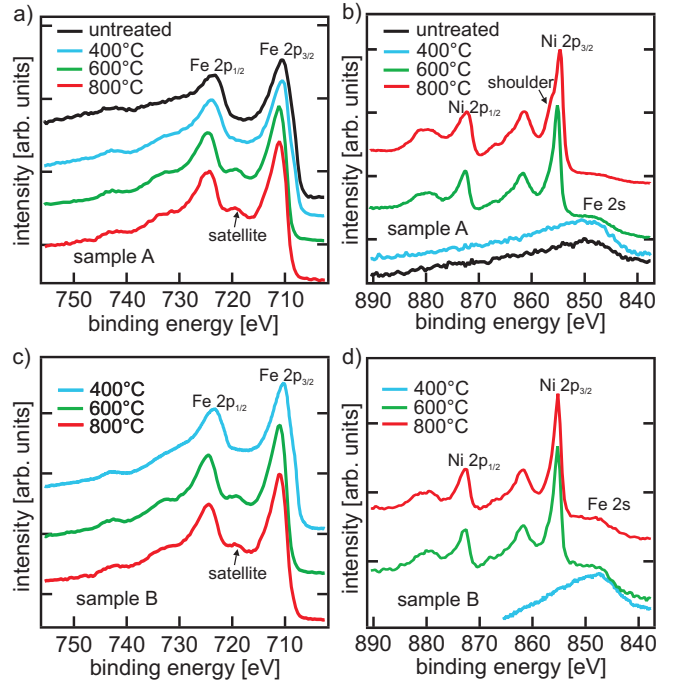


FIG. 2: Soft XPS spectra of a) Fe 2p, b) Ni 2p region of sample A and c) Fe 2p, d) Ni 2p region of sample B after each annealing step. For sample A the spectra of the untreated sample are shown exemplarily.

LEED results indicate a cube-on-cube growth for both, NiO and Fe<sub>3</sub>O<sub>4</sub> 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<sup>2+</sup> and a mixed Fe<sup>2+</sup>/Fe<sup>3+</sup> valence state, respectively. Thus, combining the results from XPS and LEED, we can conclude that the as-prepared films are consisting of stoichiometric Fe<sub>3</sub>O<sub>4</sub>/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<sub>3</sub>O<sub>4</sub> stoichiometry and the presence of mixed oxidation state.<sup>40,41</sup> For both samples, Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks are located at binding energies of 710.4 (± 0.2) eV and 723.8 (± 0.2) eV, respectively, corresponding to the values for magnetite known from literature.<sup>40</sup> Furthermore, no Ni 2p signal is visible for both samples due to the small information depth demonstrating that neither Ni diffused into the Fe<sub>3</sub>O<sub>4</sub> film nor that the Fe<sub>3</sub>O<sub>4</sub> 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  $\text{Fe}^{3+}$  and a deficiency of divalent iron.<sup>40–42</sup>

In contrast to lower annealing temperature, Ni 2p peaks becomes visible after the  $600^\circ\text{C}$  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.<sup>43,44</sup> The occurrence of such a shoulder  $\sim 1.5$  eV above the  $2p_{3/2}$  peak is reported to be characteristic for NiO.<sup>45,46</sup> The binding energy of  $855.2(\pm 0.2)$  eV of the Ni  $2p_{3/2}$  peak also confirms the origin of  $\text{NiFe}_2\text{O}_4$  and not of NiO.<sup>43,47</sup> Thus both, iron and nickel spectra obtained after annealing at  $600^\circ\text{C}$  point to a formation of  $\text{NiFe}_2\text{O}_4$  at the surface near region of both samples as a result of intermixing.

The last annealing step at  $800^\circ\text{C}$  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  $600^\circ\text{C}$ . 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.<sup>43</sup> 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  $\text{NiFe}_2\text{O}_4$  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  $(\sqrt{2} \times \sqrt{2})R45^\circ$  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  $\text{Fe}^{3+}$  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  $\text{NiFe}_2\text{O}_4$  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.

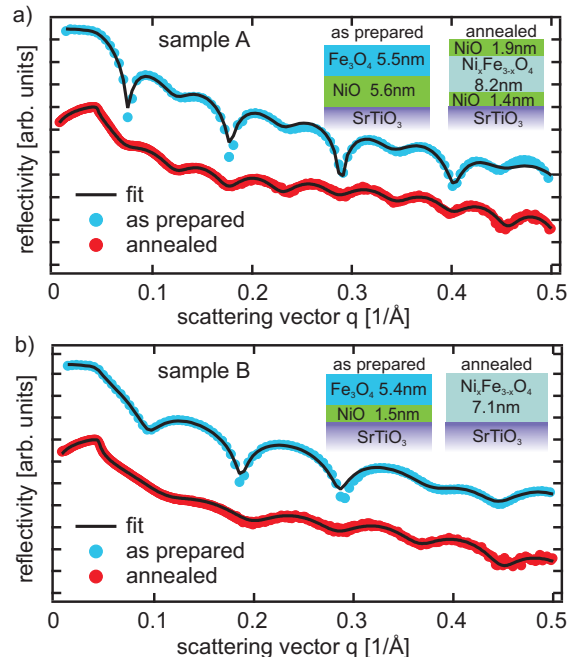


FIG. 3: Reflectivity curves and calculations from XRR measurements before and after the annealing experiments a) for sample A and b) for sample B. The insets show the underlying models.

## 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 magnetite film on top of a NiO layer on a  $\text{SrTiO}_3$  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.<sup>48</sup>

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

	substrate		layer 1			layer 2			layer 3		
sample A	$\delta$	$\sigma / \text{\AA}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$
as prepared <sup>a</sup>	$1.48 \cdot 10^{-4}$	2.4	$2.15 \cdot 10^{-4}$	1.7	5.6	$1.65 \cdot 10^{-4}$	3.9	5.5	-	-	-
annealed <sup>b</sup>	$1.50 \cdot 10^{-5}$	0.1	$1.7 \cdot 10^{-5}$	6.0	1.4	$1.58 \cdot 10^{-5}$	2.0	8.2	$1.34 \cdot 10^{-5}$	3.0	1.9
sample B	$\delta$	$\sigma / \text{\AA}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$	$\delta$	$\sigma / \text{\AA}$	$d / \text{nm}$
as prepared <sup>a</sup>	$1.48 \cdot 10^{-4}$	2.7	$2.15 \cdot 10^{-4}$	1.9	1.5	$1.65 \cdot 10^{-4}$	3.2	5.5	-	-	-
annealed <sup>b</sup>	$1.50 \cdot 10^{-5}$	0.1	$1.58 \cdot 10^{-5}$	1.0	7.1	-	-	-	-	-	-

<sup>a</sup> measured at photon energy of 2500 eV

<sup>b</sup> measured at photon energy of 8048 eV

TABLE I: Model parameters used for the XRR intensity calculations, with dispersion  $\delta$ , surface roughness  $\sigma$  and film thickness  $d$ .

thick nickel ferrite film.<sup>48</sup> The third layer on top of the nickel ferrite film consists of an oxide layer with a diluted dispersion  $\delta$  and thus a reduced electron density. Taking into account the NiO formation on top of the sample A seen in the soft XPS spectra, we can attribute the upper layer to NiO segregation to the surface. The low electron density of this layer indicate a deconstructed film or island formation on the surface.

For sample B, however, the XRR is modeled with a single homogeneous 7.1 nm thick nickel ferrite film on top of the substrate (cf. Fig. 3(b)). For both samples the thicknesses of the residual films coincide almost with the sum of the initial thicknesses of the  $\text{Fe}_3\text{O}_4$  and NiO films.

The slight increase of the overall thickness can be attributed to a volume increase of  $\sim 8\%$  due to the formation of nickel ferrite.

### C. HAXPES

In contrast to soft x-ray photoemission, HAXPES measurements allow to identify the valence states and chemical properties not only at the surface near region but with bulk sensitivity due to higher excitation energy and, thus, increased information depth.

Fig. 4 shows the HAXPES spectra for the Fe 2p core level, which is split into the Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$  peaks (cf. soft XPS spectra, Fig. 2). Spectra recorded after each annealing step for both samples are presented. The shape of the spectra is determined by the relative fraction of Fe valence states, which is used to identify the material composition.<sup>40</sup> After the initial annealing step at 400 °C, there is no satellite peak visible between the two main peaks, indicating stoichiometric  $\text{Fe}_3\text{O}_4$  for both samples. After the second and third annealing step, at 600 °C and 800 °C, respectively, a satellite peak becomes visible between the two main peaks for both samples. As it resides on the side of the Fe  $2p_{1/2}$  peak, it indicates a deficiency of  $\text{Fe}^{2+}$  ions in favor of  $\text{Fe}^{3+}$  ions compared to the initial magnetite stoichiometry. In addition, similar to the XPS results, an energy shift to higher binding energies can be seen after the second and third annealing step pointing to a formation of trivalent  $\text{Fe}^{3+}$ , too.<sup>40-42</sup> Thus, this behavior is in accordance with the results obtained from soft XPS spectra.

Fig. 5 shows the photoelectron spectra for the Ni  $2p_{1/2}$  and Ni  $2p_{3/2}$  core level of both samples. After the annealing step at 400 °C the main Ni  $2p_{3/2}$  peak is located at binding energy of  $854.5 (\pm 0.2)$  eV indicating NiO stoichiometry.<sup>43</sup> Further, for both samples, a shoulder on the high binding energy side of the Ni  $2p_{3/2}$  peak is visible, which is also typical for NiO.<sup>43,47</sup> This shoulder almost completely disappears after annealing at 600 °C of both samples. Biesinger *et al.*<sup>49</sup> identified such a peak shape without a shoulder for the spinel type material  $\text{NiFe}_2\text{O}_4$ . Besides, the Ni  $2p_{3/2}$  peak is shifted to a higher binding energy of  $855.0 (\pm 0.2)$  eV, which is comparable to binding energy reported for Ni in a  $\text{NiFe}_2\text{O}_4$  stoichiometry.<sup>43</sup> 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  $\text{Fe}^{2+}$  ions with  $\text{Ni}^{2+}$  ions in the  $\text{Fe}_3\text{O}_4$  spinel structure through interdiffusion seems to be likely.<sup>50</sup>

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  $2p_{3/2}$  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  $2p_{1/2}$  peak (due to the overlap with the Fe 2s, the Ni  $2p_{3/2}$  peak has not been considered) have been numerically integrated. From these results, the relative photoelectron yield

$$Y_{\text{Ni}} = \frac{I_{\text{Ni}}/\sigma_{\text{Ni}}}{I_{\text{Ni}}/\sigma_{\text{Ni}} + I_{\text{Fe}}/\sigma_{\text{Fe}}} = \frac{N_{\text{Ni}}}{N_{\text{Ni}} + N_{\text{Fe}} \cdot C(\varphi)} \quad (2)$$

of Ni has been calculated, using the differential photoionization cross sections  $\sigma$  reported by Trzhaskovskaya *et al.*<sup>51</sup>. Newberg *et al.*<sup>52</sup> 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

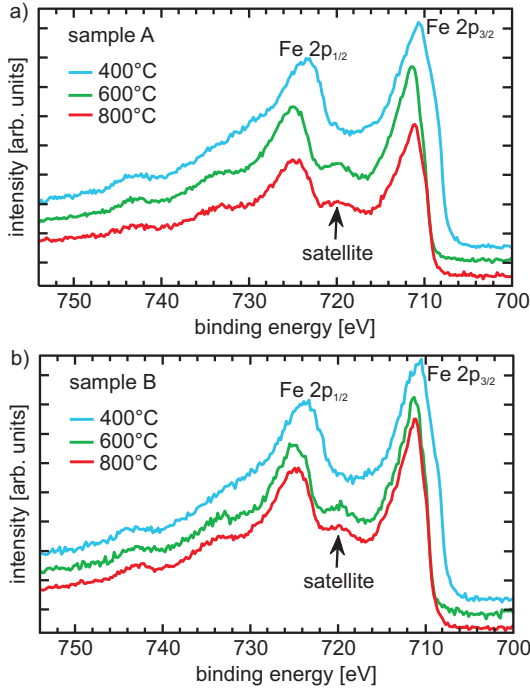


FIG. 4: HAXPES spectra of Fe 2p core level at  $10^\circ$  off-normal photoelectron emission after annealing at different temperatures a) for sample A and b) for sample B.

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  $\text{Fe}_3\text{O}_4/\text{NiO}$  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  $\text{Fe}_3\text{O}_4$  film and/or Fe into the NiO film.

Since there is no evidence of NiO in the Ni 2p HAXPES spectra after annealing at  $600^\circ\text{C}$ , a model consisting of a stoichiometric 8.2 nm thick  $\text{NiFe}_2\text{O}_4$  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  $800^\circ\text{C}$  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  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  film with  $x=1$  between two NiO films. The supposed segrega-

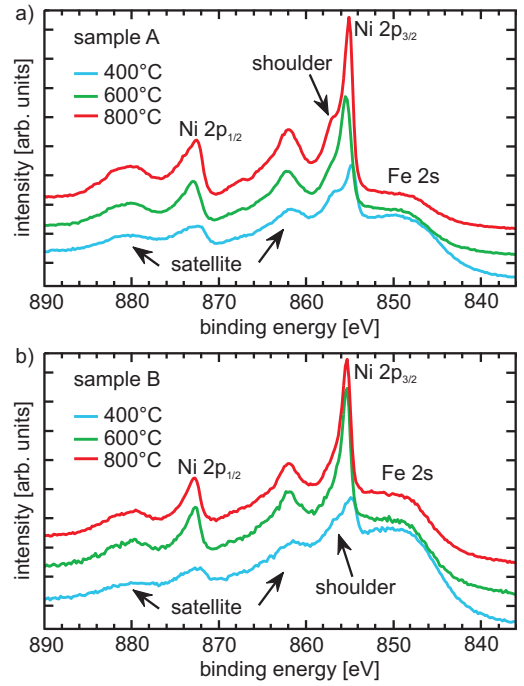


FIG. 5: HAXPES spectra of Ni 2p core level at  $10^\circ$  off-normal photoelectron emission after annealing at different temperatures a) for sample A and b) for sample B.

tion behavior of Ni and the formation of NiO at the surface could be explained by its lower surface energy of  $0.863\text{ J/m}^2$  compared to the surface energy of  $1.235\text{ J/m}^2$  for  $\text{NiFe}_2\text{O}_4(001)$ .<sup>53</sup> 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  $\text{NiFe}_2\text{O}_4$  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  $C(\varphi) \equiv 1$ . 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  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  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.

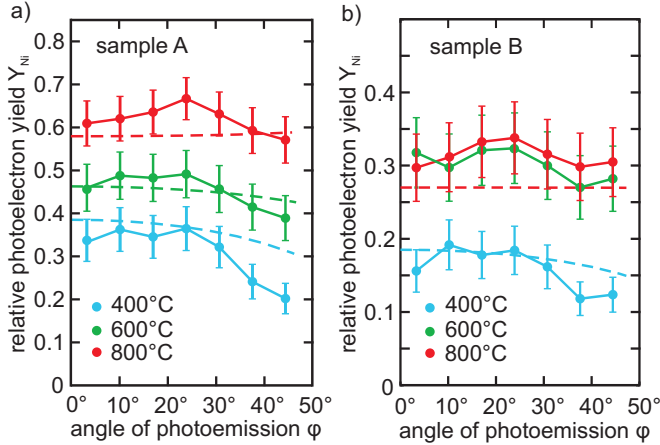


FIG. 6: Relative photoelectron yield at different off-normal emission angles a) for sample A and b) for sample B. The dashed lines show the calculated intensities using the models obtained from XRR analysis.

#### D. SR-XRD

Fig. 7 shows SR-XRD measurements and calculated CTR intensity along  $(00L)$  direction close to the perovskite  $\text{SrTiO}_3(002)_P$  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  $\text{SrTiO}_3(001)$  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  $\text{SrTiO}_3(001)$  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 for the XRR calculations of the annealed samples (cf. insets of Fig. 7 and Fig. 3).

For sample A the model consists of a  $\text{NiFe}_2\text{O}_4$  layer between two thin  $\text{NiO}$  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  $\text{NiO}$  results in a broad peak underneath the Bragg reflection of the nickel ferrite due to

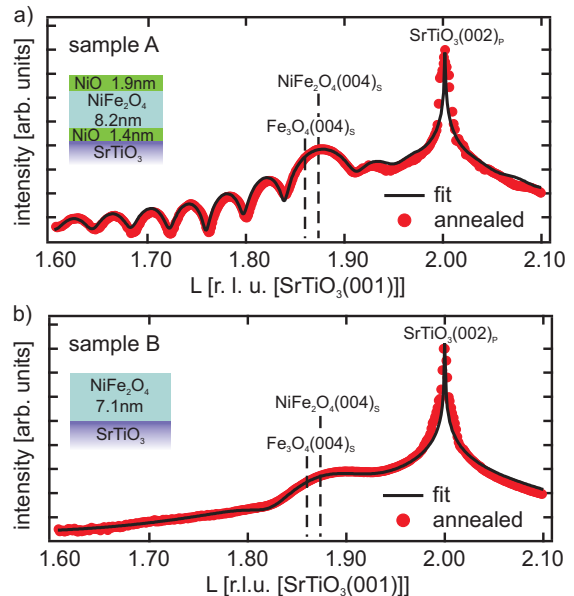


FIG. 7: SR-XRD measurements along  $(00L)$  direction and calculated intensities. The insets show the layer structures used in the calculation. The model is similar to that obtained from the analysis of the XRR (cf. inset of Fig. 3).

the small film thicknesses of the  $\text{NiO}$  films which cannot directly be seen by the bare eye in the experimental data. Furthermore, the vertical lattice constants obtained from curve fitting are  $c_{\text{NiO}} = 0.4177 \text{ nm}$  for the  $\text{NiO}$  films and  $c_{\text{NFO}} = 0.8334 \text{ nm}$  for the  $\text{NiFe}_2\text{O}_4$  layer. These results are in good agreement with the bulk values of  $a_{\text{NiO}}^{\text{bulk}} = 0.4176 \text{ nm}$  and  $a_{\text{NFO}}^{\text{bulk}} = 0.8339 \text{ nm}$ , 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  $\text{NiFe}_2\text{O}_4$  thickness of  $7.1 \text{ nm}$ . In addition, the vertical lattice constant  $c_{\text{NFO}} = 0.8304 \text{ nm}$  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  $\text{NiFe}_2\text{O}_4$ .

#### E. XMCD

XMCD has been employed after the overall annealing cycle to analyze the resulting magnetic properties element specifically after annealing at  $800^\circ\text{C}$ . 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.*<sup>54</sup> 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  $L_3$  and  $L_2$  edges<sup>55,56</sup> by considering the spin sum rule correction factors obtained by Teramura *et al.*<sup>55</sup> We find a Ni spin moment of  $0.51 \mu_B/\text{Ni}$  atom and an orbital contribution of  $0.053 \mu_B/\text{Ni}$  atom summing up to a total Ni moment of  $0.56 \mu_B$  for sample A. In case of sample B we derive  $m_{spin} = 0.91 \mu_B/\text{Ni}$  atom,  $m_{orb} = 0.122 \mu_B/\text{Ni}$  atom, and hence a total Ni moment of  $1.03 \mu_B/\text{formula unit (f.u.)}$ . The latter value is rather close to that recently found by Klewe *et al.*<sup>57</sup> on a stoichiometric  $\text{NiFe}_2\text{O}_4$  thin film.

Turning to the Fe moments we find strong indications that our heat and diffusion experiments lead to a  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  layer or cluster formation in both samples. Since we obtain  $m_{spin} = -0.028 (+0.11) \mu_B/\text{Fe}$  atom and  $m_{orb} = +0.015 (+0.007) \mu_B/\text{Fe}$  atom at the Fe sites of sample A (sample B) we find very small net contributions to the overall magnetic moments. In comparison Klewe *et al.*<sup>57</sup> found an iron spin moment of around  $0.1 \mu_B/\text{Fe}$  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  $L_{2,3}$ -XMCD spectra of sample A and B with (red) and without (blue) consideration of  $\text{Fe}_{oct}^{2+}$  ions. The resulting lattice site occupancies are 16.3%  $\text{Fe}_{oct}^{2+}$ , 32.2%  $\text{Fe}_{oct}^{3+}$ , 51.5%  $\text{Fe}_{tet}^{3+}$  (42.6%  $\text{Fe}_{oct}^{3+}$ , 57.4%  $\text{Fe}_{tet}^{3+}$ ) for sample A, and 24.0%  $\text{Fe}_{oct}^{2+}$ , 31.5%  $\text{Fe}_{oct}^{3+}$ , 44.5%  $\text{Fe}_{tet}^{3+}$  (55.6%  $\text{Fe}_{oct}^{3+}$ , 44.4%  $\text{Fe}_{tet}^{3+}$ ) for sample B including (not including)  $\text{Fe}_{oct}^{2+}$  ions into the respective fit. The result that for sample A over 50% are in  $\text{Fe}_{tet}^{3+}$  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 *i* (Fig. 8(b)) is very small if  $\text{Fe}_{oct}^{2+}$  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.<sup>44,57,58</sup> In both Fe  $L_{2,3}$ -XMCD spectra of samples A and B peak *i* is significantly smaller than results obtained very recently on  $\text{NiFe}_2\text{O}_4$  thin films grown by pulsed laser deposition (PLD),<sup>44</sup> but somewhat more intense than it is in the result of Klewe *et al.*<sup>57</sup> Also their corresponding multiplet simulation resembles our approach (not considering the  $\text{Fe}_{oct}^{2+}$  sites) rather well. The presence of peak *i* in the Fe  $L_{2,3}$ -XMCD of sample B can at least partly be explained by the lack of  $\text{Ni}_{oct}^{2+}$  ions as to the HAXPES measurements. Since peak *i* also occurs in XMCD experiments on bulk material<sup>58</sup> one can think about several additional reasons about the presence of some  $\text{Fe}_{oct}^{2+}$  ions. For instance, a small fraction of the Ni ions might be present in form of  $\text{Ni}^{3+}$  or coordi-

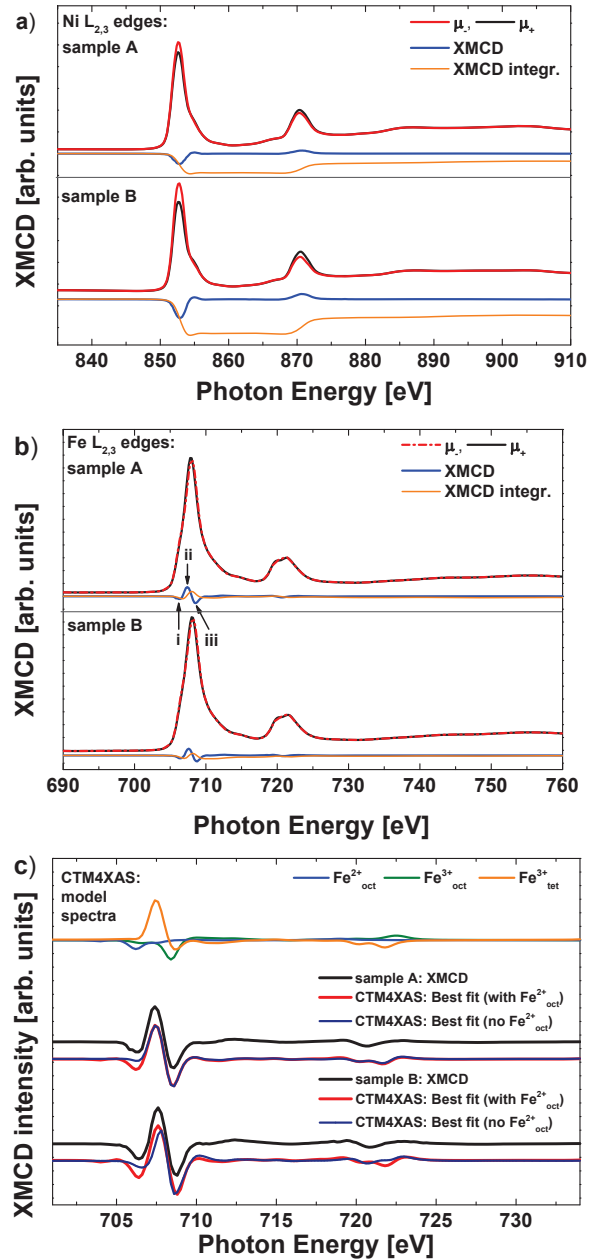


FIG. 8: a) Ni  $L_{2,3}$ -XMCD spectra of samples A and B. b) Fe  $L_{2,3}$ -XMCD spectra of samples A and B. c) Experimental Fe  $L_{2,3}$  edge XMCD of samples A and B and the corresponding XTM4XAS fits with and without consideration of octahedral coordinated  $\text{Fe}^{2+}$  ions present.

nated on tetrahedral sites as result of the interdiffusion process. Despite the fact that  $\text{Ni}^{2+}$  prefers octahedral coordination, even measurements on  $\text{NiFe}_2\text{O}_4$  bulk crystals indicate a few of the Ni ions to be on tetrahedral sites.<sup>58</sup> 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  $L_{2,3}$  and Ni  $L_{2,3}$  resonances

of oxides.<sup>58,59</sup>

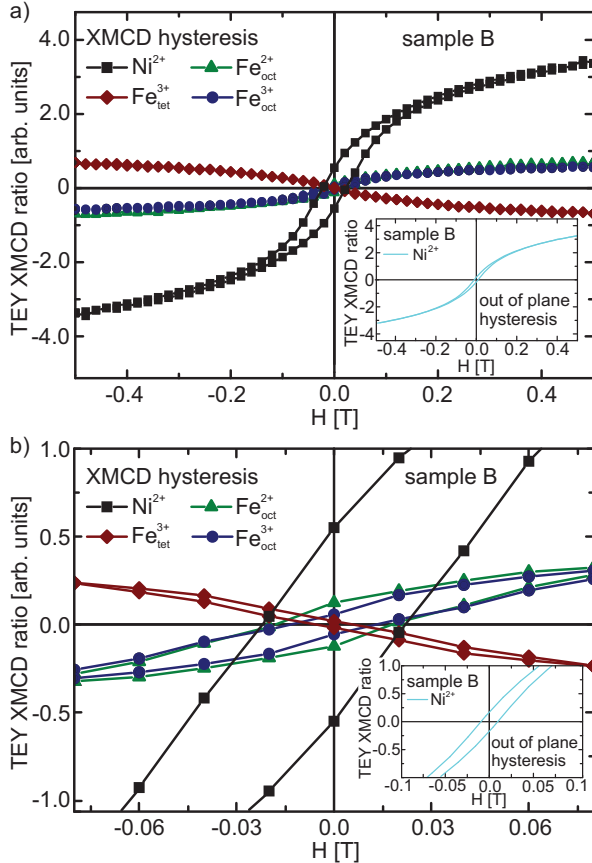


FIG. 9: (a) Element and site specific hysteresis loops of the Ni  $L_{3-}$  and Fe  $L_{3-}$  intensities of sample B. (b) Expanded view of the loops near  $H=0$  T. Insets show the Ni hysteresis loop measured in perpendicular (out of plane) geometry.

For sample B we also recorded element specific hysteresis loops at the Ni  $L_{3-}$  edge and the site specific loops at Fe  $L_{3-}$  resonances for peaks  $i-iii$  (cf. Fig. 8(b)). Fig. 9 displays the resulting magnetization loops. One can see the ferrimagnetic ordering between the  $\text{Fe}_{\text{tet}}^{3+}$  cations and the other Fe and Ni cations. For all octahedrally coordinated cations we probe a in-plane open magnetization curves, whereas the  $\text{Fe}_{\text{tet}}^{3+}$  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  $\text{NiFe}_2\text{O}_4$  thin films,<sup>44,57,60</sup> 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  $\text{NiFe}_2\text{O}_4$  epitaxial thin films<sup>61</sup> and nanoparticles.<sup>62</sup> A number of reasons might be responsible for the observed discrepancy, a strongly increased  $H_c$  might be caused by exchange coupled grains<sup>60</sup> or a high

defect density,<sup>57</sup> for instance. On the other hand, similar values for the coercive field measured here have been found on polycrystalline as well as epitaxial  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  thin films.<sup>61</sup> The bulk value of  $\text{NiFe}_2\text{O}_4$  has been reported to be  $0.01$  T<sup>62</sup> which is closer to the values obtained here.

#### IV. SUMMARY AND CONCLUSIONS

We investigated the modification of the crystallographic, electronic, and magnetic properties of  $\text{Fe}_3\text{O}_4/\text{NiO}$ -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)  $\text{Fe}_3\text{O}_4$  in three steps à 20-30 minutes in an oxygen atmosphere of  $5 \times 10^{-6}$  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  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ . 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  $\text{NiFe}_2\text{O}_4$  ( $a_{\text{NFO}}^{\text{bulk}} = 0.8339$  nm).

These findings are supported by the soft XPS and HAXPES experiments. Firstly, the formation of  $\text{Fe}^{3+}$  upon annealing at  $600^\circ\text{C}$  is confirmed by the shape and binding energy positions of the Fe 2p core level spectra. Further annealing at  $800^\circ\text{C}$  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  $600^\circ\text{C}$  and re-appear after the entire annealing cycle at  $800^\circ\text{C}$ . Due to surface sensitivity soft XPS analysis clearly reveals an occurrence of  $\text{Ni}^{2+}$  in NiO stoichiometry at the surface near region after the last annealing step. Further, HAXPES analysis shows also an increasing amount of  $\text{Ni}^{2+}$  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  $\text{NiFe}_2\text{O}_4$  was formed on top of the residual NiO film after the annealing step of  $600^\circ\text{C}$  as observed in the soft XPS and HAXPES. However, further annealing at  $800^\circ\text{C}$  results in a segregation and formation of NiO on top of a well ordered stoichiometric  $\text{NiFe}_2\text{O}_4$  of high crystalline quality. Thus, the nickel ferrite is saturated by Ni if the ferrite assumes  $\text{NiFe}_2\text{O}_4$  stoichiometry. The residual Ni attempts to form NiO on top of the nickel ferrite due to its lower surface energy compared to the surface energy of nickel ferrite.<sup>53</sup> 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  $\text{Ni}_{0.83}\text{Fe}_{2.17}\text{O}_4$ . 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  $\text{Fe}_{tet}^{3+}$  coordinated cation fraction (around 50%) compared to stoichiometric  $\text{Fe}_3\text{O}_4$ , 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  $\text{Ni}^{2+}$  ions, which exhibit magnetic moments of  $0.56 \mu_B/\text{f.u.}$  (sample A) and  $1.03 \mu_B/\text{f.u.}$  (sample B). The latter value corresponds quite well to the value very recently reported for a stoichiometric  $\text{NiFe}_2\text{O}_4$  thin film.<sup>57</sup> 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  $\text{NiFe}_2\text{O}_4$ -like thin film by means of thermal interdiffusion of  $\text{Ni}^{2+}$  ions into magnetite from  $\text{Fe}_3\text{O}_4/\text{NiO}$  bilayers.

In conclusion we presented a comprehensive study of epitaxially grown  $\text{Fe}_3\text{O}_4/\text{NiO}$  heterostructures and its structural evolution due to Ni interdiffusion as consequence of three distinct thermal annealing steps. A multi-technique approach tackling the structural, chemi-

cal, 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  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  thin films, also with compositions close to stoichiometric  $\text{NiFe}_2\text{O}_4$  with high crystalline quality by thermally induced intermixing of distinct  $\text{Fe}_3\text{O}_4/\text{NiO}$  bilayers grown on Nb-doped  $\text{SrTiO}_3(001)$ . If the initial  $\text{Fe}_3\text{O}_4$  and NiO thin film thicknesses can be controlled precisely one may obtain  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  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<sup>29</sup> and the spin Seebeck effect<sup>27,28</sup>. Thus, additional transport effects based on either charge or spin currents can be amplified or suppressed depending on the band gap properties of the  $\text{NiFe}_2\text{O}_4$ -like material.

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