Structural and magnetic properties of Fe-Ni clusters

G. Rollmann∗, S. Sahoo∗∗, and P. Entel∗∗∗

Institute of Physics, University of Duisburg–Essen, Duisburg Campus, Lotharstr. 1, 47048 Duisburg, Germany

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Structural and magnetic properties of single-elemental and mixed 5-atom and 13-atom icosahedral-like Fe-Ni clusters of different compositions have been calculated in the framework of density functional theory in the generalized gradient approximation. We have allowed for a non-collinear magnetization density and full relaxation of the atoms without imposing any symmetry constraints. We find that the the lowest-energy structures are given by distorted geometries with a maximum number of Fe–Fe bonds and a small number of Ni–Ni bonds, and the subsequent maximization of Fe–Fe and Fe–Ni bonds is suggested as a rule to predict the arrangement of the atoms in any lowest-energy isomer of an Fe-Ni cluster. Although for special geometries we obtain antiferromagnetic-like ground states with strongly reduced magnetic moments, the most stable clusters are characterized by collinear, ferromagnetic alignments of the spins.

1 Introduction

The possibility to design new magnetic materials with unique properties tailored to fit the specific needs in the desired application is very fascinating and of utmost technological importance. Nanostructured materials can provide a key for this as quantum effects in the nanometer regime leads to many physical and chemical properties showing a strong size dependence. One example for this is the magnetic moment per atom of magnetic transition metal (TM) clusters, which for small particles is not just given by a simple interpolation between the bulk value and the value for an isolated atom, but shows some oscillatory behavior with pronounced peaks for certain cluster sizes [1, 2].

A very promising field of application for nanoparticles are ultrahigh-density magnetic storage devices which make use of the natural self-organization of magnetic particles on a substrate. To achieve this purpose, a detailed understanding of the properties of magnetic nanoparticles is inevitable. But although certain properties of free clusters can be measured directly nowadays, experimental information about small, size-selected TM clusters is still very limited. Concerning pure Fe clusters, e.g., the bond length has only been measured for the dimer [3], while harmonic vibrational frequencies have been obtained for Fe2 and Fe3 [4]. Geometries of larger Fe clusters have not yet been determined experimentally. Magnetic moments of unsupported Fe, Co and Ni clusters have been measured down to clusters containing approximately 20 atoms using a Stern-Gerlach apparatus [1], but the error bars in particle size are of the order of 10%. In similar experiments, Apsel et al. have obtained magnetic moments of Ni clusters containing as little as 5 atoms with uncertainties in the moments of around 5% [2]. Extensive data come from laser photoionization and photoelectron spectroscopy studies, in which ionization potentials and electron affinities of small, size-selected magnetic TM clusters containing up to about 35 and 100 atoms have been measured [5].

∗ Corresponding author: e-mail: georg@thp.uni-duisburg.de, Phone: +49 203 379 1073, Fax: +49 203 379 5173

** e-mail: sanjub@thp.uni-duisburg.de, Phone: +49 203 379 1606, Fax: +49 203 379 3665

*** e-mail: entel@thp.uni-duisburg.de, Phone: +49 203 379 3330, Fax: +49 203 379 3665
The major part of information about the structure and morphology of small magnetic clusters comes from computational studies. Due to the development of highly accurate yet very effective numerical methods and a massive increase in computer capacities, it is now possible to investigate properties of small magnetic clusters with ab initio methods. However, in most works only mono-atomic systems have been considered (for an overview see [6, 7] and references therein). The presence of more than one species in a cluster greatly increases the complexity of the subject, thereby making the treatment by computational methods based on first principles difficult, but at the same time gives rise to interesting phenomena and the appearance of new and sometimes unique properties of the clusters.

Single-elemental Fe and Ni pentamers have been subject to a considerable number of theoretical investigations [8–20]. For Fe\textsubscript{5}, there seems to be general agreement about the geometry of the lowest-energy isomer. Whereas in an early work a square pyramidal structure of \( C_{4v} \) symmetry has been proposed [8], most recent calculations yield a ground state geometry of \( D_{3h} \) or \( C_{2v} \) symmetry, corresponding to an ideal or a distorted trigonal bipyramid [9,11–13,15–16,18–20]. The associated total magnetic moment varies from 14 to 16 \( \mu_B \) in calculations employing the local density approximation (LDA) to DFT, whereas it is increased to 16 to 18 \( \mu_B \) when gradient corrections are added. Fe\textsubscript{5} is the only Fe cluster for which a noncollinear magnetic ground state has been proposed [15, 16, 19]. The authors obtain a ferromagnetic (FM) alignment of the local moments of the atoms in the basal plane of the bipyramid, with the moments of the apical atoms canted by approximately \( \pm 31^\circ \) in opposite directions. But it could be shown that this magnetic structure is related to the assumption of \( D_{3h} \) symmetry, and that the moments are again collinear when the cluster is allowed to fully relax into a Jahn-Teller distorted \( C_{2v} \) geometry [7]. Regarding the Ni pentamer, the number of theoretical works based on first principles is smaller. By using the LDA, Reuse et al. find a trigonal bipyramidal structure with 8 \( \mu_B \) [10], Castro et al. and Reddy et al. obtain the same symmetry, but a smaller magnetic moment of 4 \( \mu_B \), with GGA [13, 14]. A value of 1.6 \( \mu_B \) per atom found experimentally [2] is in better agreement with the former result.

Due to the different behavior of Fe and Ni atoms in the pure clusters, the study of composite Fe-Ni clusters is very promising with respect to unusual and new properties, also because the corresponding bulk system shows a variety of composition-dependent anomalies and unusual effects. But in spite of this, we are not aware of any extensive, systematic theoretical investigation of mixed Fe-Ni clusters in the literature. The electronic structure of small Fe-Ni clusters containing up to four atoms altogether were calculated by Cheng and Ellis [21]. Rao et al. have studied clusters of the form (FeNi)\textsubscript{n} with \( n \leq 4 \), and also body-centered cubic (bcc) Fe\textsubscript{n−1}Ni fragments of the bulk lattice containing 9, 15 and 27 atoms [22]. They find that all clusters are FM, with magnetic moments independent of the specific cluster geometry. Concerning the small clusters, their main conclusion is that the lowest-energy isomers possess the largest number of Fe-Ni bonds. Regarding the bcc clusters, they find that the preferred position for Ni atoms is at the surface, and that for two Ni atoms it is energetically unfavorable to occupy nearest-neighbor positions.

In this paper we report results of ab initio calculations regarding geometric structure, morphology and magnetism of Fe-Ni clusters of different compositions. In the following Section the computational method is explained, after that we report in Sec. 3 results for 5-atom and icosahedral 13-atom Fe-Ni clusters in Sec. 3. We conclude by giving an outlook regarding future activities in this field.

2 Computational details

The calculations were performed in the framework of density functional theory (DFT) [23] in combination with the generalized gradient approximation (GGA) for the description of exchange and correlation effects in a functional form proposed by Perdew and Wang [24]. For each Fe (Ni) atom a number of eight (ten) valence electrons was taken into account, the remaining core electrons together with the nuclei were described by pseudopotentials following the projector augmented wave method [25] as implemented in the Vienna ab initio simulation package [26]. We have adopted periodic boundary conditions and used cubic supercells with sides of 11 Å for the 5-atom and 12 Å for the 13-atom clusters. The energy cutoff for the
plane-wave basis set was kept fixed at a value of 270 eV throughout the calculations. Integration over the Brillouin zone was done using the Γ-point only.

Geometries of the clusters were optimized by using the conjugate gradient method starting from several different initial structures. During the simulations the atoms were allowed to relax fully without imposing any symmetry constraint. We have also allowed for a non-collinear magnetization density as described in [16]. Local magnetic moments were obtained by integrating the magnetization density inside spheres of radius 1.2 Å around Fe and Ni atoms. We have calculated the degree of distortion \( \delta \) of a given cluster consisting of \( N \) atoms according to the formula

\[
\delta = \sqrt{\frac{2}{N(N-1)} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left( r_{ij} - r_{ij}^0 \right)^2 \left( r_{ij}^0 \right)^2}.
\]

(1)

Here, \( r_{ij} \) denotes the distance between atoms \( i \) and \( j \) in the cluster under consideration, while \( r_{ij}^0 \) is the distance between the same atoms in a certain reference cluster. In this work, these reference clusters were taken to be perfect trigonal bipyramids and icosahedra, respectively, with interatomic distances given by a linear interpolation between the distances in the corresponding mono-atomic, symmetric clusters, according to the composition. In case of the pure clusters, this reduces to geometry-optimized Fe\(_{13}\), Ni\(_{13}\), Fe\(_{13}\), and Ni\(_{13}\) clusters under \( I_h \) and \( D_{3h} \) symmetry constraints.

3 Results and discussion

3.1 5-atom clusters

In our calculations, we have considered all possible compositions of mixed Fe\(_n\)Ni\(_{5-n}\) clusters and have relaxed all clusters fully without symmetry restrictions, starting from different trigonal-bipyramidal-like arrangements of the atoms. The lowest-energy isomers found in our calculations are depicted in Fig. 1, detailed information on structure and magnetism is given in Table 1. The different nature of Fe and Ni

![Fig. 1](image)

Fig. 1 Ground state geometries, magnetic moments and distortions of Fe\(_n\)Ni\(_{5-n}\) clusters. Blue spheres mark Fe atoms, orange spheres represent Ni atoms. All clusters show distorted structures with the degree of distortion given in Table I.
Table 1  Energetic, magnetic and structural properties of the lowest-energy isomers of FeₙNi₅₋ₙ clusters (see Fig. 1). Binding energies are given in eV per atom, total and site-projected (spheres of 1.2 Å) magnetic moments for the Fe and Ni atoms in µ₅B, and distortions δ calculated according to Eq. (1) in %.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Eₜₐₜ</th>
<th>Mₜₜₜ</th>
<th>⟨Mₐₖ⟩</th>
<th>⟨Mₐₖ⟩</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₅</td>
<td>2.40</td>
<td>4.00</td>
<td>—</td>
<td>0.77</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe₁Ni₄</td>
<td>2.77</td>
<td>8.00</td>
<td>3.35</td>
<td>0.90</td>
<td>2.53</td>
</tr>
<tr>
<td>Fe₂Ni₃</td>
<td>3.13</td>
<td>11.98</td>
<td>3.41</td>
<td>1.09</td>
<td>3.17</td>
</tr>
<tr>
<td>Fe₃Ni₂</td>
<td>3.47</td>
<td>12.00</td>
<td>3.02</td>
<td>0.81</td>
<td>1.12</td>
</tr>
<tr>
<td>Fe₄Ni₁</td>
<td>3.74</td>
<td>16.00</td>
<td>3.21</td>
<td>1.06</td>
<td>3.86</td>
</tr>
<tr>
<td>Fe₅</td>
<td>3.95</td>
<td>16.03</td>
<td>2.90</td>
<td>—</td>
<td>4.61</td>
</tr>
</tbody>
</table>

becomes clear when comparing our results for the pure clusters. For Ni₅, we have found a nearly perfect trigonal bipyramid as ground state structure (in agreement with previous calculations mentioned above), followed by a square pyramid (C₄ᵥ symmetry) 3.4 meV per atom higher in energy. In contrast to that, the lowest-energy structure of Fe₅ shows a very large Jahn-Teller-like distortion of 4.6%, which is mainly due to an increase of one of the sides of the basal triangle from 2.38 to 2.68 Å, and a decrease in height of the pyramid (the distance between the two apical atoms) from 3.76 to 3.67 Å. The corresponding trigonal-bipyramidal state is characterized by a non-collinear arrangement of the magnetic moments, and is located 10.8 meV per atom higher in energy (see also [16, 15]).

The degree of distortion of the composite clusters is increasing when the number of Ni atoms is decreased, the only exception being Fe₂Ni₂. The lowest-energy structures are all characterized by a maximization of the number of Fe atoms located in the central triangle of the cluster. This can be interpreted as a subsequent maximization of the number of Fe–Fe and Fe–Ni bonds (or a minimization of the number of Ni–Ni bonds), or maximum trend of segregation. Note that for most compositions of bulk FM Fe-Ni alloys experiment and ab initio total-energy calculations [27] show phase segregated bcc Fe and L1₂ FeNi₃, whereby chemical clustering is encouraged on the Fe-rich side, while weak spinodal ordering occurs for the Ni-rich side of the phase diagram. For the clusters, mixing and unmixing tendencies can be related to optimum bond formation of Fe atoms as shown in the following.

The lowest-energy state for Fe₁Ni₄ is a trigonal-bipyramidal structure where the Fe atom is located in the central triangle. This can be interpreted as a subsequent maximization of the number of Fe–Fe and Fe–Ni bonds (or a minimization of the number of Ni–Ni bonds), or maximum trend of segregation. Note that for most compositions of bulk FM Fe-Ni alloys experiment and ab initio total-energy calculations [27] show phase segregated bcc Fe and L1₂ FeNi₃, whereby chemical clustering is encouraged on the Fe-rich side, while weak spinodal ordering occurs for the Ni-rich side of the phase diagram. For the clusters, mixing and unmixing tendencies can be related to optimum bond formation of Fe atoms as shown in the following.

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When another Fe atom is added, the lowest-energy structure is again determined by the fact that the Fe atoms occupy positions in the central triangle, separated by a distance of 2.41 Å. A similar structure of C₂ᵥ symmetry, which more resembles a pyramidal arrangement of the atoms, is located 23.6 meV per atom higher in energy and has a longer Fe–Fe bond length of 2.80 Å. The case of one Fe atom in the central triangle and the other occupying an apical position as well as the structure when both Fe atoms are at the top and bottom positions of the pyramid are again much higher in energy (71 and 87 meV per atom, respectively). We note that the number of Fe–Fe, Fe–Ni and Ni–Ni bonds in the lowest-energy structure is (1,6,2), compared to (1,5,3) and (0,6,3) in the isomers of higher energy.

This trend is continued as the number of Fe atoms in the cluster increases. The ‘bonding pattern’ of the ground state of Fe₃Ni₂ is (3,6,0), while the other isomers, where Fe atoms occupy apical positions, are
characterized by (3,5,1) (+69 meV) and (2,6,1) (+142 meV). Interestingly, the distortion of this cluster is lower than would be expected from the series with increasing number of Fe atoms. A detailed analysis of the energy levels would be necessary to obtain a deeper understanding of this phenomenon, but this will not be discussed here.

Finally, for Fe₄Ni₁, we find the geometry with the Ni atom at the top of the bipyramid most stable, compared to the situation when it is located in the central triangle. In the former case, the number of Fe–Fe bonds is 6, and the number of Fe–Ni bonds is 3, while it is 5 and 4 in the latter case. The energy difference of 71 meV per atom between the two isomers is quite large, which again supports the idea that the number of Fe–Fe bonds is maximal in the ground state structure. The distortion of the cluster is mainly due to a reduction of the total height and increased distances between the Fe atoms in the central triangle. In fact, with values of 3.56 Å and 2.48 Å, Fe₄Ni₁ is the most compact of all Fe-Ni pentamers.

So when we compare our results to those of Rao et al., we first note that we obtain practically the same magnetic properties of the clusters, i.e., FM alignments of the spins with approximately 3 μB per atom for Fe and 1 μB per atom for Ni. We also observe that Ni atoms do not prefer positions in the central parts of the clusters, and that Ni–Ni bonds are avoided.

But in contrast to their suggestion that the number of Fe–Ni bonds is decisive, we rather find that the number of Fe–Fe bonds seems to be more important for the determination of the ground state of a cluster with a given composition. We are led to this conclusion by a number of observations. First, for Fe₂Ni₃ the (1,5,3) isomer is more stable than the (0,6,3) isomer. A similar relationship holds for the Fe₃Ni₂ cluster, with (3,5,1) being lower in energy than (2,6,1). Finally, for Fe₄Ni₁ the ground state is given by a (6,3,0) structure, and not by a (5,4,0) arrangement of the atoms. This idea will also be tested in the next Section for a different type of Fe-Ni cluster.

### 3.2 13-atom clusters

In Fig. 2 the result of geometry optimization of Fe₁₃ with and without icosahedral symmetry constraints is shown. For the perfect icosahedron, the energy minimum corresponds to a center-to-shell distance of 2.395 Å and a total magnetic moment of 44 μB. In the following, this geometry will be referred to as the ‘symmetric Fe₁₃’ cluster. When the atoms are allowed to relax freely, the total energy is lowered considerably, but the local magnetic moments are essentially unchanged. While the value for the central atom is in the range of the bulk value of 2.2 μB, the surface atoms show enhanced moments of more than 3 μB. The degree of distortion of the relaxed cluster becomes apparent when looking at the middle panel, where the interatomic distances of the ideal and the relaxed icosahedron are compared. The value of δ calculated according to Eq. (1) is 1.9%.

Interestingly, when the central atom is taken out of the cluster leaving Fe₁₂, the distortion is reduced again, as shown in the right panel of Fig. 2. The open circles in this diagram correspond to the distances in the ideal, icosahedral Fe₁₂ cluster with an optimized center-to-shell distance of 2.275 Å, which is slightly shorter than in the symmetric Fe₁₃ cluster. The distortion of the relaxed Fe₁₂ cluster calculated by Eq. (1) is only 0.57%.

The lowest-energy states of both Fe₁₂ and Fe₁₃ are characterized by FM, collinear alignments of the local magnetic moments. But in the latter case, we have been able to stabilize an AF-like state 37.8 meV per atom above the FM ground state. The corresponding total magnetic moment of 34 μB is strongly reduced compared to the FM solution. This is partly due to the change in sign of the magnetic moment of the central atom (-1.9 μB compared to +2.6μB), but also to a reduction of the surface moments from +3.1μB to +2.8μB. The distortion of the AF cluster is with 2.1% comparable to the one of the FM cluster.

A different situation is found for the corresponding icosahedral, pure Ni clusters. The geometry of the Ni₁₃ cluster relaxed without symmetry constraints deviates only very little from the perfect icosahedral structure (center-to-shell distance of 2.32 Å). The distortion is only 0.69 %, the energy difference 1.5 meV per atom. The magnetic ground state is also FM, for this cluster we did not succeed to obtain a selfconsistent AF solution.
As was already shown in the preceding Section, the mixing of Fe and Ni atoms leads to a variety of phenomena, which are not observed in the corresponding pure clusters. An extensive investigation across the whole composition range of 13-atom Fe-Ni clusters is far beyond the scope of this work, so we restrict ourselves to one example, namely the presence of two Ni atoms in the cluster. In the following we will try to find an answer to the question, what the preferred sites for these two atoms are and whether a change in their positions has any effect on experimentally observable quantities like magnetic moments.

So we have taken into account all four possibilities of distributing the two Ni atoms on the icosahedron. The corresponding relaxed structures are depicted in Fig. 3, ordered in energy with respect to the ground state, which corresponds to a geometry where the Ni atoms occupy nearest-neighbor positions on the

**Table 2** Structural and magnetic properties of the four different Fe$_{13}$Ni$_2$ clusters (see Fig. 1 for labeling of the clusters). Energies are given in meV/atom relative to the lowest-energy structure, total and site-projected magnetic moments are in $\mu_B$, and distortions $\delta$ calculated according to Eq. (1) in %.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Energy</th>
<th>M$_{total}$</th>
<th>M$_{center}$</th>
<th>M$_{surface}$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.00</td>
<td>36.0</td>
<td>1.99 (Fe)</td>
<td>2.85 $\sim$ 3.05</td>
<td>3.13</td>
</tr>
<tr>
<td>(b)</td>
<td>5.92</td>
<td>36.0</td>
<td>1.87 (Fe)</td>
<td>2.80 $\sim$ 3.05</td>
<td>4.50</td>
</tr>
<tr>
<td>(c)</td>
<td>9.00</td>
<td>40.0</td>
<td>0.83 (Ni)</td>
<td>3.09 $\sim$ 3.11</td>
<td>1.00</td>
</tr>
<tr>
<td>(d)</td>
<td>18.08</td>
<td>30.1</td>
<td>-0.66 (Fe)</td>
<td>2.78</td>
<td>2.07</td>
</tr>
</tbody>
</table>

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surface. Energies, magnetic moments and distortions of the clusters are given in Table 2. For all isomers we obtain FM ground states characterized by a fully collinear magnetization density. The only exception is cluster (d) with the two Ni atoms opposite to each other. In this case, the magnetic moment of the central Fe atom is antiparallel to all other moments, which leads to a strong reduction of the total magnetic moment of the cluster.

When we compare our results to the results of the calculation on bcc-like Fe$_7$Ni$_2$ by Rao et al. [22], we note that in contrast to their observation, that the structures where the Ni atoms occupy any pair of corner atoms of the cube, are energetically nearly degenerate, we find that the nearest-neighbor case in our calculation is definitely preferred. Another difference is, that the geometry with one Ni atom in the center of the cube is found to be very high in energy, compared to a moderate shift in this study for the icosahedral geometry. So while Rao et al. come to the conclusion that segregation of Ni atoms is unlikely to occur for large clusters and nanoparticles, our results suggest that segregation effects play a role.

![Energy per atom](image)

**Fig. 3** Energetic relationships and magnetic moments of the four considered isomers of the Fe$_{11}$Ni$_2$ cluster. Dark spheres mark Fe atoms, light spheres represent Ni atoms. The FM cluster (a) is lowest in energy with two Ni atoms as nearest neighbors in the icosahedral shell. Clusters (b)-(c) are also FM but have higher energies, cluster (d) has the central spin reversed.

### 4 Conclusion

Total energies, geometries and magnetic properties of pure Fe and Ni and composite Fe-Ni clusters have been calculated. Although for some special structures we find AF ground states, all lowest-energy isomers are characterized by a collinear, FM magnetization density. All clusters exhibit some degree of distortion, which is more pronounced as the number of Fe atoms increases. Regarding 5-atom clusters, we observe that in the structures with the lowest total energy the number of Fe–Fe bonds is maximal, while the
number of Ni–Ni bonds is minimal. This suggests that the geometric structure of the energetic ground state of an Fe–Ni cluster is determined by a subsequent maximization of Fe–Fe and Fe–Ni bonds. This criterion was also fulfilled for Fe\textsubscript{11}Ni\textsubscript{2} clusters, in which the lowest-energy structure corresponds to a segregated cluster where the Ni atoms occupy nearest-neighbor positions on the surface. The variety of different results obtained for a single cluster and other results of TM clusters not discussed here show that further calculations are required especially with respect to promising storage materials consisting of (Fe, Co)-Pt clusters.

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