Average magnetization and local magnetic moments of Fe_N clusters ($N<230$)

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We have calculated the average magnetic moments per atom $\overline{\mu}_N$ of iron clusters, Fe_N, as a function of cluster size in the range $9 \leqslant N \leqslant 229$. The cluster geometries are assumed to be *spherical* portions of the bcc lattice. The spin-polarized electronic structure has been calculated for the assumed structures with a self-consistent tight-binding model considering the $3d$, $4s$, and $4p$ valence electrons with global charge neutrality. The nonmonotonic decrease of the $\overline{\mu}_N$ with increasing cluster size experimentally observed is obtained, although the oscillations are not well reproduced. The results are also discussed in comparison with other recent theoretical calculations. [S0163-1829(99)12821-2]

I. INTRODUCTION

The determination of the cluster geometry is the first unavoidable stage for understanding other properties such as the electronic properties (magnetism, metallic character, etc.). However, the geometrical structure is perhaps the most elusive property of small metal clusters from the experimental point of view. The experimental methods involving free clusters can provide us with some pieces of information: optical spectroscopies,[1] anomalies of the mass distribution of the produced clusters,[2,3] chemical reactivity experiments of weakly bonded molecules,[4–6] and near-threshold photoionization experiments.[7,8] Unfortunately, the experimental information is indirect and it is not enough to determine the geometrical structures without any doubt.

In the particular case of the $3d$ transition-metal clusters, a lot of experimental attention in the last ten years has been focused on the determination of the magnetic properties motivated by the possible technological applications. Based on Stern-Gerlach experiments, the works by Billas *et al.* for Fe, Co, and Ni clusters,[9] and more recently by Apsel *et al.*[10] for Ni clusters, have reported a nonmonotonic decrease of the average magnetization per atom ($\overline{\mu}_N$) with increasing cluster size. This decrease of $\overline{\mu}_N$ with increasing cluster size is accompanied by oscillations whose amplitude decreases as the size of cluster increases. They indicate, therefore, a finite-size effect and are believed to be associated with geometrical effects.[9–12] From the theoretical point of view and with the aim of understanding the oscillatory magnetic behavior of the transition-metal clusters, several geometrical shell models have been proposed.[9,11,12] In particular, in the models developed by Jensen and Bennemann[11] and later on by Aguilera-Granja *et al.*,[12] the individual magnetic moments of the different atoms are determined by their local atomic coordinations. By assuming bulklike structures (fcc, bcc) and different global cluster shapes (cube, octahedron, and cubo-octahedron) these authors found that the average magnetic moment oscillates with the cluster size, and that this magnetic ''shell structure'' reflects the progressive formation of concentric atomic layers. However, the oscillations of $\overline{\mu}_N$ experimentally observed are not in general reproduced in terms of simple geometrical shells and the calculated numerical values of $\overline{\mu}_N$ are underestimated for small cluster and overestimated for large cluster size.[11,12] Two of the possible reasons for the disagreement are (i) the electronic part in the models by Jensen and Bennemann and by Aguilera-Granja *et al.* is very crude, (ii) the geometrical structure may not be a fragment of the crystal lattice. The first point can be improved by using a better description for the electronic part and this is the line of the present work. The second point is more difficult to improve due to the absence of *ab initio* calculations for the geometrical structures of TM clusters in the range of sizes reported experimentally ($N \leqslant 700$). It is important to mention that it has also been suggested that the oscillatory behavior of $\overline{\mu}_N$ has a pure electronic origin.[17] We think that the oscillatory behavior of $\overline{\mu}_N$ results from a combination of the geometrical and the electronic part. In the particular case of Fe clusters, the *ab initio* calculations of the geometrical (and electronic) structure are restricted to clusters of relatively small size, ($N \leqslant 16$).[13,14] Although, there is a clear controversy about the geometrical structure of small Fe clusters, there are indications that for clusters larger than about 25 atoms the bcc-like structure is probable.[15,16] This is also the conclusion of recent theoretical calculations of the ionization potentials of Fe_N clusters using a tight-binding model.[18,19]

In a recent work, Guevara *et al.*[19] have reported a calculation of the average magnetic moment of iron clusters as a function of cluster size in the region studied experimentally. They use a tight-binding description that incorporates the electronic spillover, and they assume bcc-like structures. Although this model is not *ab initio*, it improves considerably the description of the electronic structure with respect to phenomenological models. These authors conclude that the electronic spillover is a key ingredient for the description of the magnetic behavior of transition-metal clusters. However, although the general trend of the nonmonotonic decrease of the average magnetization with increasing cluster size is given,

the oscillations are not correctly reproduced.

It is the aim of the present work to shed more light on this complex problem by analyzing different approximations for the electronic part. For this purpose we perform a self-consistent tight-binding calculation with a different approximation for the diagonal elements of the Hamiltonian than that of Guevara *et al.*[19] Instead of assuming the spillover, we assume global charge neutrality and allow charge transfer between inequivalent sites and different orbitals within the cluster. With this calculation we explore the influence of a different description of the electronic charge redistribution on the magnetic trends. In Sec. II we present the theoretical model used in this work. In Sec. III we present and discuss the results for the average spin polarization per atom as well as the local contributions within the cluster. The main conclusions are summarized at the end.

II. THEORETICAL MODEL

A. Electronic part

The electronic distribution of the $3d$, $4s$, and $4p$ valence electrons of Fe_N clusters are obtained by solving self-consistently a tight-binding Hamiltonian in a mean-field approximation. This Hamiltonian can be written in this way:

$$\hat{H}=\sum_{i,\alpha,\sigma}\varepsilon_{i\alpha\sigma}\hat{n}_{i\alpha\sigma}+\sum_{\substack{\alpha,\beta,\sigma\\ i\neq j}}t_{ij}^{\alpha\beta}\hat{c}_{i\alpha\sigma}^{\dagger}\hat{c}_{j\beta\sigma}, \tag{1}$$

where $\hat{c}_{i\alpha\sigma}^{\dagger}$ ($\hat{c}_{j\beta\sigma}$) are the creation (annhilitation) operators of an electron with spin σ at the orbital α (β) of the atomic site i (j), $\hat{n}_{i\alpha\sigma}$ are the corresponding number operators. $t_{ij}^{\alpha\beta}$ are the hopping integrals between $(i\alpha)$ and $(j\beta)$ orbitals that describe the electronic delocalization. These hopping integrals are obtained from the Slater-Koster approximation via the two center integrals taken from a fit to the band structure of the bcc bulk of Fe.[22] The spin-dependent energy levels $\varepsilon_{i\alpha\sigma}$ are given by

$$\varepsilon_{i\alpha\sigma}=\varepsilon_{i\alpha}^{0}+\sum_{\beta,\sigma'}U_{i\alpha\sigma,i\beta\sigma'}\Delta\nu_{i\beta\sigma'}+z_i\Omega_{\alpha}. \tag{2}$$

$\varepsilon_{i\alpha}^{0}$ stands for the energy level of the orbital α at site i in the paramagnetic solution of the bulk. The second term in Eq. (2) takes into account the correction shifts due to the electronic redistribution in the cluster. $\Delta\nu_{i\beta\sigma}=\langle\hat{n}_{i\beta\sigma}\rangle-\langle\hat{n}_{i\beta\sigma}^{b}\rangle$ is the difference between the average electronic occupation of the (i,β,σ) state of the cluster and the corresponding state in the bulk. The intra-atomic Coulomb integrals $U_{i\alpha\sigma,i\beta\sigma'}$ can be written in terms of the exchange and direct integrals $J_{\alpha\beta}=(U_{i\alpha\uparrow,i\beta\downarrow}-U_{i\alpha\uparrow,i\beta\uparrow})$ and $U_{\alpha\beta}=(U_{i\alpha\uparrow,i\beta\uparrow}+U_{i\alpha\uparrow,i\beta\downarrow})/2$. The direct integrals $U_{\alpha\beta}$ have been obtained in the following way: We assume $U_{ss}=U_{sp}=U_{pp}$, $U_{sd}=U_{pd}$, and we take the ratios $U_{ss}:U_{sd}:U_{dd}$ equal to 0.32:0.42:1 from atomic Hartee-Fock calculations.[23] The value of $U_{dd}(Fe)=5.40$ eV is obtained from the work of Pastor *et al.*[24] Concerning the exchange integrals $J_{\alpha\beta}$, we have neglected those involving s and p orbitals and J_{dd} is calculated in order to yield the average magnetic moment per atom of the cluster Fe_{26} similar to the experimental value (assuming the bcc-like structure). At the same time this choice of J_{dd} is consistent with *ab initio* calculations in Fe_9 and Fe_{15},[20,21] that is, we obtain values of $\bar{\mu}_N$ for $N=9$ and 15 in good quantitative agreement with the corresponding *ab initio* results. In terms of $U_{\alpha\beta}$ and $J_{\alpha\beta}$, Eq. (2) takes the following expresion:

$$\varepsilon_{i\alpha\sigma}=\varepsilon_{i\alpha}^{0}+\sum_{\beta}U_{\alpha\beta}\Delta\nu_{i\beta}-s_{\sigma}\sum_{\beta}\frac{J_{\alpha\beta}}{2}\mu_{i\beta}+z_i\Omega_{\alpha}, \tag{3}$$

where

$$(s_{\uparrow}=1,s_{\downarrow}=-1),$$

$$\Delta\nu_{i\beta}=\Delta\nu_{i\beta\uparrow}+\Delta\nu_{i\beta\downarrow}, \tag{4}$$

$$\mu_{i\beta}=\langle\hat{n}_{i\beta\uparrow}\rangle-\langle\hat{n}_{i\beta\downarrow}\rangle=\nu_{i\beta\uparrow}-\nu_{i\beta\downarrow},$$

in which the local magnetic moment $\mu_{i\beta}=\langle\hat{n}_{i\beta\uparrow}\rangle-\langle\hat{n}_{i\beta\downarrow}\rangle$ appears explicitly. Finally, the last term in Eq. (2) or Eq. (3) takes into account the correction shifts due to the variation of the crystal field in the cluster with respect to the bulk, which is approximately proportional to the local coordination number z_i. The potentials Ω_{α} are obtained by an interpolation between the isolated atom and the bulk.[25] In Table I we show the parameters used in our calculation.

TABLE I. Parameters (in units of eV) used in our calculation.

	U_{dd}	J_{dd}	Ω_s	Ω_p	Ω_d
Fe	5.40	0.714	0.31	0.48	−0.10

The spin-polarized electronic occupation (and thus the local magnetic moments) are determined self-consistently through the local density of electronic states:

$$\langle\hat{n}_{i\alpha\sigma}\rangle=\int_{-\infty}^{\varepsilon_F}N_{i\alpha\sigma}(E)dE. \tag{5}$$

The Fermi level ε_F is self-consistently obtained at each iteration by imposing the global charge neutrality condition:

$$\sum_{i,\alpha,\sigma}\int_{-\infty}^{\varepsilon_F}N_{i\alpha\sigma}(E)dE=8N, \tag{6}$$

N being the number of atoms of the cluster. The local density of states

$$N_{i\alpha\sigma}(E)=\frac{-1}{\pi}\lim_{\eta\to 0^{+}}\mathrm{Im}\{G_{i\alpha\sigma,i\alpha\sigma}(E+i\eta)\} \tag{7}$$

is determined by calculating the diagonal element of the Green's function $G_{i\alpha\sigma,i\alpha\sigma}(z)$ by means of the recursion method.[26] Finally the average magnetic moment per atom in a N-atom cluster can be calculated in terms of the local magnetic moments:

$$\bar{\mu}_N=\frac{1}{N}\sum_{i,\alpha}\mu_{i\alpha}. \tag{8}$$

This is the magnitude that one can compare with the Stern-Gerlach experiments of Billas *et al.*[9]

TABLE II. Details of the geometrical growth of the clusters as spherical portion of the bcc lattice of the crystal.

Shell	Square distance	Atoms	Type	Total
0	0	1	Central	1
1	3	8	Vertex	9
2	4	6	Square face	15
3	8	12	Edge	27
4	11	24	Square face	51
5	12	8	Vertex	59
6	16	6	Square face	65
7	19	24	Edge	89
8	20	24	Square face	113
9	24	24	Square face	137
10	27	8	Vertex	145
11	27	24	Square face	169
12	32	12	Edge	181
13	35	48	Square face	229

B. Geometrical part

The clusters studied here are grown around a central site and follow the body-centered-cubic (bcc) structure. We considered that the clusters grow in an onionlike structure, formed by concentric *shells*. A shell consists of the set of all atoms that following the bcc arrangement are equidistant from the center and with the same local coordination and atomic environment. This mode of growth lead us to the sequence $N=1,9,27,51,59,\ldots$. In this case, unfortunately, it is not possible to write closed relationships describing the growth process. The details of the geometrical growth, like shell number, square distance to the center of the cluster (the first-nearest-neighbor distance being $\sqrt{3}$ in these units), number of atoms per shell, type of sites of the different shells (central, square face, edge, and vertex), and total number of atoms in the cluster are presented in Table II. It is important to mention that we always consider the bulk interatomic distances.

III. RESULTS

In Fig. 1 we present our results for the average magnetic moment per atom $\overline{\mu}_N$ together with the experimental ones.[9] The theoretical results describe a nonmonotonic decrease of $\overline{\mu}_N$ with increasing cluster size. This is the general trend experimentally observed, and can be understood in terms of the atomic coordination.[11,12] As the size of the cluster increases, the bandwidth increases and the spin polarization decreases towards the bulk value. Althought this general trend is correctly described with our model assuming bcc-like structures, the absolute values of $\overline{\mu}_N$ are, in general, underestimated with respect to the experimental results (except for $N\leqslant 50$). Besides, the amplitude and position of the oscillations are in general not well described. The best quantitative agreement is obtained for clusters with sizes in the range $50\leqslant N\leqslant 100$, for which our results understimate the experimental values in no more than $0.1\mu_B$.

After comparison with the experiment, two possibilities exist as the origin of the discrepancies: the theoretical model used for the electronic calculation and the assumption of fragments of the crystal lattice for the clusters geometries. Let us discuss now the first possibility.

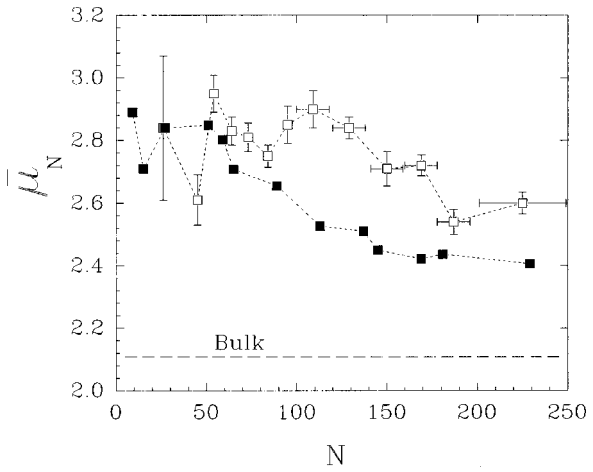

FIG. 1. Average magnetic moment per atom (in units of μ_B) obtained with our model (black squares) and through the experimental measurements of Billas *et al.* (Ref. 9) (open squares).

The model used for the description of the electronic structure has been successfully applied for the study of low-dimensional transition-metals systems like clusters[18,27,28] or surfaces[29,30] and the agreement with both *ab initio* and experimental results has been quite satisfactory when the morphology of the system has been well treated. In the case of Fe/Cr surfaces, for example, the consideration of steps[29] and roughness[30] at the interface was neccessary in order to obtain certain magnetic configurations experimentally probed. In the particular case of free-standing Ni clusters,[27,28] good qualitative agreement with the experiments[10] was obtained for those geometrical structures previously determined by molecular-dynamics simulations using a semiempirical many-body potential. It is also worth comparing our results with those obtained from an *ab initio* method. As we have discussed in the previous section, for Fe_9 and Fe_{15}, the values obtained for $\overline{\mu}_N$ are in good quantitative agreement with those obtained by Lee *et al.*[20] and Yang *et al.*[21] All this gives us confidence in the theoretical model used in this work and leads us to think that the main source of the discrepancies is the assumption of fragments of the crystal lattice for the cluster geometries. However, when considering the experimental evidences, as well as the calculation of the ionization potentials[19,25] that suggests the bcc structure as a probable geometry, it is possible that the relaxation of the interatomic distances of the bcc-like structures is a key ingredient in the interpretation of the observed oscillation of $\overline{\mu}_N$.

In a recent work by Guevara *et al.*,[19] it has been concluded that a good treatment of electronic spillover is necessary for cluster calculations with a similar model as the one proposed in the present work. These authors also assume bcc geometries for the iron clusters. In the tight-binding model with spillover, extra orbitals with *s* symmetry are added outside the cluster surface and are parametrized in order to get adequate *d*-orbital occupations [according to the electronic occupation of a (011) Fe monolayer]. In our tight-binding model no spillover is considered. We allow charge transfer between inequivalent sites and different orbitals within the global charge neutrality condition and we incorporate in the

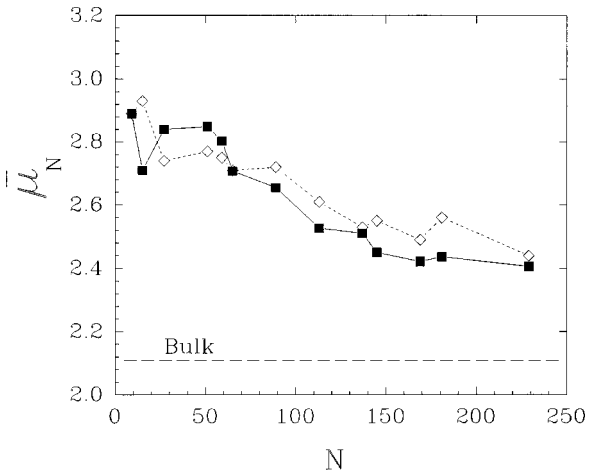

FIG. 2. Average magnetic moment per atom (in units of μ_B) obtained with our model (black squares) and by Guevara *et al.* (Ref. 19) considering the electronic spillover (open rhombus).

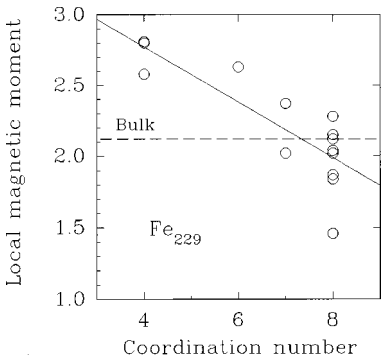

FIG. 3. Local magnetic moments (in units of μ_B) of Fe_{229} as a function of the local coordination number.

energy levels a correction shift due to the variation of the crystal fields of the clusters with respect to the bulk. It is worth comparing our results with those of Guevara *et al.*[19] for the same cluster geometries. This comparison allows us to analyze the influence of different approximations for the electronic distribution on the magnetic trends. In Fig. 2 we show the results of both models for $\bar{\mu}_N$ as a function of cluster size in the range $9 \leqslant N \leqslant 229$. They cross each other in various points and the oscillations described by both models are similar. Moreover the absolute values underestimate the experimental results in both cases. This agreement is not surprising since transition-metal clusters are in the limit $U \rightarrow \infty$, so that the charge transfer is very small. But this comparison serves also as a test of the self-consistent tight-binding model, which leads to the same magnetic trends when two different reasonable approximations for the electronic distribution are used. This allows us also to conclude that the spillover is not necessary to be considered for describing the magnetic behavior of transition-metal systems.

It is interesting to analyze the contributions of the different sites of the cluster to the average magnetization although there are no experimental techniques to probe the local magnetic moment distribution of the clusters. This analysis is easy to do with our model since the electronic and magnetic properties are determined from a local point of view through the local densities of states, $N_{i\alpha\sigma}(E)$. The local magnetic moment is very sensitive to the local coordination and atomic environment. The empirical rule that the local magnetic moment increases as the coordination number decreases holds here as Fig. 3 shows. In this figure the local magnetic moments of Fe_{229} are plotted as a function of the corresponding local atomic coordination. The plotted values are those listed in Table III for all the inequivalent sites within this cluster. We can see a rough linear correlation between the local magnetic moment μ_i and the local coordination numbers z_i at the inequivalent sites. However, the large dispersion for $z_i = 8$ indicates that not only the coordination determines the local magnetic moment, but it also depends on the local atomic environment. Moreover, there are certain inner atoms whose magnetic moment is lower than the bulk one.

In order to analyze the behavior of the local magnetization as a function of the cluster size N, we present in Fig. 4 this dependence for the central site, the first shell (the nearest neighbors of the central site), and the last outer shell. Although it is generally believed that the central atoms should have the bulk magnetization, our results indicate that the magnetic moment of the central atoms of the Fe clusters oscillates with an amplitude of about $0.5\mu_B$ around the bulk value ($2.2\ \mu_B$). It is clear that although the behavior of the central site is very spectacular, when we average the magnetic moment, its contribution is very small (of the order $1/N$) and for that reason the oscillations are not reflected in $\bar{\mu}_N$. These oscillations are smoothed out in the average process. In the case of the first shell (the nearest neighbors of the central atom) although the local moment is also very sensitive to the cluster size, the oscillations are dead and in this case the local moment converges faster to the bulk value than that of the central site. The contribution of the first shell to $\bar{\mu}_N$ is of the order $8/N$ and therefore the central site is screened very soon by the first shell as increasing N. It is interesting to remark that the experiments of Billas *et al.*[9] show a slow convergence of $\bar{\mu}_N$ towards the bulk value as

TABLE III. Local atomic environment (nearest-neighbors coordination, number, and type of atoms at the different shells) of the Fe_{229} cluster together with the local magnetic moments (in units of μ_B).

Shell	Coordination	Atoms	Type	μ_{local}
0	8	1	Central	1.46
1	8	8	Vertex	2.04
2	8	6	Square face	1.84
3	8	12	Edge	1.87
4	8	24	Square face	2.02
5	8	8	Vertex	2.15
6	8	6	Square face	2.12
7	7	24	Edge	2.02
8	8	24	Square face	2.28
9	7	24	Square face	2.37
10	4	8	Vertex	2.8
11	4	24	Square face	2.58
12	6	12	Edge	2.63
13	4	48	Square face	2.81

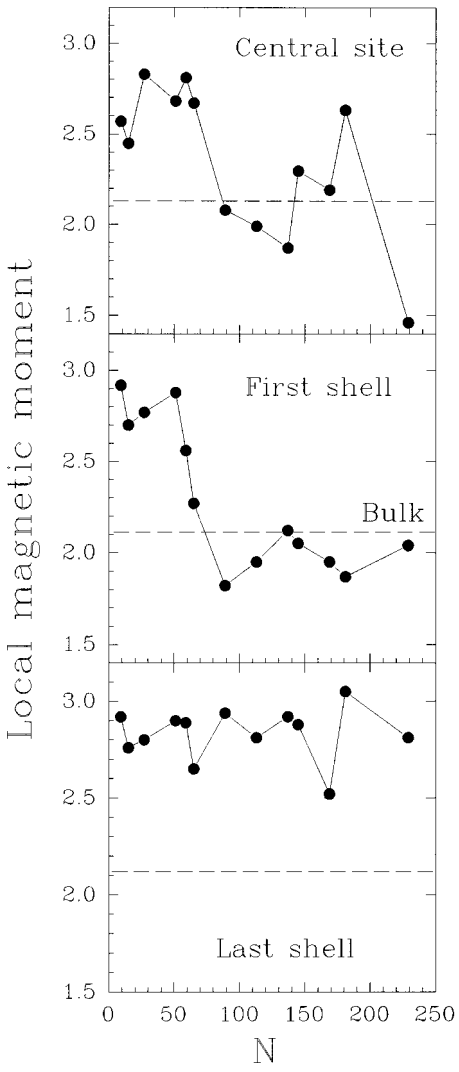

FIG. 4. Magnetic moments (in units of μ_B) of the central site (upper panel), first shell (central panel), and last outer shell (lower panel) as a function of the cluster size.

cluster size increases. In fact, this convergence is not reached for $N \leqslant 700$ and even in this size region an unexpected big oscillation is present. Finally, in the lower panel of Fig. 4 we present the contribution of the last outer shell. Regardless of the type of this site (vertex, edge, or square face), the low coordination of the surface atoms gives rise to large local magnetic moments. Thus, the last shell contributes with a value of the local magnetic moment ($\simeq 2.8\mu_B$) close to the magnetic saturation limit, with small deviations as a function of N; the lowest values correspond, in general, to the square face sites with local coordination $z_i=4$ ($N=15$, 65, 113, and 169) and the highest values correspond to the edges with local coordination $z_i=2$ ($N=27$, 89, and 181). The values for the local magnetic moments for vertex and square face sites with lower coordination than $z_i=4$ are inside the range covered by the square face and the edges sites.

IV. SUMMARY

We have calculated the average magnetic moments per atom ($\overline{\mu_N}$) and local magnetic moments of iron clusters (Fe_N) as a function of cluster size in the range $9 \leqslant N \leqslant 229$. The cluster geometries are assumed to be spherical portions of the bcc lattice. The spin-polarized electronic structure has been calculated with a self-consistent tight-binding model considering the $3d$, $4s$, and $4p$ valence electrons with global charge neutrality. The general trend for the nonmonotonic decrease of the $\overline{\mu_N}$ as increasing cluster size is well described. The results obtained in our calculation are very similar to those of Guevara *et al.*[19] though a tight-binding model that includes the electronic *spillover*. Our results suggest that the electronic *spillover* is not necessary to explain the observed magnetic behavior of these systems. However, neither our results nor the results of Guevara *et al.*[19] describe the correct oscillations experimentally observed.

The empirical rule that the local magnetic moment increases as the local coordination number decreases holds in general, although the local atomic environment also plays an important role. The magnetic moment of the central atom as a function of cluster size N displays an oscillatory behavior around the bulk value, whereas the surface atoms have a magnetic moment close to the saturation limit with small deviations as a function of N.

Finally, if we accept that the self-consistent tight-binding model is reasonably good for the electronic part, as the comparison with some *ab initio* results indicates, we think that the key ingredient for the detailed description of the magnetic behavior of the iron clusters is the correct geometrical structure. The magnetic moment of the iron systems is large and therefore the magnetic energy contributes significantly to the structure stabilization. Therefore, the next step in the present study is to incorporate an algorithm for the optimization of the geometry within the self-consistent electronic calculation, being able in this way of treating the electronic part and the geometrical part at the same level. This is the philosophy of some *ab initio* studies,[13] although they are restricted to very small sizes far from those experimentally investigated. We expect that within the tight-binding framework, this limitation can be well overcome, maintaining at the same time a sufficient degree of accuracy.

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