

## Structures of Small $\text{Fe}_{n-1}\text{Ni}$ ( $n = 2-7$ ) Clusters: A Density Functional Theory Study

SHUAIQIN YU<sup>1,\*</sup>, XIANGFENG JIA<sup>2</sup>, LIHUA DONG<sup>1</sup> and YANSHENG YIN<sup>1</sup>

<sup>1</sup>Institute of Marine Materials Science and Engineering, Shanghai Maritime University, Shanghai 201306, P.R. China

<sup>2</sup>School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan 250101, Shandong Province, P.R. China

\*Corresponding author: E-mail: sqyu@shmtu.edu.cn; shuaiqinyu0827@yahoo.com.cn

(Received: 14 October 2010;

Accepted: 27 December 2010)

AJC-9432

All possible geometrical structures of  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters were optimized at the BPW91 level in density functional theory. Theoretical results show that the Ni atom prefers to occupy the surface site and does not change the frame structures of iron atoms. Further, we analyze the stability of the lowest-energy structures for  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters and the corresponding results of the second difference in energy, the vertical ionization potential as well as the HOMO-LUMO energy gap show that the  $\text{Fe}_3\text{Ni}$  has special stability.

**Key Words:** Density functional theory, BPW91 method,  $\text{Fe}_{n-1}\text{Ni}$  cluster, Electronic property.

### INTRODUCTION

The studies on bimetallic clusters have been received great attention<sup>1</sup>. Their surface structures, compositions and segregation properties are of interest as they are important in determining chemical reactivity and have led to widespread applications in electronics, engineering and catalysis<sup>2</sup>. 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<sup>3</sup>.

Of particular interest was Fe-Ni bimetallic clusters due to their unique mechanical and magnetic properties. In addition, studies on small metal clusters are important as the high catalytic activity of metal Ni and Fe. They provide a link between the molecular state and the solid state. Moreover such study will provide a clear insight into its structure stability and its growth mechanism<sup>4</sup>. However, theoretical studies of transition metal clusters have been difficult due to the presence of *d* electrons, with complicated electronic ground state structure and with different spin multiplicities<sup>5</sup>. Especially for Fe and Ni clusters, the energies between different spin multiplicities states are so close that determining the ground state structures is always complicated and a challengeable work<sup>6</sup>. In addition, the study of Fe and Ni clusters is complicated by their ferromagnetic nature and there exists several spin states to be investigated<sup>7</sup>.

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 transition metal atoms<sup>8-12</sup> but also mixed clusters including transition metal atoms. For example, extensive density functional theory studies have been done on Cu-Co clusters<sup>13</sup>, Ag-Ni clusters<sup>14</sup> and La-Ni clusters<sup>15</sup> so on.

In this paper, we investigate the structural properties of small  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters using the BPW91 method in density functional theory. Our main objective is to determine the stable geometrical structures with their electronic states of binary  $\text{Fe}_{n-1}\text{Ni}$  clusters. This information will be useful to understand the enhanced catalytic activity and selectivity gained by using Ni-doped iron catalyst.

### COMPUTATIONAL METHOD

All density functional calculations have been done using the GAUSSIAN 98 program package<sup>16</sup>. Geometry optimizations without symmetry constraints are performed with the BPW91 method<sup>17</sup> as proposed by Gutsev and Bauschlicher<sup>18</sup> and Chrétien and Salahab<sup>19</sup> who have proved the BPW91 level provides remarkably good agreement with experiment. The optimized geometries are further verified by frequency calculations (no negative frequency).

In this paper, the LanL2DZ basis sets is selected to describe Fe and Ni atoms. The LanL2DZ basis sets become widely used in chemistry, particularly in the investigation of compounds or clusters containing heavy elements<sup>20-22</sup>. On the other hand, it has been demonstrated that the LanL2DZ basis sets are capable of providing results of very satisfactory and reasonable quality for the geometries, stabilities and spectroscopic properties of the transition metal compounds or clusters<sup>20,22,23</sup> with deviations of typically 1-6 %.

To test reliability of the method and basis sets, we calculate the bond lengths of  $\text{Fe}_2$  and  $\text{Ni}_2$  clusters and obtained the theoretical value 2.03 and 2.13 Å which is consisted with the corresponding experimental values of 2.02<sup>24</sup> and 2.16 Å<sup>25</sup>.

## RESULTS AND DISCUSSION

**Equilibrium structure:** We examine the various possible isomers of  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters at the BPW91 level and the optimized stable structures are shown in Fig. 1. For  $\text{Fe}_2\text{Ni}$ , we optimize three structures, including an equilateral triangle and two linear chains. Finally, it is identified that  $\text{Fe}_2\text{Ni}$  takes an isosceles triangle with an apex angle of 67.6° as its ground state. Another stable structure obtained during the process of optimization is a linear-chain structure (Fe-Fe-Ni) which is 0.98 eV lower than that of the ground state in energy. It is indicated that iron clusters tend to go together which is similar to that of  $\text{Fe}_2\text{Al}$ <sup>26</sup>.

The lowest-energy structure of  $\text{Fe}_3\text{Ni}$  is an edge-capped tetrahedron, which is the first 3D configuration among  $\text{Fe}_{n-1}\text{Ni}$  clusters. A number of initial configurations are considered to obtain the ground state of  $\text{Fe}_4\text{Ni}$  clusters, the optimized results show that the most stable structure is the Ni atom occupying the apex of the trigonal bipyramid which is 0.40 eV lower in energy than the structure 4b. Clearly, the Ni atom prefers to occupy the surface site.

The natural electron configurations of Fe and Ni atoms are  $3d^64s^2$  and  $3d^84s^2$ , respectively. Because they contain more valence electrons, so they are more suitable to grow towards higher-dimensional configuration. Therefore, only several three-dimensional structures are considered to be optimized for  $\text{Fe}_5\text{Ni}$ . Those stable structures obtained are arranged as the order of energy is shown in Fig. 1(5a-5c), of which the rectangular bipyramid is the ground state. Other two stable configurations (5b and 5c) are represented that the cap atom or the side atom of the capped trigonal bipyramid is replaced by an Ni atom, respectively. Fig. 1 shows that 5b structure is 0.42 eV lower than 5c in energy, which indicates Ni atom tend to occupy the surface site that further confirms the conclusion mentioned above. The lowest-energy structure of  $\text{Fe}_6\text{Ni}$  is obtained by replacing an side atom of the pentagonal bipyramid for  $\text{Fe}_7$  cluster. It is seemly indicate that the Ni atom has tendency to become a part of clusters starting at  $n = 7$ .

In a word, the doping of a Ni atom does not change the ground states of  $\text{Fe}_n$  clusters listed in Ref.<sup>8</sup>. Moreover, the iron atoms tend to go together and the Ni atom prefers to be located around iron atoms.

**Electronic properties:** The stability of these clusters can be discussed on the basis of the binding energy per atom ( $E_b$ ) and the second difference in energy ( $\Delta^2E$ ) and they are defined as formula 1 and 2.

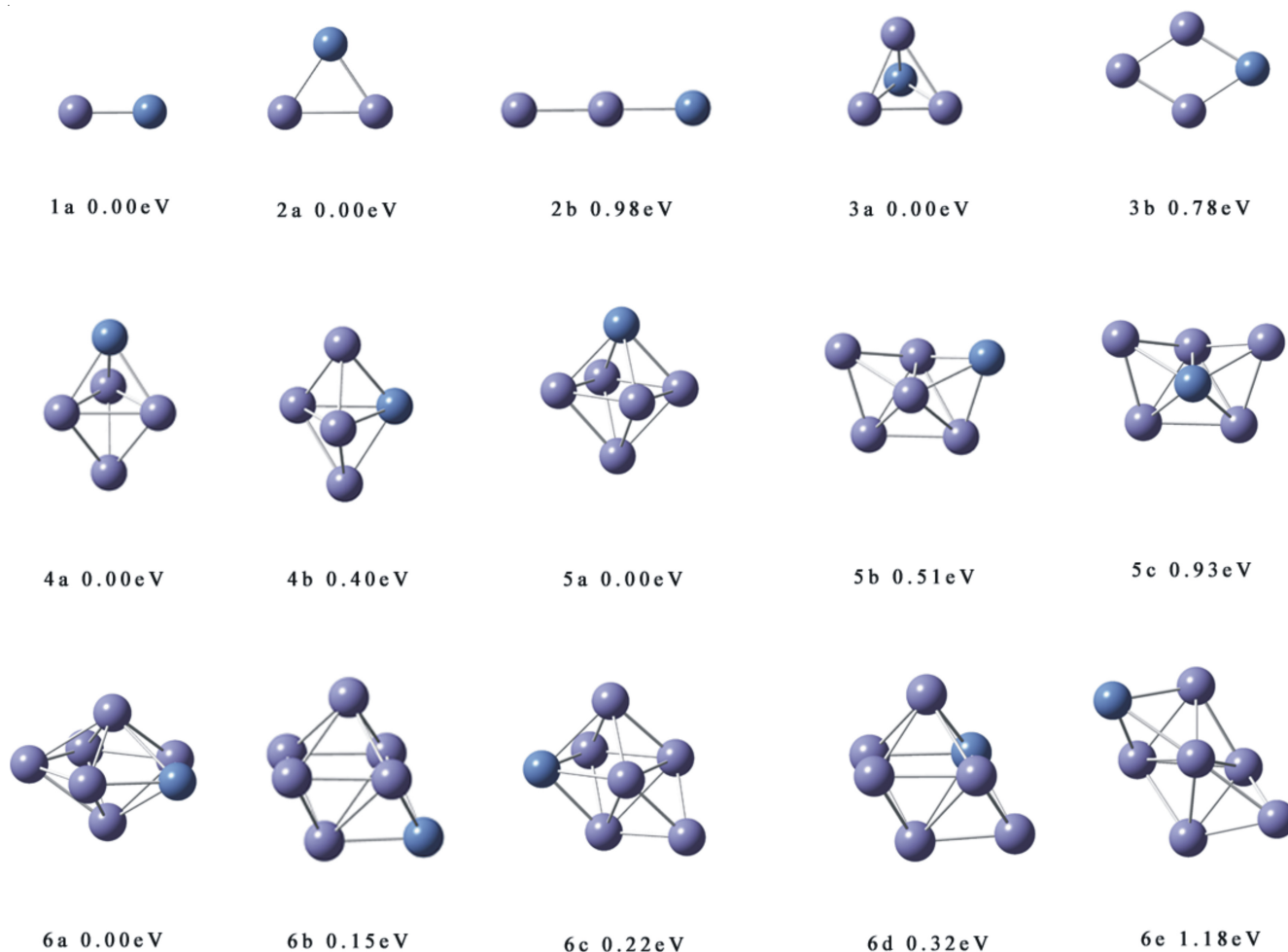


Fig. 1. Low-energy isomers for  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters at the BPW91 level. The deep blue and blue balls represent nickel atoms and iron atoms, respectively. The number under the structure is relative energies (eV) with respect to that of the corresponding lowest-energy isomers

$$E_b = \left\{ \frac{E(\text{Fe}_{n-1}\text{Ni}) - [(n-1)E(\text{Fe}) + E(\text{Ni})]}{n-1} \right\} \quad (1)$$

$$\Delta^2 E = [E(\text{Fe}_n\text{Ni}) + E(\text{Fe}_{n-2}\text{Ni})] - 2E(\text{Fe}_{n-1}\text{Ni}) \quad (2)$$

where  $E(\text{Fe}_n\text{Ni})$ ,  $E(\text{Fe}_{n-1}\text{Ni})$  and  $E(\text{Fe}_{n-2}\text{Ni})$  are the total energy of  $\text{Fe}_{n-1}\text{Ni}$ ,  $\text{Fe}_n\text{Ni}$  and  $\text{Fe}_{n-2}\text{Ni}$  and  $E_{\text{Fe}}$  and  $E_{\text{Ni}}$  are the energies of atoms Fe and Ni, respectively. The corresponding calculated results are shown in Table-1. It is seen from Table-1 that the binding energy decreases monotonically as the size of cluster increases, indicating that  $\text{Fe}_{n-1}\text{Ni}$  clusters is easier to gain energy to grow toward the evolution of bulk materials. For  $\Delta^2 E$ , Table-1 shows a peak at  $n = 6$ .

TABLE-1  
CALCULATED ENERGIES OF THE MOST  
STABLE CLUSTERS OF  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ )

Cluster	$E_b$ (eV)	$\Delta^2 E$ (eV)	Vertical ionization potential (eV)	HOMO-LUMO gap (eV)
$\text{FeNi}$	-1.48	—	7.03	0.91
$\text{Fe}_2\text{Ni}$	-1.85	-0.31	5.89	0.49
$\text{Fe}_3\text{Ni}$	-2.20	-0.37	5.96	0.44
$\text{Fe}_4\text{Ni}$	-2.56	0.02	5.99	1.91
$\text{Fe}_5\text{Ni}$	-2.78	0.06	6.49	2.31
$\text{Fe}_6\text{Ni}$	-2.93	0.02	5.94	1.45

The vertical ionization potential is another useful quantity for determining the stability of clusters and the ionized cluster with same geometry as the neutral. It is defined as the total-energy difference of the neutral cluster and the ionized cluster with same geometry as the neutral. The vertical ionization potentials calculated in Table-1 drastically decreases as cluster size, then it is starting to increase and a striking peak occurs at  $\text{Fe}_5\text{Ni}$  consisted with the result of  $\Delta^2 E$ . It is indicated that  $\text{Fe}_5\text{Ni}$  have special stability. In addition, the (HOMO-LUMO) energy gap is also a useful quantity for examining the stability of clusters. From Table-1, it is also found the  $\text{Fe}_5\text{Ni}$  cluster have larger energy gap than other  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters.

## Conclusion

In this paper, we have studied the geometries and electronic properties of  $\text{Fe}_{n-1}\text{Ni}$  ( $n = 2-7$ ) clusters at the BPW91 level. All calculated results are summarized as follows:

(i) The density functional method BPW91 combined with LanL2DZ basis sets greatly reduce the computational efforts and the bond lengths of  $\text{Fe}_2$  and  $\text{Ni}_2$  obtained by them is consisted with the corresponding experimental values.

(ii) Calculated results show that the adoping of an Ni atom does not change the geometrical configuration of corresponding  $\text{Fe}_n$  cluster.

(iii) For  $\text{Fe}_{n-1}\text{Ni}$  clusters, the Fe atoms tend to be gathered and the Ni atom is located around iron atoms.

(iv) Similar to the results of the second difference in energy, both the vertical ionization potential and the HOMO-LUMO energy gap show  $\text{Fe}_5\text{Ni}$  has special stability.

## ACKNOWLEDGEMENTS

This work is supported by the Research and Innovation of Shanghai Education Commission, China (10ZZ98), Science and Technology Program of Shanghai Maritime University, China (032219, 20080449) and National Natural Science projects (No: 20703027, 51042013), Foundation of Shandong Educational Committee (No: J09LB06).

## REFERENCES

- P. Jena, S.N. Khanna and B.K. Rao, *Physics and Chemistry of Finite Systems-From Clusters to Crystals*, Kluwer Academic Press, Vol. I and II (1992).
- G. Bozzolo, J. Ferrante, R.D. Noebe, B. Good, F.S. Honey and P. Abel, *Comput. Mater. Sci.*, **12**, 169 (1999).
- J. Xiang, S.H. Wei, X.H. Yan, J.Q. You and Y.L. Mao, *J. Chem. Phys.*, **120**, 4251 (2004).
- C. Majumder, V. Kumar, H. Mizuseki and Y. Kawazoe, *Phys. Rev. B.*, **71**, 035401 (2005).
- M.D. Morse, *Chem. Rev.*, **86**, 1049 (1986).
- T.J.D. Kumar, P.F. Weck and N. Balakrishnan, *J. Phys. Chem. C*, **111**, 7494 (2007).
- B.V. Reddy, S.K. Nayak, S.N. Khanna, B.K. Rao and P. Jena, *J. Phys. Chem. A*, **102**, 1748 (1998).
- S.Q. Yu, S.G. Chen, W.W. Zhang, L.H. Yu and Y.S. Yin, *Chem. Phys. Lett.*, **446**, 217 (2007).
- D.X. Tian, H.L. Zhang and J.J. Zhao, *Solid State Commun.*, **144**, 174 (2007).
- G.L. Qiu, M. Wang, G.L. Wang, X.F. Diao, D.Q. Zhao, Z.L. Du and Y.C. Li, *J. Mol. Struct. (Theochem.)*, **861**, 131 (2008).
- J.G. Du, H.Y. Wang and G. Jiang, *J. Mol. Struct. (Theochem.)*, **817**, 47 (2007).
- M. Castro, C. Jamorski and D.R. Salahub, *Chem. Phys. Lett.*, **271**, 133 (1997).
- J.L. Wang, G.H. Wang, X.S. Chen, W. Lu and J.J. Zhao, *Phys. Rev. B*, **66**, 014419 (2002).
- M. Harb, F. Rabilloud and D. Simon, *J. Phys. Chem. A*, **111**, 7726 (2007).
- N. Liu, Q.M. Ma, Z. Xie, Y. Liu and Y.C. Li, *Chem. Phys. Lett.*, **436**, 184 (2007).
- M. J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P. Ayala, Q. Cui, K. Morokuma, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J. A. Pople, *Gaussian 98* (Gaussian, Inc., Pittsburgh, PA, 1998).
- J.P. Perdew and Y. Wang, *Phys. Rev. B*, **45**, 13244 (1992).
- G.L. Gutsev and C.W. Bauschlicher Jr., *J. Phys. Chem. A*, **107**, 7013 (2003).
- S. Chre'tien and D.R. Salahub, *Phys. Rev. B*, **66**, 155425 (2002).
- J.G. Han, C. Xiao and F. Hageberg, *Struct. Chem.*, **13**, 173 (2002).
- L. Turker, *Theochemistry*, **548**, 185 (2001).
- J.G. Han and F. Hageberg, *Chem. Phys.*, **263**, 255 (2001).
- J.G. Han, *Chem. Phys.*, **286**, 181 (2003).
- H. Purdum, P.A. Montano, G.K. Shenoy and T. Morrison, *Phys. Rev. B*, **25**, 4412 (1982).
- J. Ho, M.L. Polak, K.M. Ervin and W.C. Lineberger, *J. Chem. Phys.*, **99**, 8542 (1993).
- S.Q. Yu and X.F. Jia, *Asian. J. Chem.*, **22**, 7075 (2010).