Influence of Ligand States on the Relationship between Orbital Moment and Magnetocrystalline Anisotropy

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The spin and orbital moments of Au/Co/Au trilayers grown on a W(110) single crystal substrate have been investigated by means of x-ray magnetic circular dichroism. Our findings suggest that the orbital moment of Co does not obtain a maximum value along the easy axis, in contrast with previous experience. This is attributed to the large spin-orbit interaction within the Au caps. Both second order perturbation theory and first principles calculations show how the magnetocrystalline anisotropy (MCA) is dramatically influenced by this effect, and how this leads to the fact that the orbital moment anisotropy is not proportional to the MCA.

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The ability to stabilize a magnetic easy axis perpendicular to the film is central to the physics of magneto-optical recording and perpendicular magnetic media, apart from the fundamental interest of spin reorientation phenomena, and has attracted an enormous interest both experimentally [1–7] and theoretically [1,8–13]. A perpendicular magnetic anisotropy can be stabilized when intrinsic magnetocrystalline anisotropy favors an out-of-plane easy axis of magnetization and is large enough to overcome the extrinsic shape anisotropy.

Models that relate the magnetocrystalline anisotropy to the atomic orbital moment have been developed and employed successfully to establish a phenomenological understanding of the magnetocrystalline anisotropy [9–12]. This theoretical framework has provided a qualitative understanding of spin reorientation phenomena [3,14–16]. The spin reorientation transition (SRT) is associated with an increase in the orbital moment upon reorientation to the new easy axis. This intuitive picture is empirically found to be consistent with many experimental observations.

Thin films of Co grown on various substrates and capped with, or sandwiched in Au, Pt, or Pd, are well-known systems that exhibit a spin reorientation [3,6,7,14,17–20]. The spin reorientation has been found to be sensitive to, e.g., the Au cap thickness, temperature, and naturally the thickness of the Co layer.

In this letter we investigate the spin reorientation in Au/Co/Au trilayers, grown on a W(110) single crystal, using x-ray magnetic circular dichroism (XMCD). These measurements are done at a constant temperature and the spin reorientation is induced upon Au capping of Co films with a thickness below 11 Å. The results of the *in situ* samples are complemented with results from an *ex situ* grown sample where the spin reorientation to out-of-plane was induced upon cooling [21]. The XMCD technique enables us to obtain spin and orbital moments on a per atom basis [22]. Using this capability, we demonstrate that the intuitive picture of relating the size of the orbital moment to the magnetocrystalline anisotropy can lead to erroneous conclusions and that the easy axis of magnetization does not always coincide with the largest orbital moment. An extended theoretical framework which contains the necessary physical interaction corroborates these findings. Especially, we will show that consideration of the Au spin-orbit coupling via hybridization to the Co atoms is central for a correct description.

The experiments were performed at beam line D1011 at MAX-lab in Lund, Sweden. This beam line provides x rays in the range 30 to 1500 eV, which includes the L absorption edges for the $3d$ transition metals, with variable polarization. Co films of different thickness were grown on a 50 Å thick Au film deposited on a W(110) single crystal. Here we present results obtained for 5 and 7 Å Co films, respectively. The bare Co films were, after characterization with XMCD and x-ray photoelectron spectroscopy (XPS), capped with Au; the 5 Å film with 3.5 Å Au in a first step with an subsequent addition of 6.5 Å Au. The 7 Å sample was, after characterization, capped in one step with 6 Å Au.

The samples prepared on the W(110) single crystal were prepared and measured *in situ*, to ensure sample cleanliness and a high degree of crystalline order, as monitored by means of XPS and LEED. The base pressure was better than 2×10^{-10} mbar. The films were produced by evaporation; Co films by means of electron bombardment heating of purified Co and the Au films through resistive heating of purified Au. A quartz microbalance (QMB) allowed the rate of all evaporators to be monitored. The QMB was calibrated using XPS for the specific geometry of each evaporator. The W single crystal was cleaned with oxygen treatments and high temperature annealing to 2300 K to remove adsorbed surface contaminants (predominantly CO and O). The *in situ* samples were deposited and measured at room temperature. The *ex situ* sample, a 20 Å Au/21 Å Co/Au trilayer, was characterized by both temperature dependent neutron reflectometry and SQUID magnetometry [18,19] and temperature dependent XMCD at MAX-lab [21]. The spin reorientation for this sample occurs between 170 and 300 K. At 170 K, a remanent magnetization is only found in the out-of-plane direction, while only an in-plane remanent magnetization is found at 300 K [21].

Here we focus on the variation of the orbital and spin moments, determined by means of XMCD sum rule analysis, associated with the spin reorientation. A representative example of the data is given in Fig. 1 for the uncapped 5 Å sample. XMCD spectra were recorded in remanence, using total electron yield, after pulsing the samples in an applied field of ~500 G along the easy axis of magnetization, exceeding the coercive field ($\lesssim$60 G) for the samples presented here.

A constant number of Co d-holes, 2.6, obtained from first principles calculations, was used in the sum rule analysis. The degree of circular polarization, 0.84 ± 0.04, was determined by measurements of a Co bulk reference. XMCD data were recorded at 45° angle of incidence and at normal incidence for in-plane and out-of-plane magnetizations, respectively. In addition, XMCD data were obtained for several other x-ray incidence angles after applying magnetic field pulses both in-plane and out-of-plane. These angle-dependent measurements exclude the existence of a canted magnetization.

The measured remanent moments are summarized in Fig. 2. The ratio $m_\ell/m_s^{\mathrm{eff}}$ [23], the effective spin moment m_s^{eff}, and the orbital moment m_ℓ are given. The effective spin moment includes a contribution from the intra-atomic magnetic dipole operator [22], but this fact has no impact for the scope of this Letter [24]. The errors are estimated from the standard deviations of the calculated moments and do not account for errors in the XMCD sum rules themselves. The results are separated for in-plane and the out-of-plane remanent magnetization represented by open and filled symbols, respectively. All bare Co films were found to exhibit an in-plane easy magnetization direction, in contrast to earlier findings for, e.g., Co on a Au(111) single crystal [25]. One may speculate that this discrepancy is due to small structural differences for the two cases. We obtain $m_s^{\mathrm{eff}} = 1.82\mu_B$/Co atom for the 7 Å Co film. The orbital moment for the uncapped situation is $0.43\mu_B$/atom. Here a SRT takes place after adding 6 Å of Au. The moments decrease upon Au capping $m_s = 1.52\mu_B$/atom and $m_\ell = 0.23\mu_B$/atom.

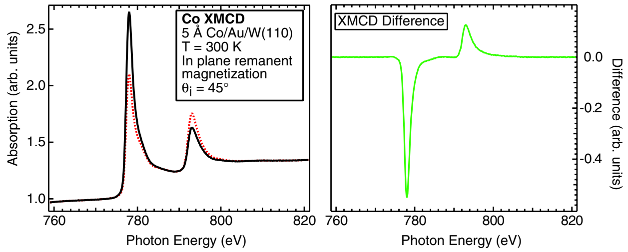

FIG. 1 (color online). XMCD data with the corresponding difference spectrum for the 5 Å sample. Data were obtained in remanence.

For the bare 5 Å Co film $m_s^{\mathrm{eff}} = 1.50\mu_B$/atom and $m_\ell = 0.31\mu_B$/atom. When adding 3.5 Å Au, a SRT occurs, which is accompanied by an increase in m_s^{eff} to $2.0\mu_B$/atom, while the orbital moment decreases slightly. After adding 6.5 Å Au onto the film, m_s^{eff} decreases to $1.89\mu_B$/atom. The m_ℓ decreases further to $0.24\mu_B$/atom. The ratios of the orbital and spin moments exhibits the same trends.

We now turn to the results obtained for the *ex situ* grown Au/Co/Au trilayer. With a Co thickness of 21 Å, this sample bridges the gap to the *ex situ* results by Weller *et al.* [3]. These authors worked at a constant temperature of 300 K, and the spin reorientation was examined while varying the Co thickness. We instead explore the temperature driven SRT. The values obtained for the spin moment, given in the right column of Fig. 2 are consistent with the ones reported by Weller *et al.* [3]. However, the relative variation of the orbital moment measured for the *ex situ* sample as the magnetization turns from in-plane to out-of-plane upon cooling is very surprising. The most striking result is the decrease of the orbital moment from

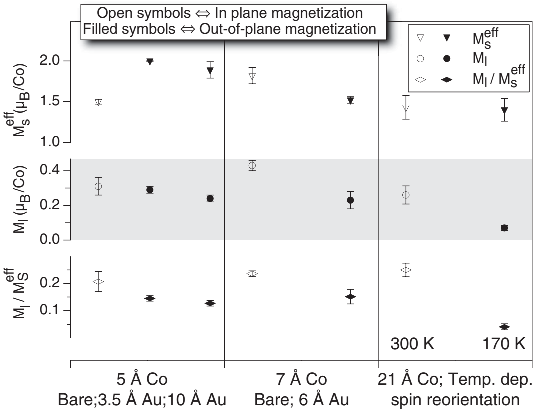

FIG. 2. Spin and orbital moments and their ratio, obtained from sum rule analysis, are given. Error bars correspond to the statistical variation in the data and do not account for errors originating from the sum rules themselves. Open symbols denote values obtained for in-plane magnetization, while closed symbols represent data for out-of-plane magnetization.

$0.26\mu_B$/atom to $0.06\mu_B$/atom. We note that this SRT is mainly driven by the temperature variation in the magnetic anisotropy energy (MAE) as the shape anisotropy contribution always favors an in-plane magnetization and is larger at lower temperatures.

Generally, a SRT is driven by a competition between the spin-orbit driven MAE and the shape anisotropy, which always favors an in-plane magnetization. In our case where small perturbations on the Co film lead to a SRT, the MAE has to favor an out-of-plane magnetization in order to nearly cancel the large shape anisotropy. Then our results in Fig. 2 contradict the well-established assumption [11] that the orbital moment anisotropy (OMA) is related to MAE in such away that the largest orbital moment is along the direction favored by MAE. The relation between the spin-orbit induced magnetic anisotropy and the orbital anisotropy is not as clear when there are more than one atomic species present and a strong hybridization between their electronic states. To investigate this in detail we now proceed with an approach very similar to that used in Ref. [11], but allow for several atomic species. That is, we study the contribution to the uniaxial anisotropy in energy and orbital moments in second order perturbation in the spin-orbit coupling $\mathcal{H}_{\mathrm{so}} = \xi \boldsymbol{\ell} \cdot \mathbf{s}$. The uniaxial MAE, ΔE_{so}, i.e., the energy difference between two magnetization directions, say $\hat{n}_1$ and $\hat{n}_2$, can be written as a sum over atomic species, q, and as a double sum over the spin indices, s (occupied), and s' (unoccupied),

$$\Delta E_{\mathrm{so}} = \sum_{qss'} \Delta E_q^{ss'} = \sum_{qss'} \{E_q^{ss'}(\hat{n}_1) - E_q^{ss'}(\hat{n}_2)\}, \tag{1}$$

where each direction dependent term is given by

$$E_q^{ss'}(\hat{n}) = -\sum_{\mathbf{k}ij} \sum_{q'} \sum_{\{m\}} n_{\mathbf{k}is,qm,q'm'} n_{\mathbf{k}js',q'm'',qm'''} \frac{\langle qms|\mathcal{H}_{\mathrm{so}}(\hat{n})|qm'''s'\rangle \langle q'm''s'|\mathcal{H}_{\mathrm{so}}(\hat{n})|q'm's\rangle}{\varepsilon_{\mathbf{k}j} - \varepsilon_{\mathbf{k}i}}. \tag{2}$$

In this equation there is a sum over all k points $\mathbf{k}$ in the Brillouin zone, all occupied states i, all unoccupied states j, all sites in the unit cell q' and a quadruple sum over magnetic quantum numbers $\{m\} = \{mm'm''m'''\}$. Here we use a set of local basis functions $|q\ell ms\rangle$, where q specifies an atomic site and ℓ, m are the azimuthal and magnetic quantum numbers, respectively. The directional dependence of the spin-orbit coupling term, comes from the spin quantization axis $\hat{n}$. Furthermore, we assume that there is only one relevant atomic shell per site. For each state, indexed by the wave vector $\mathbf{k}$ and band number i, we have an unperturbed band energy $\varepsilon_{\mathbf{k}i}$ and occupation numbers $n_{\mathbf{k}i}$, where the latter are matrices over all the basis indices since we allow for hybridization.

The OMA can in a similar way be expressed as a sum over one spin index

$$\Delta m_{\ell,q} = \sum_s \Delta m_{\ell,q}^s, \tag{3}$$

with the angular dependent terms

$$m_{\ell,q}^s(\hat{n}) = \sum_{\mathbf{k}ij} \sum_{q'} \sum_{\{m\}} n_{\mathbf{k}is,qm,q'm'} n_{\mathbf{k}js,q'm'',qm'''} (-2\mu_B) \times \frac{\langle qms|\ell_z|qm'''s\rangle \langle q'm''s|\mathcal{H}_{\mathrm{so}}(\hat{n})|q'm's\rangle}{\varepsilon_{\mathbf{k}j} - \varepsilon_{\mathbf{k}i}}, \tag{4}$$

where ℓ_z is the component of the angular momentum operator along the spin quantization axis.

From Eqs. (2) and (4) one can observe that both $\Delta E_q^{ss'}$ and $\Delta m_{\ell,q}^s$, through the sum over all sites have off-site contributions ($q' \neq q$) through the spin-orbit scattering at other sites. These contributions become significant if the hybridization is strong and simultaneously the spin-orbit coupling is larger at the other site. One can also deduce that there is a direct relation between the spin diagonal energy anisotropy term and the spin-dependent ($s = \pm 1$) orbital anisotropy contribution

$$\Delta E_q^{ss} = s \frac{\xi_q}{4\mu_B} \Delta m_{\ell,q}^s. \tag{5}$$

In this work, where we focus on contributions from Co atoms close to the Au interface, the terms $\Delta E_{\mathrm{Co}}^{\uparrow\uparrow}$, $\Delta E_{\mathrm{Co}}^{\downarrow\uparrow}$ and $\Delta m_{\ell,\mathrm{Co}}^{\uparrow}$ all vanish, due to the lack of unoccupied Co spin-up d states. Furthermore, if we would ignore the off-site spin-orbit coupling the spin-flip term $\Delta E_{\mathrm{Co}}^{\uparrow\downarrow}$ would become very small too, due to the large exchange splitting on Co. Then Eq. (5) would lead to the well-known Bruno's formula [11]

$$\Delta E_{\mathrm{so}} = -\frac{\xi_{\mathrm{Co}}}{4\mu_B} \Delta m_{\ell,\mathrm{Co}}. \tag{6}$$

However, in our case the spin-orbit coupling on Au cannot be ignored, which leads to that $\Delta E_{\mathrm{Co}}^{\uparrow\downarrow}$ is not negligible and Eq. (6) breaks down for Co atoms close to the interface.

In order to quantify this we simulate a Co/Au interface by considering a simple supercell of triangular Co and Au layers in an AB-stacking, which in case of one atomic species reduces to the hcp structure. The atomic volume has been taken as the average of those of the pure metals, while the layer distance was varied around the ideal value, $(c/a)_0 = \sqrt{8/3}$. The self-consistent electronic structure calculations were performed with the full potential linearized muffin tin orbital (FPLMTO) method including the spin-orbit coupling [26]. From these calculations both the MAE and the cobalt OMA are extracted, by comparing magnetization directions $\hat{n}$ along [100] and [001]. In order to critically test the validity of Eq. (6) the MAE is plotted against the OMA for different layer distances, c/a in

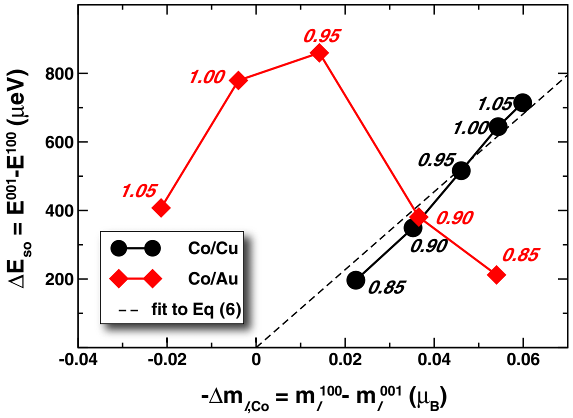

FIG. 3 (color online). MAE vs OMA for Co/Au (squares) and Co/Cu (circles) calculated for various layer distances, as indicated by the deformation parameter χ, where $\chi = (c/a)/\sqrt{8/3}$. Also, a linear fit for the Co/Cu case is shown as a dashed line. The fitting yields the value of the spin-orbit coupling parameter as 46 meV.

Fig. 3. In these results there is a strong deviation from proportionality of OMA and MAE. In the same graph we show the results for an identical set of calculations with Au substituted with Cu, in order to illustrate that a much smaller off-site spin-orbit coupling leads to a linear dependence.

In Fig. 3 we have given the deviation from the ideal ratio of out-of-plane and in-plane distances $c/a = \chi(c/a)_0$. For the Co/Cu interface one can deduce that both quantities, MAE and OMA, show almost perfectly linear dependence with the lattice deformation, while the Co/Au interface displays a strongly nonlinear MAE. The strong deviations from the expected linear dependence between MAE and OMA, as given by Eq. (6), can be traced back to the spin-flip contribution $\Delta E_{\mathrm{Co}}^{\uparrow\downarrow}$. As mentioned above, this term contributes significantly to the MAE at the Co/Au interface due to the strong spin-orbit coupling at the Au sites. In the Co/Au case there is even a calculated sign change in OMA when varying lattice spacing, which does not correspond to a SRT, as is evident from the MAE curve.

We finally present guidelines on the limiting cases of strong and negligible $d - d$ interaction between the ligand and the magnetic atoms. For the case of strong $d - d$ hybridization, it is the magnitude of the spin-orbit interaction on the ligand atoms that will determine if there will be a proportionality between the MAE and OMA. For the case of large spin-orbit interaction no simple relationship between the two quantities is found within our model. For vanishing spin-orbit interaction, a linear relationship is recovered. However, in the limit of weak hybridization the effect of the ligand is not relevant and a direct proportionality between MAE and OMA is recovered.

In conclusion we have demonstrated that spin reorientations occurring in thin magnetic films are not always associated with changes in the orbital moment that can directly be linked to the change in magneto-crystalline anisotropy. Instead we have illustrated that the changes in the orbital moment may exhibit totally different behavior. We have furthermore outlined a modified theoretical framework which contain the often used formulation by Bruno as a special case, valid in the limit of large exchange splitting and when only on-site contributions to the magneto-crystalline anisotropy is considered. When off-site spin-orbit coupling becomes important, e.g., at the Co/Au interface, no direct relationship between OMA and MAE can be expected.

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