

Magnetism of iron clusters embedded in cobalt

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We present a theoretical study of the spin magnetization of iron clusters embedded in a cobalt matrix. The calculations are performed on a large bcc cluster of 1021 atoms comprising an n atom iron core and a $(1021-n)$ atom cobalt coating, where n is varied from 59 to 641. The work is based on a spin-polarized tight-binding Hamiltonian. Comparison is made with the magnetization of $\text{Fe}_n\text{Cu}_{1021-n}$ clusters. It is found that in the copper matrix, the moments on the iron are reduced to a value close to that of bulk iron, whereas in a cobalt matrix, the iron moments are very similar to the values found in free iron clusters, in good agreement with recent experiment results. Interestingly if some alloying of the iron and cobalt is allowed in the region of the interface, we obtain an enhancement in the iron moment as compared to that of a free iron cluster of a similar size.

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I. INTRODUCTION

Nanoscale magnetic particles attract intense interest because of novel properties that are strongly dependent on their size, morphology and composition.^{1,2} The research receives added impetus because these low dimensional systems provide the key ingredient in the development of high density data storage devices. Reduced atomic coordination due to the presence of a surface plays an essential role in modifying the properties, and this was made particularly clear in experiments on free clusters of iron, cobalt, and nickel that demonstrated an enhancement in the magnetic moments with reducing cluster size.³⁻⁵ In addition certain materials, such as Rh, that are paramagnetic in bulk, exhibit magnetism when in the form of small clusters.⁶ The experimental investigation of these systems has been greatly advanced by the development of cluster sources that can produce a beam of particles with well-characterized narrow size distributions, and by element specific techniques such as x-ray magnetic circular dichroism (XMCD) that can differentiate the spin and orbital contributions to the magnetism.^{1,2}

If clusters are deposited on a surface the cluster-surface interaction can modify the free particle magnetic behavior. Generally the magnetic moment of a deposited cluster is below the free particle value. An interesting example is that of iron in the size range 200–600 atoms. Exposed clusters on a highly oriented pyrolytic graphite (HOPG) surface have their moments reduced to a little above the bulk value.⁷ However, coating the particles with Co restores their moment to around the free particle value.⁸ In addition there is a considerable enhancement over the bulk value of the orbital moment in both the exposed and the cobalt coated iron clusters. In the case of exposed particles, the magnetization was monitored as a function of surface coverage.⁹ The spin moment was found to be rather insensitive to the coverage, while the orbital moment reduced rapidly to its bulk value. We focus in this paper on the spin contribution to the magnetic moment and report calculations on Fe clusters embedded in Co. We find that not only does a coating of Co result in a moment on the Fe that is very similar to its free cluster value in agreement with the XMCD measurements,⁸ but further enhance-

ment of the Fe moment is possible if some diffusion of Co atoms across the Fe/Co interface is allowed to take place.

There have been extensive theoretical studies of the magnetism of single element clusters. *Ab initio* calculations¹⁰⁻¹⁵ are limited to a small number of atoms, while parametrized tight binding methods¹⁶⁻²⁰ of various levels of sophistication can explore systems of several hundred atoms, or more if symmetry or the recursion technique are used. The calculations give a reasonable account of the size dependent magnetization^{18,19} observed in Fe, Ni, and Co, and accord with the experimental observation that the largest Rh cluster showing magnetism is in the size range 50–100 atoms.²⁰⁻²³

Most of the work on two element systems has been either on layer materials or on clusters of a few atoms on a surface. Studies of embedded clusters are more limited.²⁴⁻³³ Many of the calculations focus on small clusters, but there have been a number of papers that have considered clusters larger than 50 atoms.^{26,27,30,31} Recently, Paduani and Krause³³ have studied a variety of Fe-Co alloy and multilayer systems using the first-principles molecular cluster discrete variational method. They model different Fe-Co systems with 15-atom embedded clusters of various compositions. They find that the local magnetic moment for Fe atoms is very dependent on the environment while the local moment for Co is nearly constant.

The systems that are close packed in bulk have a structure that is more clearly defined than the bcc ones such as Fe. Clusters of Co or Ni adopt an icosahedral structure, with a characteristic shell filling clearly evident in experiments.³⁴ The situation in Fe is much less clear,³⁴⁻³⁶ with some indication of competition between different cluster geometries, but a bcc structure at all cluster sizes is usually assumed.^{18,19} For simplicity we shall assume a bcc structure for clusters in this paper both for the Fe core and for the Co coating. This assumption is not unrealistic. In the case of thin Fe-Co films, the cobalt layer can be stabilized in a bcc structure up to a thickness of about 2 nm.^{37,38}

Our calculations are based on a tight-binding model developed earlier and applied to single element nonspin-polarized systems.^{39,40} In the following section we describe briefly its extension for two element spin-polarized clusters.

In Sec. III results are presented on the spin magnetism of free Fe clusters and Fe clusters with coatings of Co or Cu. We also consider the effect in the cobalt embedded clusters of alloying just inside the Fe/Co interface.

II. THEORETICAL METHOD

Our tight-binding (TB) model, which can be reliably used from bulk, through to surfaces and clusters of elemental materials, has been described extensively in our previous publications.^{39,40} Here we will summarize briefly the extension of the methodology⁴⁰ to spin-polarized and binary systems.

We use a minimal orthogonal basis set containing s , p , and d orbitals. The on-site energy levels are assumed to depend only on the angular momentum l of the orbitals λ and are given by⁴⁰

$$\epsilon^{i\lambda} = a_l + b_l \rho_i^{2/3} + c_l \rho_i^{4/3} + d_l \rho_i^2, \quad (1)$$

where ρ_i is the local ‘‘density’’ around atom i ,

$$\rho_i = \sum_{j \neq i} \exp[-\gamma_{JI}(r_{ij}/r_0 - 1)] f_c(r_{ij}), \quad (2)$$

where $I(J)$ denotes the type of atom on site $i(j)$, γ is a parameter that will depend on the atom types such as Fe, Co, Cu. If $I=J$, r_0 is the equilibrium nearest neighbor distance in the bulk, otherwise it takes the value of arithmetic average. $f_c(r)$ is a cutoff function with chosen cutoff distance and steepness.⁴⁰ The two-center intra-atomic elements, which arise from the overlap of wave functions $|i\lambda\mu\rangle$ with neighbor atomic potentials V_j , are included to improve the TB transferability.^{39,40} To extend to binary systems, these terms are assumed to depend on distance r_{ij} and atomic types I, J

$$I_{ll'\mu}(r_{ij}) = (c_{IJ,1} + c_{IJ,2} r_{ij}/r_0) \times \exp[-c_{IJ,3}(r_{ij}/r_0 - 1)] f_c(r_{ij}), \quad (3)$$

where $I_{ll'\mu}(r_{ij}) = \langle i\lambda\mu | V_j | i\lambda'\mu' \rangle$, l denotes s , p , d , and μ denotes σ , π , δ . According to the definition of I , normally $c_{IJ} \neq c_{JI}$.

Similarly to the traditional TB scheme,⁴¹ the two-center interatomic Hamiltonian elements are determined by ten Slater-Koster hopping parameters $V_{ll'\mu}$. We assume the hopping parameters depend on the bond length r_{ij} as

$$V_{ll'\mu}(r_{ij}) = (h_{IJ,1} + h_{IJ,2} r_{ij}/r_0) \times \exp[-h_{IJ,3}(r_{ij}/r_0 - 1)] f_c(r_{ij}). \quad (4)$$

We have made the approximation $h_{IJ} = h_{JI}$. If $I=J$, the TB parameters c_{IJ} in Eq. (3) and h_{IJ} in Eq. 4 take the values of those of the pure elements.⁴⁰ If $I \neq J$, c_{IJ} and h_{IJ} correspond to the TB parameters between different elements.

The repulsive pair potential Φ as a function of interatomic distance

$$\Phi(r_{ij}) = p_{IJ,1} \exp[-p_{IJ,2}(r/r_0 - 1)] f_c(r_{ij}) \quad (5)$$

depends on atomic type I and J in binary systems. Obviously $p_{IJ} = p_{JI}$.

To extend the TB formalism to spin-polarized systems, an additional energy related to charge transfer and spin-polarization is defined as

$$E_{\text{SP}} = \frac{1}{2} \sum_i U_i (n_i - n_i^0)^2 - \frac{1}{4} \sum_{i, ll'} J_{i, ll'} m_{il} m_{il'} + \frac{1}{4} \sum_i J'_{id} (n_{id} - n_{id}^0)^2 m_d^2, \quad (6)$$

where n_i^0 is the number of valence electrons of the corresponding atom and n_{id}^0 is the bulk d -orbital occupancy. The quantities n_i , m_{il} , and n_{id} in Eq. (6) are defined as

$$n_i = \sum_{l\sigma} n_{il\sigma},$$

$$m_{il} = n_{il\uparrow} - n_{il\downarrow}, \quad (7)$$

$$n_{id} = n_{id\uparrow} + n_{id\downarrow}.$$

The problem needs to be solved self-consistently and the total energy is to be minimized with respect to the local occupations $n_{il\sigma}$ within global charge neutrality. The second term of Eq. (6) corresponds to the exchange energy due to spin polarization, while the introduction of the third term makes the exchange and Coulomb repulsion parameters depend on local environment, i.e., the spin split is smaller in atomic limit than in bulk limit for the same local magnetic moment m_{id} while the Coulomb repulsion is larger in atomic limit due to larger local magnetic moment. Generally, the third term only gives a minor correction because the local d occupancies of transition metals only slightly change with local environment.¹⁸

The TB parameters for pure Fe, Co, and Cu are determined as described in our previous publication.⁴⁰ In fitting the parameters related to interaction between different elements, the TB parameters for pure Fe, Co, and Cu are kept fixed and a constant shift to the on-site energy levels is used to make the Fermi energy of different pure metals the same. Similarly to the fitting for pure elemental materials, the binary parameters are determined by the simultaneous fit to the energy levels and total energies of a number of binary clusters of up to 55 atoms in size, as well as the total energies of a few hypothetical ordered binary alloys all obtained from density functional calculations.

The electron-electron interaction parameters except U_i for Fe and Co in Eq. (6) are determined by a fit to spin-polarized *ab initio* results of a number of small clusters and bulk bcc or fcc structures over a bond length range around the theoretic equilibrium states. As shown previously,⁴⁰ the results are not sensitive to the precise values of U_i . Because the magnetic moments are dominated by the d -orbital contribution, we have neglected those exchange integrals $J_{ll'}$ between s and p orbitals. The magnetic moments are very sensitive to the values of J_{dd} , which are 0.95 eV for Fe and 1.16 eV for Co. The determined interaction parameters are tested against some well-understood systems.

TABLE I. Geometrical growth of O_h clusters as a portion of bcc lattice. The number of subshells n_{shell} (sets of equivalent atoms), number of atoms in each main shell n_{main} , and total number of atoms are given for up to sixth main shell.

main	n_{shell}	n_{main}	Total
0	1	1	1
1	2	14	15
2	3	44	59
3	6	110	169
4	8	170	339
5	12	302	641
6	13	380	1021

III. RESULTS

The focus of this paper is iron clusters embedded in a cobalt matrix, but to check our method on a well-understood system, we begin by predicting the magnetic moments of a (100) free-standing Fe monolayer and Fe (100) surface at the experimental lattice constant of bcc Fe. A 13-layer slab structure is used to model the surface. The TB calculated local moments are $3.2\mu_B$ for the monolayer, $2.99\mu_B$ for the (100) surface layer, and $2.26\mu_B$ for the center layer respectively, in excellent agreement with the full-potential linearized augmented-plane-wave method calculations.⁴²

The clusters studied in this paper are constructed around a central site and follow the bcc structure with the theoretical lattice constant of Fe. The clusters were constructed layer by layer along the (100) and (110) directions of the bcc structures. The resulting main shell-closed clusters are covered with 6 (100) faces and 12 (110) faces. Because the separation distance of (100) planes ($\frac{1}{2}a$ where a is bcc lattice constant) is smaller than that of (110) planes [$(\sqrt{2}/2)a$], a particular main shell may contain two (100) layers. Main shell filling maintains this cluster shape. Subshells are filled with succes-

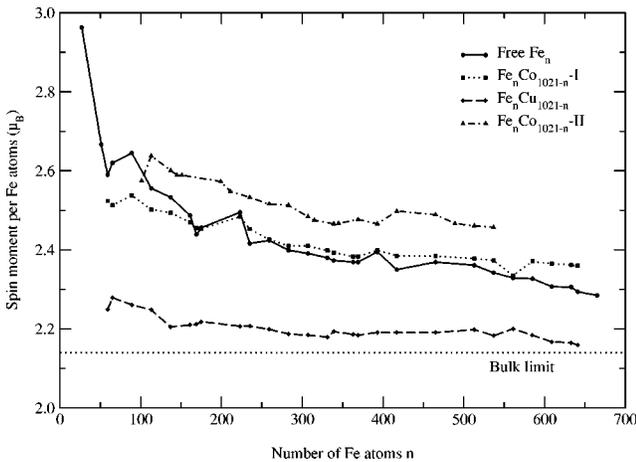


FIG. 1. Averaged local magnetic moments of Fe atoms in free Fe clusters (Free Fe_n), Cu coated Fe clusters ($\text{Fe}_n\text{Cu}_{1021-n}$), and Co coated Fe clusters ($\text{Fe}_n\text{Co}_{1021-n}$ -I). $\text{Fe}_n\text{Co}_{1021-n}$ -II are clusters with some Co atoms substituted for Fe atoms inside the interface of the Co coated Fe clusters.

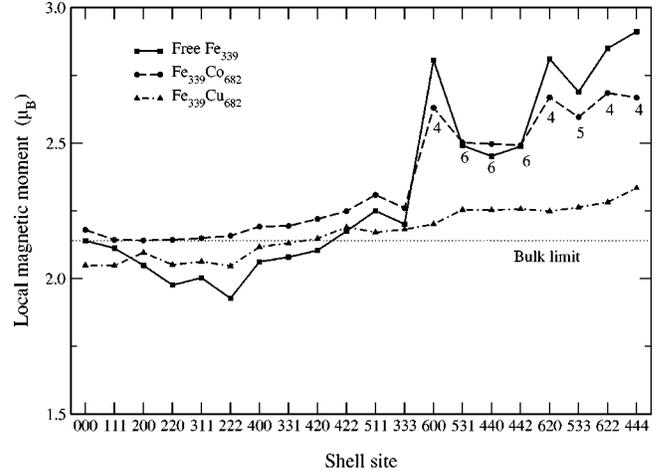


FIG. 2. Local magnetic moments of Fe atoms for free and for Co or Cu coated Fe_{339} . The subshell sites are labeled as lattice positions such as (000) and (111), in units of one-half the lattice constant. The figures close to the plots give the numbers of Fe nearest neighbors for each surface or interface subshell. Obviously other subshells have eight Fe nearest neighbors.

sive O_h symmetry occupation of free sites with the largest number of first nearest neighbors (FNN's) or those with smallest distance from cluster center if the numbers of FNN's of several available sets are equal. The details of the pattern of main-shell filling are listed in Table I. The order of filling of the subshells will be apparent in Figs. 2 and 3.

Previous calculations of iron clusters^{18,19} assumed a spherical growth pattern. Up to the size of about 200 atoms, the present proposed growth is similar to the onionlike spherical growth. We find from our TB calculations that the total energy of regularly shaped Fe clusters generated as described are lower than those of the same size spherically shaped clusters.

Using symmetry-adapted basis functions, we can easily diagonalize the Hamiltonian matrix for systems containing more than 1000 atoms. In Fig. 1 we present our results for

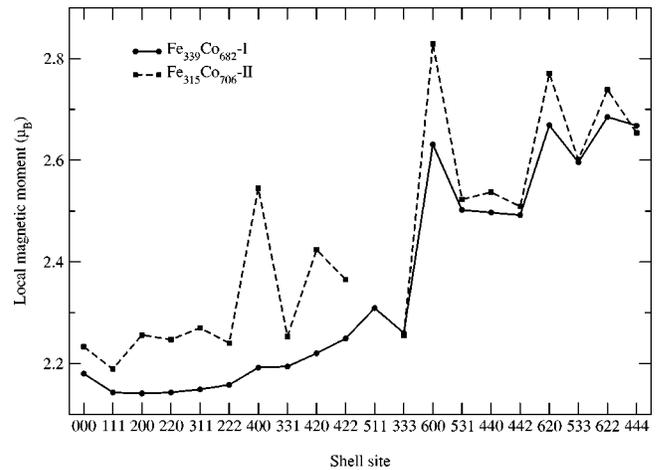


FIG. 3. Comparison of the local magnetic moments of Fe for Co coated Fe clusters with and without cobalt atoms diffused into the iron core. $\text{Fe}_{315}\text{Co}_{706}$ -II is constructed from $\text{Fe}_{339}\text{Co}_{682}$ -I by replacing 24 Fe atoms of shell (511) with Co atoms.

the averaged local magnetic moments per iron atom of the cobalt coated iron clusters together with those of free iron clusters and copper coated ones. For the Co (Cu) coated clusters, the Fe cores are covered by at least one layer of Co (Cu) which ensures that the nearest neighbor coordination of all Fe atom is the same as in bcc bulk Fe. Two plots for Co coated Fe clusters are shown in Fig. 1. ($\text{Fe}_n\text{Co}_{1021-n}$ -I) clusters have the n Fe atoms filling inner subshells with the Co atoms in the outer ones. An ($\text{Fe}_n\text{Co}_{1021-n}$ -II) cluster is constructed from a ($\text{Fe}_{n+p}\text{Co}_{1021-n-p}$ -I) one by replacing all p Fe atoms in a subshell in the interface region with Co atoms. Such a cluster will give an indication of possible effects arising from the diffusion of Co atoms across the interface.

It is well known, both theoretically^{18,19} and experimentally,^{4,5} that the magnetic moments of free iron clusters are enhanced compared to the bulk materials, and that the average magnetization per atom decreases nonmonotonically to the bulk value with increasing cluster size. As shown in Fig. 1, our calculated averaged magnetic moments for free clusters are reasonably in agreement with previous up to 200-atom size theoretical results,^{18,19} and correctly reproduce the experimental trend^{4,5} of converging to the bulk value with some oscillation. When free iron clusters are deposited on a surface such as HOPG or a noble metal, the spin magnetic moment at Fe atom sites reduces from the free cluster value to something close to the bulk limit⁷. The enhancement of the magnetic moment of free clusters, due to the large proportion of surface atoms is largely cancelled out by the cluster-surface interaction present in supported clusters. This behavior is seen in the plot in Fig. 1 for Fe embedded in Cu. The magnetization is reduced to marginally above the bulk value, behavior very similar to the experimental observations on Fe clusters deposited on HOPG.⁷

Coating the Fe core with Co instead of Cu produces very different behavior as is shown in the $\text{Fe}_n\text{Co}_{1021-n}$ -I plot in Fig. 1. Despite the fact that the coordination of the surface Fe atoms is the same as that of the bulk, the average magnetic moment on the Fe is close to or, for larger clusters, very slightly higher than that of free iron clusters. The element-specific nature of XMCD measurements provides an experimental probe of the average moment on the Fe core.^{2,8} Our results on Fe embedded in Co are in good agreement with the experimental results for 200–600 Fe atom clusters (Fig. 24 in Ref. 2).

It has been pointed out before that Fe is magnetically weak because of an insufficient electron-electron interaction to bandwidth ratio, while in Fe-Co alloys this interaction for the Co atoms could increase the exchange splitting of the Fe 3*d* bands^{33,43}. The local magnetic moments for each subshell of Fe_{339} in different environments are depicted in Fig. 2. The results for other cluster sizes are similar to this one. Referring first to the free Fe cluster, the enhancement over the bulk moment comes mainly from the surface shell (number 4 in the notation of Table I), which contains 170 atoms in sub-shells labeled (600) to (444). The coordination numbers of the surface atoms are noted on the figure. A coating of Cu, restores the bulk coordination number, and yields a magnetization that is close to that of bulk. With Co atoms as neighbors, however, the reduction of the fourth shell Fe moments

is much less. The Co neighbors provide an effective enhancement to the exchange splitting of the Fe that virtually compensates for the bandwidth increase that occurs because of their presence.

For Fe clusters embedded in a Co film, XMCD data show that the number of Fe 3*d* holes per atom is indistinguishable from the bulk demonstrating that the grains consist mainly of pure Fe with intermixing confined to the particle surfaces.⁸ However, Fe and Co are intermiscible, and this may result in some Co atoms diffusing through the interface region into the Fe particle. To model the effect of this diffusion, we replace some of the Fe atoms in Co coated Fe clusters by Co atoms. For ease of calculation, we maintain cluster symmetry by replacing all the atoms in one subshell. It can be seen from plot $\text{Fe}_n\text{Co}_{1021-n}$ -II of Fig. 1 that this substitution produces a distinct enhancement in the average local moment on the Fe compared with free Fe clusters for sizes larger than 100 atoms.

In order to see where the enhancement comes from, we show the local moment of different shell sites on a typical cluster in Fig. 3. The cluster $\text{Fe}_{315}\text{Co}_{706}$ -II is constructed by replacing 24 Fe atoms at shell (511) of $\text{Fe}_{339}\text{Co}_{682}$ -I with Co atoms. The increased moment comes largely from five shells (400), (420), (600), (620), and (622), which are first nearest neighbor sites of (511). The effective enhancement to the exchange splitting on Fe sites produced by Co neighbors operates not only on atoms on the surface of the Fe core but also in the core region itself. The sensitivity of the magnetic moments of Fe to the local environment has also been observed in a recent study of Fe-Co alloys and multilayers.³³

IV. SUMMARY

We have calculated the average spin magnetic moment in Fe clusters over the size range 100–600 atoms. The well-known enhancement over bulk values was found in free clusters, while a coating of Cu reduced the moment to roughly that found in bulk. With a coating of Co, however, the moment is comparable to that of free clusters. This is in close agreement with experiment. The behavior is interpreted as an increase in the effective exchange splitting on Fe resulting from the presence of Co atoms in the immediate environment. Most interestingly, we find that still further enhancement of the average Fe moment is possible if some Co atoms are introduced into the interface region of the Fe core.

The work points to the potential of the Fe/Co system in applications requiring a high magnetic density, and emphasizes the possibility of tailoring the properties of magnetic nanostructures by controlling the grain size and the composition of two component systems.

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