Hcp-icosahedron structural transformation induced by the change in Ag concentration during the freezing of $(CoAg)_{561}$ clusters*

Xiao Xu-Yang(肖绪洋)†

School of Electronics Engineering, Chongqing University of Arts and Sciences, Chongqing 402160, *China*

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The synergy effect of alloy elements in bimetallic clusters can be used to tune the chemical and physical properties. Research on the influences of alloy concentration and distribution on the frozen structure of bimetallic clusters plays a key role in exploring new structural materials. In this paper, we study the influence of Ag concentration on the frozen structure of the $(AgCo)_{561}$ cluster by using molecular dynamics simulation with a general embedded atom method. The results indicate that the structure and chemical ordering of the $(AgCo)_{561}$ cluster are strongly related to Ag concentration. Hcp-icosahedron structural transformation in the frozen $(CoAg)_{561}$ cluster can be induced by changing Ag concentration. The chemical ordering also transforms to Janus-like Co–Ag from core-shell Co–Ag.

Keywords: bimetallic cluster, freeze, molecular dynamics, structural transformation

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1. Introduction

Specific chemical and physical properties in bimetallic clusters have led to wide applications in catalysts, sensors, microelectronic and optoelectronic devices.[1] These properties are strongly related to the geometric shape, crystal structure, and chemical ordering of the clusters.[2] These cluster structures can be tuned by doping with different alloy elements or by varying the alloy concentration.[3−5] In addition, the formation of a stable structure is usually frozen from the liquid phase. Therefore, a study on the influence of atomic concentrations on the frozen structure of a bimetallic cluster is very important in exploring the structural evolution in bimetallic clusters.

In previous studies, it was found that many special structures appeared in bimetallic clusters at a given alloy concentration. A Co–Ag cluster with 30% Ag froze to form a core-shell structure with an hcp-like Co core.[6] Ag–Pd clusters with Pd atoms segregating at the subsurface layer were obtained by the collision of a large Ag_{135} cluster with a small Pd_{16} cluster.[7] In addition, it was also found that different chemical orderings (such as core-shell, Janus-like, onion-like) can be produced at different alloy concentrations.[8−10] It was also found that the chemical ordering of the $(AgCo)_{201}$ clusters can transform to Janus-like or three-shell onion-like structures from core-shell structures with a variation in Co concentration.[11] All the results indicate that the structure and the chemical ordering of bimetallic clusters can be tuned by varying the alloy concentration. Therefore, the structural evolution of bimetallic clusters with the variation in alloy concentration plays a key role in finding new structures and exploring the origin of special structures.

The frozen structure was frozen from the liquid state. Therefore, the influence of initial structure on the frozen structure can be ignored.[12] Furthermore, higher atomic energy obtained from higher temperature can make the cluster easily reach an equilibrium state and form a stable structure. The freezing process is more similar to the experimental process and can be used to compare with the experimental results. However, this causes a difficulty in studying the frozen structure. The atomic behaviour cannot be tuned in the simulation by controlling the initial structure and atomic distribution of the cluster. Therefore, it is necessary to study the evolution of the frozen structure in the bimetallic cluster in the overall concentration range by selecting special physical parameters. This is important in exploring the effect of atomic concentration on the frozen structural evolution of bimetallic

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†Corresponding author. E-mail: xuyxiao@126.com

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clusters.

In this study, molecular dynamics simulation with a general embedded atom method is used to study the influence of Ag concentration on the frozen structure of Co–Ag clusters. Co and Ag are selected as the objectives on account of the following reasons. (i) The structural transformation from fcc to hcp in Co-based bimetallic clusters can be tuned by manipulating the thermodynamic behaviour and interaction process of the cluster. This is helpful for discovering the influence of doping alloy element on structural evolution. (ii) The surface energy of Ag (1065 mJ·m^{-2}) is much lower than that of Co (2197 mJ·m^{-2}),[13] which might make Ag segregate easily and form core-shell, three-shell onion-like, or Janus-like chemical ordering, separately. All the Ag concentrations (from 0 at% Ag to 100 at% Ag at an increment of 10 at%) are considered in this study. The pair distribution function and snapshot are used to study the frozen structure.

2. Simulation details

In this study, the pure Ag cluster including 561 atoms with a cuboctahedral shape was first truncated from a $30a_0 \times 30a_0 \times 30a_0$ ($a_0 = 0.40862$ nm) large Ag bulk. The Ag–Co bimetallic clusters were obtained by randomly substituting Ag atoms with Co atoms according to the Ag concentration. Molecular dynamics simulation with a general embedded atom method was used to study the freezing of the clusters. The model has been used to study the melting of Ag–Pd clusters.[14] The accuracy of the embedded atom method in simulating bimetallic clusters has been described in Refs. [15] and [16]. The model has also been used to study the configuration evolution of the Ag–Co clusters.[11] The time step was 1.0 fs. All the clusters were relaxed for 0.2 ns at 2000 K to ensure that the cluster was melted completely. Furthermore, the temperature was much higher than the melting points for all the clusters. This could make atoms in the cluster obtain higher energy and easily reach an equilibrium state. Then, the clusters were cooled down to 200 K with a cooling rate of 0.5 K/ps. The initial temperature and the cooling rate are similar to those in previous works,[17] and can make the clusters obtain stable structures. The frozen structures were obtained by relaxing the cluster at 200 K for 0.2 ns.

3. Results and discussion

In order to define the influence of doping Ag atoms on the frozen structure of the Co–Ag cluster, the frozen structures of pure Ag_{561} and Co_{561} were first studied using their snapshots and pair distribution functions. Figure 1 gives the pair distribution functions of the frozen structures of Ag_{561} and Co_{561} and their corresponding snapshots. It can be seen that the frozen structure of Ag_{561} has an icosahedral character, which is formed by six 5-fold symmetry axes and a quasispherical shape with 20 (111)-like facets. The result is consistent with that of pair distribution function. For Co_{561}, the frozen structure is formed by the stacking of the (111) facets in an AB order. It can also be found that the hcp character peaks appear at 0.41 nm and 0.48 nm. All the results indicate that the Co_{561} formed an hcp structure. It is also found that the hcp structure was formed at the freezing point and not subjected to structural transformation in the cooling process. The hcp structure in the frozen Co_{561} is different from the result of the previous study.[17] In the previous study, the icosahedron was formed for Co_{531} after the cluster had frozen to 200 K from 2000 K with a cooling rate of 0.5 K/ps. It is found that the only difference is that the Co_{561} was relaxed for 0.2 ns at 2000 K by comparing their freezing conditions. This indicates that the relaxation at 2000 K makes the atom obtain enough energy to form a Co bulk-like structure for Co_{561}. The difference between the frozen structures of Ag_{561} and Co_{561} is conducible to studying the influence of Ag concentration on the frozen structure of the $(AgCo)_{561}$ cluster.

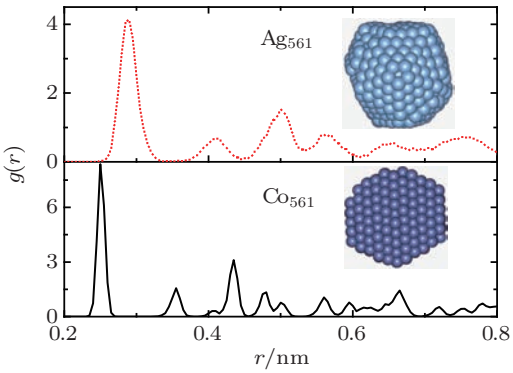


Fig. 1. (colour online) Pair distribution functions and snapshots of the frozen structures of clusters Ag_{561} and Co_{561}.

All the frozen structures of the Co–Ag clusters with different Ag concentrations were studied using the above-mentioned pair distribution function, which is shown in Fig. 2. Clearly, for the Co–Ag clusters with Ag concentrations of 10%, 20%, and 30%, there are hcp character peaks appearing at 0.41 nm and 0.48 nm. This indicates that these three clusters froze to form an hcp structure. For the Co–Ag clusters with

Ag concentrations of 40% and 50%, the hcp character disappears. The peaks are similar to those of the pure Ag_{561}. In other words, these two clusters froze to form an icosahedron. With the increase in Ag concentration, the position of the first peak changes to 0.28 nm from 0.25 nm. This indicates that the lattice constants of the cluster increase with the increase in Ag concentration. These clusters have characteristic peaks of icosahedron. The intensities of the peaks are weaker than those of the Co–Ag clusters with Ag concentrations of 40% and 50%, and the ordering of the icosahedron decreases. The difference between the frozen structures of the Co–Ag clusters with different Ag concentrations indicates that the hcp or icosahedral structure of the frozen Co–Ag bimetallic cluster can be tuned by varying the Ag concentration. In addition, there are no hcp or icosahedrons coexisting at the present Ag concentrations.

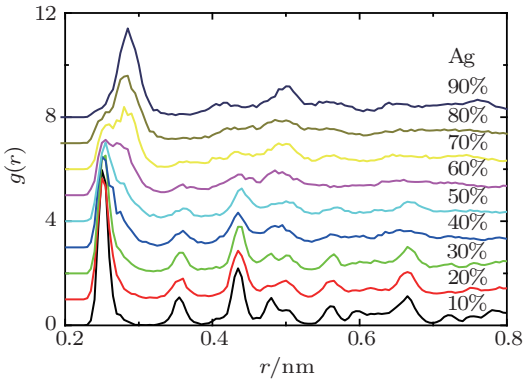


Fig. 2. (colour online) Pair distribution functions of Co–Ag clusters with different Ag concentrations.

The configurations and chemical orderings were studied using the overviews and cross sections of the frozen clusters, as shown in Fig. 3. The clusters with Ag concentrations of 10%, 20%, and 30% were formed by the stacking of (111) facets in an AB order by observing the atomic arrangement at a smaller size. The icosahedron with a symmetry axis was obviously formed by the clusters with Ag concentrations of 40%, 60%, and 70%. For the clusters with Ag concentrations of 50%, 80%, and 90%, the icosahedral characters in the atomic arrangement are not obvious in spite of the icosahedrons displayed by their pair distribution functions. In addition, the atomic morphologies in the surface layers of the frozen icosahedrons are also different. The icosahedral characters of the Co–Ag clusters with Ag concentrations of 40% and 50% are not more obvious than the others. This is because the atomic misfits are large for Co and Ag atoms. For these two concentrations, Ag atoms formed a coating layer. The lattice distortion between the Ag coating layer and the inner Co atoms makes the surface Ag layer distorted, which influences the icosahedral character of the surface layer. It is reasonable to conclude that the icosahedral character in the surface layer becomes obvious with the doped Ag atoms exceeding a given concentration. In other words, structural transformation in a bimetallic cluster can be induced by doping alloy elements with a certain concentration. The chemical ordering was studied using the cross section passing through the centre. A Co–Ag core-shell was formed for the clusters with Ag concentrations of 10%–50%. A Janus-like motif was formed for the clusters with Ag concentrations of 60% and 70%, and for the clusters with Ag concentrations of 80% and 90%, Co atoms aggregated into two small clusters and embedded in the subsurface layer of the clusters. This is because the cluster

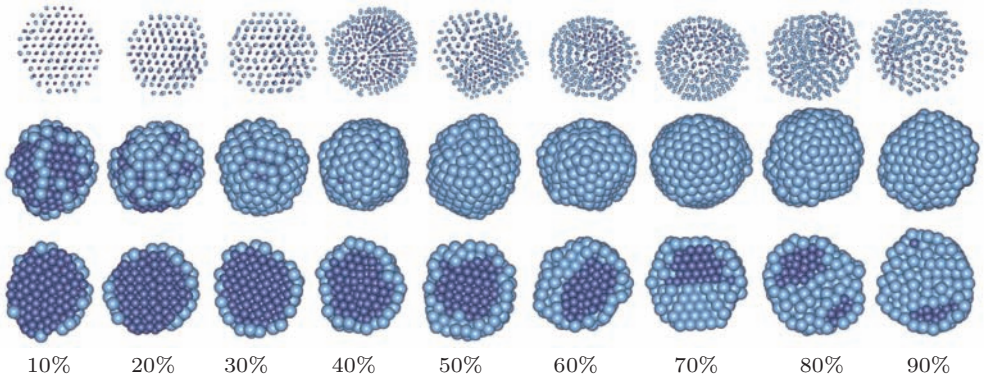


Fig. 3. (colour online) Frozen configurations of the clusters with different Ag concentrations. The first row shows all the atoms at a smaller size to display their inner arrangement. The second row shows only surface atoms. The third row shows cross sections, each passing through the centre of the cluster. The bright spheres are Ag atoms, and the dark spheres are Co atoms.

is stable for Co atoms embedded in the subsurface layer of the cluster.[11] In this study, it is also found that Ag atoms segregate to the surface layer of the cluster. Ag atoms on the surface layer of the clusters can inhibit the formation of the hcp structure and induce the clusters to form icosahedrons when the Ag concentration exceeds a given concentration. There is no action for lower Ag concentration.

4. Conclusions

A molecular dynamics simulation with a general embedded atom method is used to study the frozen structures of Co–Ag clusters in the overall Ag concentration range. It is found that Co bulk-like hcp is formed by the pure Co_{561} and $(CoAg)_{561}$ with a lower Ag concentration ($\leq 30\%$ Ag). The $(CoAg)_{561}$ clusters froze to form icosahedrons from Co bulk-like hcp with the increase in Ag concentration. The hcp-icosahedron structural transformation is induced by varying the Ag concentration. This is because the segregated Ag atoms form a coating layer and induce the structural transformation. In addition, chemical orderings like Co–Ag core-shell, Janus-like motif, and two small Co clusters embedded in the subsurface layer of the clusters are formed with the variation in Ag concentration.

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