Strong changes in the magnetic properties of ultrathin Co/Cu(001) films due to submonolayer quantities of a nonmagnetic overlayer

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We have studied the evolution of the magnetic properties of the Co/Cu(001) system as a Cu overlayer is deposited, using the magneto-optical Kerr effect (MOKE) *in situ*. We observe striking, nonmonotonic variations in the coercive field H_c, the *M-H* loop amplitude M_{max}, and the ratio of remanent to saturation magnetization S upon the deposition of submonolayer quantities of Cu. We propose that the observed effects arise due to overlayer-induced changes in the electronic structure. As a consequence both the magnetic anisotropy of the films and the magneto-optical response vary strongly. We show that the entire Co film is affected, in that a single Cu atom at the surface can affect the behavior of more than 40 Co atoms throughout the thickness of the film, illustrating the importance of the segregation of substrate atoms during the growth of such films. Distinct behavior occurs according to the range of overlayer thickness, implying that separate physical mechanisms dominate for different coverages. At submonolayer thicknesses we propose that a step-induced uniaxial magnetic anisotropy term is very strongly modified by the presence of a partial Cu overlayer. Concurrent changes in the magneto-optical signal are attributed to the electronic structure of the partial Cu/Co interface. For overlayer thicknesses in the monolayer range, electronic effects associated with the completed interface occur, in particular a reduction of the Curie temperature T_C and a possible suppression of the magnetic moment of the Co atoms.

I. INTRODUCTION

It is now a well-established experimental fact that nonmagnetic overlayers can drastically affect the magnetic properties of ultrathin magnetic films. Motivated by an early observation by Przybylski and Gradmann,[1] Weber *et al.*[2] investigated the Fe/W(110) system systematically, and found that submonolayer coverages of Ag, Pd, and O_2 enhance the Curie temperature T_C. More recently, several studies of the effects of nonmagnetic overlayers on systems with out-of-plane remanent magnetization have been published,[3–8] which focus on the behavior of the anisotropies of the systems. In particular, Engel *et al.*[5–7] have studied the influence on the perpendicular magnetism of Co/Pd(111) and Co/Au(111) films during the growth of Au, Cu, Ag, and Pd overlayers. They observe a nonmonotonic dependence of the coercive field H_c on the nonmagnetic overlayer thickness, which they attribute to an "anomalous perpendicular anisotropy" induced by the interface; a quantitative analysis of the magnetic surface anisotropy in such systems has since been reported by Kohlhepp and Gradmann.[9] For systems with out-of-plane anisotropies it is well known that the presence of an interface has a strong effect, associated with the broken symmetry of the system. For films with in-plane anisotropy, however, symmetry considerations suggest that any effect will be much weaker. In this paper, extending a preliminary investigation,[10] we present the results of a careful study of the effects of small coverages of a nonmagnetic overlayer on the magnetic properties of Co/Cu(001) films, which exhibit in-plane magnetization. Our results show that films with in-plane magnetization can display strong variations in their magnetic properties as a nonmagnetic overlayer is deposited.

Two important considerations in the present context are the role of the electronic structure at the interface and within the magnetic layer, and that of the morphology and structure of the Co film and the interface. Both Engel *et al.*[5–7] and Beauvillain *et al.*[8] conclude that the changes in total anisotropy they observe in their perpendicularly magnetized samples are due to the evolution of the electronic band structure, which strongly affects the magnetic interface anisotropy. The evolution of interface states with overlayer thickness has been studied by Brookes, Chang, and Johnson[11] and Hartmann *et al.*[12] for various magnetic systems, using spin-resolved photoemission spectroscopy. Both studies observe overlayer-induced features that evolve in the submonolayer range and peak at around one monolayer (ML). Studies of films grown on vicinal surfaces, consisting of atomically flat terraces separated by monatomic steps, indicate that the structure of the surface under investigation, in particular the presence of steps in the film, plays an important role in determining the magnetic properties of the film[13–18] (e.g., via magnetoelastic effects), and that the coverage length scale required for overlayer-induced effects can be smaller than 1 ML.

Although Co/Cu(001) films have been extensively studied, conflicting results in terms of their magnetic properties have been published.[19,20] In comparing these studies, it is important to note the difference in growth temperatures (which were 300 and 450 K, respectively), particularly in the light of recent work by Kief and Egelhoff and co-workers,[21,22] which shows that the threshold temperature for the segregation of Cu substrate atoms to the surface is 375 K. Exceeding this limit means that the growing Co layer is sandwiched between the Cu substrate and

a segregated Cu overlayer. Some qualitative observations of the effect of a Cu overlayer on the magnetic properties of this system have been published; reported effects due to several ML's of Cu include a reduction of the Curie temperature,[20] of the out-of-plane anisotropy constant,[23] and of the coercive field.[24] Krams *et al.*[23] state that the in-plane anisotropy does not vary strongly with Cu coverage for the overlayer thicknesses they study.

In the present work, we have carefully studied the variation of the magnetic properties of Co/Cu(001) films upon Cu deposition, with the emphasis on submonolayer coverages of Cu. In this way, we attempt to simulate the surface segregation in a controlled manner, and we measure the magnetic properties using the magneto-optical Kerr effect (MOKE). In an extension of our preliminary study,[10] the thickness d_{Co} of the Co layers has been varied between 1 and $6d_c$, d_c being the thickness for long-range order to occur and which is estimated to lie between 1 and 1.7 ML at 300 K.[19,20,22,23,25] The increased range of Co thicknesses studied allows us to test whether the observed features in the behavior are due to surface effects (in which case they should be less pronounced for thicker films) or volume effects. Furthermore, we are able to identify common features in the Cu overlayer thickness-dependent behavior. These findings shed light on several models proposed as possible explanations for the behavior observed and mentioned in our earlier study.[10] We shall show that in all cases the magnetic properties of the Co films display a striking sensitivity to the presence of the Cu overlayer, and report a nonmonotonic behavior of the coercive field H_c, the saturation magneto-optical signal M_{max}, and the squareness S of the M-H loop (which we have defined as the ratio of remanent to saturation magnetization) upon submonolayer coverages of Cu. The complex behavior suggests that different mechanisms dominate at different coverages. We discuss the results in terms of the magnetic anisotropies and the influence of the electronic structure as the interface evolves, and suggest that at submonolayer coverages, the behavior is extremely sensitive to the presence of steps on the substrate.

II. EXPERIMENTAL DETAILS

All experiments were carried out in ultrahigh vacuum (UHV) with a base pressure of 1.0×10^{-10} mbar, and a pressure of below 5.0×10^{-10} mbar during deposition of both Co and Cu. The single-crystal Cu(001) substrates were cleaned by cycles of Ar^+ sputtering (1 kV) and annealing to 700 K; this yielded a well-ordered surface according to the resulting low-energy electron diffraction pattern, with the Auger spectrum revealing no contamination. Three separate, similarly prepared Cu crystals (denoted A, B, and C) were used during the experiment, thus excluding any possibility of our observations being an artifact of a particular substrate crystal. The crystals were spark cut to within 0.5° of the (001) face. Growth of both Co and Cu was performed at room temperature, with typical deposition rates of 0.1 and 0.05 ML/min, respectively.

Magnetic measurements were performed at 300 K, using MOKE *in situ* in the transverse geometry,[26] with a Helmholtz coil generating a magnetic field (±170 G) along the easy [110] axis.[26,27] Each individual experiment consisted of the following steps:

(i) Growth of a Co film to a particular thickness; in previous work[24] we have investigated the variation of H_c as a function of Co thickness d_{Co} for uncovered films. In Fig. 1(a) we show measurements of H_c extended to $d_{Co}=6.0d_c$ (d_c is the critical thickness for the onset of ferromagnetism, as described above), accompanied in Fig. 1(b) by the variation of the saturation Kerr intensity with d_{Co}. The sharp onset of a finite coercive field and magnetization thus provides a highly reliable thickness reference. We maintain a constant evaporation rate using the integral flux monitor of a commercial evaporator (Omicron EFM3), which we calibrate in units of d_c, and cross reference via the measured coercive field and the data of Fig. 1(a) for films of up to $\approx4d_c$. In the course of this investigation, a variety of Co thicknesses of between 1.0 and $6.0d_c$ were studied.

(ii) Growth of a Cu overlayer in small submonolayer steps, recording the M-H loops (at room temperature) as a function of Cu thickness. The absolute Cu overlayer thickness d_{Cu} is obtained via Auger spectroscopy, with an error of $\approx30\%$. However, a constant evaporation rate is again maintained during the Cu growth, and thus the form of the variation of H_c, S, and M_{max} as functions of d_{Cu} in relative units can be accurately determined and compared between experiments. Cu films were grown to thicknesses of $\approx1-5.25$ ML depending on experimental factors.

III. RESULTS

In this section, we first present examples of the evolving magnetic behavior observed as a Cu overlayer is

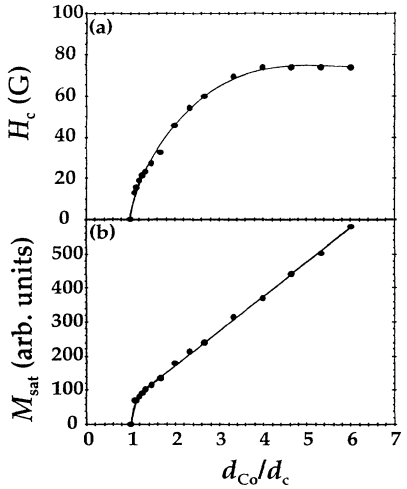

FIG. 1. The thickness dependence of (a) H_c and (b) M_{max} as a function of the Co thickness. The sharp onset of both quantities at the critical thickness d_c enables us to judge the relative Co thickness very accurately. The lines are guides to the eye; errors are within the dot size.

grown. We then present results for some particular cases, to help elucidate the possible origins of the observed behavior.

A. General features

As a typical example of the evolution of the magnetic behavior as an overlayer is deposited, we display in Fig. 2 *M-H* loops at various stages of the Cu overlayer growth for Co/Cu(001) films of four different Co thicknesses, $d_{Co}=1.35d_c$, $1.5d_c$, $1.8d_c$, and $2.6d_c$. It can be seen that in all cases H_c is reduced after deposition of around 0.2 ML Cu, but increases again as more Cu is grown. It is also evident that the hysteresis loops around the ≈ 0.2 ML point become almost perfectly square. An analysis of all *M-H* loops in these experiments yields the data displayed in Figs. 3 and 4. These four growth sequences illustrate clearly the main features of the behavior of the magnetic properties of ultrathin Co/Cu(001) films as a Cu overlayer is grown: nonmonotonic changes of the loop amplitude M_{max}, the squareness S (where we have defined $S=M_{remanent}/M_{saturation}$), and the coercive field H_c with submonolayer coverages of Cu are clearly visible in all cases (note the difference in the H_c scale between the two plots to enable the features in the thinner films' behavior

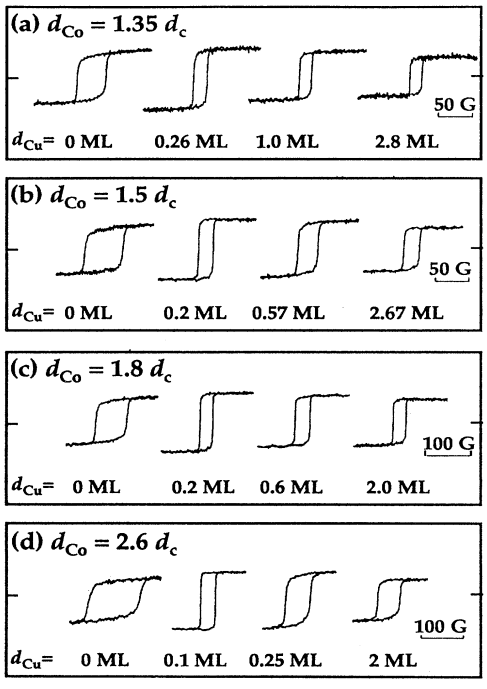

FIG. 2. Examples of *M-H* loops evolving during Cu overlayer growth. Data for four different Co thicknesses are shown: $1.35d_c$ in (a), $1.5d_c$ in (b), $1.8d_c$ in (c), and $2.6d_c$ in (d). (a) and (d) were grown on one substrate crystal, denoted *B*, while (b) and (c) were grown on another, denoted *A*. Beneath each *M-H* loop the Cu overlayer thickness d_{Cu} is given. The heights of the loops in a given sequence can be compared directly. Note the difference in magnetic-field scales for between sequences.

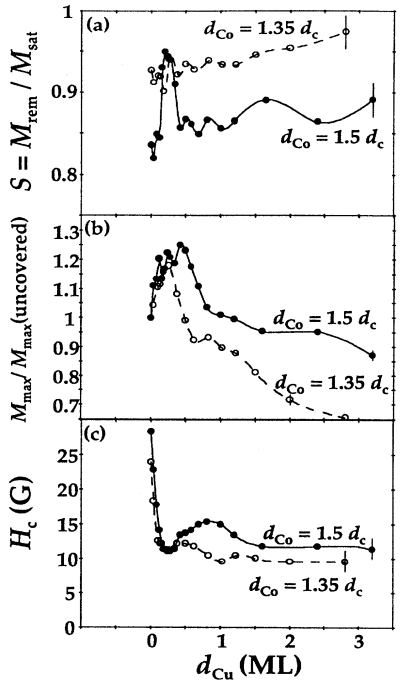

FIG. 3. The results of a careful analysis of the Cu growth sequence of a $1.35d_c$ thick Co/Cu(001) film (substrate *B*: open circles, dotted line) and of a $1.5d_c$ thick Co/Cu(001) film (substrate *A*: full circles, solid line), revealing the nonmonotonic behavior of the squareness S in (a), the loop amplitude M_{max} in (b), and the coercive field H_c in (c). The lines are guides to the eye; a representative error bar is given for each variable.

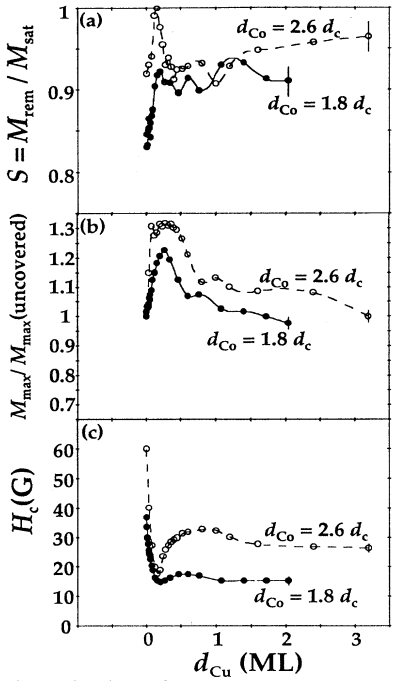

FIG. 4. The behavior of the magnetic properties S, M_{max}, and H_c with Cu deposition for a $1.8d_c$ thick Co/Cu(001) film (substrate *A*: full circles, solid line), and a $2.6d_c$ thick Co/Cu(001) film (substrate *B*: open circles, dotted line). The lines are guides to the eye; a representative error bar is given for each variable.

to be seen clearly). In particular, for all four films, H_c exhibits a sharp minimum at the same thickness at which M_{max} peaks, ≈ 0.2 ML Cu.

We see that the peak in M_{max} is always somewhat broader than the minimum in H_c. The behavior of S can be seen to be complex: for the $2.6d_c$ and $1.5d_c$ Co films there is a pronounced peak in S that correlates well with the sharp minimum in H_c and not as closely with the peak in M_{max}—this could indicate that S is being influenced by changes in either the anisotropy or domain pinning in the sample. However, this feature is less well defined for the $1.8d_c$ and $1.35d_c$ Co films, possibly since S is subject to larger errors than M_{max} and H_c. As the Cu overlayer is grown to higher thicknesses, S continues to vary in an unpredictable way. The differing initial values of S for the different growth runs appear to be a property of the substrate crystal used; the $1.5d_c$ and $1.8d_c$ films both have $S_{initial} \approx 0.83$ and were grown on the same substrate crystal (referred to as substrate A, represented by full circles and solid lines in Figs. 3–7), and the $1.35d_c$ and $2.6d_c$ films both have $S_{initial} \approx 0.92$ and were grown on another Cu crystal (substrate B, represented by open circles and dotted lines).

Besides the most prominent features of a sharp minimum in H_c and a strong enhancement of M_{max}, we always see a secondary maximum in H_c at thicknesses in the range 0.5–0.9 ML Cu. In considering the loop amplitude M_{max}, we observe a peak enhancement at $d_{Cu} \approx 0.2$ ML. Although the coercivities (and thus the Co film thicknesses) vary dramatically, H_c always drops by a factor of ≈ 3 to a sharp minimum, and the peak in M_{max} is around 20–30 % greater than the initial value of M_{max} in all cases (although this enhancement is less pronounced in thinner Co films). All samples have a final value of M_{max} that is close to or less than the value for the uncovered Co/Cu(001) film. We next describe further experiments, designed to clarify specific aspects of this behavior.

B. Thicker Co films

So far we have only shown results for Co films up to $2.6d_c$. To determine whether the observed features are a consequence of effects at the surface or changes that occur to the bulk of the sample, we have investigated a much thicker Co film, of thickness $6.0d_c$, on substrate A. The data from this sample are shown in Fig. 5, showing a selection of loops in Fig. 5(a), the behavior of S in Fig. 5(b), and the variation of H_c and M_{max} in Figs. 5(c) and 5(d), respectively. It can be seen that we still observe the minimum in H_c and the peak in M_{max}. However, for this sample the behavior of S is somewhat different than in the thinner samples; upon deposition of ~ 0.1–0.2 ML of Cu the loops again become very square [see Fig. 5(a)]; however with subsequent Cu deposition there is much less variation in S than in previous cases, with $S \geq 0.97$ at all times.

The importance of this particular experiment lies in the fact that we still see the minimum in H_c and the peak in M_{max} for such a thick sample ($6d_c = 7.8 \pm 1.8$ ML). This

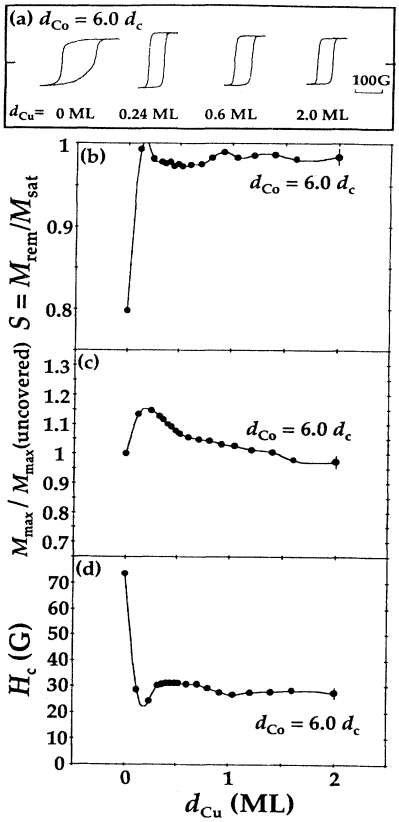

FIG. 5. The behavior of a $6.0d_c$ thick Co/Cu(001) film (substrate A) with Cu deposition. A selection of loops are given in (a), and in (b), (c), and (d) we show the magnetic properties S, M_{max}, and H_c, respectively. The lines are guides to the eye; a representative error bar is given for each variable.

means that the Cu overlayer atoms are affecting the entire Co film rather than just the surface; a simple calculation for 0.2 ML of Cu on a 7.8 ML Co film shows that a single Cu atom can therefore influence the magnetic properties of some 40 Co atoms in the bulk of the sample, and given that we see measurable effects for coverages lower than 0.2 ML, this value is a conservative estimate. This fact is very important in considering possible models for the observed behavior.

C. Thick Cu overlayers

Another interesting feature of the data can be seen in Figs. 3 and 4: at $d_{Cu} \approx 2$–3 ML, M_{max} starts to decrease sharply. To clarify the behavior in this region, a $1.95d_c$ Co/Cu(001) film was grown (substrate A), and subsequently measurements were made for values of d_{Cu} extended to 5.25 ML. The results are shown in Fig. 6, and a local minimum of M_{max} at $d_{Cu} \approx 2$ ML is clearly visible, followed by a maximum at $d_{Cu} \approx 3$ ML. The behavior of H_c [Fig. 6(c)] agrees with the general trends (Sec. III A), but there is no pronounced peak visible in S in this case [Fig. 6(a)], which may be due to the lower resolution in

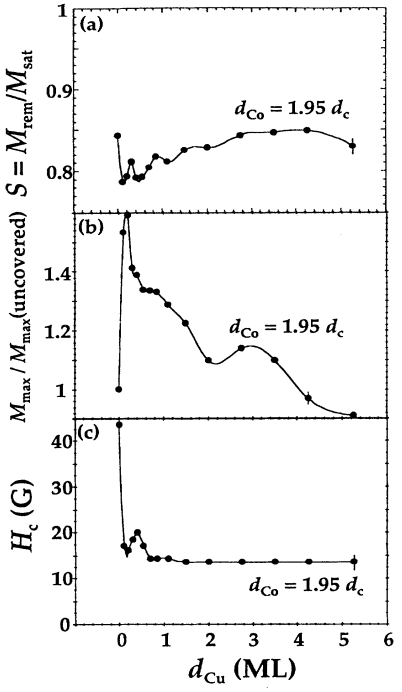

FIG. 6. The behavior of the magnetic properties S, M_{max}, and H_c with Cu deposition for a $1.95d_c$ thick Co/Cu(001) film (substrate A), with the Cu overlayer grown to 5.25 ML. The lines are guides to the eye; a representative error bar is given for each variable.

d_{Cu} for this experiment.

In Fig. 6, it is also important to note the reduction of M_{max} after 5.25 ML Cu deposition—the loop height is reduced by 15% from the value of M_{max} for the uncovered Co/Cu(001) film; additionally, referring to Fig. 3, for the $1.5d_c$ Co film a reduction in M_{max} of 7% is measured after only 2.5 ML Cu deposition. A straightforward numerical calculation shows that a reduction of this magnitude cannot be due to attenuation of the optical signal by the Cu layer. A possible explanation for the reduction of M_{max} at larger Cu thickness, suggested by the observations of Schneider *et al.*,[20] is that we are observing the effect of a reduction of T_C upon Cu deposition in line with their published results, and further, that the magnitude of the reduction is different for samples of different thickness because the original T_C of the films is different. An alternative explanation is the effect of the adsorbed Cu atoms on the electronic structure; calculations by Wu and Freeman[28] show that the presence of Cu substrate atoms can suppress the moment on the Co atoms by up to 10%, so a similar effect due to the overlayer is not unlikely.

D. Co films in the vicinity of d_C

To address the possible effect of changes in T_C, we have performed experiments on thinner Co/Cu(001) films (grown on substrate B), to identify the thickness regime over which the Cu overlayer is able to reduce T_C. Using our previous investigations of Co films on Cu(001),[24,29] a Co film is grown of a thickness such that it is just ferromagnetic when uncovered. If the initial effect of the Cu is to reduce T_C, it should then be possible to drive the film into the paramagnetic state by depositing Cu; this would be manifested in the transition from a ferromagnetic M-H loop (with a well-defined coercive field) to a paramagnetic M-H loop with zero remanence. This is exactly what has been observed experimentally, as can be seen in Fig. 7(a). At zero Cu coverage we observe a ferromagnetic loop with coercive field $H_c = 6$ G, from which the Co film thickness is judged to be $1.005d_c$. As Cu is deposited, H_c drops very quickly [as can be seen in Fig. 7(a) for $d_{Cu} = 0.4$ ML], and after ≈ 2 ML Cu deposition a paramagnetic loop is observed. This clearly proves a reduction of T_C, in line with the results of Schneider *et al.*,[20] despite the fact that we have not measured T_C directly. Figure 7(b) shows the evolution of M_{max} for this film as a function of d_{Cu}, and Fig. 7(c) that of H_c and, once the paramagnetic phase is entered, the paramagnetic susceptibility χ (determined graphically, from the slope of the recorded loops at zero field). From Fig. 7(c) it can be seen that once H_c has fallen to zero it never recovers; in fact χ continues to drop with further Cu deposition. By comparison with our previous studies of paramagnetic

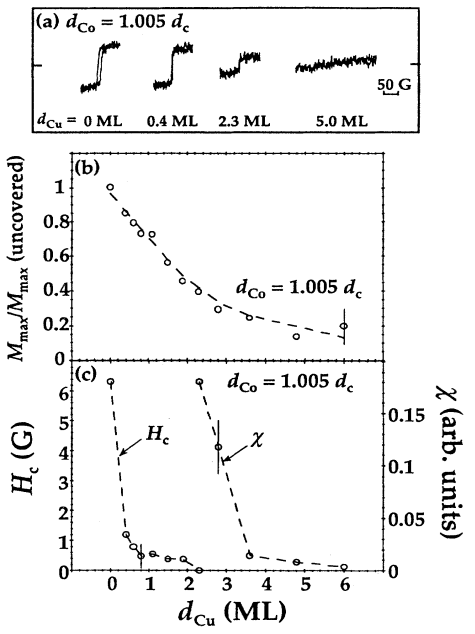

FIG. 7. The observed behavior of a Co film of thickness $d_{Cu} = 1.005d_c$ grown on substrate B. M-H loops for different Cu overlayer thicknesses are shown in (a): as the Curie temperature T_C is lowered (as described in the text), there is a clear transition from the ferromagnetic state to the paramagnetic state. The heights of the loops can be compared directly. (b) shows the behavior of M_{max}, and (c) shows the behavior of both H_c and χ (which is determined graphically, in arbitrary units). The lines are guides to the eye; a representative error bar is given for each variable.

Co/Cu(001),[29] this implies that the film is going further into the paramagnetic region and that therefore T_C is decreasing monotonically in this region.

However, the monotonic decrease in T_C described above occurs at Cu thicknesses at which, in previous growth sequences, H_c and M_{max} maintain reasonably constant values; in contrast, it is the submonolayer regime in general that we have seen the nonmonotonic behavior of H_c, M_{max}, and S. Consequently, we have performed a separate experiment on another extremely thin Co/Cu(001) film, concentrating on lower Cu coverages than used in the experiment of Fig. 7. A Co film was grown (on a third Cu crystal, substrate C) with a coercive field of $H_c = 3.8$ G, from which we judge the thickness to be $d_{Co} = 1.002 d_c$. A Cu overlayer was then deposited, and in Fig. 8(a) we show a selection of loops for this growth sequence, with Figs. 8(b) and 8(c) showing the subsequent variation of M_{max} and H_c, respectively. In this case we see H_c going to zero within experimental accuracy [see Fig. 8(a)] but subsequently recovering; it then again becomes unresolvable in the monolayer coverage range, similar to the results for the sample of Fig. 7, but in this case a detailed study for Cu thicknesses above 2 ML was not carried out. From this data it appears that for films in the vicinity of d_c, nonmonotonic changes in the magnetic properties are indeed occurring for Cu thicknesses in the submonolayer range, but this behavior is not detected for the sample of Fig. 7 due to the lower Cu thickness resolution in that experiment. It is therefore quite likely that we are seeing different effects occurring in different ranges of d_{Cu}, with electronic effects at larger Cu thicknesses causing a reduction in T_C.

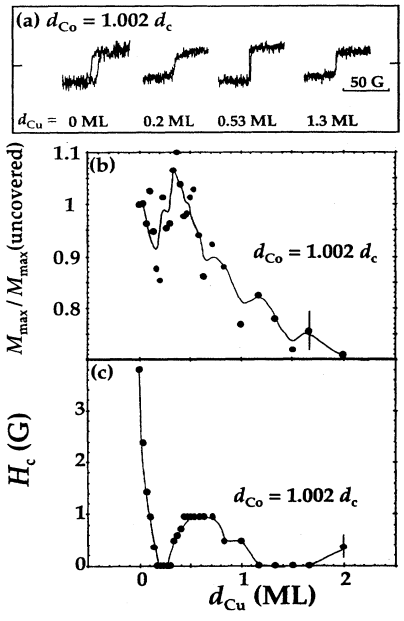

FIG. 8. The behavior of a $1.002 d_c$ Co/Cu(001) film (substrate C) as a Cu overlayer is deposited. In (a) a selection of loops are shown, and for $d_{Cu} = 0.2$ ML we see $H_c = 0$ G within experimental accuracy. In (b) the behavior of M_{max} is displayed, which can be seen subject to scatter at low Cu coverages, and in (c) we show the variation of H_c. The lines are guides to the eye; a representative error bar is given for each variable.

E. Thermal segregation of substrate Cu

As mentioned earlier, one motivation for simulating the surface segregation of Cu atoms in this way was to possibly reconcile the apparently contradictory results in the literature,[19,20] bearing in mind the threshold temperature for Cu segregation, 375 K,[21,22] is between the temperatures at which these studies were carried out. If this is indeed the cause of the discrepancy, we should see similar features to those presented above if we grow a Co/Cu(001) structure at 300 K and subsequently anneal it to above the segregation threshold temperature. To this end we have grown a film of thickness $1.02 d_c$ and heated it in short bursts to 400 K, cooling it rapidly back to 300 K between steps. As Fig. 9 shows, we do observe a minimum in H_c as a function of annealing time, and after a longer time H_c approaches a constant value that is lower than that for the as-grown film. This proves that our attempted simulation of the segregation, by growing Cu overlayers at 300 K, is valid. Variations of M_{max} in this experiment are unpredictable, which may be due to the segregation process causing pits several nanometers deep in the sample surface,[30] resulting in a less uniform Co film.

IV. DISCUSSION

We now discuss in turn the observed behavior of H_c, S, and M_{max}, in relation to several possible models: variation in T_C, surfactant behavior of the overlayer, a step-induced uniaxial anisotropy, and electronic changes due to the absorbing Cu atoms. We shall consider which of these mechanisms plays a role in either the submonolayer coverage range or the monolayer coverage range, and which can be ruled out.

By reducing H_c to zero in Co films in the vicinity of d_c, we have already shown that the Curie temperature is reduced in these films if a sufficiently thick overlayer is deposited (Fig. 7). However, this process alone cannot be responsible for all the features we observe for the follow-

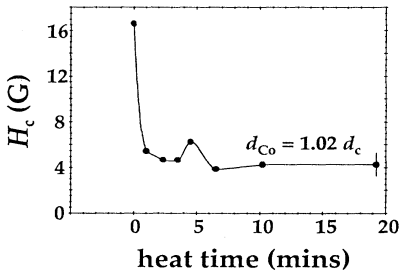

FIG. 9. The variation of H_c as a $1.02 d_c$ Co/Cu(001) film (substrate C) was heated in short bursts to promote segregation of substrate Cu atoms, as described in the text, showing a clear minimum in H_c. The line is a guide to the eye; a representative error bar is shown.

ing reason: for epitaxial magnetic films in the ultrathin regime, T_C is a strong function of film thickness[20,31–33] and, for Co/Cu(001) films, climbs to well above 300 K for Co thicknesses as low as 2.5 ML and is well above 1000 K for the thickest ($6d_c$) film studied.[20,32,34] This means that any effects due purely to a variation in T_c should be much less pronounced for thicker Co films, whereas we observe the effects to be roughly the same for all Co thicknesses we study. A reduction in T_C alone is therefore insufficient to explain all the features we observe. The reduction of M_{max} at coverages above $d_{Cu} \approx 2$ ML, observed for a variety of Co thicknesses, consequently implies that electronic effects, i.e., a reduced spin polarization of the Co atoms or change in magnetocrystalline anisotropy due to hybridization,[28,35–37] may be important in this coverage range.

It has been suggested that the reduction in H_c could be brought about by an improvement in the film quality, the Cu overlayer acting as a surfactant, smoothing the film and reducing the number of domain pinning sites in the sample; such surfactant effects have been reported during the growth of metal films in the presence of species such as CO, O_2, and Sb.[38,39] Relevant to this, Allenspach *et al.*[40] have seen evidence for an increase in domain size for a demagnetized Co/Cu(001) sample upon addition of a Cu overlayer, using spin-polarized scanning electron microscopy (spin-SEM). Since we see effects of a similar magnitude even for our thickest film studies, $6d_c$, this would mean that surface pinning sites affect the entire film. This model is able to account for the initial drop in H_c, but offers no reasons for the concurrent increase in S (unless our films are in a multidomain state at remanence, which is unlikely, as discussed below), nor does it explain the subsequent increase in H_c or the observed peak in M_{max}.

Referring to the experiments on Co films in the vicinity of d_c (Figs. 7 and 8), it appears that we are seeing different effects at different Cu coverages: at higher Cu coverages, above about 2 ML, we definitely observe a monotonic reduction T_C (Fig. 7); however, in the submonolayer thickness range (Fig. 8), we again see nonmonotonic behavior of H_c. An important aspect of this latter experiment is the *M-H* loop with no resolvable hysteresis, recorded for 0.2 ML Cu coverage. This could be due to one of two effects: first, that T_C has been lowered below room temperature at this point and we are recording a paramagnetic loop. Bearing in mind the subsequent recovery of a finite coercive field, this would then imply that the behavior in this coverage range is due to nonmonotonic variations in T_C. This is unlikely since similar nonmonotonic variation in H_c is also observed in the thicker Co films, for which T_C is well above room temperature. We therefore rule out this explanation. The second possible effect is that the free energy of the sample has a predominantly uniaxial magnetic anisotropy at this Co thickness, and that the easy axis is changing with Cu coverage. The *M-H* loop with zero remanence in Fig. 8 would then correspond to hard-axis behavior, with the easy axis subsequently reverting back to the [110] direction with further Cu deposition. Such a model is suggested by the spin-SEM and MOKE results of Weber *et al.*,[14] who have studied the effects of minute amounts of Cu and Co grown on a nominally Cu(001) single-crystal substrate miscut by 1.6°. A uniaxial anisotropy arises from the presence of steps on the substrate, with the easy axis initially parallel to the steps. As small amounts of Cu are deposited, they report a change of the easy axis by 90°, then essentially fourfold symmetric behavior, followed by a return to the initial behavior at higher Cu coverages.

This behavior is qualitatively in agreement with measurements of temperature-induced magnetic anisotropies in the Co/Cu(117) system by Wulfhekel *et al.*,[13] if one takes into account our findings about the segregation of substrate Cu atoms at raised temperatures (Sec. III E). They report that the magnetic easy axis is initially parallel to the step edges, resulting in a square *M-H* loop recorded with the applied field parallel to the steps and a rounded loop with the field perpendicular. On raising the temperature to ≈ 100 °C they observe a change in the magnetic anisotropy of the sample, to being nearly fourfold with a small uniaxial component perpendicular to the steps. This gives a rounded *M-H* loop parallel to the steps and a square loop perpendicular to the steps; then on heating above ≈ 115 °C, they see a second anisotropy change, with the easy axis reverting irreversingly to its initial direction. The similarity between this result and that of Weber *et al.*[14] can be accounted for if we take the first heating step of Wulfhekel *et al.*[13] as provoking a small amount of segregation of the Cu substrate atoms, and the second step corresponding to further Cu segregation, as expected in this temperature range (Sec. III E and Ref. 21).

In our work, the fact that we do not record perfectly square ($S = M_{rem}/M_{sat} = 1$) loops at all times can only be due to either incomplete saturation at the maximum external field (leaving a multidomain state at remanence), or to the fact that at zero field, the magnetization direction of the sample is rotated slightly away from the direction along which we are applying the field. Since Co/Cu(001) films are known to occupy a single domain state over millimeter-sized areas upon growth,[22,41,42] and *M-H* loops recorded in larger applied fields show no significant variation in M_{max}, we can be certain that at maximum applied field, the magnetization of the sample is fully aligned along the direction of the field. This implies that, for our experimental setup, the remanent magnetization of the sample is slightly rotated away from the direction along which we apply the field, i.e., the magnetization is not lying perfectly along the crystallographic [110] axis. We postulate that this misalignment is due to a small step-induced uniaxial anisotropy in our samples, allowing us to propose the following model for the general behavior of S. For substrates A and B (i.e., for the data of Figs. 2–7), this anisotropy causes the remanent magnetization of uncovered Co/Cu(001) films to lie away from the [110] axis; the deposition of around 0.2 ML Cu reduces the step anisotropy (via hybridization effects between Co step atoms and the neighboring adsorbed Cu atoms[28,37]) and the [110] direction becomes easier, leading to the increases in S that we observe. The step anisot-

ropy must then reassert itself upon subsequent Cu deposition, causing S to decrease at higher coverages. Additionally, if magnetization reversal is governed by mobile domain walls, then the [110] axis becoming easier could also result in a decrease in H_c, as we observe.

The question that must now be asked is whether the step-induced anisotropies we propose can be large enough to account for the changes in remanence we observe. We can consider the in-plane anisotropy contribution to be made up of an effective fourfold term K_p^{eff} and an effective uniaxial term k_u^{eff}, so that

$$E(\phi)=K_p^{\text{eff}}(d_{\text{Co}},d_{\text{Cu}})\sin^2 2\phi + k_u^{\text{eff}}(d_{\text{Co}},d_{\text{Cu}})\cos^2(\pi/4-\phi)\ , \quad (1)$$

where ϕ is the in-plane azimuthal angle to the [100] crystallographic axis (after Krams *et al.*[23]), and the effective in-plane anisotropy terms K_p^{eff} and k_u^{eff} contain volume and surface components and depend on both the Co and Cu thicknesses. We consider uncovered films with $d_{\text{Co}}=2$ ML, taking Krams's values for the components of K_p^{eff} (our K_p^{eff} is equivalent to $K_{\text{in-plane}}$ in their work). The equilibrium direction for the remanent magnetization, $\phi_0=\phi(\partial E/\partial\phi=0)$ is related to S via $S=\cos(\pi/4-\phi_0)$, from which the ratio of k_u^{eff} to K_p^{eff} can be found. Using our experimental values of S for uncovered films ($S=0.83$ and 0.92 for substrates A and B, respectively), and using Krams's values for the fourfold anisotropy terms, we estimate $k_u^{\text{eff}}\approx -5\times10^{-6}\ \text{J m}^{-2}$. We can compare this with the work of Albrecht *et al.*,[43] who report that the anisotropy energy due to a single step along the [001] direction in the Fe/W(110) system is -1.0×10^{-13} J m^{-1}. The step anisotropy energy per unit area is thus the energy per step divided by the mean step separation (i.e., the mean terrace width). For the purposes of comparison, we assume that steps along major crystallographic directions in the Co/Cu(001) system are going to have energies of a similar order to those in the Fe/W(110) system described by Albrecht *et al.* For the values of S that we record, we therefore estimate the required mean step separation to be ≈ 100 Å. Since terraces on clean Cu(001) substrates are generally of the order of a few hundred angstroms[44–46] this figure is not unrealistic, thus supporting our model of a step-induced anisotropy.

It is to be noted at this point that for this model of step-induced behavior to be applied to the $1.002d_c$ film discussed earlier, the M-H loop with zero remanence (Fig. 8) implies that in this case (substrate C) the [110] axis gets *harder* as 0.2 ML Cu is deposited. This is consistent with the model if the steps on substrate C are aligned parallel to the applied field, in contrast to those on substrates A and B. The above discussion therefore offers a plausible explanation for the observed behavior of S and H_c.

We must next look for an explanation for the behavior of M_{max} that is consistent with this model of the behavior of the magnetic anisotropy. Calculations by Wang, Wu, and Freeman[28,35–37,47] show that a close link exists between the electronic structure and the magnetocrystalline anisotropy, and that Cu atoms at a Co interface (either as a substrate or overlayer) strongly affect the electronic states of the Co film; Engel *et al.*[5–7] and Beauvillain *et al.*[8] both conclude that the most likely explanation for the change they observe in the out-of-plane anisotropy K_u upon deposition of an overlayer is that the details of the electronic band structure are changing. This theory, though, applies to continuous overlayer films, and it has been shown that interface states in the band structure of similar systems peak at around 1 ML.[11,12] Electronic structure changes could, however, occur at submonolayer coverages if the arriving Cu atoms collect initially at step edges, a growth mode that has been seen in other systems.[18,48]

The enhancement of the loop amplitude M_{max} that we observe is a particularly surprising result, clearly repeatable despite being subject to more scatter than the minimum in H_c. By comparing our increase in M_{max} with the dependence of the magnetization M on Co thickness for Co/Cu(001) films in the critical region, first reported by Smardz *et al.*[19] and as shown by our data in Fig. 1(b), we see that the increase in M_{max} for the deposition of about 0.2 ML of Cu is comparable to the increase in M for a similar quantity of Co. If we were directly measuring the magnetization, this observation would imply the unlikely conclusion that the Cu atoms carry a magnetic moment comparable to that of Co atoms. However, it is possible that we are seeing a slight polarization of the Cu atoms due to the Co moments; experiments have shown a polarization of Cu atoms upon deposition onto a Co(001) substrate,[49–51] with the moment induced on the Cu atoms being around 3% of the moment on the Co atoms (this is comparable to theoretical studies of the same system[52]). Referring again to our model of steps on the substrate, straightforward considerations of local atomic coordination numbers suggest that Co step atoms should have a slightly higher moment than terrace atoms, as is shown to be the case for the Fe/W(110) system by Albrecht *et al.*[53] Cu atoms adsorbing at the steps could therefore be subject to a stronger polarization than those sitting on the terraces. Since Carl and Weller show that extremely small paramagnetic moments induced in nonmagnetic layers can give rise to a large enhancement of the Kerr signal,[54] we conclude that the enhancement we observe is a magneto-optical effect wherein the optical response of the sample is affected by the slightly polarized overlayer atoms.

For the spin polarization of the Cu atoms to peak at a similar thickness to that at which the coercivity is most strongly affected requires that the spin polarization of the Cu atoms be dependent on the morphology of the incomplete layer. If the incoming Cu atoms initially adsorb at the steps, as proposed above, then this picture is consistent with the reports of Albrecht *et al.*[43,53] on Fe/W(110) systems, which describe enhanced magnetic moments and anisotropies at steps in magnetic layers. The adsorbing Cu atoms then simultaneously become relatively strongly polarized thus enhancing the magneto-optical response *and* reduce the step-induced uniaxial anisotropy, due to the electronic structure of these incomplete Cu overlayers. However, this model requires further theoretical analysis and experimental scanning tun-

neling microscopy (STM) studies for verification. We note that Gehring and Roberts[55] have addressed the possible increase of the Verdet constant V (which governs the magneto-optical response). Using a phenomenological crystal-field approach, they show that the required reduction in the anisotropy is only accompanied by an increase in V if they include a uniaxial in-plane anisotropy term arising from an in-plane crystallographic distortion.

V. CONCLUSIONS AND SUMMARY

Our observations can now be qualitatively explained by assuming that as Cu is deposited onto the Co film, the electronic structure of the system is changed via hybridization of the Cu and Co electronic states. A clear distinction emerges between the cases of submonolayer coverage and completed monolayer coverage, and the magnetic properties we observe are affected in the following ways:

(i) In the submonolayer coverage range, comparison with the work of Weber *et al.*[14] and Wulfhekel *et al.*[13] suggests that the substrate morphology is likely to be critically important in determining how the Cu overlayer affects the magnetic anisotropy. In particular, the presence of steps may encourage locally ordered growth in the early stages, thus explaining why such small amounts of Cu are able to have so strong an effect. In this model, a small uniaxial anisotropy term, associated with the steps, changes as the Cu is deposited. This picture offers an explanation for the observed behavior of S and H_c. The electronic structure is so sensitive to the presence of the Cu atoms that a single Cu atom on the surface effectively influences the properties of at least 40 Co atoms throughout the bulk of the magnetic layer.

(ii) At Cu coverages higher than ≈ 2 ML, we see a reduction in the Curie temperature T_C for thin Co films ($d_{\mathrm{Co}} \leq 1.005 d_c$), as shown in Sec. III C and in line with previous reports.[20] Electronic structure changes affecting all the Co thicknesses studied occur in this coverage range, with hybridization effects influencing the magnetic anisotropy and possibly suppressing the magnetic moment of the Co atoms, and hence the magneto-optical signal, in line with published theoretical studies.[28,35–37] This latter point may account for the reduction in M_{max} at larger Cu thicknesses for thicker Co films, in which T_C reductions would be undetectable.

(iii) It is well known that a change in the electronic structure can affect the magneto-optical interaction, and that, in particular, a very small induced polarization on the Cu atoms[49–52] may have a profound effect on the magneto-optical response, as reported for the Ru/Co system.[54] Thus the observed enhancement of the loop amplitude M_{max} is likely to be a magneto-optical enhancement rather than an enhancement of the absolute magnetization M of the system.

In summary, we have studied the effects of ultrathin Cu overlayers on ultrathin ferromagnetic Co films with in-plane anisotropy, and we have presented experimental data for a range of Co thicknesses and Cu substrates, showing that unexpectedly strong changes in the magnetic properties occur in this regime. Qualitatively similar variations in H_c and M_{max} with d_{Cu} occur in all cases, although the exact dependence varies with both d_{Co} and the choice of substrate. The loop squareness S appears to be particularly sensitive to the substrate used, implying that the details of the behavior can be affected by slight differences in the sample morphology. This finding is consistent with our attributing the behavior to the influence of a step-induced magnetic anisotropy. We show that Cu atoms at the surface can affect the entire volume of the Co film, and that there is evidence for both an anisotropy change within the plane of the film and for a strong concurrent variation in the magneto-optical characteristics of the film. From consideration of the available data, it is clear that STM studies of overlayer morphology and growth in this system would be very valuable. Our results emphasize the importance of the interaction between a magnetic layer and an overlayer, which can give rise to striking and largely unexplored effects in the submonolayer range. Furthermore, they highlight the strong effects that surface segregation during growth can have on the magnetic properties of such systems, in that interactions at the atomic level can have a profound influence on the macroscopic behavior.

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