Density functional theory study of Mg_nNi_2 (n = 1–6) clusters*

Li Jing(李 晶)[a], Liu Xiao-Yong(刘小勇)[a],
Zhu Zheng-He(朱正和)[b], and Sheng Yong(盛 勇)[a]†

[a] College of Material Science and Engineering, Sichuan University, Chengdu 610065, China
[b] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

(Received 13 April 2011; revised manuscript received 9 September 2011)

The geometries of Mg_nNi_2(n = 1–6) clusters are studied by using the hybrid density functional theory (B3LYP) with LANL2DZ basis sets. For the ground-state structures of Mg_nNi_2 clusters, the stabilities and the electronic properties are investigated. The results show that the groundstate structures and symmetries of Mg clusters change greatly due to the Ni atoms. The average binding energies have a growing tendency while the energy gaps have a declining tendency. In addition, the ionization energies exhibit an odd–even oscillation feature. We also conclude that n = 3, 5 are the magic numbers of the Mg_nNi_2 clusters. The Mg_3Ni_2 and Mg_5Ni_2 clusters are more stable than neighbouring clusters, and the Mg_4Ni_2 cluster exhibits a higher chemical activity.

Keywords: Mg_nNi_2 clusters, density functional theory, geometrical structures, stability

PACS: 31.15.A–, 36.40.Vz, 71.15.Mb **DOI:** 10.1088/1674-1056/21/3/033101

1. Introduction

Because of their special physical and chemical properties, metal clusters have drawn extensive attention in different fields, such as physics, chemistry and materials, etc.[1−5] In particular, research on mixed clusters has become an advanced topic.[6−12] Magnesium (Mg) clusters have some unique physical and chemical properties. The atomic interactions within magnesium clusters will change with the number of atoms, which shows the qualities of nonmetal-to-metal transitions. Jellinek and Acioli[13] have studied the structures and the electronic properties of Mg_n (n = 2–22) clusters by density functional theory (DFT). Kumar and Car[14] studied the structures and bonding natures of Mg_n (n = 2–13) clusters by using the local density approximation (LDA), and found that Mg_4 and Mg_{10} are magic clusters. As an important transition metal element, nickel (Ni) can be used not only as a permanent magnet material, but also employed as an important alloying element. Therefore, it is reasonable that the pure Ni clusters have received widespread attention.[15,16] Because the hydrogen storage capacity of material can be effectively improved by adding a small amount of Ni into Mg, the studies of Ni-doped Mg clusters have a great significance in practice.

The Mg_xNi_y ($x+y \leq 5$) clusters have been investigated by Zhang *et al.*[17] through using DFT. The results suggest that the Ni atoms change the groundstate structures and symmetries of Mg clusters considerably. And the clusters with a larger number of Ni bonds are more stable. Moreover, the $MgNi_2$ clusters are stable comparatively, and the Mg_2Ni_3 clusters exhibit higher chemical activities. However, it is noted that the results in Ref. [17] focus mainly on the energies and charge distributions of $Mg_xNi_y(x+y \leq 5)$ clusters. The Mg_xNi_y system was studied in a limited way, without intensive discussion about the clusters' stabilities and electronic properties.

In this paper, we present a systematic theoretical investigation of the Mg_nNi_2 clusters. The prime motivation is to understand the evolution of structures and electronic properties of Mg_nNi_2 clusters. To this end, we carry out extensive research on the equilibrium geometry, stability, highest-occupied and lowest-unoccupied molecular orbital (HOMO–LUMO) gap, ionization potential (IP) and electron affinity (EA) of Mg_nNi_2 clusters up to $n = 6$ by using DFT. The findings in this paper provide a meaningful reference for the study of Mg alloy clusters and Mg-based alloy materials.

*Project supported by the National Natural Science Foundation of China (Grant No. 10676022).
†Corresponding author. E-mail: shengyong69@163.com
© 2012 Chinese Physical Society and IOP Publishing Ltd

In Section 2, we give a brief description of the main features of the computational methods used in the work. A deep discussion about geometries, stabilities and electronic properties of Mg_nNi_2 clusters is presented in Section 3. Finally, our conclusion is given in Section 4.

2. Computational method

The structures of Mg_nNi_2 ($n = 1$–6) clusters were optimized and their energies were calculated by using the hybrid DFT (B3LYP) with LANL2DZ basis sets. All the computations were performed using a Gaussian03 program package.[18] To find the lowest energy structures of Mg_nNi_2 clusters, we designed as many initial configurations as possible. These configurations are optimized under different spin multiplicities, and the lowest energy structures without imaginary frequency are considered to be the most stable structures. There are two methods to design the initial configurations. One is based on the ground-state structures of pure Mg clusters. We designed the initial configurations with two Ni atoms, which are capped, displaced or filled into Mg clusters. The other is to take examples from ground-state structures and isomers of Mg_nNi clusters.[17] The Mg atoms are replaced by Ni atoms to construct the initial configurations. The convergence criteria of energy, force and displacement are 10^{-7} a.u., 10^{-4} a.u./Bohr and 10^{-3} Bohr respectively.

For the purpose of evaluating the accuracy of the calculation level, we investigate Mg_2, Ni_2 and MgNi clusters by employing a B3PW91 density functional technique with TZVP basis sets. The results calculated by different methods are presented in Table 1, which are very close to the experimental values. Satisfactory agreement indicates that the method we used should be reasonable to describe the MgNi system. On this basis, the parameters of the ground-state structures are further discussed, such as average bond length, average binding energy, the second-order difference of energy and energy gap, etc.

3. Results and discussion

3.1. Geometry

The ground-state structures of Mg_nNi_2 (n = 1–6) clusters are shown in Fig. 1. They each have a triplet spin multiplicity. In Fig. 1, the darker spheres represent the Ni atoms, while the lighter spheres denote the Mg atoms. Furthermore, the na represents the ground-state structure of Mg_nNi_2 clusters, and the nb and nc refer to the metastable configurations. The geometric parameters of Mg_nNi_2 clusters are given in Table 1.

Table 1. Geometric parameters and energies of the ground-state structures of Mg_nNi_2 ($n = 1$–6) clusters.

Clusters	Symmetry	Average bond length/nm	E_b/eV	HLG/eV	Δ_2E/eV	IP/eV	EA/eV
Mg_2	$D_{\infty h}$	0.3961, 0.3803[a] 0.4147[b], 0.3891[c]	0.0064, 0.0075[a] 0.002[b]	3.3342, 3.5405[a] 3.565[b]			
Mg_3	D_{3h}	0.3590[b]	0.018[b]	3.129[b]			
Mg_4	T_d	0.3237[b]	0.093[b]	2.966[b]			
Mg_5	D_{3h}	0.3396[b]	0.087[b]	2.449[b]			
Ni_2	$D_{\infty h}$	0.2376, 0.2035[a] 0.2078[b], 0.215∼0.22[d]	0.7969, 0.7708[a] 0.620[b]	2.2572, 2.5347[a] 2.857[b]			
MgNi	$C_{\infty v}$	0.2492, 0.2475[a] 0.2532[b]	0.4542, 0.3649[a] 0.357[b]	1.8585, 1.9568[a] 1.742[b]			
$MgNi_2$	$D_{\infty h}$	0.2440	1.8222	3.1320		6.8257	0.3880
Mg_2Ni_2	D_{2h}	0.2619	2.0991	2.4425	–0.1756	5.8836	0.7220
Mg_3Ni_2	Cs	0.2516	2.3004	2.4202	–0.0305	6.2426	0.9291
Mg_4Ni_2	C_{4v}	0.2546	2.4396	0.7031	–0.0656	6.1742	1.7454
Mg_5Ni_2	Cs	0.2540	2.5485	1.4082	–0.0305	5.3391	1.4012
Mg_6Ni_2	C_1	0.2525	2.6339	1.3165		4.8913	0.3127

[a] For comparison, the Mg_2, Ni_2 and MgNi clusters are calculated by using a B3PW91 functional with a TZVP basis set. [b] Ref. [17]. [c] Experimental value of Mg–Mg bond length, see Ref. [19]. [d] Experimental value of Ni–Ni bond length, see Ref. [20].

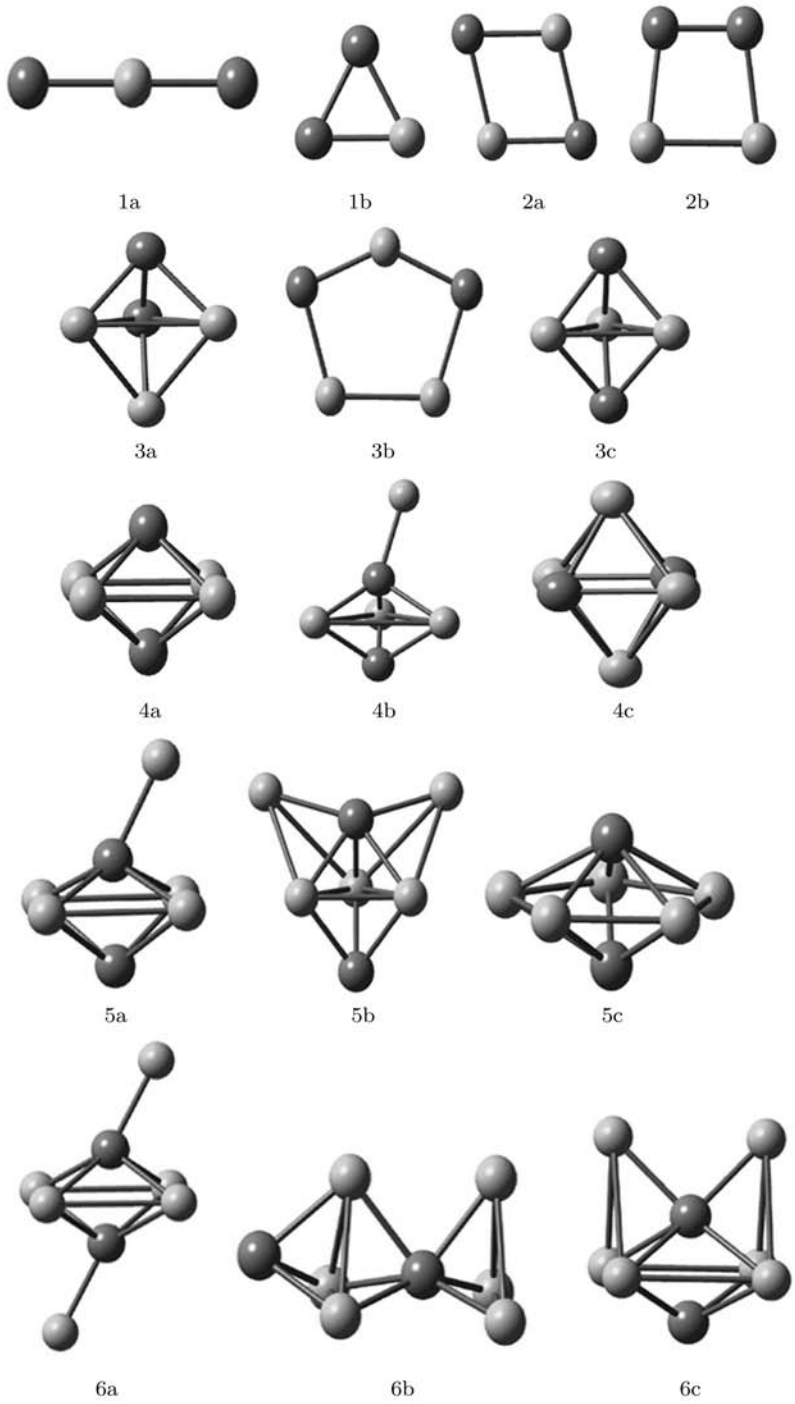


Fig. 1. Geometries of Mg_nNi_2 ($n = 1$–6) clusters.

As the number of atoms increases, the number of isomers augments correspondingly. The isomers are selected for the purpose of reflecting the growth patterns of ground-state structures. The evolution of ground-state structures, which can be seen from Fig. 1, are from a linear structure to a planar structure, and to a three-dimensional structure. The ground-state structure of the $MgNi_2$ cluster is linear rather than a triangle, which implies that both the ground state structure and the symmetry of pure Mg clusters have an obvious change because of the Ni atoms. For Mg_2Ni_2 clusters, both the planar and the three-dimensional structures are taken into account. The results show that the rhombus structure is the most stable structure and the tetrahedron structure is not converged. The energy of the metastable configuration 2b is 1.882 eV higher than that of the ground-state structure. The geometries of Mg_3Ni_2 clusters

have both planar and three-dimensional structures. The ground-state structure is of a triangular bipyramid with C_s symmetry. It can be considered as the fact that two atoms of the ground-state structure of the Mg_5 cluster are replaced by two Ni atoms. The energies of the ground-state structure are 1.022 eV and 0.658 eV, which are lower than those of the other two metastable structures 3b and 3c respectively. Starting from the Mg_4Ni_2 clusters, the low-lying isomers are all three-dimensional structures. The ground-state structure of the Mg_4Ni_2 cluster, whose tops are occupied by two Ni atoms, is of a quadrilateral bipyramid with C_{4v} symmetry, and there is a noticeable change compared with the ground-state structure of Mg clusters. The energies of the metastable structures 4b and 4c are 0.113 eV and 0.509 eV, which are both higher than the ground-state structure. The ground-state structure of the Mg_5Ni_2 cluster, which is based on the ground-state structure of the Mg_4Ni_2 cluster, is of a quadrilateral bipyramid connected by a Mg atom at the top. Nevertheless, the structure, which is formed by replacing two Mg atoms of the ground-state structure of the Mg_7 cluster with Ni atoms, is the metastable structure 5c. The energies of the metastable structures 5b and 5c are 1.033 eV and 0.596 eV, which are higher than those of the ground-state structure of the Mg_5Ni_2 cluster respectively. The ground-state structure of the Mg_6Ni_2 cluster is derived from the ground-state structure of the Mg_5Ni_2 cluster by connecting another Ni atom with a Mg atom at the top of the quadrilateral bipyramid. The energies of metastable structures 6b and 6c are 0.849 eV and 0.439 eV, which are higher than those of the ground-state structure of Mg_6Ni_2 cluster respectively.

From the analysis above, it follows that the ground-state structures of Mg_nNi_2 clusters are based on the triangular bipyramid and quadrilateral bipyramid. Most structures derived from the ground-state structures of pure Mg clusters are metastable structures. It is noted that the average bond lengths of the Mg_nNi_2 clusters are smaller than those of the Mg_n clusters with the same number of atoms, which means that the Ni atoms enhance the stabilities of Mg clusters. It is no wonder that the Ni atoms tend to bond with more Mg atoms, thereby achieving a more stable structure.

3.2. Stability

In further studies of cluster stability, the average binding energy (E_b) as a function of n is plotted in Fig. 2. E_b is the main basis of judging the stability of clusters. It can be expressed as the following formula:

$$E_b(Mg_nNi_2) = [nE(Mg) + 2E(Ni) - E(Mg_nNi_2)]/(n+2), \quad (1)$$

where $E(Mg_nNi_2)$, $E(Mg)$ and $E(Ni)$ represent the energies of the Mg_nNi_2 cluster, Mg atom and Ni atom, respectively. As shown in Fig. 2, the average binding energies of the lowest energy structures increase with the number of Mg atoms. It reflects that the clusters become more stable as the number of Mg atoms increases. In spite of the fact that the binding energies of the Mg_nNi_2 and Mg clusters increase with n, the Mg_nNi_2 cluster binding energies are higher than those of Mg clusters of the same size (Table 1). To a certain extent, it is due to the fact that the electronegativity of a Ni atom (1.91) is higher than that of a Mg atom (1.31), which also means that the interaction of Mg–Ni bonds are stronger than that of Mg–Mg bonds.

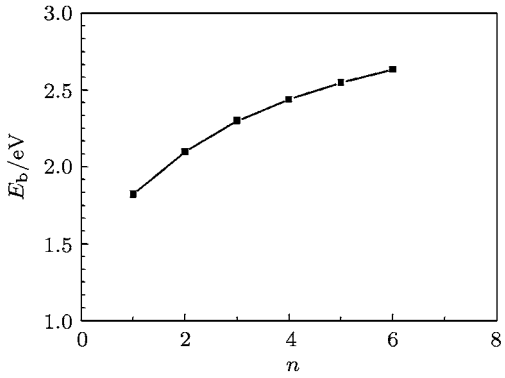


Fig. 2. Average binding energies of Mg_nNi_2 (n = 1–6) clusters.

The size dependence of the HOMO–LUMO energy gaps for the lowest energy structures of Mg_nNi_2 (n = 1–6) clusters is plotted in Fig. 3. The HOMO–LUMO energy gap reflects the ability for an electron to jump from the occupied orbital to the unoccupied orbital, which represents the intensity of the chemical activity. A large HOMO–LUMO gap generally corresponds to a closed-shell electronic configuration with high stability.

In Fig. 3, we note that the HOMO–LUMO energy gaps of the ground-state structures of Mg_nNi_2 clusters have a declining tendency as a whole with an increasing number of Mg atoms. The energy gaps of Mg_nNi_2 clusters are larger than those of Mg clusters with the same size (Table 1). It means that the chemical activities of Ni-doped Mg_nNi_2 clusters are higher. Moreover, the closure of the HOMO–LUMO gap is

customarily interpreted as an indication of the transition to a metallic state. Kumar and Car[21] suggested that the divalent metal cluster bond changes from a weak chemical bond to a metallic bond with the increase of size. During the transition, the energy gaps will become smaller. It is in close agreement with our results.

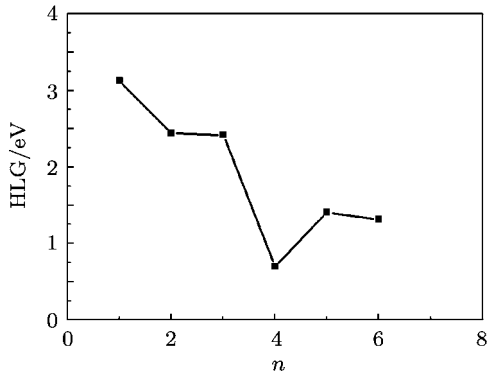


Fig. 3. Energy gaps of Mg_nNi_2 (n = 1–6) clusters.

Compared with the neighbouring clusters, $Mg_3Ni_2$and Mg_5Ni_2 clusters have large energy gaps, which indicate that their chemical activities are low, and they are stable comparatively. It is noticeable that the energy gap reduces from 2.42 eV of a Mg_3Ni_2 cluster to 0.70 eV of a Mg_4Ni_2 cluster, which verifies that the size of cluster has a great influence on the HOMO–LUMO energy gap.

The value of the energy gap determines the probability of the molecules jumping from the ground state to the excited state. Generally speaking, the larger the value of the energy gap, the larger the energy of electron excitation, i.e., the smaller the probability of electronic transition. It implies that the molecules are more stable in a certain state. On the contrary, the molecules with smaller energy gaps are easier to jump to the excited state. Namely, their chemical activities are higher. The HOMO–LUMO orbital diagrams of Mg_nNi_2 clusters are shown in Fig. 4. We can visually view the bond types of Mg and Ni atoms and the characteristic of the delocalization effect.

Another sensitive quantity that characterizes the relative stability of clusters as a function of cluster size is second-order energy difference Δ_2E. The higher the value of second-order energy difference, the more stable the cluster. The corresponding Δ_2E is defined as

$$\Delta_2E(Mg_nNi_2) = E(Mg_{n+1}Ni_2) + E(Mg_{n-1}Ni_2) - 2E(Mg_nNi_2), \quad (2)$$

where $E(Mg_{n+1}Ni_2)$, $E(Mg_{n-1}Ni_2)$ and $E(Mg_nNi_2)$ are respectively the total energies of the most stable $Mg_{n+1}Ni_2$, $Mg_{n-1}Ni_2$ and Mg_nNi_2 clusters. The results are plotted in Fig. 5. The second-order energy differences between the clusters with odd n are higher than with even n. It is a consequence of the electron pairing effect. Figure 5 shows that the local maxima of second-order energy differences appear at n = 3 and 5, which means that Mg_3Ni_2 and Mg_5Ni_2 are magic clusters. Considering the results of both the second-order energy difference and energy gaps, we find that Mg_3Ni_2 and Mg_5Ni_2 clusters own higher stability.

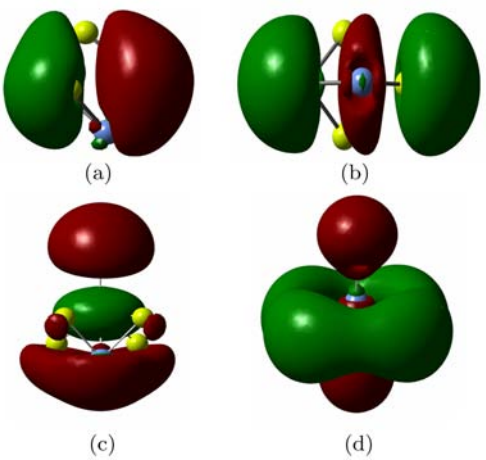


Fig. 4. (colour online) HOMO–LUMO orbital diagrams of $Mg_nNi_2(n = 1-6)$ clusters. (a) Mg_3Ni_2, HOMO; (b) Mg_3Ni_2, LUMO; (c) Mg_5Ni_2, HOMO; (d) Mg_5Ni_2, LUMO.

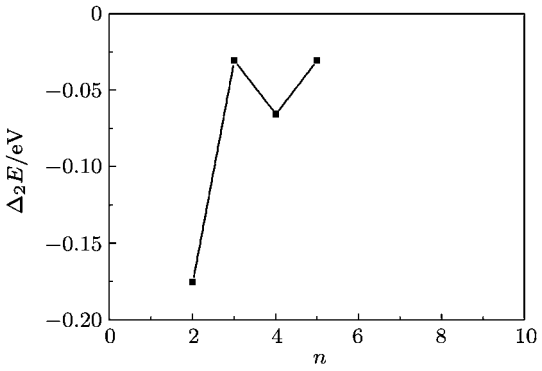


Fig. 5. Second-order energy difference of Mg_nNi_2 (n = 1–6) clusters.

3.3. Electronic properties

For investigating the stability of Mg_nNi_2 clusters, the IP and EA are calculated and the obtained results are presented in Fig. 6. The IP of the cluster refers to the bonding energy of a neutral cluster losing an electron. The higher the value of IP, the higher the

cluster stability. The electron affinity, reflecting the bonding energy of a neutral cluster receiving an electron, is equal to the total energy difference between the neutral cluster and the anionic cluster. The corresponding IP and EA are respectively defined as

$$\mathrm{IP}(\mathrm{Mg}_n\mathrm{Ni}_2) = E(\mathrm{Mg}_n\mathrm{Ni}_2^+) - E(\mathrm{Mg}_n\mathrm{Ni}_2), \quad (3)$$

$$\mathrm{EA}(\mathrm{Mg}_n\mathrm{Ni}_2) = E(\mathrm{Mg}_n\mathrm{Ni}_2) - E(\mathrm{Mg}_n\mathrm{Ni}_2^-), \quad (4)$$

where $E(\mathrm{Mg}_n\mathrm{Ni}_2^+)$, $E(\mathrm{Mg}_n\mathrm{Ni}_2^-)$ and $E(\mathrm{Mg}_n\mathrm{Ni}_2)$ represent the energies of $\mathrm{Mg}_n\mathrm{Ni}_2^+$, $\mathrm{Mg}_n\mathrm{Ni}_2^-$ and $\mathrm{Mg}_n\mathrm{Ni}_2$ clusters, respectively.

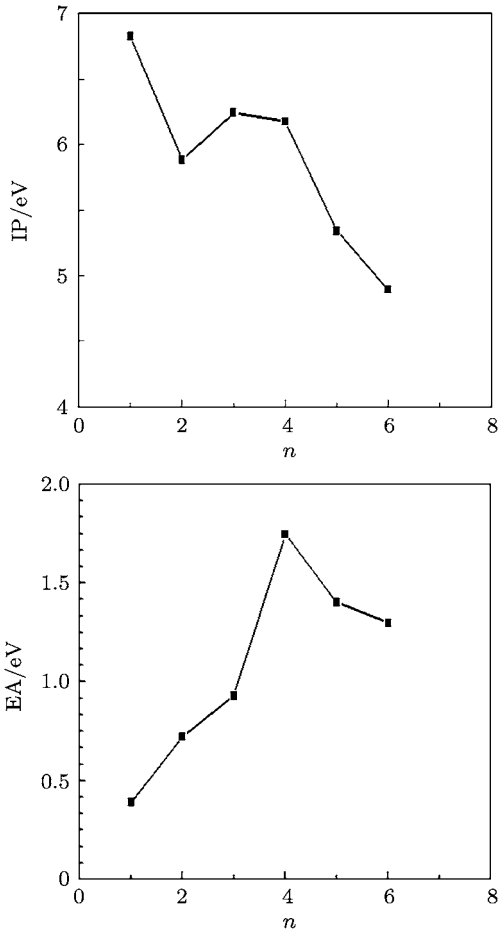


Fig. 6. Ionization potential (IP) and electron affinity (EA) of $\mathrm{Mg}_n\mathrm{Ni}_2$ (n = 1–6) clusters.

As shown in Fig. 6, the IPs have a declining tendency as a whole as n increases. The IPs exhibit odd–even oscillations with the size of cluster increasing. The odd–even pattern is a consequence of the electron pairing effect. In our calculation level, the valence shells of Mg and Ni are $2p^6 3s^2$ and $3d^8 4s^2$ respectively. In the case where a cluster has an even number of valence electrons, the extra electrons must go into the next orbital, which costs energy, resulting in a higher value of IP. When n is odd, the IP of $\mathrm{Mg}_n\mathrm{Ni}_2$ clusters is great comparatively. And the peaks occur at n = 3, 5 for $\mathrm{Mg}_n\mathrm{Ni}_2$ clusters, which indicates that n = 3, 5 are the magic numbers. Compared with the neighbouring clusters, the $\mathrm{Mg_3Ni_2}$ cluster and the $\mathrm{Mg_5Ni_2}$ cluster are more stable, which is consistent with the analysis above.

On the other hand, the EAs have a growing tendency as a whole with n increasing and exhibit no odd–even oscillations. The dependence of EA on effective nuclear charge, atomic radius and electron configuration may account for this phenomenon. It is noticeable that the value of EA increases from 0.93 eV of a $\mathrm{Mg_3Ni_2}$ cluster to 1.75 eV of a $\mathrm{Mg_4Ni_2}$ cluster. And n = 4 is the local maximum which means that the chemical activity of a $\mathrm{Mg_4Ni_2}$ cluster is higher. This echoes the analysis above and signifies that the variation in geometry also affects the electronic properties of $\mathrm{Mg}_n\mathrm{Ni}_2$ clusters. The electron affinities of $\mathrm{Mg_3Ni_2}$ and $\mathrm{Mg_5Ni_2}$ clusters are low comparatively, i.e., they are more stable than the neighbouring clusters.

4. Conclusion

We extensively investigate the geometrical structures of $\mathrm{Mg}_n\mathrm{Ni}_2$ (n = 1–6) clusters and their relative stabilities, by using the hybrid DFT B3LYP with LANL2DZ basis sets. The results are summarized as follows.

1) The Ni dopants make the pure Mg cluster ground-state structures and symmetries change obviously and the stabilities of Mg clusters are improved. Triangular bipyramids and quadrilateral bipyramids play a dominant role in the evolution of the ground-state structures. The Ni atoms tend to bond with more Mg atoms, thereby achieving more stable structures.

2) The average binding energies of the lowest energy structures increase with the number of Mg atoms, while the HOMO–LUMO energy gaps of the ground-state structures have a declining tendency as a whole. The energy gaps of $\mathrm{Mg}_n\mathrm{Ni}_2$ clusters are larger than those of the pure Mg clusters. Moreover, the ionization energies exhibit odd–even alternations, but the electron affinities do not. Integrating the results of the second-order energy difference, energy gap and ionization potential, we conclude that $\mathrm{Mg_3Ni_2}$ and $\mathrm{Mg_5Ni_2}$ clusters are more stable than neighbouring clusters, and the n = 3, 5 are the magic numbers. The $\mathrm{Mg_4Ni_2}$ cluster owns a higher chemical activity, owing to its larger energy gap and lower electron affinity.

References

[1] Ge G X, Yan H X, Jing Q and Zhang J J 2011 *Acta Phys. Sin.* **60** 033101 (in Chinese)

[2] Qi K T, Mao H P, Wang H Y and Sheng Y 2010 *Chin. Phys.* B **19** 033602

[3] Zhao J J 2001 *Phys. Rev.* A **64** 043204

[4] Salahub D R 1987 *Adv. Chem. Phys.* **69** 447

[5] Liu Z F, Lei X L, Liu L R, Liu H Y and Zhu H J 2011 *Chin. Phys.* B **20** 023101

[6] Calaminici P 2004 *Chem. Phys. Lett.* **387** 253

[7] Jackson K A 1993 *Phys. Rev.* B **47** 9715

[8] Yang M, Jackson K A, Koehler C, Frauenheim T and Jellinek J 2006 *J. Chem. Phys.* **124** 024308

[9] Jin R and Chen X H 2010 *Acta Phys. Sin.* **59** 6955 (in Chinese)

[10] Jaque P and Toro-Labbé A 2004 *J. Phys. Chem.* B **108** 2568

[11] Che X F and Chen H S 2011 *Acta Phys. Sin.* **60** 043601 (in Chinese)

[12] Zhang X R, Gao C H, Wu L Q and Tang H S 2010 *Acta Phys. Sin.* **59** 5429 (in Chinese)

[13] Jellinek J and Acioli P H 2002 *J. Phys. Chem.* A **106** 10919

[14] Kumar V and Car R 1991 *Z. Phys.* D **19** 177

[15] Reuses F A, Khanna S N and Brenel S 1995 *Phys. Rev.* B **52** 11650

[16] Luo C L, Zhou T H and Zhang Y 2000 *Acta Phys. Sin.* **49** 54 (in Chinese)

[17] Zhang X R, Gao C H and Liu X F 2009 *Journal of Jiangsu University of Science and Technology* **23** 468 (in Chinese)

[18] Frisch M J, Trucks G W and Schlegel H B 2003 Gaussian 03 (Revision A.7, Gaussian, Inc., Pittsburgh, PA)

[19] Ruette F, Sanchez M, Anez R, Bermubez A and Sierraalta A 2005 *J. Mole. Struct. Theochem* **729** 26

[20] Morse M D 1986 *Chem. Rev.* **86** 1049

[21] Kumar V and Car R 1991 *Phys. Rev.* B **44** 8243