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Magnetic versus crystal-field linear dichroism in NiO thin films

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We have detected strong dichroism in the Ni $L_{2,3}$ x-ray absorption spectra of a monolayer NiO film. The dichroic signal appears to be very similar to the magnetic linear dichroism observed for thicker antiferromagnetic NiO films. Detailed analysis reveals, however, that the dichroism is caused by crystal-field effects in the monolayer film, which is a nontrivial effect because the high spin Ni $3d^8$ ground state is not split by low-symmetry crystal fields. We present a practical method for identifying the independent magnetic and crystal-field contributions to the linear dichroic signal in spectra of NiO films with arbitrary thicknesses and lattice strains. Our findings are also relevant for $3d^5$ and $3d^3$ systems such as $LaFeO_3$, Fe_2O_3, VO, $LaCrO_3$, Cr_2O_3, and Mn^{4+} thin films.

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Magnetic linear dichroism (MLD) in soft-x-ray absorption spectroscopy (XAS) has recently developed into a powerful tool to study the magnetic properties of antiferromagnetic thin films.[1–5] The contrast one obtains as a result of differences in the magnitude and orientation of local moments is essential to determine the spin anisotropy and parameters like the Néel temperature (T_N), as well as to map out spatially the different magnetic domains that are present in antiferromagnetic films.[6–14] Such information is valuable for the research and application of magnetic devices using exchange bias.

Much of the modern MLD work has been focused on NiO and $LaFeO_3$ thin films, and the observed dichroism has been attributed entirely to magnetic effects.[6–14] Other sources that could contribute to linear dichroism, however, such as crystal fields of lower than octahedral symmetry, have been neglected or not considered. Indeed, one would expect that such low-symmetry crystal fields are negligible for bulk-like NiO and $LaFeO_3$ films, and, more fundamentally, that such crystal fields will not split the high-spin Ni $3d^8$ or Fe $3d^5$ ground state. We have illustrated this insensitivity in Fig. 1 for the Ni^{2+} case, where the energy level diagram in an O_h environment is compared to that in a D_{4h} point group symmetry.[15] In contrast, an exchange field will split the Ni^{2+} ground state into three levels with $M_S=-1,0,1$ with an energy separation given by the exchange coupling J; see Fig. 1. The basis for obtaining strong dichroism in the Ni $L_{2,3}$ ($2p \rightarrow 3d$) absorption spectra is that dipole selection rules dictate which of the quite different final states can be reached and with what probability for each of the initial states. The isotropic spectrum of each of these three states will be the same, but each state with a different $|M_S|$ value will have a different polarization dependence.[1–5] A completely analogous argumentation can be given for the orbitally highly symmetric high spin $3d^5$ and $3d^3$ cases, e.g., Mn^{2+}, Fe^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}.

In this paper we report on XAS measurements on monolayer (ML) NiO films which are grown on a Ag(100) substrate and capped by a 10 ML MgO(100) film. We have observed strong linear dichroism in the Ni $L_{2,3}$ spectra, similar to that measured for thicker NiO films. From a detailed analysis, however, we discovered that the dichroism cannot be attributed to the presence of some form of magnetic order, but entirely to crystal-field effects. The analysis provides us also with a practical guide of how to disentangle the individual contributions to the linear dichroic signal, i.e., the contribution from magnetic interactions versus that from low-symmetry crystal fields. This is important for a reliable determination of, for instance, the spin moment orientation in NiO as well as $LaFeO_3$, Fe_2O_3, VO, $LaCrO_3$, Cr_2O_3, and Mn^{4+} manganate ultra thin films, surfaces and strained films, where the low-symmetry crystal-field splittings may not be negligible as compared to the exchange field energies.

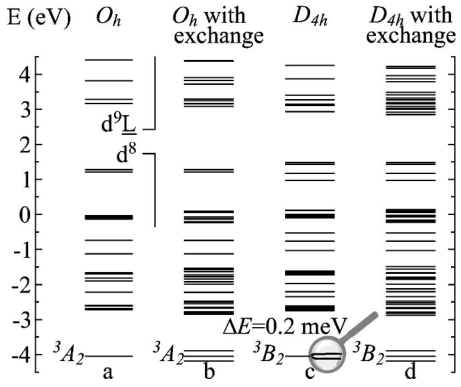

FIG. 1. Energy level diagram for Ni^{2+} ($3d^8$) in: (a) O_h symmetry with $pd\sigma=-1.29$ and $10Dq=0.85$ eV; (b) O_h symmetry with additional exchange field of 0.16 eV; (c) D_{4h} symmetry with $pd\sigma=-1.29$, $10Dq=0.85$, and $Ds=0.12$ eV; (d) D_{4h} symmetry with additional exchange. The $3d$ spin–orbit interaction is included, but the states are labeled as if the spin–orbit interaction was not present.

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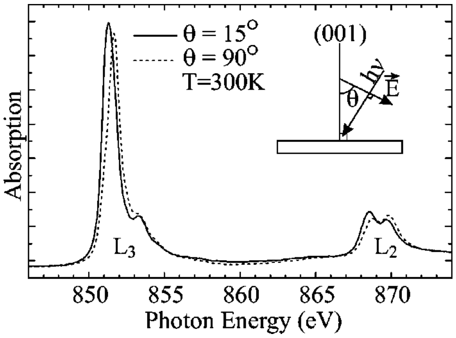

FIG. 2. Experimental polarization dependent Ni $L_{2,3}$ XAS of 1 ML NiO(100) on Ag(100) covered with MgO(100). θ is the angle between the light polarization vector and the (001) surface normal ($\theta = 90°$ means normal light incidence).

The polarization-dependent XAS measurements were performed at the Dragon beamline of the NSRRC in Taiwan. The spectra were recorded using the total electron yield method in an XAS chamber with a base pressure of 3×10^{-10} mbar. The photon energy resolution at the Ni $L_{2,3}$ edges ($h\nu \approx 850$–880 eV) was set at 0.3 eV, and the degree of linear polarization was $\approx 98\%$. A NiO single crystal is measured *simultaneously* in a separate chamber upstream of the XAS chamber in order to obtain a relative energy reference with an accuracy of better than 0.02 eV. The 1 ML NiO film on Ag(100) was prepared in Groningen, by using NO_2 assisted molecular beam epitaxy. Immediately after the NiO growth, the sample was capped *in situ* with an epitaxial 10 ML MgO(100) film. Reflection high-energy electron diffraction (RHEED) intensity oscillations recorded during growth of thicker films demonstrated the layer-by-layer growth mode and provided an accurate thickness calibration.[16,17]

Figure 2 shows the polarization-dependent Ni $L_{2,3}$ XAS spectra of the 1 ML NiO film, taken at room temperature. The angle between the light polarization vector and the (001) surface normal is given by θ ($\theta = 90°$ means normal light incidence). The general line shape of the spectra is very similar to that of thicker NiO films and bulk NiO.[5]

Figure 3 presents a close-up of the L_2 edge, the region most often used to measure the magnitude of the magnetic linear dichroic effect in antiferromagnetic NiO films.[6–8,11–14] The spectra of the 1 ML NiO film show a very clear polarization dependence. This linear dichroic effect is as strong as that for a 20 ML NiO film grown on MgO(100) (taken from Alders *et al.*[5]), albeit with an opposite sign, as can be seen from Fig. 3. Relying on the analysis by Alders *et al.*[5] for the antiferromagnetic 20 ML film, one may be tempted to conclude directly that the spin orientation in the 1 ML film is quite different from that of the 20 ML film, i.e., that the spins for the 1 ML would be lying more parallel to the interface while those of the thicker films are pointing more along the interface normal. However, Alders *et al.*[5] have also shown that the magnetic ordering temperature of NiO films decreases strongly if the film is made thinner. In fact, for a 5 ML NiO film on MgO(100), it was found that T_N is around or below room temperature, i.e., that no linear dichroism can be observed at room temperature. A simple extrapolation will therefore suggest that 1 ML NiO will not be magnetically ordered at room temperature. This is in fact supported by the 80 K data of the 1 ML NiO on Ag(100) as shown in Figs. 3 and 4: the spectra and the dichroism therein are identical to those at 300 K, indicating that T_N must be at least lower than 80 K.

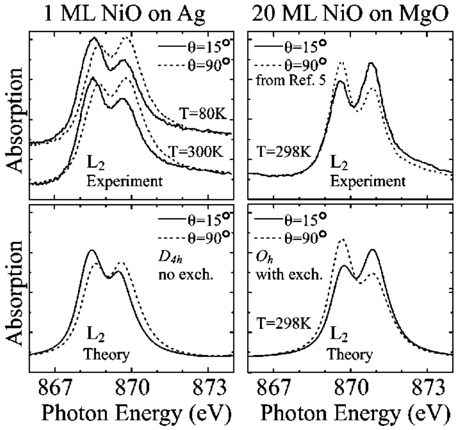

FIG. 3. Polarization dependence of the Ni L_2 XAS of 1 ML NiO on Ag(100) covered by MgO(100). The 20 ML NiO on MgO spectra are taken from Ref. 5. The theoretical spectra for the 1 ML NiO are calculated in D_{4h} symmetry without exchange, and for the 20 ML in O_h with exchange.

In order to resolve the origin of the linear dichroism in the 1 ML NiO system, we now resort to the Ni L_3 part of the spectrum. A close-up of this region is given in Fig. 4. We can easily observe that the strong polarization dependence of the spectra is accompanied by an energy shift ΔE of 0.35 eV in the main peak of the L_3 white line. This shift seems small compared to the 852 eV photon energy being used, but it is very reproducible and well detectable since the photon energy calibration is done with an accuracy of better than 0.02 eV thanks to the simultaneous measurement of a NiO single crystal reference. We now take this energy shift as an indicator for the presence and strength of local crystal fields with a symmetry lower than O_h, i.e., crystal fields that do not split the ground state but do alter the energies of the XAS final states, and, via second-order processes, also causes spectral weight to be transferred between the various peaks as we will show below.

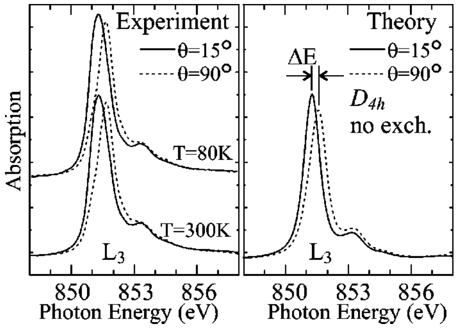

FIG. 4. Experimental and theoretical polarization dependence of the Ni L_3-XAS of a 1 ML NiO(100) on Ag(100) covered with MgO(100). The theoretical spectra are calculated in D_{4h} symmetry without exchange.

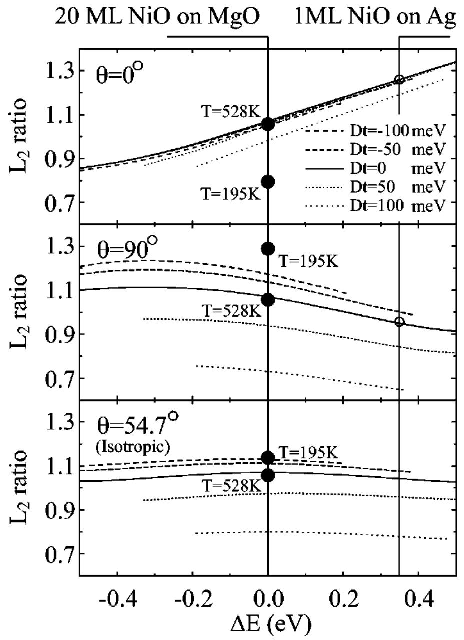

FIG. 5. Calculated ratio of the two peaks in the L_2 edge as a function of ΔE, which is the shift in energy of the L_3 main peak in going from grazing ($\theta = 0°$) to normal ($\theta = 90°$) incidence of the linearly polarized light. The L_2 ratio is calculated for $\theta = 90°$, $\theta = 0°$, and for the isotropic spectrum.

To understand the Ni $L_{2,3}$ spectra quantitatively, we perform calculations for the atomic $2p^6 3d^8 \rightarrow 2p^5 3d^9$ transitions using a similar method as described by Alders *et al.*,[5] but now in a D_{4h} point-group symmetry and including hybridization. The method uses the full atomic multiplet theory and includes the effects of the solid. It accounts for the intra-atomic $3d$–$3d$ and $2p$–$3d$ Coulomb and exchange interactions, the atomic $2p$ and $3d$ spin–orbit couplings, the O $2p$–Ni $3d$ hybridization with $pd\sigma = -1.29$ eV, and an O_h crystal-field splitting of $10Dq = 0.85$ eV. The local symmetry for the Ni ion sandwiched between the Ag(100) substrate and the MgO(100) film is in principle C_{4v}, but for d electrons one can ignore the odd part of the crystal field, so that effectively one can use the tetragonal D_{4h} point-group symmetry. As we will explain below, the D_{4h} parameters Ds and Dt (Ref. 18) are set to 0.12 and 0.00 eV, respectively, and the exchange field (acting on spins only) to zero. The calculations have been carried out using the XTLS 8.0 program.[19]

The right panel of Fig. 4 shows the calculated L_3 spectrum for the light polarization vector perpendicular and parallel to the C_4 axis ($\theta = 90°$ and $\theta = 15°$, respectively). One can clearly see that the major experimental features are well reproduced, including the 0.35 eV energy shift between the two polarizations. This shift can be understood in a single electron picture. The ground state has the $\underline{3d}_{x^2-y^2} 3d_{z^2}$ configuration, where the underline denotes a hole. The final state has a $2p^5 \underline{3d}_{x^2-y^2}$ or $2p^5 \underline{3d}_{z^2}$ configuration. For z polarized light the $3d_{z^2}$ state can be reached, but the $3d_{x^2-y^2}$ cannot, and the final state will be of the form $2p^5 \underline{3d}_{x^2-y^2}$. For x polarized light the final state will be of the form $2p^5 \underline{3d}_{z^2-y^2} = \sqrt{3/4}(2p^5 \underline{3d}_{z^2}) + \sqrt{1/4}(2p^5 \underline{3d}_{x^2-y^2})$. In a pure ionic picture, the $2p^5 \underline{3d}_{x^2-y^2}$ state will be $4Ds + 5Dt$ lower in energy than the $2p^5 \underline{3d}_{z^2}$ state. In the presence of the O $2p$–Ni $3d$ hybridization, we find that $Ds = 0.12$ and $Dt = 0.00$ eV reproduce the observed 0.35 eV shift.

Going back to the L_2 edge, we can see in Fig. 3 that the calculations can also reproduce very well the observed linear dichroism in the 1 ML NiO spectra. In fact, one now could also see the same 0.35 eV shift at this edge, although it is not as clear as in the L_3 edge. We would like to stress here that the good agreement has been achieved without the inclusion of an exchange splitting, i.e., the dichroism is solely due to the low-symmetry crystal-field splitting. It is a final state effect and the change in the ratio between the two peaks of the L_2 edge as a function of polarization can be understood as follows. In O_h symmetry the first peak is due to two final states, one of T_2' and one of E_1' symmetry. The second peak is due to a final state of T_1' symmetry. All three states have the $2p^5 \underline{3d}_{e_g}$ configuration. If one reduces the crystal field to D_{4h} symmetry the peaks will split. The T_2' state will split into two states of B_2' and E_1' symmetry, the E_1' into A_1' and B_1', and the T_1' into A_2' and E_1'. The energy splitting can be measured, but this is much easier done using the L_3 edge. We note that each of the two peaks in the L_2 edge will have a state of E_1' symmetry, so that these two will mix and transfer spectral weight. This can be seen with isotropic light, but will show up more pronounced as a linear dichroic effect if polarized light is used.

In contrast to the 1 ML NiO case, the good agreement between theory and experiment for the polarization dependent spectra of a 20 ML NiO film[5] have been achieved by assuming the presence of an antiferromagnetic order with an exchange field of about 0.16 eV in a pure local O_h symmetry. It is surprising and also disturbing that a low-symmetry crystal field could induce a spectral weight transfer between the two peaks of the L_2 white line such that the resulting linear dichroism appears to be very similar as a dichroism of magnetic origin. It is obvious that the ratio between the two peaks cannot be taken as a direct measure of the spin orientation or magnitude of the exchange field in NiO films[5] if one has not first established what the crystal-field contribution could be.

We now can identify two strategies for finding out which part of the linear dichroism is due to low-symmetry crystal-field effects. The first one is to study the temperature dependence as we have done above. Here, we have made use of the fact that those crystal fields do not split the high-spin ground state, so that there are no additional states to be occupied with different temperatures other than those already created by the presence of exchange fields. Thus, there should not be any temperature dependence in the crystal-field dichroism. The linear dichroism due to magnetism, however, is temperature dependent and scales with $\langle M^2 \rangle$. By going to temperatures high enough such that there is no longer any temperature dependence in the linear dichroism, i.e., when all magnetic ordering has been destroyed, one will find the pure crystal-field-induced dichroism.

The second strategy to determine the low-symmetry crystal-field contribution is to measure carefully the energy shift ΔE in the main peak of the Ni L_3 white line for $\theta=0°$ vs $\theta=90°$. We now calculate the ratio between the two peaks of the Ni L_2 edge as a function of ΔE, and the results are plotted in Fig. 5 for $\theta=90°$, $\theta=0°$, and $\theta=54.7°$ (isotropic spectrum). Since ΔE is a function of Ds and Dt combined, we have carried out the calculations with Ds as a running variable for several fixed values of Dt, and plotted the resulting L_2 ratios vs ΔE. We now can use Fig. 5 as a road map to determine how much of the linear dichroism in the Ni L_2 edge is due to crystal-field effects and how much due to magnetism. We can see directly that the 1 ML data lie on curves with the same Dt, meaning that the measured L_2 ratios are entirely due to crystal fields. The same can also be said for the 20 ML NiO on MgO at 528 K, which is not surprising since this temperature is above T_N. However, for the 20 ML NiO at 195 K, one can see that the data points do not lie on one of the Dt curves (one may look for larger Dt curves, but this results in line shapes very different from experiment) or let alone on curves with the same Dt, indicating that one needs magnetism to explain the L_2 ratios. In other words, knowing the L_2 ratio and ΔE together allows us to determine the magnitude of the exchange interaction and the orientation of the spin moments. It is best to use the $\theta=0°$ spectra, since here the L_2 ratio is determined almost by ΔE alone and is not too sensitive to the individual values of Ds and Dt.

To conclude, we have observed strong linear dichroism in the 1 ML NiO on Ag, very similar to the well-known magnetic linear dichroism found for bulk-like antiferromagnetic NiO films. The dichroism in the 1 ML, however, cannot be attributed to the presence of some form of magnetic order, but entirely to crystal-field effects. We provide a detailed analysis and a practical guide of how to disentangle quantitatively the magnetic from the crystal-field contributions to the dichroic signal.

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