Hyperfine fields at Co clusters in bulk Ag and Cu by a first-principles study: the role of the nearest neighbourhood

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Abstract
The hyperfine field distribution at substitutional Co clusters in fcc Cu and
Ag hosts as a function of the chemical composition of the Co nearest
neighbourhoods is studied. These clusters contain up to 135 Co and the
theoretical *ab initio* calculations are performed with the real-space-LMTO-ASA
method. We find that Co hyperfine fields exhibit an almost linear dependence
on the number of host atoms in the first co-ordination shell. This result
supports what has been recently suggested by an empirical model based on
results inferred from NMR experiments. Nevertheless, we also observe a site
dependence that is not completely described by this simple empirical model
and discuss the role played by further neighbourhoods.

1. Introduction

Magnetic clusters in non-magnetic media have attracted great interest in the last decade due
to the discovery of giant magnetoresistance (GMR) in such systems [1, 2]. Special attention
has been devoted to Co clusters inside a Cu and Ag medium. As the transport properties
are closely related to structural characteristics, to understand the GMR behaviour in these
materials a detailed structural description is highly desirable. Because it is sensitive to local
environment, hyperfine field (HF) measurements, using different techniques, have been used
to study structural characteristics of these systems. The approach through hyperfine quantities
has the advantage of being able to distinguish very small particles and to differentiate bulk from
interface atoms. We must note that interface features are crucial because interface scattering
seems to be the main mechanism that generates the GMR. Nevertheless, the interpretation
of the spectra obtained in these disordered systems is rather complicated and can sometimes

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be misleading. Therefore, reliable theoretical calculations can be a very useful tool to guide the accomplishment of this task. There are recent HF measurements in Co–Cu [3–5] and Co–Ag [6] granular systems using the NMR technique performed with the aim of characterization through local properties. The spectra resolved in these works clearly show two different HF distributions: one region with HFs similar to those of fcc Co and another with less intense HFs. A fundamental assumption has been made in the interpretation of these spectra. The authors assume that the magnitude of the HF at a given Co site is determined by the chemical composition of its nearest neighbourhood (NN) and also that there is a linear correlation of the HF value with the number of atoms of each species in the first shell. More specifically, they first assume that Co atoms with an NN composed exclusively of Co atoms will have the same HF as fcc Co. Then, the substitution of each Co neighbour by Ag would lead to a decrease of about 1.3 T in the magnitude of the Co HF [6]. For the Cu matrix, this decrease would be slightly larger, about 1.6 T [3, 4, 7] or 1.8 T [5]. It is important to note that this model has been earlier derived from measurements performed on systems which have structures very different from granular systems such as Co alloys with small impurity concentrations or planar interfaces [6,7]. In this paper we use theoretical calculations to explicitly investigate the role played by the chemical composition of the NN of Co sites on the magnitude of the HFs at Co clusters in a Ag or Cu matrix. We perform *ab initio* electronic structure calculations for Co clusters with up to 135 atoms at substitutional positions in fcc Cu and Ag hosts and analyse the HF behaviour as a function of the number of host atoms in the NN of each Co site. Our aim with this study is to discuss the validity of the empirical model, cited above, for the analysis of HF spectra of Co clusters in Cu or Ag. We must also note that the lack of symmetry involved in these metallic systems usually makes them very difficult to study by theoretical electronic structure methods.

2. Theoretical approach

Here we use the real-space linear muffin-tin orbital in the atomic sphere approximation (RS-LMTO-ASA) method [8] to calculate the Fermi contact contribution to the HF. We note that this is usually the dominant contribution to the HF in these systems [9, 10]. For simplicity, we denote by HF both the measured HF and the theoretically obtained Fermi contact contribution to the HF, unless otherwise stated. The RS-LMTO-ASA is a first-principles (or *ab initio*) real-space approach based on the Kohn–Sham scheme of the functional theory [11]. Here we use the Von Barth–Hedin parametrization [12] for the exchange and correlation term of the local spin density approximation. This well established self-consistent approach has already been thoroughly 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 [13–16]. A detailed description of the general procedure and the calculation of HFs can be found elsewhere [8, 15, 17]. We must note that a few thousand atoms in an fcc arrangement with the host lattice parameters are used to simulate the bulk. The Co clusters are placed around the centre of these systems to avoid surface effects. We call attention to this point because it is the proper description of the solid embedding that has been shown to make the RS-LMTO-ASA one of the best suited approaches to treat metallic systems with a lack of periodicity. We must note that here our main focus is directed to general trends and, as in previous works, we do not include lattice relaxation effects. As discussed there, in the case of the HFs in these granular systems, these effects are small and they should not affect the generally observed trends [13, 14]. The clusters are built as a set of substitutional Co impurities consisting of a given central atom and its successive neighbouring shells. In this way, atoms belonging to the same neighbourhood of the central atom are equivalent and can be calculated only once in each self-consistent cycle. We note that in the analysis of our HF results as a function of the NN

Table 1. Number of host nns of each non-equivalent site of Co atoms in each cluster. The clusters are denoted by the number of Co atoms they contain (N). Co0 denotes the central site of each cluster and the atoms in its nth neighbourhood are denoted as Con.

Site	$N = 1$	$N = 13$	$N = 19$	$N = 43$	$N = 55$	$N = 79$	$N = 87$	$N = 135$
Co0	12	0	0	0	0	0	0	0
Co1		7	5	1	0	0	0	0
Co2			8	4	4	0	0	0
Co3				7	5	3	2	0
Co4					7	5	5	1
Co5						6	6	4
Co6							9	3
Co7								6

composition we shall not consider the frequency with which a given site appears in each cluster (multiplicity). This means that every non-equivalent site is counted only once in the analysis. This procedure is adopted here because the error in the HF result is not of statistical type, but due to numerical uncertainties in the calculation that are inherent to the implementation of the theoretical approach we have used. The inclusion of the multiplicity of the atoms does not change the general features observed here, but the HF uncertainties corresponding to Co sites belonging to neighbourhoods composed by many atoms would then be considered with an unrealistic weight. We consider clusters with up to 135 Co atoms in Ag and Cu hosts, which are labelled by the number of Co atoms they contain. For easy reference we show in table 1 the number of host (Cu or Ag) atoms that belong to the NN of each Co site in all clusters studied here. In order to understand easily the results presented in this table, it is useful to remember that in an fcc structure each atom has 12 nearest neighbours (nns). It is also to be noticed that, as the clusters become larger, there will be more Co sites that have their NN composed only of Co atoms.

3. Results and discussion

As we discussed in a previous work [14], the HFs at Co sites in these granular systems present a clear systematic trend in both matrices. In all cases we see that the intensity of the HF tends to decrease as we go towards the interface. After this, a similar trend has also been confirmed in two independent calculations: (a) using the discrete variational method [9] for Co clusters with up to 55 atoms in Cu and (b) also using the RS-LMTO-ASA method for Co clusters with up to 79 Co atoms in Cu, but in a slightly different theoretical approach [10]. We now try to inspect correlations of the magnitudes of the HFs at the Co sites with both their NN chemical composition and cluster size. In order to do this, we use the HF results we already obtained in a previous work [14]. As we mentioned above, the new analysis presented here aims at the discussion of the validity of the empirical model used in the interpretation of the experiments, which assumes a linear variation of the HF with the number of Cu or Ag atoms in the Co NN. We must note that in our analysis we compare results for different situations but obtained through the same theoretical approach. In this case, the numerical uncertainties due to the approximations used here (although they are known to affect, to a limited extent, the direct comparison among theoretical and experimental results) should not affect the theoretically observed systematic behaviour of the HF values as a function of characteristic environments. We show in figure 1 our theoretical HF results at each Co site in Ag, plotted as a function of the number of host atoms in its NN, nn_{Ag}, according to table 1. The error bars in figure 1 represent
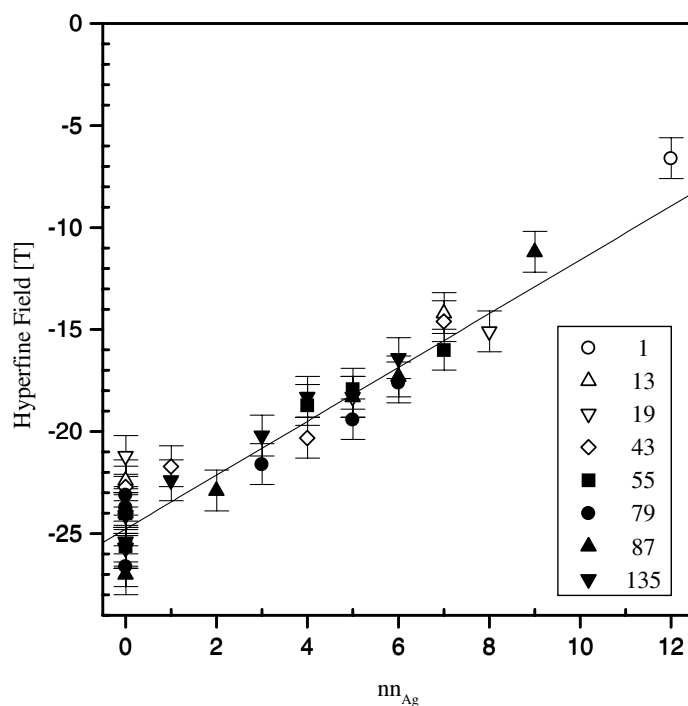
Figure 1. Hyperfine fields at each Co site in Ag, plotted as a function of nn_{Ag}, the number of host atoms in its NN. The error bars represents an estimate of the maximum error introduced by different computational implementations to the RS-LMTO-ASA calculation of the HF (see text). Different symbols correspond to different cluster sizes.

an estimate of the maximum error introduced by different computational implementations [10] to the RS-LMTO-ASA calculation of the HF. As discussed in the previous section, due to these uncertainties, for this particular analysis we do not consider the multiplicity of the equivalent sites. From the results presented in figure 1 we see a certain dispersion on the plotted data (vertical distribution). Nevertheless, the HFs at sites that have the same chemical composition of the first neighbourhood are remarkably close in value. This is surprisingly true, with the only exception of Co sites which have only Co atoms in their NN. This feature clearly indicates the dominant influence of the NN on the HF values. On the other hand, it is important to note that Co atoms with the same NN chemical distribution can have different further neighbourhoods. Due to this fact, most of the dispersion on the Co HF values for a given number of host nns can be attributed to different environments. This is clearly seen in the case $nn_{Ag} = 0$, where the dispersion is of the order of 6 T, a value that is certainly much larger than the eventual fluctuations in the theoretical calculations, expressed by the HF error bars. This fact shows that the influence of further neighbours, although to a much smaller extent than the NN, has a sizeable effect. We now try to examine these tendencies in a more detailed way. In figure 1 we show with a solid line a linear fit performed with the HF values we found at the Co sites in each considered cluster in Ag. This is done to compare the suggested experimental model with our theoretical results for the HF distribution as a function of Co NN chemical composition. The offset and slope found in this fit are $-24.5(\pm 0.3)$ and $1.33(\pm 0.07)$ T, respectively. We first note that the uncertainties on the coefficients obtained in this fit are very small. This is an indication that the assumed linear variation with nn_{Ag} can describe the HF behaviour very well.
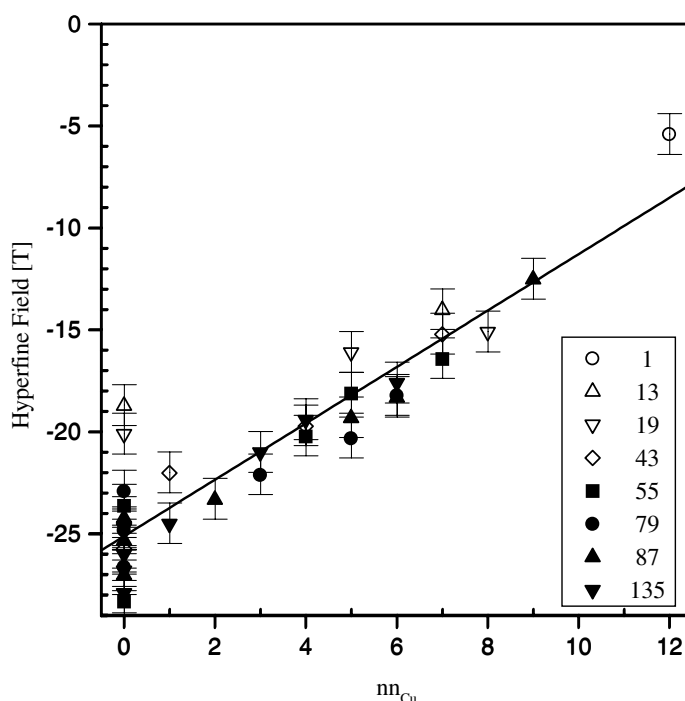
Figure 2. Hyperfine fields at each Co site in Cu, plotted as a function of nn_{Cu}, the number of host atoms in its NN. The error bars represents an estimate of the maximum error introduced by different computational implementations to the RS-LMTO-ASA calculation of the HF (see text). Different symbols correspond to different cluster sizes.

We also note that the offset (-24.5 ± 0.3 T) has a value that is very similar to -25.9 T, which is the HF value we obtain for pure fcc Co with the Ag lattice parameter. Moreover our results show that the slope obtained with the linear fit is in excellent agreement with the values 1.2 and 1.3 T/nn_{Ag} suggested by the experimental model [6].

In figure 2 we show for Co clusters in the Cu matrix the same analysis performed as for Co clusters in Ag. We can see that for a Cu host, the dispersion of the Co HF results, for each nn_{Cu}, is slightly more significant. Nevertheless, the observed general behaviour is similar to that we find when Ag is the host (figure 1). With a linear fit we have found $1.4(\pm0.1)$ T/nn_{Cu} as the slope and $-25.1(\pm0.5)$ T as the offset. We note that for idealized fcc Co with the Cu experimental lattice parameter we have found a -27.1 T HF and for the fcc Co with the proper Co experimental lattice parameter a -28.0 T HF. Both values are close to the offset obtained from our linear fit. For Co in a Cu matrix, the experimental model suggests $1.6(1)$ T/nn_{Cu} [3, 4, 7] and 1.8 T/nn_{Cu} [5] as the slope of the HF variation with nn_{Cu}. We see that the agreement of our theoretical results with the experimental model is remarkable. Nevertheless we note that for Co clusters in Cu there seems to be a more significant influence of further neighbours. This broader range of the Cu host influence on the Co atoms when compared with the Ag matrix can be expected. Since in these granular systems Co and Cu local densities of states always lie closer than Co and Ag local densities of states, we see a larger overlap and hybridization effects in the Cu host. The experimental model assumes that all Co atoms that do not have any host atom in their NN will have the pure fcc Co HF. To simulate this situation, we have made a second linear fit to the theoretical results neglecting
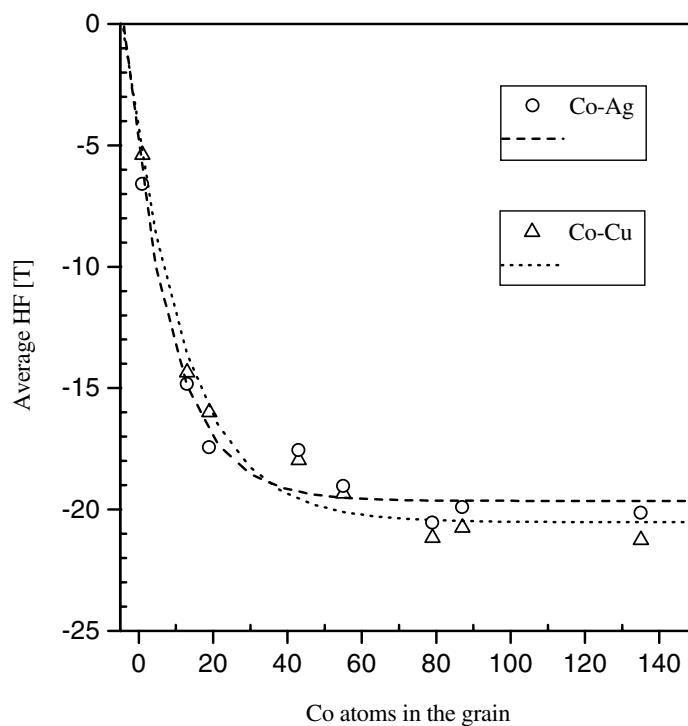
Figure 3. Average hyperfine fields for each cluster in Cu and Ag hosts.

the dispersion of the HF results we found for Co sites with $nn_{host} = 0$. In this case, we have attributed to these Co sites the HF value we calculated for pure fcc Co with the corresponding host lattice parameter. If we compare the coefficients obtained in these two fits we see that the offsets are almost the same in the two cases, while the slopes are 14% (for Ag) and 20% (for Cu) larger than previously obtained. These changes suggest that the influence of further neighbours on the Co HFs is one order of magnitude smaller than the influence of the NN.

Another interesting analysis we perform here is the study of the average Co HF trends as a function of Co cluster size (number of atoms) in Ag and Cu. We note that for the average HF calculation the multiplicities of the atoms have been taken into account. We show in figure 3 our theoretical results for the average Co HF as a function of the number of Co atoms in the clusters we have considered. We see that for any Co cluster size the average HFs in Ag and Cu hosts are very similar, although we observe a slightly faster decrease in the case of the Cu host. We also see that the average HFs tend rapidly to stable values, which are around 7 T smaller in magnitude than the HFs we found for pure fcc Co with the lattice parameter of Cu (-27.1 T) and Ag (-25.9 T). We note that the behaviour observed here for very small clusters must be related to the large number of atoms belonging to an interface region. However, as we increase the cluster size the contribution of bulk atoms becomes more and more important and we would expect a further decrease in the magnitude of this value for even larger grains.

4. Conclusions

Through theoretical *ab initio* calculations we have explicitly investigated the role played by the composition of the NN on the HFs at Co sites in clusters with up to 135 atoms in Ag

and Cu matrices. Using the RS-LMTO-ASA method we have calculated the Fermi contact contribution to the HF as a function of the number of host nns. The HF trends obtained at the Co sites allow us to conclude that the influence of the number of host nns is dominant and exhibits an almost linear correlation. The slopes obtained in these linear fits are in very good agreement with the values inferred from empirical models. Nevertheless we have also shown that the HF values are sensitive to further neighbours, especially in the case of Co clusters in a Cu host, but with an effect that is one order of magnitude smaller. Finally, we have shown that the average HF value as a function of the number of atoms in the cluster tends to stabilize very rapidly in both hosts. To our knowledge, this is the first time that such a correlation has been investigated theoretically in a proper way and our results can be used as theoretical support for the interpretation of complex experimental spectra, especially those obtained by NMR, in granular systems.

Acknowledgments

References

[1] Berkowitz A E *et al* 1992 *Phys. Rev. Lett.* **68** 3745
[2] Xiao J Q, Jiang J S and Chien C L 1992 *Phys. Rev. Lett.* **68** 3749
[3] Panissod P, Malinowska M, Jedryka E, Wójcik W, Nadolski S, Knobell M and Schmidt J E 2001 *Phys. Rev. B* **63** 4408
[4] Malinowska M, Wójcik W, Nadolski S, Jedryka E, Mény C, Panissod P, Knobell M, Viegas A D C and Schmidt J E 1999 *J. Magn. Magn. Mater.* **98-99** 599
[5] Sinnecker E H C P, Oliveira I S, Tiberto P and Guimarães A P 2000 *J. Magn. Magn. Mater.* **218** L132
[6] Pogorelov Yu G, Kakazei G N, Souza J B, Kravets A F, Lesnik N A, Azevedo M M P, Malinovska M and Panissod P 1999 *Phys. Rev. B* **60** 12 200
[7] Mény C, Jedryka E and Panissod P 1993 *J. Phys.: Condens. Matter* **5** 1547
[8] Frota-Pessôa S 1992 *Phys. Rev. B* **48** 7148
   Peduto P R, Frota-Pessôa S and Methfessel M 1991 *Phys. Rev. B* **44** 13 283
   Ferreira S and Frota-Pessôa S 1995 *Phys. Rev. B* **51** 2045
[9] Gomez J A and Guenzburger D 2001 *Phys. Rev. B* **63** 134404
[10] Frota-Pessôa S and Legoas S B 2000 *Hyperfine Interact.* **7** 1
[11] Hohenberg P and Kohn W 1964 *Phys. Rev. B* **136** 864
   Kohn W and Sham L J 1965 *Phys. Rev. A* **140** 1133
[12] Barth V and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[13] Nogueira R N and Petrilli H M 1999 *Phys. Rev. B* **60** 4120
[14] Nogueira R N and Petrilli H M 2001 *Phys. Rev. B* **63** 012405
[15] Petrilli H M and Frota-Pessôa S 1993 *Phys. Rev. B* **48** 7148
[16] Frota-Pessôa S *et al* 1993 *Phys. Rev. Lett.* **71** 4206
[17] Petrilli H M and Frota-Pessôa S 1990 *J. Phys.: Condens. Matter* **2** 135