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## Near - surface electronic structure An x - ray absorption spectroscopy s

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# Near-surface electronic structure in strained Ni-ferrite films: An x-ray absorption spectroscopy study

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## ABSTRACT

We report on the x-ray absorption spectra (XAS) and x-ray magnetic circular dichroism (XMCD) of a series of NiFe<sub>2</sub>O<sub>4</sub> (Ni ferrite) films grown on symmetry matched substrates and measured in two geometries: out-of-plane and near in-plane. The Ni ferrite films, grown by pulsed laser deposition, are epitaxial and the substrates used (ZnGa<sub>2</sub>O<sub>4</sub>, CoGa<sub>2</sub>O<sub>4</sub>, MgGa<sub>2</sub>O<sub>4</sub>, and MgAl<sub>2</sub>O<sub>4</sub>) introduce a systematic variation in the lattice mismatch between the substrate and the film. Modeling of the XAS and XMCD spectra, both measured with the surface sensitive total electron yield mode, indicates that the Ni<sup>2+</sup> cations reside on the octahedrally coordinated lattice sites in the spinel structure. Analyses of the Fe XAS and XMCD spectra are consistent with Fe<sup>3+</sup> cations occupying a subset of the octahedral and tetrahedral sites in the spinel oxide lattice with the addition of a small amount of Fe<sup>2+</sup> located on octahedral sites. The Ni<sup>2+</sup> orbital to spin moment ratio ( $\mu_l/\mu_s$ ), derived from the application of XMCD sum rules, is enhanced for the substrates with a small lattice mismatch relative to NiFe<sub>2</sub>O<sub>4</sub>. The results suggest a path for increasing the orbital moment in NiFe<sub>2</sub>O<sub>4</sub> by applying thin film growth techniques that can maintain a highly strained lattice for the NiFe<sub>2</sub>O<sub>4</sub> film.

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## I. INTRODUCTION

Magnetically ordered insulators with anti-ferromagnetic interactions are of crucial importance to diverse applications including power electronics,<sup>1</sup> active and passive microwave and mm-wave components,<sup>2</sup> spintronic devices,<sup>3,4</sup> and they are also the parent compounds of many classes of high-temperature superconductors.<sup>5</sup> The incorporation of magnetic insulators<sup>6,7</sup> into integrated electronics generally requires either polycrystalline or epitaxial thin films. In the case of epitaxial films, strain imparted by the substrate can have profound effects on the properties of the film.<sup>8–17</sup>

Extremely high strain states have been generated in epitaxial oxide thin films; for perovskite ultrathin films grown on symmetry-matched perovskite substrates, strain states as high as 6% have been realized.<sup>18</sup> Moreover, epitaxial strain in oxide thin films has been exploited to produce higher temperature superconductors;<sup>9</sup> stabilize ferromagnetism;<sup>19,20</sup> activate piezo- and ferroelectricity;<sup>18</sup> modify dielectric constants and optical bandgaps;<sup>21</sup> and drastically alter catalytic activity.<sup>22</sup> As many magnetic insulators based on the spinel structure can also be grown in thin film forms, a natural issue to explore is the role of epitaxial strain on the properties of

10 May 2025 17:15:32

such spinel oxide thin films. Among the broad group of magnetic insulators,<sup>6</sup> spinel ferrites<sup>23–25</sup> are commonly used for applications requiring high-resistivity, low loss performance at high frequencies, and high magnetic permeability. Ni ferrite ( $\text{NiFe}_2\text{O}_4$ )<sup>3,26</sup> is a magnetically soft spinel compound that in the bulk exhibits a Curie temperature over 850 K,<sup>27</sup> high electrical resistivity,<sup>28</sup> large bandgap,<sup>29</sup> and retains a significant magnetization of  $\sim 50$  emu/g, or about  $2.1 \mu_B$  per formula unit.<sup>30–32</sup> In thin film form and when grown on well-lattice matched substrates,  $\text{NiFe}_2\text{O}_4$  is an intriguing spintronic material with very low Gilbert damping,<sup>33</sup> making it attractive for applications that rely on spin transport and magnon propagation.<sup>34,35</sup> Also,  $\text{NiFe}_2\text{O}_4$  is a low cost material with useful catalytic properties.<sup>36,37</sup> Spin transport across interfaces relies on the electronic structure near the surface of the growing  $\text{NiFe}_2\text{O}_4$  film, and similarly catalytic reactions are mediated by the electronic states on the surface. As the electronic structure of materials can be modified significantly by strain,<sup>38,39</sup> it is of considerable importance to explore the electronic states of strained  $\text{NiFe}_2\text{O}_4$  films in the near-surface region.

Spinel oxide compounds have the general formula  $\text{AB}_2\text{O}_4$ . The A cations are divalent while the B cations are trivalent; in *spinel ferrites* the B cations are  $\text{Fe}^{3+}$ . Spinel oxides have a relatively open cubic crystal structure where the  $\text{O}^{2-}$  anions form a fcc lattice, leading to a network of tetrahedrally ( $T_D$ ) and octahedrally ( $O_H$ ) coordinated sites for the cations. The cations in the spinel structure are distributed among one half of the available  $O_H$  sites and one eighth of the  $T_D$  sites. Magnetically, the dominant exchange interaction in spinel compounds is the anti-ferromagnetic exchange between the  $T_D$  and the  $O_H$  sub-lattices, while the  $T_D$ – $T_D$  and  $O_H$ – $O_H$  interactions are ferromagnetic.  $\text{NiFe}_2\text{O}_4$  (or NFO) is an *inverse spinel*, where the  $\text{Fe}^{3+}$  cations are divided equally between the  $O_H$  and  $T_D$  sites, leading to near-complete cancellation of the  $\sim 5 \mu_B$  moment per  $\text{Fe}^{3+}$  cations, while the divalent Ni cations with a moment of  $\sim 2 \mu_B$  reside on the remaining  $O_H$  sub-lattice sites and provide most of the net moment in NFO.

In this article, we report on an x-ray spectroscopic study of NFO films grown on different spinel oxide substrates:  $\text{ZnGa}_2\text{O}_4$  (ZGO),  $\text{CoGa}_2\text{O}_4$  (CGO),  $\text{MgGa}_2\text{O}_4$  (MGO), and  $\text{MgAl}_2\text{O}_4$  (MAO). The selection of different spinel oxide substrates is significant for two main reasons. First, in contrast to films grown on substrates with rocksalt or perovskite lattices, such as MgO or  $\text{SrTiO}_3$ , the similar crystal symmetry between the spinel substrate and NFO film helps reduce defects such as formation of anti-phase boundaries. Second, the four different spinel substrates permit tuning of the lattice mismatch between the film and substrate.

The bulk cubic lattice constant of NFO ( $a_{\text{bulk}}^{\text{NFO}}$ ) has been reported as  $8.345 \text{ \AA}$ <sup>33</sup> and  $8.337 \text{ \AA}$ ,<sup>40</sup> and hence we will refer to the average value of  $8.341 \text{ \AA}$ . ZGO ( $a^{\text{ZGO}} = 8.333 \text{ \AA}$ <sup>40</sup>) is almost perfectly matched with NFO, leading to a lattice mismatch of only 0.10%. At the other extreme, MAO ( $a^{\text{MAO}} = 8.086 \text{ \AA}$ <sup>33</sup>) has a smaller lattice parameter, leading to a much larger lattice mismatch of 3.06%. The CGO ( $a^{\text{CGO}} = 8.328 \text{ \AA}$ ,<sup>33</sup> 0.16%) and MGO ( $a^{\text{MGO}} = 8.280 \text{ \AA}$ ,<sup>33</sup> 0.73%) substrates provide intermediate values of lattice mismatch.

We examined the x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) spectra of the Fe and Ni  $L_{2,3}$  core levels from NFO films grown on the four spinel

substrates. These element-specific x-ray spectroscopies rely on strong dipole allowed  $2p \rightarrow 3d$  electronic transitions and hence provide access to the  $3d$  final states of NFO. In strongly ionic materials, XAS and XMCD are sensitive to crystal fields and can thus be used to investigate symmetry lowering around specific cations in strained films. In this study, XAS and XMCD spectra were all acquired in the total electron yield (TEY) mode. TEY is much more surface sensitive than transmission XAS/XMCD measurements, even when then transmission measurements are acquired in the substrate luminescence yield (LY) mode. XAS/XMCD acquired with TEY, therefore, provide an assessment of the  $3d$  final states of NFO in the near-surface region.

## II. EXPERIMENT

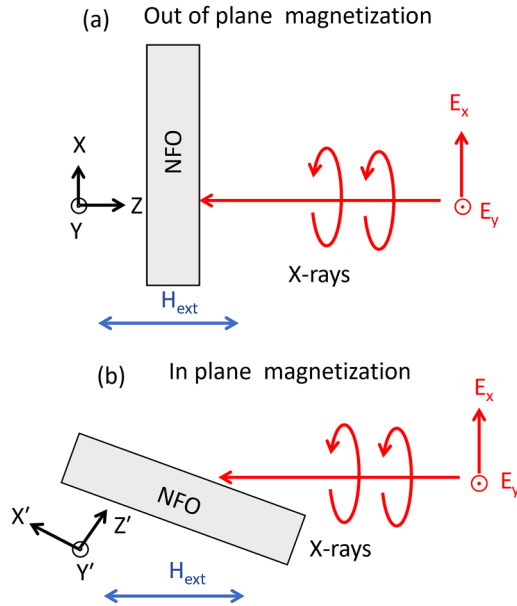
As mentioned, all NFO films are grown on ZGO, CGO, MGO, and MAO substrates and we refer to the resulting films as film\substrate (e.g., NFO\ZGO). All the substrates are spinel oxides and the films are grown using pulsed laser deposition on the [001] oriented surfaces of the spinel oxide substrates. For details on the growth of the films, please refer to Ref. 33. The deposition conditions are selected to promote epitaxial growth of the NFO films with different degrees of strain in the films, although strain relieving defects in the films increase considerably with increasing lattice mismatch between the NFO film and the spinel substrate. The thickness of the NFO films was 74 nm for the NFO\ZGO and NFO\MAO samples and 40 nm for NFO\CGO and NFO\MGO. All samples were uncapped with the exception of NFO\CGO, where a 5 nm platinum (Pt) cap was deposited for magneto-transport measurements (not reported). A summary of the samples studied is provided in Table I.

To probe magnetic configuration and electronic states of the near-surface region of the NFO films, we utilize XAS<sup>41,42</sup> measured in TEY mode. XAS spectra are recorded for the  $L_3$  ( $2p_{3/2}$ ) and  $L_2$  ( $2p_{1/2}$ ) edges of Ni and Fe cations in the NFO samples. In TEY, the sample drain current is recorded as a function of the incident energy of the x-ray photons, resulting in a distribution of primary, Auger, and secondary electrons. In the soft x-ray regime, suitable for the XAS measurements of the  $L_{2,3}$  edges of second row transition metals, the primary electrons have very low kinetic energy and are not capable of exciting a large number of secondary electrons. The TEY signal is dominated by very low energy secondary electrons generated by multiple inelastic scattering of Auger electrons. As these low energy electrons have a low probability of traveling to

TABLE I. Summary of samples studied.

Substrate	Lattice mismatch (%)	Film thickness (nm)	Cap ?
$\text{ZnGa}_2\text{O}_4$ (ZGO)	0.10	74	No
$\text{CoGa}_2\text{O}_4$ (CGO)	0.16	40	Yes (Pt—5 nm)
$\text{MgGa}_2\text{O}_4$ (MGO)	0.73	40	No
$\text{MgAl}_2\text{O}_4$ (MAO)	3.06	74	No

10 May 2025 17:15:32



**FIG. 1.** Schematic of the experimental setup for (a) out-of-plane (OOP, normal incidence) and (b) in-plane (IP, 70° off-normal incidence) configuration. Circularly polarized x rays are incident upon the sample. In (a) the electric field vectors ( $E_x$  and  $E_y$ ) of the x rays are parallel to the sample plane. In (b), the sample is rotated by 70° and  $E_y$  remains parallel to the sample plane but  $E_x$  will mainly have a component along the sample normal. The magnetic field ( $H_{\text{ext}}$ ) of  $\pm 3$  T is applied along the x-ray beam direction in both experimental geometries.

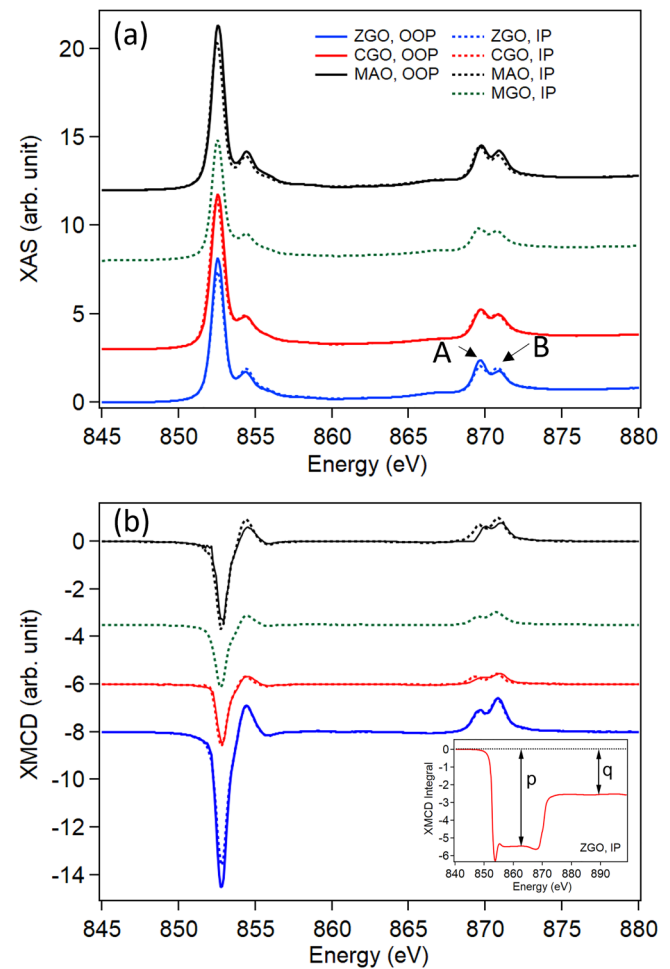
the surface and escaping the sample, the TEY mean probing depth is only a few nm from the surface of the thin film.<sup>43</sup>

Most of the XAS spectra in this paper were measured at the PM2-VEKMAG beamline at the BESSY-II synchrotron of the Helmholtz-Zentrum, Berlin, Germany. The measurements were performed at two different configurations (Fig. 1). For the out-of-plane (OOP) configuration, the sample was oriented with the film normal direction parallel to the photon Poynting vector and a saturating magnetic field ( $H_{\text{ext}}$ ) of  $\pm 3$  T was applied in a direction parallel to the x-ray propagation direction. For the in-plane (IP) geometry, the sample was rotated by 70° while the magnetic field direction was unchanged (Fig. 1). The field was therefore predominantly in-plane. At the PM2-VEKMAG beamline, the incident soft x-ray beam had a fixed polarization of 77% RCP and XMCD<sup>44,45</sup> spectra were generated by recording an XAS spectra and then reversing the polarity of the magnetic field from +3 to −3 T. This experimental configuration was used for the OOP and IP TEY XAS measurements for the NFO//ZGO, NFO//CGO, and NFO//MAO films. For the NFO//MGO sample, only IP measurements in the TEY mode were recorded at beam line 4.0.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA. The NFO//MGO sample was oriented at an angle of 45° away from the x-ray Poynting vector and saturating field of  $\pm 1$  T was applied parallel to the sample surface. All spectra presented were acquired at room temperature.

### III. RESULTS AND DISCUSSIONS

In Figs. 2(a) and 2(b), the Ni XAS and XMCD spectra are shown for both the in-plane (dotted lines) and out-of-plane (solid lines) configurations. The XAS spectra contain two parts. The  $L_3$  edge ( $2p_{3/2}$  level) between  $\approx 850$ –857 eV is dominated by a main peak at about 852.6 eV followed by a well-defined but weaker peak at 854.3 eV. In contrast, the  $L_2$  edge ( $2p_{1/2}$ ) is comprised of two peaks, which we label “A” and “B,” with roughly similar intensities. The Ni XAS and XMCD spectra are consistent for all the samples and also with previously published Ni-spectra for ferrites.<sup>46–48</sup> For NFO//MGO, only in-plane spectra were acquired.

The Ni  $L_{2,3}$  spectra are generally similar to one another. To assess small differences in the spectra, we calculate the normalized



**FIG. 2.** (a) Polarization averaged XAS spectra of the Ni  $L_{2,3}$  edges for both the IP and OOP configurations. (b) XMCD scans of the Ni  $L_{2,3}$  edges. An offset in the vertical axis is added to the spectra for clarity. The IP and OOP spectra are shown by dotted and solid lines, respectively. The primary peaks at the  $L_2$  edge are labeled by “A” and “B.” The XMCD integral for the ZGO, IP sample is shown in the inset of (b).

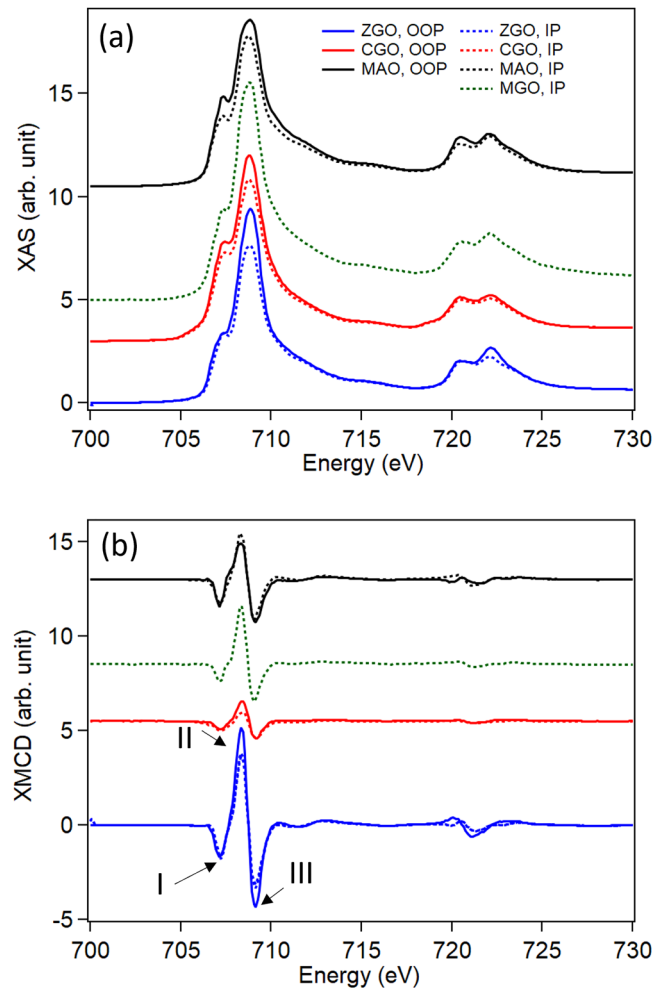
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XAS intensity difference at Ni  $L_3$  edge,  $\Delta R = (I_{OOP} - I_{IP})/I_{OOP}$  for the NFO//ZGO and NFO//MAO samples and we have observed that the intensity difference is around 9.0% and 9.4% for the ZGO and MAO substrates, respectively. Saturation effects originating from the variation in effective electron escape depth relative to the photon penetration depth can be amplified at high angles of incidence,<sup>49</sup> and such effects can lead to variations in the XAS intensity on the order of the observed variations for NFO//ZGO and NFO//MAO. Hence, the relative similarity of  $\Delta R$  for the ZGO and MAO substrates may contain contributions from both intrinsic effects, originating from changes in the electronic structure of the  $\text{NiFe}_2\text{O}_4$  films on the different substrates, and extrinsic effects originating from spectral saturation. Turning to the  $L_2$  region of the spectra, in all cases, peak A has a larger intensity than peak B. For the case of the NFO//MGO and NFO//CGO films, changing from an IP to an OOP geometry produces little difference in the ratio of the A and B peaks. We note that the Pt cap on the NFO//CGO sample may suppress variations between the IP and OOP geometries because of the saturation effects noted above. However, for the NFO//ZGO, the A and B peaks become almost equal in intensity for the IP alignment; in other words, the intensity of peak B has increased relative to peak A.

The shape of the XMCD spectra also shows a high degree of similarity between the different samples and measurement geometries. The spectra are characterized by a dominant negative feature at the  $L_3$  edge coinciding with the main  $L_3$  peak in the XAS spectra; in contrast, the secondary  $L_3$  XAS peak at 854.3 eV generates a positive feature in the XMCD spectra. At the  $L_2$  edge, the sign of the XMCD signal is positive for both the A and B peaks for all samples and measurement conditions. However, in the dichroism spectrum, the B peak is generally higher in intensity than the A peak. In general, we conclude that the overall shape of the  $\text{Ni}^{2+}$  XMCD spectra is consistent with earlier reports for  $\text{NiFe}_2\text{O}_4$ ,<sup>46–48</sup> and to a first approximation the spectra are insensitive to the lattice mismatch of the  $\text{NiFe}_2\text{O}_4$  with the substrate. However, the integrated intensity distribution between the  $L_3$  and  $L_2$  edges displays subtle shifts, as discussed below. In the inset of Fig. 2(b), we show the integrated XMCD spectrum of ZGO, IP, where we also indicate the “p” and “q” parameters<sup>45</sup> which are used to calculate the orbital to spin angular momentum ( $\mu_\ell/\mu_s$ ) in Fig. 5.

Figures 3(a) and 3(b) present the XAS and XMCD spectra for the Fe  $L_3$  ( $\approx 705$ – $712$  eV) and  $L_2$  ( $\approx 719$ – $723$  eV) edge for the IP and OOP configuration. The  $L_3$  edge is characterized by two main spectral features: a weaker peak at  $\sim 707.3$  eV and the dominant  $L_3$  peak  $\sim 708.8$  eV. In some cases, the weaker peak at  $\sim 707$  eV appears as more of a shoulder on the main  $L_3$  feature. In prior reports,<sup>46</sup> this weaker feature has been associated with a small contribution from  $\text{Fe}^{2+}$  cations which may be introduced in the sample via oxygen vacancies and other defects. As is the case with the Ni spectra, the Fe  $L_2$  features are comprised of two primary features. Among the different samples, the Fe XAS spectra at the  $L_3$  edge has a larger amplitude for out-of-plane configuration with respect to the in-plane one for NFO//ZGO, NFO//CGO, and NFO//MAO.

For the XMCD spectrum of the Fe  $L_3$  edge, the normalized XMCD exhibits a distinctive negative/positive/negative structure [labeled I, II, III in Fig. 3(b)], which was also previously observed



**FIG. 3.** (a) Polarization averaged XAS spectra of the Fe  $L_{2,3}$  edges for both the IP and OOP configurations. (b) XMCD scans of the Fe  $L_{2,3}$  edges. An offset in the vertical axis is added to the spectra for clarity. The IP and OOP spectra are shown by dotted and solid lines, respectively. The primary spectral features of the Fe  $L_3$  edge are marked by “I,” “II,” and “III.”

for other spinel ferrites.<sup>23,46,50</sup> The lowest energy negative feature I is most likely a contribution from a small amount of  $\text{Fe}^{2+}$  originating from defect states.<sup>51</sup> XMCD spectral features II and III are associated with  $\text{Fe}^{3+}$  cations on  $T_d$  and  $O_h$  sites, respectively. The opposite signs of the two features, and the dominant negative feature on the octahedrally-coordinated  $\text{Ni}^{2+}$  XMCD spectra, confirms that cations on the  $O_h$  and  $T_d$  site are coupled antiferromagnetically. In all the XMCD spectra, the intensity of feature I is smaller compared to the intensity of both features II and III. For NFO//ZGO, the out-of-plane intensity is larger compared to the in-plane intensity for II and III. For NFO//MAO, the Fe XMCD features I and III have the nearly the same amplitude for both IP and OOP configuration whereas feature B has a larger

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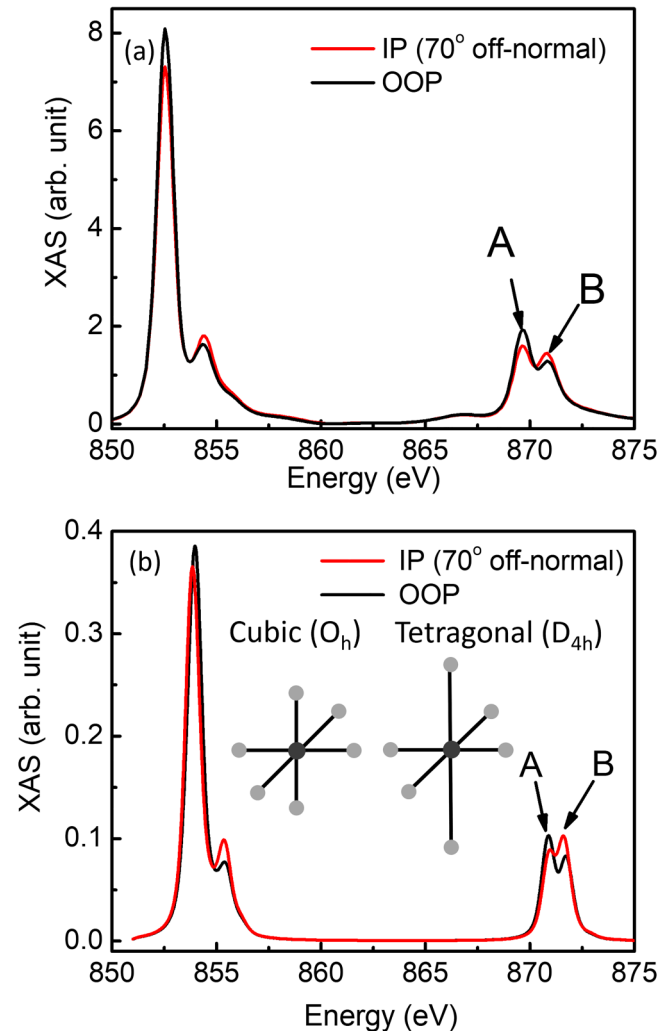


intensity for the IP spectra than the OOP one. Overall, however, the overlapping spectral features from the diverse Fe cations found in many spinel ferrites, complicates the detailed analysis of the Fe spectra.

To get a qualitative insight into the electronic states of the  $\text{NiFe}_2\text{O}_4$ , we model the Ni XAS spectra using the CTM4XAS (charge transfer multiplet for XAS) software package<sup>52</sup> for both the IP and OOP configurations. The charge transfer multiplet approach is well suited to ionic compounds such as  $\text{NiFe}_2\text{O}_4$  where localized excitations of core-level electrons lead to atomic-like spectra dominated by dipole-allowed transitions between different angular momenta states which are then modified by crystal field and charge transfer effects. To generate the model Ni spectra, the atomic Slater integrals  $F_{dd}$ ,  $F_{pd}$ , and  $G_{gd}$  are reduced by a factor of 0.7 for all three integrals. The spin-orbit coupling is reduced by 0.977 from atomic values for the core states and is left unchanged for the valence level final states. Lifetime and instrumental broadening effects are included by convolving the individual delta function-like multiplet spectra with Lorentzian and Gaussian distributions of 0.2 eV each. The parent symmetry of the  $\text{Ni}^{2+}$  spectra is  $O_h$ , reflecting the lattice site occupation of the Ni cations and we set the cubic crystal field ( $10Dq$ ) parameter to 1.0 eV. For certain spectra, we simulate the effects of a tetragonal distortion of the cubic  $\text{NiFe}_2\text{O}_4$  unit cell by reducing the symmetry of the calculations from  $O_h$  (cubic) to  $D_{4h}$ ; this is implemented by setting the  $D_s$  and  $D_t$  parameters to non-zero values.

In Fig. 4(a), we present the Ni  $L_{2,3}$  XAS spectra for the IP and OOP conditions acquired from the NFO//ZGO sample. This sample has the lowest lattice mismatch between the  $\text{NiFe}_2\text{O}_4$  film and the spinel oxide substrate. We focus on the  $L_2$  edge and note that for the OOP configuration (black trace), the peak labeled A has a much higher intensity than peak B. For the IP condition (red trace), the intensity of peak A is reduced while peak B's intensity increases. The two spectral features are nearly equal in intensity for the IP condition. In Fig. 4(b), we present model calculations for the IP and OOP conditions. For purely cubic symmetry, a change in the ratio of peak A to peak B can only be realized by assuming extremely large and unphysical values of  $10Dq$ . However, by reducing the symmetry to  $D_{4h}$ , realized by setting the  $D_s$  value to 0.05 eV, a clear reduction of A/B intensity ratio is realized. We therefore conclude that there may be a small amount of tetragonal distortion in the  $\text{NiFe}_2\text{O}_4$  epitaxial film even for substrates with low lattice mismatch (0.10% in the case of NFO//ZGO).

Finally, we return to the experimental XMCD spectra for Ni and use the XMCD sum rules to calculate the ratio of the orbital to spin angular momentum ( $\mu_\ell/\mu_s$ ) from the integral of the XMCD spectra.<sup>45</sup> In Fig. 5, we present these ratios as a function of the lattice mismatch between the  $\text{NiFe}_2\text{O}_4$  film and the different spinel oxide substrates. While the data set is sparse as there are not that many single crystal spinel oxide substrates available with the appropriate unit cell size, an interesting relationship is suggested by the data. For the systems with relatively low lattice mismatch (NFO//ZGO and NFO//CGO) there is little difference between  $\mu_\ell/\mu_s$  measured in the IP or OOP configurations; no conclusions can be drawn for the NFO//MGO sample as only IP data were collected. For the NFO//ZGO system, which has a very low lattice mismatch of 0.10%,  $\mu_\ell/\mu_s$  is about 0.15–0.16, and this ratio seems

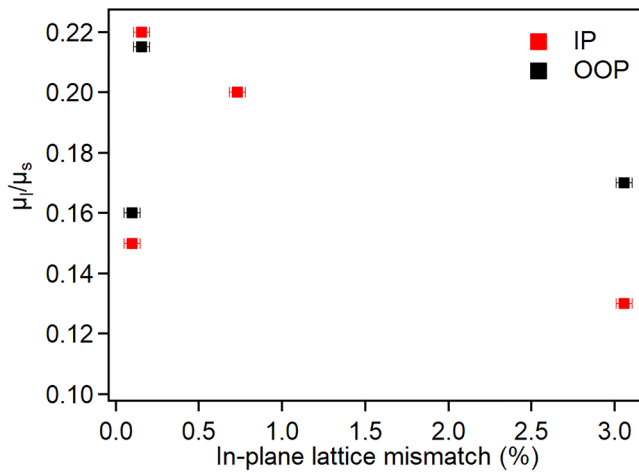


**FIG. 4.** (a) Experimental XAS spectra for the Ni  $L_{2,3}$  edges (predominantly  $\text{Ni}^{2+}$ ) for the NFO//ZGO sample. Both IP and OOP configurations are presented at  $H_{\text{ext}} = 3$  T. (b) Simulated XAS spectra from a charge transfer multiplet model; crystal field parameters are  $10Dq = 1.0$  eV and  $D_s = 0.05$  eV. The primary peaks on the  $L_2$  core level are marked by "A" and "B."

to grow to 0.20–0.22 for NFO//CGO and NFO//MGO samples with slightly higher lattice mismatch.

For the NFO//MAO system with a large lattice mismatch of 3.06%, there is a relatively large split in  $\mu_\ell/\mu_s$  for IP ( $\mu_\ell/\mu_s \simeq 0.13$ ) and OOP (0.17). The average value between the two configurations is about 0.15 and is quite close to  $\mu_\ell/\mu_s$  for NFO//ZGO, the sample with the lowest amount of lattice mismatch. However, the NFO//MAO film is relatively thick (74 nm) and a large number of anti-phase boundaries and other strain-relaxing defects have been reported in this sample.<sup>33</sup> The near-surface region of the 74 nm thick film, which is the portion of the film sampled by the XAS measured with TEY, is relaxed close to the bulk  $\text{NiFe}_2\text{O}_4$  lattice

10 May 2025 17:15:32



**FIG. 5.** Orbital to spin magnetic moment ratio ( $\mu_L/\mu_S$ ) for Ni obtained from the experiment as a function of lattice mismatch for both IP and OOP configurations. Low values of lattice mismatch, where the NFO film is coherently strained, result in an enhanced  $\mu_L/\mu_S$ . The horizontal error bars account for differences in the reported values of the bulk NFO lattice parameter.<sup>33,40</sup>

parameter. In other words, the near-surface region of the NFO\MAO film is in a strain state similar to bulk  $\text{NiFe}_2\text{O}_4$ . Under such conditions, the electronic states sampled by XAS in TEY mode for the NFO\MAO and NFO\ZGO films are similar.

#### IV. CONCLUSIONS

We report on the Fe and Ni  $L_{2,3}$  XAS and XMCD spectra for  $\text{NiFe}_2\text{O}_4$  samples grown on different substrates, namely,  $\text{ZnGa}_2\text{O}_4$ ,  $\text{CoGa}_2\text{O}_4$ ,  $\text{MgGa}_2\text{O}_4$ , and  $\text{MgAl}_2\text{O}_4$ . These substrates share the same spinel symmetry as the  $\text{NiFe}_2\text{O}_4$  films but provide a different degree of lattice mismatch between the film and substrate. The Fe  $L_3$  XMCD spectra exhibit a negative/positive/negative structure, similar to other spinel ferrites, and the significant amplitude of the lowest energy negative XMCD feature may indicate the presence of  $\text{Fe}^{2+}$  cations in the samples, possibly introduced by oxygen vacancies in the films. The Ni XAS spectra are generally similar across all samples and measurement geometry. The Ni  $L_2$  edge is characterized by a two-peak structure and there is a trend of a reduction of the low energy peak (peak A) to high energy peak (B) intensity ratio when the XAS is measured at more glancing incidence (IP configuration). Our CTM4XAS modeling qualitatively reproduced this trend in the Ni  $L_2$  edge XAS spectra and suggests there may be a small tetragonal distortion in the system even for very low values of lattice mismatch.

Finally, we report on the Ni  $\mu_L/\mu_S$  for the different samples and measurement conditions. While the data set is sparse, there is a trend to a larger  $\mu_L/\mu_S$  with increasing lattice mismatch. However, this increase is not apparent in samples with large (3.06%) lattice mismatch. As the NFO\MAO film with the large lattice mismatch was relatively thick, this suggests an intriguing possibility. The density of strain relieving defects such as misfit dislocations

increases above some critical thickness and it may be feasible to stabilize highly strained films in very thin  $\text{NiFe}_2\text{O}_4$  films, similar to the strategy employed to realize unusually high strain states of over 6% in perovskite on perovskite thin films.<sup>18</sup> This may open up a route to achieve very high orbital moments in  $\text{NiFe}_2\text{O}_4$  and related compounds by growing very thin films to maintain the desired strain state. Combining such highly strained, but low defect density, films with the low damping already realized in thicker  $\text{NiFe}_2\text{O}_4$  films,<sup>33,40</sup> may be a useful path for making further use of orbital angular momentum in spintronic and magnonic applications.

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#### AUTHOR DECLARATIONS

##### Conflict of Interest

The authors have no conflicts to disclose.

#### Author Contributions

**S. Saha:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **R. Knut:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **A. Gupta:** Investigation (equal); Resources (equal). **F. Radu:** Data curation (supporting); Investigation (equal); Resources (supporting); Writing – review & editing (equal). **C. Luo:** Data curation (equal); Investigation (equal); Resources (equal); Writing – review & editing (equal). **O. Karis:** Conceptualization (equal); Writing – review & editing (equal). **D. A. Arena:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Supervision (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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10 May 2025 17:15:32