Step-induced unusual magnetic properties of ultrathin Co/Cu films: ab initio study

A. V. Smirnov\textsuperscript{(a)} and A. M. Bratkovsky\textsuperscript{(b)}

\textsuperscript{(a)}Institut für Festkörperphysik, Technische Hochschule, D-64289 Darmstadt, Germany
\textsuperscript{(b)}Hewlett-Packard Laboratories, 3500 Deer Creek Road, Bldg. 26U, Palo Alto, CA 94304-1392

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Abstract

We have performed ab initio studies to elucidate the unusual magnetic behavior recently observed in epitaxial Co films upon absorption of submonolayers of Cu and other materials. We find that a submonolayer amount of Cu on a stepped Co/Cu (100) film changes dramatically the electronic and magnetic structure of the system. The effect is mainly due to hybridization of Co and Cu $d$-electrons when copper forms a “wire” next to a Co step at the surface. As a result, a non-collinear arrangement of magnetic moments (switching of the easy axis) is promoted.

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Recently, a remarkable new phenomenon in magnetism of systems with reduced dimensionality has been reported. It has been found that copper coverages as small as three-hundredths of a monolayer are sufficient to rotate discontinuously the magnetization direction of Co films (up to 20 atomic layers thick) [1]. The analogous situation takes place also for other overlayers covered with submonolayers of Ag, Au, and even oxygen [2]. Buckley et al. [3,4] have also concluded that in their experiments single Cu atom at the surface can affect the behavior of more than 40 Co atoms throughout the thickness of the film. This is perhaps one of the most remarkable new phenomena in ultrathin film studies, which currently attracts much attention [1–8] because of potential applicability for magnetic storage devices. The authors [1–4] have reasonably speculated that the observed unusual magnetic behavior can be explained by overlayer-induced changes in the electronic structure in combination with steps at the surface. Steps on the Co film, which arise from a slight misorientation of the surface, can act as sinks for Cu atoms diffusing on it, and thus cause Cu “wires” to nucleate and grow.

To gain more insight into magnetic behavior of ultrathin films on an atomistic level, it is necessary to study micromagnetism by \textit{ab initio} methods. These should address the effects of small coverages of nonmagnetic overlayers as well as surface and interface steps on the magnetic properties of such films. Only a few first-principles calculations of magnetic properties of ultrathin Co films have been performed, but only for ideal surfaces [9,10]. Although it is widely recognized that atomic-scale defects can strongly affect magnetic properties, to the best of our knowledge, there have been no previous theoretical studies of the magnetic nanostructure of ultrathin Co/Cu films with a non-ideal surface, although some attempts to calculate magnetic properties with surface irregularities were undertaken (for instance, for Fe/Cr-based systems [11,12]).

The purpose of the present work is \textit{ab initio} analysis of the step-induced magnetic properties of thin Co films, including the effects of submonolayer quantities of a non-magnetic overlayer, and their relation to “magnetic switching”.

For the calculations of the electronic structure, we made use of the tight-binding (TB)
LMTO method [13] in real-space (RS) [14], which we successfully applied previously for studies of magnetism in complex disordered systems [14–17]. Here, we use the TB-LMTO method for first-principles calculations of both ferromagnetic and constrained non-collinear magnetic two atomic layers (AL) cobalt films with non-ideal surface on the Cu substrate.

The specific form of the \textit{ab initio} TB-LMTO Hamiltonian in the atomic sphere approximation is the same as in Ref. [17]. Our structural models are based on the supercell approach: the unit cell contains 144 atomic spheres (some used to simulate vacuum) positioned at the sites of the fcc lattice and distributed in 12 AL for [001] and [1\bar{1}0] directions and 1 AL for the [110] direction – Cu atoms of the substrate occupy the lower 5 AL, the top 4 AL are filled by the empty spheres, and the central 3 AL are used for the Co film with a step (Fig. 1). The distance between neighbors corresponds to the measured lattice constant of fcc-Cu, \(a_{\text{Cu}} = 3.615 \text{ Å} \), Ref. [6]. For the real-space calculations by the recursion method [18] we have used up to \(\sim 3000\)-atom cluster built from the cell according to the symmetry of the lattice.

We apply periodic boundary conditions in the plane of the surface. For the perpendicular Z-direction ([001]), our calculations for 2- and 3-AL cobalt films on a copper substrate show no noticeable differences from either a semi-infinite Cu crystal below and vacuum above the Co film or with periodicity for the Z axis; therefore we shall present our results for the latter case. It is worth mentioning that 18 nearest neighbors were taken into account for constructing the Hamiltonian matrix; all the Cu and empty spheres were equal size, but the Co spheres were slightly larger (\(S_{\text{Co}}/S_{\text{Cu}} = a_{\text{Co}}/a_{\text{Cu}} = 1.019\)) [6]. In our calculations, we require self-consistent convergence better than 0.0008 electron/(a.u.)\(^3\) for the average root mean square deviation between the input and output of both electron and spin densities.

To begin with, we discuss the results of our calculations for “ideal” reference systems (two atomic layers of Co on the surface of fcc-Cu and the same with 1 AL (Co or Cu) as overlayer), see Table I. The calculated densities of states (DOS) for minority spin carriers are shown in Fig. 2. These states are actively involved in formation of electronic structure, while majority spin states in Co are almost full. Our data are in favor of a simple ‘bond-counting’ argument that for a pure Co-film a reduced coordination number for atoms in a film narrows the \(d\)-
band and increases the exchange splitting. Thus, we observe an enhanced local magnetic
moment at the surface as compared to the bulk crystal atoms \( M_{3\text{AL-Co}}/M_{\text{fcc-Co}} \approx 1.11 \). On the other hand, the interaction of Co atoms with a non-magnetic Cu overlayer suppresses the magnetic moment in the Co film; we observe a strong hybridization of the Cu overlayer \( d \)-states with corresponding Co minority \( d \)-states (Fig. 2). The same tendency has been noted in Ref. [10] for a 1 AL Co film. One can clearly see that Co DOS shows strong changes in the energy range down to about 0.15 Ry below the Fermi level. The states involved are mainly Co \( 3z^2−1, xz, \) and \( yz \), which change abruptly upon deposition of Cu [10].

Now we are in a position to analyze possible changes of magnetic properties due to the surface steps. We consider the case of 2.5 AL Co films (Fig. 1), where there is a Co terrace of equal size with a trough (both infinite in the [110] direction and replicated in the [110] direction). Such a surface defect results in a substantial increase of magnetic moments on the Co surface atoms in the trough and some decrease of the moments on other atoms (in comparison with Co atomic layers of the reference system). Near the steps, a discontinuity (kink) in the value of the magnetic moment is clearly seen. The average magnetic moment on Co atoms is about 1.70 \( \mu_B/\text{Co} \), the same as for the 3 AL Co film. Average values for each layer are given in Table I. Upon deposition of Cu wires one would expect strong changes in magnetic behavior of the system due to mainly two reasons: Co-Cu hybridization and electron charge redistribution. Incidentally, the fact that the majority Co \( d \)-band is almost full means that charge transfer would change mainly a number of minority carriers on a site, so that the number of transferred electrons will be approximately equal to the change of a magnetic moment on the same site.

Results of calculations for 2.5 AL Co films with 1-, 2- and 3-Cu wires placed in the trough near the step are presented in Table I and Fig. 3. The deposited Cu substitutes an empty site adjacent to a step and consequently squeezes out about 0.6 electron. This charge redistribution involves all (!) terrace Co sites causing significant changes in magnetic moments. Namely, addition of just one overlayer chain of Cu atoms increases the terrace magnetic moment on 0.06 \( \mu_B/\text{atom} \) and decreases the moment on the nearest neighboring
Co sites up to 11%; the moment for the Co atoms in the second plane beneath the copper wire increases from 1.56 $\mu_B$ up to 1.64 $\mu_B$.

There are many ways to add a second Cu wire. We have considered only the one where Cu atoms are adsorbed on the terrace level (in the 3rd “central” AL). Our calculations show that the growth of a continuous Cu overlayer is preferable, that is, the energy of systems with 2 adjacent Cu chains attached to the Co steps is lower than for the case when each Cu wire is placed symmetrically near separate atomic steps.

The dependence of the nanomagnetic structure on the number of Cu overlayer atoms is shown on Fig.3. The values of the Co magnetic moments under the copper steadily decrease when the amount of Cu increases (the average magnetic moment on Co shows the same tendency, Table I), approaching its mean value (1.54 $\mu_B$) for a completed Cu overlayer. At the same time, the magnetic moments on Co terrace atoms go up, and, therefore, the jump in the moment value increases together with the number of deposited Cu atoms. This, as well as the charge redistribution, may promote a frustration of the directions of magnetic moments, as we shall now discuss.

Because of the low symmetry of the system we consider, there are no constraints preventing the system from developing a complex (non-collinear) magnetic order. To investigate this possibility, we have performed a series of calculations with a ‘frozen’ magnetic configuration as shown in Fig.4. There the angle between the moments on two cobalt wires close to the Cu/Co boundary and the moments on all other atoms has been fixed at a right angle with respect to each other. We have then performed self-consistent calculations for the charge and spin densities (the procedure is analogous to that used in a ferromagnetic case [20]). We have found that this constrained non-collinear configuration is slightly lower in energy ($< 2$ mRy/atom) than the collinear ferromagnetic one [20]. This clearly shows a tendency towards a non-collinear magnetic order, which has been also confirmed by calculations with unrestricted spin directions.

Summarizing, for the first time we have performed ab initio studies of ultrathin Co/Cu films with consideration of the effects of both a stepped surface and Cu overlayer atoms on the
magnetic properties. We have found that they both can radically change the nanomagnetic structure of the film. We have found that deposition of a copper ‘wire’ causes a long-range charge and moment redistribution over a large number of adjacent Co sites, as a result of strong $d$-$d$ hybridization between Co and Cu atoms. The results of calculations with a constrained magnetic arrangement have clearly showed a tendency towards a non-collinear magnetic ordering in the ultrathin Co films with a non-ideal surface due to a hybridization between $d$-electrons on Cu and Co.

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* Permanent address: Kurchatov Institute, 123182 Moscow, Russia.

+ Corresponding author. Electronic address: alexb@hpl.hp.com

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TABLES

TABLE I. The calculated values of the magnetic moments for various Co films (in $\mu_B$), and for different numbers of Cu overlayer atoms (for details see text). For films with surface irregularities, the averaged values for each atomic layer (AL) are given. $< M >$ is the average magnetic moment on all Co atoms. For comparison, the measured value for a thick fcc Co film (on Cu) is 1.68 $\mu_B$ [19], and the calculated magnetic moment for fcc Co crystal, $M_{\text{fcc-Co}}$ is 1.65 $\mu_B$ (1.66$\mu_B$ from the LMTO calculations [19]).

| Film           | 1st AL | 2nd AL | 3rd AL (ES) | $< M > / \mu_B$ |
|----------------|--------|--------|-------------|-----------------|
| 2AL-Co         | 1.55   | 1.83   | 0.03        | 1.69            |
| 3AL-Co         | 1.66   | 1.60   | 1.83        | 1.70            |
| 2.5AL-Co       | 1.603  | 1.755  | 1.771       | 1.697           |
| 2.5AL-Co+1 Cu-wire | 1.607 | 1.733  | 1.829       | 1.702           |
| 2.5AL-Co+2 Cu-wires | 1.613 | 1.702  | 1.842       | 1.694           |
| 2.5AL-Co+3 Cu-wires | 1.619 | 1.668  | 1.850       | 1.685           |
| 2AL-Co+1AL-Cu  | 1.64   | 1.54   | 0.01 (Cu)   | 1.59            |
FIGURES

FIG. 1. Structural model and magnetic nanostructure for 2.5 AL Co films on a Cu substrate (schematic). Co atoms are indicated by a bold contour. Vacuum is simulated by the empty spheres (ES). The values of the magnetic moment are shown inside each site. All magnetic moments are parallel to each other. In the present calculations all atoms of the “central” layers are assumed to be non-equivalent; for other sites non-equivalence is considered only for different atomic layers, excluding boundary layers.

FIG. 2. The local density of states (DOS) for spin-down (minority) $d$ states of 2 AL Co films with Cu (a) and Co (b) mono-overlayers; dashed lines correspond to the DOS for fcc Cu (a) and Co (b) bulk crystals.

FIG. 3. Magnetic moments for 2.5 AL Co films with one (a), two (b), and three (c) Cu wires. The position of the Cu atoms is shown by dashed lines. The Co atoms with numbers 2 and 24 correspond to the atoms at the terrace middle. The structural model is shown in Fig.1.

FIG. 4. Structural model and local magnetic moments for 2.5 AL Co films on a Cu substrate with 2 Cu wires near the atomic step (schematic). For symbols, see Fig.1. The magnetic moments of the unshadowed Co atoms are perpendicular to the rest of the Co atoms.