First-Principles Calculation of the Anomalous Perpendicular Anisotropy in a Co Monolayer on Au(111)

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We perform fully relativistic spin-polarized local spin density calculations for Au covered Co monolayer on Au(111). In accord with a trend observed in experiments we obtain an enhancement of perpendicular magnetic anisotropy as a function of the Au coverage. The close relationship found between the anisotropies of orbital magnetic moments and the anisotropy energies leads to an interpretation of our results in terms of familiar perturbation theory. By using this framework the anomalous behavior of the magnetic anisotropy energies can be well explained due to changes in the *sp-d* hybridization at the interface of Co monolayer and Au cap. [S0031-9007(96)01047-2]

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Since many overlayer and superlattice systems have been predicted to be useful for purposes of high-density magneto-optical storage, theoretical investigations of the magnetic anisotropy of such systems became of particular interest. Despite extensive experimental and theoretical efforts, a complete, material-specific understanding of the surface magnetic anisotropy, as yet, has not been achieved. Recently several authors have discussed the anomalous perpendicular anisotropy in ultrathin Co films on Au and Pt (111) surfaces. In particular, Engel *et al.* [1,2] performed careful experiments which revealed that deposition of additional Ag, Cu, Au, or Pd layers—forming a trilayer—increases the perpendicular anisotropy as can be seen in their *in situ* polar magneto-optical Kerr effect (PMOKE) measurements. Furthermore, they found the surprising fact that the anisotropy energy has a maximum for coverages between 1 and 2 monolayers (ML). Both facts were also observed by Ould-Mahfoud *et al.* [3] and Beauvillain *et al.* [4] also by PMOKE experiments. Each experimental paper discusses several possibilities as the theoretical reason of the observed behavior. One reason could be the magnetoelastic anisotropy, but no abrupt change in the structure is observed in the experiments. Although, in principle, a strong lattice mismatch can lead to such a contribution, it has been pointed out by Beauvillain *et al.* [4] that this can explain neither the measured peak nor the amplitude of the anomalous anisotropy. These authors suggest the modified electronic structure due to the overlayer as a reason of the observed behavior.

In this paper we report results of spin-polarized fully relativistic electronic structure calculations using the screened KKR method for a single monolayer of Co on Au(111) with a different number of additional covering layers of Au. Our aim is to show that the experimental results can be reproduced (both qualitatively and quantitatively) by such calculations, confirming in turn that the reason for the dependence of the magnetic anisotropy energy on the overlayer coverage is caused by the corresponding changes in the electronic structure. Such calculations have the advantage that local quantities like charges, spin-only and orbital moments, as well as local energetical contributions to the magnetic anisotropy can be calculated easily, whereas the various factors contributing to the measured magnetic anisotropy data, such as the reduced coordination and symmetry, changes in the electronic structure, or lattice strain at the interface of the constituents, can hardly be separated experimentally.

Self-consistent calculations within the local spin density approximation (LSDA) [5], the atomic sphere approximation (ASA), and with a magnetic field pointing perpendicular to the surface were carried out in turn for each multilayer $\mathrm{Au}_n/\mathrm{Co}/\mathrm{Au}(111)$, where n denotes the number of Au cap layers on top of a Co/Au(111) surface. In our studies $n = 0, 1, 2, 3, 4$, or ∞, where ∞ means that the Co layer was embedded as an interlayer into bulk Au. Similarly to Ref. [6], the fully relativistic spin-polarized screened KKR method has been used to carry out the actual band structure calculations, so relativity, spin-polarized scattering, and the semi-infinite geometry were all treated on the same footing. We assumed a perfect fcc lattice with the experimental lattice constant of the bulk gold ($a = 7.681$ a.u.) throughout all space and no lattice strain was taken into account. The Co layer was assumed to be ferromagnetically ordered. For this particular setup, in each case, two layers of empty sphere potentials between the perfect vacuum and the surface, as well as at least two layers of Au between the perfect bulk and the Co layer, were treated self-consistently. During the self-consistent procedure, the energy integrations were performed along a semicircular contour in the complex plane using a 16-point Gaussian sampling on an asymmetric (logarithmic)

mesh. For the Brillouin zone integrations, 45 $\mathbf{k}_\parallel$ points in the irreducible wedge of the two-dimensional (2D) Brillouin zone (IBZ) have been used.

The evaluation of the magnetic anisotropy energy (MAE) is based on the so-called force theorem [7,8]. For each system $Au_n/Co/Au(111)$, therefore, two subsequent calculations were performed using the previously determined self-consistent potentials, namely, one with the magnetic field perpendicular to the surface ($\perp$), and one with the magnetic field pointing along the x axis of the 2D lattice ($\parallel$). Here we used 990 $\mathbf{k}_\parallel$ points in IBZ close to the Fermi energy and 631–325 $\mathbf{k}_\parallel$ points for energies away from the real axis to ensure a relative accuracy below 5% for the difference between the band energies with respect to the two orientations, $\Delta E_b = E_b^\parallel - E_b^\perp$. The MAE is then given by the sum of ΔE_b and the magnetostatic dipole-dipole interaction ΔE_{dd} [6],

$$\Delta E = \Delta E_b + \Delta E_{dd} . \quad (1)$$

The calculated MAE's are shown in Fig. 1 together with the experimental results as deduced from the measurements of Ref. [4] for thicker Co films by extrapolation to the monolayer limit. For the uncovered monolayer the theory predicts in-plane orientation with a small anisotropy energy. This result can be related to previous theoretical results for a free-standing Co monolayer [9,10], yielding a negative MAE greater than 1 eV in magnitude. The effect of the Au substrate is quite similar to that of Cu where the magnitude of the anisotropy energy is considerably reduced, however, its sign remains negative [10]. In contrast, the experimental curve in Fig. 1 exhibits the out-of-plane direction of the magnetization even in the absence of Au coverage ($n = 0$). This might be due to the approximate extrapolation scheme used when deriving this curve from the experimental data and/or to the fact that perfect pseudomorphism of Co on Au is never obtained experimentally.

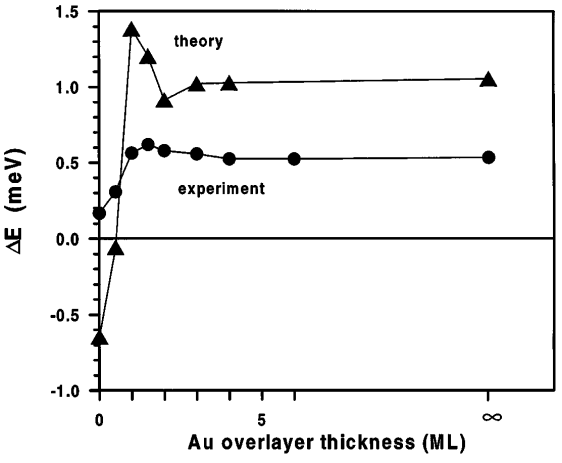

FIG. 1. Total magnetic anisotropy energies ΔE for a Co monolayer on Au(111) with different Au coverages. Triangles: calculated results; circles: experimental results from Ref. [4]. Solid lines serve as a guide to the eye.

By depositing an additional layer of Au onto the Co layer, both in theory and in experiment, there is an abrupt increase in the MAE implying a strong tendency to perpendicular magnetization. For more than 1 ML coverage the MAE slightly drops and rapidly converges with increasing coverage to its interface value. It should be noted that the theoretical values for the noninteger coverages were obtained by supposing a random distribution of the Au atoms and vacancies at the lattice positions of the incomplete surface layer. The effect of this substitutional disorder on the electronic structure of the system was then taken into account in a mean field theory, namely in terms of the coherent potential approximation [11,12].

As can be seen from Fig. 1, all qualitative features of the experimental data are well reproduced, in particular the maximum at about 1 ML coverage. The theoretical values, however, are bigger than the experimental values by a factor of 2. This factor can be accounted for by intermixing at the Au/Co interface(s) and/or by surface roughness effects. Intermixing is expected to damp the effect of symmetry breaking at the Au/Co interface and therefore reduce the anisotropy. This naive argument is supported by first principles calculations for $Fe_nCu(001)$ multilayers [13], where 15% intermixing already halves the band energy anisotropy.

Since the spin-only magnetic moment of Co is fairly insensitive to the presence of a Au cap and the induced moments on the Au layers are almost negligible, the dependency of ΔE_{dd} on n is of minor importance. Therefore, the calculated shape of the MAE (ΔE) with respect to n is overwhelmingly due to the band energy part ΔE_b. Within multiple scattering theory, it is natural to partition the band energy into contributions associated with particular layers investigating thus to what extent the different layers contribute to the MAE. In Table I these layer resolved band energies are shown. The main contribution to ΔE_b comes from the cobalt layer, however, for the covered samples a remarkable increase of ΔE_b arises also due to the Au layers closest to the

TABLE I. Calculated layer resolved band energy differences $\Delta E_b = E_b^\parallel - E_b^\perp$ (in meV) for $Au_n/Co/Au(111)$ films. In the first row, integer arguments with a prime label layers on the substrate side and those without a prime label the cap layers. For $n = 0.5$ and 1.5 only the Au contributions are shown for the surface layers Au(1) and Au(2), respectively.

n		...	Au(2)	Au(1)	Co	Au(1′)	Au(2′)
0					−0.626	0.045	0.001
0.5				0.121	−0.087	0.058	0.005
1				0.197	1.207	0.157	0.018
1.5			−0.007	0.183	0.952	0.142	0.014
2			0.012	0.161	0.711	0.144	0.011
3		−0.015	0.002	0.156	0.834	0.153	0.014
4	0.001	0.000	0.014	0.145	0.793	0.147	0.013
∞	0.001	−0.002	0.012	0.149	0.821	0.149	0.012

Co layer. Obviously, the contributions from both the Co layer and the neighboring Au layers reach their maximum at 1 ML Au coverage giving rise to the characteristic peak seen in Fig. 1. This indicates that the changes in the hybridization between the Co and Au layers introduced by the cap layers is the main course of the anomalous magnetic anisotropy.

As proposed originally by van Vleck [14], the magnetic anisotropy arises primarily from the spin-orbit coupling (SOC) interaction. For 3*d* transition metals the SOC energy is fairly small as compared to the 3*d* bandwidth, which allows one to use perturbation theory to the magnetocrystalline anisotropy [15]. One particular result of this theory is that for ferromagnetic monolayers the MAE is closely related to the anisotropy of the orbital magnetic moment $\Delta m_{\mathrm{orb}} = m_{\mathrm{orb}}^{\parallel} - m_{\mathrm{orb}}^{\perp}$. For a more than half filled *d* shell and by neglecting spin-channel coupling a negative proportionality between ΔE and Δm_{orb} can be predicted, as confirmed recently also by means of x-ray magnetic circular dichroism for thicker Au/Co/Au films [16,17].

In order to test the validity of this prediction, in Fig. 2 the calculated Δm_{orb}'s are shown (with a negative sign) as a function of the thickness of the Au cap. In agreement with the observed in-plane anisotropy, for the uncapped case an enhancement of the orbital magnetic moment with respect to the parallel direction is found. For the capped cases displaying perpendicular anisotropy this enhancement is dramatically reduced, i.e., the perpendicular orbital magnetic moment is increased relative to $n = 0$, however, Δm_{orb} does not change sign as would be expected from the simple model above. Nevertheless, comparing Fig. 2 to Fig. 1 reveals that the shape of Δm_{orb} accurately follows that of ΔE. This at least implies that the changes in ΔE induced by the Au overlayer can be interpreted in simple terms of perturbation theory. Apparently the corresponding changes in the minority spin band of Co have to be examined.

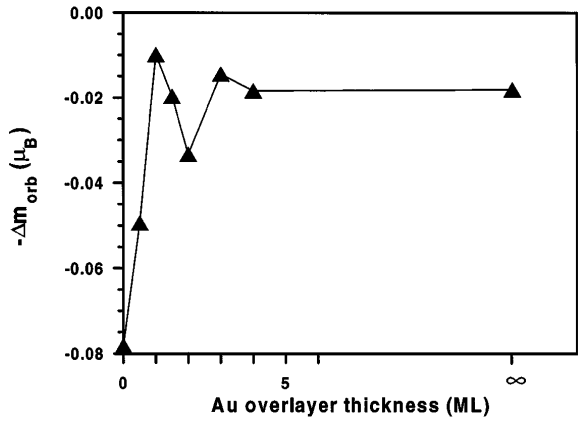

FIG. 2. Calculated values of orbital moment anisotropies, $\Delta m_{\mathrm{orb}} = m_{\mathrm{orb}}^{\parallel} - m_{\mathrm{orb}}^{\perp}$, as shown with a negative sign, for Au_n/Co/Au(111) multilayers. The solid line serves as a guide to the eye.

The most striking changes due to different Au coverages were found in the minority d_{z^2} and d_{yz}-like states of Co as shown in Fig. 3 [18]. Because of SOC induced interaction with the $d_{xz,yz}$ states (namely, through L_x and L_y coupling), the large d_{z^2}-like density of states at the Fermi level (E_F) clearly explains the in-plane anisotropy for $n = 0$. For $n = 1$ the d_{z^2} peak at E_F considerably reduces, while a d_{yz} peak at E_F arises, whereas the d_{xz} component of the density of states (DOS) remains practically unchanged. Subsequently, a corresponding peak at E_F was observed in the *s* and *p*-like DOS of the cap Au. Note that the lattice positions closest to a Co atom in the neighboring Au layers are nearly aligned along the *yz* direction. So a strong tendency to perpendicular anisotropy is expected due to L_z coupling between d_{yz} and d_{xz} states as indeed obtained in our calculations. Since for $n = 2$ the Au(1) layer (see Table I) becomes more distant from the surface accompanied by an increase of the energetical separation of the Au *sp* and Co *d* bands, the hybridization between them obviously reduces, pushing thus the d_{yz} states of Co somewhat away from E_F [see Fig. 3(b)]. Following from the above considerations this results in a decrease of the MAE. Clearly subsequent deposition of Au layers hardly influences the Au(1) layer anymore. In order to visualize the role of the relative energetical position of the Co and Au(1) bands to the MAE, in Fig. 4 we plotted the difference between the calculated Madelung

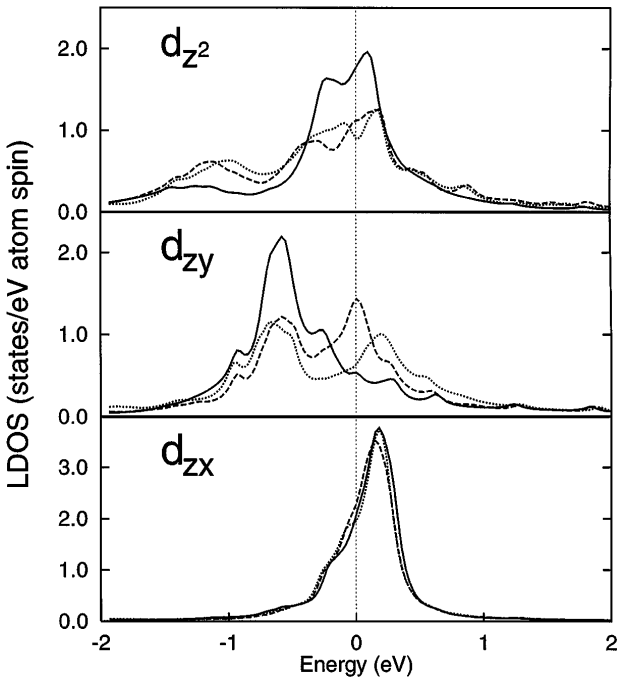

FIG. 3. Minority spin densities of states of d_{z^2}, d_{yz}, and d_{xz} character for Co in Au_n/Co/Au(111) multilayers. Solid line: $n = 0$, dashed line: $n = 1$, dotted line: $n = 2$. The Fermi level is chosen to be the origin of the energy scale.

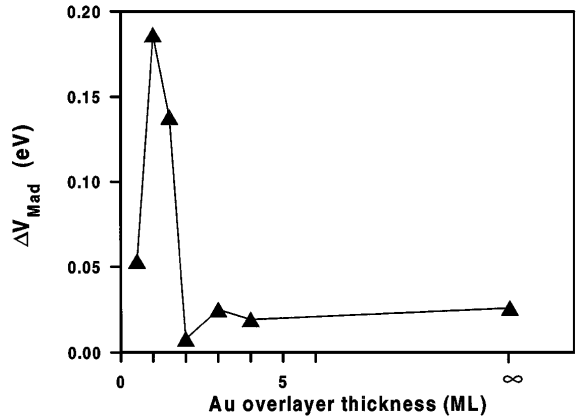

FIG. 4. Difference between the calculated Madelung potentials of the Au(1) and the Co layer in $Au_n/Co/Au(111)$ multilayers. The solid line serves as a guide to the eye.

potentials of Au(1) and Co, ΔV_{Mad}, and found a good correlation to the variation of ΔE in Fig. 1.

In conclusion, we showed that the anomalous characteristics of the MAE observed in the $Au_n/Co/Au(111)$ system can be well reproduced by electronic structure calculations. As the function of coverage, the orbital moment anisotropy is found to be proportional to the MAE in agreement with the prediction of simple perturbation theory. The anomalous behavior of the MAE can then be well understood in terms of overlayer induced changes in the electronic structure, governed by the relative energetical positions of the Au and Co bands [19].

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[18] The z axis is perpendicular to the layers; the x and y axes are in plane, with x along a nearest neighbor direction.

[19] After submission of the paper we became aware of a very similar study of L. Zhong *et al.* on the Co/Cu(111) system.