The Ground State Structures and Magnetic Properties of Zr_nNi ($n = 1$–9) Clusters from First Principles Calculation

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(Received August 23, 2016; revised version April 10, 2017; in final form May 3, 2017)

The ground state structures and magnetic properties of Zr_nNi ($n = 1$–9) clusters are studied by using first principles calculation. Firstly, we find the ground state configurations of Zr_nNi ($n = 1$–9) clusters. Secondly, the magic clusters (Zr_2Ni and Zr_7Ni) of Zr_nNi clusters are found by the comparisons of average binding energies, the second-order energy difference and energy gaps between the highest occupied orbital and the lowest unoccupied orbital of the ground state of Zr_nNi clusters. Thirdly, the calculated results show that magnetic moment of Zr_nNi ($n = 1$–2) clusters is 4 μ_B; however, the magnetic moment of Zr_nNi clusters is about 2 μ_B for $n = 3$–9 (exception for $n = 7$). Finally, it is found that the magnetic moment of Zr_nNi cluster mainly comes from Zr atom and Ni atom is the electron acceptor from the Mulliken population analysis.

DOI: 10.12693/APhysPolA.131.1507

PACS/topics: first-principles calculations, Zr_nNi clusters, the geometric structure of balance, stability and magnetic properties

1. Introduction

Atomic cluster shows new physical phenomena due to quantum size effect, macroscopic quantum tunneling effect and surface effect, which make it fit for the design and synthesis of new materials, thus, atom cluster attract the attention of many theoretical and experimental workers in recent 30 years [1–14].

Transition metal cluster shows new properties in the geometry, electronic structure and magnetic characteristics, so it becomes the focus of attention of people [15–20]. Zirconium (Zr) is used as the cladding of fuel in the nuclear industry due to its less absorption of neutron. Zr is also used for refining alloy instead of steel because its strong corrosion resistance to common acid, alkali and salt, besides, also has been used in surgery and chemical industry, all of these are the reasons why people pay attention to Zr_n and corresponding mixed clusters [21–25]. Wang et al. find that the magic numbers of stabilities are $n = 2$, 5, and 7 and the atomic averaged magnetic moments of the Zr_n ($n \neq 2$) display an odd-even oscillation features, the tetrahedron $Cs\,Zr_4$ structure has the biggest atomic averaged magnetic moment of 1.5 μ_B/atom [22]; Zhao et al. find that the relative stabilities of Zr_5Fe, Zr_7Fe and $Zr_{12}Fe$ are stronger than that of other sized clusters and they are all magnetic clusters for Zr_nFe ($n = 2$–13) [24]; Ren et al. find that the relative stabilities of Zr_4Co, Zr_7Co, Zr_9Co, and $Zr_{12}Co$ are stronger than other sized clusters, and the magnetic moment of Zr_nCo clusters mainly comes from the localized d electron [25]. It is found that the magnetic moment of the smaller clusters Zr_2Fe, Zr_4Fe, ZrCo, and Zr_2Co mainly came from Zr atoms based on the analysis of the data in Refs. [24, 25]. As transition element, nickel (Ni) has lots of physical and chemical properties, Ni can be used not only as permanent magnetic material but also as an important alloy element. Not only pure Ni clusters are the focus of attention [9, 26], Ni–Nb alloy has been used in superconducting magnet, the systems show many peculiar properties in the structure and electronic properties when Ni is doped in semiconductor silicon, germanium and bivalent alkali metal clusters [27–29]. Ni and Zr alloy has superconducting property [30], what is more important is that it has many advantages compared with other alloy glass, such as positive hall coefficient [31], quantum interference effect [32], big induction conductivity of anisotropy [33], besides, it can exist in large doping concentration scope, therefore the Zr–Ni alloy attracts people's attention [34–36]. However, by now the research on geometrical structure and other properties of Zr_nNi clusters in experiment and theory is rare.

The geometric structures, average binding energies, the second-order differences of energy, the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the magnetic properties of Zr_nNi clusters and the magnetic moment of Zr (Ni) atom are studied in this paper, the results are useful for related research.

2. Computational method

In order to find the ground state structures of Zr_nNi clusters, a large number of possible initial structures for each size of the clusters are considered in this paper. Three ways are adopted to construct the initial configurations of Zr_nNi. The first method to get the initial configurations of Zr_nNi is by using Ni to replace M atom of the equilibrium configurations of Zr_nM (M = Fe, Co)

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clusters [24, 25]; in the second method a variety of possible configurations are built by Ni atom blocking (or gap filling) based on all the balance configurations of Zr_n clusters [21–23] or by possible replacement of Zr atom in Zr_{n+1} clusters to get the initial configurations of Zr_nNi clusters. The third way to look for the initial configurations of Zr_nNi clusters is taking the equilibrium configuration of titanium [37, 38] and cadmium [39] clusters for reference.

The calculations in full geometry optimization are performed using spin-polarized density functional method in Dmol3 simulation package (ver. 3.2) [40] and the calculations in the electronic structure are performed using effective nuclear potential and a double numerical basis including a *d*-polarization function, and the exchange and correlation potential is GGA-PW91 method [41]. The convergence criteria of self consistent field is 10^{-5} Ha, the convergence criteria of force is 0.04 Ha/nm, displacement convergence criteria is 0.0005 nm in the process of geometric optimization and the convergence standard energy is 10^{-5} Ha. Zr_nNi clusters who have even number of electrons are studied starting from spin singlet, the method of spin non-restriction is used in the calculation, and all possible spin multiplicity are optimized. In order to verify the reliability of the method used in this article, firstly, dimer Zr_2, whose experimental data can be contrasted, are calculated. The result show that the Zr–Zr bond length (0.2324 nm) is consistent with the results of calculation well [22, 23, 42, 43], which means that the method chosen in this paper is reasonable.

3. Results and discussion

3.1. Geometrical structures of Zr_nNi clusters

The equilibrium structures of Zr_nNi clusters are shown in Fig. 1, the dark balls are on behalf of Ni atoms and the light color balls are on behalf of Zr atoms. The balance structures of clusters are marked as *na*, *nb*, *nc*, and so on for any specific size and their energies change from low to high, where *na* stand for ground state of Zr_nNi cluster. Physical quantities such as spin multiplicities, symmetry and energy difference of equilibrium structure (*nb*, *nc*, and so on) and ground state (*na*) on Zr_nNi are listed in Fig. 1. In fact, the spin multiplicities are fully considered for all configurations. The energies of all spin states are considered and calculated for all the balance configurations. But in the following only the lowest energy states of steady state are talked.

The symmetric configuration of ZrNi ground state is 1a, of which spin state is quintuplet, Zr–Ni bond length is 0.2446 nm. For Zr_2Ni clusters, its ground state is an isosceles triangle structure as $2a$ (C_{2v}), whose apex angle is 65.23°, Zr–Ni bond length is 0.2406 nm, Zr–Zr bond length is 0.2593 nm and spin state is also quintuplet, which shows Zr–Zr bond length is longer than that of Ni–Zr in Zr_2Ni cluster agreeing with the result in Ref. [44]; another kind of configuration is linear type with Ni in the center of symmetry, its energy is 1.940 eV higher than the ground state energy. The ground state ($3a$) of

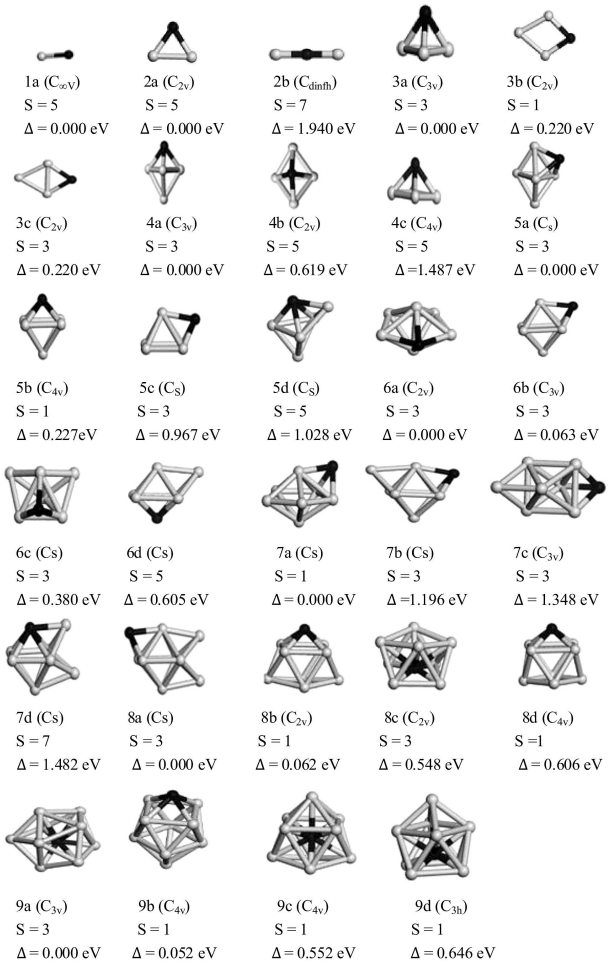

Fig. 1. The equilibrium structures, symmetries, multiplicity S and energy difference ΔE between equilibrium state and base state of Zr_nNi clusters. (1) The dark balls are on behalf of Ni atoms and the light color balls are on behalf of Zr atoms. (2) The equilibrium structures of clusters are marked as *na*, *nb*, *nc*, and so on for any specific size. (3) Spin multiplicity, symmetry and energy difference of equilibrium structure (*nb*, *nc*, and so on) and ground state *na* of Zr_nNi are listed in figure.

Zr_3Ni is spin triplet with C_{3v} tetrahedron symmetry, other structures of Zr_3Ni are of C_{2v} symmetry as shown, $3b$ and $3c$, they are spin singlet and spin triplet respectively, both their energy is 0.220 eV higher than that of Zr_3Ni ground state. The balance geometric structures of Zr_4Ni are obtained as shown, $4a$ (C_{3v}), $4b$ (C_{2v}), $4c$ (C_{4v}) in Fig. 1. They are double cone, twin double cone and right square pyramid, the energies of $4b$ (C_{2v}), $4c$ (C_{4v}) are 0.619 and 1.487 eV higher than that of $4a$ (C_{3v}), respectively. $4a$ (C_{3v}) is the ground state of Zr_4Ni and its spin is triplet. The ground state ($5a$) of Zr_5Ni is triangular bipyramid and whose spin state is triplet, the geometric configuration (Cs) of which is gained by blocking a Ni atom to the ground state Zr_5 [23], and the rest of the balance structures of Zr_5Ni are also shown as 5b (C_{4v}), 5c (C_s) and 5d (C_s) in Fig. 1, and their energies are 0.227, 0.976, and 1.028 eV higher than the energy of the ground

state. It can be seen from Fig. 1 that the pentagon double cone structure $6a$ (C_s) is the ground state and its spin state is triplet, the rest of the balance structure as shown $6b$ (C_{3v}), $6c$ (C_s) and $6d$ (C_s) and their energies are 0.063, 0.380, and 0.605 eV higher than that of its ground state, respectively. The ground state of Zr_7Ni is spin singlet with geometric configuration as $7a$ (C_s), which is obtained by blocking a Ni atom to a little distortion double cone, and the rest of the three isomers are shown as $7b$ (C_s), $7c$ (C_{3v}) and $7d$ (C_s), their energies are 1.196, 1.348, and 1.482 eV higher than the energy of its ground state. It is found that Zr_7Ni ground state is the most stable of Zr_nNi clusters through the following analysis, which is similar to the results of literatures [24, 25], where Zr_7Fe and Zr_7Co are the stable states of Zr_nFe and Zr_nCo. The ground state structure of Zr_8Ni clusters is shown as $8a$ (C_s), whose spin is triplet, which is not the same as the Zr_8Fe and Zr_8Co structures in literature [24, 25], the balance of the other structure as shown $8b$ (C_{2v}), $8c$ (C_{2v}), $8d$ (C_{4v}), their energies are 0.062, 0.548, and 0.606 eV higher than that of the ground state. The structure of the ground state on Zr_9Ni is shown as $9a$ (C_{3v}), whose spin is triplet, the other balance structures for Zr_9Ni are shown as $9b$ (C_{4v}), $9c$ (D_{3h}), $9d$ (C_{4v}), their energy is 0.052, 0.552, and 0.646 eV higher than that of the ground state, respectively.

3.2. The relative stability of Zr_nNi clusters

Average binding energy E_b, the second-order difference energy $\Delta_2 E$ and energy gap E_{gap} (energy difference between HOMO and LUMO) of the ground state have been calculated and the results have been listed in Table I.

TABLE I

Atomic averaged binding energy E_b, the second-order difference energies $\Delta_2 E_n$, and energy gap E_{gap} between HOMO (the highest occupied orbital) and LUMO (the lowest unoccupied orbital) for the ground state Zr_nNi ($n = 2$–9) clusters.

Cluster	E_b [eV]	$\Delta_2 E_n$ [eV]	E_{gap} [eV]
ZrNi	1.420		0.008
Zr_2Ni	2.960	0.195	0.320
Zr_3Ni	3.423	–0.585	0.220
Zr_4Ni	3.813	0.171	0.115
Zr_5Ni	4.044	0.105	0.163
Zr_6Ni	4.195	–0.504	0.129
Zr_7Ni	4.371	0.937	0.443
Zr_8Ni	4.403	–0.467	0.208
Zr_9Ni	4.476		0.338

In order to describe their properties, the results have been shown in Figs. 2–4, respectively. The average binding energy and the definition of second-order difference energies are as follows:

$$E_b(n) = \frac{(nE_t(\mathrm{Zr}) + E_t(\mathrm{Ni}) - E_t(\mathrm{Zr}_n\mathrm{Ni})}{n+1}, \quad (1)$$

$$\Delta_2 E(n) = E_t(\mathrm{Zr}_{n+1}\mathrm{Ni}) + E_t(\mathrm{Zr}_{n-1}\mathrm{Ni}) - 2E_t(\mathrm{Zr}_n\mathrm{Ni}). \quad (2)$$

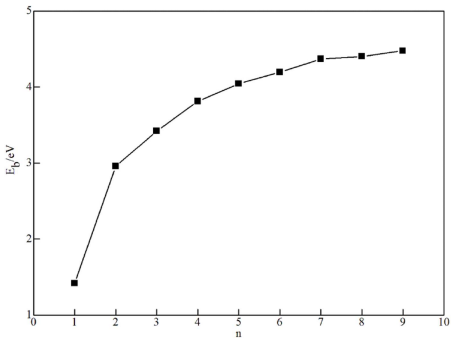

Fig. 2. Size dependence of average binding energy E_b of the ground state Zr_nNi clusters.

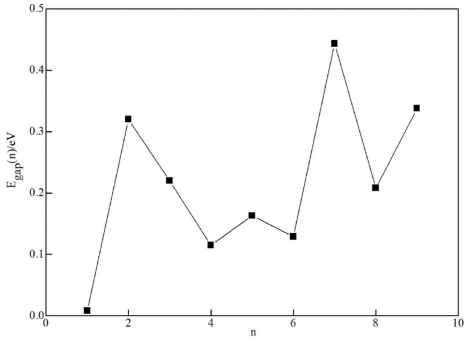

Fig. 3. Size dependence of energy gap E_{gap} of the ground state Zr_nNi clusters.

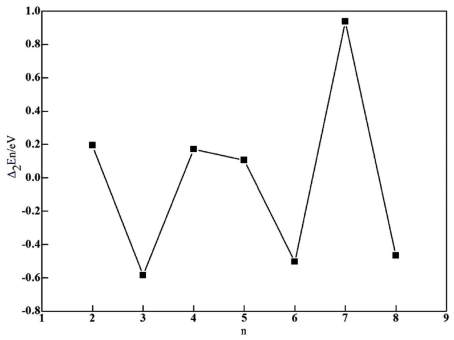

Fig. 4. Size dependence of the second-order difference energies $\Delta_2 E_n$ of the ground state Zr_nNi clusters.

Here $E_t(\mathrm{Zr})$, $E_t(\mathrm{Ni})$, $E_t(\mathrm{Zr}_{n-1}\mathrm{Ni})$, $E_t(\mathrm{Zr}_n\mathrm{Ni})$, and $E_t(\mathrm{Zr}_{n+1}\mathrm{Ni})$ represent energies of the corresponding atoms and clusters, respectively. Figure 2 shows that the average binding energy increases with the size of cluster becoming large. The average binding energy of cluster grows rapidly for n changing from 1 to 2 and 6 to 7, however the change of the binding energy is slower for n changing from 2 to 5 and 7 to 9. There is a local maximum for $n = 2$, 7, which means that these clusters are more stable than their neighboring clusters. As we know the size of the E_{gap} reflects the ability of the electronic transition from HOMO to LUMO, to some extent, E_{gap} represents the ability to participate in chemical reactions. Figure 3 shows the change rule of E_{gap} with its size, from which it can be seen that local maximum of E_{gap} appears at $n = 2$, 5, 7, which further indicates

the stability of the corresponding clusters are higher than other clusters. In the field of clusters physics, the greater the second-order energy difference the more stable of clusters. Figure 4 shows the change law of $\Delta_2 E$ with its size. It can be seen that when $n = 2, 7$, $\Delta_2 E$ appears local maximum, which means that these clusters are more stable being coincident with the results of E_{gap}. Both the energy gap and second-order energy difference of Zr_7Ni are the biggest in all clusters, and its value is far greater than other clusters, suggesting that the singlet state of Zr_7Ni is the most stable of all Zr_nNi ($n = 1$–9), the exceptional stability to the singlet state of Zr_7Ni can be explained by the jellium model of metal clusters [45]. Zr has 4 valence electrons whereas Ni has 10. In Zr_7Ni, there are $7 \times 4 + 10 = 38$ valence electrons. 2 of them can be considered to complete Ni $3d$ orbital and the remaining 36 electrons may be considered for the construction of a closed super atomic shell. It is not difficult to draw from Figs. 2–4 that Zr_2Ni and Zr_7Ni are magic number of Zr_nNi, they can be gotten by capping a Ni atom to the stable structures of Zr_2 and Zr_7 [23], respectively.

3.3. Magnetic property of Zr_nNi clusters

The occupied number of electrons orbital can be gotten by the analysis of the Muliken population, and the average magnetic moment has been obtained by calculating the difference of electron occupation number between spin up state and spin down state. The total magnetic moment of the clusters, magnetic moment of Zr and Ni atoms of the ground state are presented in Table II. It can be seen from Table II that the magnetic moment of clusters system mainly comes from the contribution of Zr atom, and the magnetic moment of clusters can be divided into two parts: Zr_nNi clusters almost have stable magnetic moment 4 μ_B for $n = 1$–2, however the magnetic moment of Zr_nNi is basically stable in 2 μ_B for $n = 2$–9 (except for $n = 7$) clusters, which is very similar to Ge_nFe clusters [46]. It also can be seen that Ni atom gets charge from Zr atom by the Mulliken population analysis.

TABLE II

Total magnetic moment of Zr_nNi, average atomic magnetic moment of Zr atom, atomic magnetic moment of Ni atom and charge C_{Ni} of Ni atom on the ground state Zr_nNi ($n = 2$–9) clusters.

Cluster	Magnetic moment [μ_B]			Charge [e]
	Zr_nNi	Zr	Ni	Ni
ZrNi	4.0	2.983	1.017	-0.129
Zr_2Ni	4.0	3.734	0.266	–0.124
Zr_3Ni	1.999	1.638	0.361	–0.089
Zr_4Ni	2.0	2.003	–0.003	–0.039
Zr_5Ni	1.998	1.754	0.246	–0.129
Zr_6Ni	1.968	1.447	0.521	–0.088
Zr_7Ni	0	0	0	–0.210
Zr_8Ni	1.999	1.764	0.235	–0.162
Zr_9Ni	2.261	2.155	0.106	–0.247

3.4. The electronic properties of a typical cluster Zr_2Ni

The total and partial density of states of Zr and Ni atom for both up and down spins on the typical cluster Zr_nNi ($n = 2$) are shown in Fig. 5 in order to verify our calculated result that the magnetic moment of Zr_nNi cluster mainly coming from Zr atom is reasonable, from which it can be seen that the total density of states of Ni and Zr atom for both up and down spins are not symmetrical and the magnetic moment of Zr_2Ni cluster mainly comes from Zr atom, the partial density of states of Ni and Zr atom for both up and down spins are not symmetrical and the magnetic moment of Ni and Zr atom mainly comes from the electrons of $3d$ orbital. Both the electronic properties of a typical cluster Zr_nNi (n=2) and the results in Refs. [24] and [25] that the magnetic moment of the clusters Zr_2Fe, Zr_4Fe, ZrCo and Zr_2Co mainly came from Zr atom show our result is credible.

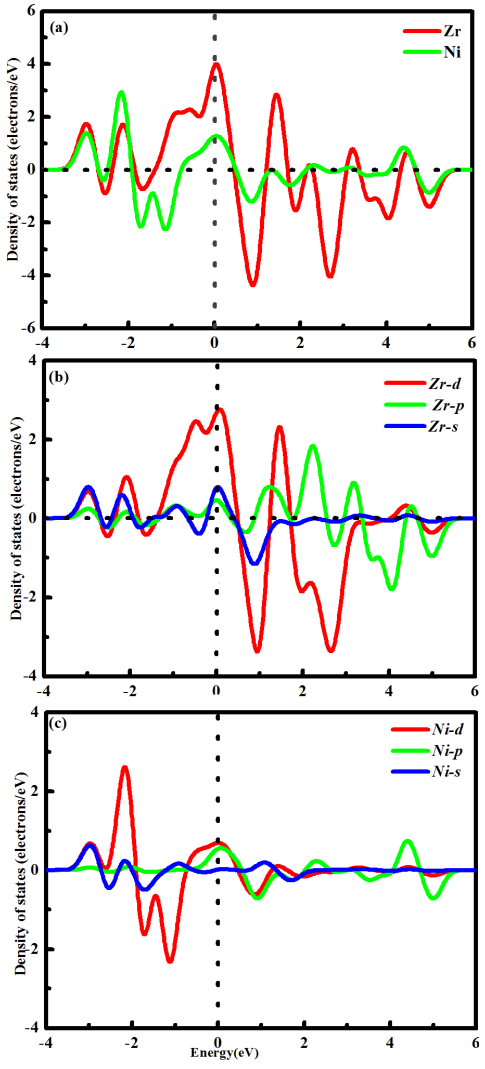

Fig. 5. The total and partial density of states of Zr and Ni atom in Zr_2Ni cluster ((a),(b) and (c) are total and partial density of states of Zr and Ni atom in Zr_2Ni cluster).

4. Conclusion

In this paper, the first principles which is based on density functional theory are used to study Zr_nNi ($n = 1$ to 9) clusters, the generalized gradient approximation (GGA) is carried out in the optimization and calculation of energy and magnetic features. The results are as follows:

(1) Zr_7Ni is the most stable of all Zr_nNi ($n = 1$ to 9) clusters, who have the largest average binding energies, energy gap and the second-order difference of energy.

(2) The magnetic moment of the ground state Zr_nNi clusters is about 4 μ_B for $n = 1$–2, however the magnetic moment is about 2 μ_B for $n = 2$–9 (except for $n = 7$) from the Muliken population analysis.

(3) Ni atoms get certain charge from Zr atoms and Ni atoms are the electron acceptor for Zr_nNi clusters.

Acknowledgments

This research was supported by the National Natural Science Foundation of China under grant No. 11405280 and the Scientific Research Projects Start-up Foundation of High Level Talented Person of Zhoukou normal college under grant No. ZKNUB2013005.

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