Controlling Orbital Moment and Spin Orientation in CoO Layers by Strain


1Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
2H. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, 50937 Köln, Germany
3Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan
4Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan
5National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30077, Taiwan

(Received 8 November 2004; published 28 October 2005)

We have observed that CoO films grown on different substrates show dramatic differences in their magnetic properties. Using polarization dependent x-ray absorption spectroscopy at the Co L2,3 edges, we revealed that the magnitude and orientation of the magnetic moments strongly depend on the strain in the films induced by the substrate. We present a quantitative model to explain how strain together with the spin-orbit interaction determine the 3d orbital occupation, the magnetic anisotropy, as well as the spin and orbital contributions to the magnetic moments. Control over the sign and direction of the strain may, therefore, open new opportunities for applications in the field of exchange bias in multilayered magnetic films.

DOI: 10.1103/PhysRevLett.95.187205 PACS numbers: 75.25.+z, 71.70.–d, 75.70.–i, 78.70.Dm

The discovery of the exchange bias phenomenon in surface-oxidized cobalt particles about 50 years ago [1] marks the beginning of a new research field in magnetism. Since then, several combinations of antiferromagnetic (AFM) and ferromagnetic (FM) thin film materials have been fabricated and investigated [2,3], motivated by the potential for applications in information technology. Numerous theoretical [4–8] and experimental [9–14] studies have been devoted to unravel the mechanism(s) responsible for exchange biasing. However, no conclusive picture has emerged yet. A major part of the problem lies in the fact that there is insufficient information available concerning the atomic and magnetic structure of the crucial interface between the AFM and FM material. The important issue of, for instance, spin reorientations in the AFM films close to the interface is hardly considered [15–19], and the role of epitaxial strain herein has not been discussed at all.

In this paper, we study the magnetic properties of CoO thin films epitaxially grown on MnO(100) and on Ag(100), as model systems for an AFM material under either tensile or compressive in-plane stress. Our objective is to establish how the magnetic anisotropy as well as the spin and orbital contributions to the magnetic moments depend on the lowering of the local crystal field symmetry by epitaxial strain. Using polarization dependent x-ray absorption spectroscopy (XAS) at the Co L2,3 (2p → 3d) edges, we observe that the magnitude and orientation of the magnetic moments in the CoO/MnO(100) system are very different from those in CoO/Ag(100). We present a quantitative model to calculate how local crystal fields together with the spin-orbit interaction determine the magnetic properties.

The actual compositions of the CoO/MnO(100) and CoO/Ag(100) systems are (14 Å)MnO/(10 Å)CoO/(100 Å)MnO/Ag(001) and (90 Å)CoO/Ag(001), respectively. The two samples were grown by molecular beam epitaxy (MBE), evaporating elemental Mn and Co from alumina crucibles in a pure oxygen atmosphere of 10−7 to 10−6 mbar. The base pressure of the MBE system is in the low 10−10 mbar range. The thickness and epitaxial quality of the films are monitored by reflection high energy electron diffraction measurements. With the lattice constant of bulk Ag (4.09 Å) being smaller than that of bulk CoO (4.26 Å) and MnO (4.44 Å), we find from x-ray diffraction that CoO on Ag is slightly compressed in-plane ($a_\parallel = 4.235$ Å, $a_\perp = 4.285$ Å) and from reflection high energy electron diffraction that CoO sandwiched by MnO is about 4% expanded in-plane ($a_\parallel = 4.424$ Å). The sandwich structure was used to maximize the CoO thickness with full in-plane strain. Details about the growth will be published elsewhere [20].

The XAS measurements were performed at the Dragon beam line of the National Synchrotron Radiation Center (NSRRC) in Taiwan using in situ MBE grown samples. The spectra were recorded using the total electron yield method in a chamber with a base pressure of 3 × 10−10 mbar. The photon energy resolution at the Co L2,3 edges ($h\nu = 770–800$ eV) was set at 0.3 eV, and the degree of linear polarization was $\approx 98\%$. The sample was tilted with respect to the incoming beam, so that the Poynting vector of the light makes an angle of $\alpha = 70^\circ$ with respect to the [001] surface normal. To change the polarization, the sample was rotated around the Poynting vector axis as depicted in Fig. 1, and $\theta$, the angle between the electric field vector $\vec{E}$ and the [001] surface normal, can be varied between 20° and 90°. This measurement geometry allows for an optical path of the incoming beam which is independent of $\theta$, guaranteeing a reliable comparison of the spectral line shapes as a function of $\theta$. A CoO single crystal is measured simultaneously in a separate chamber to obtain...
a relative energy reference with an accuracy of better than 0.02 eV.

Figure 2 shows the polarization dependent Co $L_{2,3}$ XAS spectra of the CoO/MnO(100) (left panels) and CoO/Ag(100) (right panels) systems, taken at temperatures both far below (top panels) and far above (bottom panels) the Néel temperature of the CoO thin film, which is about 290 K for CoO/MnO(100) and 310 K for CoO/Ag(100) as we will show below. The angle $\theta$ between the electric field vector $\vec{E}$ and the [001] surface normal is varied between 20° and 90°. The spectra have been corrected for electron yield saturation effects [21]. The general line shape of the spectra shows the characteristic features similar to that of bulk CoO [22], ensuring the good quality of our CoO films. Very striking in the spectra is the clear polarization dependence, which is stronger at 77 K than at 400 K. Important also is that the polarization dependence of the CoO/MnO(100) system is opposite to that of the CoO/Ag(100): For instance, the intensity of the first peak at $h\nu = 777$ eV is always higher for $\theta = 20^\circ$ than for $\theta = 90^\circ$ in CoO/MnO(100), while it is always smaller in CoO/Ag(100).

In order to resolve the origin of the polarization dependence in the CoO spectra, we have investigated the temperature dependence in more detail. Figure 3(a) depicts the polarization contrast of the peak at $h\nu = 777$ eV, defined as the difference divided by the sum of the peak height in the spectra taken with the $\theta = 20^\circ$ and $\theta = 90^\circ$ polarizations. One can clearly see a significant temperature dependence for both systems, and a closer look also reveals the presence of a kink at about 290 K for CoO/MnO(100) and 310 K for CoO/Ag(100), which can be associated with the Néel temperatures of the CoO thin films as we will show below. We therefore infer that at high temperatures the polarization contrast is caused solely by crystal field effects and that at low temperatures the magnetism must also contribute to the contrast. In other words, we are observing crystal field induced linear dichroism at high temperatures and a combination of crystal field induced and magnetic linear dichroism at low temperatures. Important is to note that the opposite sign in the dichroism for the CoO/MnO(100) and CoO/Ag(100) systems implies that the orientation of the magnetic moments is perpendicular and the sign of the crystal field splittings is opposite in the two systems.

To analyze the Co $L_{2,3}$ spectra quantitatively, we perform calculations for the atomiclike $2p^63d^7 \rightarrow 2p^53d^8$ transitions using a similar method as described by Alders et al. [23] but now in a $D_{4h}$ point group symmetry and including covalency. The method uses a Co$_6$ cluster which includes the full atomic multiplet theory and the local effects of the solid [22,24]. It accounts for the intratomic $3d$-$3d$ and $2p$-$3d$ Coulomb and exchange interac-

![FIG. 1](image1.png)

FIG. 1. Experimental XAS geometry, with polarization of the light in the horizontal plane. $\theta$ is the angle between the electric field vector $\vec{E}$ and the [001] surface normal, and $\alpha$ is the tilt between the Poynting vector and the surface normal.

![FIG. 2](image2.png)

FIG. 2 (color online). Experimental and calculated Co $L_{2,3}$ XAS spectra of (left panel) CoO in (14 Å)MnO/(10 Å)CoO/(100 Å)MnO/Ag(001) at $\theta = 20^\circ$ and $\theta = 90^\circ$, far below (top panel, $T = 77$ K) and far above (bottom panel, $T = 400$ K) the Néel temperature of the CoO thin film; (right panel) the same for CoO in (90 Å)CoO/Ag(001).
FIG. 3. Temperature dependence of the polarization contrast in the Co L\(2,3\) spectra: (a) peak contrast, defined as the difference divided by the sum of the intensity, integrated over the entire L\(2,3\) range. Solid and empty circles are the experimental data. The solid lines are the theoretical simulations.

The results of the calculations are shown in Fig. 2. We have used the parameters already known for bulk CoO [24,25] and have to tune only the parameters for \(D_S\), \(D_t\), and the direction of the exchange field. For the CoO/MnO(100) system, we find an excellent simulation of the experimental spectra for \(D_S = -40\) meV, \(D_t = -13\) meV, and an exchange field parallel to the [001] surface normal. For the CoO/Ag(100) system, we obtained the best fit for \(D_S = 13\) meV, \(D_t = 4\) meV, and an exchange field perpendicular to the [001] surface normal. These two sets of parameters reproduce extremely well the spectra at all temperatures, as is also demonstrated in Fig. 3(a), showing the excellent agreement between the calculated and measured temperature dependent polarization contrast of the first peak. Most important is obviously the information that can be extracted from these simulations. We find that the magnetic moments in CoO/MnO(100) are oriented out of plane, and, in strong contrast, those in CoO/Ag(100) are in-plane. We also find for CoO/MnO(100) a 2.46\(\mu_B\) spin and 1.36\(\mu_B\) orbital contribution to the 3.82\(\mu_B\) total magnetic moment. By comparison, the numbers for CoO/Ag(100) are smaller: 2.14, 1.00, and 3.14\(\mu_B\), respectively. The crystal field parameters give also a very different splitting in the \(t_{2g}\) levels: about \(-56\) meV for CoO/MnO(100) and +18 meV for CoO/Ag(100), which is fully consistent with our structural data in that the CoO in CoO/MnO(100) experiences a large in-plane expansion (tensile strain) while the CoO in CoO/Ag(100) is only slightly contracted in-plane (compressive strain).

Shape anisotropy cannot explain why the spin of the thinner CoO film, i.e., CoO/MnO(100), is oriented out of plane while that of the thicker film, i.e., CoO/Ag(100), is in-plane. In order to understand intuitively the important interplay between strain and spin-orbit interaction for the magnetic properties of materials with a partially filled 3\(d\) \(t_{2g}\) shell, we will start with describing the energetics of the high spin Co\(^{2+}\) \((3d^7)\) ion in a one-electron-like picture. In \(O_h\) symmetry, the atomic 3\(d\) levels are split into 3 \(t_{2g}\) and 2 \(e_g\) orbitals, so that two holes reside in the spin-down \(e_g\) orbitals and one hole in one of the spin-down \(t_{2g}\). Introducing a tetragonal distortion, in which the \(c\) axis (out of plane) is made different from the \(a\) axis (in-plane), the \(t_{2g}\) levels also become split. In the limit that this splitting is much larger than the spin-orbit interaction, we will find for CoO with \(c/a \ll 1\) that the \(t_{2g}\) hole will occupy a linear combination of \(d_{xy}\) and \(d_{yz}\) orbitals. The spin-orbit interaction will then produce a \(m_l = -1\) state, i.e., a state with an orbital moment of \(1\mu_B\) directed perpendicular to the plane of the film. The spin moment will be also out of plane, since it is coupled via the spin-orbit interaction to the orbital moment. For CoO with \(c/a \gg 1\), we will get a \(t_{2g}\) hole in the \(d_{xy}\) orbital, i.e., a state with a quenched orbital momentum [26]. For the actual CoO/Ag(100) system, we find that \(c/a\) is indeed larger than 1 but only slightly and with a \(t_{2g}\) splitting which is smaller than the spin-orbit interaction. As a result, the orbital moment is not quenched [27]. In fact, it is directed in-plane and, thus, also the spin moment. For the CoO/MnO(100) system, the \(c/a\) is smaller than 1, and the orbital and spin moment are indeed directed out of plane. The size of the orbital moment as calculated in the cluster model is somewhat larger than \(1\mu_B\), but this is merely due to the presence of Coulomb and exchange interactions in the multiplet structure [27,28] not considered in the simple one-electron structure.
calculations reproduce the measured integrated polarizations for the initial state. To illustrate this, let us make the simplification where the parallel with the easy axis (Ag) energy calculated for the film plane is about 4.8 meV. The same single ion anisotropy contributions to the magnetic moments. Control over the sign

\[ E = K_0 + K_1 \sin^2(\eta) + K_2 \sin^4(\eta) \]

where \( n \) denotes the hole number and the subscript the orbital type. For an isotropic orbital occupation, the integrated contrast would be 0 and an extremely stable beam. We thank Lucie Hamdan and Henk Bruiningen for their skillful technical and organizational assistance in preparing the experiment. The research in Cologne is supported by the Deutsche Forschungsgemeinschaft through SFB 608.

[25] Parameters for CoO cluster: \( \Delta = 6.5, U_{dd} = 6.5, U_{dd} = 8.2, p_{d} = -1.2, T_{p} = 0.7, 10Dq = 0.525, \zeta = 0.066, H_{ck} = 0.0126, \) Slater integrals 80% of Hartree Fock values; CoO/MnO(100); \( D_{S} = -0.04, D_{t} = -0.013, \) CoO/(Ag(100)); \( D_{S} = 0.013, D_{t} = 0.004, \) all values in eV.
[27] M. W. Haverkort et al. (to be published).