

Role of Co in enhancing the magnetism of small Fe clusters

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Using *ab initio* calculations, we study the magnetic features of the Fe_mCo_n , $m+n \leq 6$ clusters and investigate the role of Co in enhancing the magnetism of the Fe grains. Our results show that the role of Co appears to be that of inducing structural changes in the grain which may lead to enhanced magnetic moments for the Co-Fe clusters as a result of the rehybridization process and the following respecification of the effective band filling. Since the structural changes can efficiently be introduced by suitable templates, we point out that the anticipated role of Co in enhancing the magnetism of the Fe grains is not unique. This finding is in agreement with the recent experimental results.

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I. INTRODUCTION

The yearly linear increase in the magnetic storage capacity has suffered a slowdown recently as a result of reaching the superparamagnetic (SPM) limit in the magnetic storage technology and lends urgency for developing magnetic materials for circumventing this problem. As a result, efforts have been underway in fabricating advanced magnetic-storage materials. Much emphasis has been focused at magnetic materials of granular type as it has recently been found that *binary metallic clusters* consisting mainly of transition metal grains (clusters) may offer the possibility of breaking the SPM limit and, therefore, lead to magnetic storage densities in the range of 1–10 Tb/in². To reach this target, it is necessary to fabricate magnetic storage materials consisting of grains with sizes in the range of 2–10 nm. (For an extensive recent review, see Ref. 1 and references therein.) The key factors for achieving this objective require the magnetic grains to exhibit high saturation magnetic moments and room-temperature blocking temperatures. The latter feature calls for grains of large magnetic anisotropic energy (MAE), while the achievement of the former is at odds with the existing boundaries set by the so-called Slater–Pauling curve which specifies their (bulk phase) maximum value to be $2.45 \mu_B$ per atom (known also as the SPM limit). In the present work, we focus on one of those key factors that can ensure enhanced storage densities. In particular, we are searching for those factors that influence the development of saturation magnetic moments in a magnetic grain with values larger than those achieved so far. It should be recalled that improved magnetic grains with enhanced magnetic moments (as compared to those achieved so far) will allow the use of higher magnetic fields at the write heads than is available with the existing materials with a resulting increase in bit density.

A. Binary Fe-Co alloys and clusters

A material that has attracted theoretical and technological interest due to its unusual magnetic features is the Fe-Co alloy. This is because the bulk $\text{Co}_x\text{Fe}_{1-x}$ alloy is known to exhibit the largest known magnetic moment per atom with a maximum value of $\approx 2.45 \mu_B$ achieved for Co concentration, $x=30\%$. By virtue of this, and the fact that small grains exhibit magnetic moments (per atom) larger than those of the corresponding bulk phase, it is believed that binary Co-Fe grains could lead to large magnetic moments exceeding the SPM limit. Binns and co-workers,^{2,3} performing x-ray magnetic circular dichroism (XMCD) measurements on Co-coated Fe clusters of small volume (Fe/Co) ratio, have reported an increase in the magnetic moment (above the Slater–Pauling curve) of Fe atoms when coated with Co. This was verified recently by the theoretical works of Xie and Blackman⁴ and of Bergman *et al.*⁵ Bergman *et al.*⁵ attributed the enhanced magnetism of the Co-coated Fe clusters to Co-induced intra-atomic spin-density transfer from low- to high-spin states in the Fe atoms.

The interest in the issue of the Co-induced enhancement of the Fe grains has been renewed recently not only because these grains are very promising for breaking the Slater–Pauling limit, but also following the experimental results of Pratzner *et al.*⁶ who found maximum values for the magnetic moment in pure Fe than in $\text{Co}_x\text{Fe}_{1-x}$ monolayers on W(110) substrate. Using a fresh approach to interpret these results, one can claim that the role of Co in the magnetic enhancement of the free Fe-Co grains competes with the influence of the W(110) *template* in the deposited Fe-Co films on the W(110) substrate, i.e., both Co and the W(110) substrate appear to play parallel or common roles in enhancing the magnetism of the Fe grains. The main issue, therefore, is determining those factors which are inherent in the magnetic

enhancement of Fe grains, resulting either from the presence of Co or due to the action of a template (substrate). Our aim in the present work is to provide conclusive answers to these questions with a view to provide useful help in the design and fabrication of improved magnetic storage materials.

It is well known that the magnetic moment of a bimetallic magnetic grain (cluster) includes contributions derived from intrinsic and extrinsic cluster properties. The former depend on the *atomic* electronic configurations, the band filling factors and the spin-orbit coupling of the cluster's constituent atoms. These seem to be associated with the presence of Co in the case of the free Fe-Co grains. The latter, on the other hand, depend on the *molecular* electronic configuration of the ground state of the grain and result from the hybridization of the atomic orbitals of the electrons of the cluster's constituent atoms. As a result, they depend on the geometry, the composition and, in general, the structural configuration of the grain.⁷ All of these factors can be influenced by the W(110) template when used in conjunction with the Fe-Co films. A mutual dependency seems to exist between the attainable geometry of the cluster and the resulting hybridization with the result of this interplay depending on the band filling factors and the energetics of the available bonding orbitals.^{7,8}

By evaluating the role of each of the factors that could contribute to the enhancement of the grain magnetism, one could exploit the recent technological advances by growing binary grains with a given predetermined composition and possibly, a large magnetic anisotropy, ensuring large grain-magnetic-moment and high blocking temperature.^{1,8,9} This could be realizable, for example, by confining the growth in judiciously chosen templates, or by coating the grain with an appropriate material.^{8,9} Following this growth pathway, it seems reasonable to expect the response of the intrinsic properties of the constituent cluster atoms to the cluster (extrinsic) environment to play a dominant role in establishing the electronic and magnetic behavior of the grain.

In view of the above, an important issue to be addressed is whether one can trace the way the intrinsic properties of the constituent atoms of the binary cluster are affecting the structural properties of the cluster.^{7,8} This will greatly help in specifying possible pathways for enhancing the magnetic moment of bimetallic grains since they specify the attainable structural configuration of the cluster and the corresponding hybridization level of the atomic orbitals of its constituent atoms. It should be noted that cluster states with large orbital magnetic moment (OMM) do not always correspond to states which are energetically most favorable.¹⁰ However, by *pinning* the cluster geometry during the growth process one can circumvent this limitation and obtain confined grain states with the largest possible OMM. Nevertheless, the OMM contribution has to be considered in relation to the enhancement or the reduction of the spin magnetic moment (SMM) of the cluster as the SMM depends strongly on the ligand (or molecular) fields associated with the confined cluster geometry.

B. Results for small transition metal clusters

To obtain answers to these questions, we have embarked on a detailed study of the structure, stability as well as the

magnetic features of small binary magnetic clusters consisting of transition metals (TMs) (V, Fe, Co, Ni, Cu) and semi-conducting elements (C, Si).^{7,8,11-13} Our results led us to the following three basic conclusions:

(i) In the case of V, it is found that a significant increase in its magnetic moment, μ_V , occurs when it forms clusters with any of the TMs; Fe, Co, Ni. This increase leads to μ_V values greater than the corresponding atomic values, while at the same time μ_X ; X=Fe, Co, Ni suffers a significant reduction. This behavior has recently been verified experimentally (see, for example, Refs. 14–16). We attribute this to the electronic redistribution in the various molecular orbitals (MOs) in contradistinction to the atomic orbital (AO) distribution of free atoms. A common feature seen in all the VX_n binary clusters studied is the antiferromagnetic (AF) alignment of the magnetic moments of the X-cluster atoms with respect to that of the V.

(ii) In the case of Co, it is found that in CoX_n clusters the Co magnetic moment, μ_{Co} , is in general not significantly affected by any choice of the element X (metal or semiconductor). Furthermore, its moment is significantly smaller than that of the free atom but larger than the corresponding bulk value and aligns ferromagnetically (FM) with respect to μ_X . This result is reminiscent of the magnetic behavior of Co in bulk binary alloys of 3d-TMs (see, for example, Ref. 17).

(iii) Fe is found to exhibit an intermediate behavior between V and Co when forming clusters with other elements, i.e., Fe may undergo either a reduction or an enhancement in its magnetic moment; it may induce small or large magnetic moments on neighboring nonmagnetic materials and it may lead to FM or AF configurations of magnetic moments of the cluster atoms. It is worth noting that no systematic trend in the behavior of Fe (as a constituent cluster material) is seen and its behavior appears to depend strongly on the geometric configuration i.e., on the coordination number and, interestingly, on the orientation of bonds.

C. Objectives and computational method

Having obtained these general trends, we focus our emphasis on the general issue of the enhancement of the grain magnetism and investigate the role of those factors (intrinsic or extrinsic) that can lead to nanograins with large magnetic moments using *ab initio* methods. Much emphasis is put on the Fe-Co clusters since recent experiments have indicated these grains to be the most promising ones for fabricating materials for magnetic storage capabilities beyond the SPM limit.¹ The calculations are performed using the density functional theory (DFT) at the Becke three parameter hybrid functionals; Lee, Yang, and Parr (B3LYP) level of approximation using the GAUSSIAN program¹⁸ and the LANL2DZ basis set (which includes effective core potentials and relativistic effects).⁷ In particular, we discuss the magnetic features of the Fe_nCo_m , $n+m \leq 6$, clusters as dictated by the results of accurate *ab initio* calculations (DFT/B3LYP). The objective of the present work is to understand the underlying physics that leads to such an enhancement of the magnetic moment of Fe-Co clusters and propose possible pathways for their fabrication.

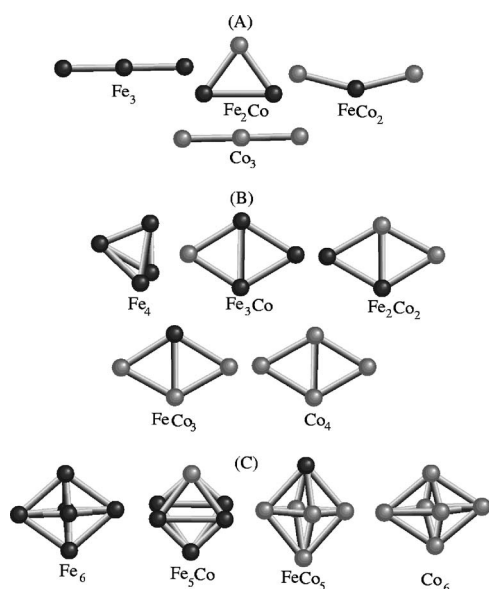


FIG. 1. Relaxed ground state geometries of Co-Fe clusters consisting of three, four, and six atoms. The geometries of the five atom clusters are shown in Fig. 4.

II. RESULTS AND DISCUSSION

The ground-state geometry of the fully relaxed Co-Fe clusters are shown in Figs. 1 and 4. As it is computationally prohibitive to search the entire configuration space, we have restricted our search for optimal cluster geometries by taking starting configuration structures obtained from our previous work using the tight-binding methods.¹⁹ For the trimers, however, we made a complete search. For the four-, five-, and six-atom clusters, we restricted the search mainly to tetrahedral, triangular-bipyramid, and tetragonal-bipyramid structures, respectively. Depending on the cluster size, only two to three isomers were found in an energy interval of 0.5 eV. Finally, the Mulliken population analysis was used for calculating the contributions from spin-up and spin-down states to the total charges around each atomic site; deviation from the neutral charge state at a particular site will be referred to as the *charge transfer* to this site.

A common feature of our results is that the Co-Fe clusters studied exhibit high-spin ground states, while one of the next favorable cluster states exhibits much smaller spin multiplicity than the ground state. The activation barrier between these two states is in the range of 0.25–0.50 eV, although there were a few cases with much larger activation barrier. This is a rather surprising feature since these states with such different spin multiplicities did not exhibit any noticeable structural differences. On the other hand, it is worth noting that this low-spin (LS) and high-spin (HS) feature of cluster states is a very interesting result since it demonstrates that even at the small cluster regime one rediscovers the feature of the LS-HS states of the bulk binary (consisting of any pairs of Fe, Co, Ni, Cu) alloys of transition metals.¹⁷

Our results for the magnetic moment of the constituent Co-Fe cluster atoms with respect to their charge state and their interatomic distances are presented in Figs. 2 and 3, while more detailed information about the entries in these

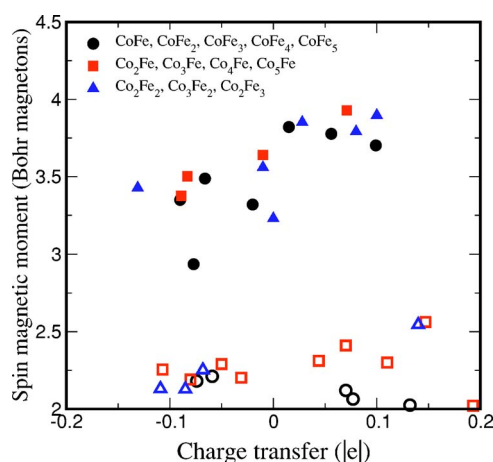


FIG. 2. (Color online) Variation of the magnetic moments of constituent Co-Fe cluster atoms with respect to their charge state; solid (open) symbols refer to Fe (Co) atoms. Circles (squares) refer to clusters with one Co (Fe) atom, respectively, while triangles refer to clusters with number of Co or Fe atoms greater than one. Positive charge means that the atoms lose charge to their surrounding atoms.

figures is included in Table I. In these figures, the results include the distribution of magnetic moments for three classes of clusters as denoted in the legend. The classes were chosen in such a way so as to illustrate the variations of the magnetic moments in clusters having one Fe atom, one Co atom and finally, more than one Fe and Co atom. It should be noted that our results for the ground state structure and magnetic moment for the Fe_n , $n=1-6$, obtained earlier with the tight-binding molecular dynamics (TBMD) method¹⁹ are identical with those reported by Dieguez *et al.*²⁰ who have used the Spanish initiative for electronic simulations with thousands of atoms (SIESTA) method (except in the value of the magnetic moment of Fe_5). As is apparent from Fig. 2, there is a strong correlation between charge transfer and the magnetic moment μ_{Fe} of the Fe cluster atoms. In particular, when the electronic charge, Q_{Fe} , is transferred onto Fe atoms, there is a corresponding reduction in their μ_{Fe} . By contrast,

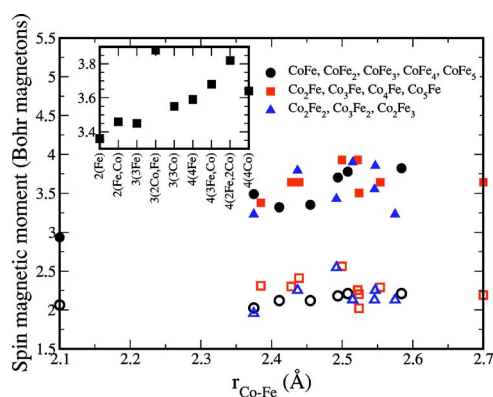


FIG. 3. (Color online) Variation of the magnetic moments of constituent Fe-Co cluster atoms with respect to their interatomic distances. Symbols are same as in Fig. 2. The inset shows the variation of μ_{Fe} with the coordination number $N(nFe, mCo)$ of Fe atoms with n and m denoting the number of Fe bonds to Fe and Co nearest neighbors, respectively ($n+m=N$).

TABLE I. Detailed information of results shown in Figs. 2 and 3: $(2S+1)$, $r_{\text{Fe-Co}}$, Q_X , and μ_X , $X=\text{Fe,Co}$ denotes the spin multiplicity of the ground state, the Fe-Co distance, and the net charge and magnetic moment of the X atom, respectively. Distances are given in Å, the charge in units of $|e|$ and the magnetic moments in μ_B .

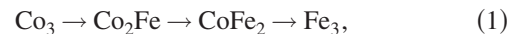
| Cluster | $2S+1$ | $r_{\text{Fe-Co}}$ | Q_{Fe} | μ_{Fe} | Q_{Co} | μ_{Co} |
|---------------------------------|--------|--------------------|-----------------|-------------------|-----------------|-------------------|
| CoFe | 6 | 2.100 | -0.077 | 2.936 | 0.077 | 2.064 |
| CoFe ₂ | 10 | 2.375 | -0.066 | 3.488 | 0.132 | 2.025 |
| CoFe ₃ | 14 | 2.494 | 0.099 | 3.702 | -0.074 | 2.181 |
| CoFe ₄ | 18 | 2.584 | 0.015 | 3.821 | -0.059 | 2.211 |
| CoFe ₄ | 18 | 2.508 | 0.056 | 3.777 | -0.059 | 2.211 |
| CoFe ₄ | 18 | 2.452 | 0.080 | 3.760 | -0.060 | 2.211 |
| CoFe ₅ | 20 | 2.411 | -0.020 | 3.320 | 0.070 | 2.120 |
| CoFe ₅ | 20 | 2.455 | -0.090 | 3.350 | 0.070 | 2.120 |
| FeCo ₂ | 9 | 2.385 | -0.089 | 3.376 | 0.044 | 2.311 |
| FeCo ₃ | 12 | 2.522 | 0.071 | 3.928 | -0.107 | 2.255 |
| FeCo ₃ | 12 | 2.500 | 0.071 | 3.928 | 0.147 | 2.562 |
| FeCo ₄ | 13 | 2.524 | -0.083 | 3.502 | 0.193 | 2.021 |
| FeCo ₄ | 13 | 2.524 | -0.083 | 3.502 | -0.031 | 2.202 |
| FeCo ₅ | 16 | 2.439 | -0.010 | 3.640 | 0.070 | 2.410 |
| FeCo ₅ | 16 | 2.428 | -0.010 | 3.640 | 0.110 | 2.300 |
| FeCo ₅ | 16 | 2.554 | -0.010 | 3.640 | -0.050 | 2.290 |
| FeCo ₅ | 16 | 2.700 | -0.010 | 3.640 | -0.080 | 2.190 |
| Co ₂ Fe ₂ | 13 | 2.492 | -0.131 | 3.428 | 0.140 | 2.545 |
| Co ₂ Fe ₂ | 13 | 2.515 | 0.100 | 3.897 | -0.109 | 2.131 |
| Co ₂ Fe ₃ | 17 | 2.437 | 0.080 | 3.792 | -0.068 | 2.252 |
| Co ₂ Fe ₃ | 17 | 2.547 | 0.028 | 3.852 | -0.068 | 2.252 |
| Co ₃ Fe ₂ | 14 | 2.546 | 0.016 | 3.551 | -0.085 | 2.128 |
| Co ₃ Fe ₂ | 14 | 2.575 | -0.004 | 3.231 | -0.085 | 2.128 |
| Co ₃ Fe ₂ | 14 | 2.375 | -0.004 | 3.231 | 0.153 | 1.956 |

when Fe atoms lose charge to the neighboring Co atoms, the Fe atoms experience an increase in their μ_{Fe} . It is worth pointing out that despite the small amounts of charge transfer involved, the calculated changes in μ_{Fe} are significant. The relationship $\mu_{\text{Fe}}=f(Q_{\text{Fe}})$ seems to be correlated with the interatomic distance $r_{\text{Co-Fe}}$ between neighboring Fe and Co atoms. In particular, it is observed that increased (reduced) values of μ_{Fe} are associated with larger (smaller) $r_{\text{Co-Fe}}$ values as shown in Fig. 3. In the inset of this figure, the variation of μ_{Fe} with the coordination number $N(n\text{Fe}, m\text{Co})$ of the Fe atoms is indicated with n and m denoting the number of Fe bonds to Fe and Co nearest neighbors, respectively ($n+m=N$).

In striking contrast to the Fe atoms of the Fe_nCo_m clusters ($n+m \leq 6$) studied, one can see from Figs. 2 and 3 that the Co cluster atoms are neither affected by changes in their bonding lengths to the Fe atoms nor by changes in their charge state. This result is consistent with the recent results of Bergman *et al.*⁵ on their work dealing with the magnetism of Fe clusters embedded in a Co matrix. This finding also agrees with the behavior of Co when forming binary clusters with other elements.⁷

Our results seem to point to the following interesting trends. Upon substituting one Co atom by an Fe atom in the

N -atom $\text{Co}_{N-m}\text{Fe}_m$ cluster, on the one hand we observe an increase of the binding energy per atom, while on the other hand the average magnetic moment, μ_N , per cluster atom increases approximately by $\Delta\mu_N \approx 1/N$ following the process: $\text{Co}_{N-m}\text{Fe}_m \rightarrow \text{Co}_{N-m-1}\text{Fe}_{m+1}$, for $0 \leq m \leq (N-1)$. Thus, in the sequence:



$\Delta\mu_{N=3}=0.33 \mu_B$. For $N=4, 5, 6$, we found $\Delta\mu_N$ to be, respectively, 0.25, 0.20, and 0.17 μ_B for the processes: $\text{Co}_N \rightarrow \text{Co}_{N-1}\text{Fe}$. These results are the cluster analogs of the bulk-phase findings of James *et al.*¹⁷ according to which the absolute value of the magnetic moment of the ferromagnetic state of a binary Fe-alloy increases linearly with the increasing number of unlike nearest neighbors.

The relationship $\Delta\mu_N=f(N)=1/N$ appears to hold also for the processes $\text{Co}_{N-m}\text{Fe}_m \rightarrow \text{Co}_{N-m-1}\text{Fe}_{m+1}$ for $1 \leq m \leq (N-1)$ if the substitution of Co by an Fe atom does not lead to significant changes in the cluster symmetry. However, when a substitution of an Fe atom by Co is followed by a structural change, then $\Delta\mu_N$ was found to be much larger than $1/N$ (see lower part of Fig. 4) breaking, thus, the bulk feature of the linear dependence of μ_{Fe} on unlike nearest neighbors.

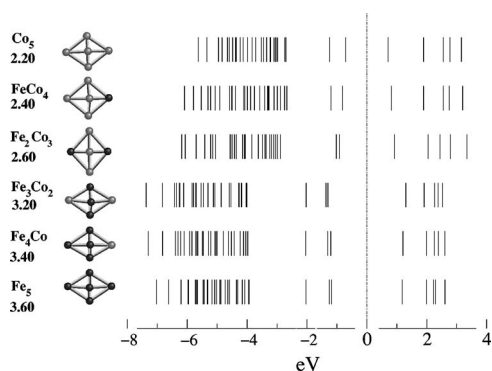


FIG. 4. Geometric configurations of the relaxed ground state of five-atom Fe-Co clusters. The average magnetic moment per cluster atom (given in Bohr magnetons) is shown at the left of the cluster, while the energy spectrum of the majority (alpha-spin) MOs is shown at right. The clusters Fe_5 and Fe_3Co_2 exhibit a distorted D_{3h} symmetry; the Fe_4Co exhibits a distorted C_{3v} symmetry; Fe_2Co_3 and FeCo_4 exhibit distorted C_{2v} and C_s symmetry, respectively. Finally, Co_5 exhibits the distorted C_{3v} (or distorted C_{2v}) symmetry.

Following these observations and the fact that the average magnetic moment μ_{Co} per Co atom in the Co_N clusters does not vary monotonically with the number N of the cluster atoms, it can be anticipated that one can find cluster compositions and configurations with very high magnetic moment by substituting Co with Fe atoms.

While the above results may give legitimacy to the assumption that the most important factor for enhancing the magnetic moment of the Fe clusters is to maximize the number of Co neighbors for the Fe atoms,⁵ it also supports other reported results^{5,7} predicting that the μ_{Co} is insensitive to the precise nature of its surroundings. The latter prediction implies that an increased Co content in the Fe clusters will lead to a reduction in the magnetic moment of the resulting Fe-Co grain. As a result, it may seem reasonable for someone to assume that the key to high saturation magnetic moment is to maximize the number of Co neighbors to the Fe clusters, while keeping the total number of atoms in the cluster to a minimum.⁵ However, recent experimental results⁶ have shown that Co-Fe alloys of reduced dimensionality and, in particular, Co-Fe monolayers grown on W(110) exhibit not only their maximum Curie temperature for zero Co concentration but also show a considerable differentiation in their Slater–Pauling diagram as compared to that of the $\text{Co}_x\text{Fe}_{1-x}$ bulk alloy.

These observations, taken together, show that the hypothesis of the Co-induced enhancement of the Fe clusters is not so simple or true, in general, and the matter needs to be addressed further. Thus, on the basis of our present and previous results,^{7,8} we examine the magnetic enhancement of the Fe clusters through our proposed arguments referring to the way the ligand fields (or the molecular fields) dictate the hybridization of the atomic orbitals of the constituent cluster atoms and its role in the attainable cluster geometry. In this view, the Co atoms appear to be the means inducing the changes in the point group symmetry of the Fe atoms leading, thus, to rehybridization processes and consequently to changes in the magnetic moment of the Fe atoms. This inter-

TABLE II. Spin multiplicity and atomic magnetic moments per atom for the atoms of clusters shown in Fig. 4; $\bar{\mu}$, $\bar{\mu}_{\text{Fe}}$, $\bar{\mu}_{\text{Co}}$ denote averages per cluster atom, over Fe atoms and over Co atoms of the cluster, respectively. Results for Co_4 , Fe_4 , and Fe_6 are also included for comparison.

| Cluster | $2S+1$ | $\bar{\mu}$ (μ_B) | $\bar{\mu}_{\text{Fe}}$ (μ_B) | $\bar{\mu}_{\text{Co}}$ (μ_B) |
|--------------------------|--------|-------------------------|-------------------------------------|-------------------------------------|
| Co_4 | 11 | 2.50 | | 2.500 |
| Co_5 | 12 | 2.20 | | 2.200 |
| Co_4Fe | 13 | 2.40 | 3.50 | 2.125 |
| Co_3Fe_2 | 14 | 2.67 | 3.40 | 2.067 |
| Co_2Fe_3 | 17 | 3.20 | 3.83 | 2.255 |
| CoFe_4 | 18 | 3.40 | 3.70 | 2.200 |
| Fe_5 | 19 | 3.60 | 3.60 | |
| Fe_4 | 15 | 3.50 | 3.50 | |
| Fe_6 | 21 | 3.33 | 3.33 | |

pretation becomes apparent in Fig. 4 where we plot the energy level diagram for the majority spin MOs (Ref. 21) of the $\text{Co}_{5-m}\text{Fe}_m$, $m=0,1,2,3,4,5$, series along with the corresponding structure and average magnetic moment per cluster atom for each member of the series. It is clear from this figure that by substituting one or two Fe atoms by Co in the Fe_5 cluster, no significant changes are observed in either the structural or electronic configuration of the cluster. These clusters retain the properties of the parent Fe_5 cluster. However, as more Fe atoms are substituted by Co, the Co_5 now acts as the parent cluster inducing changes in the structural and the electronic configuration of the cluster. Additionally, it can be observed from Fig. 4 that it is not Co which induces the splitting of the highest occupied molecular orbital (HOMO) levels and the significant shifts of the HOMO and the lowest unoccupied molecular orbital (LUMO) levels toward the Fermi level. It is apparent from Fig. 4 that these effects are the consequence of structural changes induced by Co.

Finally, it is worthwhile to note the following feature: While in going from Fe_4 to Fe_5 , the average magnetic moment, μ_{Fe} , per Fe atom increases by $0.1 \mu_B$ (i.e., from 3.5 to $3.6 \mu_B$), the μ_{Fe} value per cluster atom for Fe_4Co is found to be $3.4 \mu_B$, i.e., a lesser value. However, as is apparent from Table II, the substitution of one Fe-atom by a Co-atom in the Fe_5 cluster enhances the average magnetic moment of the Fe atoms, $\bar{\mu}_{\text{Fe}}$. Thus, one observes an interplay between an enhancement of $\bar{\mu}_{\text{Fe}}$ and a reduction (on the average) of the magnetic moment of the cluster measured as the average magnetic moment per cluster-atom $\bar{\mu}$. Our results, thus, lead to the following definitive statements.

(i) Small magnetic grains exhibit enhanced magnetic moments exceeding the (bulk) Slater–Pauling limits (see, for example, Ref. 19). The value of these magnetic moments can be tailored by choosing the size, the shape, and the composition of the grain.

(ii) As previously reported by us,⁷ the magnetic moment of the Co atom is not affected by the nature of its neighboring atoms and their geometric arrangement, in agreement with other reported results.^{4,5}

(iii) Fe atoms in small Fe grains tend to increase their magnetic moment if some of their neighboring Fe atoms are substituted by Co atoms.

(iv) There are certain cases in which the addition of Co does not necessarily lead to an increase in the magnetic moment of the Fe grains. This depends on the degree of the structural changes imposed on the grain by the substitution of Fe by Co.

It is, therefore, obvious that the widely used term *enhanced magnetic moments* has a relative meaning. However, it is apparent that in relation to the magnetic storage issue, this term is associated with the possibility of producing magnetic storage films exhibiting saturated magnetic moments greater in value than those limited by the SPM limit. It should be recalled, however, that as we pointed out in the above, although the fabrication of magnetic grains with enhanced magnetic moments is a prerequisite for the production of improved magnetic storage materials, this is not the only feature that has to be improved. In particular, the magnetically improved grains must also have to respond positively to the following requirements.¹

(i) Retain their large magnetic moments when deposited on an appropriate substrate. In the case of Fe grains, this can be achieved by coating them by Co and as experimental and theoretical work has shown, coating the Fe clusters with Co significantly increases their spin moment without reducing the orbital contribution.

(ii) Be organized in regular arrays (on the substrate) which can allow on the one hand, large grain densities (in order to retain large magnetizations per unit area) and on the other hand, storing a data bit on a single grain effectively.

(iii) Have large MAE in order to exhibit room-temperature blocking temperatures, that is, to have their magnetization stable against thermal excitations.

The present results provide some answers to the questions underlying the physics behind the increase of the grain magnetism that appears in the most promising binary clusters, namely the Fe-Co grains. The present results go beyond simply reinforcing the well-known observation that the magnetic moment of Fe in clusters, layers, and bulk phase can be modified by a change of the structure. They delve deeper and demonstrate that these structural changes have as their origin the presence of the Co atoms and attribute the changes in the magnetic moments of the grains to the role of Co in establishing the orbital rehybridization and the associated HS states of the grains. The latter may also be affected by an additional contribution of the Co atoms which can be assigned to the extra *d* holes associated with the Co atoms. As we pointed out in our previous reports,^{7,8} the *d* band filling is a major factor which dictates the structural, electronic, and the magnetic behavior of a material. Furthermore, it is worth noting that the present small-cluster results reaffirm the trends found for bulk phases¹⁷ and generalize conclusions arrived at for the bulk phase. Thus, it can be seen that the rehybridization following the structural changes in small clusters may lead to a nonlinear variation of the magnetic moment of Fe with the number of the surrounding Co atoms in contradistinction to the linear variation and the weak dependence on crystal structure (chosen among face-centered-cubic, body-centered-cubic, and hexagonal-close-packed

ones) found for the bulk phase.¹⁷ Another example is the increase of the magnetic moment of atoms in surfaces and in large clusters which has been explained as a band effect in bulk phase, namely the narrowing of the *d* bandwidth due to the smaller coordination number of these atoms. Thus, it has been demonstrated that in very small clusters, the increase of the magnetic moment of the cluster atoms, in addition to the contribution from effects due to the reduced coordination numbers, includes significant contributions that arise from the rehybridization and *d*-band filling processes which follow the point group symmetry of each particular cluster atom.^{7,8,11–13}

III. CONCLUSIONS

The present findings for the small Fe-Co clusters and their systematic comparison with the corresponding data of the bulk phase, allow one to claim that a possible pathway to enhance the magnetism of the Fe-Co grains beyond the SPM limit is to combine the conclusions arrived at within the rigid-band model (i.e., Slater–Pauling conclusions) with those derived from considering the effect of possible rehybridizations (of the corresponding AOs of the constituent cluster atoms) which lead to enhanced high spin electronic configurations for the grains. One way to obtain such appropriate hybridizations appears to be the use of appropriate templates either in the form of a coating material or as a substrate. Putting these conclusions in another way, one can say that the Co-induced structural changes and the resulting rehybridization of the grain orbitals specify the effective band filling and, therefore, dictate the magnetic behavior of the grain.

It is worth noting that according to our proposed explanation, the presence of Co is not a necessary condition for enhancing the magnetism of the Fe clusters; it may be replaced by an appropriate template which could induce the necessary hybridization leading to large magnetic moments of the Fe grains. This observation is justified by the recent experimental results of Pratzner *et al.*⁶ who found maximum values for the magnetic moment in pure Fe than in $\text{Co}_x\text{Fe}_{1-x}$ monolayers on W(110) substrate. In this experiment, the role of Co seems to be played by the W(110) substrate acting as a template.

In conclusion, the present work proposes a plausible reason that makes Co appear as an agent in enhancing the magnetic moment of Fe grains. Our results attribute to Co the role of the inducer of local structural changes in the Fe grains and refute any claim attributed to it of playing a unique role in magnetically enhancing the Fe grains. This role can also be equally well played by an appropriately chosen template for the Fe-grain growth.

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¹J. Bansman, S. H. Baker, C. Binns, J. A. Blackman, J. P. Bucher, J. Dorantes-Davila, L. Favre, D. Kechrakos, A. Kleibert *et al.*, Surf. Sci. Rep. **56**, 189 (2005).

²C. Binns, S. H. Baker, M. J. Maher, S. C. Thornton, S. Louch, S. S. Dhesi, and N. B. Brookes, Eur. Phys. J. D **16**, 189 (2001).

³C. Binns, S. H. Baker, K. W. Edmonds, P. Finetti, M. J. Maher, S. C. Louch, S. S. Dhesi, and N. B. Brookes, Physica B **318**, 350 (2002).

⁴Y. Xie and J. A. Blackman, Phys. Rev. B **66**, 085410 (2002).

⁵A. Bergman, E. Holmstrom, A. M. N. Niklasson, L. Nordstrom, S. Frota-Pessoa, and O. Eriksson, Phys. Rev. B **70**, 174446 (2004).

⁶M. Pratzner and H. J. Elmers, Phys. Rev. B **69**, 134418 (2004).

⁷A. N. Andriotis, G. Mpourmpakis, G. Froudakis, and M. Menon, J. Chem. Phys. **120**, 11901 (2004).

⁸A. N. Andriotis, G. Mpourmpakis, G. Froudakis, and M. Menon, New J. Phys. **4**, 78 (2002).

⁹A. L. Elias *et al.*, Nano Lett. **5**, 467 (2005).

¹⁰A. N. Andriotis and M. Menon, Phys. Rev. Lett. **93**, 026402 (2004).

¹¹G. Mpourmpakis, G. E. Froudakis, A. N. Andriotis, and M. Menon, Phys. Rev. B **68**, 125407 (2003).

¹²G. Mpourmpakis, G. E. Froudakis, A. N. Andriotis, and M. Menon, J. Chem. Phys. **119**, 7498 (2003).

¹³M. Menon, A. N. Andriotis, and G. Froudakis, Nano Lett. **2**, 301 (2002).

¹⁴Y. Huttel, G. van der Laan, T. K. Johal, N. D. Telling, and P. Bencok, Phys. Rev. B **68**, 174405 (2003).

¹⁵A. Scherz, P. Pouloupoulos, R. Nunthel, J. Lindner, H. Wende, F. Wilhelm, and K. Baberschke, Phys. Rev. B **68**, 140401(R) (2003).

¹⁶N. H. Hoa Hong, J. Sakai, W. Prellier, A. Hassini, A. Ruyter, and F. Gervais, Phys. Rev. B **70**, 195204 (2004).

¹⁷P. James, O. Eriksson, B. Johansson, and I. A. Abrikosov, Phys. Rev. B **59**, 419 (1999).

¹⁸M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann *et al.*, GAUSSIAN 98 (Revision A.11) (1998).

¹⁹A. N. Andriotis and M. Menon, Phys. Rev. B **57**, 10069 (1998).

²⁰O. Dieguez, M. M. G. Alemany, C. Rey, P. Ordejon, and L. J. Gallego, Phys. Rev. B **63**, 205407 (2001).

²¹As far as we show clusters that all possess high spin states, we show only the majority (alpha-spin) molecular orbitals energy levels assuming (correctly) that the changes in the energy levels come from the alpha orbitals. We neglect showing the beta-spin molecular orbitals energy levels because beta orbitals lay close in energy to the alpha ones and have almost the same MO character.