Magnetism of Co nanoparticles supported on the Cu(111) substrate: Size and environment dependence

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We report a tight-binding calculation of the magnetic properties of triangular Co nanoparticles with two monolayers height supported on the (111) substrate of Cu. This system has been recently characterized through scanning tunneling microscopy measurements. The spin-polarized electronic structure is self-consistently determined by solving a tight-binding Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons. Different particle sizes as well as different particle concentrations over the surface are considered in order to investigate the influence of the local environment on the magnetic map of the system. The resulting trends are discussed by comparing with those obtained from available measurements for free-standing Co clusters, and with the asymptotic limit of a Co bilayer on Cu(111). [S0163-1829(97)08301-X]

I. INTRODUCTION

The magnetic properties of free and supported transition metal (TM) nanoparticles have attracted increasing attention in the past decade. From the scientific point of view, the study of these systems allows one to understand many important and fundamental phenomena, like the electronic delocalization and the hybridization effect, because of their bridge character between the isolated atom and the corresponding massive systems. Therefore, the evolution of magnetism from the microscopic to the macroscopic regime may be analyzed with the study of nanometer-scale clusters. Besides, the large variety of magnetic behaviors exhibited by these materials, like the enhanced magnetic moments and giant magnetoresistance, has opened new prospects in the development of material science; for instance, the construction of devices like magnetic sensors is, nowadays, a reality. From the technological point of view, supported or embedded clusters have more practical applications than the free ones.

Cobalt nanoparticles have been widely investigated. Molecular beam deflection measurements of Billas *et al.*[1] and Douglass *et al.*[2] for free-standing Co clusters show how magnetism develops with increasing cluster size. More recently, Chen *et al.*[3] have used a microemulsion technique to synthesize Co particles and their size-dependent magnetic properties have been also measured. All the above experimental groups have found enhancements in the range 25–40% with respect to Co bulk in the average spin-polarization of Co clusters with about 50 atoms. This augmentation of the spin-polarization is attributed to the loss of coordination at the surface atoms of the nanoparticle. The convergence to the bulk magnetic moment of Co is reached for clusters of about 600 atoms in size.[1] It is interesting to note that no detailed experimental knowledge about the geometrical structure of small Co particles is available,[4] but the strong dependence of the magnetic properties with the geometrical structure is well known.

This surface effect leading to enhanced magnetic moments should also exist when the clusters are deposited on surfaces or when they are formed during the first stage of the growth process of an overlayer on a substrate under certain conditions (low temperature and high velocity of deposition). Scanning tunneling microscope (STM) studies by de la Figuera *et al.*[5] for Co deposited on the Cu(111) substrate by molecular beam epitaxy show that Co grows forming nanoparticles of triangular shape, and these islands do not coalesce during the growth process up to at least 5 monolayer height. Two types of particles have been characterized: the first type follows the fcc sequence $ABCab$, and the other type grows in a stacking fault hcp sequence $ABCba$ (uppercase letters denote Cu planes and lowercase Co planes). Both configurations occur with about the same proportion. Furthermore, at the initial stage of the growth, almost all the Co particles are two monolayers high.

From the microscopic study of the magnetic properties of these supported Co nanoparticles, important aspects can be learned about the magnetism of the resulting granular surface and about the interface formed when thicker coverages of Co are deposited. It is clear that the magnetic coupling at the interface plays a fundamental role in the behavior of the subsequent multilayers. In this context, the experimental results concerning the oscillations between ferromagnetic (F) and antiferromagnetic (AF) coupling of the Co layers through a Cu spacer in the (111) orientation do not lead to a uniform picture of the phenomena.[6,11,12] It has been suggested, for instance, that the antiferromagnetic coupling observed between Co layers across Cu in this orientation, which is the basis of the magnetoresistance enhancement, can be mediated by minority components of grains with orientation close to (100) at the interface.[6] In the same spirit it has been suggested[5,13] that the formation of Co nanoparticles at the Cu(111) interface may be the origin of the controversial experimental results on the magnetic behavior of these multilayers.

For the ideal Co overlayers deposited on Cu substrates, the most precise result nowadays are given by *ab initio* calculations. The Co/Cu(111) system has been studied very recently by Zhong *et al.*[7] using the full potential linearized augmented-plane-wave (FLAPW) method. In that calculation, the magnetocrystalline anisotropy has been determined

for a fully relaxed structure, and the authors have pointed out that the change in the strength of the interfacial hybridization is due to both the surface effect and atomic relaxation. There has been also reported very recently[8] an *ab initio* full potential linear muffin tin orbital (FPLMTO) study of the spin and orbital moments of the Co monolayer on Cu(100), leading to the conclusion that the enhancement shown by the resulting spin moments at the surface is due to the reduced coordination number. The orbital moments become also enhanced at the surface. These results are in agreement with the experimental data.[9] For the Co/Cu(111), angle-resolved photoemission measurements[10] indicate that the magnetic exchange splitting for 1–2 monolayers of Co on Cu(111) is nearly the same than for bulk Co. However, the authors conclude also that ''the interaction between Co and Cu is rather weak indicating that Co on top of Cu behaves like a quasi-two-dimensional transition metal.''

At the present time, no measurements are available for the magnetic properties of supported Co clusters. From the theoretical point of view, there exist only the *ab initio* KKR calculations of Lang *et al.*[14] for Co microclusters deposited on Cu(001). However, these first principles calculations are restricted to very small cluster sizes (one atom, dimer, trimer) due to the complexity of treating the large number of inequivalent atoms involved in a realistic sample.

It is the aim of the present work to perform a theoretical study of the magnetic trends of the Co nanoparticles formed during the first stage of the growth on Cu(111). The morphology of the system is modeled approximately guided by the experimental main features observed through STM by de la Figuera *et al.*[5] The interesting points in the present study are as follows.

(a) Analyze the surface effect (loss of coordination at the different atomic sites within the cluster).

(b) Dependence of the magnetic properties of the Co nanoparticles with the size and with the growth sequence (fcc or hcp).

(c) Possible magnetic interaction via exchange between the Co particles as a function of the particle concentration over the substrate.

In order to study the general magnetic trends of the system, the spin polarized electronic distribution has been calculated in all the inequivalent sites within the system. The local density of states, magnetic map, magnetic order, and average magnetization are determined by self-consistently solving a tight-binding Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons. The quantitative predictions of this model are tested for the ideal Co/Cu(111) and Co/Cu(100) systems taken as reference the *ab initio* results.[7,8] The trends with size obtained for the Co nanoparticles are compared with the experimental measurements for free-standing Co clusters.

The rest of the paper is organized as follows. In Sec. II we present our theoretical method. The results are presented and discussed in Sec. III and the main conclusions of the work are summarized at the end.

II. THEORETICAL MODEL

A. Hamiltonian

The electronic structure is determined by solving self-consistently a tight-binding Hamiltonian for the $3d$, $4s$, and $4p$ valence electrons in a mean field approximation:

$$H=\sum_{i,\alpha,\sigma}\epsilon_{i\alpha\sigma}N_{i\alpha\sigma}+\sum_{\substack{i,\alpha,\sigma\\ i\neq j}}t_{ij}^{\alpha\beta}c_{i\alpha\sigma}^{\dagger}c_{j\beta\sigma}. \tag{1}$$

Here $c_{i\alpha\sigma}^{\dagger}$ ($c_{j\beta\sigma}$) are the operators for the creation (annihilation) of an electron with spin σ and orbital state α (β) at the atomic site $i(j)$, and $N_{i\alpha\sigma}$ is the corresponding number operator. The electronic delocalization within the system is described by the hopping integrals $t_{ij}^{\alpha\beta}$ between orbitals α and β at sites i and j, which are assumed to be spin-independent. The hopping integrals between atoms of the same element are fitted to reproduce the *ab initio* band-structure calculations for the pure element.[15] The heteronuclear hoppings at the nanoparticle-substrate interface are obtained as the average of the corresponding homonuclear hoppings. This has been proven to be a very good approximation in calculations for ideal Co overlayers on Cu(111).[16]

The spin-dependent diagonal terms $\epsilon_{i\alpha\sigma}$ in our Hamiltonian include the electron-electron interaction through a correction shift of the energy levels, and take the following expression:

$$\epsilon_{i\alpha\sigma}=\epsilon_{i\alpha}^{0}+z_{\sigma}\sum_{\beta}\frac{J_{\alpha\beta}}{2}\mu_{i\beta}+\Omega_{i\alpha}. \tag{2}$$

Here, $\epsilon_{i\alpha}^{0}$ are the bare energy of the orbital α at site i (that is, excluding Coulomb interactions). The second term is the correction shift due to the spin-polarization of the electrons at site i, that is, $\mu_{i\beta}=\langle N_{i\beta\uparrow}\rangle-\langle N_{i\beta\downarrow}\rangle$. In this second term, $J_{\alpha\beta}$ are the exchange integrals and z_{σ} is the sign function ($z_{\uparrow}=+1$; $z_{\downarrow}=-1$). The d-electron exchange integral $J_{dd}(\mathrm{Co})=0.95$ eV is fitted to yield the spin-polarization of Co bulk ($1.53\mu_B$), calculated with the *ab initio* LMTO method. The ratio $J_{dd}(\mathrm{Co})/J_{dd}(\mathrm{Cu})=1.36$ is also taken from a LMTO calculation.[17] Exchange integrals other than J_{dd} are neglected. Finally, the size and orbital-dependent potentials $\Omega_{i\alpha}$ assure the local neutrality condition [$n_d(i)=n_d(\mathrm{bulk})$; $n_{sp}(i)=n_{sp}(\mathrm{bulk})$ at each site i], which is well fulfilled in systems containing the present transition metals.[16]

B. Self-consistent calculation

Our goal is to determine the magnetic moment distribution in our system, consisting of Co nanoparticles deposited on the (111) semi-infinite substrate of Cu, that is, to obtain $\mu_{i\alpha}$ at each site i and orbital α. The magnetic order as well as macroscopic quantities like the average magnetization are directly obtained from these microscopic magnitudes.

To this end, we solve self-consistently our Hamiltonian for all the inequivalent sites considered. Cu atoms below the second interface layer are assumed to be of bulk type since their density of states is nearly the same as in the bulk. Thus, the self-consistent calculation involves all nonequivalent atoms of the Co particle, as well as Cu atoms of the first two underlayers with different environment.

The magnetic moments distribution can be determined by integrating the majority and minority local densities of states (LDOS) up to the Fermi energy:

$$\mu_{i\alpha}=\int_{-\infty}^{\epsilon_F}[\rho_{i\alpha\uparrow}(\epsilon)-\rho_{i\alpha\downarrow}(\epsilon)]d\epsilon. \tag{3}$$

The LDOS is directly related to the diagonal elements of the Green function:

$$\rho_{i\alpha\sigma}(\epsilon) = -\frac{1}{\pi}\mathrm{Im}[G_{i\alpha\sigma,i\alpha\sigma}(\epsilon + iO^{+})]. \quad (4)$$

These diagonal elements of the Green function are calculated by using the recursion method,[18] with a sufficient number of levels in the continued fraction to assure the stability of the results. The self-consistent procedure starts giving an input of $\mu_{i\alpha}$ and $\Omega_{i\alpha}$ at each site i and orbital α from which the diagonal elements of the Hamiltonian are constructed. By solving the resulting Hamiltonian within the recursion technique we obtain the LDOS. From them, a new distribution of magnetic moments $\mu'_{i\alpha}$ is obtained. The potentials $\Omega_{i\alpha}$ are also updated at each iteration. The procedure finishes when the input $\mu_{i\alpha}$ and output $\mu'_{i\alpha}$ coincide and the local neutrality condition is reached within an accuracy of 10^{-4}.

The advantages of this method are as follows:

(1) It is formulated in the real space. Thus, no symmetry restrictions are required.

(2) It allows the self-consistent calculation for systems composed of a very large number of inequivalent sites, because no diagonalization is required.

(3) The magnetic properties are determined from a local point of view.

However, this method has also disadvantages related to its parametrical character and approximations. Before discussing the results, we would like to note precisely just how sensitive our model is to reasonable variations in the choice of parameters. We will consider also the effects of the main approximations. With respect to the hopping integrals, we have tested a variation of about 10% in the relative bandwidths of Co and Cu. The quantities of interest, i.e., local magnetic moments and magnetic orders, do not change qualitatively. Thus, the trends are independent of the choice of the hopping integrals within that range.

There are two main approximations in our model: the local neutrality condition and the mean field treatment. First principle calculations by Wang and Freeman[19] for ideal surfaces of transition metals indicate that the charge transfer is negligible in these materials, assuring the accuracy of the local electroneutrality as a first approximation. Our mean field treatment necessarily exaggerates the exchange splitting, and thus, the magnetization, which is reduced by *ab initio* methods considering many body correlation effects. It is important also to note that, if many-body effects are important, the one-particle DOS may not be comparable to the excitation spectrum which is measured in photoemission.

We estimate the accuracy of the numerical predictions of our model by comparing our results for the ideal Co/Cu(111) and Co/Cu(100) with those obtained through the *ab initio* FLAPW model[7] and FPLMTO,[8] respectively. Our local magnetic moment for the Co monolayer on Cu(111), amounts to $2\mu_B$ which is higher than the *ab initio* value[7] ($1.60\mu_B$) by $\simeq 20\%$. For the Co monolayer on Cu(100) we obtain $2.13\mu_B$, which is higher than the *ab initio*[8] ($1.85\ \mu_B$) by $\simeq 13\%$. Therefore, the average spin-polarization is overestimated in our model by $\simeq 17\%$. The self-consistent tight-binding method seems to be less accurate for the late transition metals, Co, Ni, and Cu, where the *sp* electrons play a more important role than for the other elements. Thus, the computed absolute values have to be taken with care, and for this reason we will concentrate our discussion on the magnetic trends of the system, that is, the relative differences of the magnetic moments at inequivalent atoms within the cluster, the convergence of the average magnetization towards the ideal Co bilayer when the cluster size increase, and the possibility of magnetic interaction between the Co clusters. For a local quantitative description one should go beyond our model, by using an *ab initio* technique including the correlation effects. Our self-consistent tight-binding model has been successfully applied in previous works to the study of free-standing clusters,[20] clusters embedded in matrices,[21] and rough interfaces of Fe/Cr systems.[22] We guess that for the late transition metals one could improve the accuracy of the model by improving the transferability of the parameters. One possibility would be to fit them to first principles results for finite systems instead of fitting them to the bulk. In our particular case, we will explore in the future a fit of the parameters to *ab initio* KKR results for small Co microclusters on Cu,[14] and also to the ideal Co bilayer on Cu(111).

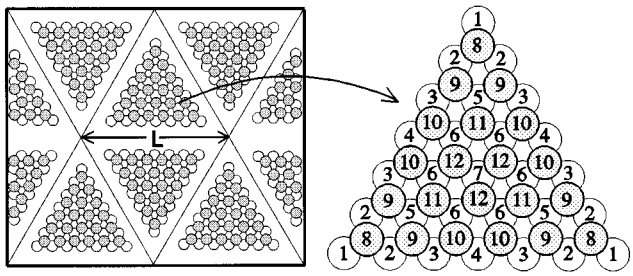

FIG. 1. The triangular Co nanoparticles deposited on Cu(111). A portion of the semi-infinite system is shown. These particles with a corner pointing up are grown in a hcp sequence (*ABCba*), whereas those with a corner pointing down are grown in a fcc sequence (*ABCab*). Note the equal ratio between fcc and hcp types, as experimentally observed through STM (Ref. 5). For a fixed island size, the distance L characterizes the particle concentration. In the detail, the inequivalent Co sites are illustrated for a typical cluster of 49 atoms (sites 1–7 belong to the interface plane and sites 8–12 to the surface plane). For simplicity, the inequivalent Cu sites are not indicated.

III. RESULTS

The surface morphology, modeled approximately to the STM observations, is shown in Fig. 1. The triangular Co nanoparticles of two monolayers height are placed at translationally symmetrical positions over the Cu(111) semi-infinite substrate. This corresponds to the hexagonal atomic distribution at the (111) surface of a fcc system. In order to simulate the observed[5] equal ratio between the fcc and hcp growth sequences, half of the supported clusters follow the *ABCab* growth sequence whereas the other half are deposited in the *ABCba*. This leads to a 60° rotation of one type with respect to the other, as it is also experimentally determined.[5] In the detail of Fig. 1 all the inequivalent Co sites (for a typical cluster of 49 atoms) are identified according to their geometrical and chemical environment. For sim-

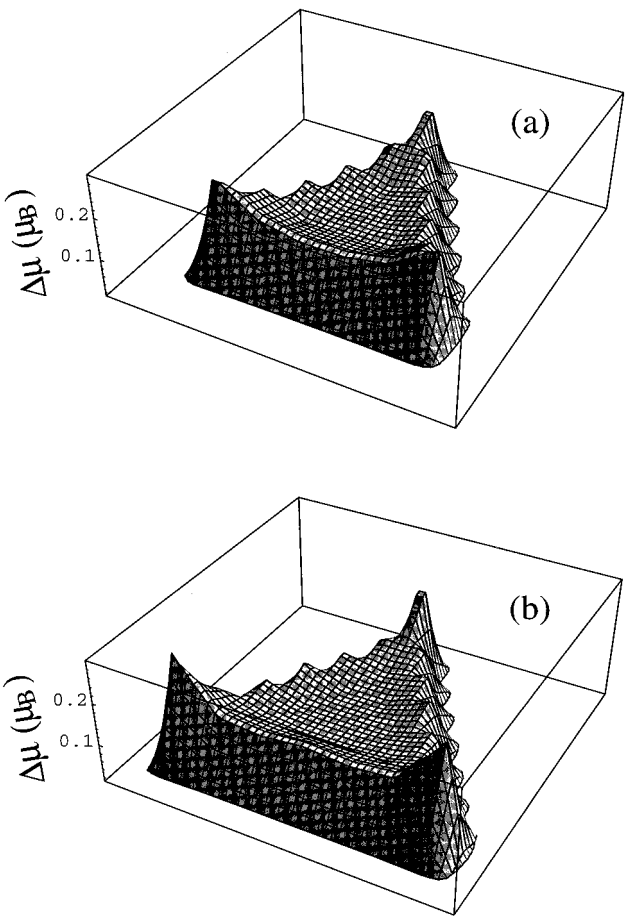

FIG. 2. Profile of the increase of the local magnetic moments for a supported fcc cluster of 49 atoms with respect to the ideal fcc-Co bilayer: (a) surface atoms; (b) interface atoms. The local magnetic moments of the surface and interface of the ideal fcc Co bilayer are taken as reference in (a) and (b), respectively.

plicity the inequivalent Cu sites in the first two surface layers are not indicated in the figure. In all these Co and Cu inequivalent sites, the LDOS and local magnetic moments are calculated self-consistently.

In order to investigate what is the influence of the growth sequence and cluster size, we have considered both types of isolated supported clusters with sizes of 16, 49, 100, and 169 atoms. These sizes correspond to the succesive clusters of two monolayer height that one can generate with triangular shape. For all sizes, we obtain a ferromagneticlike order within the Co cluster. This result is consistent with the strong ferromagnetism of bulk Co and the noble character of the Cu substrate. In Fig. 2 is shown, for a fcc Co cluster of 49 atoms, the difference between the local magnetic moments and the magnetization of the corresponding atoms of the ideal Co bilayer on Cu(111). Several trends obtained from our calculations are discussed in the following paragraphs.

In all cases, the local magnetic moments for the fcc and hcp clusters are very similar, since the Cu environment is nearly the same (differs only in one second neighbor); furthermore, Cu is a noble metal substrate, which only hybridizes appreciably with the Co states lying 1.5 eV below the Fermi level. Indeed, the Cu states around the Fermi energy have predominantly sp character, with a negligible density

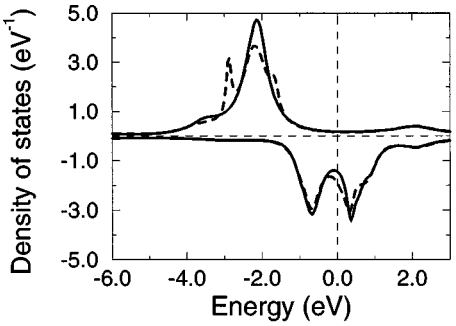

FIG. 3. Local density of states at the corner atom of the surface plane of the cluster of 49 atoms (type 8 in Fig. 1). The solid line corresponds to the hcp growth mode and the broken line to the fcc growth mode.

of states. The weak interaction between Co and Cu has been also pointed out from angle-resolved photoemission measurements[10] for a Co monolayer deposited on Cu(111). We obtain that the magnetization induced by Co through hybridization in the Cu interface is negligible ($\simeq 0.01\mu_B$). This is in agreement with the *ab initio* results of Zhong *et al.*[7] for Co/Cu(111). However, it is interesting to note that although the integrated magnitudes (local magnetic moments) do not appreciably depend on the growth sequence, the corresponding LDOS at some particular sites reflects the different environment. For instance, in Fig. 3 is illustrated the LDOS at the corner atom of the surface plane of the cluster of 49 atoms for both the fcc and hcp growth modes. One observes a different electronic structure, with a high density peak at about 3 eV below the Fermi level in the case of the fcc growth. In contrast, the LDOS for the hcp case does not reflect this state, but a higher density of states at the most pronounced peak of the majority band.

Appreciable changes are obtained, however, between the local moments of the different Co atoms within a given cluster as shown in Fig. 2. This is again related to their local environment, particularly to the local coordination number. The atoms which display the lowest moment are those located at the Co/Cu interface in the center of the island [Fig. 2(b)]. The largest moment is displayed by the Co atoms situated at the corner of the surface plane [Fig. 2(a)]. These are the less coordinated Co atoms and, thus, approach the atomic limit. An enhancement in the local magnetic moments has been also obtained by Lang *et al.*[14] for Co microclusters deposited on Cu(001) through an *ab initio* KKR method. These surface effects, that hold for every cluster size and for both fcc and hcp growths, are reflected in the LDOS shown in Fig. 4 for the fcc supported cluster of 49 atoms. One can observe the transition from the electronic localization (low coordination, narrow LDOS), to the electronic delocalization (increasing coordination, broadening of the LDOS) as going from the corner atom towards the side atom and the central atoms.[23] As discussed above, the magnetic enhancement differs for the inequivalent sites of the cluster (essentially corner, side, and central Co atoms located at the surface or at the interface planes). Moreover, the distribution of inequivalent sites depends on the cluster size and, therefore, so does the average magnetization. There are no magnetic measurements available for supported Co nanoparticles so far, but interesting conclusions can be drawn by comparing with the experi-

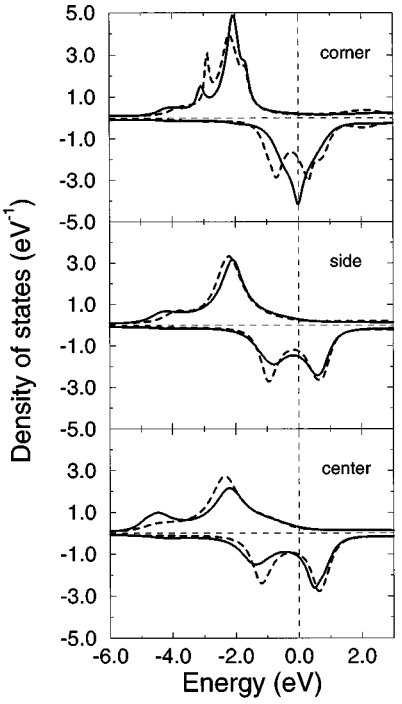

FIG. 4. Local density of states at particular sites (corner, side, and center atoms) of the fcc supported Co nanoparticles of 49 atoms. The solid line corresponds to the atoms at the interface plane whereas the broken line corresponds to the atoms at the surface plane.

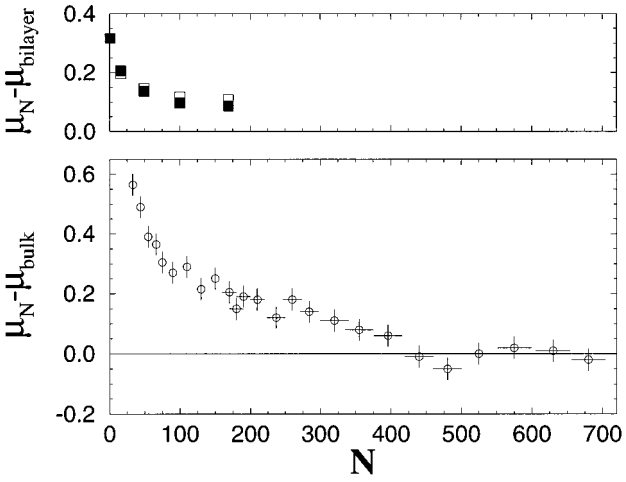

FIG. 5. Average magnetization per Co atom as a function of cluster size relative to the ideal fcc Co bilayer. Open and filled squares correspond to our calculations for hcp and fcc supported Co clusters, respectively. The experimental results for the average magnetization of free-standing Co clusters (open circles and error bars), relative to the bulk (Ref. 1), are also included for the sake of comparison.

mental results for free-standing Co clusters.[1–3] This comparison is worth it since in our nearly two-dimensional Co clusters, most of the atoms are of surface type. In Fig. 5, we show the evolution of the average magnetization per atom as a function of the cluster size towards the value for the ideal Co bilayer on Cu(111). Also, for the sake of comparison, we show for the free-standing clusters the evolution of the same quantity towards the value for the Co bulk (taken from the experiment of Billas *et al.*[1]). All the experimental groups[1–3] have found an augment of 25–40 % in the average magnetization of Co clusters of about 50 atoms as compared to the bulk. Our supported particles are mostly composed of atoms of surface type, whereas in the compact free-standing clusters, a core of Co atoms of bulk-type starts to develop. This bulk-type atoms tend to reduce the average magnetization of the cluster. Since the atoms at the center of the supported cluster have lower moments than those at the corner or at the sides, the average magnetization of the cluster decreases as the cluster size increases. Moreover, the limit of infinite size for the free-standing clusters is the bulk, whereas for the supported clusters is the ideal Co bilayer deposited on Cu(111). This trend is recovered as an asymptotic limit in our calculation (see Fig. 5). The convergence to the bilayer limit seems to be relatively slow, as it is also the case for free-standing clusters, where the bulk limit is reached only for a size of about 600 atoms. In Fig. 5, one can also observe the small but persistent difference in the average magnetization between the fcc and hcp supported nanoparticles. This small difference, however, is out of the range of the experimental accuracy.

Up to now, we have discussed the situation corresponding to isolated supported Co particles ($L \rightarrow \infty$ in Fig. 1). It is also interesting to investigate the behavior of the system when the particle concentration is increased. For this purpose, we have considered typical Co particles of 49 atom size and we have moved the distance between them by changing the parameter L of Fig. 1. In this way, we have studied the resulting surface magnetization at different Co coverages: $L = 25.55$ Å ($\simeq 0.98$ Co ML) and $L = 33.21$ Å ($\simeq 0.59$ Co ML).

In order to characterize the possible magnetic interaction via exchange between adjacent Co clusters, we have considered the rhombohedrical unit composed by a fcc and a hcp cluster shown in Fig. 1. As input in the calculation we started with two different spin arrangements (note that the initial spin configuration can change during the self-consistent procedure). One case corresponds to all the magnetic moments pointing in the same direction in both fcc and hcp cluster types. This leads to a situation in which all the Co particles over the surface have moments in the same direction and, therefore, the surface has a net average magnetization. In the other case, the magnetic moments of the fcc clusters point in opposite direction to those of the hcp clusters. This gives rise to a starting situation in which each Co particle on the surface is surrounded by three Co particles (the nearest ones) whose magnetic moments point in opposite direction. In this case the initial antiferromagnetic superstructure over the surface leads to a zero average surface magnetization. If the magnetic interaction via exchange is strong and the clusters are close enough, one expects that the initial antiferromagnetic superstructure will transform into the ferromagnetic one during the self-consistent procedure, because Co has a strong tendency to ferromagnetism. In our calculation, both antiferromagnetic and ferromagnetic superstructures are obtained as self-consistent solutions for all the considered con-

centrations, even for $L=25.55$ Å (0.98 Co ML). Moreover, the energy difference between the antiferromagnetic and ferromagnetic superstructures is zero and, furthermore, no differences in the absolute values are obtained as compared to the isolated cluster situation ($L\rightarrow\infty$). These results indicate that the magnetic interaction between the Co particles supported in the Cu substrates is very small, at least beyond a distance between nanoparticles of $\simeq 5.5$ Å.

The giant magnetoresistance appears when the magnetic moments of ferromagnetic slabs or clusters, separated by nonmagnetic materials, are ordered antiferromagnetically or at random. Then, the application of a magnetic field produces a ferromagnetic ordering and an important decrease of the resistivity. We wonder if this type of measurement could confirm our results.

IV. SUMMARY

We have calculated the magnetic properties of Co nanoparticles supported on the (111) substrate of Cu. The morphology of the system is approximately modeled according to the experimental sample by accounting for the main features observed through STM.[5] The main general trends obtained are the following.

(a) The local magnetic moments of the Co particles grown in a fcc ($ABCab$) sequence are very similar to those of the particles grown in a hcp ($ABCba$) sequence, independently of the cluster size.

(b) The Co atoms with the lowest moment are those at the center of the particle in the interface plane (the atom with higher coordination). The largest moment is displayed by the Co atoms at the corner of the surface plane (the less coordinated ones).

(c) The average magnetization of the supported Co clusters decreases as increasing cluster size, approaching the limit of the ideal Co bilayer deposited on Cu(111). A similar trend has been experimentally observed for free-standing clusters, although in this case, the limit corresponds to the bulk.

(d) Our calculation indicates that the magnetic interaction via exchange between the Co particles is very small beyond a distance between particles of $\simeq 5.5$ Å. This result could be experimentally analyzed by means of magnetoresistance measurements.

We want to point out, however, that although this study gives a reliable insight into the general trends of the problem, it would be very interesting to compare with the results of a more sophisticated, but expensive, *ab initio* calculation. For model systems less complicated than those studied here, like the ideal monolayer of Co on Cu(111) and Co on Cu(100), there are recent *ab initio* calculations showing similar trends than our results for these systems, although our method tends to overestimate the spin polarization by about 17%. In the mean time, our purpose is to improve the transferability of the parameters of our model by fitting them to *ab initio* results for small Co clusters supported on Cu. Our hope is that the numerical output using these improved parameters will compare well, qualitatively and quantitatively, with *ab initio* calculations when available.

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[23] But, even if the Co-Cu interaction is considered to be weak, when one covers the supported Co particles with a Cu film, the surface effect will not be present and the Co magnetization will decrease. In order to show that our model can deal with this effect, we have performed a calculation for the Cu_4/Co/Cu(111) ideal sandwich, and we obtain a magnetic moment in Co strongly reduced with respect to the one in Co/Cu(111) (where the Co-vacuum interface is present).