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J. Kortus

Center for Computational Materials Science

T. Baruah

Center for Computational Materials Science

M. R. Pederson

Center for Computational Materials Science

C. Ashman

Virginia Commonwealth University

Shiv N. Khanna

Virginia Commonwealth University, snkhanna@vcu.edu

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Magnetic moment and anisotropy in Fe_nCo_m clusters

J. Kortus,^{a)} T. Baruah,^{a)} and M. R. Pederson

Center for Computational Materials Science, Code 6390-Naval Research Laboratory, Washington, DC

C. Ashman and S. N. Khanna^{b)}

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

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Electronic structure calculations of Fe_nCo_m ($n+m=5$ and 13) are used to examine the effects of alloying on the magnetic moment and magnetic anisotropies. Our density-functional studies show that many mixed clusters have moments comparable to or higher than the pure clusters. The mixed clusters, however, have very low anisotropies and could be ideal as soft magnetic materials. It is shown that shape, composition, and compositional ordering must be considered for optimization of anisotropy energies. © 2002 American Institute of Physics. [DOI: 10.1063/1.1482793]

Extensive research over the past decade has shown that small clusters offer a class of magnetic properties. Clusters of itinerant ferromagnetic solids Fe, Co, and Ni have higher magnetic moments per atom than the corresponding bulk;¹ clusters of nonmagnetic solids like Rh are spin polarized;^{1,2} and atomic moments in clusters of Mn, which exhibits complex magnetic order in the bulk, are ferromagnetically aligned.^{3,4} The reduction in particle size also leads to new dynamical behaviors. For a particle with a size smaller than the typical magnetic domain size, the atomic moments are exchange coupled and the particles behave as a single magnet with a combined moment from the individual atoms. However, the anisotropy energy (AE) that determines the minimum energy required to reorient this combined magnetic moment decreases with size and typically becomes comparable to thermal energies in particles of about 10 nm. These particles then undergo superparamagnetic (SP) relaxation.^{5–8} A fundamental understanding of the magnetic anisotropy energy (MAE), which controls the onset of SP behavior is therefore requisite to the design of molecular scale magnets.

While there has been considerable effort in the past to understand the evolution of the magnetic moment, the few theoretical attempts to understand the MAE in clusters have been limited to semiempirical approaches.¹⁰ Recently Zhou *et al.*¹¹ have shown that the MAE in clusters and low-dimensional systems can be affected by the orbital-correlation terms. However in the absence of a precise recipe for derivation of the orbital-polarization or correlation correction within density-functional theory, the conclusions of these papers can best be regarded as informative albeit qualitative.

The purpose of this letter is to examine the magnetic moment and the magnetic anisotropy in small Fe_nCo_m clusters. Bulk FeCo alloys exhibit the highest saturation magnetization and the limiting value, occurring around 35% Co, known as the Slater–Pauling limit, has long been regarded as the highest possible magnetization. Can this limit be over-

come in clusters and, as a related issue, do the Fe_nCo_m clusters exhibit higher magnetization than pure Fe or Co clusters? The bulk alloys are used as soft magnetic materials due to their small magnetic anisotropy. The magnetic anisotropy of clusters is not known and the factors that control the magnetic anisotropy in these reduced sizes are not well understood. This line of inquiry is motivated by the possibility that the small anisotropy of the solid alloys may be enhanced by a chemical ordering of atoms in specialized geometries. To address these issues, we have carried out studies on several Fe_nCo_m clusters. Here, we present results on five and 13 atom clusters.

Our studies employed a linear combination of atomic-orbitals approach Naval Research Laboratory Molecular Orbital Library (NRLMOL)¹² within the generalized-gradient approximation (GGA)¹³ to the density-functional theory. The basis sets used contained 20 bare Gaussians with exponents varying from 0.0452 to $3.866\,748 \times 10^6$ for Fe and 0.048 28 to $4.208\,47 \times 10^6$ for Co contracted to 11 *s*-like, 5 *p*-like and 4 *d*-like orbitals resulting in 46 basis functions for each atom. This large basis set shows great stability and gives reliable geometries. Detailed information on the construction of the Gaussian basis sets can be found in Ref. 14.

One focus of the present work is the calculation of the MAE. The main contribution to this quantity comes from the spin–orbit coupling and except for the cases where the second-order term is zero (due to symmetry), the most significant contribution comes from this term. For intrinsically uniaxial or lower-symmetry systems such as those discussed here the second-order contribution to the MAE is given by the change in the second-order spin–orbit energy (Δ_2) as the angle (θ) between the axis of symmetry and the quantization axis varies between 0 and $\pi/2$. For lower-symmetry systems, the second-order MAE depends on two angles. We have just proposed an implementation of the spin–orbit coupling that uses the exact representation given by $U(\mathbf{r}, \mathbf{p}, \mathbf{S}) = -1/2c^2 \mathbf{S} \cdot \mathbf{p} \times \nabla \Phi(\mathbf{r})$. In addition to including some non-spherical contributions that would be absent in a standard $\mathbf{L} \cdot \mathbf{S}$ representation, the numerical implementation is particularly well suited to local-orbital methods such as NRLMOL.¹⁵ Please note, while the scalar relativistic corrections (mass velocity and Darwin terms) have a $1/c^2$ contri-

^{a)}Also at: Department of Physics-Georgetown University, Washington, DC 20057.

^{b)}Electronic mail: khanna@hsc.vcu.edu

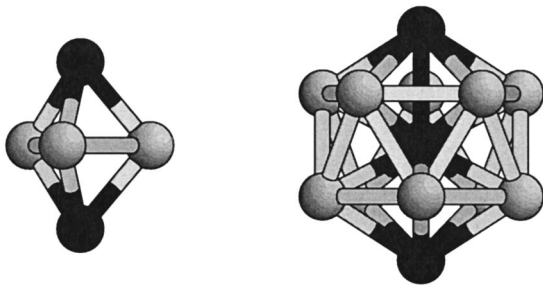


FIG. 1. The uniaxial geometrical configurations studied here include triangular bipyramid geometries ($N=5$) and distorted icosahedrons ($N=13$). For the mixed clusters, the dopant atoms were placed along the uniaxial axis.

tribution to the single-electron Hamiltonian, these terms do not effect the second-order MAE for systems with real Kohn–Sham orbitals.

Some of the intermediate 13-atom clusters studied here have either no or a very small energy gap. As such the second-order perturbation method discussed in Ref. 15 is not obviously applicable so an exact-diagonalization method was developed. For a simple comparison, we found that the $S = 3 \mu_B$ Fe_2 dimer has a second-order MAE of 5.36 K which is in good agreement with the 5.23 K result obtained from exact diagonalization.

In Fig. 1, we show the configurations studied in this work. The five- and 13-atom clusters are chosen because they allow for uniaxial structures. For pure uniaxial configurations, it is possible to further enhance the uniaxial character via substitution of different transition metal atoms along the axis of symmetry. This procedure allows for uniaxial clusters with compositions Fe_3Co_2 , $\text{Fe}_{10}\text{Co}_3$, Co_3Fe_2 , and $\text{Co}_{10}\text{Fe}_3$. For the smaller clusters ($N=5$), the uniaxially symmetric stable geometries have been further optimized for these stoichiometries with no symmetry constraints in order to find the influence of geometry on the MAE.

We start by comparing some of the present results with previous calculations. In Table I, we show the magnetic moments and the magnetic anisotropies of mixed Fe_nCo_m clusters. For Co_5 , our calculated ferromagnetic ground state has D_{3h} symmetry, a magnetic moment of $13\mu_B$ and a binding energy of 11.67 eV. Fan *et al.*¹⁶ have performed symmetry restricted density-functional calculations on Co_5 and find a C_{4v} ground state with a magnetic moment of $13\mu_B$ and a binding energy of 11.45 eV. Castro *et al.*, on the other hand, find a ground state with a moment of $9\mu_B$. The magnetic

TABLE I. Symmetry group, magnetic moments, MAE, and smallest highest occupied molecular orbital–lowest unoccupied molecular orbital gaps for the ground-state Fe_nCo_m 5 atom clusters. EA (EP) means easy-axis (plane). TA stands for a system with three different axes. Anisotropy energies have been calculated using both second-order perturbation expressions (Ref. 10) and exact diagonalization methods. The two methods agree to 0.5–1.0 K for all cases. The ^a indicates majority–minority gap,^b indicates minority–majority gap.

Cluster	Symmetry		Moment μ_B	MAE (K)	GaP (eV)
Co_5	D_{3h}	EA	13	6	0.41 ^a
Co_3Fe_2	D_s	TA	13	27/15	0.06 ^b
Co_2Fe_3	D_{3h}	EP	16	21	0.59 ^a
Fe_5	C_{2v}	EP	16	14	0.20 ^b

TABLE II. Magnetic moment and MAE for relaxed 13-atom clusters with three central atoms constrained along the z axis (MAE- z) and fully unconstrained (MAE) for the Fe_nCo_m clusters. For Co_{13} , the fully relaxed cluster has a moment of $21 \mu_B$.

Cluster	Moment (μ_B)	MAE- z (K)	MAE (K)
Co_{13}	21	0	0
$\text{Co}_{10}\text{Fe}_3$	30	56	63
$\text{Fe}_{10}\text{Co}_3$	41	51	9
Fe_{13}	44	41	41

moments of Co_m clusters calculated by these authors increase monotonically from Co_2 to Co_4 , but Co_5 has a lower moment than even Co_4 . Possibly, these authors did not examine higher spin states. For Fe_5 , our calculated moment is in agreement with earlier calculations by Castro *et al.*¹⁷ The bond lengths are slightly different and we find a binding energy of 11.86 eV as compared to their calculated values of 10.98 eV. Postnikov *et al.*,¹⁸ and Hobbs *et al.*,¹⁹ have carried out *ab initio* molecular dynamics simulations on Fe_5 using GGA and local density approximation (LDA). While Hobbs *et al.* find a moment of $14.00 \mu_B$ in the LDA, Postnikov *et al.*¹⁸ find a moment of $18.00 \mu_B$. For the GGA, Postnikov *et al.* and Hobbs *et al.*^{18,19} find moments of $18.00 \mu_B$. Since these studies are based on pseudopotentials, it is possible that the differences between these authors and the all electron calculation by us and Castro *et al.*¹⁷ are due to the treatment of the core.

In Ref. 8, moments as a function of size for large Fe, Ni, and Co clusters are measured. While the smallest clusters in these studies are still large compared to those discussed here a reasonable extrapolation of $2.6 \mu_B$ and $3.2 \mu_B$ for Co and Fe agrees well with the present results. The magnetic moments per atom in bulk Co and Fe are $1.72 \mu_B$ and $2.22 \mu_B$, respectively. Further, our predicted MAE for the pure clusters are well below room temperature. This is consistent with the Stern–Gerlach experiments on Fe_n and Co_n clusters cooled down to 77 K where the clusters are deflected in the same direction indicating a SP relaxation.⁹

We now discuss 13-atom clusters. We have investigated Co_{13} , $\text{Co}_3\text{Fe}_{10}$, $\text{Co}_{10}\text{Fe}_3$, and Fe_{13} clusters assuming C_{5v} and D_{2h} symmetries. For the mixed clusters, the substituted atoms have been added to preserve the uniaxial symmetry (Fig. 1). All 13-atom clusters are found to be easy-plane systems. The total magnetic moments obtained are given in Table II. It is seen that the magnetic moment increases as Co is substituted by Fe. In particular $\text{Fe}_{10}\text{Co}_3$ has a moment of $3.15 \mu_B/\text{atom}$ which is almost 35% higher than the Slater–Pauling limit. The question arises as to whether the clusters are magnetically softer or harder than the corresponding solids.

Starting from the Hamiltonian obtained from self-consistent field (SCF) calculations without spin–orbit coupling, we calculated the spin–orbit matrix elements as described in Ref. 15 and obtained the MAE from exact diagonalization. Our earlier studies have shown that the magnetic anisotropy is mainly determined by the mixing of electronic states close to the Fermi energy. To further illustrate this dependence, we introduced an electronic temperature that allows the occupation of unoccupied states. The calculated AE as a function of the broadening temperature is

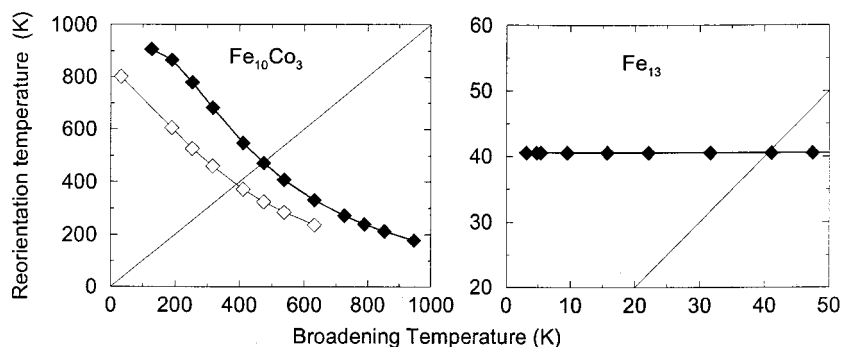


FIG. 2. Anisotropy energy as a function of electronic broadening temperature for clusters with imposed C_5 symmetry. The open squares for $\text{Fe}_{10}\text{Co}_3$ are results from SCF calculations at the same temperature as the broadening temperature. The intersection with the straight line corresponds to the moment reorientation temperature.

shown in Fig. 2. The results on the magnetic anisotropy at various electronic temperatures can also be used to estimate the blocking temperature, i.e., temperature above which the moments will reorient in different directions. This is given by the temperature at which the MAE becomes equal to the thermal energy.

The Fe_{13} cluster has a large energy gap of 0.2 eV, therefore temperature changes which are small compared to this gap will not change the occupation of states or the anisotropy. The $\text{Fe}_{10}\text{Co}_3$ cluster, however, showed a surprisingly high moment reorientation temperature of 480 K. However, this result was obtained only by varying the temperature for the spin-orbit coupling. A change in temperature for a metallic system also changes the SCF wave functions and energies. Therefore, we carried out SCF calculations at the same electronic temperature as used in the spin-orbit part, allowing for full electronic relaxation at that broadening temperature. The results are also shown in Fig. 2. The SCF anisotropy curve is now shifted downwards, resulting in a reorientation temperature of about 400 K.

Degeneracies at the Fermi level indicate possible Jahn-Teller relaxations, therefore we allowed for geometry relaxation by lowering symmetry constraints. First, we restricted the movement of the three central atoms along the z axis, all other outer atoms were symmetry unconstrained. The degeneracies at the Fermi level vanish and all clusters gain Jahn-Teller energy. Relaxing the symmetry has a dramatic effect on MAE, which decreases significantly. Removing all constraints, the largest change is found for the case of $\text{Fe}_{10}\text{Co}_3$. The axial arrangement of the Co atoms is lost and the MAE decreases significantly. Fe_{13} does not show any great changes in geometry or MAE as expected. Results for the MAE are given in Table II.

It is interesting to compare the aforementioned results with the bulk. $\text{Fe}_x\text{Co}_{1-x}$ alloys exhibit the highest magnetization at a Co concentration of around 30% and are associated with an increase in the local moment on Fe sites from a bulk value of $2.2 \mu_B/\text{atom}$ to almost $2.8 \mu_B/\text{atom}$ (Ref. 20) for Fe sites surrounding Co. In clusters, the Fe sites in Fe_{13} already have a moment of $3.38 \mu_B/\text{atom}$ and the addition of Co does not lead to any enhancement of the magnetic moment. However, the introduction of chemical ordering via three Fe atoms in $\text{Co}_{10}\text{Fe}_3$ and by three Co atoms in $\text{Fe}_{10}\text{Co}_3$ does increase the anisotropy compared to pure clusters when the atoms are constrained along the z axis. Similar behavior is also observed in five-atom clusters.

To summarize, the present studies show that the small

Fe_n and Fe_nCo_m clusters exhibit high magnetic moments per atom that are about 35% higher than the Slater-Pauling limit. However, the clusters have small magnetic anisotropy energies indicating that bulk magnetic alloys can be made softer by going to nanosizes. What is most surprising is that whereas bulk Co has a higher anisotropy than pure Fe or mixed Fe-Co alloys, Co_n clusters have the lowest anisotropy. The present work also shows that a high magnetic anisotropy requires a strong coupling between occupied and unoccupied states close to the Fermi energy. One possible way to accomplish this may be to generate unreactive, compositionally ordered uniaxial clusters with small gaps.

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