Large Variations in the Magnetization of Co Clusters Induced by Noble-Metal Coating

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We report calculations of the electronic and magnetic properties of small Co clusters, coated with Ag or Cu, performed with a parametrized tight-binding method. For a given number of Co atoms in a cluster, we obtain a large range of magnetization values, depending on the size and shape of the coating. The noble metal develops a net polarization that changes appreciably the total magnetic moment of the cluster. This result is reinforced by *ab initio* calculations for mixed slabs, where the corrugation of a nonmagnetic covering also produces important variations in the total magnetic moment. [S0031-9007(98)07909-5]

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Small metallic clusters have been the subject of wide investigation in recent years. This is due to the fact that many of their properties (structural, electronic, optical, and magnetic) differ from those of the corresponding bulk. In particular, the magnetic properties of small transition metal clusters are attractive from a technological point of view because of possible magnetic recording applications.

Recently Eastham *et al.* [1] measured, by using x-ray dichroism, the magnetization of mixed clusters of Co and Cu deposited on a Si substrate, obtaining an average cluster magnetization per Co atom that is always lower than the one corresponding to Co thin films. They show that the magnetization behavior depends on cluster size and on the relative concentration of Co and Cu in a nonobvious way. The average magnetization per Co atom goes from around $1.3\mu_B$ to less than $0.25\mu_B$.

Granular magnetic solids, consisting of single-domain ferromagnetic particles embedded in an immiscible medium, have also been studied in recent years because of their potential use in magnetic recording, optical devices, and sensors. For example, giant magnetoresistance has been observed recently in granular films of magnetic clusters embedded in a nonmagnetic metal [2,3]. This property is a consequence of the macroscopic magnetization, and is therefore related to the grain size distribution and to the intergranular magnetic interactions [4]. On the other hand, other authors [5,6] have observed that the presence of a magnetic layer generates a response within a nonmagnetic medium (Cu, Ag, Au) that oscillates with varying noble metal coverage, even at distances as large as 100 Å.

There has been a large computational effort in studying homonuclear free clusters [7,8], and also supported or adsorbed ones [9]. However, there are only a few calculations on mixed clusters, while the amount of experimental work has been growing steadily. *Ab initio* calculations by Chuanyun *et al.* [10] for Co clusters embedded in Cu and also the tight-binding calculations by Vega *et al.* [11] for Fe clusters embedded in Cr are some examples.

In this contribution, we study clusters of Co coated with Cu or Ag ($Co_N X_M$, X = Cu, Ag, $N + M$ up to 405) having the structure of parts of an fcc lattice. Although the cluster sizes attainable are somewhat smaller than the experimental ones of Ref. [1], the purpose of this systematic study is to analyze the behavior of the magnetic moment of these coated clusters as a function of shape, size, and composition, as the magnetic properties of mixed transition metal clusters are not necessarily given by the average behavior of the corresponding bulks [12]. We show that the polarization of the noble metal which coats the Co clusters is very sensitive to the symmetry of the system; for example, Ag can develop an antiferromagnetic (AF) or ferromagnetic (F) alignment with Co by changing the atomic arrangement of the noble metal. Therefore, the polarization of the conduction electrons of the noble metal coating can lead to large variations in total magnetic moment of the cluster, while keeping the magnetization of each of the Co atoms quite unaltered.

For the cluster calculations, we use a parametrized tight-binding Hamiltonian as in previous works [7]. It considers s, p, and d orbitals and uses parameters taken from the corresponding bulk materials. Magnetism is obtained from a Hubbard-like term solved in the unrestricted Hartree-Fock approximation, which implies that only collinear magnetism is considered. The single-site and hopping elements of the Hamiltonian are taken to be the bulk values, obtained from Andersen's canonical linear muffin-tin orbital, atomic sphere approximation (LMTO-ASA) paramagnetic bands [13]. The hoppings are assumed to be spin independent and for the heteronuclear case Co-X (X = Cu, Ag), that appears at the interfaces, they are averaged as in Ref. [14]. Extra empty orbitals, s', are added to the basis set, outside the clusters, to account for the

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electron spillover at the surfaces. They are parametrized so as to obtain adequate d orbital occupations at the surfaces, as the s'-orbital site energy is related to the average coordination of the surface atoms. Enough s' orbitals are added so that each cluster atom, bulk or surface, has the bulk coordination [7].

Our calculations are restricted to isomers of high symmetry (O_h or D_{4h}), closed shells of atoms surrounding a central atom in an fcc structure. We consider this structure to be the probable one for these clusters, as both components are fcc in the bulk phase and also because recent experiments show that Co clusters grow in the fcc structure for small sizes [15]. By using techniques of group theory, we can calculate up to 405 atom clusters (17 shells).

(a) Co-Cu clusters.—As Co and Cu bulk equilibrium distances are very close, we parametrize both diagonal and off-diagonal elements of the Hamiltonian as if all of the interatomic distances in the clusters were equal to their average value. The first clusters considered are those reported in Ref. [10], so that the results can be compared with *ab initio* calculations. We find excellent agreement in the total magnetic moments and some differences in the distribution within the shells.

The dependence of the cluster magnetic moment with Cu coating is studied by calculating for clusters of the type $Co_N Cu_M$, with $N + M$ ranging from 13 to 405 [16]. Figure 1 shows the results obtained for clusters with a core of 13 Co atoms. Both the average magnetic moment and the total magnetic moment show an oscillatory behavior as a function of coating thickness, although the core contribution has a smaller range of variation. Because of hybridization with the Cu atoms, the polarization of the Co atoms is always less than for the free Co_{13} cluster. For some particular coatings, the noble metal becomes AF with respect to Co and therefore yields smaller cluster magnetic moments per Co atom, in some cases even smaller than for bulk Co. This effect seems to be related to the shape of the added Cu shells. When the coated cluster has low coordinated atoms in the last shell, that is, a rather open or corrugated cluster surface, it develops a F polarization.

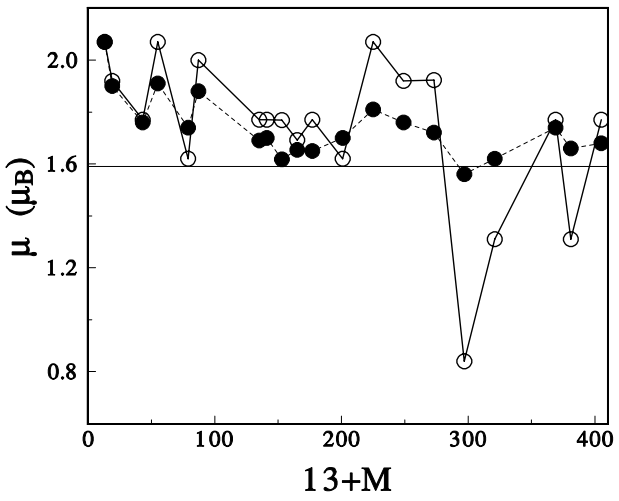

FIG. 1. Magnetic moment per Co atom vs increasing number of Cu atoms for $Co_{13}Cu_M$ clusters. ○ corresponds to the total magnetic moment, ● to the magnetic moment of the Co core.

Because of the extreme sensitivity of the polarization of the noble metal to surface symmetry, clusters with the same Co core of 13 atoms can have a magnetic moment per Co atom going from more than $2\mu_B$ to less than $1\mu_B$.

(b) Co-Ag clusters.—Bulk Co and Ag have very different lattice constants, and therefore the interatomic distances to be used in the cluster calculations have to be determined. For this purpose, we used 3D calculations performed with an *ab initio* method. In particular, we optimized the lattice constant of different $Co_n Ag_m$ ordered alloys using the WIEN97 code [17], which is an implementation of the linearized augmented plane wave method, based on density functional theory. It uses the local spin density approximation for exchange and correlation, and includes scalar relativistic effects. For all the alloys considered, the optimized Co-Ag distance is very close to the arithmetic weighted mean of the Co-Co and Ag-Ag nearest neighbor distances present in the unit cell. Based on this result, we have used for the Co-Ag interaction in the cluster calculations the average of the corresponding bulk values and for Co-Co and Ag-Ag ones their bulk values.

As in the case of Cu coating, we have studied $Co_N Ag_M$ clusters with $N + M$ ranging from 13 to 405. In contrast to what happened for Cu coated clusters, many of the cases considered give a net AF polarization of the Ag coating. Therefore, the total magnetic moment of the clusters is smaller than that of the bare Co clusters. However, the magnetization of the Co core per atom is larger than the Co bulk value. From Fig. 2 it is evident that the total magnetic moment not only depends on the number of Co atoms of the core but also on the number and shape of the surrounding Ag atoms. The net polarization of Ag oscillates, but for an increasing number of shells it leads, in most of the examples shown, to a net AF polarization. In this sense it is interesting to point out that, even for the largest cluster sizes considered, the outer Ag shells and the spilled-over electrons acquire an AF polarization. Few cases here have F polarization and show relative maxima in the magnetization per atom; they are related to a corrugated outer Ag shell, with some poorly coordinated Ag atoms (spikes).

The fact that Cu has a tendency to align more ferromagnetically than Ag with respect to Co is easily understood by considering the relative energy positions of the respective d bands. In the first case, the majority bands nearly overlap and the magnetic polarization of the noble metal is due to minority band hybridization, leading thereafter to a mostly F polarization of the Cu atoms. This alignment can be enhanced by surface corrugation. In the second case, the d bands of Ag lie lower in energy than the Co ones and the larger hybridization is given among majority bands, triggering then a mostly AF alignment of the Ag

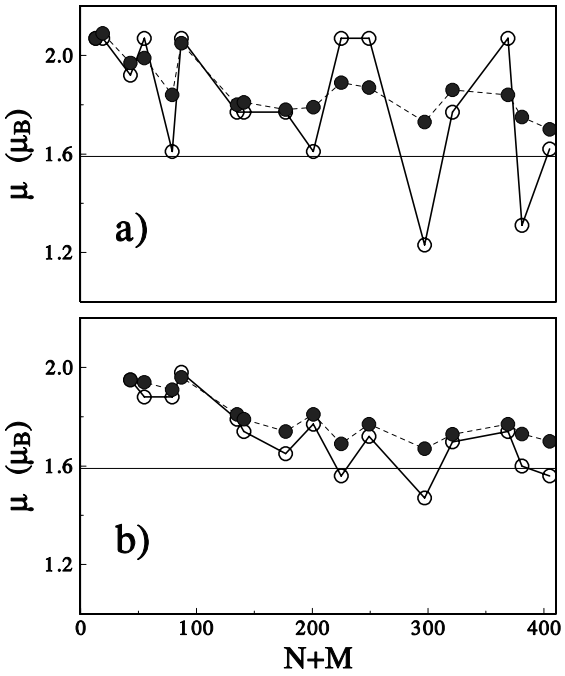

FIG. 2. Same as Fig. 1 for (a) $Co_{13}Ag_M$ and (b) $Co_{43}Ag_M$ clusters.

atoms which, contrary to Cu coating, can be reversed by the system symmetry and the surface corrugation.

In the two examples shown in Table I the total magnetic moment per Co atom decreases from $2.08\mu_B$ to $1.23\mu_B$. This large decrease reflects the fact that in the second cluster there are many more AF Ag atoms surrounding the Co core than in the first one. The polarization of the d orbitals of the Ag atoms dies down very fast, while the sp one is still rather large in the outermost shell. This explains the remarkable fact that, for a fixed number of Co atoms, there is an astonishingly broad range of cluster magnetizations that can be attained by just changing the Ag covering.

To show that the large variations of the magnetic moment are not an artifact of the parametrized tight-binding calculations, we have performed *ab initio* [17] calculations for three examples of mixed 2D periodic systems. Surface corrugation effects on the magnetization values are also obtained, thus confirming the outcome of the cluster calculations.

In the first case, we consider a trilayer slab of fcc structure, grown in the (001) direction, where the central layer is a 2D ordered AgCo (or CuCo) alloy and the outer layers are of pure noble metal. This is part of the $CoAg_3$ alloy in the $L1_2$ optimized structure. An interslab distance of 3 times the slab width is intercalated between slabs, so that they do not interact with each other and allow a periodic 3D calculation. In this case each Co atom is surrounded by 12 Ag (or Cu) nearest neighbors and 4 Co next nearest neighbors. The slab surfaces are perfect planes. For the second example, we add another atomic plane on each side of the previous slab with only 50% of the noble metal atoms, showing a (2×2) surface structure. In this case, each Co atom has the same first and second nearest neighbors as before but the surface is not smooth (first approximation to the spikes). A third example studies a full Co monolayer (ML) covered either by two smooth Ag layers on each side, or by a corrugated surface obtained by removing 50% of the atoms in the external Ag layer. For this last example, we take the Ag-Ag bulk distance in the plane and an optimized Co-Ag interplanar distance.

TABLE I. Local magnetic moments per atom, orbital, and shell for two Co-Ag clusters, in μ_B. The first column indicates shell number starting from the center of the clusters.

	$Co_{13}Ag_{212}$				$Co_{13}Ag_{284}$		
Shell	μ_d	μ_{sp}	μ_{tot}	Shell	μ_d	μ_{sp}	μ_{tot}
1 (Co)	1.94	−0.09	1.85	1 (Co)	1.94	−0.10	1.84
2 (Co)	1.92	−0.03	1.89	2 (Co)	1.77	−0.05	1.72
3 (Ag)	0.04	−0.06	−0.02	3 (Ag)	0.04	−0.08	−0.04
4 (Ag)	0.02	−0.03	−0.01	4 (Ag)	0.01	−0.05	−0.04
5 (Ag)	0.02	−0.01	0.01	5 (Ag)	0.01	−0.04	−0.03
6 (Ag)	0.00	0.00	0.00	6 (Ag)	−0.01	−0.02	−0.03
7 (Ag)	0.00	0.01	0.01	7 (Ag)	0.00	−0.01	−0.01
8 (Ag)	0.00	0.01	0.01	8 (Ag)	−0.01	−0.01	−0.02
9 (Ag)	0.00	0.01	0.01	9 (Ag)	0.00	−0.01	−0.01
10 (Ag)	0.00	0.02	0.02	10 (Ag)	0.00	−0.01	−0.01
11 (Ag)	0.00	0.01	0.01	11 (Ag)	0.00	−0.02	−0.02
12 (Ag)	0.00	0.02	0.02	12 (Ag)	0.00	−0.01	−0.01
13 (Ag)	0.00	0.02	0.02	13 (Ag)	0.00	−0.02	−0.02
				14 (Ag)	0.00	−0.02	−0.02
				15 (Ag)	0.00	−0.02	−0.02
	$\mu_{s',\text{tot}} = 0.64$				$\mu_{s',\text{tot}} = -0.83$		
	$\mu_{\text{tot}} = 27$				$\mu_{\text{tot}} = 16$		

TABLE II. Magnetic moments (in μ_B) for slabs of Co-Cu and Co-Ag, with smooth and corrugated noble metal surfaces. The first and second examples are slabs with an ordered alloy Co-Cu(Ag) surrounded by noble metal layers, while the third case is a slab of a full Co ML surrounded by Ag. The noble metal atoms are labeled with increasing index as they approach the surface. "int" indicates the polarization of the interstitial region (of sp character).

	Co-Cu alloy		Co-Ag alloy		Full Co(ML)-Ag	
	Smooth	Corrugated	Smooth	Corrugated	Smooth	Corrugated
Co	1.03	1.24	1.47	1.53	1.63	1.56 and 1.66
Cu1(Ag1)	.01	.04	−.03	.00	.02	−.01
Cu2(Ag2)	.01	.03	−.02	.00	−.00	.01
Cu3(Ag3)	...	.02	...	.01	...	...
int	−.09	−.08	−.13	−.03	−.01	−.13
tot. per Co atom	.99	1.36	1.23	1.52	1.64	1.54

The results are shown in Table II, where the magnetic moment of each atom in the unit cell and in the interstitial region are displayed. As for the tight-binding calculated cluster, changing from a perfectly planar surface to a more corrugated one changes the polarization of Co and of the noble metal atoms, and therefore the total magnetic moment of the unit cell per Co atom.

From our calculations, we conclude that Cu and Ag atoms become polarized even at large distances from the Co cores. Their net polarization can be F or AF and is mostly due to the sp orbitals. This long-range effect reflects itself in the broad range of magnetization values that clusters with the same Co core can display depending on the covering. For a given Co core, the overall dependence of the cluster magnetization as a function of noble metal thickness is very similar for Cu and Ag coating (Figs. 1 and 2). This reflects the importance of symmetry effects.

The present calculations attempt the modelization of coated clusters in vacuum. However, the conclusion drawn about the broad range of attainable magnetization values will not change if the coated systems are embedded or deposited on some other material. We have repeated some of the calculations suppressing the spillover, a situation which would simulate a substrate or host as Si, and again for a given Co core the magnetization value depends strongly on noble metal thickness.

The results obtained provide a remarkable qualitative agreement with the recent experiments by Eastham *et al.* [1], for Co clusters embedded in Cu and supported on a Si surface. As in Ref. [6], it is the confinement of sp electrons in the noble metal that produces oscillations with noble metal thickness, which are greatly influenced by the surface roughness.

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