

Controlling Orbital Moment and Spin Orientation in CoO Layers by Strain

Beamline

11A Dragon beamline

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We have observed that CoO films grown on different substrates show dramatic differences in their magnetic properties. Using the polarization dependent Co- $L_{2,3}$ XAS spectra, we revealed that the magnitude and orientation of the magnetic moments strongly depend on the strain in the films induced by the substrate. We presented 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.

The discovery of the exchange bias phenomenon in surface-oxidized cobalt particles about 50 years ago marks the beginning of a new research field in magnetism. Since then several combinations of anti-ferromagnetic (AFM) and ferromagnetic (FM) thin film materials have been fabricated and investigated, motivated by the potential for applications in information technology. Although numerous theoretical and experimental studies have been devoted to unravel the mechanism responsible for exchange biasing, 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 in the previous works is hardly considered, and the role of epitaxial strain herein has not been discussed at all. In this work 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.

The actual CoO/Ag(100) system consists of 90Å CoO grown on a Ag(100) single crystal surface and the CoO/MnO(100) system is a sandwich of (14Å)MnO/(10Å)CoO/(100Å)MnO/Ag(001) layers. With the lattice constant of bulk Ag (4.09Å) being smaller than that of bulk CoO (4.26Å) and MnO (4.444Å), we find from X-ray diffraction that CoO on Ag is slightly compressed in-plane ($a_{\parallel} \approx 4.235\text{Å}$, $a_{\perp} \approx 4.285\text{Å}$), and from reflection high energy electron diffraction that CoO sandwiched by MnO is about 4% expanded in-plane ($a_{\parallel} \approx 4.424\text{Å}$). The sandwich structure was used to maximize the CoO thickness with full in-plane strain.

Figure 1 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 the former and 310 K for the latter as we will show below. The angle θ between the electric field vector E and the [001] surface normal, is varied between 20° and 90° . Very striking in the spectra is the clear polarization dependence, which is stronger at 77 K than at 400 K. Important is also 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, we have investigated the temperature dependence in more detail. Figure 2a 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. We therefore infer that at high temperatures the polarization contrast are 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 get quantitative information we calculate the Co $L_{2,3}$ spectra with the well-proved configuration

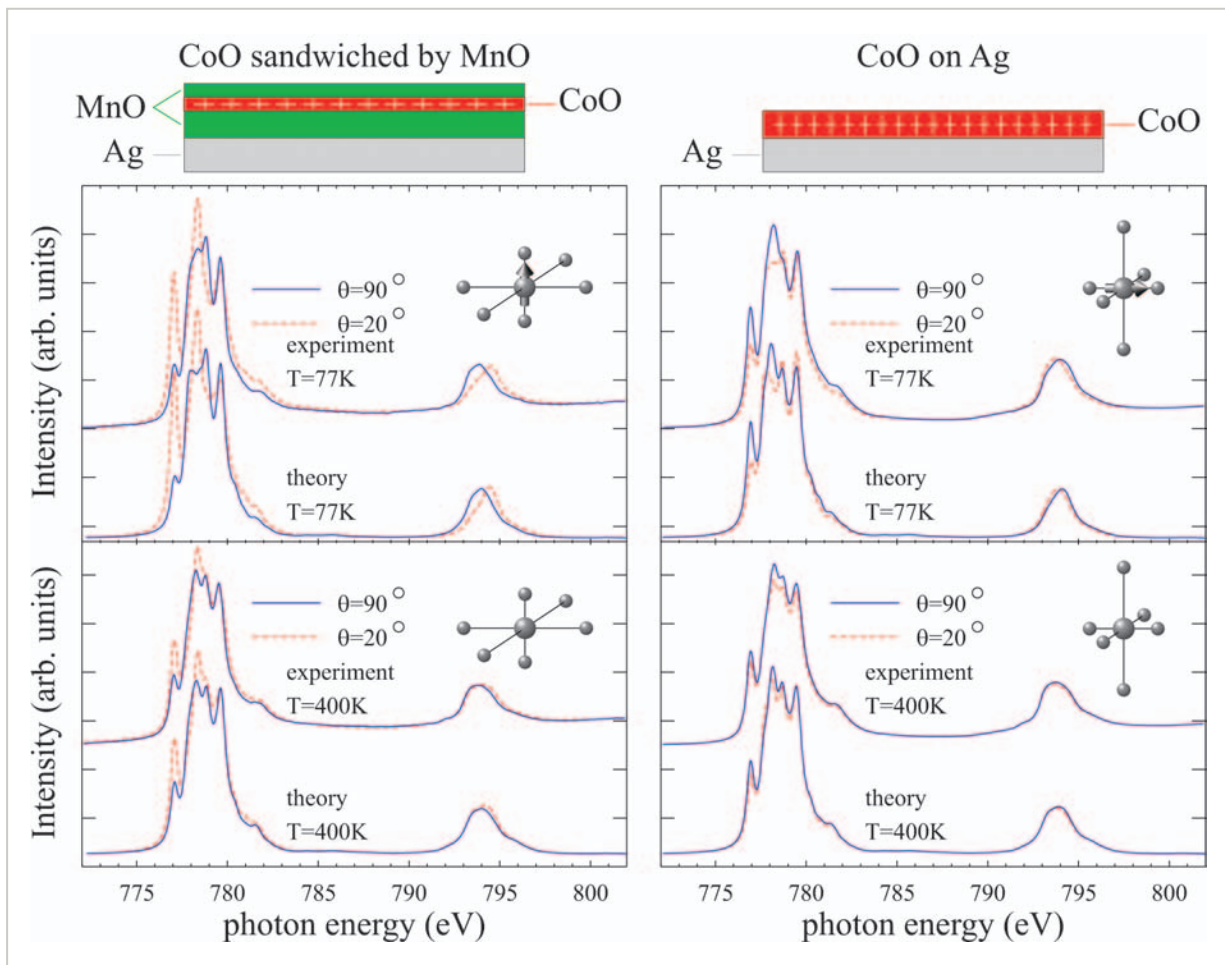


Fig. 1: Experimental and calculated Co $L_{2,3}$ XAS spectra of left panel: CoO in (14Å)MnO/(10Å)CoO/(100Å)MnO/Ag(001) at $\theta=20^\circ$ and $\theta=90^\circ$, far below (top panel, $T=77$ K) and far above (bottom panel, $T=400$ K) the Néel temperature of the CoO thin film; right panel: the same for CoO in (90 Å)CoO/Ag(001).

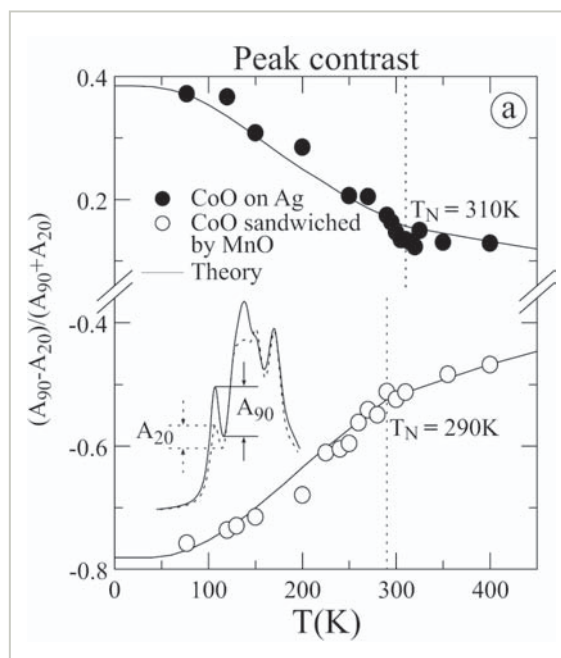


Fig. 2: Temperature dependent polarization contrast in the Co $L_{2,3}$ spectra, defined as the difference divided by the sum of the height of the peak at 777 eV, taken with $\theta = 20^\circ$ and $\theta = 20^\circ$ polarizations. Filled and empty circles are the experimental data. The solid lines are the theoretical simulations.

interaction cluster model, which includes the full atomic multiplet theory and the local effects of the solid. It accounts specifically also the local crystal field parameters $10Dq$, Ds and Dt , and a Brillouin type temperature dependent exchange field which acts on spins only and which vanishes at T_N . Figure 1 compares experimental and theoretical spectra for the CoO/MnO(100) with $Ds = -40$ meV, $Dt = -13$ meV and an exchange field parallel to the [001] surface normal and for the CoO/Ag(100) with $Ds = 13$ meV, $Dt = 4$ 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. 2a, showing the excellent agreement between the calculated and measured temperature dependent polarization contrast of the first peak at 777 eV.

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) to be 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 $3d$ 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 $3d$ 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_{xz} 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. 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. 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.

Based on the parameters extracted from the excellent simulations of the spectra, we have esti-

mated the magnetocrystalline anisotropy within the CoO films. We calculated the single ion anisotropy by comparing the total energy of the CoO₆ cluster for different *exchange field directions*. This energy is expressed as $E = K_0 + K_1 \sin^2(\eta) + K_2 \sin^4(\eta) + K_3 \sin^4(\eta) \sin^2(\varphi) \cos^2(\varphi)$, where η is the angle between the exchange field and the c-axis, and φ is the azimuthal angle. We find for CoO/MnO(100) $K_1 = 3.4$ meV, $K_2 = 1.4$ meV and $K_3 = 0.1$ meV, while for CoO/Ag(100) we obtain $K_1 = -1.7$ meV, $K_2 = 0.1$ meV, and $K_3 = 0.1$ meV. In other words, for CoO/MnO(100) the energy difference between the spin directed parallel with the easy axis ($\eta = 0^\circ$, perpendicular to the film) and parallel with the hard axis ($\eta = 90^\circ$, lying in the film plane) to be about 4.8 meV. The same single ion anisotropy energy calculated for the CoO/Ag(100) is about -1.6 meV, i.e. the hard axis is perpendicular and the easy axis parallel to the film plane. These energies are more than 2 orders of magnitude larger than the dipolar anisotropy within the film.

To conclude, CoO films grown on different substrates show dramatic differences in their magnetic properties. Strain induced local crystal fields 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, especially when using magnetic ions with a partially filled t_{2g} shell.

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Experimental Station

XAS chamber of the Universität zu Köln, Germany

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