Structural stabilities and electronic properties of Mg$_{28-n}$Al$_n$ clusters: A first-principles study

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In this paper, we have constructed the alloy configurations of Mg$_{28-n}$Al$_n$ by replacing atoms at various possible positions, starting from the stable structures of Mg$_{28}$ and Al$_{28}$ clusters. According to the symmetry of the cluster structure, the isomers of these initial structures have been screened with the congruence check, which would reduce computational hours and improve efficiency. Using the first-principles method, the structural evolution, mixing behavior and electronic properties of Mg$_{28-n}$Al$_n$ clusters are investigated for all compositions. We conclude that Al atoms prefer to reside in the central positions of Mg–Al clusters and Mg atoms tend to occupy the peripheral location. The negative mixing enthalpies imply the stabilities of these Mg–Al clusters and thus possible applications in catalysis and hydrogen storage materials. Among Mg$_{28-n}$Al$_n$ clusters, Mg$_{24}$Al$_4$, Mg$_{21}$Al$_7$, Mg$_{14}$Al$_{14}$, Mg$_{26}$Al$_2$ and Mg$_{27}$Al$_1$ present relatively high thermodynamic stabilities, and the electronic properties of these stable structures are discussed with the charge distributions around the Fermi level. © 2017 Author(s).

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INTRODUCTION

Bimetallic clusters$^1$ continue to be attractive due to their unexpected stabilities and extraordinary electronic properties, with a variety of applications in catalysis,$^2$ optics$^3$ and spintronic.$^4$ In comparison with pure clusters, the properties of bimetallic clusters vastly rely on the chemical compositions,$^5$ cluster size$^6,7$ and the detailed atomic structures, crucial for the regulation in practice. For instance, in the Ag$_{3-x}$Au$_x$ ($x=0–3$), the binding energies of CO increase with increasing the number of Au atoms, and the s–d energy gap was found to become smaller by increasing the Au content in the case of anionic clusters.$^8$ Note that bimetallic clusters display not only magic size but also magic compositions,$^9$ characterized by the relatively high stability. Among Ni$_{13-n}$Ag$_n$ ($n=0–13$) clusters, the magic composition NiAg$_{12}$ exhibits the unique properties including the high coordinated structure and the total magnetic moment of zero, as well as maximum HOMO–LUMO gap.$^4$

Aluminum is a light-weight and low-cost metal material, while Al clusters and doped-Al clusters have been widely investigated.$^{10}$ The mixed metal systems of magnesium and aluminum are lighter and cheaper than other Al–based alloy,$^{11,12}$ having superiorities in the development of new materials for hydrogen storage.$^{13}$ Based on the density functional theory (DFT), small stable Mg–Al clusters such as MgAl$_4$$^{14}$ and Mg$_4$Al$_4$ were theoretically investigated. Osorio and

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co-workers discussed the potential energy surface of Mg$_x$Al$_{28}$ ($x, y=1$–$4$) and found that MgAl$_4$, Mg$_2$Al$_4$ and Mg$_4$Al$_4$ present high stabilities. From the famous magic cluster of Al$_{13}$, previous theoretical studies were also focused on the structural and electronic properties of hydrogenated MgAl$_{12}$ clusters.

According to a spherical jellium$^{21}$ which the electronic configuration of clusters approaches a closed shell, magic clusters have the valence electron count of 2,8,18,20,34,40. . . . The neutral and anionic MgAl$_n$ ($n=3$–20) have been carried out by the combination of the Particle Swarm Optimization (CALYPSO)$^{22–24}$ method and the time-dependent DFT calculation,$^{25}$ indicating that the MgAl$_6$ cluster shows high stability due to the magic number of 20. Expected stabilities were found in Mg$_2$Al$_{5}$, Mg$_3$Al$_{11}$ with 20 and 40 valence electrons. However, Mg$_2$Al$_7^-$, Mg$_2$Al$_{11}^-$ and Mg$_2$Al$_{11}^-$ non-magic clusters exhibit unexpected stabilities,$^{12}$ revealing that applications of the jellium model may be inapplicable in some cases of the Mg–Al clusters.

Probing the ground state structures of bimetallic clusters is more complex than the corresponding pure clusters, due to the existence of homotops$^{26}$ which have the same number of total atoms, component and geometrical structures, but different in the atom arrangement.$^5$ With the increasing of the bimetallic cluster size, the number of homotops increases rapidly.$^{27}$ For the medium and large bimetallic clusters, the structure prediction will become time-consuming because of numerous possible candidates. Paiva et al. focused on probing the most stable candidates of Mg–Al clusters of the total atoms number up to 55.$^{11}$ They predicted the 10 lowest energy structures for given chemical component using the genetic algorithm of Gupta potential function and re-optimized these structures with the DFT calculation. The investigation exposed that the atomic arrangement of Mg–Al clusters has a tendency of core-shell segregation.$^3$

In this paper, taking 28-atom as an example, we perform a detailed investigation of the medium size Mg–Al clusters with the congruence check. Here, we consider two initial morphologies, the pure Mg$_{28}$ and Al$_{28}$ clusters reported in the literatures. In order to probe the stable structures, the candidates of Mg–Al clusters are from the substitution by Al atoms on Mg atoms of the pure Mg$_{28}$ cluster and vice versa, followed by the re-optimization using the first-principles calculations. This task is complicated for 28-atom bimetallic clusters because of the large number of equivalent homotops. We adopt the molecular eigen-subspace projection function (EPF)$^{28}$ method to screen non-equivalent homotops and study the geometries, structural evolution and electronic properties of 28-atom Mg–Al clusters. For comparison, the CALYPSO method is used to conduct a global structure search for some given components.

**CALCULATION METHODS**

We performed the calculations of Mg–Al cluster based on DFT method, as implemented in the Vienna ab initio simulation package (VASP).$^{29–32}$ The projector augmented wave (PAW) method was adopted and the exchange-correlation functional was formulated by Perdew–Burke–Ernzerhof (PBE) within the generalized gradient approximation (GGA). The energy cutoff was set to be 350 eV for the plane wave basis set, and the converged criteria of the force on each atom was fixed on 0.01 eV/Å, with a K mesh of $1 \times 1 \times 1$. In order to eliminate the interactions of two neighbor clusters, the vacuum distances were set to be more than 10 Å. We considered the valence electron configuration of $3s^2$ for Mg atoms, and $3s^23p^1$ for Al atoms.

In order to describe the structural stabilities of a binary alloy cluster, we have calculated a mixing enthalpy which is defined as:

$$\Delta H = \frac{E(Mg_{28-n}Al_n)}{28} - (1 - x)\frac{E(Mg_{28})}{28} - x\frac{E(Al_{28})}{28}$$

The total energy of the Mg–Al cluster noted by $E(Mg_{28-n}Al_n)$ is compared to the energy of the stable structures of pure Mg$_{28}$ and Al$_{28}$ cluster, while $\chi$ and $1-\chi$ denote the percentage of Al and Mg atoms, respectively. A negative value of mixing enthalpy indicates a favorable mixing tendency. When we used the CALYPSO method to predict structures,$^{34,35}$ at least 1000 isomers were probed on the same molecular formula to achieve a lower energy structure, and the 30 lowest energy isomers were further optimized to predict the ground state structure.
RESULTS AND DISCUSSIONS

Initial structures

To obtain the possible stable alloy clusters, we start from the stable structures of Mg$_{28}$ cluster$^{36}$ and Al$_{28}$ cluster$^{37,38}$ with Mg–Mg distances of 3.07 Å and Al–Al distances of 2.70 Å, respectively. We choose two systems of pure Mg$_{28}$ clusters: one is the stable structure reported in the literature as shown in Figures 1(a); the other one is given in Figures 1(b) where the four atoms in the middle of the cluster have a smaller offset position. Brown and blue balls represent Mg and Al atoms, respectively. The following diagrams have the same marks. The Mg atoms of these two Mg$_{28}$ initial structures are gradually replaced by Al atoms at various possible positions with $n=1$–4. Based on the symmetry of cluster structure, the isomers of Mg–Al clusters are screened with the congruence check and re-optimized by theoretical calculations. Note that the alloy clusters in Figs. 1(b) show relatively high stability. Thus, we use the Mg$_{28}$ structure shown in Figs. 1(b) for the possible alloy clusters. Similarly, we create initial Mg$_{28–n}$Al$_n$ $(n=24–27)$ structures with Mg-substituting of the stable structure of Al$_{28}$ shown in Figs. 1(c).

According to the congruence check, the total number of Mg–Al isomers reaches 8712 when the number of Al atoms $n=5$, and 8614 when the number of Mg atoms is 5, therefore the traversal calculation is no longer used. We analyze the structural evolution of Mg$_{28–n}$Al$_n$ $(n=1–4, 24–27)$ and conduct over 20 different isomers as starting geometries for Mg–Al clusters with $n=5$–13, 15, 17, 19, 21, 23. The CALYPSO method is also used to conduct a global structure search for $n=2$–5, 7, 10, 11, 14, 20, 22, 24, 26.

Structures of Mg$_{28–n}$Al$_n$ $(n=1–6)$ clusters

The lowest energy structure and some representative isomers of Mg$_{28–n}$Al$_n$ $(n=1, 2)$ clusters are displayed in Figure 2. As illustrated in Figs. 2(a), the most stable structure of Mg$_{27}$Al$_1$ can be considered as the Mg$_{28}$ cluster with the Al atom locating at the center of the alloy cluster. The following two systems have the Al atom occupying the interior sites with relative energies of 0.128 eV and
FIG. 3. The most stable isomers of Mg$_{28-n}$Al$_n$ clusters from \(n=3\) to \(6\), (a) Mg$_{25}$Al$_3$ (b) Mg$_{24}$Al$_4$ (c) Mg$_{23}$Al$_5$ (d) Mg$_{22}$Al$_6$.

0.164 eV. The structures that Al atoms occupy the surface have high energy and poor thermodynamic stability characteristics. For Mg$_{26}$Al$_2$ shown in Figs. 2(b), the most stable structure is greatly deformed compared with the Mg$_{28}$ cluster, having the two Al atoms in the central position adjacent to each other. Two Al atoms are located in the internal of alloy cluster for the third and fourth isomers, which are 0.312 eV and 0.329 eV higher than the most stable structure. From high energy structures, the more Al atoms are located on the surface, the worse system stability.

Figure 3 shows the lowest energy structures of the Mg$_{28-n}$Al$_n$ clusters with \(n=3\) to \(6\). Our results indicate that these four optimized structures have large deformations compared with the initial structures. Mg$_{25}$Al$_3$ has been found that three Al atoms are adjacent in the center of the cluster, with two Al–Al distances of 2.727 Å and 2.816 Å. In Mg$_{24}$Al$_4$, four Al atoms are aggregated into a tetrahedral structure with Al–Al bonds from 2.711 Å to 2.888 Å, while Mg$_{23}$Al$_5$ has an additional Al atom capping Al$_4$ group, forming a double tetrahedron structure with Al–Al distances in the ranges of 2.682–3.024 Å. Mg$_{22}$Al$_6$ is based on the structure of Mg$_{23}$Al$_5$, capping an additional Al atom on the double tetrahedral structure with Al–Al distances in the ranges of 2.682–3.024 Å. Thus, in the lowest energy structures of the Mg$_{28-n}$Al$_n$ (\(n=3\)–\(6\)) clusters, Al atoms tend to occupy the central position of the alloy cluster forming a tetrahedral structure. Al atoms prefer to be adjacent since the Al–Al bond is stronger than the Mg–Al interaction.

**Structures of Mg$_{28-n}$Al$_n$ (\(n=20–27\)) clusters**

Figure 4 shows the lowest energy structure and some representative isomers of Mg$_{28-n}$Al$_n$ (\(n=27, 26\)) clusters. For Mg$_1$Al$_{27}$ and Mg$_2$Al$_{26}$, the ground state geometries correspond to the pure Al$_{28}$ cluster. As illustrated in Figs. 4(a), the Mg$_1$Al$_{27}$ with lowest energy is the one with the Mg atom on the side edge of alloy cluster, followed by the one which the Mg atom is at the vertex with the relative energy of 0.068 eV. The highest energy isomer has the relative energy of 1.095 eV with the Mg atom in the core of alloy cluster. For Mg$_{26}$Al$_2$ shown in Figs. 3(b), the lowest energy system has the structure which two Mg atoms are scattered on the side edge of the clusters. The following system has two Mg atoms on the two opposite edge of alloy cluster with the relative energy of 0.020 eV. As long as there is an Mg atom in the core of Mg$_{26}$Al$_2$ clusters, isomers have high energy,
and among them the system which the two Al atoms are adjacent has the highest relative energy of 1.318 eV.

For a further increase of Mg atoms component, the ground state structures of Mg$_4$Al$_{24}$, Mg$_6$Al$_{22}$ and Mg$_8$Al$_{20}$ clusters are displayed in Figure 5. It can be seen that these Mg–Al clusters are clearly deformed compared with the initial structures and the Mg atoms tend to be segregated on the surface of the cluster. For Mg$_4$Al$_{24}$, the structure has an open cage like the Al$_{13}$ icosahedron. For Mg$_6$Al$_{22}$, we can find two groups whose structures are similar to distorted icosahedrons. One group has Al–Al separations in the ranges of 2.632–3.106 Å, Mg–Al distances from 2.910Å to 3.067 Å, and Mg–Mg separation of 3.071 Å. The other group has Al–Al separations in the ranges of 2.664–3.270 Å, Mg–Al distances from 2.862Å to 3.015 Å, and Mg–Mg separation of 3.040 Å. Mg$_8$Al$_{20}$ shown in Figs. 5(c) also includes two icosahedron fragments. Overall, the structures of these clusters with the Al atoms number $n=24, 22, 20$ are based on icosahedrons and the remaining atoms stay outside the icosahedrons.

**Mixing properties**

The mixing enthalpies of the Mg–Al clusters for the entire component have been computed as Figure 6 shown. In the same component series, the maximum negative value of the mixing enthalpy implies the most stable cluster. It can be seen that the mixing enthalpies are negative for all compositions, demonstrating that these structures are beneficial to the formation of Mg–Al alloy at the cluster scale. Among Mg$_{28-n}$Al$_n$ ($n=0–28$) clusters, Mg$_{24}$Al$_4$, Mg$_{21}$Al$_7$, Mg$_{14}$Al$_{14}$, Mg$_2$Al$_{26}$ and Mg$_1$Al$_{27}$ have relatively a good capability for thermodynamic stability. Note that parts of the structures probed by CALYPSO method have lower energy; however this method is at high computational cost.
FIG. 7. The charge density within $[E_F - 1 \text{eV}, E_F]$. The isosurfaces (yellow) compared to the peak amplitudes are 75%/60%/60%/50%/60% for (a) Mg$_{24}$Al$_4$ (b) Mg$_{21}$Al$_7$ (c) Mg$_{14}$Al$_{14}$ (d) Mg$_2$Al$_{26}$ (e) Mg$_1$Al$_{27}$.

The alloy configurations by replacing atoms with the congruence check can be a method of researching alloy clusters.

**Electronic properties**

In the following, we focus on electronic properties of Mg$_{24}$Al$_4$, Mg$_{21}$Al$_7$, Mg$_{14}$Al$_{14}$, Mg$_2$Al$_{26}$, and Mg$_1$Al$_{27}$ which are relatively high stability systems in term of the mixing enthalpy, analyzing the charge density with in $[E_F - 1 \text{eV}, E_F]$ as shown in Figure 7. For Mg$_{24}$Al$_4$, the charges are mainly located around the Al$_4$ tetrahedron in the center of the alloy cluster, while a few charges are distributed on the surface, suggesting that the chemical reactivity of the surface is relatively poor. In Mg$_{21}$Al$_7$, only a few charges cover the Mg–Mg bonds compared with the charge distribution around the Al atoms. The charge density in Mg$_{14}$Al$_{14}$ shows that the electrons distribute around Al and Mg atoms and the charge distribution around the Al atoms is larger than that of Mg atoms. For Mg$_2$Al$_{26}$, the charge density is mainly concentrated around the Al atoms on the top sites of the cluster, the same as Mg$_1$Al$_{27}$. Thus, in Mg$_{21}$Al$_7$, Mg$_{14}$Al$_{14}$, Mg$_2$Al$_{26}$ and Mg$_1$Al$_{27}$, most of the charges are located on the surface position, providing the active centers for chemical reaction such as absorbing hydrogen atoms. For all of these stable structures, the charge distributions near the Fermi level tend to be around the Al atoms.

**CONCLUSION**

In summary, we have investigated bimetallic Mg–Al clusters using the density functional theory. The calculations reveal that Al atoms prefer to gather around the center of the clusters, while Mg atoms segregate to the surface, leading to a core-shell like structure. The mixing enthalpies of structures are found to be negative for all components, illustrating that these Mg–Al alloy clusters are energetically favorable against the phase segregation. The five systems Mg$_{24}$Al$_4$, Mg$_{21}$Al$_7$, Mg$_{14}$Al$_{14}$, Mg$_{26}$Al$_2$ and Mg$_{27}$Al$_1$ present outstanding stabilities and the charge distributions around the Fermi level of these clusters prefer to be around the Al atoms. These may play a guiding role in the research of the Mg–Al alloy stability under the finite size and the development of new functional materials.

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