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Competition between two- and three-dimensional growth of Co clusters deposited on Cu(001): Influence on the magnetic properties

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Using a quasi–*ab initio* molecular-dynamics method we have studied two-dimensional (2D) versus three-dimensional (3D) structures in Co clusters deposited on Cu(001) finding that the magnetism plays a relevant role. For the magnetic Co_{25} supported cluster, the influence of such a 2D to 3D structural change on the magnetic properties (magnetic-moment distribution an average magnetization) is investigated through self-consistent calculations within a *spd* tight-binding model parametrized to *ab initio* results for the ideal Co monolayer on Cu(001).

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The development of new high-density magnetic storage devices is one of the hot topics in high-technology research.[1] One of the key aspects is the search of novel magnetic materials with two main requirements: size integration (nanoscale structures), and high localized magnetic moments. Supported magnetic clusters are considered one of the best candidates due to their enhanced and very localized magnetic moments. Recent advances in experimental techniques like lithography and pattern transfer seem to date the production of size-controlled periodic arrays of clusters in the very near future, boosting the research in this field.[2] For technical applications it is crucial to assure the stability of the magnetization of each nanoparticle avoiding the interaction between the clusters. The best way to do it is to consider magnetic clusters deposited on inert substrates, like noble metals.

Particular interest has been focused on Co nanoparticles deposited on noble substrates, especially on Cu. It has been pointed out that these Co nanostructures should display enhanced magnetic moments and that the magnetic interaction between them should be negligible even for very high cluster concentration rates.[3] It is well known that the local environment (geometry and coordination) influences strongly the magnetic behavior of these systems. Different measurements of the magnetization for free-standing Co clusters[4–6] as a function of the cluster size found enhancements of about 25–40 % with respect to the magnetic moment in bulk. This effect is due to the loss of coordination at the surface atoms of the particle and should also exist for Co clusters deposited on Cu. The experimental data concerning the growth of Co on a Cu substrate showed a different growth scenario depending on the experimental conditions, due to the competition between kinetics and energetics in the deposition process. Some of the experimental groups have found a good epitaxial layer-by-layer growth of Co on Cu substrate,[7–13] while others observed segregation and intermixing phenomena at the Co/Cu interface,[14,15] or the formation of compact Co clusters on the Cu substrate.[14,16,17] What is clear is that at the initial stage of Co monolayer growth, small Co clusters are formed on the Cu surface. For Co deposited on Cu(111), scanning tunnel microscope observations[16] have shown the formation of two-monolayer height Co islands on the Cu substrate. Recent atomic scale calculations[18] for Co clusters on Cu (111) indicated the transition from two-dimensional (2D) structures (planar supported clusters) to three-dimensional (3D) structures above a certain size, estimated around 25 atoms. It is expected that this type of structural transition affects the magnetic properties of the system, but at the same time the magnetism can play an important role in those structural transitions.

In the present communication, we explore 2D versus 3D structures in Co_N clusters deposited on Cu (001) in connection to their magnetic properties. For this orientation there is no direct experimental observation or theoretical indication about the structure of the Co clusters formed on the Cu(001) substrate during the first stages of the growth. For this purpose we consider several 2D and 3D atomic arrangements for certain Co_N clusters in the range $16 \leqslant N \leqslant 25$ and we optimize them using a quasi-*ab initio* molecular-dynamics method, both with magnetic and nonmagnetic parameterizations. We calculate the corresponding binding energies and compare the magnetic and nonmagnetic situation. For the optimized geometries of the magnetic Co_{25} cluster, the local magnetic moments at each inequivalent site and the average magnetization are analyzed by means of self-consistent spin-polarized calculations within a *spd* tight-binding model parametrized to *ab initio* results for the ideal Co monolayer on Cu(001), and we compare the results with those obtained for the unrelaxed geometries.

We take the Co_{25} cluster as a reference because the 2D-3D transition has been predicted around this size when the Cu substrate is in the (111) orientation. The atomic arrangements of the Co_{25} cluster on the Cu(001) substrate have been optimized using a quasi-*ab initio* molecular-dynamics method within the tight-binding model based on fitting the interatomic potentials to accurate first-principle calculations of selected cluster-substrate properties for Co clusters on Cu.[19] This improvement in the fit includes implicitly in the

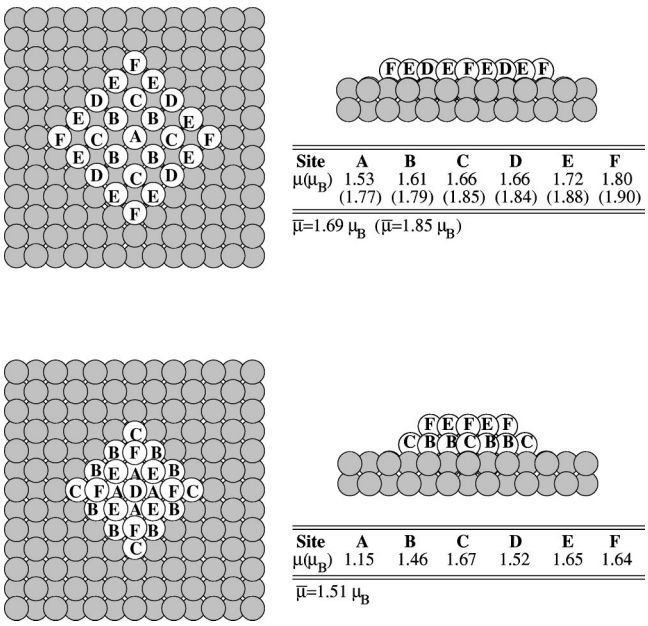

FIG. 1. Geometries of 2D and 3D relaxed Co clusters with 25 atoms supported on Cu(001) together with the magnetic-moment distribution and average magnetic moment per cluster atom ($\bar{\mu}$). For the sake of comparison, also the local magnetic moments and average magnetization corresponding to the unrelaxed planar structure (ideal fcc lattice positions) are reported between parenthesis. Black balls correspond to Cu substrate sites while white balls are the Co atoms in the clusters. All the inequivalent sites in the Co clusters are indicated with capital letters. Only a portion of the semi-infinite system is illustrated.

potentials the magnetic character of the systems, as well as information about the local environment, in particular the finite size of the supported clusters and the interface. However, in order to analyze the role played by the magnetism, we have also performed the optimization using another set of interatomic potentials fitted to first-principle calculations of selected cluster properties in the nonmagnetic configuration. The potentials are formulated in the form proposed by Rosato, Guillope, and Legrand (RGL)[20] with a modified form of the repulsive part. The minimum-energy configurations of Co clusters on Cu(001) surface were obtained using a quenched molecular-dynamics minimization technique.

We have considered two typical geometries for Co_{25}: a two-dimensional (planar) and a three-dimensional one. The planar geometry (see Fig. 1) is represented by a $Co_{5\times5}$ relaxed square island, while the three-dimensional one is a relaxed two-monolayer height structure composed from 16 and 9 atoms in the bottom and top layers, respectively (see Fig. 1). From our molecular-dynamics calculations when the magnetism is taken into account the 3D structure is more stable than the planar one, as proved by the energy gained (-0.13 eV per Co atom). This two-layer 3D structure is chosen because the growth in the bilayer mode has been observed experimentally.[16] Although we cannot speak about the most stable 3D structure (because this would implicate an extensive molecular-dynamics (MD) study for a very large number of initial configurations), we have tested the possibility of a trilayer growth mode and found that, at least up to this cluster size, the two-layer atomic configurations are more stable. We will come again to this point later.

The positions of the Co atoms in the clusters are different from the ideal fcc sites of the Cu lattice due to the strain relaxation at the Co/Cu interface (recently it was shown that Co clusters and Cu substrates are not flat due to the strain relief.[21]) The horizontal interatomic distances within both planar and bilayer 3D clusters are compressed about 4% as compared to the Cu ideal lattice values, being the edge Co atoms relaxed towards the center of the Co clusters. The in-plane relaxations of the Cu atoms in the uppermost Cu(001) plane are nearly negligible. Only the substrate Cu atoms under the Co clusters (Co/Cu interface) exhibit small horizontal distortions (about 1 %). The interface Co atoms in the clusters are relaxed down to the substrate by 9% (central atoms) and 3% (edge atoms). Since the Cu atoms under the Co clusters are pushed down into the substrate in the same way due to the out-of-plane relaxations,[21] the average distance between the Co atoms and the Cu underneath remains nearly the same as the Cu-Cu interatomic distance in the fcc Cu bulk. The Cu atoms that are not adjacent to the Co clusters do not vary significantly from the ideal lattice sites. Since it is well known the close relation between magnetism and atomic structure, an important question arises at this point. Is the magnetism in any sense a driving force in the 2D-3D structural transition? In order to shed some light on this question, we have repeated the MD relaxations for both the planar and the 3D bilayer structures of Co_{25} with the nonmagnetic parametrization, that is switching off the magnetic contribution, although the most stable solution is, of course, the magnetic one. We have found that in this case the planar structure is more stable than the 3D bilayer structure (with an energy gain of 0.03 eV per Co atom). It is therefore clear that magnetism favors the 2D-3D structural transition that takes place for larger sizes if magnetism is switched off. In the case of the nonmagnetic calculations, all Co atoms of the supported cluster approach very close to the substrate because the forces acting on nonmagnetic Co adatoms are considerably larger than the forces acting on magnetic ones.[22] This leads to a strong interaction between the Co atoms and the substrate (the relaxation down to the substrate is about 18% in the nonmagnetic situation). Taking into account that the 2D-3D structural transition is favored by the magnetism it is expected that for clusters smaller than Co_{25} the bilayer 3D structure will be also more stable than the planar one. In fact, the 2D-3D transition could take place at sizes smaller than $N=25$. We have performed the structural optimizations also for Co_{17} and Co_{23} supported magnetic clusters. First we take the planar Co_{17} cluster and also the planar Co_{16} + one Co atom located on top of Co_{16}. We find that the second structure is more stable than the planar one (energy gain of 0.24 eV), indicating that already at this cluster size the bilayer growth mode is more probable. This growth mode, in fact, is preserved at least up to Co_{25}. For an intermediate size, Co_{23}, we consider two cases: a bilayer cluster and also a bilayer Co_{22} + one Co atom located on top of Co_{22}. This second case can be seen as the first stage of a three-layer growth mode for this cluster size. Here also the

bilayer structure is again more stable. In the absence of magnetism, as we have pointed out before, the planar 2D growth would be stable up to at least Co_{25}. In resume, the magnetism is a driving force, not only for the 2D-3D structural transition, but also for the atomic relaxation of the supported Co_N clusters, and the bilayer growth mode takes place at least up to Co_{25}.

Let us come again to Co_{25} in order to analyze the influence of the 2D-3D transition and the atomic relaxation on the magnetic properties. The local magnetic moments at each inequivalent sites of both planar and 3D clusters have been calculated. 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. In our case the Co atoms are placed nearly in Cu fcc sites at the surface, so the hopping integrals fitted to the Co fcc bulk will not reproduce the interaction properly. Therefore, we have used a genetic algorithm code[23] to fit the hopping integrals in order to reproduce the band structure of a Co fcc bulk with the lattice parameter of Cu. The *ab initio* tight-binding linear muffin-tin orbital (TB-LMTO) method[24] was used in this case. The *d*-electron exchange integral of Co is fitted to yield the spin-polarization of a Co monolayer on the Cu(100) substrate calculated previously with the *ab initio* TB-LMTO method.[24,25] The ratio between the Co and Cu *d*-electron exchange integrals is also taken from first-principle calculations.[25] Our self-consistent tight-binding model has been successfully applied in previous works to the study of the magnetic properties of free-standing clusters,[26] clusters embedded in matrices,[27] rough interfaces,[28] and supported nanostructures.[3,29] The values of the magnetic moments and the average magnetization per atom for both the planar and bilayer 3D structures can be seen in Fig. 1. Both structures are ferromagnetic and every Co atom within the clusters has a significant magnetic moment which in most cases is bigger than the fcc Co bulk magnetization ($1.56\mu_B$), in particular for the planar structure. The Co atoms that display a higher magnetic moment are those at the corner of the cluster (the less coordinated ones), while the smaller magnetic moments correspond to atoms at the center of the cluster (the most coordinated). It is well known that for free-standing clusters, changes in the geometry affect significantly the magnetization. This effect has been reported experimentally for free-standing Ni clusters by Apsel *et al.*[30] and analyzed theoretically by Bouarab *et al.*[31] and Aguilera *et al.*[32] They have found oscillations in the average magnetic moment as a function of cluster size due to the changes in the geometry of the clusters (magnetic magic numbers). We found that the 2D-3D transition has a noticeable influence on the magnetic-moments distribution in the cluster and therefore on the average magnetization. The average magnetization for the stable 3D cluster is about 10% smaller than for the planar structure. This is consistent with the increase of the average coordination as going from 2D to 3D structures for the same cluster size. Figure 2 reports the total density of states (DOS) at both 2D and 3D supported clusters. It can be observed the larger degree of electronic delocalization in the DOS of the 3D structure as compared to the 2D one. To our best knowledge, experimental information on the magnetic moments of

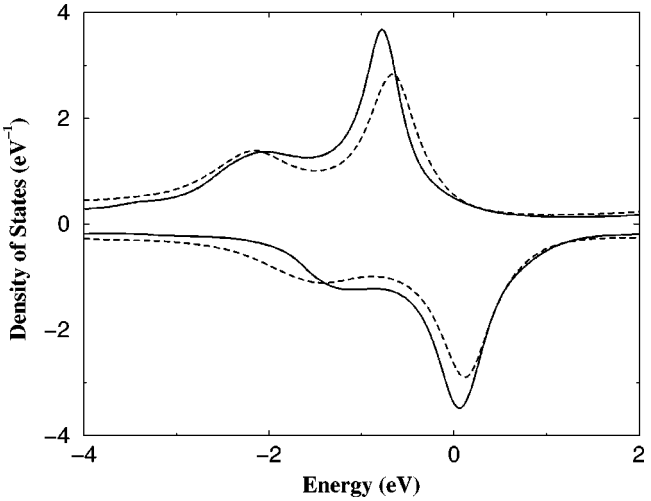

FIG. 2. Average total densities of states for the 2D (solid line) and 3D (dashed line) Co_{25} clusters deposited on Cu(001). The Fermi level is at 0 eV.

Co clusters supported on Cu confirming these predictions has not been reported so far. It is expected that beyond a certain cluster size, larger than 25 atoms, the ground-state geometry will be more spherical than the two-monolayer height structure of our Co_{25} 3D cluster. In that case the average magnetization should decrease approaching the Co bulk limit. For storage applications it is crucial to get high magnetic moments in the nanoparticles, so our result could be useful as an indication of how to select the sizes of the particles to get the best magnetic response.

In the fitting of the parameters of our model we calculated, using *ab initio* TB-LMTO, the magnetization of an ideal Co overlayer on the Cu(001) and obtained a magnetic moment of $1.77\mu_B$ per atom. In Fig. 1 one can see that the magnetic moments of the planar Co_{25} cluster are smaller than the magnetic moment of the ideal Co overlayer on Cu (an exception being the Co atoms in the corners). Considering that the coordination of Co atoms in the overlayer is larger than the average coordination in this finite cluster, our result is, at first glance, in disagreement with the general trend of the lower magnetic moment for more coordinated systems, but another fact has to be taken into account. As we mentioned before the clusters are compressed in the surface plane with respect to fcc Cu.[21] The resulting reduction in the Co-Co interatomic distances increases the electronic kinetic energy; the *d* bandwidth increases giving rise to a reduction of the magnetic moment, which explains why the magnetic moment of such a planar Co_{25} cluster is smaller than for the ideal Co monolayer on Cu(001). We have also calculated the local magnetic moments for the 2D Co_{25} cluster considering the Co atoms placed in the ideal fcc lattice positions on the Cu(001) substrate (no relaxed geometry). The results obtained are reported in parenthesis in Fig. 1. The average magnetization of this configuration is $1.85\mu_B$, about 9.5% higher than the value obtained for the relaxed planar configuration, and also higher than the magnetization for the Co overlayer on Cu(001), as it is expected. These results show again the strong relation between atomic structure and magnetism and

probe the relevance of the geometrical structure optimization for the investigation of electronic properties of low-dimensional systems.

In summary, using a MD scheme in combination with a self-consistent *spd* tight-binding model, both parametrized to *ab initio* results, we have reported on the magnetic properties for competing two-dimensional and three-dimensional structures of Co clusters deposited on Cu(001). We obtain that the magnetism is a driving force, not only for the 2D-3D structural transition, but also for the atomic relaxation. When magnetism is not considered in the structural optimization, the forces acting on nonmagnetic Co adatoms result considerably larger than forces acting on magnetic ones. This leads to a strong interaction between Co atoms and the substrate, with a larger relaxation down to the substrate than in the magnetic case. The 2D-3D structural transition takes place for larger sizes when magnetism is not taken into account. The most stable solution corresponds always to the magnetic configuration, and in this case, the 3D structure with two-monolayer height is more stable than both the planar one and the 3D structures with three-monolayers height for clusters larger than Co_{16} up to at least Co_{25}. Due to the lower average coordination of the planar 2D structure, its average magnetization is about 10% higher than for the bilayer 3D structure. The in-plane relaxations of the planar cluster give rise to a reduction of the magnetization as compared to the ideal Co monolayer on Cu(001). Since the general belief is that finite transition metal systems should display enhanced magnetization, our result puts in evidence the relevance of performing structural optimization for the calculation of the magnetic properties. It would be interesting to investigate the growth process of these supported Co nanoparticles to determine the one-dimension to two-dimension structural transition and the corresponding effects in the magnetic behavior. We await experimental confirmation of our predictions.

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