Correlation of magnetism and structure for ultra thin Au/Co/Au films: evidence for magnetoelastic effects

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Abstract. The spin-reorientation transition of thin Au/Co/Au films, grown \textit{in-situ} on W(110), is studied in XMCD and EXAFS experiments. At 300 K, for \textit{in-situ} grown Co on a Au(111) film, the dominant easy magnetization direction was found to be in the surface plane, for the uncapped Co/Au bilayers. This is a novel observation, in terms of easy magnetization direction for low thickness Co on Au. After capping with Au, a sizeable out-of-plane magnetization is observed below a thickness of four atomic Co layers. When the spin-reorientation transition occurs because of Au capping, a 5 Å thin Co layer undergoes structural changes of lattice parameters $\Delta a/a = -1.2\%$ and $\Delta c/c = +6.6\%$. The observation of structural changes which accompany the spin reorientation transition, contradicts previous work on Co/Au(111), and allows to quantify the magnetoelastic energy contribution, connected with the presence of the Co/Au interface.

1. Introduction

The magnetic anisotropy of ultrathin ferromagnetic films has been extensively studied, given the interest in the microscopic origin of the Perpendicular Magnetic Anisotropy (PMA). PMA can be stabilized when intrinsic magnetocrystalline anisotropy favors the out-of-plane easy axis of magnetization and is large enough to overcome the extrinsic shape anisotropy. In terms of the electronic structure the microscopic origin of the surface/interface anisotropy has been related to the anisotropy of the orbital moment [1, 2]. A recent X-ray Magnetic Circular Dichroism (XMCD) study of \textit{in-situ} prepared Au/Co/Au(111)/W(110) films does not support this picture, as there is no increase of the Co perpendicular orbital moment, which accompanies the in-plane to out-of-plane Spin Reorientation Transition (SRT) [3]. The magnetic characterization of a similar system has been studied at constant Co thickness as a function of temperature. The temperature-driven SRT was found to occur at a Co thickness of $\sim$18 Å at room temperature [4]. The thickness-driven SRT occurs at much smaller Co thickness in our case. These apparently conflicting observations highlight the need for an \textit{in-situ} structural study. In this system, there is a large in-plane lattice mismatch of $\sim$14% between

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Au(111) and Co(0001). Sellmann et al. reported that the in-plane strain starts to get relaxed at a critical thickness of ~6 Å [4]. Marsot et al. applied Co K-edge Extended X-ray Absorption Fine Structure (EXAFS) analysis on uncapped Co/Au(111) films, and found that Co grows non-pseudomorphically from the first stage of the growth, keeping its own lattice parameters, which leads to the expectation that the magnetoelastic energy does not contribute to the PMA of this system [5]. However, such a conclusion may not be generally true. The strain of the Co layer naturally depends on the growth conditions e.g. the substrate temperature and the deposition rate. Thus, a further in-situ structural study of the Co/Au interface and the inner Co layers of a film using the very same sample, on which the magnetic characterization has been done, is required.

Here we discuss Co L-edge EXAFS and its analysis for in-situ prepared Au/Co/Au(111)/W(110) films. The L-edge EXAFS has the advantage that it provides structural information, at the same time and for the same samples, together with the magnetic information as obtained by the XMCD. However, for the 3d transition metals there are three overlapping L₁, 2, 3 edges and any quantitative EXAFS analysis is difficult to perform. In order to overcome this difficulty, we apply the Bayes-Turchin approach, as developed by Krappe and Rossner, which has been successfully applied to the analysis of overlapping L-edge EXAFS of Fe [6, 7].

2. Experimental

Co L-edge XMCD and EXAFS measurements were performed at the synchrotron radiation laboratory MAX-lab in Lund, Sweden at beamline D1011. This beamline provides soft x-rays with variable polarization in the energy range 30 to 1500eV from a bending magnet [8]. Co films of various thicknesses were grown at room temperature by electron-beam evaporation on a 50Å thick Au(111) film grown in-situ on a W(110) single crystal. The W single crystal was cleaned by means of oxygen treatments and high temperature annealing to 2300 K. The cleanliness and surface order were monitored by means of XPS, XAS and LEED. Co was evaporated with a rate of ~1ML/min. The evaporation rates were monitored using a quartz microbalance. The base pressure was better than 2x10⁻¹⁰mbar. The XMCD measurements were performed in remanence after magnetizing the samples using magnetic field pulses in the direction parallel or perpendicular to the film surface. The EXAFS spectra were measured in-situ, following the magnetic characterization by means of XMCD and resonant x-ray reflectivity. The absorption spectra, taken in the electron yield mode, are normalized to the incident x-

![Figure 1](image1.png)

**Figure 1.** Dominant magnetic easy-axis diagram at 300K for the in-situ grown Au/Co/Au/W(110) system. Open squares and asterisks indicate the samples for which the XMCD measurements were performed in the present study. In-plane and out-of-plain remanent magnetization can be stabilized in the shaded area marked by ‖ and ⊥, respectively.

![Figure 2](image2.png)

**Figure 2.** Co L-edge EXAFS χ(k) spectra of the 5Å Co films and the hcp Co reference. Theoretical μ₀ is used in extracting and normalizing χ(k). The anomalies at ~6 Å⁻¹ and in the case of the 5Å films at ~8.6 Å⁻¹ is due to the L₁ edge of the theoretical μ₀ and an experimental artefact in measured I₀, respectively.
ray intensity $I_0$ by the photocurrent of a gold mesh. As a reference for the EXAFS analysis, EXAFS spectra of an in-situ grown thick Co film (~100 Å) on Cu(111), which is known to exhibit the hcp(0001) structure [9], were also measured.

3. Results

3.1. Magnetic anisotropy

We briefly summarize the results of the XMCD measurements here. More details and further analysis will appear elsewhere [10]. Figure 1 shows the magnetic anisotropy diagram for in-situ grown Au/Co/Au films on a W(110) single crystal. The diagram shows the dominant magnetic easy axis direction as determined by the XMCD measurements in magnetic remanence at 300K. There are clear differences compared to earlier reported results on similar systems [4, 11]. For the present in-situ grown Co on a Au(111) film, the dominant easy direction magnetization is found in plane, for the uncapped Co/Au bilayers in the whole thickness range we studied, down to $t_{Co}=5$ Å. The thickness-driven SRT occurs at much lower Co thickness, at around 8Å. Furthermore, there is no large change in the Co 3$d$ orbital magnetic moment, to be correlated with the occurrence of the SRT [3].

3.2. EXAFS analysis

In the EXAFS analysis of overlapping $L$-edges we apply the Bayes-Turchin approach [6, 7]. This method is based on a Bayesian approach originally proposed by Turchin and Nozik [12]. This approach can be described as a regularization procedure for an ill-posed fit problem; it allows to start with a large parameter space and to determine the parameter subspace, which contains those parameters, which are determined by the experimental data. It also provides a precise way of treating the atomic background $\mu_0(k)$ together with a careful treatment of the errors which come both from the experiment and the model. Readers are referred to references [6, 7] for a complete description of the method. In this report we present a selection of results obtained for an uncapped 5Å Co film and the 5Å Co film capped with a 3.5Å Au overlayer, where the magnetic easy axis is in-plane and out-of-plane, respectively, see figure 1. A detailed analysis of more extended data set will be published elsewhere [13]. Figure 2 shows Co $L$-edge EXAFS spectra of three Co films measured at normal incidence using linearly polarized x-rays, plotted versus the photoelectron wave number, referring to the Co $L_3$ absorption-edge energy. The spectra include three overlapping $L_1, 2, 3$ edges and are

| Table 1. | Fit results using the fixed value $S_0=0.9$. A priori values are obtained from the bulk hcp Co structure. $R_i$ is the half path length of each single scattering path $i$. $\sigma^2_{\text{struct}}$ is the structural part of the Debye-Waller parameters. $N_i$ is the path degeneracy. |
|----------|---------------------------------|-------------------------|-------------------------|
| parameters | a priori Co/Cu(111) reference | a posteriori Co(5Å)/Au thin film | a posteriori Au(3.5Å)/Co(5Å)/Au thin film |
| $R_1$(Å) | 2.498 | 2.499 ± 0.002 | 2.406 ± 0.008 | 2.496 ± 0.025 |
| $R_2$(Å) | 2.510 | 2.513 ± 0.002 | 2.561 ± 0.004 | 2.532 ± 0.011 |
| $R_3$(Å) | 3.541 | 3.541 ± 0.002 | 3.474 ± 0.010 | 3.496 ± 0.016 |
| $R_4$(Å) | 4.070 | 4.070 ± 0.002 | 4.057 ± 0.045 | 4.071 ± 0.031 |
| $R_5$(Å) | 4.341 | 4.341 ± 0.002 | 4.202 ± 0.012 | 4.344 ± 0.017 |
| $R_6$(Å) | 4.347 | 4.348 ± 0.002 | 4.457 ± 0.022 | 4.454 ± 0.024 |
| $R_7$(Å) | 4.782 | 4.782 ± 0.002 | 4.756 ± 0.028 | 4.741 ± 0.028 |
| $R_8$(Å) | 5.020 | 5.020 ± 0.002 | 5.025 ± 0.022 | 5.019 ± 0.028 |
| $\sigma^2_{\text{struct}}$(Å$^2$) | 0.00100 | 0.00212 ± 0.00014 | 0.00493 ± 0.00035 | 0.01048 ± 0.00035 |
| $N_1$ | 2.00 | 2.00 | 1.99 ± 0.29 | 2.02 ± 0.26 |
| $N_2$ | 2.00 | 2.00 | 1.80 ± 0.21 | 2.18 ± 0.22 |
| $N_3$ | 2.00 | 2.00 | 2.02 ± 0.29 | 2.02 ± 0.26 |
| $N_4$ | 2.00 | 2.00 | 2.03 ± 0.29 | 2.02 ± 0.26 |
| $N_5$ | 4.00 | 4.00 | 3.90 ± 0.28 | 3.82 ± 0.26 |
| $N_6$ | 4.00 | 4.00 | 4.01 ± 0.28 | 3.88 ± 0.26 |
| $N_7$ | 8.00 | 8.00 | 8.02 ± 0.29 | 8.03 ± 0.26 |
| $N_8$ | 2.00 | 2.00 | 1.93 ± 0.29 | 1.91 ± 0.26 |
normalized to the summed and smoothed embedded atom absorption coefficients $\mu_{0,L}(s) \ (s = 1-3)$, calculated by means of the FEFF8.4 code [14]. The summed $\mu_{0,L}(k_s)$ are subtracted to obtain $\chi(k)$. The anomaly in the $\chi(k)$ at ~6.0Å$^{-1}$ is due to the $L_1$ edge region in the theoretical $\mu_0$. We also note that the spectra for the 5Å films have a step-like experimental artefact at ~8.6 Å$^{-1}$ due to an anomaly in the measured $I_0$ signal. In the fitting procedure larger uncertainties are assigned to these spectral regions in order to eliminate any possible effect on the structural parameters. We used as the a priori model parameters [6] the structural parameters of bulk hcp cobalt. The total number of parameters in the fitting procedure is 24 for Co/Cu(111) and 32 for the Co/Au thin films. These are the background spline-parameters $\delta I_0$, the shell radii $R_i$, the structural disorder $\sigma^2_{\text{struct}}$, and the path degeneracy $N_i$. 8 single scattering paths and 56 multiple scattering paths are included in the model. The path degeneracies are kept constant for the hcp Co/Cu(111) reference. The amplitude reduction factor $S_0^2$ and the edge energy $E_0$ are fixed to the value which yields the correct result for the reference data of the thick Co film. For the thermal part of the Debye-Waller parameter $\sigma^2$ calculated values from the Debye temperature of bulk hcp Co are used. The results of the curve fitting are summarized in table 1. The a priori values for the structural parameters are also shown in the table. Note that the values of parameters which stay at the a priori values after the fit do not imply that those values are determined by the experiment; instead, this means that nothing new is learned from the experiment concerning those parameters and the a posteriori error in this case is mostly determined by the width of the a priori probability distribution [6, 7]. In the present case the nearest two shell radii $R_1$ and $R_2$ are well determined by the data. The lattice parameters $a$ and $c$ from the result of $R_1$ and $R_2$ are $a=2.56$ Å and $c=3.80$ Å for the uncapped 5 Å Co/Au film, $a=2.53$ Å and $c=4.05$ Å for the 5 Å Co capped with 3.5 Å Au. This gives, for the strain $\epsilon_{11} = (a-a_{\text{bulk}})/a_{\text{bulk}}$ and $\epsilon_{33} = (c-c_{\text{bulk}})/c_{\text{bulk}}$, $(\epsilon_{11}, \epsilon_{33})=(2\%, -6.7\%)$ and $(\epsilon_{11}, \epsilon_{33})=(1\%, -0.6\%)$ for the uncapped Co(5Å)/Au film and the Au(3.5Å)/Co(3.5Å)/Au film, respectively. In the case of the uncapped Co(5Å)/Au film, the Co layers are significantly more compressed in the direction perpendicular to the film surface than the bulk elastic constants yields $(\epsilon_{33}=2(C_{13}/C_{33})\epsilon_{11}=-0.57\epsilon_{11}$ in the case of hcp Co [15]). This is substantially relaxed when the film is capped by Au. In addition, a large Debye-Waller parameter $\sigma^2_{\text{struct}}$, indicating a strong local disorder for the Co-Co bonds, was observed for the 5Å Co films. This effect is more prominent for the Au-capped Co films. The increase of disorder upon Au capping may be related to the formation of interfacial dislocations which may accompany the relaxation of the strain. An increase of the local disorder at low Co thickness is also reported by an earlier Co/Au(111) EXAFS study [5], and the present values of $\sigma^2_{\text{struct}}$ are close to the values reported there. This observation establishes the increase in disorder as a structural effect correlated with the occurrence of the SRT. We observe here two types of structural effects: both the local strain in the maximum of the pair distribution function, as well as an increase in its width.

Figure 3. Bayes-Turchin fit of the Fourier filtered EXAFS of (a) hcp Co/Cu(111) reference, (b) Co(5Å)/Au and (c) Au/Co(5Å)/Au. A priori and a posteriori spectra are shown in solid curves. Solid curves with bars are experimental data with effective uncertainties (see text).
4. Discussion

Our \textit{in situ} EXAFS results show large structural strains for the Co thin films. At the same time the Co thickness where the SRT occurs, shifts to a smaller thickness as compared to previous reports [4]. Moreover our uncapped Co/Au films show an in-plane easy magnetization direction at room temperature for the whole Co thickness region we studied, in variance with previous studies [11]. To find out whether it is possible to explain this difference in the magnetic anisotropy in terms of linear magnetoelastic coupling, we examine a simple phenomenological model which takes into account the magnetoelastic term, $K_\text{ME}$. For a thin film in general, the effective uniaxial magnetic anisotropy constant, $K_\text{eff}$, can be expressed as $K_\text{eff}=K_1^{\text{eff}}+K_\text{ME}$, where the first-order effective magnetic anisotropy constant $K_1^{\text{eff}}$ is given by $K_1^{\text{eff}}=K_{\text{dipole}}+K_{\text{bulk}}+[K_{\text{1st interface}}+K_{\text{2nd interface}}]/t$ [16]. For the present system of hexagonal symmetry, assuming an isotropic in-plane tensile strain, the lowest-order contribution to the magnetoelastic term, $K_\text{ME}$, is given as a function of the magnetoelastic constants $B_i$ by $K_\text{ME}=(B_1+2B_3)\varepsilon_{11}+B_2\varepsilon_{33}$ [16, 17]. For bulk hcp Co, $B_1=-0.80\times10^7$ Jm$^{-3}$, $B_2=-2.90\times10^7$ Jm$^{-3}$ and $B_3=2.81\times10^7$ Jm$^{-3}$ are the values of the magnetoelastic constants. According to our EXAFS analysis the Co/Au thin films exhibit positive $\varepsilon_{11}$ and negative $\varepsilon_{33}$. The bulk magnetoelastic constants give for the corresponding coefficients in $K_\text{ME}$, $B_1+2B_3 > 0$ and $B_2 < 0$, implying positive values of $K_\text{ME}$ for the strain we observed. This means a further stabilization of the \textit{out-of-plane} magnetization contrary to the anisotropy diagram in figure 1, where the \textit{in-plane} magnetization is more stabilized as compared to earlier reports, although $K_\text{ME}$ is in the right order of magnitude to give rise to the observed orientation of the magnetization. On that account, our EXAFS/XMCD study strongly suggests that the magnetoelastic constants differ from the bulk value as reported in the literature [17, 18]. From the results of further EXAFS analysis of a few more cases which will be described in a forthcoming article [13], we find that there exists a rather small range of the values of the magnetoelastic constants which reproduce the magnetization easy axis in figure 1 assuming $K_\text{ME}$ to be linear in the strains. That is, we obtain that $B_1+2B_3$ must be negative with a value of about $-1$ to $-4\times10^7$ Jm$^{-3}$, and $B_2$ must be positive, in the range of $0$ to $5\times10^7$ Jm$^{-3}$ in order to reproduce the observed magnetic anisotropy.

To illustrate this result, we simulate $K_\text{eff}$ assuming $B_1+2B_3=-3.0\times10^7$ Jm$^{-3}$ and $B_2=1.3 \times10^7$ Jm$^{-3}$. This is shown in figure 4, as a function of the Co thickness, $t$. Several lines are shown in figure 4, assuming constant strains for the case of uncapped, capped with 0.5 ML Au, capped with >1ML Au. For the interface term $K_s$ we used values reported for in the literature [11, 19]. These values describe well our magnetic anisotropy diagram. If there is no strain in the Co layer, the magnetic anisotropy favors an out-of-plane magnetization up to $t\approx10\AA$ for the uncapped Co/Au films. A positive $\varepsilon_{11}$ and a negative $\varepsilon_{33}$ make the slope steeper with these values of the magnetoelastic constants. In the case of $(\varepsilon_{11}, \varepsilon_{33})=(1\%, -0.6\%)$, the magnetic anisotropy energy of in-plane and out-of-plane magnetizations are approximately balanced for the Au(0.5ML)/Co(8Å)/Au film. Larger strain is necessary to stabilize the in-plane magnetization for the uncapped 5Å Co/Au film. It can be concluded that, if this picture applies, the Au cap layer induced SRT of the 5Å Co/Au film is driven for a large part by the relaxation.

![Figure 4. $K_\text{eff}$ as a function of Co film thickness and strains. The values of $B_1+2B_3=-3.0\times10^7$ Jm$^{-3}$ and $B_2=1.3 \times10^7$ Jm$^{-3}$ are used.](image-url)
of the strain caused by the Au capping, whereas the $K_s$ term is responsible for the SRT in the thicker films.

5. Summary

We have performed Co $L$-edge XMCD and EXAFS measurements of in situ prepared Co/Au/W(110) and Au/Co/Au/W(110) ultrathin films, which exhibit a different magnetic anisotropy as compared to previously reported results. In particular, for an uncapped 5 Å Co/Au film, we observe an in-plane strain $\varepsilon_{11}$ of $\sim$2% and an out-of-plane strain $\varepsilon_{33}$ of $\sim$-6.7%. These are considerably relaxed after Au capping. We propose a simple model which based on the magnetoelastic energy, leads to the easy magnetization direction as obtained by XMCD. A range of the linear magnetoelastic constants which are compatible with the XMCD observations is found to be $B_1+2B_3=-1$ to $4\times10^7$ Jm$^{-3}$ and $B_2=0$ to $5\times10^7$ Jm$^{-3}$. These are of the same order of magnitude as the bulk constants, but are of opposite sign. We find that combined in situ XMCD-EXAFS at the $L$ edges, together with the advanced Krappe-Rossner Bayesian method of EXAFS data-analysis used here, can be a powerful tool for this type of study. Ultimately, a more realistic modeling of the interface should also take into account the structural disorder and the film morphology necessary for a better microscopic understanding of the magnetic properties.

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References

[1] Weller D, Stöhr J J, Nakajima R, Carl A, Samant M G, Chappert C, Mégy R, Beauvillain P, Veillet P and Held G A 1995 Phys. Rev. Lett. 75 3752
[2] Stöhr J 1999 J. Magn. Magn. Mater. 200 470
[3] Andersson C, Sanyal B, Eriksson O, Nordström L, Karis O, Arvanitis D, Konishi T, Holub-Krappe E and Hunter Dunn J 2007 Phys. Rev. Lett. 99 177207
[4] Sellmann R, Fritzschke H, Maletta H, Leiner V and Siebrecht R 2001 Phys. Rev. B 64 054418
[5] Marsot N, Belkhou R, Magnan H, Le Fèvre P, Guillot C, Chandersis D 1999 Phys. Rev. B 59 3135
[6] Krappe H J and Rossner H H 2004 Phys. Rev. B 70 104102
[7] Rossner H H, Schmitz D, Imperia P, Krappe H J and Rehr J J 2006 Phys. Rev. B 74 134107
[8] Hunter Dunn J, Hahlin A, Karis O, Arvanitis D, LeBlanc G, Andersson Å and Lindgren L-J 2004 AIP Conf. Proc. 705 65
[9] Rath Ch, Prieto J E, Müllner S M, Miranda R and Heinz K 1997 Phys. Rev. B 55 10791
[10] Andersson C 2006 PhD Thesis (Uppsala University) and Persson A et al. in preparation
[11] Allenspach R, Stampamoni M and Bischof A 1990 Phys. Rev. Lett. 65 334
[12] Turchin V F 1985 Lecture Notes in Physics 236 33
[13] Sakamaki M et al. in preparation
[14] Ankoudinov A L, Nesvizhskii A I and Rehr J J 2003 Phys. Rev. B 67 115120
[15] Schober H R and Dederichs H 1979 in Landolt Börnstein New Series III Vol. 11a (Berlin: Springer)
[16] Bruno P 1993 IFF-Ferienkurs 24 24.1 (Forschungszentrum Jülich)
[17] Gutjahr-Löser Th, Sander D and Kirschner J 2000 J. Magn. Magn. Mat. 220 L1
[18] Tian Z, Sander D and Kirschner J 2009 Phys. Rev. B 79 024432
[19] Chappert C, Le Dang K, Beauvillain P, Hurdequint H and Renard D 1986 Phys. Rev. B 34 3192