Aligning spins in antiferromagnetic films using antiferromagnets

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We have explored the possibility to orient spins in antiferromagnetic thin films with low magnetocrystalline anisotropy via the exchange coupling to adjacent antiferromagnetic films with high magnetocrystalline anisotropy. We have used MnO as a prototype for a system with negligible single-ion anisotropy. We were able to control its spin direction very effectively by growing it as a film on antiferromagnetic CoO films with different predetermined spin orientations. This result may pave the way for tailoring antiferromagnets with low magnetocrystalline anistropy for applications in exchange bias systems. Very detailed information concerning the exchange coupling and strain effects was obtained from the Mn $L_{2,3}$ soft x-ray absorption spectroscopy.

The study of the exchange bias phenomena in multi-layered magnetic systems is a very active research field in magnetism, not the least motivated by the high potential for applications in information technology. Various combinations of antiferromagnetic (AFM) and ferromagnetic (FM) thin film materials have been fabricated and intensively investigated [1, 2]. There seems to be an agreement among the experimental and theoretical studies that the largest exchange bias effects can be found in systems containing AFMs with a high magnetocrystalline anisotropy, such as CoO. The simple underlying idea is that the anisotropy helps to fix the spin orientation in the AFM while switching the magnetization in the FM.

Our objective is to explore the possibilities to control and to pin the spin direction in AFM oxides having low magnetocrystalline anisotropy, e.g. transition-metal oxides with the $3d^3$, $3d^5$, or $3d^8$ ionic configurations. If successful, this would help to extend the materials basis for the AFMs used in exchange bias systems. One could then consider thin films of not only NiO but also LaCrO$_3$, LaFeO$_3$, γ-Fe$_2$O$_3$, and R$_3$Fe$_5$O$_{12}$ [3]. At first sight, our chances may seem bleak since a recent study on ultra thin NiO films reveals that the magnetic anisotropy results from a detailed balance between the influence of strain and thickness on the already very weak dipolar interactions in the AFM [4, 5]. On the other hand, the few studies available in the literature on combinations of AFM/AFM films revealed that the interlayer exchange coupling can be very strong [6, 7, 8, 9, 10, 11, 12]. We took these findings as starting point of our work.

We have used MnO as an ideal model for an antiferromagnetic system with negligible single-ion anisotropy. We have grown MnO as a thin film epitaxially on two different types of CoO single crystal films. In one CoO film the spin direction is oriented perpendicular to the surface, and in the other parallel to the surface [13]. Using soft x-ray absorption spectroscopy at the Mn $L_{2,3}$

edges, we observed that the spin direction of the MnO film strongly depends on the type of CoO film the MnO is grown on, and that it is dictated by the spin orientation of the CoO film and not by the strain or dipolar interactions in the MnO film. Interlayer exhange coupling is thus a very effective manner to control spin directions and may be used for tailoring AFMs with low magnetocrystalline anisotropy for exchange bias applications.

The actual MnO/CoO systems studied are (14Å)MnO/(10Å)CoO/(100Å)MnO/Ag(001) and (22Å)MnO/(90Å)CoO/Ag(001). The two samples were grown on a Ag(001) single crystal 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 (RHEED) measurements. With the lattice constant of bulk Ag, CoO, and MnO being 4.09Å, 4.26Å, and 4.444Å, respectively, we find from x-ray diffraction (XRD) and RHEED that the in-plane lattice constants in each film are essentially given by the thickest layer which is almost bulk like. Compared to the bulk, the 10Å CoO sandwiched by MnO is about 4% expanded in-plane ($a_\parallel \approx 4.424$Å), while the 90Å CoO directly on Ag is slightly compressed in-plane ($a_\parallel \approx 4.235$Å, $a_\perp \approx 4.285$Å). The MnO is in both samples compressed, but much more so for the one on the 90Å CoO film. Details about the growth will be published elsewhere [14]. We have recently shown that the spin direction is oriented perpendicular to the surface in the CoO film under tensile in-plane stress, and that it is parallel to the surface in the film with the slightly compressive in-plane stress [13].

The XAS measurements were performed at the Dragon beamline of the NSRRC in Taiwan using *in-situ* MBE grown samples. The spectra were recorded using the total
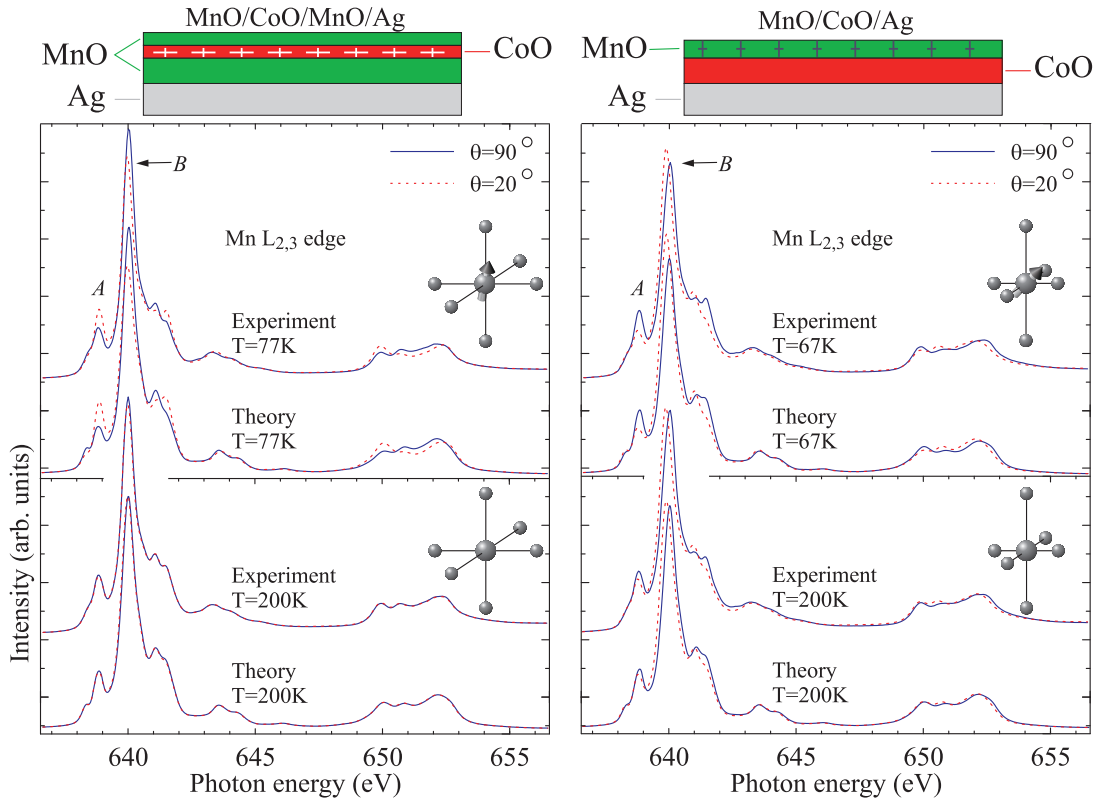
FIG. 1: (color online) Experimental and calculated Mn $L_{2,3}$ XAS spectra of MnO in (left panel) (14Å)MnO/(10Å)CoO/(100Å)MnO/Ag(001) and (right panel) (22Å)MnO/(90Å)CoO/Ag(001) for $\theta = 20°$ and $\theta = 90°$. Spectra below (T=77K) and above (T=200K) the T_N of the MnO film are shown in the top and bottom parts, respectively.

electron yield method in a chamber with a base pressure of 3×10^{-10} mbar. The photon energy resolution at the Mn $L_{2,3}$ edges ($h\nu \approx 635 - 655$ eV) was set at 0.2 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 $\alpha = 70°$ with respect to the [001] surface normal. To change the polarization, the sample was rotated around the Poynting vector axis, so that θ, the angle between the electric field vector $\vec{E}$ and the [001] surface normal, can be varied between $20°$ and $90°$ [13]. This measurement geometry allows for an optical path of the incoming beam which is independent of θ, guaranteeing a reliable comparison of the spectral line shapes as a function of θ. A MnO single crystal is measured *simultaneously* in a separate chamber to obtain a relative energy reference with an accuracy of better than 0.02 eV.

Fig. 1 shows the polarization dependent Mn $L_{2,3}$ XAS spectra of the MnO/CoO samples with CoO spin-orientation perpendicular (left panel) and parallel (right panel) to the surface, taken at temperatures far below (top part) and far above (bottom part) the Néel temperature (T_N) of the MnO thin film, which is about 130 K as we will show below. The spectra have been corrected for electron yield saturation effects [15]. The general line

shape of the spectra shows the characteristic features of bulk MnO [16], ensuring the good quality of our MnO films. Very striking in the spectra is the clear polarization dependence, which is the strongest at low temperatures. Important is that below T_N the dichroism, i.e. the polarization dependence, of the two samples are opposite: for instance, the intensity of the peak A at $h\nu = 639$ eV is higher for $\theta = 20°$ than for $\theta = 90°$ in MnO/CoO where the spin orientation of the CoO is out of plane, while it is smaller in the other sample. Above T_N, the dichroism almost vanishes. Nevertheless, small but clear and reproducible shifts in the spectra as a function of polarization can be seen: peak B at 640 eV has a shift of about 30 meV for the MnO sandwiching the 10Å CoO film, and 150 meV for the MnO overlaying the 90Å CoO film.

In order to resolve the origin of the dichroism in the spectra, we have investigated the temperature dependence in more detail. Fig. 2 depicts the polarization contrast of peak A, defined as the difference divided by the sum of the peak height in the spectra taken with the $\theta = 20°$ and $\theta = 90°$ polarizations. In going from low to high temperatures, one can see a significant temperature dependence for both samples (with opposite signs), which flattens off at about 130K, indicating the T_N of these MnO thin films. We therefore infer that at low
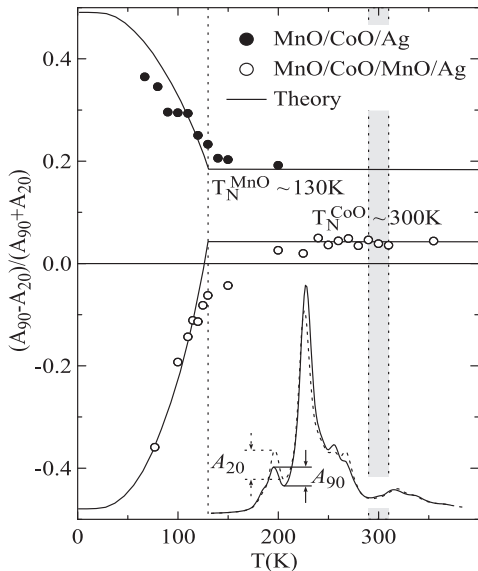
FIG. 2: Temperature dependence of the polarization contrast in the Mn $L_{2,3}$ spectra, defined as the difference divided by the sum of the height of peak A at $h\nu = 639$ eV, taken with $\theta = 20°$ and $\theta = 90°$ polarizations. Filled and empty circles are the experimental data. The solid lines are the theoretical simulations. The shaded area represents the T_N of the CoO layers under the MnO film.

temperatures the strong dichroic signal is caused by the presence of magnetic ordering. Important is to note that the opposite sign in the dichroism for the two samples implies that the orientation of the magnetic moments is quite different. Here we note that MnO films grown on Ag *without CoO* do not show any dichroism down to the lowest temperatures, indicating the crucial role of the CoO in orienting the magnetic moments of the MnO.

To understand the Mn $L_{2,3}$ spectra quantitatively, we perform calculations for the atomic-like $2p^6 3d^5 \rightarrow 2p^5 3d^6$ transitions using a similar method as described by Kuiper *et al.* [17] and Alders *et al.* [18], but now in a D_{4h} point group symmetry and including covalency. The method uses a MnO$_6$ cluster which includes the full atomic multiplet theory and the local effects of the solid [16, 19]. 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 $2p$ - Mn $3d$ hybridization, 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. The calculations have been carried out using the XTLS 8.0 programm [19].

The results of the calculations are shown in Fig. 1. We have used the parameters already known for bulk MnO [19, 20], and have to tune only the parameters for Ds, Dt, and the direction of the exchange field. For the MnO sandwiching the 10Å CoO we find an excellent simulation of the experimental spectra for $Ds = 9.3$ meV, $Dt = 2.6$ meV, and an exchange field parallel to the [112] direc-

tion. For the MnO overlaying the 90Å CoO we obtained the best fit for $Ds = 48.6$ meV, $Dt = 11.1$ meV, and an exchange field along the [211] direction. These two sets of parameters reproduce extremely well the spectra at all temperatures. This is also demonstrated in Fig. 2, showing the excellent agreement between the calculated and measured temperature dependence of the dichroism in peak A. Most important is obviously the information concerning the spin direction that can be extracted from these simulations. We thus find that the magnetic moments in the MnO are oriented towards the surface normal when it is grown on the CoO film which has the spin direction perpendicular to the surface, and that it is lying towards the surface when it is attached to the CoO film which has the parallel alignment. In other words, it seems that bulk-like MnO domains are stabilized that follow the CoO spin-direction as much as possible.

In order to find out whether the spin direction in the MnO thin films is determined by the exchange coupling with the CoO, or whether it is given by strain and dipole interactions in the films as found for NiO thin films on non-magnetic substrates [4, 5], we now have to look more closely into the tetragonal crystal fields in the MnO films. The values for the tetragonal crystal field parameters Ds and Dt, which we have used to obtain the excellent simulations as plotted in Fig. 1, can actually be extracted almost directly from the high-temperature spectra, where the magnetic order has vanished and does not contribute anymore to the polarization dependence.

The top panels of Fig. 3 show a close-up of the spectra taken at 200K, i.e. above T_N. One can now observe the small but clear and reproducible shifts in the spectra as a function of polarization: the shift in peak A is denoted by Δ_A and in peak B by Δ_B. In order to understand intuitively the origin of these shifts, we will start to describe the energetics of the high spin Mn^{2+} ($3d^5$) 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, all containing a spin-up electron. The L_3 edge of Mn^{2+} should then consist of two peaks: in exciting an electron from the $2p$ core level to the $3d$, one can add an extra spin-down electron either to the lower lying t_{2g} or the higher lying e_g shell, producing peaks A and B, respectively. In the presence of a tetragonal distortion, both the t_{2g} and e_g levels will be split, resulting in a polarization dependent shifts Δ_A and Δ_B, analogous as found for NiO [21].

Due to the intra-atomic $2p$-$3d$ and $3d$-$3d$ electron correlation effects, the relationship between the shifts in the spectra and the crystal field splittings become non-linear. Using the cluster model we are able to calculate this relationship for a Mn^{2+} $3d^5$ system and the results are plotted in Fig. 3. Using this map, we find for the MnO sandwiching the 10Å CoO that $\Delta_{t_{2g}} = 15$ meV and $\Delta_{e_g} = 50$ meV, and for the MnO overlaying the 90Å CoO that $\Delta_{t_{2g}} = 90$ meV and $\Delta_{e_g} = 250$ meV ($Ds=(\Delta_{e_g}+\Delta_{t_{2g}})/7$, $Dt=(3\Delta_{e_g}-4\Delta_{t_{2g}})/35$). The crystal field splittings for the
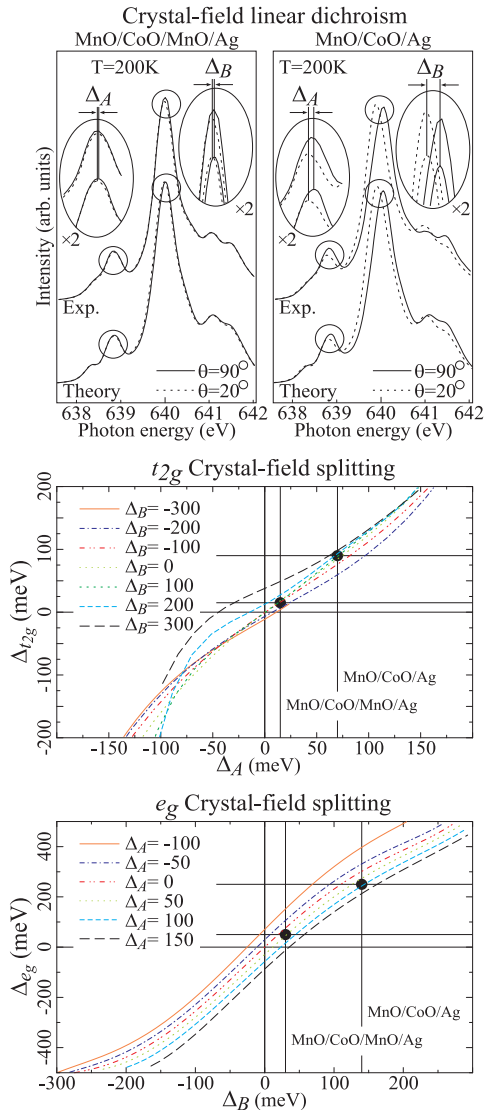
FIG. 3: (color online) (top panel) Close-up of the experimental and calculated Mn L_3 XAS spectra at 200K, i.e. above T_N of (left) (14Å)MnO/(10Å)CoO/(100Å)MnO/Ag(001) and (right) (22Å)MnO/(90Å)CoO/Ag(001); Δ_A and Δ_B are the polarization dependent shifts in peaks A and B, respectively; (middle and bottom panels) Relationship between $\{\Delta_A, \Delta_B\}$ and the tetragonal $\{\Delta_{e_g}, \Delta_{t_{2g}}\}$ splittings.

second sample are much larger than for the first sample, fully consistent with our structural data in that the MnO in the second sample experiences a much stronger compressive in-plane strain. Important is now to recognize that the crystal field splittings for the two samples have the same sign, i.e. that both MnO films are compressed in plane. This implies that strain together with the dipolar interactions cannot explain the quite different spin-orientations of the two MnO systems. We conclude that the magnetic anisotropy mechanism present in, for instance, NiO thin films on non-magnetic substrates [4, 5], is overruled by the stronger interlayer exchange coupling

[6, 7, 8, 9, 10, 11, 12] between the CoO and MnO layers.

The T_N for these thin MnO layers is found to be at about 130 K. It is surprising that it is not reduced as compared to the bulk value of 121 K [22], since generally one would expect such to happen with decreasing thickness as was observed for NiO on MgO [18]. The origin for this is not clear at this moment. It is possible that the in-plane compressive stress gives an increase of the Mn $3d$ - O $2p$ hybridization, which in turn could produce an increase of the superexchange interaction strength [3] and thus also of T_N. Another, more exciting, possibility emerges from the recent experimental and theoretical work on AFM/AFM multilayers such as FeF_2/CoF_2 and CoO/NiO [6, 7, 8, 9, 10, 11, 12]. Experiments have revealed that multilayers could even have a single magnetic ordering transition temperature lying in between the two T_Ns of the constituent materials. The phenomenon has been ascribed to the very strong interlayer exchange coupling.

In conclusion, we have shown that it is possible to control the spin direction in MnO very effectively by growing them as thin films on antiferromagnetic CoO films with different predetermined spin orientations. Using detailed Mn $L_{2,3}$ soft x-ray absorption spectroscopy, we are also able to show that it is not strain but interlayer exchange coupling which plays a decisive role herein. This result may pave the way for tailoring antiferromagnets with low magnetocrystalline anistropy for applications in exchange bias.

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