Structure and magnetic properties of Fe-Ni clusters

B. K. Rao, Susana Ramos de Debiaggi,* and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000
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Using a first-principles molecular-orbital approach, we study the equilibrium geometries and binding energies of small Fe-Ni clusters containing up to four Fe and four Ni atoms. We find that the clusters are ferromagnetic with magnetic moments enhanced relative to the bulk values. For some specific cluster sizes and compositions, different isomers (corresponding to different geometries and clearly different energies) are found to have the same magnetic moment. This behavior is in contrast to the common understanding that magnetism usually depends on the cluster geometry. Calculations have also been carried out by modeling $Fe_{n-1}Ni$ ($n = 2,9,15,27$) clusters as fragments of a bcc lattice to determine the preferred site of Ni and its effect on the magnetic properties. The results are used to analyze the recent experimental study of the magnetic properties of FeNi nanoparticles.

I. INTRODUCTION

Theoretical and experimental studies in the last two decades have demonstrated that magnetism of materials is strongly affected[1] by their dimensionality, size, and inter-atomic separation. This has been clearly illustrated in the studies of multilayers and gas phase atomic clusters where sizes can be controlled at the atomic level. The strong size dependence of cluster properties have opened new possibilities to design materials with specific and tailored properties.[2] In this sense, transition metal clusters are of special interest due to their central role in both magnetism and catalysis. Although mixed transition metal clusters can be produced, most of the current work being done in this area primarily involves systems containing only one atomic component. A systematic microscopic understanding of the properties of mixed transition metal clusters is still lacking.

The study of the magnetic properties of monoatomic ferromagnetic nanoparticles, and more generally low-dimensional systems such as surfaces and multilayers, has demonstrated that the magnetic moment is enhanced over the bulk value. The magnetic moment is quite sensitive to the overlap of the electronic distribution between neighboring sites, with the magnetic moment decreasing as the overlap increases.[3] Consequently, it is also expected that an increase of the coordination would tend to reduce the moment. Using a Stern-Gerlach magnet, Apsel et al.[4] have measured the effective moment of Ni_n clusters containing 5–740 atoms. By applying the superparamagnetic model,[5] the magnetic moments were found to be larger than the bulk value ($0.6 \mu_B$), and decreased monotonically with the size of the cluster. Similar results were also obtained earlier by de Heer and co-workers[6] on Fe, Co, and Ni clusters. Theoretical studies using both *ab initio*[3,7–10] and semiempirical tight-binding models[11] have qualitatively explained the experimental trend in homonuclear transition metal clusters. However, magnetic properties of mixed transition-metal clusters have not yet received similar attention.

In this paper, we present theoretical studies of the magnetic properties of mixed Fe-Ni clusters. The choice of this system was motivated by many interesting properties of Fe-Ni alloys. In the bulk phase, Fe-Ni alloys are among the most widely studied magnetic materials and they pose many anomalies as a function of composition. For example, in the ''Invar'' alloy phase[12] containing 36% Ni, the Fe-Ni alloy exhibits extremely small thermal expansion coefficient, maximum lattice constant, and maximum magnetic moment. To study how the magnetic properties of Fe-Ni alloy would behave in the nanophase; Li et al.[13] recently synthesized ultrafine particles by varying the alloy composition. The particle size ranged from 10 to 100 nm with a mean size of 30–40 nm. For Fe content below 60%, the authors found the particles to have fcc structure with a lattice constant around 3.5 Å while for larger Fe concentration, the particles had bcc structure with a much reduced lattice constant of around 2.8 Å. The most interesting result of their study, however, is that the saturation magnetization of the ultrafine particles of Fe-Ni was consistently lower than their bulk value for all range of composition studied. This is particularly surprising as one expects the particles to have higher magnetic moments with reduced size due to increasing number of surface atoms.

In order to explain this anomalous behavior, Guevara et al.[14] have investigated the magnetic properties of a Fe-Ni cluster in the Ni-rich region, near to the $FeNi_3$ composition by assuming that the cluster has the bulk structure with 47 Fe atoms and 178 Ni atoms. They used a tight-binding model with parameters taken from the bulk. The most stable solution they obtained is a ferromagnetic one, with an average magnetic moment of $1.25 \mu_B$ per atom, which is slightly larger than the bulk alloy value for that composition. The authors also found the existence of many antiferromagnetic solutions lying very close in energy to the ferromagnetic one. The authors have, however, cautioned the reader that due to the approximate nature of their calculations the energy differences may not be very accurate. However, they believed that the lowering of magnetization in the nanophase could be due to coexistence of ferro- and antiferromagnetic solutions. It should be remarked that other effects such as disorder and segregation, which were not taken into account, could also play a role in the decrease of the total magnetization of the system.

There are very few *ab initio* theoretical calculations in the literature on the properties of Fe-Ni clusters. Kaspar and Salahub[15] had earlier used molecular-orbital calculations with the self-consistent-field $X\alpha$ scattered-wave method to explain, from a molecular point of view, several of the Invar anomalies. For this, clusters containing 13 atoms ($Fe_{13}, Fe_{12}Ni, Ni_{13}$) were used as a model of the bulk. The presence of strongly antibonding majority-spin orbitals and nonbonding minority-spin orbitals at the Fermi level was shown to account for the anomalies in the Invar concentration range.

Small Fe-Ni clusters containing up to four atoms were later studied by Cheng and Ellis[10] using the discrete variational method and local-density approximation to the density-functional theory. Their aim was to determine effective many-body potentials (pairwise, three and four-body potentials) by fitting to the calculated binding energy as a function of interatomic distance. However, their results for the magnetic moment of Fe_2 and Ni_2 dimers are in disagreement with some recent theoretical results (see Table I).

In this paper we have studied the structural and magnetic properties of Fe-Ni clusters using *ab initio* self-consistent molecular-orbital theory[16] within the density-functional formulation. We present here two series of results. First, we examine the equilibrium geometries, binding energies, and magnetic moments of free $(FeNi)_n$ clusters with $n \leq 4$. In the second part, we model Fe-Ni clusters in the Fe rich composition range by considering them as a portion of the bulk phase having bcc symmetry. Our objectives have been to investigate if the magnetic moments of small FeNi clusters are indeed smaller than their bulk value and if there are energetically nearly degenerate isomers that exhibit antiferromagnetic ordering. The study of the equilibrium geometries will also enable us to see if there is any tendency of Fe and Ni to segregate, i.e., if Fe-Ni bonding is less favored over Fe-Fe and Ni-Ni bonding. By comparing the results of free clusters with those where clusters mimic the bulk structure, we can study the sensitivity of the magnetic moment to cluster topology. In the following, we discuss these results and their possible connection with related experimental measurements.

II. COMPUTATIONAL PROCEDURE

The calculations have been carried out using molecular-orbital theory where the cluster wave function was constructed as a linear combination of atomic orbitals centered at the atomic sites. The atomic orbitals were represented by a double numerical basis with added polarization function available in the DMOL software.[17] The total energies were calculated using the density-functional theory and generalized gradient approximation for the exchange-correlation potential. For the latter, we have used the Becke-Perdew-Wang form of the functional.[18]

We carried out two separate calculations. In the first, we have studied the equilibrium structure, energetics, and magnetic properties of free $(FeNi)_n$ clusters containing up to four Fe and Ni atoms. The geometries were optimized by relaxing the structures until the forces vanished at each atomic site.
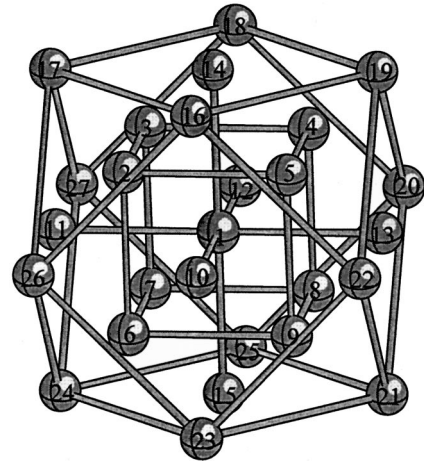

FIG. 1. A 27-atom cluster mimicking the bcc structure of the Fe-Ni alloy in the Fe-rich phase.

Different initial configurations were tried to examine if the clusters possess any nearly degenerate isomers.

In the second set of calculations, we studied the energetics and magnetic properties of $Fe_n, Fe_{n-1}Ni$ ($n=9, 15, 27$), and Fe_7Ni_2 clusters having a structure of that of the bcc phase of bulk iron. The energies of $Fe_{n-1}Ni$ clusters were then calculated by placing the Ni atom on successive shells (see Fig. 1). The objective was to see if Ni in a Fe nanoparticle would prefer to reside on the surface or within the bulk and if this preference affects the total magnetic moment of the cluster. In the following we present these results separately.

III. RESULTS AND DISCUSSIONS

A. Optimized geometries, electronic structure, and magnetic properties of $(FeNi)_n$ ($n \leq 4$) clusters

We begin with a discussion of the results on dimers: Fe_2, Ni_2, and FeNi. The present results are compared with some earlier calculations[7–10] using various levels of theory in Table I. The measured bond lengths of Fe_2 range from 1.75 Å to 2.04 Å, while that of Ni_2 is 2.16 Å. All calculated bond lengths agree well with the experiment.[19,20] For FeNi no experimental bond length is available, but our calculated value agrees well with those of Cheng and Ellis.[10] However, the magnetic moments of the dimers calculated by Cheng and Ellis are not in agreement with our calculations as well as those of earlier authors. It is important to note that the bond lengths of all the three dimers are very close to each other. However, there are marked differences between various calculations of the binding energy per atom. This disagreement in the binding energies occurs partly due to the errors in the energies of the free atoms as well as due to the treatments of the exchange-correlation energy functional. However, the relative energies of the isomers are expected to be influenced less since they do not involve inaccuracies in the energies of the free atoms.

In Fig. 2 we plot the equilibrium geometries of the $(FeNi)_n$ ($n \leq 4$) clusters. The resulting binding energies, $E_b = [E(Fe_nNi_n) - nE(Fe) - nE(Ni)]/n$ and magnetic moments per atom are given in Table II. We note that the geometry of

TABLE I. Binding energies per atom, bond lengths, and total magnetic moments for Fe_2, Ni_2, and FeNi dimers.

	Authors	Fe_2	Ni_2	FeNi
R_e(Å)	Present	2.02	2.14	2.08
	Ref. 7	2.00	2.10	
	Ref. 10	2.22	2.12	2.06
	Ref. 8	2.01		
	Ref. 9		2.13	
	Expt. (Refs. 19, 20)	1.73–2.04	2.16	
BE (eV)/atom	Present	1.70	2.83	2.33
	Ref. 7	1.62	1.74	
	Ref. 10	1.42	1.44	1.39
	Ref. 8	1.13		
	Ref. 9		1.31	
	Expt. (Refs. 19, 20)	0.61–1.28	2.07	
$\mu(\mu_B)$	Present	6	2	4
	Ref. 7	6	2	
	Ref. 10	8	2.28	6
	Ref. 8	6		
	Ref. 9		2	
	Expt. (Refs. 19, 20)	6	2	

TABLE II. Binding energies per atom and magnetic moments per atom of $(FeNi)_n$ clusters.

		BE (eV)/ atom	Magnetic moment (μ_B)/atom
FeNi	Fig. 2(a)	2.33	2
$(FeNi)_2$	Fig. 2(b)	3.19	2
$(FeNi)_3$	Fig. 2(c)	3.66	2.33
$(FeNi)_4$	Fig. 2(d)	3.73	2
$(FeNi)_4$	Fig. 2(e)	3.87	2

larger than the Ni_2 bond length of 2.14 Å in Table I. This implies that the relative bonding between Ni atoms in $(FeNi)_n$ clusters is weak and the stability of these clusters could be enhanced by promoting Fe-Fe and Fe-Ni bonds. We will see if that remains the case not only in larger $(FeNi)_n$ clusters but also in clusters used to model the bcc phase of bulk FeNi alloy. The total magnetic moment of $(FeNi)_2$ is 8 μ_B with 3.14 μ_B localized at each Fe site and 0.86 μ_B localized at each Ni site. The magnetic moments/atom in Fe_2 and Ni_2 are, respectively, 3 μ_B and 1 μ_B. Thus, Fe and Ni appear to retain their magnetic character as they would in very small homoatomic clusters.

Fe_3Ni_3 forms a three-dimensional structure. The evolution of this structure from that of $(FeNi)_2$ can be viewed by noting that the planar rhombus structure of $(FeNi)_2$ bends as the third Fe atom binds to two Fe atoms and one Ni atom in a tetrahedral coordination. The stability of this structure arises by maximizing the number of Fe-Ni bonds (there are six Fe-Ni bonds, while there are two Fe-Fe bonds and one Ni-Ni bond). The total magnetic moment of $(FeNi)_3$ is 14 μ_B with the magnetic moments at the three Fe and three Ni sites distributed as 3.63, 3.63, 3.44 μ_B and 1.13, 1.12, 1.06 μ_B.

We found two isomers of Fe_4Ni_4 with very different geometries. The lowest-energy structure [Fig. 2(e)] is 1.1 eV lower than its higher-energy isomer [Fig. 2(d)]. It should be pointed out that the ground-state geometry in Fig. 2(e) is again dominated by a propensity of Fe-Ni bonds (there are 8 Fe-Ni bonds while there are only two Fe-Fe and two Ni-Ni bonds). The higher-energy isomer [Fig. 2(d)], on the other hand, contains four Fe-Ni bonds, four Fe-Fe bonds, and four Ni-Ni bonds. A closer examination of the ground-state geometry of $(FeNi)_4$ in Fig. 2(e) reveals that it is built of two bent rhombus structures of $(FeNi)_2$, reminiscent of the structure in Fig. 2(b), lying on top of each other. Since we observed the appearance of the same structure in Fig. 2(c), it indicates that the $(FeNi)_2$ may be a building block in larger $(FeNi)_n$ clusters. Building blocks are usually energetically more preferred structures. This is also the case here. From Table II we see that the gain in the binding energy per atom in adding an FeNi pair increases by 0.86 eV in going from FeNi to $(FeNi)_2$, while it increases only by 0.47 eV from $(FeNi)_2$ to $(FeNi)_3$ and 0.18 eV from $(FeNi)_3$ to $(FeNi)_4$. Thus, $(FeNi)_2$ can be considered as a magic number and hence the building block of larger clusters.

The magnetic moment per atom of both the isomers of $(FeNi)_4$ have the same magnetic moment, namely, 2 μ_B.

the $(FeNi)_2$ is planar with a Fe-Ni distance of 2.29 Å and Fe-Fe distance of 2.16 Å. Note that these distances are close to their respective dimer values given in Table I. However, the Ni-Ni distance in $(FeNi)_2$ is 4.04 Å, which is much
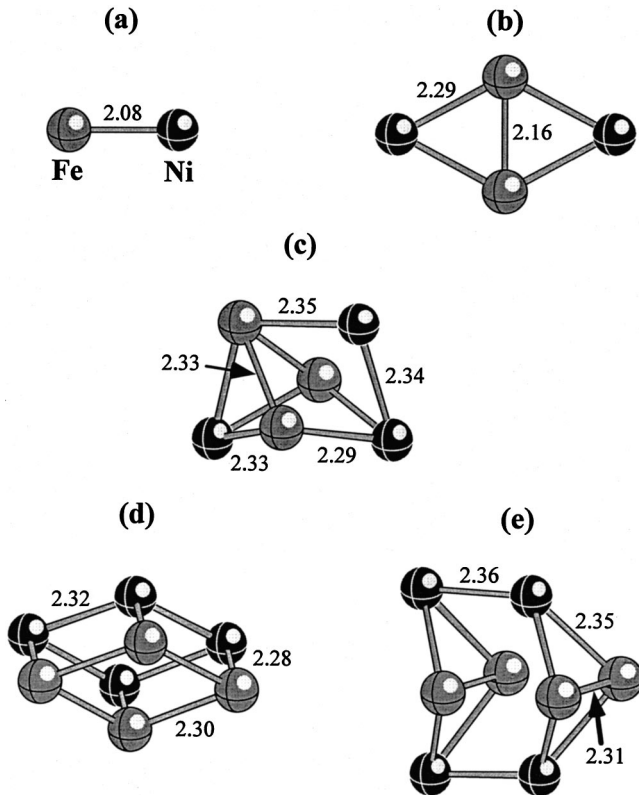

FIG. 2. Equilibrium geometries of $(FeNi)_n$ ($n \leqslant 4$) clusters. For Fe_4Ni_4, geometries of two isomers with close energies are given.
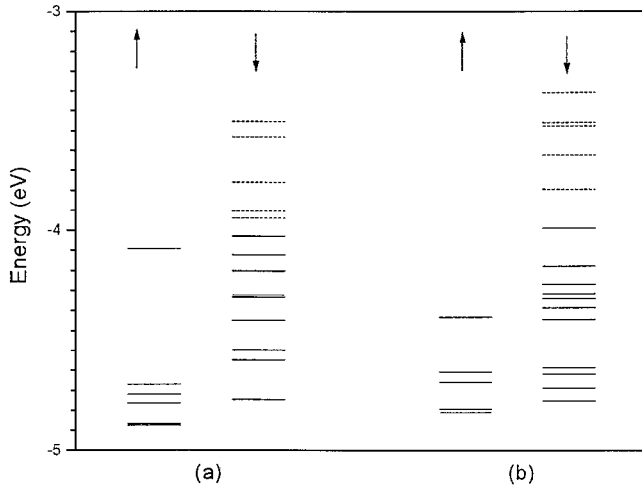
FIG. 3. Molecular-orbital energy levels of majority and minority spin states of (FeNi)$_4$ isomers—(a) higher-energy state, (b) ground state.

This is rather unusual, as it is well known that the geometry of a cluster has strong effect on its magnetic moment. To understand this anomaly, we plot in Fig. 3 the molecular-orbital energy levels for majority and minority spin states of these two isomers. The highest occupied molecular orbital (HOMO) corresponding to minority spin ($\downarrow$) electrons of the ground-state isomer plotted in Fig. 3(b) is 0.4 eV above the HOMO of the majority spin ($\uparrow$). This energy difference is large and as the structure changes to a different isomer, it is unlikely that the rearrangement in the spin $\uparrow$ and spin $\downarrow$ levels can significantly influence the total population of the two spin states. This is what indeed happens. As seen from Fig. 3(a), the HOMO of spin $\uparrow$ electrons move to higher energy while those of spin $\downarrow$ move slightly lower. But this does not affect the total population of either spin state. Hence the magnetic moments of both the isomers remain unchanged.

What we find interesting in these small clusters is that the magnetic moments are not only larger than their bulk composition, but they also remain insensitive to their size. More importantly, the magnetic moment per FeNi pair remains at $4\mu_B$ of which Fe retains nearly $3\mu_B$. We found no evidence of an antiferromagnetic coupling in these clusters nor the segregation of like atoms. As expected, the magnetic moments in the cluster phase remain larger than that in the bulk phase for bimetallic systems, which at the 50:50 Fe-Ni composition is about $3.5\ \mu_B$/pair.

B. Fe$_n$Ni clusters as models of the bcc crystalline phase

In this part, we have confined Fe$_{n-1}$Ni clusters to assume the bcc structure of Fe (Fig. 1). The lattice constant was chosen to be that of bulk Fe, which is 2.87 Å. We have considered clusters containing 9, 15, and 27 atoms. The preferred site of Ni was obtained by minimizing the total energy with respect to all possible sites that Ni could assume. We first discuss results on pure Fe clusters since these have been studied for Fe$_9$ and Fe$_{15}$ clusters earlier by other authors.[21,22] In Table III we compare our calculated moments with earlier results. We note that the binding energy per atom increases

TABLE III. Binding energies per atom and magnetic moments per atom in Fe$_9$, Fe$_{15}$, and Fe$_{27}$ clusters.

System	B.E. (eV)/atom	Magnetic moment/atom (μ_B)		
		Present	Ref. 22	Ref. 21
Fe		4.0		
Fe$_9$	2.70	2.89	2.89	2.89
Fe$_{15}$	3.61	3.20	2.67	2.93
Fe$_{27}$	3.67	2.96		

monotonically with cluster size and for the Fe$_{27}$ cluster, the binding energy per atom of 3.67 eV is somewhat smaller than the bulk cohesive energy of 4.28 eV. The magnetic moment atom agrees with previous first-principles calculations.[21,22] Although the magnetic moment per atom decreases with cluster size as expected, for the Fe$_{27}$ cluster (i.e., $2.96\mu_B$), it is still larger than the bulk value of $2.2\mu_B$. This is because clusters contain a large proportion of surface atoms. Thus, the magnetic moments of Fe clusters in the cluster phase are larger than the bulk value irrespective of their geometry. This is also borne out in the experimental study of the gas phase clusters.[6] Note that the magnetic moments of ultrafine Fe-Ni particles measured by Li et al.[13] is consistently smaller than their bulk values for all ranges of composition, i.e., the magnetic moments of pure Fe nanoparticles and pure Ni nanoparticles measured by Li et al., are also smaller than their respective bulk values. This is not only in disagreement with previous theory but also with the experiment on gas phase clusters. This suggests that the observed reduction in the magnetization must be due to other factors. We will discuss this possibility later in the section.

To study the effect of Ni substitution in the Fe lattice, we have replaced the Fe on the central (site #1) and on successive layers in the Fe$_n$ clusters (Fig. 1). The total energies and corresponding magnetic moments of these clusters were calculated without relaxing the geometry. The resulting binding energies, E_b defined as

$$E_b = [E(\text{Fe}_{n-1}\text{Ni}) - (n-1)E(\text{Fe}) - E(\text{Ni})]/n$$

and the magnetic moment per atom are given in Table IV. As pointed out earlier in the discussion of the FeNi dimer, the replacement of a Fe atom by Ni increases the binding energy by 1.26 eV and lowers the magnetic moment by $2\mu_B$. In the Fe$_8$Ni cluster, we have calculated the energy difference and changes in the magnetic moment by replacing the Fe atom at the central site (#1) and first-layer site (#2). Table IV shows that while the energy is gained in both cases, replacing the Fe atom on the first layer by Ni in Fe$_9$ is 0.98 eV more preferable than that when the central Fe is replaced. The changes in the magnetic moments, on the other hand, remain unaffected, namely, the total moment is lowered by $2\mu_B$ in both cases. It is energetically preferable for Ni to occupy the surface site of a cluster.

In Fe$_{14}$Ni, Ni has been assigned to occupy the central site (#1) or the outer layer sites (#2 and #10). The binding energy results in Table IV again shows that it is energetically favor-

TABLE IV. Binding energy and magnetic moment of $Fe_{n-1}Ni$ clusters ($n=2, 9, 15, 27$) with Ni occupying various sites shown in Fig. 1. The binding energy is defined as $E_b=[E(Fe_{n-1}Ni)-(n-1)E(Fe)-E(Ni)]/n$.

System	B.E. (eV)/atom			Magnetic moment (μ_B)/atom			$\Delta\mu=\mu(Fe_{n-1}Ni)-\mu(Fe_n)(\mu_B)$	
Ni site:	#1	#2	#10	#1	#2	#10	#1	#2
FeNi	2.33			2.0			−2.0	
Fe_8Ni	2.74	2.85		2.67	2.67		−2.0	−2.0
$Fe_{14}Ni$	3.65	3.66	3.69	3.07	3.07	3.07	−2.0	−2.0

able for Ni to occupy the surface site and this occupancy is 0.54 eV more preferable than the central site. Once again, the magnetic moments of these clusters are unaffected by the precise site occupied by Ni and the magnetic moment of $Fe_{14}Ni$ is lowered by $2\mu_B$ compared to that of Fe_{15}. We have also studied a $Fe_{26}Ni$ cluster by replacing the central Fe site with a Ni atom. While the cluster gains 0.77 eV, its magnetic moment is again lowered by $2\mu_B$.

From the above studies several conclusions can be made. (1) The substitution of a surface Fe atom by Ni is preferred for all clusters studied and the net energy gain ranges between 0.5 eV to 1.3 eV. (2) The magnetic moment of a $Fe_{n-1}Ni$ cluster is $2\mu_B$ less than a Fe_n cluster independent of the location of the Ni atom. (3) The average magnetic moment per atom of a $Fe_{n-1}Ni$ cluster is larger than their bulk values.

C. Ni site distribution in a Fe_7Ni_2 cluster

In order to determine if the successive addition of Ni atoms to a Fe cluster having the bulk bcc phase would lead the Ni atoms to form nearest neighbors, and the possible role this could play on the resulting magnetic moment, we have studied various forms of the Fe_7Ni_2 cluster. Here the two Ni atoms could assume four different configurations: sites 1, 2; 2, 3; 2, 7; and 2, 8 in Fig. 1. The Ni atoms occupying sites 1 and 2 would form nearest neighbors. The separation between Ni atoms would continually increase as they occupy sites 2 and 3, sites 2 and 7, or sites 2 and 8. The binding energies per atom of these four different configurations along with the resulting magnetic moment per atom are given in Table V. The binding energies of Fe_7Ni_2 clusters with two Ni atoms occupying the cube corners are nearly the same whether the Ni atoms are nearest neighbors (sites 2 and 3), next nearest neighbors (sites 2 and 7), or farther apart (sites 2 and 8) as

TABLE V. Total binding energy (defined as the energy needed to dissociate the cluster into individual atoms) and magnetic moments/atom of Fe_7Ni_2 cluster with the Ni pair occupying four possible configurations of a bcc cluster shown in Fig. 1.

Site occupation of Ni pair	Total B.E. (eV)	Magnetic moment (μ_B)/atom
#1, #2	26.11	2.67
#2, #3	27.03	2.44
#2, #7	26.96	2.44
#2, #8	27.00	2.44

seen in Fig. 1. The reason for this surprising result is that in each case the number of nearest-neighbor Fe-Ni bonds is the same, i.e., two. Note that it is energetically unfavorable for Ni atoms to become nearest neighbors as the configuration with Ni atoms occupying sites 2 and 3 is about 0.9 eV higher. We had earlier observed the same trend in small Fe-Ni clusters where the geometries were fully optimized. Thus, we believe that in large FeNi clusters and nanoparticles, segregation of Ni atoms is unlikely. On the other hand, Ni atoms are expected to occupy the surface sites of a Fe cluster as long as they do not form nearest neighbor for a given composition.

We also find from Table V that the magnetic moment of Fe_7Ni_2 for the energetically preferable configurations is reduced by $4\mu_B$ from that of the Fe_9 cluster. Thus, for every Ni that replaces a Fe atom, the magnetic moment is reduced by $2\mu_B$. However, the total magnetic moment of a Fe_xNi_y cluster is still larger than the bulk phase with the same composition.

IV. CONCLUSIONS

Using density-functional theory and generalized gradient approximation, we have calculated the equilibrium geometry, binding energies, and magnetic properties of FeNi clusters, for different sizes and Ni content. Two different series of calculations have been performed: $(FeNi)_n$ ($n\leq4$) clusters with fully optimized geometries and $Fe_{n-1}Ni$ ($n=9, 15, 27$) clusters as fragments of a bulk bcc lattice.

The equilibrium geometries found for small $(FeNi)_n$ clusters have a large number of FeNi bonds, and energetically preferable isomers are those where Fe-Ni bonds are maximized. All clusters are found to be ferromagnetic. A remarkable result, which contrasts the behavior found for certain homoatomic systems, is the fact that the magnetic moment per atom of these clusters are almost insensitive to the specific geometry of the clusters. In all cases, the magnetic moment is higher than the bulk value and almost constant; $2\mu_B$/atom.

In $Fe_{n-1}Ni$ ($n=9, 15,$ and 27) clusters mimicking the bulk bcc structure, we found that the system is ferromagnetic with magnetic moments higher than the bulk value. The magnetic moment of a $Fe_{n-1}Ni$ cluster is $2\mu_B$ less than a Fe_n cluster, independent of the location of the Ni atom. More importantly, this reduction is independent of the location of the Ni atom. For low Ni concentration, Ni prefers to move toward the surface as observed from the point of view of the energetics.

The closest experimental results to compare with are those of Li *et al.*, which refer to nanometer FeNi particles. Their measurements reveal a decrease of the saturation magnetization in the whole composition range of Ni content, which is opposite to our finding. It should be pointed out that the experiment deals with a powder sample, and it has been suggested by Guevara and Llois[14] that the anomaly in the magnetic behavior in ultrafine particles could come from phase segregation, antiferromagnetic coupling of Ni and Fe, or defects. It should be pointed out that the measurements of the saturation magnetization of pure nanocrystalline Fe (6-nm size) revealed a reduction by about 40% relative to the saturation magnetization of bulk α-Fe.[23] This reduction is attributed to a number of factors; the interatomic spacing in the interfacial region are different from bulk α-Fe, the boundary regions differ structurally and chemically from the crystalline state, and the orientation of magnetization between two neighboring nanocrystallites is governed by anisotropy and magnetic interaction across the interface. In our studies, such factors do not arise as we are dealing with isolated clusters.

Our *ab initio* calculations indicate that Ni segregation, at least for low Ni content, is energetically not favored. More importantly, the Ni-Ni distance does not change the magnetic properties of the cluster, which remains ferromagnetic and with a magnetic moment higher than the bulk. We also found no evidence of antiferromagnetic coupling between Fe- and Ni sites. From Fig. 8 in Ref. 13, it can be observed that even in the pure (homoatomic) ultrafine particles (pure Ni and Fe particles) the magnetic moments are reduced with respect to the bulk values. This result is in clear contradiction with the trend observed for free clusters, due to the enhanced magnetism of surface atoms. The present calculations for small FeNi clusters as well as the earlier one for a larger cluster ($Fe_{47}Ni_{178}$), using tight-binding empirical approximation,[14] indicate that the magnetic moments in isolated nanoparticles are enhanced, not reduced. It is well known that nanoparticles of magnetic elements exhibit superparamagnetic behavior and in the free clusters the observed magnetic moment in a Stern-Gerlach experiment[4] is known to be less than its intrinsic magnetic moment. Thus, further experimental and theoretical studies on FeNi clusters in the gas phase and ultrafine particles will be very worthwhile.

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*Permanent address: Dpto. De Fisica, Universidad Nacional del Comahue, Buenos Aires 1400, 8300 Neuquen, Argentina.

[1] F. Liu, M. R. Press, S. N. Khanna, and P. Jena, Phys. Rev. B **39**, 6914 (1989) and references therein.

[2] B. K. Rao, S. N. Khanna, and P. Jena, J. Cluster Sci. **10**, 477 (1999).

[3] B. V. Reddy, S. K. Nayak, S. N. Khanna, B. K. Rao, and P. Jena, J. Phys. Chem. A **102**, 1748 (1998).

[4] S. E. Apsel, J. W. Emmert, J. Deng, and L. A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996).

[5] S. N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).

[6] I. M. L. Billas, A. Chatelain, and W. A. de Heer, Science **265**, 1682 (1994).

[7] M. Castro, C. Jamorski, and D. R. Salahub, Chem. Phys. Lett. **271**, 133 (1997).

[8] B. Nash, B. K. Rao, and P. Jena, J. Chem. Phys. **105**, 11 020 (1996).

[9] S. E. Weber and P. Jena, Chem. Phys. Lett. **281**, 401 (1997).

[10] H.-P. Cheng and D. E. Ellis, J. Chem. Phys. **94**, 3735 (1991).

[11] A. N. Andriotis, N. Lathiotakis, and M. Menon, Chem. Phys. Lett. **260**, 15 (1996).

[12] C. E. Guillaume, C. R. Acad. Sci. **125**, 235 (1897).

[13] X. G. Li, A. Y. Chiba, and S. Takahashi, J. Magn. Magn. Mater. **170**, 339 (1997).

[14] J. Guevara and A. M. Llois, Rev. Mexicana Fis. **44**, 22 (1998).

[15] J. Kaspar and D. Salahub, Phys. Rev. Lett. **47**, 54 (1981).

[16] W. J. Hehre, J. L. Radom, P. V. R. Scheleyer, and J. A. Pople, *Ab initio Molecular Orbital Theory* (Wiley, New York, 1986).

[17] DMOL CODE, Biosym Technologies, Inc., San Diego, CA, 1995.

[18] W. Kohn and L. J. Sham, Phys. Rev. **136**, B864 (1964); P. Hohenberg and W. Kohn, Phys. Rev. **140**, A1133 (1965); A. D. Becke, Phys. Rev. A **38**, 3098 (1988); J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1991).

[19] H. Purdum, P. A. Montano, G. K. Shenoy, and T. Morrison, Phys. Rev. B **25**, 4412 (1982); D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, *ibid.* **32**, 7290 (1985); S. S. Lin and A. Kant, J. Phys. Chem. **73**, 2450 (1969); I. Shim and K. A. Gingerich, J. Chem. Phys. **77**, 2490 (1982); L. Lian, C.-X. Su, and P. B. Armentrout, *ibid.* **97**, 4072 (1992).

[20] J. Ho, M. L. Polak, K. M. Ervin, and W. C. Lineberger, J. Chem. Phys. **99**, 8542 (1993).

[21] L. Keeyung, J. Callaway, and S. Dhar, Phys. Rev. B **30**, 1724 (1984).

[22] Y. Yang, K. H. Johnson, D. R. Salahub, J. Kaspar, and R. P. Messmer, Phys. Rev. B **24**, 5673 (1981).

[23] See review by H. Gleiter in Nanostruct. Mater. **1**, 1 (1992).