Local magnetic properties of Co grains in bulk Ag and Cu: A first-principles study

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Here we use the real space–linear muffin-tin orbital–atomic sphere approximation method to perform a systematic study of the site and grain size dependence of local magnetic moments and hyperfine fields at Co grains (up to 135 atoms) in fcc Ag and Cu hosts. We found a very stable value for the local moment at Co atoms in Ag hosts, whereas the average local moment for Co grains in Cu tends to be slightly larger for larger grains. We show that free and embedded Co clusters have very different magnetic behavior. The Co hyperfine fields present similar values in both matrices and exhibit a systematic site dependence.

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The discovery of giant magnetoresistance (GMR) in granular materials[1,2] generated a great interest in the study of these systems. Special attention has been devoted to Co grains inside Cu and Ag mediums. As the transport properties are closely related to structural characteristics, an accurate description is required in order to understand the GMR behavior in these materials. To estimate the size of the grains it is a common practice to assume that all Co atoms have the same local magnetic moment and that the grains are supposed to be noninteracting. However, this simple model has been shown to be not well suited to this characterization, mainly for Co-Cu systems. Many recent works have discussed this problem studying the possible interactions between the Co particles.[3] Hyperfine field (HF) measurements using different techniques have also been used to study structural characteristics of these systems. Because it is sensitive to local environments, this kind of approach has the advantage of being able to distinguish very small particles and differentiate bulk from interface atoms. We must note that interface features are crucial because, as has been indicated in Refs. 1 and 2 and confirmed in Ref. 4, interface scattering is the main mechanism that generates the GMR. We must note that the lack of symmetry involved in these systems makes them very difficult to be studied by theoretical electronic structure methods.

Here, we study the local magnetic properties of Co grains in fcc Ag and Cu hosts. We use the real space–linear muffin-tin orbital in the atomic sphere approximation (RS-LMTO-ASA) method to calculate local magnetic moments (LM's) and the Fermi contact contribution to the HF's. This is the usually dominant contribution to the HF in these systems. The RS-LMTO-ASA is a first-principles real space approach based on the density functional theory with the local spin density approximation (LSDA) for the exchange correlation term. This approach has already been used with success in the study of different transition metal systems with local defects such as substitutional or interstitial impurities and sets of substitutional impurities.[5–7] A detailed description of the general procedure and the calculation of HFs can be found elsewhere.[8–10] We should note that large clusters of a few thousand atoms in a fcc arrangement with the host lattice parameter are used. We call attention to this point because it is the proper description of the solid embedding what has been shown to make the RS-LMTO-ASA one of the most well suited approaches to treat metallic systems with lack of periodicity.

Finally we note that the evaluation of the numerical uncertainty on the self-consistent LSDA calculation of measurable quantities is a difficult task and can be misleading. Two distinct aspects must be considered in this case. When compared directly to the experimental results, the uncertainty on our theoretical values can be roughly estimated to be around 0.1 μ_B for local magnetic moments and 4 T for HF's. This has been shown by previous experience with dilute transition metal alloys in standard situations (when orbital contributions can be neglected), and is mainly due to the approximations inherent to the implementation of the LSDA. Nevertheless one should keep in mind that, contrary to what is usually observed when energy related quantities and insulators or semiconductors are considered (typically, gap energies), the use of different parametrizations or charge density gradient corrections for the exchange and correlation term has no great impact on local magnetic properties of transition metal alloys (as local magnetic moments). On the other hand, the comparison of local magnetic properties at sites in different spatial configurations, within the framework of the RS-LMTO-ASA approach when performed under the same numerical conditions and always involving the same atomic species, leads to a natural and systematic error cancellation. Therefore, in the comparative analysis of local magnetic moments obtained at sites with different neighboring configurations, clear and regular trends can be inferred, even when much smaller differences (up to 1 order of mag-

TABLE I. Average magnetization per Co atom, in units of μ_B, for different grain sizes in Ag and Cu hosts. The grains are labeled by the number of Co atoms in the grains.

	Ag	Cu
13	1.83	1.54
19	1.84	1.56
43	1.77	1.57
55	1.84	1.56
79	1.83	1.59
87	1.83	1.59
135	1.82	1.61

TABLE II. Local magnetic moments, in units of μ_B, for each nonequivalent Co site at a single impurity and Co_nAg systems ($n=13$, 19, 43, 55, 79, 87, and 135). The single impurity and the central atoms of each grain are denoted as Co0 and the atoms in the nth neighborhood of the central sites are denoted as Con.

	1	13	19	43	55	79	87	135
Co0	1.66	1.92	1.93	1.89	1.88	1.86	1.86	1.87
Co1		1.82	1.85	1.89	1.89	1.89	1.88	1.87
Co2			1.80	1.86	1.82	1.91	1.90	1.88
Co3				1.68	1.84	1.82	1.88	1.89
Co4					1.80	1.82	1.83	1.91
Co5						1.81	1.79	1.71
Co6							1.67	1.85
Co7								1.78

nitude smaller, which is the usual convergence criterium for orbital occupations) are involved.

Here we present local and average magnetic moments of the grains studied and the HF's for each nonequivalent Co atom of the grains. The grains are built from a set of substitutional Co impurities in the hosts, consisting of a central atom and its successive neighboring shells. We neglect relaxation effects as it has been shown that they give a small contribution[5] and therefore they should not affect the general trends. We considered grains with up to 135 Co atoms in Ag and Cu hosts, which will be labeled by the number of Co atoms they contain. From the results presented in Table I, we see that the average LM's for different Co grains in Ag are very similar, with a small fluctuation around the value 1.83 μ_B. This value is very close to the LM 1.86 μ_B we found for pure fcc Co calculated with the lattice parameter of Ag. This observation confirms the tendency we have suggested in a previous work for smaller clusters.[5] However, the average moments of Co atoms in Cu hosts present a small but clear increase in magnitude for larger grains. We note that all these values are smaller than the value 1.68 μ_B we obtained for pure fcc Co with the lattice parameter of Cu. From Table II, we see that the invariance of the average LM's of Co grains in Ag reflects the fact that the individual LM's are also similar. Nevertheless, the isolated impurity has a smaller moment than Co atoms in the grains and Co atoms near the interface have LM's slightly smaller than those placed in innermost positions. This indicates that the vicinity of Ag atoms instead of Co attenuates the magnetic moments. Such tendency, as we see from Tables II and III, is also observed for Cu hosts but with a stronger intensity and the influence of the Cu atoms seems to have a longer range than Ag. This difference in behavior is due to the relative position of the impurities and host density of states. The relative position of Co and Cu d bands are much closer than the relative position of Co and Ag. Therefore, the hibridization between Co and Cu is larger than Co and Ag.

TABLE III. Same caption as Table II, but for Co_nCu systems.

	1	13	19	43	55	79	87	135
Co0	1.07	1.55	1.65	1.69	1.70	1.68	1.68	1.66
Co1		1.54	1.58	1.64	1.63	1.67	1.68	1.68
Co2			1.49	1.55	1.62	1.64	1.64	1.65
Co3				1.54	1.55	1.60	1.61	1.65
Co4					1.49	1.54	1.58	1.61
Co5						1.54	1.56	1.63
Co6							1.59	1.58
Co7								1.58

From Tables II and III we see that there are some fluctuations of the LM's depending on the position with respect to the central atom. However, we note that all s, p, and d partial contributions to the Co LM's (not shown at the tables) become less intense as we get near the surface of the grain. As the s and p moments are aligned antiparallel to the d moments, sometimes the change of the s and p moments may lead to a weak increase in the LM's of Co atoms that are placed nearest to the interface. We should note that, although these fluctuations are small, this behavior might be related to the oscillations in the moments observed for free clusters[11–13] but as a much weaker effect. The results we obtained here show a different behavior than reported in Ref. 14, where Co clusters with 13, 19, and 43 atoms in Cu are calculated using the discrete variational method with local spin density. They have found a similar behavior for the embedded and free clusters, both presenting a decrease in the moments at inner positions. Moreover, their values for the total moments for the embedded clusters are 20% larger than

TABLE IV. Hyperfine fields (T) for each nonequivalent Co site at a single impurity and Co_nAg systems ($n=13$, 19, 43, 55, 79, 87, and 135). The single impurity and the central atoms of each grain are denoted as Co0 and the atoms in the nth neighborhood of the central sites are denoted as Con.

	1	13	19	43	55	79	87	135
Co0	−6.6	−22.4	−21.2	−22.7	−25.6	−26.6	−27.0	−25.7
Co1		−14.2	−18.3	−21.7	−24.0	−23.7	−24.0	−25.4
Co2			−15.1	−20.3	−18.7	−23.1	−23.8	−25.7
Co3				−14.6	−17.9	−21.6	−22.9	−24.1
Co4					−16.0	−19.4	−18.3	−22.4
Co5						−17.6	−17.3	−18.3
Co6							−11.2	−20.2
Co7								−16.4

TABLE V. Same caption as Table IV, but for Co_nCu systems.

	1	13	19	43	55	79	87	135
Co0	−5.4	−20.6	−20.0	−25.7	−28.3	−26.6	−27.6	−27.9
Co1		−14.0	−16.0	−22.0	−23.6	−24.8	−25.6	−26.8
Co2			−15.3	−19.7	−20.2	−22.9	−24.3	−26.0
Co3				−15.2	−18.1	−22.1	−23.6	−24.7
Co4					−16.4	−20.3	−19.6	−24.5
Co5						−18.2	−18.0	−19.4
Co6							−13.1	−21.0
Co7								−17.6

ours. The results recently presented in Ref. 15 for Co clusters in Cu are also larger than ours in a similar way. However, the values they obtained for Co clusters in Ag are closer to the ones we obtained, being less than 10% smaller. Now, if we compare our results with those calculated for free Co clusters with the same numbers of atoms and symmetry,[12,14–18] we see that the average LM's we obtain are always smaller than the ones obtained for free clusters. However, more importantly, we note that the tendency of the moments at the interface atoms to decrease is opposite to what has been observed for free clusters, where the smaller coordination number leads to an enhancement of the magnetic moments. The values we obtained for the LM's of Co grains in Cu are in a better agreement with the results for planar interfaces Co/Cu.[19] However, grains present a more intense influence of the host in Co LM's and in a broader range. This must be due to the fact that in grains the interface atoms have more host neighbors than in flat interfaces.

In Ref. 18, Co clusters with 13 atoms surrounded by up to 15 neighboring Cu or Ag shells were calculated. The authors reported that induced moments at the host atoms at the vicinity of the grains were small but did not decrease with the distance to the cluster, and it was suggested that this should also represent the behavior for granular systems. We note that we have not found this behavior, as the induced moments we found become smaller than 0.005 μ_B after a few neighborhoods and tend to almost disappear. The differences we found from our results to those obtained in Refs. 14, 15, and 18 discussed above seem to indicate that the study of the magnetic behavior of granular systems requires a very accurate description of the correct embedding of the grains in the hosts.

Finally, we note that the behavior we observed for Co magnetic moments in Ag agrees with the assumption very often used to analyze measured results of magnetization and to estimate the size of the grains, which considers all Co atoms as possessing a LM of 1.77 μ_B.[20] The values we found are a little larger than the value for pure fcc Co. This may be due to the fact that we are not considering relaxation effects, which might cause a slight decrease in the LM's without affecting the general trends. The differences between the behavior of the Co moments in Ag and Cu leads to the fact that, while considering the Co LM's in Co-Ag as a constant is a good approximation, this seems not to be true for Co-Cu systems.

The HF's for Co grain atoms present a clear systematic trend in both hosts. These results are shown in Tables IV and V. In all cases we see that the intensity of the HF tends to decrease as we go toward the interface. The most external atoms in each grain have values around −15 T in all cases, and inner atoms tend to stabilize their HF's around −26 T. The values for internal atoms are similar to those for pure Co calculated with the lattice parameter of Ag (−25.9 T) and Cu (−27.1 T). The similarity of these values indicate that, although the magnetic behavior of Co grains in Ag and Cu seems to be different, the hyperfine behavior is very similar, not only presenting the same trends but also the same magnitudes. These results are in good agreement with those inferred from measurements. The nuclear magnetic resonance spectra of Co-Ag multilayers[21] and Co/Cu granular systems[22] present a distribution with two peaks: the first one lies around −17 T and is related to Co atoms at interface positions; the other one (around −22 T) is close to the HF for pure fcc Co and is related to atoms in internal positions of the grains. Our results present an even stronger difference between inner and interfacial HF's than suggested by the experiments, but they reinforce the assumption that with the light shed by theoretical calculations, HF measurements may be a powerful tool for the characterization of these grains. They can clearly distinguish between atoms at interface and inner positions.

To summarize, using a well established approach to deal with local magnetic properties of bulk systems, we have found that the LM's for Co atoms in small grains in Ag are similar. However, for Co grains in Cu there is a small increase in the average moments as the grains become larger. The HF's we obtained for Co grains in Cu and Ag exhibit a similar behavior. We also showed that the magnetic behavior of the Co grains in these matrices are definitely different than for free clusters.

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