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Magnetic circular x-ray-dichroism study of Co/Pt(111)

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Magnetic circular x-ray-dichroism measurements at the Co $L_{2,3}$ edges of the Co/Pt(111) interface are presented. Ultrathin Co films, deposited and measured at room temperature, order magnetically above a thickness of 1.8 monolayers and show magnetic anisotropy perpendicular to the surface up to coverage of at least 5 monolayers. An enhancement of the orbital magnetic momentum relative to the bulk value of Co metal is observed. A further increase after addition of a thick Pt overlayer reveals the influence of hybridization at the Co/Pt interface. Observations of magnetic surface alloys with perpendicular anisotropy are also reported. [S0163-1829(96)50918-5]

In the last few years there has been an explosive growth of interest in artifically thin film layered systems due to their variety of technological applications.[1,2] However, several of these interface or surface related phenomena, for example, the magnetic anisotropy perpendicular to the film surface, are still not well understood. In samples with alternate ultrathin layers of a 3*d* ferromagnet and another transition metal, an enormous progress in both preparation techniques and theoretical interpretation have considerably decreased the discrepancy between experimental results and theoretical predictions.[1]

Since the work of Néel,[3] an interface, as a symmetry break of a system, is expected to provoke contributions to the magnetic anisotropy through the changes in the electronic band structure.[4,5] Detailed investigations of the interface structure are often lacking, nevertheless it is known that interface roughness and interdiffusion tend to decrease the strength of the perpendicular magnetic anisotropy (PMA).[6] One exception to this is a positive contribution of the interface alloy to the PMA as, for example, in Co/Cr multilayers.[7]

Several models were proposed to explain the PMA in artificially layered structures $X/Y/X$, where X stands for a 3*d* metal and Y for a 4*d* or 5*d* metal. Generally, the spin-orbit parameter of 4*d* and 5*d* metals is considerably larger than that of 3*d* metals. Hybridization and exchange at the interfaces should therefore have an important influence on the anisotropy.[8]

First experimental observations supporting the link between PMA and an enhancement of the orbital momentum m_{orb} were recently reported.[9] The experimental verification of m_{orb} anisotropy in other directions than the easy axis is still lacking, since this requires high magnetic fields to saturate the sample with respect to its intrinsic anisotropy. Obviously, measurements in the remanent state will determine automatically m_{orb} parallel to the anisotropy direction.

X-ray magnetic circular dichroism (MCD) measurements can determine, via the sum rules,[10,11] the magnetic spin and orbital momentum, m_{spin} and m_{orb}, respectively. The angular dependence of the MCD signal gives directly information about the direction of the mean magnetic moment. Certain parameters that are difficult to determine in 3*d* transition metals, such as the number of 3*d* holes and the total absorption intensity related to the transitions into these states, can be neglected if only the ratio $R_{o/s}=\langle L_Z\rangle/\langle S_Z\rangle$ is determined. This ratio remains constant even in the case of incomplete remanence. Recent verification of the sum rules from band structure calculations in proximity of the surface[13] revealed that only the $\langle L_Z\rangle$ sum rule remains valid to within 5–10 %. The rule for the spin moment can be influenced by the magnetic dipole operator $\langle T_Z\rangle$, but in the case of the bulk Co (Refs. 11 and 12) it is generally neglected.

Co/Pt is without doubt one of the most investigated systems showing PMA in multilayers,[14] sandwiches,[15] and alloyed thin films.[16] It was predicted theoretically that one Co monolayer on Pt(111) should show PMA.[17] Experimentally, perpendicular domains were observed for a 4 ML thick Co film on a Pt surface.[18] A strong hybridization was calculated for the Co/Pt interface.[17] This effect is limited to the first two layers at the interface but changes the spin density over a longer range. The theoretically predicted increase of the magnetic moment for a Co surface amounts to 10%, but the ratio of $R_{o/s}$ stays constant.[19]

One of the greatest interface contributions, favorable for PMA, was observed on Pt capped Co/Pt(111) films.[15] Sev-

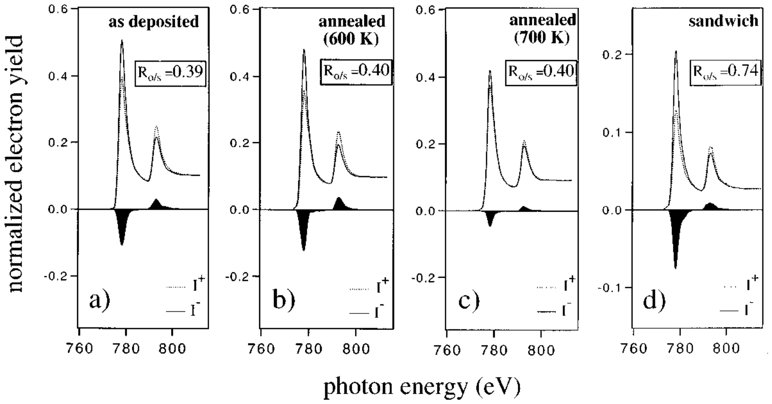

FIG. 1. Circular polarized x-ray absorption spectra at the $L_{2,3}$ edges for opposite remanent sample magnetization and the MCD signal for a 5 ML thick Co film on Pt(111) and the measured $\langle L_Z\rangle/\langle S_Z\rangle$ ratio $R_{o/s}$; (a) as deposited; (b) same film after annealing at 600 K for 20 min.; (c) same film after additional annealing at 700 K for 20 min.; (d) a 5 ML thick Co film on Pt(111) recovered by 15 ML Pt (‘‘sandwich’’).

eral groups have started to investigate the growth of Co on a Pt(111) single crystal in order to characterize the details of the interface structure (Ref. 20, and references therein). The misfit of the Co/Pt(111) interface is about 10%. It was observed that near a coverage d_{Co} of 1.8 monolayers (ML), the Co films on Pt(111) relax close to their bulk positions.[15,20] The relaxation is related to the observation of spots in the low-energy electron diffraction (LEED) pattern. Surface-extended x-ray-absorption fine structure (SEXAFS) experiments[21] at Co *K* edge performed on films of thickness d_{Co} between 2 and 10 ML indicate that this relaxation does lead locally to the structural anisotropy of hcp Co. Thus, possible deformation of the unit cell must be smaller than 1% compared to bulk Co.

The interface remains sharp even after annealing the sample for about 20 minutes at 550 K.[20] At higher temperatures interdiffusion sets in. Depending on d_{Co} and the annealing conditions, surface alloys of several compositions are formed.[20,21]

Covering the Co by a thick fcc Pt (15 ML) layer leads to a second Pt/Co interface less sharp compared to the first one.[20,21] The experiments were performed at the Laboratoire pour l’Utilisation du Rayonnement Electromagnétique (LURE) in Orsay on the SU-23 beam line equipped with four plane grating monochromators covering a photon energy range from 80 to 1000 eV. The beam line is installed behind an asymmetric hybrid wiggler which is optimized to give a high degree of circularly polarized radiation below and above the orbit plane of the positrons. The circular polarization of the light was fixed at 60%. Core level photoemission spectroscopy (PES) at various incident energies was used to check sample cleanliness. The attenuation of the Pt $4f_{7/2}$ intensity can be used to calibrate the Co flim thickness and the core level shift, reflecting changes in this chemical environment gives an insight in possible interdiffusion at the interface.[20]

Circular polarized x rays were obtained by moving the prefocusing mirror 2 mm below the positron orbit plane yielding a degree of circular polarization of (60±5) %. During almost all of our experiments the polarization (right helicity) was kept constant and only the direction of sample magnetization was changed. The external field (±0.8 T) direction was 45° off the sample normal in order to get information about the easy axis of the film. All MCD measurements were made at room temperature on samples with remanent magnetization using total electron yield. Base pressure in the experimental chamber was in the 10^{-11} Torr range.

The electron yield spectra were normalized to the absorption intensity before the absorption edges, and a linear background was subtracted from the spectra to remove the contribution from the substrate. This procedure gives the absorption signal as the percentage of the total electron yield. We estimate an error for the difference between two spectra of about 15%, which prevents us from discussing small changes of the MCD signal.

The measurements were performed at different photon incident angles Θ in order to determine the maximum MCD signal. The angle Θ of the maximum intensity indicates directly the orientation of the easy axis relative to the surface normal of the film. We neglect the saturation effects due to the total yield method, since only a small deviation (5%) from the cosine dependence for a $\Theta<65°$ is expected for layers under 10 ML.[22]

Figure 1 shows two absorption spectra and their difference for a 5 monolayer thick Co film taken with opposite sample magnetization. Note that no correction for incomplete photon polarization has been applied to the MCD signal. The MCD signal is comparable with results already reported.[9,12,23]

Recently, it was proposed that the absolute value of the MCD intensity at the L_3 edge can be used to monitor the degree of long-range magnetic ordering.[23] This only makes sense as long as the samples compared have a constant ratio $R_{o/s}$. To accomplish this, the MCD intensity is normalized to the total absorption intensity for linear polarized x rays, which is supposed to be identical to the average of the spectra taken with left- and right-handed polarized light. The result of this normalization as a function of Co thickness is shown in Fig. 2(a). Below 1.8 ML no MCD signal is found, indicating the absence of remanent ferromagnetic ordering at room temperature for this thickness range. Figure 2(a) displays also the intensity ratio of L_2 and L_3 edges (linear polarization) which has a constant value. The same results were obtained on a Co(0001) single crystal (this work) and on Co/Cu(100).[23] Comparing our results with the measurements on Co/Cu(100) (in plane magnetization and $R_{o/s}=0.33$) and taking into account the different degree of circularly polarized light, we find that in our experiments the 4–5 ML thick Co films show remanence close to 100%.

Figure 2(b) shows $R_{o/s}$ as a function of the Co film thickness on Pt(111). The cosine of the angle Θ showing the

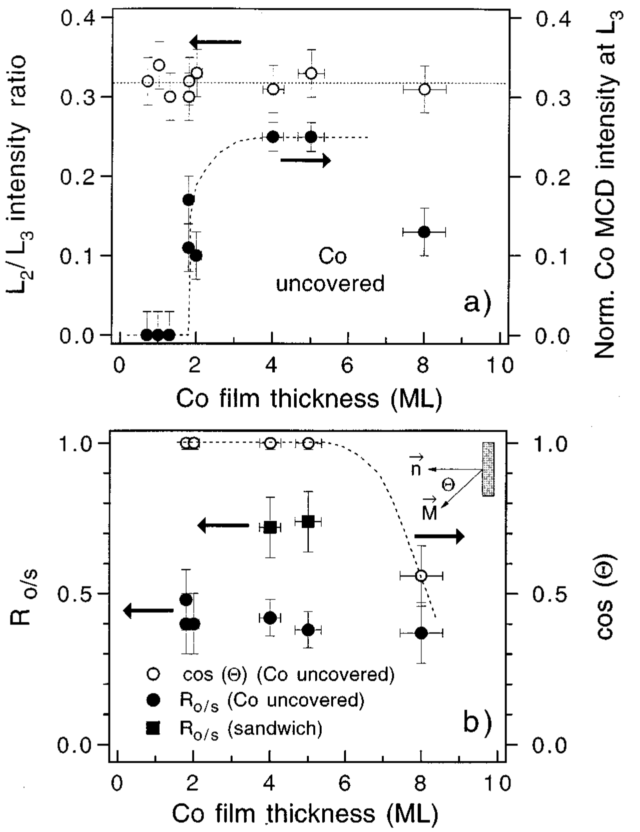

FIG. 2. (a) Ratio of the average absorption intensity at the L_2 and the L_3 edge (left) and the MCD signal normalized to the total absorption intensity at the L_3 edge (right) as a function of the Co thickness. (b) Measured $R_{o/s}=\langle L_Z\rangle/\langle S_Z\rangle$ ratio (left) and the cosine of the angle Θ between the sample normal and the direction of the remanent magnetization (right) as a function of the Co thickness for the uncovered Co films. The $R_{o/s}$ ratio after additional deposition of 15 ML Pt (''sandwich'') is also indicated. In the inset the definition of Θ is shown.

maximum MCD signal is also indicated. A perpendicular orientation is observed for thicknesses up to 5 ML, whereas for the 8 ML the easy axis is rotated to 56° off normal. Measurements on Co films on Au(111) show that the rotation of the easy axis from perpendicular to in plane as a function of d_{Co} occurs via an intermediate state, where the easy direction lies on a cone of half-angle Θ.[24] The authors define a crossover thickness t^*, where $\Theta=45°$. In comparison to their work, we can estimate a t^* for our uncovered Co films of about 7 ML.

Figures 1(b) and 1(c) show the influence of annealing a 5 ML thick Co film. Annealing at 600 K for 20 min leads to a slight interdiffusion at the interface as deduced from the photoemission spectra. The small variations of the MCD L_3 and L_2 signals observed have to be investigated more precisely and will not be discussed here. After additional annealing at 700 K, a Co/Pt surface alloy is formed (mean Co concentration $50\pm15\%$)[20,21] leading to well-defined LEED pattern of a (111) fcc surface, with a intermediate lattice parameter between that of Co and Pt.[20] The decrease of the MCD signal indicates changes in the magnetic properties of the sample, but the PMA is still observed. At the same time, $R_{o/s}$ remains constant within the experimental error. It is interesting to stress that in this case Co atoms are distributed over about 10 ML. For this thickness a pure Co films already show in plane magnetization.

The addition of the second interface, formed by the deposition of 15 ML of Pt on top of the Co layer, considerably enhances the relative orbital moment [Figs. 1(d) and 2(b)]. These sandwiches showed square *ex situ* polar Kerr hysteresis loops with 100% remanence for $d_{\mathrm{Co}}=4$–5 ML. For smaller Co coverages the coercive field increases considerably[15,25] and no inversion of the magnetization was possible with the available magnetic field (0.08 T). Note that the relative intensity loss in Fig. 1(d) compared to the uncovered Co films is related to the small effective sampling depth of the secondary electrons in total yield, already observed in previous work.[23]

An increase of the intensity of the white lines at the L_3 and the L_2 edge, already reported for Co/Pd and Co/Pt multilayers with very thin d_{Co},[9] was also observed in our samples, but the effect was limited to uncovered Co/Pt(111) samples with $d_{\mathrm{Co}}\leqslant2$ ML and Pt/Co/Pt(111) sandwiches with $d_{\mathrm{Co}}\leqslant4$ ML. The small critical Co thickness for the observation of this effect supports the idea that the changes in the total electron density are limited to the interface layer and are related to the Co 3*d*-Pt 5*d* hybridization, as predicted theoretically.[17]

It is well known that at room temperature a critical film thickness is necessary for magnetic ordering. For Co/Cu(100) this thickness is found to be 1.8 ML.[23,26] The authors relate this observation to structural changes in the growth mode. Similarly, in the Co/Pt(111) system, the magnetic ordering coincides with the LEED observation of relaxation on a large scale. Since no hysterisis curve measurements are known for the magnetic Co films on Pt(111), we cannot say if the smaller normalized MCD intensity at the L_3 edge for $d_{\mathrm{Co}}\approx2$ ML [Fig. 2(a)] is related to an incomplete remanence and/or to changes of the ordering temperature with thickness.

Usually the phenomenological description of the effective uniaxial anisotropy K_U is given by $K_U=K_V+2K_Sd_{\mathrm{Co}}^{-1}$,[15] where K_V and K_S are, respectively, the volume and interface anisotropies constants. Despite the form anisotropy and the observation of a contribution from the Co/vacuum interface opposed to the PMA,[24,27] the large critical thickness t^* indicates the presence of a high interface term K_S originating from the Co/Pt(111) interface, favoring PMA. In the case of comparable Pt/Co/Pt(111) sandwich samples K_S was evaluated as 1.15 mJ/m^2.[15] Comparing critical thicknesses with those of our uncovered samples we estimate a similar K_S for our films.

As far as the $R_{o/s}$ ratio is concerned, we can only discuss relative changes since we did not measure a bulk Co sample. $R_{o/s}$ values reported in the literature vary from 0.19 (Ref. 12) to 0.33.[23]. Our result seems to indicate an important enhancement of m_{orb} in agreement with recent measurement on Co/Cu(100) interface.[28] In this paper the authors show an enhancement of Co orbital moment by a factor 2 at a single interface as compared to the bulk Co.

In our experiments, the fact that the addition of the second interface increases $R_{o/s}$ considerably reveals clearly that this is related to the Co/Pt interface itself, since our SEXAFS measurements indicate no significant structural changes provoked by the Pt deposition. The deformation of the Co lattice cannot therefore be decisive for the enhancement of $R_{o/s}$. So, the rise of $R_{o/s}$ must be electronic in nature, hence correlated to a hybridization phenomenon.

Considering these results in relation to the magnetic anisotropy, it is evident that the deposition of Pt on top of Co films enhances K_U, since t^* increases from about 7 ML (this work) to 15 ML.[15] If m_{spin} is constant, it seems that K_U scales with m_{orb} as recently proposed[9] since $R_{o/s}$ doubles after deposition of Pt overlayer.

The negligible influence of annealing of the 5 ML shows that despite the interdiffusion at the interface a constant $R_{o/s}$ value is observed. In particular for the surface alloy (annealing at $T=700$ K) the PMA is still observed which underlines the influence of the spin-orbit coupling and hybridization between Co and Pt. Nevertheless, it would be interesting to follow the thickness dependence of m_{orb} and m_{spin} separately which requires measurements in high magnetic fields. At the same time we stress that it would be possible to use the MCD measurements for the determination of anisotropy constants using the experimental geometry of Kerr studies.

In conclusion, the influence of hybridization at the Co/Pt interface on the enhancement of the $R_{o/s}$ was shown. A minimum thickness of 1.8 ML was determined for remanent magnetic ordering at room temperature for Co films on Pt(111). The critical thickness t^* for the observation of the PMA is about 7 ML. First indications of magnetic surface alloy formation with PMA were given.

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