

Magnetic magic numbers are not magic for clusters embedded in noble metalsR. Robles,¹ R. C. Longo,² A. Vega,¹ C. Rey,² V. Stepanyuk,³ and L. J. Gallego²¹*Departamento de Física Teórica, Atómica, Molecular y Nuclear, Universidad de Valladolid, E-47011 Valladolid, Spain*²*Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15782, Santiago de Compostela, Spain*³*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

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Atomic scale simulations show that Co clusters embedded in Cu surfaces are always more stable than the adsorbed clusters often observed experimentally. Spin-polarized electronic structure calculations based on a self-consistent tight-binding method reveal that, unlike gas-phase clusters, ferromagnetic Co clusters embedded in Cu do not exhibit “magnetic magic numbers.” This is explained in terms of the coordination geometry imposed on the clusters by the substrate.

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I. INTRODUCTION

Low-dimensional magnetic systems have received considerable attention in recent years because of their potential application in new high-density magnetic storage devices (see, e.g., Ref. 1). Supported magnetic clusters are of particular interest due to their enhanced and very localized magnetic moments. Since it is crucial to ensure the stability of the magnetization of each cluster while avoiding its interacting with other clusters, the best candidates as substrates are noble metals.

Particular attention has been focused on Co clusters and other Co structures deposited on Cu substrates. However, published data on the structures of these systems have been somewhat contradictory; this is an important question, since determination of the geometrical structure adopted by the clusters is the first step towards understanding other properties, such as their magnetic moments. Zimmerman *et al.*² found that Co nanoparticles burrow into clean Cu (001) at 600 K. Atomic scale simulations by Stepanyuk *et al.*³ corroborated this burrowing and showed that it is promoted by the Co clusters becoming coated with Cu, which leads to high pressure at the interface; while Pentcheva and Scheffler,⁴ using the full-potential linearized augmented plane-wave (FP-LAPW) method, found that, on Cu (001), Co bilayers covered by a Cu layer are more stable than exposed Co bilayers, which is consistent with experimental observation of surface Cu atoms following annealing of Cu (001) covered with Co.⁵ However, supported or partially embedded Co structures have also been observed. For instance, Nouvertné *et al.*⁶ used FP-LAPW calculations to interpret their scanning tunneling microscopy images as showing that Co atoms are incorporated in the Cu (001) surface layer, where they act as nucleation centers for the small Co islands that are observed in CO titration experiments; at the Cu (111) surface Pedersen *et al.*⁷ observed three-layer-high Co islands that had just one subsurface layer and were surrounded by a rim of Cu; and de la Figuera *et al.*⁸ observed two-layer-high triangular Co islands on top of the Cu (111) surface.

In the work described here we determined the ground-state configurations of Co_n clusters ($n \leq 10$) at the (001) and (111) surfaces of Cu (by quenching Co clusters from numer-

ous starting configurations on and beneath the Cu surfaces), and we calculated the magnetic properties of the ground-state clusters. We found that embedded clusters are always more stable than adsorbed clusters, and that, although they are ferromagnetic, their magnetic moments decrease almost monotonically with increasing cluster size, in strong contrast with those of free clusters of magnetic transition metals, which exhibit so-called “magnetic magic numbers.”

II. DETAILS OF THE COMPUTATIONAL METHOD, RESULTS, AND DISCUSSION

We computed the ground-state structures of Co_n clusters ($n=2-10$) at the (001) and (111) surfaces of Cu using the many-body potential that was employed by Stepanyuk *et al.*³ and Levanov *et al.*⁹ in their study of Co/Cu (001) systems, which was constructed on the basis of the second-moment approximation to the tight binding (TB) method.¹⁰ Details of the data to which the potential was fitted, and the optimized values of the potential parameters, have been given in Ref. 9. The inclusion in the data set of the binding energies of small Co clusters supported on the Cu (001) surface (calculated using the first-principles Korringa-Kohn-Rostoker Green’s-function method) makes this potential especially suitable for studying ground-state Co cluster structure at Cu surfaces. In particular, magnetic effects are included implicitly by these energy calculations including spin-polarization effects.

The Cu (001) surface was modelled by the top (001) layer of a 15-layer slab of atoms with the bottom four layers fixed and periodic boundary conditions in the [100] and [010] directions. Each layer comprised 242 Cu atoms. The atoms in the slab were initially arranged as in bulk Cu, but before addition of the Co atoms the top 11 layers were relaxed to the minimum-energy configuration using a conjugated gradient procedure.¹¹ This initial relaxation induced a contraction of about 0.5% in the top interlayer space, which is consistent with the experimental value of $(1.1 \pm 0.4)\%$ reported in Ref. 12. Similarly, the Cu (111) surface was modelled by the top (111) layer of a 15-layer slab of atoms with the bottom four layers fixed and periodic boundary conditions in the $[\bar{1}10]$ and $[\bar{1}\bar{1}2]$ directions. In this case, each layer comprised 360 Cu atoms. Initial relaxation of the slab (without

Co atoms) reduced the top interlayer distance by about 0.75%, in good agreement with the observed inward relaxation of $(0.7 \pm 0.5)\%$ for this surface.¹³ For both surfaces we computed the lowest-energy structures of Co_n clusters by considering numerous initial configurations both on and beneath the surface for each value of n and, for each configuration, calculating the minimum energy of the cluster + substrate system using a quenched molecular-dynamics (MD) minimization technique.¹⁴

Using the cluster geometries and interatomic distances obtained as described above, we computed the magnetic moments distribution of the Co/Cu systems using a self-consistent TB method similar to that employed by Robles *et al.*¹⁵ in their study of the structural and electronic properties of Ni clusters at the Al (001) surface. The main difference is that in the present work the parameters of the TB model (hopping and exchange integrals) were obtained from a single fit to *ab initio* results for a Co monolayer embedded three layers below the Cu (001) surface that were obtained using the TB linear muffin-tin orbital (LMTO) method;¹⁶ an embedded monolayer was used so as implicitly to take into account hybridization between Co and Cu atoms and the influence of the surface, Co clusters having been found to embed themselves in the Cu substrates with three layers of Cu above the main cluster layer (see below).

Figure 1 shows the predicted ground-state structures of Co_n clusters ($n=2-10$) at the (001) and (111) surfaces of Cu. All the clusters are embedded in the substrate. Although this might be unexpected, Co and Cu being almost immiscible in bulk form,¹⁷ similar intermixing has recently been found for other metals that are immiscible in the bulk (see, e.g., Ref. 3 and those cited therein). Hence our results show that the supported and partially embedded Co clusters observed at Cu surfaces by Nouvertné *et al.*,⁶ Pedersen *et al.*,⁷ and de la Figuera *et al.*⁸ were probably metastable.

Evidently under the influence of the Cu environment, the arrangement of the Co atoms in the embedded clusters conforms to the Cu lattice, except that their average nearest-neighbor Co-Co distances are closer to that of bulk Co than to the Cu-Cu distance of bulk Cu, which has a lattice parameter about 2% larger than that of Co (in these small clusters the resulting deviations of the atoms from lattice point locations are minimal). Beneath both surfaces, the “growth” pattern of the cluster strikes a balance between construction of the most compact cluster possible [as in the transitions from Co_5 to Co_6 under the (001) surface and from Co_3 to Co_4 under (111)] and extension parallel to the nearby surface [as in the transitions from Co_6 to Co_7 under (001) and from Co_7 to Co_8 under (111)]; overall it is the former trend that predominates, although the latter results in the most populous plane through the cluster generally lying parallel to the surface. The only significant exception is Co_8 under the (001) surface, although the least-energy configuration shown [two atoms in each of four (001) layers] is actually almost isoenergetic with a configuration obtained in consonance with the second of the above-mentioned trends by adding the missing corner atom to Co_7 . The balance between the pursuit of compactness and extension parallel to the surface appears to depend, reasonably enough, on proximity to the surface: al-

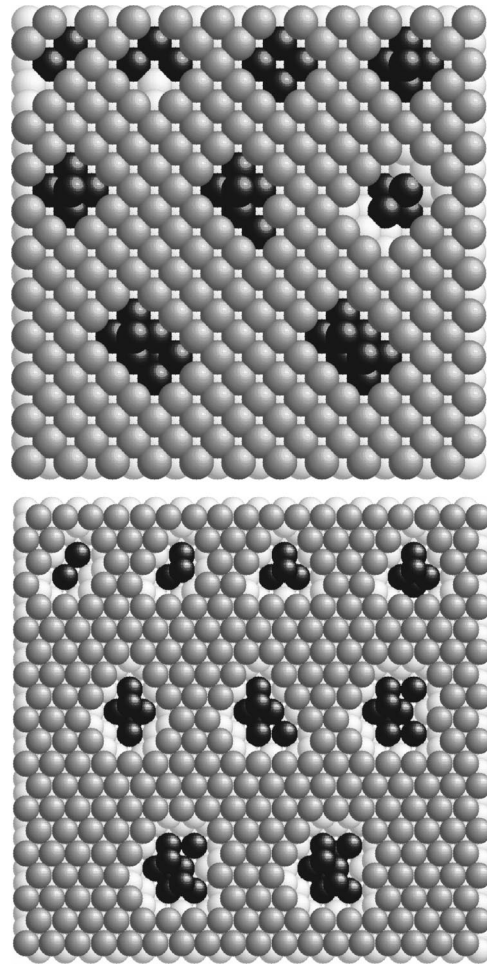


FIG. 1. Predicted ground-state structures of Co_n clusters ($n=2-10$) at the (001) and (111) surfaces of Cu (upper and lower panels, respectively). Dark spheres represent Co atoms and grey spheres represent top-layer Cu atoms; for clarity, some Cu atoms of the first and second layers of the substrate, and the Cu atoms pushed out on top of the surface by the embedded Co clusters, have been removed to allow visualization of the latter, which except for $n=8$ in Cu (001) lie mainly in layer 3 with one or two atoms in layers 2 and/or 4. In Cu(001), Co_8 has two atoms each in layers 2–5.

though the presumably metastable clusters observed experimentally at the surface^{6–8} were mainly two layers high, and Gómez *et al.*¹⁸ found that two-dimensional Co clusters deposited on Cu (111) transform into three-dimensional clusters above a certain critical size, Izquierdo *et al.*,¹⁹ in calculations explicitly including magnetic effects, found that two-dimensional Co_n clusters deposited on Cu (001) are stable up to $n=16$.

Before applying the self-consistent TB model to investigate the magnetic moments of the embedded clusters, we first used it to calculate the electronic structure of a Co monolayer supported on the Cu (001) surface, and compared the resulting local densities of electronic states (LDOS) with those obtained using the *ab initio* TB-LMTO method. This provides a test of the transferability of the TB parametrization, since in the supported layer the Co atoms have a differ-

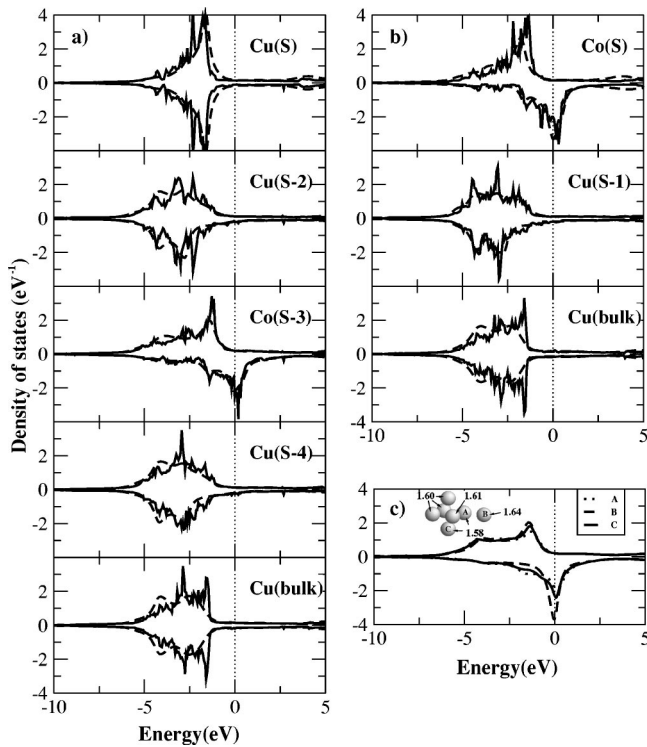


FIG. 2. LDOS in selected sites of (a) the system formed by a Co monolayer embedded three layers below the Cu (001) surface, (b) the system formed by a Co monolayer supported on the Cu (001) surface, and (c) the cluster Co_7 embedded in the Cu (001) substrate with its main layer in substrate layer 3. For (a) and (b), calculations were performed using both the *ab initio* TB-LMTO method (continuous line) and the TB method (dashed line); for (c), the TB method was used (the number associated with each atom represents its magnetic moment, in μ_B). The vertical dotted lines at 0 eV indicate the Fermi level.

ent environment from what they have in the embedded layer, for which the TB model was optimized. Figures 2(a) and 2(b) show the LDOS in selected layers of the systems formed by a Co monolayer embedded three layers below the Cu

(001) surface and a Co monolayer supported on the same surface, as calculated using the TB and *ab initio* TB-LMTO methods. The agreement between the results of the two methods is quite good, especially in that the TB method (i) gives the main peaks of the Co LDOS correctly, (ii) reproduces the sharp peaks of the Cu surface quite well, and (iii) properly predicts the hybridization-induced broadening undergone by the occupied bands in Cu layers adjacent to the Co layer, particularly near the Fermi energy.

Figure 3 shows the average magnetic moment per atom of embedded Co_n clusters at the (001) and (111) surfaces of Cu as a function of n . The clusters are ferromagnetic, with an average magnetic moment that decreases almost monotonically from $1.65\mu_B$ to $1.58\mu_B$ and between these extremes is slightly larger for the sub-(001) than for sub-(111) clusters. All the observed values are smaller than those found by a TB method for small Co_n clusters supported on Cu (001), which decrease with increasing n from $1.96\mu_B$ for Co_2 to $1.67\mu_B$ for Co_9 ,²⁰ and considerably smaller than those of free Co_n clusters (cf., for example, $2\mu_B$ for Co_2 and $2.5\mu_B$ for Co_4 ; see Fig. 3 and Ref. 21).

In previous work on average atomic magnetic moments $\bar{\mu}$ in clusters,²² dependence on cluster size has been found to be explicable in terms of average atomic coordination number CN and average within-cluster nearest-neighbor distance d (“geometric effects”), $\bar{\mu}$ decreasing with decreasing d and increasing CN. These effects—with CN now including Co-Cu as well as Co-Co coordination—appear sufficient to explain not only the differences in $\bar{\mu}$ among free, supported and embedded clusters noted above, but also the gradual monotonic decrease with increasing size observed in this work among embedded clusters, in which, as in the case of supported clusters, the atoms are essentially constrained to occupy the points of a pre-established lattice. This imposed regularity prevents the radical changes in CN and d that can and do occur in free clusters as cluster size n increases, and which give rise to the overall downward trend of $\bar{\mu}(n)$ plots for free clusters of magnetic transition metals being overlain

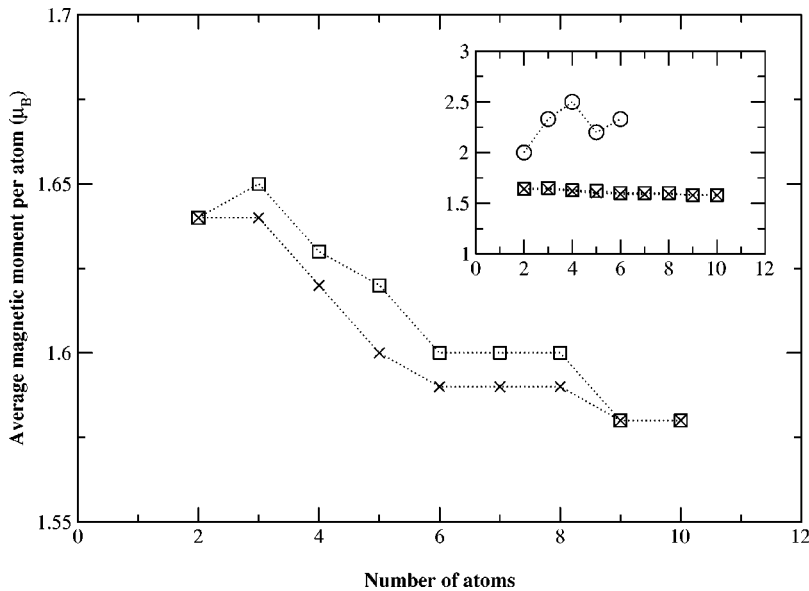


FIG. 3. Average magnetic moment per atom (in μ_B) of embedded Co_n clusters at the (001) and (111) surfaces of Cu, as a function of n (squares and crosses, respectively). In the inset, we compare these results with those obtained by Andriotis and Menon²¹ for free Co clusters using a TB MD method.

by considerable irregularity, with peaks at “magnetic magic numbers” corresponding to clusters with low CN and/or large d ; the best examples of this irregularity are Ni clusters, which have been studied in detail both experimentally and theoretically (see Ref. 22 and those cited therein), but it has also been observed in a density-functional study of small Fe clusters²³ and in a TB MD study of Co clusters,²¹ some of the results of which are shown here in the inset to Fig. 3.

The role of d in Co clusters embedded under Cu surfaces (in which, as noted above, d is less than the Cu lattice parameter) is emphasized by our finding that their $\bar{\mu}$ values (1.58 – $1.65\mu_B$) are smaller than the $1.69\mu_B$ obtained for a hypothetical fcc bulk Co with the lattice constant of Cu. The role of CN is emphasized by the effect of a more general bond number being observable even in the magnetic moments of individual atoms in the embedded clusters: the fact that the magnetic moments of the Co atoms nearest the surface are slightly larger than those of Co atoms with the same Co environment that lie farther from the surface [compare, for example, the top and bottom atoms in Fig. 2(c)] is attributable to their having fewer second-neighbor bonds. Though small, this difference is significant because it is systematic in all the clusters.

Although the above arguments appeared sufficient to explain our results, there remained the possibility that the low values of sub-Cu (001) and sub-Cu (111) Co clusters were also partly due to Co-Cu hybridization, Cu being a noble metal. To investigate this we analyzed in detail the magnetic moments and LDOS of individual atoms in the embedded clusters. Figure 2(c) shows, as a typical example, the results obtained for Co₇ beneath the Cu (001) surface. The atom

with fewest Co neighbors, and hence the most Cu neighbors, has the highest magnetic moment ($1.64\mu_B$), while the two atoms with most Co and fewest Cu neighbors have the lowest magnetic moments ($1.58\mu_B$); moreover, it is the LDOS for the atom with the largest magnetic moment that has the narrower peak. Since Co-Cu hybridization must tend to reduce the magnetic moment upon increasing the number of Cu neighbors, it may be concluded that hybridization cannot be the dominant influence.

III. SUMMARY AND CONCLUSIONS

To sum up, we have studied the structure of Co clusters at Cu surfaces by allowing both the clusters and the substrate to relax. We found that the clusters burrowed into the substrate, and calculation of their magnetic moments showed that the magnetic moment per atom decreased essentially monotonically as cluster size increased. This is attributed to the influence of the substrate lattice on coordination numbers and interatomic distances in the clusters, which as functions of cluster size cannot undergo the sudden changes that are responsible for “magnetic magic numbers” in series of free clusters. It seems likely that these conclusions are valid in general for ferromagnetic clusters embedded at noble metal surfaces.

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