

## Magnetic Dichroism and Spin Structure of Antiferromagnetic NiO(001) Films

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We find that Ni  $L_2$  edge x-ray magnetic linear dichroism is fully reversed for NiO(001) films on materials with reversed lattice mismatch. We relate this phenomenon to a preferential stabilization of magnetic  $S$  domains with main spin component either in or out of the plane, via dipolar interactions. This suggests a way to selectively control spin structures in  $3d$  systems with small spin-orbit coupling.

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Many forefront magnetic devices and applications are based on the exchange bias effect, i.e., the breaking of time reversal symmetry and the onset of unidirectional magnetic anisotropy in a field-cooled antiferromagnet-ferromagnet (AF-F) system [1]. Examples are domain stabilizers in magnetoresistive recording heads, novel permanent magnets, and spin-valve and magnetic tunnel junctions for nonvolatile magnetic memory cells [2,3]. A general theory of exchange bias, necessary to optimize performances and develop new devices, is still lacking. However, it is by now widely accepted that the key to understanding this intriguing phenomenon is the AF spin structure [1], and, in particular, the dynamical changes thereof over deep layers of the AF far away from the AF-F interface [4–13]. Nevertheless, the effective role of the AF spin structure remains unclear due to the great difficulty to experimentally unravel and control complex AF domain patterns, which constitute one of the main obstacles to a full understanding of the exchange bias. These difficulties have been recently overcome using magnetic linear dichroism (MLD) in linearly polarized soft x-ray absorption spectroscopy (XAS). MLD, in fact, directly probes local moments and spin anisotropy in AF by measuring the difference between the absorption coefficient across a core threshold for different angles between the light polarization and the sample crystallographic axes [14–18], and provides a source of magnetic contrast

with chemical and surface sensitivity [19–24]. Using the Ni  $L_2$  MLD effect, magnetic domains have been imaged at NiO(001) surfaces [19–21] and spin orientations have been directly observed at the interface of NiO(001) with Co [22] and Fe [23], as well as in other AF-F interfaces [24]. In particular, Zhu *et al.* [10] used Ni  $L_2$  MLD to show that the onset of exchange bias in NiO/Co<sub>84</sub>Fe<sub>16</sub> bilayers is accompanied by a preferential repopulation of NiO AF domains with in-plane main spin component, which was proposed as the key step in the exchange bias process. Moreover, they suggested that the magnitude of the exchange bias field is proportional to the availability of AF domains with main spin component parallel to the AF-F interface [10].

Here we show that the Ni  $L_2$  MLD is fully reversed for NiO(001) films close to materials with reversed lattice mismatch, and we relate this phenomenon to a preferential stabilization of AF  $S$  domains with main spin component either in or out of the interface plane, via dipolar interactions in a tetragonally distorted NiO lattice. This suggests a way to selectively control the spin structure of  $3d$  systems with small spin-orbit coupling, to design AF-F layers useful to test exchange bias theories [10], and to combine high exchange bias fields [10] to the technologically appealing properties of NiO such as high blocking temperature, corrosion resistance, and chemical stability [12,13].

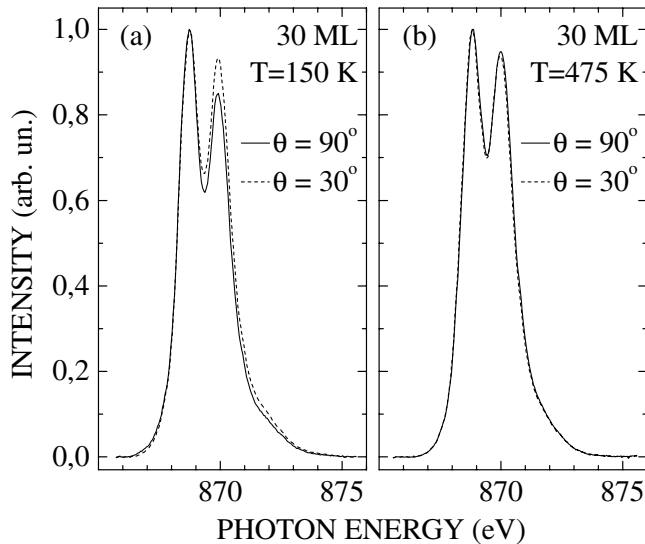


FIG. 1. Polarization and temperature dependent Ni  $L_2$  edge of 10 ML MgO(001)/30 ML NiO(001)/Ag(001) film.  $\theta$  is the angle between light polarization and surface normal.

Epitaxial NiO(001) films were prepared by NO<sub>2</sub> assisted molecular beam epitaxy on a Ag(001) single crystal held at 455 K [25]. Immediately after the growth, the NiO(001) films were *in situ* capped with an epitaxial MgO(001) layer 10 monolayers (ML) thick, and next stored in a dry atmosphere. Low (LEED) and reflection high energy (RHEED) electron diffraction showed that both capped and noncapped NiO(001)/Ag(001) films have a rock-salt ( $1 \times 1$ ) termination [25]. Periodic RHEED intensity oscillations demonstrated the layer-by-layer growth mode and provided an accurate thickness calibration procedure [25,26]. The MLD experiments were performed at the Superesca beam line of the Elettra Synchrotron Light Source in Italy (Fig. 1) and at the Dragon beam line of the National Synchrotron Radiation Research Center in Taiwan (Figs. 2 and 3). Temperature and polarization dependent XAS spectra were recorded in total electron yield mode (TEY), with the electric field vector making angles  $\theta$  of 15°, 30°, and 90° with the NiO(001) surface normal. Reproducibility was accurately verified by repeatedly measuring the XAS spectra in sequential temperature cycles.

Figure 1 shows the polarization and temperature dependent Ni  $L_2$  spectra of a 10 ML MgO(001)/30 ML NiO(001)/Ag(001) film, for clarity normalized to one at the low energy peak. The spectra are similar to those reported by Alders *et al.* [16] for a noncapped 20 ML NiO(001)/MgO(001) film. Well below the bulk NiO Néel temperature ( $T_N = 520$  K) the  $L_2$  ratio, i.e., the  $L_2$  low to high energy peak intensity ratio, decreases with  $\theta$ , while approaching  $T_N$  the MLD effect, taken as the change of the  $L_2$  ratio with the angle  $\theta$ , vanishes. At  $T = 475$  K the  $L_2$  ratio is 1.06 for both  $\theta = 30^\circ$  and  $\theta = 90^\circ$  [Fig. 1(b)], in excellent agreement with the value of 1.056 reported

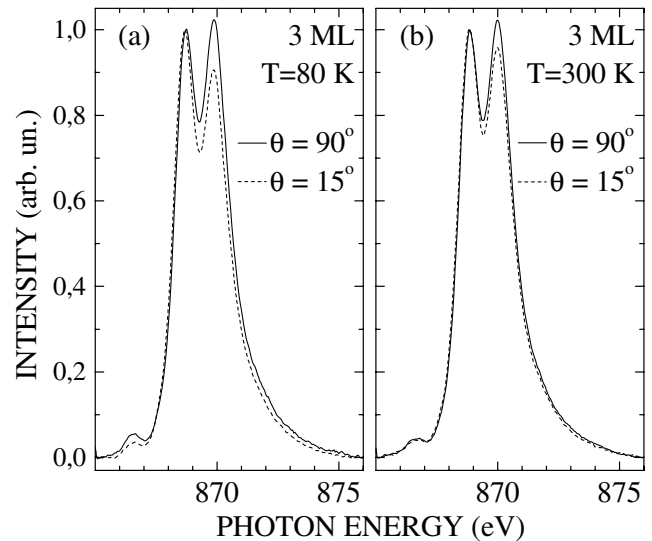


FIG. 2. Polarization and temperature dependent Ni  $L_2$  edge of 10 ML MgO(001)/3 ML NiO(001)/Ag(001) film.  $\theta$  is the angle between light polarization and surface normal.

by Alders *et al.* [16] for the same conditions. At  $T = 150$  K, however, the  $L_2$  ratio is 1.071 and 1.176 for  $\theta = 30^\circ$  and  $\theta = 90^\circ$  [Fig. 1(a)], respectively, giving a *positive* MLD effect of +8.9%, while for the same angles at  $T = 195$  K Alders *et al.* [16] report values of 0.879 and 1.283, respectively, i.e., a MLD of +31.5%.

Figure 2 shows the polarization and temperature dependent Ni  $L_2$  spectra of a 10 ML MgO(001)/3 ML NiO(001)/Ag(001) film. Surprisingly, these spectra exhibit a dramatic inversion of the dichroism, as compared to those of Fig. 1. At  $T = 80$  K [Fig. 2(a)], the  $L_2$  ratio is 1.103 and 0.977 for  $\theta = 15^\circ$  and  $\theta = 90^\circ$ , respectively, giving a *negative* dichroism of  $-12.9\%$ . At

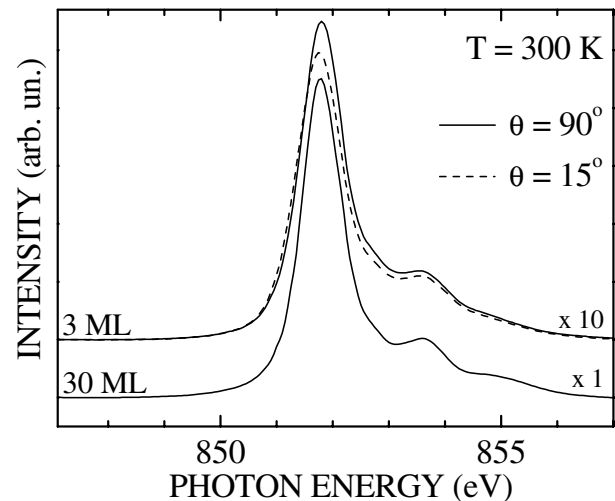


FIG. 3. Polarization dependent Ni  $L_3$  edge of 10 ML MgO(001)/3 ML NiO(001)/Ag(001), and  $\theta = 90^\circ$  Ni  $L_3$  edge of 10 ML MgO(001)/30 ML NiO(001)/Ag(001), at  $T = 300$  K.

$T = 300$  K [Fig. 2(b)], the dichroism is still negative, and is also still large ( $-6.7\%$ ), very likely because the Néel temperature of the thin NiO(001)/Ag(001) film is substantially higher than 300 K [26], or, as discussed below, because of a crystal field effect. However, the absolute magnitude of the dichroism is reduced by almost a factor of 2 upon going from 80 to 300 K.

In general, dichroism effects in linearly polarized XAS spectroscopy are determined not only by local exchange fields and magnetic moments, but also by the local crystal field symmetry [14–18]. Therefore, the observed dichroism inversion might in principle be a result of the symmetry changes accompanying the transition from a three-dimensional to a two-dimensional system taking place when the NiO film thickness is reduced from 30 ML down to 3 ML. In fact, Haverkort and Tjeng [17] have very recently shown that a strong inversion of the Ni  $L_2$  dichroism occurs in 10 ML MgO(001)/1 ML NiO(001)/Ag(001) due to a final state effect connected with the lifting of the degeneracy of the  $e_g$  and  $t_{2g}$  orbitals in  $D_{4h}$  symmetry. Moreover, they find that the  $O_h$  to  $D_{4h}$  symmetry transition introduces also a strong polarization dependence in the Ni  $L_3$  spectra of the NiO(001) monolayer, showing up as a shift as large as 0.4 eV of the  $L_3$  white line main peak with the angle  $\theta$  [17].

Figure 3 shows the polarization dependent Ni  $L_3$  edge of a 10 ML MgO(001)/3 ML NiO(001)/Ag(001) film at  $T = 300$  K (top curves). These spectra have the same line shape as that of a 10 ML MgO(001)/30 ML NiO(001)/Ag(001) film (bottom curve). However, a 0.1 eV shift of the Ni  $L_3$  main peak is clearly visible comparing the  $\theta = 15^\circ$  and  $\theta = 90^\circ$  spectra of the 3 ML film. This shift indicates that the average  $\text{Ni}^{2+}$  local symmetry is significantly different from  $O_h$ , and, therefore, the crystal field contribution to the Ni  $L_{23}$  line shape of the 3 ML film is not negligible [17]. Nevertheless, even for a pure  $D_{4h}$  symmetry, the crystal field does not split the ground state, and, consequently, does not introduce any temperature dependence in the Ni  $L_2$  dichroism [17]. Therefore, the strong temperature dependence of the Ni  $L_2$  shown in Fig. 2 demonstrates that at least half of the dichroism of the 3 ML film at  $T = 80$  K is a genuine MLD effect due to local exchange fields and magnetic moments [14–17].

Exchange interactions affect the XAS spectra line shape in two ways. First, they split up the ground state and the excited states into Zeeman sublevels. The transitions from the ground state manifold to the dipole allowed final states manifold are strongly polarization dependent and, due to the finite temperature statistical occupation of the sublevels, they are also temperature dependent [14–16]. Second, an exchange field introduces off-diagonal matrix elements between various multiplets in the final state yielding a transfer of spectral weight [16] which is also temperature dependent, since the local exchange field is a thermally averaged mean field quan-

tity. The latter effect provides a direct way of measuring the local exchange field in the final state of XAS excited with isotropic light [16]. However, it is a much smaller effect than the former, which provides instead a straightforward way to measure the *direction* of the local magnetic moments and the strength of the local exchange field in the ground state, using polarization and temperature dependent XAS [14–16]. For NiO, in particular, a general expression was derived which directly relates the Ni  $L_2$  ratio to the angle between the Ni easy spin direction and the light polarization [16]. Using this relation, it was shown that in epitaxial NiO(001)/MgO(001) films the eight magnetic domains with main spin component perpendicular to the interface ( $S_\perp$  domains), i.e., those along the  $[\pm 1 \pm 1 \pm 2]$  directions, are preferentially stabilized over the 16 domains with main component parallel to the interface ( $S_\parallel$  domains), i.e., those along the  $[\pm 1 \pm 2 \pm 1]$ ,  $[\pm 2 \pm 1 \pm 1]$ , directions, yielding a net *positive* MLD effect. Applying the same analysis to the magnetic component of the 3 ML film dichroism (Fig. 2) we then reach the conclusion that in epitaxial NiO(001)/Ag(001) thin films a preferential stabilization occurs which favors instead magnetic domains with main spin component parallel to the interface ( $S_\parallel$ ).

For a deeper understanding of these experimental results, we have calculated the dipolar energies in a uniformly strained AF NiO lattice [27]. In bulk AF NiO, exchange-striction induced rhombohedral contractions of the rock-salt crystal structure along  $\langle 111 \rangle$  directions yield a large dipolar uniaxial anisotropy which constrains the spin to align ferromagnetically within  $\{111\}$  and antiferromagnetically between neighboring  $\{111\}$  planes [28]. Spin-orbit coupling, single-ion anisotropy, and nonclassical dipolar interactions introduce a  $10^{-3}$  times smaller anisotropy which constrains the spin direction within the  $\{111\}$  plane to point along the  $\langle 11-2 \rangle$  threefold set of axis [29,30]. The resulting magnetic domain pattern has the spin pointing along each of the 24 directions indicated above. We performed first-order perturbation theory [27] using as unperturbed magnetic states the eigenvectors of the bulk AF NiO dipolar Hamiltonian, and as a perturbation a dipolar Hamiltonian which explicitly includes a uniform tetragonal strain  $\varepsilon = (c/a) - 1$ , with  $c$  and  $a$  as the lattice parameters along  $[001]$  and  $[010]$ , respectively. We find that the inclusion of a tetragonal strain into a bulk AF NiO lattice lifts the spin direction degeneracy and preferentially stabilizes  $S_\perp$  domains, for  $\varepsilon < 0$  (compression), and  $S_\parallel$  domains, for  $\varepsilon > 0$  (expansion). A similar result is obtained for uniformly strained AF films. In the latter case, however, the finite thickness  $\tau$  (number of monolayers) introduces an additional perturbation to the dipolar anisotropy, similar to the well-known shape anisotropy of FM thin films, and a set of critical values  $\{\varepsilon, \tau\}$  is found for  $\varepsilon = (1.34 - 1.67\tau)^{-1}$ , which separates regimes in which either  $S_\perp$  or  $S_\parallel$  domains are preferentially stabilized.

Our simple dipolar model does not include single-ion anisotropy nor the presence of a gradient of strain in the sandwiched NiO film. Therefore, it provides only a rough quantitative estimate of the critical  $\{\varepsilon, \tau\}$  values. Nevertheless, based on the above results, it is easy to understand why differently unbalanced magnetic domain populations are obtained in tetragonally compressed NiO(001)/MgO(001) [31] and tetragonally stretched NiO(001)/Ag(001) films [32] ( $a_{mgo} = 4.212 \text{ \AA} > a_{nio} = 4.176 \text{ \AA} > a_{ag} = 4.086 \text{ \AA}$ ).

Moreover, our model may naturally explain the discrepancy between the Ni  $L_2$  ratios measured on 10 ML MgO(001)/30 ML NiO(001)/Ag(001) [Fig. 1(a)] and 20 ML NiO(001)/MgO(001) [16] films. The critical thickness for lattice relaxation is  $\approx 100$  ML and 20 ML for NiO films on MgO(001) [31] and Ag(001) [32], respectively. Therefore, while the 20 ML NiO(001)/MgO(001) film has a predominantly  $S_{\perp}$  domain occupation and a positive MLD effect [16], the 10 ML MgO(001)/30 ML NiO(001)/Ag(001) might have an occupation of mainly  $S_{\parallel}$  within the first 20 ML from the NiO(001)/Ag(001) interface and mainly  $S_{\perp}$  in the outermost layers closer to the MgO(001)/NiO(001) interface, so that the net MLD effect is positive, due to the high surface sensitivity of the TEY detection mode [33], but has a strongly reduced magnitude compared to the 20 ML NiO(001)/MgO(001) film. Above  $T_N$  the long range magnetic order and the MLD effect are lost, and the Ni  $L_2$  ratio of the NiO films on both MgO(001) and Ag(001) converges exactly to the same value [Fig. 1(b)].

The magnetic anisotropy of  $3d$  oxides is determined by dipolar fields and by the coupling of spin, orbital, and lattice degrees of freedom, via  $\mathbf{l}\cdot\mathbf{s}$  spin-orbit interactions. The latter are negligible in compounds with an orbital singlet atomic ground state, such as MnO. However, since  $\mathbf{l}\cdot\mathbf{s}$  does not have matrix elements coupling the  $e_g$  states with each other, spin-orbit coupling is negligible also in NiO and other compounds having a ground state  $3d$  occupation with totally filled  $t_{2g}$  and incomplete  $e_g$  orbitals, so that also in these compounds the magnetic anisotropy is strongly dominated by dipolar interactions. Therefore, our experimental results for NiO(001) films on Ag(001) and MgO(001), together with the results of our model calculations, suggest that the influence of the lattice strain on the magnetic anisotropy should be a general effect for  $3d$  systems in which spin-orbit coupling is small compared to dipolar interactions. Nevertheless, in compounds such as FeO and CoO spin-orbit coupling will split up the partly filled  $t_{2g}$  orbitals and greatly influence the magnetic anisotropy, while the dipolar interactions and the changes thereof due to lattice distortions here should play a minor role.

In summary, we found that the Ni  $L_2$  MLD is fully reversed for NiO(001) films close to materials with reversed lattice mismatch, and we related this phenomenon to a preferential stabilization of AF  $S$  domains with main

spin component either in or out of the interface plane, via dipolar interactions in the strained lattices. This is expected to be a general effect for  $3d$  systems with small spin-orbit coupling, and suggests a way to design AF-F layers with selectively controlled spin structures of particular relevance in the field of exchange bias.

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