Density functional theory study on Ni-doped Mg_nNi ($n = 1 - 7$) clusters*

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The possible geometrical and the electronic structures of small Mg_nNi ($n = 1 - 7$) clusters are optimised by the density functional theory with a LANL2DZ basis set. The binding energy, the energy gap, the electron affinity, the dissociation energy and the second difference in energy are calculated and discussed. The properties of Mg_nNi clusters are also discussed when the number of Mg atom increases.

Keywords: density functional theory, magnesium nickel clusters, structure of ground state
PACC: 3640, 3640B, 3120A, 3120B

1. Introduction

Metal clusters have been a hot research topic for more than 20 years because of their unique structures and properties. Research on small clusters conduces to an understanding of the physical and the chemical properties that are different between the block and the atoms, and it can also administer to a better understanding of the mechanism formation and a series of relevant laws of metal clusters.[1−8] Magnesium alloys have been widely used because of their excellent properties such as high strength, heat resistance, wear resistance, low density, good thermal conductivity, and other excellent performance. Magnesium clusters and other atom doped clusters have also been extensively studied.[9−12] In recent years, the study of pure transition metals and mixed transition metal clusters has developed quickly.[13,14] Nickel is an important transition element with excellent corrosion resistance properties, and it can also be used as a permanent magnetic material. Nickel can also be employed as an important alloying element with its physical and chemical properties. On the other hand, Nickel has very good applications in the hydrogen storage materials, and magnesium-nickel hydrogen storage alloys have the most potential to develop into hydrogen storage alloys. Most of the researches on nickel doped clusters have focused on the Magnesium–Nickel–Hydrogen system,[15−21] but the researches about magnesium with nickel doped have rarely been reported. In order to explore the micro-mechanism of the magnesium clusters doped with nickel, we use the Gaussian03 procedures to do the calculation and study the structure and the electronic properties of the Mg_nNi ($n = 1-7$) clusters.

2. Method

The possible geometrical and electronic structures of small Mg_nNi ($n = 1 - 7$) clusters are optimised by using the density functional theory (DFT) with LANL2DZ basis set. The binding energy, the energy gap, the electron affinity, the dissociation energy, and the second difference in energy are calculated. Optimisation processes are based on energy system convergence, the convergence of energy is better than 10^{-6} a.u. In order to save time and improve efficiency, the optimisation process is divided into two steps: The first step is to optimise the structure with a given bond length, bond angle and dihedral angle of the initial value in the convergence precision of 10^{-4} a.u.; the second step is to optimise the structure by using the result of the first step in the convergence precision of 10^{-6} a.u., and we set the structure with a lowest energy but no imaginary frequency to be the ground state structure of clusters. In order to verify the validity of the method, we compare our calculated Mg–Mg

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bond length 5.2156 Å (1 Å=0.1 nm) in Mg_2Ni with the experimental data 5.2107 Å given by DAG NOREUS and others,[17,21] and it can be seen that they are very close to each other, thereby showing our method to be reasonable.

3. Results and discussion

3.1. Geometry

The ground-state geometries of Mg_nNi clusters are shown in Fig. 1, where the dark atoms are Ni atoms, panel (a) refers to the structure of ground state and panels (b) and (c) represent the isomer structures. The ground state structures of the clusters in Fig. 1 show that Ni atom occupies the surface location of the cluster when the number of Mg atoms is in a range from 1 to 4, but Ni atom gradually falls from the surface into centre when the number of Mg atoms changes from 5 to 7.

We can see that different from Mg_3 cluster's most stable triangle structure, Mg_2Ni cluster forms a linear structure with the Ni atom locating in the centre. It can be seen that the Mg–Ni bond forms more easily than Mg–Mg bond. The first 3D structure appears at $n = 3$ as a tetrahedron structure, and the Ni atom occupies a vertex of the tetrahedron. In the ground state of the Mg_4Ni cluster, Ni atom bonds four Mg atoms, i.e. Ni atom occupies the centre of the tetrahedron with C_{2v} symmetry, Ni atom bonds four Mg atoms, and only two pairs of Mg atoms form two Mg–Mg bonds.

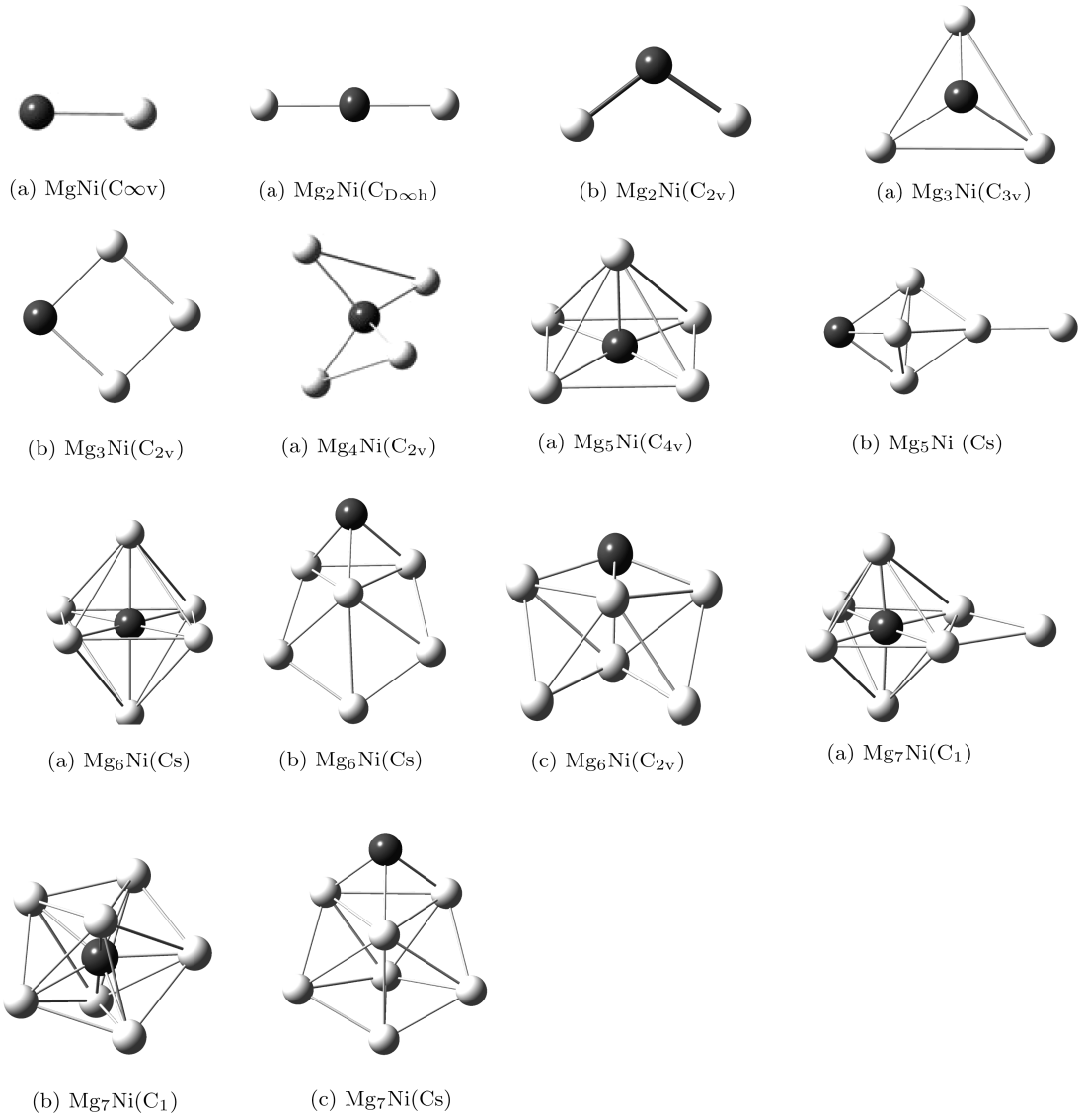


Fig. 1. Structures of Mg_nNi ($n = 1 - 7$) clusters.

For the configuration of Mg_5Ni cluster, it does not form the most stable octahedron like Mg_6 cluster, but forms a four-pyramid structure. The Ni atom slides into the inside of the cluster. The structure shows that the Ni atom tends to slide into the cluster to obtain the most stable structure. The ground state structure of Mg_6Ni shows that Mg atoms form an octahedron structure with Cs symmetry. In this structure Ni atom completely falls into the interior of geometry. It can also be seen that the ground state structure of Mg_7Ni cluster develops from Mg_6Ni cluster. Because of the binding energy of Mg–Ni is larger than that of Mg–Mg, so Mg–Ni bond forms more easily. In the ground state structure of Mg–Ni clusters, Ni atom tends to bind most of Mg atoms. The ground state geometries of Mg_2Ni, Mg_4Ni, Mg_6Ni and Mg_7Ni clusters all show this characteristic. The ground state structures of Mg_6Ni and Mg_7Ni show that they are formed by adding Mg atoms to Mg_5Ni cluster's ground state structure. It shows that the Mg_5Ni is more stable than others.

3.2. Stability and electronic properties

The stability of cluster structure can be checked by each atom binding energy (E_b), the second difference in energy ($\Delta^2 E$) and HOMO–HUMO energy gap (E_g), which are respectively expressed as

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

$$\Delta^2 E[Mg_nNi] = E[Mg_{n+1}Ni] + E[Mg_{n-1}] - 2E[Mg_nNi], \quad (2)$$

$$E_g = E_{LUMO} - E_{HOMO}. \quad (3)$$

In formula (1), E[Mg] and E[Ni] are calculated by the same method and basis set. The binding energy of each atom in the cluster system can be represented as E_b, it reflects the energy changes of the whole cluster. From Fig. 2 we can see that E_b increases with the number of atoms increasing. Because of the surface effect of small clusters is obvious, the converging of its binding energy to the block material is very slow. Second difference in energy is a very sensitive physical quantity to the stability of clusters: a bigger second difference in energy indicates a higher stability of clusters. Figure 2 also shows that the second difference in energy changes as cluster size increases, it varies between positive and negative values, and tends to become moderate. From the curve b in Fig. 2 we can see a peak at a Mg_5Ni cluster's point which shows that the Mg_5Ni cluster is stabler. Comparing the Mg_5Ni cluster with the Mg_6Ni and Mg_7Ni clusters, we can see that the ground state structure of Mg_5Ni cluster is the magic number structure, the ground state structure of clusters will develop from Mg_5Ni cluster's structure when the number of Mg atom is greater than 5. From Fig. 2 it follows that the ground structure of Mg_5Ni cluster is stabler, and it indicates that the large cluster structure is based on the octahedron, and the Ni atom is located in the centre of clusters.

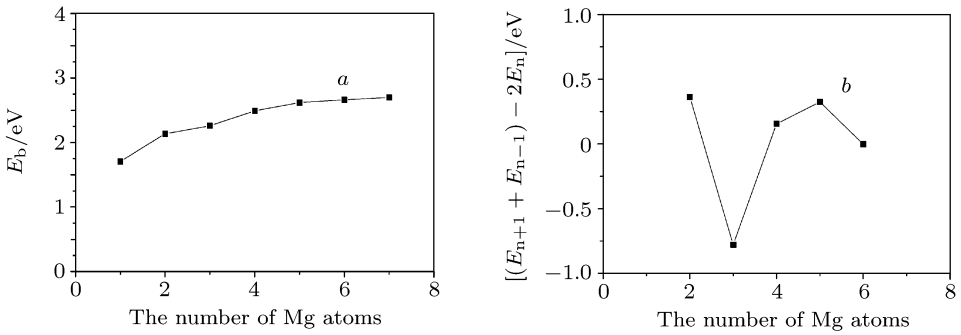


Fig. 2. Binding energy of clusters (curve a) and second difference in energy (curve b).

The energy gap between HOMO and LUMO reflects the ability for electron to jump from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. When the gap is greater, it is more difficult to transit from an excited electronic state to an unoccupied state, and the cluster's chemical activity is stabler.

From Fig. 3 we can see that the energy gap reduces as the number of Mg atoms increases. Comparing Fig. 2 with Fig. 3, we can see that the second difference in Mg_5Ni cluster is the highest, but its energy gap is decreasing. The analysis of natural orbitals shows that the Mg atom 3s orbital hybridises with the Ni atom 3d orbital, and the 3d orbital has about 10 electrons, it can be regarded as full shell, so Mg_5Ni is more stable.

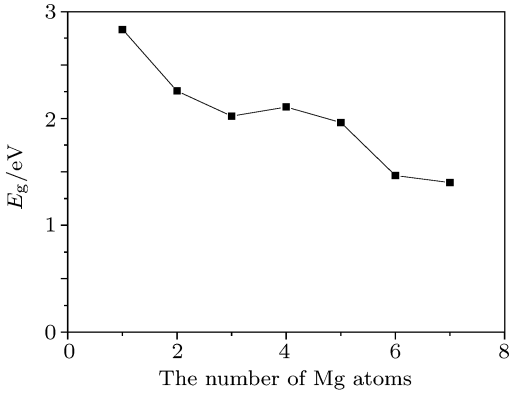
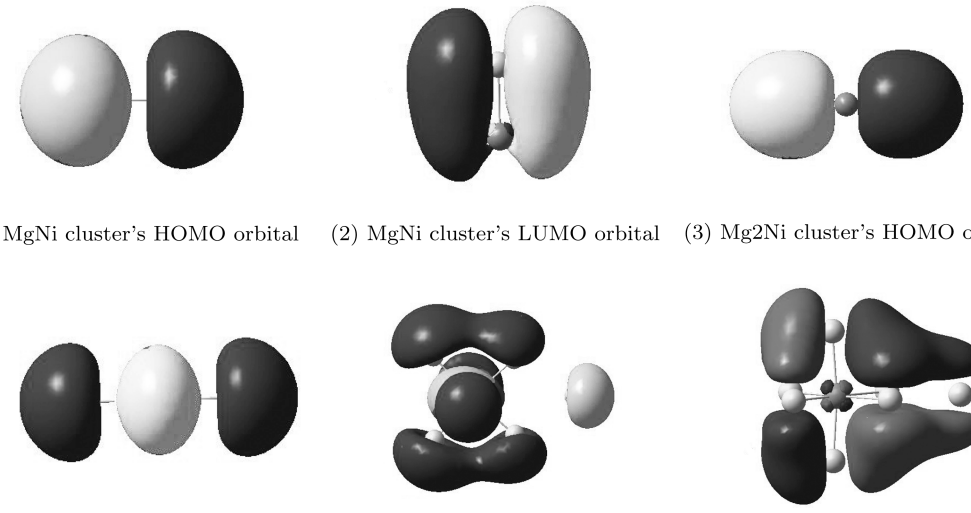


Fig. 3. Relation between HOMO–LUMO energy gap and size of clusters.

HOMO–LUMO energy gap reflects the chemical activity of cluster; a smaller energy gap means a higher chemical activity. From Fig. 4 we can see that the orbitals of clusters become more delocalized as the number of Mg atoms increases, so the energy gaps will be shown as in Fig. 3, i.e. it reduces as the number of Mg atoms increases, and the chemical activity also increases.



(1) MgNi cluster's HOMO orbital (2) MgNi cluster's LUMO orbital (3) Mg2Ni cluster's HOMO orbital

(4) Mg2Ni cluster's LUMO orbital (5) Mg7Ni clusters HOMO orbital (6) Mg7Ni cluster's LUMO orbital

Fig. 4. HOMO–LUMO orbital diagram of MgNi, Mg_2Ni and Mg_7Ni clusters.

3.3. Bonds

The bond between atoms is closely related to the structure. In order to study the combination of various structure parameters and bonds, we list the average bond length, the average bond lengths of Mg–Ni bond and Mg–Mg bond in Table 1. From Fig. 5 it follows that the average bond length increases as the number of atom increases but more and more gently, and the average length of Mg–Mg reduces as the number of atoms increases. It can also be seen that the change of Mg–Mg bond length is greater than that of Mg–Ni bond length, with one Mg atom added to the ground state structure on $Mg_{n-1}Ni$ cluster as $n = 5 - 7$.

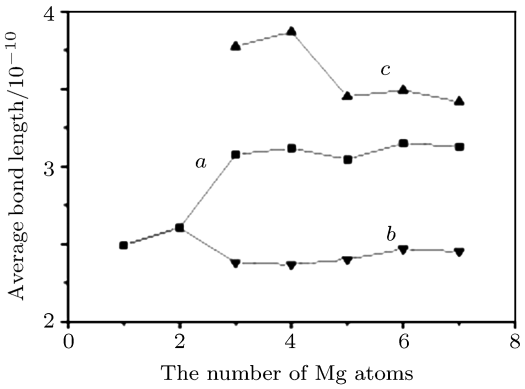


Fig. 5. Average length of all bonds (curve *a*), average length of Mg–Ni bonds (curve *b*), and average length of Mg–Mg bonds (curve *c*).

Table 1. Geometries and electronic characteristic parameters of Mg_nNi ($n = 1 - 7$) clusters.

cluster	multiplicity	symmetry	E/a.u	R/nm	R_{Mg-Mg}/nm	R_{Mg-Ni}/nm	E_b/eV	Δ^2E/eV	E_g/eV
MgNi	3	$C_{\infty v}$	–170.1010	0.2492		0.2492	1.7059		2.8316
Mg_2Ni	3	$C_{D\infty h}$	–170.9389	0.2608		0.2608	2.1355	0.3605	2.2566
Mg_3Ni	1	C_{3v}	–171.7636	0.3078	0.3774	0.2381	2.2602	–0.7801	2.021
Mg_4Ni	1	C_{2v}	–172.6197	0.3119	0.3868	0.2369	2.491	0.1545	2.1056
Mg_5Ni	3	C_{4v}	–173.4645	0.3048	0.3452	0.2402	2.6191	0.3236	1.9609
Mg_6Ni	3	C_s	–174.3003	0.315	0.3492	0.2468	2.6644	–0.002	1.4653
Mg_7Ni	3	C_1	–175.1361	0.3129	0.3419	0.2453	2.6986		1.3992

4. Conclusion

The ground state structure of Ni-doped Mg_nNi ($n = 1 - 7$) clusters and their properties are calculated by the density functional theory with a LANL2DZ basis set. The results show that the Mg–Ni bond forms more easily than the Mg–Mg bond and the Ni atom tends to bond most of the Mg atoms. The Ni atom tends to fall into the inside of clusters from the surface gradually as the number of Mg atoms increases, the Ni atom entirely falls into the cluster when $n > 5$. The octahedron will be the most stable structure of the multi-atom clusters ($n > 5$), and the Ni atom is loaded into the cluster. The stable structure will develop and change on the base of the octahedron as the number of Mg atoms increases.

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