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Structures and stabilities of small $Fe_{6-x}Ni_x$ clusters

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The structures and stabilities of $Fe_{6-x}Ni_x$ (x=0-5) clusters have been systematically studied at the BPW91 level in density functional theory. Theoretical results show that the doping of Ni atoms do not change the rectangular bipyramid of Fe_6 cluster, and structural features are determined by the ratio between the number of Ni atoms and Fe atoms. When the number of Ni atoms is less than 3, $Fe_{6-x}Ni_x$ clusters have the similar high stability as Fe_6. However, the stabilities of cluster decrease when the number of Ni atoms is equal or larger than 3.

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1. Introduction

Transition-metal (TM) clusters are a subject of particular interest due to their reactivity, electronic, magnetic and catalytic properties. Therefore, many experimental and theoretical studies have already been carried out on TM clusters. For nickel clusters, Reuse *et al.* [1] systematicall studied Ni_n (n=2-6, 8, 13) clusters using an approach based on a linear combination of atomic orbitals and molecular orbitals within the density functional formalism. Menon *et al.* [2] obtained the optimized geometries of Ni_n (n=2-10) clusters using the tight-binding approximation in molecular dynamics. Grigoryan *et al.* [3] systematically studied the energetics, structure, growth, and stability of Ni_n (n=2-150) clusters by a combination of the embedded-atom method in the version of Daw, Baskes, and Foiles, the variable metric/quasi-Newton method, and the Aufbau/Abbau method. Ma *et al.* [4-5] have studied the electronic structures of small Ni_n, Co_n and Fe_n (n=2-3) clusters using first-principles calculations based on the density functional theory.

For iron clusters, Wang *et al.* [6-7] studied the electron affinity of Fe_n (n=1-34) clusters using Photoelectron Spectroscopy. Loh *et al.* [8] studied the binding energies of iron cluster ions (1^+) (Fe_n^+) (n=2-10) with xenon by using Collision-induced dissociation. On the theoretical side, Ouyang *et al.* [9] studied the geometrical structures of small Fe_n clusters at the UB3LYP/Lanl2dz level; Ballone and Jones [10] performed DFT-LSDA calculations based on the Car-Parrinello (CP) method [11] to predict the structures and magnetic moments of Fe_n clusters; Gutsev *et al.* [12] used several different functionals in DFT to study the Fe_n (n=2-6) clusters; Diéguez *et al.* [13] performed an extensive study of the structures, binding energies, and magnetic moments of Fe_n clusters up to n=17 using a fully self-consistent DFT-based method; Köhler *et al.* [14] investigated magnetic and structural properties of iron clusters up to Fe_{32} using a density-functional based tight-binding scheme.

The studies on bimetallic clusters have also been received great attention. Their chemical and physics properties may vary the composition and atomic ordering as well as the size of the clusters [15]. Though large advances have been made in experimental physics to produce measurable quantities of size selected clusters, it lacks the ability to directly explore and assign cluster geometries and discriminate between possible isomers [16].

Recently, with the appearance of the DFT theory which has the ability to directly explore and assign cluster geometries and discriminate between possible isomers, some meaningful improvements have been achieved in the property studies of not only TM atoms but also mixed clusters including TM atoms. For example, extensive DFT studies have been done on Cu-Co clusters [17], Ag-Ni clusters [18] and La-Ni clusters [19] so on.

For Fe-Ni alloy clusters, we have successfully studied Structures of small $Fe_{n-1}Ni$ (n=2-7) Clusters using the BPW91 method in DFT [20]. In this paper, we investigate geometric structures of the bimetallic nanoclusters $Fe_{6-x}Ni_x$ (x=0-5) using the same method. In addition, we also analyze their stabilities (vertical ionization potential(VIP), highest occupied molecular orbital(HOMO), lowest unoccupied molecular orbital(LUMO), as well as the HOMO-LUMO difference) as a function of the size and chemical compositon.

2. Computational method

In this paper, $Fe_{6-x}Ni_x$ (x=0-5) microclusters have been investigated theoretically by applying BPW91 method [21] as proposed by Gutsev and Bauschlicher [22]. In addition, Chrétien and Salahab [23] have also proved the BPW91 level provides remarkably good agreement with experiment.

The LanL2DZ basis sets is selected to describe Fe and Ni atoms, because the LanL2DZ basis sets are capable of providing results of very satisfactory and reasonable quality for the geometries, stabilities, and spectroscopic properties of the TM compounds or clusters [24,25,26] with deviations of typically 1-6%.

We have successfully studied Fe_n (n=2-8) clusters [27] and $Fe_{n-1}Ni$ (n=2-7) clusters [20] using BPW91 method and LanL2DZ, especially for Fe_n (n=2-8) clusters, the theoretical results agree well with the experimental data. Therefore, the BPW91 method combining with LanL2DZ basis sets is the most effective level of theory available for the analysis of TM metallic systems.

All density functional calculations have been done using the Gussian98 program package [28], and the optimized geometries are further verified by frequency calculations (no negative frequency).

3. Results and discussion

Equilibrium structure: We examine various possible isomers of $Fe_{6-x}Ni_x$ (x=0-5) clusters at the BPW91 level, and the optimized stable structures are shown in Fig. 1. For any given size clusters, the structures are shown according to the energy from low to high and represented by *xa*, *xb*, *xc* and so on, of which *x* is the number of Ni atoms, *a* always `represent the ground state of $Fe_{6-x}Ni_x$ clusters, b, c and so on is relative energies (in eV) with respect to that of the lowest-energy structures.

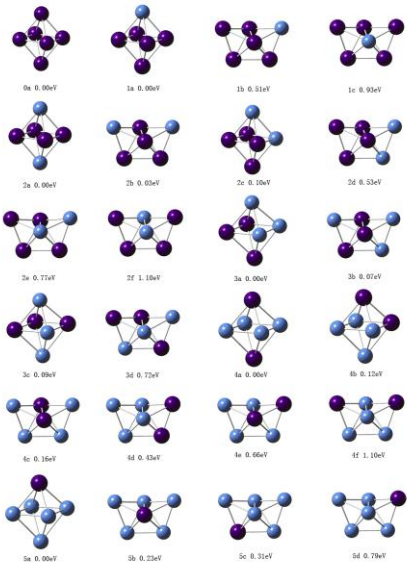

Fig. 1. Low-energy isomers for $Fe_{6-x}Ni_x$ (x=0-5) clusters at the BPW91 level. The deep blue and blue balls represent iron atoms and nickel atoms, respectively. The number under the structure is relative energies (in eV) with respect to that of the corresponding lowest-energy isomers

For Fe_5Ni, the ground state is the same rectangular bipyramid as that of Fe_6 cluster, other two stable configurations(2b and 2c) are represented that the cap atom or the side atom of the capped trigonal bipyramid replaced by an Ni atom, respectively. Fig. 1 shows that the energy of 2b and 2c structure is 0.51eV and 0.93eV, obviously, the 2b structure is more stable than 2c, which is indicated that Ni atom tend to occupy the surface site of Fe_6 cluster. For Fe_4Ni_2, structure 2a and 2b have higher stability than other isomers, of which structure 2a is the rectangular bipyramid, while structure 2b is the capped trigonal bipyramid. The two stable structures have in common is that the Fe atoms tend to be gathered and Ni atoms seem to be located around a Fe core with a maximum of Fe-Ni bonds. From Fig. 1, it can be seen that the energy difference between structure a and b is very small which is only 0.03eV. To further determined the ground state, we calculated the ionization energy of structure 2a and 2b, and the responding results are 6.53eV and 6.21eV, respectively. Obviously, structure 2a is more stable than 2b, which is indicated that the doping of Ni atoms do not change the ground state of Fe_6 cluster.

For Fe_3Ni_3, the ground state is still the rectangular bipyramid. Differently, Fe atoms and Ni atoms all tend to be gathered together. More interestingly, Ni atoms are brought together, and the iron atoms seem to be located around a Ni core for Fe_2Ni_4 and $FeNi_5$.

In a word, although the doping of Ni atoms does not change the rectangular bipyramid of Fe_6 cluster, the configuration are determined by the ratio between the number of Ni and Fe atoms. When the number of Ni atoms is less than the number of Fe atoms, Fe atoms tend to be gathered together, and Ni atom tend to be located around a Fe core with a maximum of Fe-Ni bonds. When the number of Ni atoms is the same as Fe atoms, Fe atoms and Ni atoms all tend to be gathered together. When the number of Ni atoms is larger than Fe atoms, the Ni atoms tend to be gathered, setting a Ni core, with outer Fe atoms.

Stabilities: To further analyze the stabilities for $Fe_{6-x}Ni_x$ (x=0-5) clusters, the vertical ionization potential(VIP), the highest occupied molecular orbital(HOMO), lowest unoccupied molecular orbital(LUMO), and the HOMO-LUMO difference for the most stable clusters at their ground state geometry as the chemical composition are studied, and the corresponding theoretical results are listed in Table 1.

VIP is an useful quantity for determining the stability of clusters. It is defined as the total-energy difference of the neutral cluster and the ionized cluster with same geometry as the neutral. From Table 1, it can be seen that the VIPs take on oscillation tendency when the number of Ni atoms is less than 3, and maxima is found at x=1, indicating Fe_5Ni have higher stability than other clusters, which is consistent with the result of $Fe_{n-1}Ni$(n=2-7) cluster in Ref. [20]. But the VIPs decrease as the number of Ni atoms increases when the number of Ni atoms is equal or larger than 3.

In addition, the HOMO, LUMO as well as HOMO-LUMO difference are also useful quantities for examining the stability of clusters. From Table 1, We can found the the HOMOs for Fe_5Ni and Fe_4Ni_2 are smaller than that of Fe_3Ni_3, Fe_2Ni_4 and $FeNi_5$, and are very near to that of Fe_6, while the LUMOs for Fe_5Ni, Fe_4Ni_2 and Fe_3Ni_3 are higher than that of Fe_2Ni_4 and $FeNi_5$, and closer to that of Fe_6. Generally speaking, the HOMO is smaller and the LUMO is higher, the cluster is more stable. Therefore, it is clear that Fe_5Ni and Fe_4Ni_2 clusters have higher stability than Fe_3Ni_3 Fe_2Ni_4 and $FeNi_5$ clusters. The same conclusion can be obtained by the HOMO-LUMO difference. It can be seen from Table 1, the HOMO-LUMO differences for Fe_5Ni and Fe_4Ni_2 are 2.31eV and 2.32 eV, respectively, which is closer to Fe_6 cluster (2.34eV). However, the HOMO-LUNO differences decrease sharply when the number of Ni atom is up to 3, even reach 0.39 eV for Fe_2Ni_4 and 0.32 eV for $FeNi_5$.

Table 1. Calculated energies of the most stable clusters of $Fe_{6-x}Ni_x$ (x=0-5)

Cluster	VIP(eV)	HOMO(eV)	LUMO(eV)	HOMO-LUMO gap(eV)
Fe_6	6.45	-0.16281	-0.07695	2.34
Fe_5Ni	6.49	-0.16593	-0.08097	2.31
Fe_4Ni_2	6.44	-0.16615	-0.08084	2.32
Fe_3Ni_3	6.39	-0.15570	-0.08200	2.00
Fe_2Ni_4	6.24	-0.15639	-0.14219	0.39
$FeNi_5$	6.15	-0.15556	-0.14407	0.32

Obviously, the stabilities of $Fe_{6-x}Ni_x$ is associated with the number of Ni atoms. when the number of Ni atom is less than 3, the stability of $Fe_{6-x}Ni_x$ is very close to that of Fe_6, but when the number of Ni atoms is equal or even larger than 3, the stabilities decrease as the number of Ni atoms increases.

4. Conclusion

In this paper, we investigated the geometries and stabilities of nickel doping on small iron clusters by using BPW91 method. All calculated results are summarized as follows:

(i) The doping of nickel atoms do not change the lowest-energy structure of Fe_6 cluster. (ii) The geometric structure of the clusters is determined by the ratio between the number of Fe and Ni atoms. When the number of Ni atoms is less than iron atoms, Fe atoms tend to be gathered together, and Ni atom tend to be located around a Fe core with a maximum of Fe-Ni bonds. When the number of Ni atoms is the same as Fe atoms, Fe atoms and Ni atoms all tend to be gathered together. When the number of Ni atoms is larger than Fe atoms, the Ni atoms tend to be gathered, setting a Ni core, with outer Fe atoms. (iii) Similar to the results of VIPs, the HOMO, LUMO and the HOMO-LUMO difference are directly related to the adoping number of Ni atoms. When the number of Ni atoms is equal or larger than 3, the stabilities of $Fe_{6-x}Ni_x$ decrease as the number of Ni atoms increases.

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