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Surface segregation of Ag–Cu–Au trimetallic clusters

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Abstract
Segregation phenomena of Ag–Cu–Au trimetallic clusters with icosahedral structure are investigated by using a Monte Carlo method based on the second-moment approximation of the tight-binding (TB-SMA) potentials. We predict that the Ag atoms segregate to the surface of the Ag–Cu–Au trimetallic icosahedral clusters. The Ag concentrations in the surface layer of the clusters are about 11–29 at.% higher than the overall Ag concentration in all the cases studied. The simulation results also indicate that the Au atoms are mainly distributed in the middle shell and the Cu atoms are located in the center for the 147-, 309-, 561- and 923-atom clusters at 300 K. The segregation phenomena of the Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic clusters are mainly due to the different surface energies of the Ag, Au and Cu atoms. It is found that the size and composition have little effect on the segregation phenomena of Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic cluster.

1. Introduction
Due to their potential applications in the optical, magnetic and catalytic fields [1–4], metal clusters have evoked a lot of interest in recent years. Alloying clusters are more complex than monometallic clusters because of the introduction of new metallic components. It is found that trimetallic clusters possess much higher catalytic activity and selectivity, compared with the corresponding monometallic and bimetallic clusters [5, 6]. It should also be mentioned that the properties of trimetallic clusters can be tuned by size, composition and atomic ordering. For example, it was predicted in Ni–Cu–Rh clusters that the order–disorder transition and surface segregation phenomenon occur, depending on the cluster size, shape, composition and atomic ordering [7].

Trimetallic clusters have been prepared experimentally to improve the catalytic performance of the bimetallic clusters by the incorporation of a third metal. Most recently, Toshima et al have reported a new method to synthesize Pd–Ag–Rh trimetallic clusters with a triple core/shell structure by mixing Pd–core/Ag–shell bimetallic clusters with Rh atoms [5]. Zhang et al have also prepared Pt–Ru–Co trimetallic clusters by the reduction of an aqueous Pt–Ru–Co precursor solution with a parallel micro-emulsion system [6]. However, it is still difficult to understand the structural properties of trimetallic clusters in detail by experimental methods. The application of some theoretical methods shows great promise for understanding the detailed structures of trimetallic clusters. One of these methods is the statistical–mechanical free-energy concentration expansion method (FCEM), which is capable of studying multi-component alloy clusters. Rubinovich et al have studied Ni–Cu–Pd, Ni–Cu–Al and Ni–Cu–Rh trimetallic clusters by using the FCEM method, and found the surface segregation phenomena in these clusters [7, 8]. In addition, orbital-free DFT molecular dynamic simulations have been employed by Aguado et al to analyze the structural and melting properties of Li–Na–Cs trimetallic clusters [9].

In this work, attention is paid to the Ag–Cu–Au trimetallic clusters. There are three reasons for the selection of the Ag–Cu–Au system. First, the Ag–Cu–Au system is made up of relatively noble metals whose properties are well known [10]. Second, due to the medical applications of the alloys [11], the Ag–Cu–Au bulk alloys have been studied
of which is a size addition, metal clusters exhibit structural magic numbers, each characterized by using experimental methods [15]. Moreover, 923 atoms (L and 923 atoms with icosahedral structures are simulated. The potentials. The Ag–Cu–Au trimetallic clusters of 147, 309, 561 segregation in Ag–Cu–Au trimetallic clusters by using Monte Carlo (MC) methods have been successfully used to simulate the segregation processes in the bulk alloys [16–18] and alloying clusters [19–28]. The surface segregation in Ag–Cu–Au bulk alloys [29] has been studied by using Monte Carlo simulations. However, few reports are available for the surface segregation of Ag–Cu–Au trimetallic clusters.

The knowledge of the internal structure and size of metal clusters is particularly important for the understanding of their properties. Unlike the bulk metal materials, which possess the face-centered-cubic (fcc) or other crystalline structures, extensive experimental [30–32] and theoretical investigations [33, 34] have found that metal clusters up to several thousands of atoms in size exhibit noncrystalline icosahedral (ih) or other multiply twinned structures (MT). The icosahedral structure contains 20 fcc tetrahedra built up by hexagonal planes, and possesses the fivefold rotation symmetry and 20 external (111) facets [35, 36]. Therefore, the icosahedral cluster is related to the high surface-to-volume ratio and stability, which is preferred by relatively small clusters as observed in experimental studies [30–32]. In addition, metal clusters exhibit structural magic numbers, each of which is a size N corresponding to a perfectly symmetric ideal structure. In general, magic metal clusters are more stable and better observed in experiments [35, 37]. For an icosahedral structure with L shells (the central atom is denoted as L = 1), the magic number of atoms corresponding to a perfectly symmetric ideal icosahedron is [35]. NL = \( \frac{5}{2}L^3 - \frac{5}{2}L^2 + \frac{1}{2}L - 1 \). Thus, we can get the ideal icosahedral structures with the magic numbers of N = 147, 309, 561 and 923 atoms (L = 4, 5, 6 and 7, respectively), which are the subject of our investigation in this work.

The purpose of this work is to study the surface segregation in Ag–Cu–Au trimetallic clusters by using Monte Carlo simulations. The metal–metal interactions are modeled by the second-moment approximation of the tight-binding potentials. The Ag–Cu–Au trimetallic clusters of 147, 309, 561 and 923 atoms with icosahedral structures are simulated. The structure characteristics and the segregation of the Ag–Cu–Au trimetallic clusters at different compositions are discussed.

2. Computational details

2.1. Potential model and parameters

In Monte Carlo runs, we adopted the second-moment approximation of the tight-binding (TB-SMA) potential to model the interactions between atoms [38]. The TB-SMA potential function provides an accurate description of many basic properties of crystalline and non-crystalline bulk phases and surfaces [39], and obtains reasonable predictions of the structure [40–42] and thermodynamic properties [43, 44] of metal clusters. In addition, the TB-SMA potential has been used successfully in previous atomic-scale simulation studies of monometallic clusters [40, 45–47] and metal alloy clusters [41–44, 48–51], and shows excellent agreement with experimental and theoretical values such as surface energies and diffusion energy barriers, indicating that the TB-SMA potential rationally represents the interactions between atoms in Monte Carlo simulations of metal alloy clusters.

Within the TB-SMA potential, the total energy of a system is expressed as

\[
E_{\text{total}} = \sum_i (E_R^i + E_B^i),
\]

where \( E_R^i \) and \( E_B^i \) are the Born–Mayer ion–ion repulsion and band terms, respectively. Both terms can be written for an atom \( i \) as

\[
E_R^i = \sum_j A e^{-p (r_{ij}/r_0 - 1)} \quad (2)
\]

\[
E_B^i = -\sum_j \xi^2 e^{-2q (r_{ij}/r_0 - 1)}^{1/2}, \quad (3)
\]

where \( r_0 = a_0/\sqrt{2} \) (\( a_0 \) is the independent lattice constant for each pure system and for alloying clusters) and \( r_{ij} \) is the distance between atoms \( i \) and \( j \) in a cluster.

For the Ag–Cu–Au clusters, the parameters are of different values for the different interactions (Ag–Ag, Cu–Cu, Au–Au, Ag–Cu, Ag–Au and Cu–Au). The potential parameters \( A, \xi, p \) and \( q \) for the homometallic interactions (Ag–Ag, Cu–Cu, Au–Au) were achieved by fitting to the experimental values of the cohesive energy, lattice parameters and independent elastic constants of the pure metals [38]. The potential parameters \( A, \xi, p \) and \( q \) of the heteroatomic Cu–Au interaction were obtained by fitting to the experimental values of the cohesive energy, lattice parameters and independent elastic constants of the pure metals [38]. The parameters \( A, \xi, p \) and \( q \) of the heteroatomic Ag–Cu and Ag–Au interactions were fitted to the solubility energy [41, 48]. All these potential parameters used in this work are listed in Table 1.

2.2. Monte Carlo simulations

Based on the Metropolis algorithm [52], Monte Carlo (MC) simulation methods have been successfully used to study the surface segregation phenomena of metal bulk alloys [16, 29, 53] as well as metal alloy clusters [19–28]. These MC methods were proved to be particularly advantageous in

<table>
<thead>
<tr>
<th>( A ) (eV)</th>
<th>( \xi ) (eV)</th>
<th>( p )</th>
<th>( q )</th>
<th>( r_0 ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag–Ag</td>
<td>0.1028</td>
<td>1.178</td>
<td>10.928</td>
<td>3.139</td>
</tr>
<tr>
<td>Cu–Cu</td>
<td>0.0855</td>
<td>1.224</td>
<td>10.960</td>
<td>2.278</td>
</tr>
<tr>
<td>Au–Au</td>
<td>0.2061</td>
<td>1.790</td>
<td>10.229</td>
<td>4.036</td>
</tr>
<tr>
<td>Ag–Cu</td>
<td>0.0986</td>
<td>1.2274</td>
<td>10.700</td>
<td>2.805</td>
</tr>
<tr>
<td>Ag–Au</td>
<td>0.149</td>
<td>1.4874</td>
<td>10.494</td>
<td>3.607</td>
</tr>
<tr>
<td>Cu–Au</td>
<td>0.1539</td>
<td>1.5605</td>
<td>11.05</td>
<td>3.0475</td>
</tr>
</tbody>
</table>

* Reference [38]; † Reference [41, 48]; ‡ Reference [48].
studying segregation phenomena in the equilibrium alloy structure, because they can circumvent slow physical dynamic processes (such as diffusion) in the system and provide an averaged composition profile over a thermodynamic equilibrium ensemble [22, 25, 54].

In Monte Carlo simulations, the segregation processes are simulated by changing the chemical type of the atoms and slightly displacing the atoms from their original positions [16]. Two approaches can be used: grand canonical ensemble and canonical ensemble. The grand canonical ensemble simulation proceeds by picking an atom and then changing its type. In this approach, the equilibrium composition is obtained by maintaining the correct chemical potential difference $\Delta \mu$ between the two species [16]. In our previous works, we studied the metal Cu–Au and Pd–Pt clusters by using the grand canonical ensemble MC method [55, 56]. In contrast, the canonical ensemble simulation proceeds by interchanging two randomly picked different type atoms [16]. In this approach, starting from some atomic configurations, the successive configurations are generated in proportion to the probabilities of a configuration occurring in the equilibrium ensemble [22, 25, 26]. By using this method, the compositions of the metal clusters are fixed, corresponding to the compositions prepared in experiments. In this work, we focus on segregation phenomena in equilibrium structures of the clusters at fixed compositions rather than on the evolution towards equilibrium of the system. Therefore, the canonical MC method is a suitable technique. It is noticed that the canonical MC methods have been successfully used in several other surface segregation calculations of bimetallic Pt–Re [22], Pt–Ni [25], Pt–Mo [26] and Ag–Co [23] clusters with satisfactory results. Consequently, in our MC study of the Ag–Cu–Au trimetallic clusters, the canonical ensemble statistical mechanics was used, where the total number of atoms of each species and the simulation temperature remain unchanged.

In each MC step, the sampling scheme includes two types of trials:

1. Small displacement of a randomly selected atom from its original position in an arbitrary direction.
2. Two different atoms picked randomly are interchanged.

The trial is accepted if it results in a decrease in the configuration energy of the system. However, if the configuration energy is increased, trials are accepted with a probability $P$ proportional to the Boltzmann factor:

$$P = \exp\left(-\frac{\Delta E}{k_B T}\right),$$

(4)

where $k_B$ is the Boltzmann constant, $T$ is the simulation temperature and $\Delta E$ is the configuration energy difference.

Operation (1) corresponds to the relaxation and vibration movements, while operation (2) accounts for the segregation phenomenon in the Ag–Cu–Au trimetallic clusters. In operation (1), the magnitude of the atomic displacement is in the range $0$, $r_{\text{max}}$, where the maximum displacement $r_{\text{max}}$ at a given temperature is adjusted in order to retain the acceptance probability of a new configuration close to 0.5 during the simulation process.

In our MC simulations, 20000 MC steps were performed for each atom in the calculated clusters. The first 10000 steps per atom were used to reach the equilibrium, where the fluctuation of the total energy was less than 0.2%, and the following 10000 steps per atom were used for an average of the structural properties. In this work, the simulation temperature was fixed at 300 K. There was no periodic boundary condition applied in the cluster. Three compositions of $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$, $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ and $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{60}$ were selected for exploring the structural properties of the Ag–Cu–Au trimetallic clusters.

Aiming at understanding the cluster structure in detail, we calculated the reduced pair correlation functions of the Ag–Cu–Au trimetallic clusters, $g_{\text{cm}}^\ast(r)$. We define $g_{\text{cm}}^\ast(r)$ as the pair correlation function around the center of mass for the trimetallic clusters and $g_{\text{cm}}^\ast(r) = g_{\text{cm}}(r)/(V/N^2)$. Then, the reduced pair correlation function $g_{\text{cm}}^\ast(r)$ is given by $g_{\text{cm}}^\ast(r) = \langle \delta(\mathbf{r} - \mathbf{r}_{\text{cm}} - r) \rangle / N_{\text{att}}$, where $n$ is the atom number counted and $\mathbf{r}_{\text{cm}}$ is the coordinates of the center of mass at each MC step. The reduced pair correlation function was calculated from the block ensemble average after equilibrium, in which a block contains 10000 configurations.

3. Results and discussion

The surface segregations of Ag–Cu–Au trimetallic clusters are affected by the size of the clusters. We plot in figures 1(a)–(c) the calculated concentrations of Ag, Cu and Au atoms in the surface, subsurface and third (from surface to center) layers of the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters changing with the cluster size, respectively. It is found from figure 1(a) that the Ag atoms are enriched in the surface layer of the equilibrium $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters with different sizes. The Ag concentration in the surface layer is 26–29 at.% higher than the overall Ag concentration in the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters. It is also found in figure 1(a) that the Ag concentrations in the subsurface and third layers are much lower than the overall Ag concentration in the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters, while the Ag concentrations in the subsurface and third layers increase with the cluster size.

The calculated Au concentrations in the surface, subsurface and third layers of the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters changing with the cluster size are shown in figure 1(b). It is found in figure 1(b) that the Au concentration in the subsurface layer is 19–26 at.% higher than the overall Au concentration in the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters, indicating that the Au atoms segregate to the subsurface layer of the equilibrium $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters of different sizes. In contrast, the Au concentrations in the surface and third layers are much lower than the overall Au concentration in the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ clusters, as shown in figure 1(b).

In figure 1(c), we present the Cu concentrations in the surface, subsurface and third layers of the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters changing with the cluster size. It is observed from figure 1(c) that the Cu concentration in the third layer is much higher than the overall Cu concentration in the clusters, suggesting that the Cu atoms mainly aggregate in the third layer of the equilibrium $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ icosahedral clusters of different sizes. It can be also found from figure 1(c) that the extent of Cu segregation to the third layer decreases with the increase of cluster size. Furthermore, the Cu concentrations in the subsurface and surface layers are much lower than the overall Cu concentration in the $\text{Ag}_{20}\text{Cu}_{60}\text{Au}_{20}$ clusters.
Figure 1. Calculated Ag, Au and Cu concentrations in the surface, subsurface and third (from surface to center) layers of the Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters as a function of the cluster size at 300 K. (a) Ag concentration, (b) Au concentration, (c) Cu concentration.

lower than the Cu concentration in the third layer of the clusters.

To further explore the equilibrium structures of the Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters, the snapshots and reduced pair correlation functions of the clusters are supplied. We show in figure 2(a) final snapshots of the Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters with the sizes of 147, 309, 561 and 923 atoms at 300 K. Clearly, the Ag atoms are enriched on the surface, and the Au atoms are mainly in the middle shell, while the Cu atoms stay in the center for the 147-, 309-, 561- and 923-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters at 300 K. This observation is consistent with our calculated concentrations of Ag, Au and Cu atoms in the surface, subsurface and third layers of the Ag$_{60}$Cu$_{20}$Au$_{20}$ icosahedral clusters, as shown in figure 1. Similar results can also be found in the reduced pair correlation functions. Figure 2(b) shows the reduced pair correlation functions of 561-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters at 300 K. It can be observed from figure 2(b) that the Ag atoms are enriched on the surface and the Au atoms occupy the middle shell, while the Cu atoms stay in the center of the 561-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ cluster. The segregation phenomena of the Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic clusters are mainly due to their different surface energies. The richer Ag atoms on the surface and the segregation of Au atoms on the subsurface enables minimization of the cluster surface energy, due to the lower surface energy of Ag (78 meV Å$^{-2}$), compared with Au (97 meV Å$^{-2}$) and Cu (114 meV Å$^{-2}$) [57, 58].

To understand the composition effect on the segregation phenomena of the Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic clusters, we further calculated the concentrations of Ag, Cu and Au atoms in the Ag–Cu–Au trimetallic clusters. We show in figure 2(a) final snapshots of the Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters with the sizes of 147, 309, 561 and 923 atoms at 300 K. Clearly, the Ag atoms are enriched on the surface, and the Au atoms are mainly in the middle shell, while the Cu atoms stay in the center for the 147-, 309-, 561- and 923-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters at 300 K. This observation is consistent with our calculated concentrations of Ag, Au and Cu atoms in the surface, subsurface and third layers of the Ag$_{60}$Cu$_{20}$Au$_{20}$ icosahedral clusters, as shown in figure 1. Similar results can also be found in the reduced pair correlation functions. Figure 2(b) shows the reduced pair correlation functions of 561-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ clusters at 300 K. It can be observed from figure 2(b) that the Ag atoms are enriched on the surface and the Au atoms occupy the middle shell, while the Cu atoms stay in the center of the 561-atom Ag$_{60}$Cu$_{20}$Au$_{20}$ cluster. The segregation phenomena of the Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic clusters are mainly due to their different surface energies. The richer Ag atoms on the surface and the segregation of Au atoms on the subsurface enables minimization of the cluster surface energy, due to the lower surface energy of Ag (78 meV Å$^{-2}$), compared with Au (97 meV Å$^{-2}$) and Cu (114 meV Å$^{-2}$) [57, 58].

To understand the composition effect on the segregation phenomena of the Ag, Au and Cu atoms in the Ag–Cu–Au trimetallic clusters, we further calculated the concentrations of Ag, Cu and Au atoms in the different atomic layers of the Ag$_{60}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters. Figure 3 shows the calculated Ag concentrations in the surface layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters changing with cluster size. It is found in figure 3 that the Ag concentrations in the surface layers are 11–26 at.% higher than the overall Ag concentration in the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters. Moreover, the Ag concentrations in the surface layers increase with cluster size. Therefore, we can conclude that the Ag atoms generally
segregate to the surface of the Ag–Cu–Au trimetallic clusters for the compositions of Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$.

Figure 4 show the total Au concentrations in the surface and subsurface layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ clusters as a function of the cluster size at 300 K.

Figure 5 show the Cu concentrations in the third (from surface to center) layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ clusters as a function of the cluster size at 300 K.

Figure 6. Snapshots (gray atoms, Ag; light atoms, Au; black atoms, Cu) and the reduced pair correlation functions of the 561-atom Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ clusters. (a) The 561-atom Ag$_{20}$Cu$_{60}$Au$_{20}$ clusters. (b) The 561-atom Ag$_{20}$Cu$_{20}$Au$_{60}$ clusters.

icosahedral clusters changing with the cluster size. Apparently, the Au concentrations in the surface and subsurface layers are higher than the overall Au concentration in the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters, which means that the Au atoms are enriched in the surface and subsurface layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters. The reason for the Au segregation to the surface layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters is that the Ag concentrations in the two clusters are too low to occupy all the surface sites. Thus the Au atoms can occupy the remaining surface sites of the clusters. In figure 5, we show the Cu concentrations in the third layers of the Ag$_{20}$Cu$_{60}$Au$_{20}$ and Ag$_{20}$Cu$_{20}$Au$_{60}$ icosahedral clusters changing with the size of the cluster. We found that the Cu concentrations in the third layers are much higher than the overall Cu concentration in
the Ag_{20}Cu_{60}Au_{20} and Ag_{20}Cu_{20}Au_{60} clusters. This suggests that
the Cu atoms are enriched in the third layers of the Ag_{20}Cu_{60}Au_{20} and Ag_{20}Cu_{20}Au_{60}
icosahedral clusters. This observation is in agreement with the behavior of Cu atoms
aggregated in the third layers of the Ag_{60}Cu_{20}Au_{20} cluster, as shown in figure 1(c).

To further observe the segregation phenomena of Ag, Cu and Au atoms in the Ag_{20}Cu_{60}Au_{20} and Ag_{20}Cu_{20}Au_{60}
icosahedral clusters, the snapshots and reduced pair correlation functions of the 561-atom Ag_{20}Cu_{60}Au_{20} and Ag_{20}Cu_{20}Au_{60}
clusters are shown in figures 6(a) and (b), respectively. It is found in figure 6(a) that the Ag atoms lie in the surface layer of
the Ag_{20}Cu_{60}Au_{20} cluster, and Au atoms are mainly enriched in the surface and subsurface layers of the cluster, while the
inner core of the cluster are filled with the Cu atoms. This observation is consistent with the results shown in figures 3–5.
For the Ag_{20}Cu_{20}Au_{60} cluster, the Ag atoms are enriched on the surface of the cluster and the Cu atoms mainly aggregate
in the center of the cluster. In contrast, the Au atoms mainly occupy the middle shell of the cluster, as shown in figure 6(b).

4. Conclusions

We have investigated segregation phenomena of Ag–Cu–Au trimetallic clusters by using the Monte Carlo simulation
method, based on the second-moment approximation of the tight-binding potentials. It is found that the Ag atoms
generally segregate on the surface of the clusters and the Au atoms lie in the subsurface of the clusters, while the Cu
atoms aggregate in the center of the clusters. These regular segregation phenomena of Ag, Cu and Au atoms in the Ag–
Cu–Au trimetallic cluster are mainly due to their different surface energies (Ag, 78 meV Å^{-2}; Au, 97 meV Å^{-2}; Cu,
114 meV Å^{-2}). It is also found that the size and composition are of little effect on the segregation phenomena of Ag and Cu
atoms in the Ag–Cu–Au trimetallic cluster. In summary, the simulation results are useful to understand the structural
properties of trimetallic clusters. It is also expected that these simulation results would provide helpful information for the
preparation of trimetallic clusters.

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