Enhancement of Orbital Magnetism at Surfaces: Co on Cu(100)

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By combining magnetic circular x-ray dichroism experiments with first principles electronic structure calculations, we demonstrate that the orbital contribution to magnetism can be strongly enhanced at surfaces. This effect is illustrated for Co grown on a Cu(100) surface, where the first layer of Co shows an enhancement of the orbital moment ($0.26\mu_B$) by a factor of 2 as compared to the bulk. The lowering of the symmetry at the surface, the enhanced spin moment, and the increased value of the density of states at the Fermi level are factors that generally give the observed enhancements.

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Lately one has witnessed intense theoretical [1–5] and experimental [6–13] efforts in understanding orbital magnetism, especially in studies involving surface physics. Such studies are well motivated for several reasons. First, the quenching of orbital moments, well established in bulk materials of cubic symmetry, could be partly lifted on the surface and, in particular, at surface steps, resulting in unexpected behavior. Moreover, this aspect of magnetism is interwoven with other physical phenomena, such as the magnetocrystalline anisotropy and the magnetic Kerr angle. For bulk materials it has been shown that one can probe the orbital magnetic moment M_L by measurements of the g factor [6], by means of neutron scattering experiments [7], and recently by means of magnetic circular x-ray dichroism (MCXD) experiments even for atoms at a surface or an interface [8,10–13]. Depending on the chemical environment, a specific element is expected to have different spin and orbital moments. This has indeed been shown, by both theory and experiment, to be the case in the bulk. One may anticipate modified orbital moments also at the surface. Previous theoretical works have predicted such behavior [4,5]. However, experimental work has yet to give a quantitative proof of this [14], and it is the purpose of this Letter to provide such evidence.

On quite general grounds the orbital moment of delocalized electron states should, to a large extent, depend on the shape and width of the density of states (DOS). In particular, one may expect enhanced orbital moments at surfaces due to the following modifications of the DOS. (i) At the surface the d bands become more narrow causing larger spin moments which, due to the spin-orbit coupling, produces enhanced orbital moments. (ii) At the surface the crystal field partitioning of the electronic levels is modified, due to the reduced symmetry. Thus the lower symmetry at the surface results in a reduced crystal field quenching of the orbital moment, and from this one also expects an enhanced orbital moment. (iii) The value of the DOS at the Fermi level, E_F, is larger than in the bulk. Previously it was shown that a large DOS at E_F results in an enhanced orbital moment [15]. Other effects may also play a role but the ones listed above are the main reasons for an enhancement of the orbital moment at the surface. One should bear in mind that there may be exceptions to the above three points [(i)–(iii)].

Let us now illustrate these points using the electronic structure of two, for the present analysis, pertinent systems, bulk fcc Co and a monolayer of Co on Cu(100). In Fig. 1 we show the DOS for bulk fcc Co and compare it with the Co projected DOS for 1 monolayer (ML) of Co on Cu(100). The DOS of Fig. 1 were calculated by means of a full potential electronic structure method based on the local density approximation, designed to treat both surface as well as bulk materials [16,17]. The spin moments corresponding to the DOS in Fig. 1 are $1.72\mu_B$ and $1.85\mu_B$ for bulk Co and the Co overlayer, respectively. The corresponding values for the orbital moment are $0.13\mu_B$ and $0.26\mu_B$, respectively. The relative enhancement of the or-

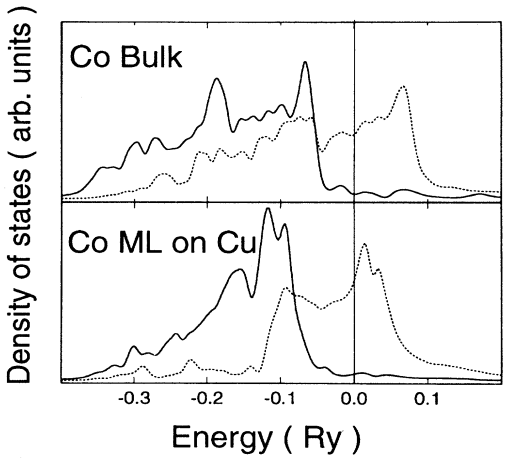

FIG. 1. Calculated DOS for bulk fcc Co and the surface projected DOS for a monolayer of Co on Cu(100). The solid lines show the DOS for the spin-up electrons, while the dotted lines show the DOS for the spin-down electrons. In both cases the experimental lattice constant of Cu is adopted.

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bital moment at the surface is thus very large, much larger than the enhancement of the spin moment. The data of Fig. 1 illustrate all the above mentioned reasons for large orbital moments at the surface [(i)–(iii)]. Similar calculations for a monolayer of Fe on Cu(100) and a monolayer of Ni on Cu (100) confirmed the previous analysis and gave for the same reasons enhanced orbital moments at the surface (see below) [18].

In order to test the theoretical predictions presented above we performed MCXD measurements on Co ultrathin films grown on a Cu(100) surface as a function of film thickness. Only thickness dependent experiments provide data which can be used to assess the theory and allow for a quantitative comparison. The choice of the Co/Cu(100) system as a prototype for such an investigation is motivated by several reasons. (a) This is one of the few systems in the thin film literature where a regular layer by layer growth is found at room temperature in the range 2–20 ML as shown by x-ray absorption and photoelectron diffraction measurements [19,20]. For thinner films a transition from heteroepitaxial to homoepitaxial growth has also been characterized [21]. (b) The magnetic properties of this system appear to be more simple than those of other $3d$ metal overlayers with a larger lattice mismatch to the Cu(100) substrate, where a reorientation of the magnetization is observed as a function of overlayer thickness [22]. These experimental findings make the Co/Cu(100) system a good prototype for a successful comparison of experimental data to *ab initio* electronic structure calculations.

The MCXD measurements were performed using the SX 700 plane grating monochromators at BESSY. The Co films were evaporated and characterized *in situ*. The effective electron escape depth λ for our experimental setup was determined independently to be 17(3) Å [23]. For films with a thickness $d \leq 2.2$ ML, their critical temperature T_c and other critical properties were characterized *in situ* [12]. A high quality monodomain magnetic response is found, corresponding to magnetic domain sizes of at least 10^6 Å^2 for $d \geq 2$ ML [24]. For several samples the MCXD response as a function of the of x-ray incidence angle was investigated as well. This allows one to quantify and correct saturation effects that can occur in the measurements [23]. These angular dependent measurements independently confirm the measured value of λ [23]. Data were taken in a temperature range between 40 and 350 K, and for many samples measurements were performed at several reduced temperatures T/T_c. More experimental details are given elsewhere [12,23,24].

Typical MCXD spectra for a thin Co film (3.5 ML) are shown in Fig. 2(a). By subtracting the normalized absorption spectra of Fig. 2(a) one obtains the MCXD difference spectrum of Fig. 2(b). The MCXD difference spectrum of a thick Co film is also shown. In order to compare these spectra taken at different reduced temperatures the MCXD difference of the thick film is scaled in such a way that the strongest MCXD response at the

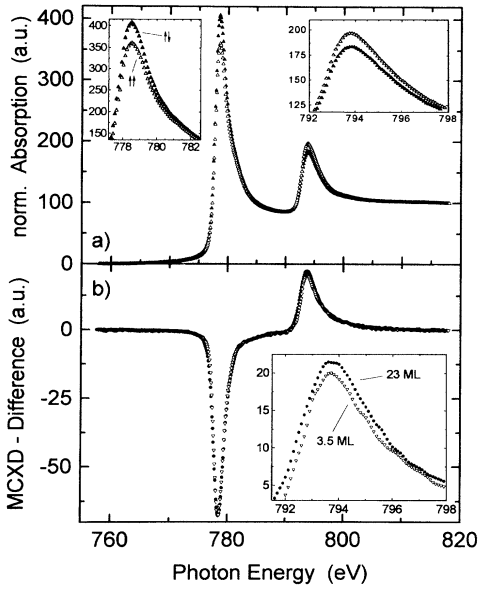

FIG. 2. (a) The normalized absorption spectrum for 3.5 ML Co/Cu(100). Open triangles indicate the photon spin parallel to the remanent magnetization, full triangles antiparallel. (b) MCXD difference for the 3.5 ML film (triangles) and a thick 23 ML film (circles). Both are normalized to the same L_3 intensity to demonstrate that the dichroic response around the L_2 edge is relatively smaller for the thin film.

L_3 edge coincides for both samples [Fig. 2(b)]. It can be seen that the two scaled difference spectra coincide within the noise level over a wide photon energy range except for those photon energies yielding a magnetic response at the L_2 edge. Based on MCXD sum rules that link the dichroic areas below the spectra of Fig. 2 to the ground state orbital and spin moment contributions [8,9], this observation implies a qualitative difference in the orbital and spin magnetism between these two Co overlayers. The spectra of Fig. 2(b) unambiguously demonstrate thatthe area under the L_2 peak is smaller for the thin film, indicating an increased orbital contribution. It is important to investigate the MCXD spectra of the Co overlayers systematically, not only over a wide range in thickness but also over a large temperature range. We find that the relative reduction of dichroic response as shown in Fig. 2(b) is correlated to the film thickness only. No correlation is observed as a function of reduced temperature ($0.02 \leq T/T_c \leq 0.8$). In order to further link the observed differences in the MCXD signal to ground state magnetic properties and compare with theory, we use MCXD sum rules [9]. To obtain an accurate comparison, we will limit ourselves only to the discussion of the difference spectra that, after neglecting the magnetic dipole contribution—as was proposed earlier [9,25], yield the ratio between the orbital (M_L) and the spin (M_S) contribution to the magnetic moment. Only a relative comparison, using the difference spectra as a function of the Co overlayer thickness, can be used to quantify the small

changes recorded in the experimental spectra [Fig. 2(b)]. As observed earlier, an analysis involving also an experimental determination of the number of d holes involves the fitting of steps in the absorption spectra of Fig. 2(a), a procedure introducing several free parameters as well as supplementary assumptions regarding the number of d holes [23].

The results of the M_L/M_S ratio are shown in Fig. 3, as a function of Co thickness. A systematic increase in M_L/M_S is observed with decreasing thickness d down to a value of $d \geq 2$ ML. Below 2 ML this ratio appears to scatter. As a complement to the experimental work we have calculated the M_L/M_S ratio by means of first principles calculations. The calculated data are collected in Table I, and we note that for both the monolayer of Co on Cu and the surface of fcc Co the spin and orbital moments are enhanced compared to the bulk. The enhancement of the orbital moment is much stronger ($\sim$100%) than the spin moment so that the M_L/M_S ratio is also enhanced at the surface. Following the theoretical results, in Table I (third row), a quantitative comparison between theory and experiment is also made (Fig. 3). We reproduced the experimental data using three different M_L/M_S ratios, corresponding to the interface (A), the surface (C), and the remaining ($d-2$) Co layers (B). Introducing a single scaling factor, so that the experimental points match the theoretical value for bulk films, parameter B was determined and subsequently fixed. Furthermore, in order to adequately reproduce the measured signal, the decay in intensity of the deep lying Co layers has to be modeled using the effective electron escape depth λ, being 17 Å [23], as discussed above. For $d \geq 3$, by performing a summation over the number of Co layers, one obtains an expression for the weighted experimental M_L/M_S contribution of d Co layers with an interlayer spacing D:

$$\left(\frac{M_L}{M_S}\right)_{\text{exp}} = \frac{Ae^{-D(d-1)/\lambda} + B\sum_{n=3}^{d} e^{-D(n-2)/\lambda} + C}{\sum_{n=0}^{d-1} e^{-nD/\lambda}}. \quad (1)$$

Equation (1) is used to obtain $(M_L/M_S)_{\text{exp}}$ as an analytical function of d, producing a fit to the experimental data points. The full curve of Fig. 3 represents the best fit to the experiment varying only parameters A and C in the fitting procedure. These parameters are summarized in Table I (fourth row). It is important to note that the parameters in Eq. (1) are unambiguously determined, i.e., the interface contribution vanishes for thick films and the M_L/M_S ratio approaches the bulk value for increasing d. In contrast, for $d \leq 5.5$ the interface term dominates. A meaningful determination of both parameters (A and C) is thus possible as the full thickness dependence is experimentally available. Our data, shown in Fig. 3, demonstrate the first quantitative evidence for increased orbital magnetic contributions at a surface. Previous observations using photoemission experiments on a clean surface were only of a tentative nature and no precise numerical determination could be given [14]. Also previous observations of an enhanced M_L/M_S ratio in a Co/Pd multilayer [10] do not appear to be related to a lowering of dimensionality, but rather to intermixing between Co and Pd. For Co/Pd and Co/Pt multilayers [26] the enhancement was not sound. In contrast, the expected thickness dependence is exactly what we obtain from the data reported in Fig. 3. The rapid increase of M_L/M_S down to $d \geq 2$ ML follows the expected 1/d law, weighted for the electron escape depth and the three different M_L/M_S contributions, as discussed above. Moreover, it is very rewarding that the agreement between theoretical and experimental values of M_L/M_S is good for the surface of fcc Co (Table I) as well as for the Co monolayer on Cu. To illustrate that the effect of Co on Cu is not an isolated example we have, as stated above, calculated the spin and orbital moments for a monolayer of Fe on Cu(100) and for a monolayer of Ni on Cu(100) [18]. The M_L/M_S ratio for the surface atoms are 0.045 and 0.195, respectively, which is to be compared to the bulk values of 0.036 and 0.100, respectively. We have also performed measurements of the Ni on the Cu(100) system, with varying thickness of the Ni overlayers [27]. In the latter study we also find an enhancement of M_L/M_S for the surface atoms in agreement with the theoretical results, quite comparable to the one of Co on Cu system. A detailed description of this work goes, however, beyond the scope of the present Letter [18,27].

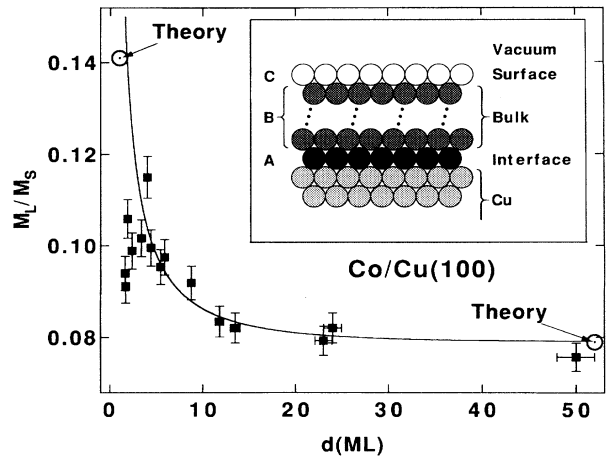

FIG. 3. The ratio of orbital versus spin moment M_L/M_S as a function of film thickness d. The open circles give the theory taken from Table I. The full squares show the experiment. The solid line is a fit using Eq. (1) with the parameters given in the last row of Table I. Note that the fit was performed only for $d \geq 3$ ML, corresponding to well-defined, epitaxial growth. The surface, interface, and bulk contributions used in Eq. (1) are schematically shown in the inset.

The quantitative agreement between theory and experiment also supports the assumption that the dipolar contribution to the MCXD signal is small. There is, to our knowledge, no experimental systematic study in the literature of this contribution that has been neglected in previous work [8–25]. We also note that our data points cover an

TABLE I. Calculated values for M_L, M_S, and their ratio for fcc Co. The calculations were performed using the Cu lattice constant. The experimental values for M_L/M_S are also given (parameters A, B, and C, see text).

Quantity	1 ML Co/Cu(100)	Co(fcc, bulk)	Co(fcc, surface)
M_L/μ_B	0.261	0.134	0.234
M_S/μ_B	1.850	1.724	1.921
$(M_L/M_S)_{\text{th}}$	0.141	0.078	0.122
$(M_L/M_S)_{\text{exp}}$	$A = 0.19(5)$	$B = 0.078$	$C = 0.11(3)$

extended reduced temperature range over which the magnetization and anisotropy constants of ultrathin films vary almost by an order of magnitude [28]. It is therefore improbable that the effect of dipolar or anisotropy fields is correlated to our experimental findings for $d \geq 2$ ML. We observe that for small thicknesses, below 2 ML, the experimental data points deviate from the expected theoretical behavior. It should be noted that around this thickness the transition from homoepitaxial to heteroepitaxial growth takes place. In this thickness range the Co atoms tend to form small islands [21] and T_c changes abruptly by more than 150 K [12]. It cannot, therefore, be expected that the simple layer by layer analysis presented above can hold for this situation. The present set of data clarifies also previous measurements, where for Co/Cu(100) no increase in M_L/M_S was found for $d = 1.8$ ML [12]. The data of Fig. 3 clearly indicate that this quantity depends very sensitively on the film morphology, and in order to obtain meaningful results an almost perfect layer by layer growth has to be realized experimentally.

In conclusion, we have presented evidence for an increased orbital moment for prototype surface systems. The quantitative agreement between theory and experiment allows one to establish simple criteria regarding the electronic structure of a system for the occurrence of such a phenomenon. We have isolated several different mechanisms which drive enhanced orbital moments at surfaces, e.g., the lowering of the symmetry, the enhanced spin moment, and the increased value of DOS (E_F). It therefore makes possible the manipulation of the orbital contribution to the magnetic moments of interfaces and surfaces on a microscopic level.

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[1] M. S. S. Brooks and P. Kelly, Phys. Rev. Lett. **51**, 1708 (1983).
[2] G. Y. Guo *et al.*, Phys. Rev. B **50**, 3861 (1994).
[3] P. Strange *et al.*, J. Phys. Condens. Matter **1**, 3947 (1989).
[4] O. Eriksson *et al.*, Solid State Commun. **78**, 801 (1991); O. Eriksson *et al.*, Phys. Rev. B **45**, 2868 (1992).
[5] R. Wu, D. Wang, and A. J. Freeman, Phys. Rev. Lett. **71**, 3581 (1993); R. Wu and A. J. Freeman, *ibid.* **73**, 1994 (1994).
[6] *New Series* (Landolt-Börnstein, Berlin, 1987), Vol. III/19a; F. Schreiber *et al.*, Phys. Rev. B **51**, 1 (1995).
[7] M. Wulff *et al.*, Phys. Rev. B **39**, 4719 (1989).
[8] G. Schütz, M. Knülle, and H. Ebert, Phys. Scr. **T49**, 302 (1993).
[9] B. T. Tole *et al.*, Phys. Rev. Lett. **68**, 1943 (1992); P. Carra *et al.*, *ibid.* **70**, 694 (1993).
[10] Y. Wu *et al.*, Phys. Rev. Lett. **69**, 2307 (1992).
[11] M. G. Samant *et al.*, Phys. Rev. Lett. **72**, 1112 (1994).
[12] M. Tischer *et al.*, J. Magn. Magn. Mater. **135**, L1 (1994).
[13] W. L. O'Brien and B. P. Tonner, Phys. Rev. B **50**, 12 672 (1994).
[14] G. van der Laan *et al.*, Phys. Rev. Lett. **69**, 3827 (1992).
[15] O. Eriksson *et al.*, Phys. Rev. B **41**, 11 807 (1990); H. Ebert *et al.*, J. Appl. Phys. **67**, 4576 (1990).
[16] J. M. Wills and O. Eriksson (unpublished); J. M. Wills and B. R. Cooper, Phys. Rev. B **36**, 3809 (1987); D. L. Price and B. R. Cooper, *ibid.* **39**, 4945 (1989).
[17] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[18] O. Hjortstam *et al.* (to be published).
[19] O. Heckmann *et al.*, Surf. Sci. **312**, 62 (1994).
[20] Hong Li and B. P. Tonner, Surf. Sci. **237**, 141 (1990).
[21] A. K. Schmid and J. Kirschner, Ultramicroscopy **42-44**, 483 (1992).
[22] B. Schulz and K. Baberschke, Phys. Rev. B **50**, 13 467 (1994).
[23] J. Hunter Dunn *et al.*, J. Phys. C **7**, 1111 (1995).
[24] A. Aspelmeier *et al.*, J. Magn. Magn. Mater. **146**, 256 (1995).
[25] In Ref. [5] it has been suggested that the dipolar term could increase at low symmetry configurations. We note, however, that even if we adopt the results of these theoretical predictions we can only account for about 30% of the observed increase in M_L/M_S, an effect almost within the experimental error.
[26] D. Weller *et al.*, Phys. Rev. B **49**, 12 888 (1994).
[27] M. Tischer, Ph.D. thesis, Freie Universität Berlin, May, 1995.
[28] G. André *et al.*, Surf. Sci. **326**, 275 (1995).