Vol 18 No 5, May 2009
1674-1056/2009/18(05)/1843-07

Chinese Physics B

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Evolution of three-shell onion-like and core-shell structures in $(AgCo)_{201}$ bimetallic clusters*

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(Received 15 September 2008; revised manuscript received 13 October 2008)

This paper studies the structural evolution of $(AgCo)_{201}$ clusters with different Co concentrations under various temperature conditions by using molecular dynamics with the embedded atom method. The most stable position for Co atoms in the cluster is the subsurface layer at low temperature (lower than 200 K for the $Ag_{200}Co_1$ cluster). The position changes to the core layer with the increase of temperature, but there is an energy barrier in the middle layer. This makes the Ag–Co cluster form an Ag–Co–Ag three-shell onion-like configuration. When the temperature is high enough [higher than 800 K for $(AgCo)_{201}$ clusters with 50% Co], Co atoms can obtain enough energy to overcome the energy barrier and the cluster forms an Ag–Co core-shell configuration. Amorphization for the onion-like and core-shell clusters is induced by the large lattice misfit at Ag–Co interfaces. The structural evolution in the Ag–Co cluster is related to the release of excess energy.

Keywords: bimetallic cluster, structure, molecular dynamics
PACC: 3640J, 6146

1. Introduction

Ferromagnetic nanoparticles embedded in a non-ferromagnetic matrix or capped by noble metals have resulted in special magnetic properties.[1] Much work on magnetic granular films consisting of such nanoparticles has been carried out in order to investigate the phenomenon of giant magnetoresistance,[2] which is necessary for developing high density data storage materials.[3] The rapid growth of the areal storage density results in smaller magnetic particles, furthermore, their magnetic properties are strongly related to the structures of clusters and cluster assemblies in atomic scale.[4] Therefore, they should be researched from an atomic viewpoint. But it is difficult to investigate directly by using experimental approaches. Computer simulation methods, in particular molecular dynamics (MD), have become a powerful means of investigating atomic behaviour.

Recently, research on the thermodynamic properties of bimetallic clusters by using MD has already exhibited some new features which distinguish them from pure metals.[5–8] Since silver has a much lower surface energy (1065 mJ/m^2) and a larger atomic radius, it has become a main element to create nanoparticles with special structure and morphology. The MD simulations showed that core-shell and three-shell onion-like metallic clusters can be grown by depositing hetero atoms onto an Ag matrix.[9,10] Since Pd atoms preferentially segregate at the subsurface layer of the Ag cluster at low temperatures, Ag–Pd clusters with Pd atoms segregating at the subsurface layer were obtained by the collision of an Ag cluster with a Pd cluster.[11] For an Ag–Co bimetallic cluster, a core-shell structure of the Ag–Co cluster with a partial HCP-like Co core was obtained by cooling the cluster.[12] The structural and thermodynamic properties of Ag–Co nanoparticles at equilibrium states were also studied by using the metropolis Monte Carlo method.[13,14] They found that the core-shell structures contribute a lot to the structures and thermodynamic behaviour. But, this research only focused on the equilibrium states of the clusters, many questions about the evolution toward equilibrium states remain and should be addressed in further studies, especially for Ag–Co clusters over the complete range

*Project supported by the National Natural Science Foundation of China (Grant No 50374027), the program for New Century Excellent Talents in University (Grant No NCET-06-0289), and the 111 project of China (Grant No B07015).
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of Co concentrations under different temperatures. In addition, an understanding as to why the formation of three-shell and core-shell structure occurs so frequently is still lacking. Therefore, it is worthwhile to study these in order to understand the growing mechanism of magnetic alloy film.

In this study, the structural evolution of $(AgCo)_{201}$ clusters with different Co concentrations under various temperature conditions was explored by relaxing the clusters for 1 ns to make the clusters evolve toward their equilibrium states. The pair distribution function was used to explore the evolution of the cluster structures under different conditions. Generally, both the surface energy and interface energy were characterized by excess energy,[10,13] which was used to define the variation of the energy during the structural evolution process in this study. In addition, the energies of the clusters were calculated with a Co atom embedding different layers of the Ag_{200} cluster, which was used to analyse the energy dependence of the evolution of three-shell onion-like and core-shell structures.

2. Computational details

The present MD calculations employed a fifth-order Gear predictor–corrector algorithm[15] to integrate the equations of Newton. The time step was 2 fs. The scaling method was adopted during the simulation to control the system temperature. Canonical ensemble MD simulations were performed with free boundary conditions for clusters and periodic boundary conditions for bulks. Our group has used the model to simulate the thermodynamic behaviour and interaction of bimetallic clusters.[16−19] In general, potential functions of single elements are not suitable to simulate alloys due to their different choice of the cutoff distance. Zhou *et al* have developed a general alloy potential.[20,21] This potential was described with the identical analytic form based on the embedded atom method (EAM), which has been extended to enable calculations of alloys with any combination of 16 metals. The specific design of the EAM forces the potentials to smoothly go to zero at the same cutoff distance. For a bimetallic system, the alloy pair potential was defined by using the alloy model proposed by Johnson.[22] The potential has been successfully used to simulate the growth of nanoscale multilayer films.[21] Dorfbauer *et al* have applied it to calculate the cooling structure of Co–Ag clusters.[12]

The cluster started with geometries constructed from a $10a_0 \times 10a_0 \times 10a_0$ large FCC bulk. The lattice constant a_0 of the bulk Ag in the simulation is 0.40862 nm. The truncated cluster has a truncated octahedral structure with 201 atoms. This is because no structure transformation occurs for these clusters during the heating process. It is helpful to explore configuration evolution in the clusters without considering the influence of structure transformation on the energy. The structures of the bimetallic $(Ag_{201-m}Co_m)_{201}$ clusters were obtained by randomly substituting m Ag atoms with Co atoms. The concentrations of cobalt are 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%, respectively. Long runs, usually 5×10^5 time steps (1 ns) in duration, were used to obtain fully relaxed configurations.

3. Results and discussion

At first, the heating processes of pure Ag_{201} and Co_{201} clusters were simulated to define the melting range of bimetallic clusters. The Ag_{201} and Co_{201} clusters were heated up to 1300 K from 300 K. The temperature step was 20 K, with 0.06 ns trajectory steps propagated for each temperature cycle. Both the temperature step and time step were the same as the methods of Dorfbauer *et al*.[12] The melting points of Ag_{201} and Co_{201} clusters are 800 K and 1180 K, respectively. According to the melting points, 200 K, 500 K, and 1000 K were selected as the simulated temperatures. The reason is that the dependence of the evolution toward equilibrium states not only on Co concentrations but also on temperatures for clusters can be defined by simulating the cluster relaxation under different temperatures.

Figure 1 gives the energy per atom curves as a function of time for $(AgCo)_{201}$ clusters with different Co concentrations. Abrupt decreases of the energies corresponding to their initial energies were founded for the clusters with 30%, 40%, 50%, and 60% Co. However, for the clusters with other Co concentrations, the energies fluctuate near a steady state, there is a very small and virtually invisible decrease except for 70% Co. On the other hand, the phenomena of the abrupt decreases of the energies occur after the clusters relax for 1 ns at 500 K except for the cluster with 90% Co.

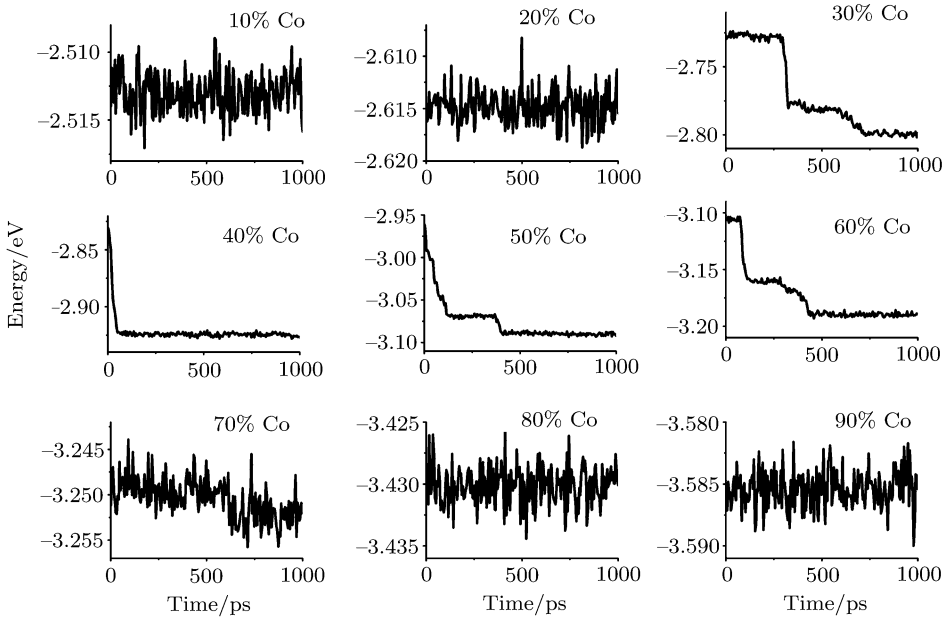


Fig.1. Time evolution of the energy per atom for $(AgCo)_{201}$ clusters with different Co concentrations at 200 K.

Corresponding to the evolution of the energies, the cluster configurations also make some obvious changes. Figure 2 portrays the cross sections of the clusters with different Co concentrations after relaxing for 1 ns at 200 K, 500 K and 1000 K, respectively. By comparing with the initial ideal configurations, clearly, the configurations of the clusters with 10%, 20%, 70%, 80%, and 90% Co at 200 K are almost identical to their initial ideal configurations, while the clusters with 30%, 40%, 50%, and 60% Co form Ag–Co–Ag three-shell onion-like configurations. Comparing with the results of Fig.1, we find that the forming processes of the three-shell onion-like configurations are followed by the significant decrease of the energies, viz., the stable configurations under these conditions are three-shell onion-like. For the clusters at 500 K, apart from the cluster with 90% Co, the configurations of the clusters with other concentrations change by comparing with the initial ideal configurations. Three-shell onion-like configurations are formed for the clusters with 30%, 40%, 50%, and 60% Co and not for the clusters with 10%, 20%, 70%, and 80% Co.

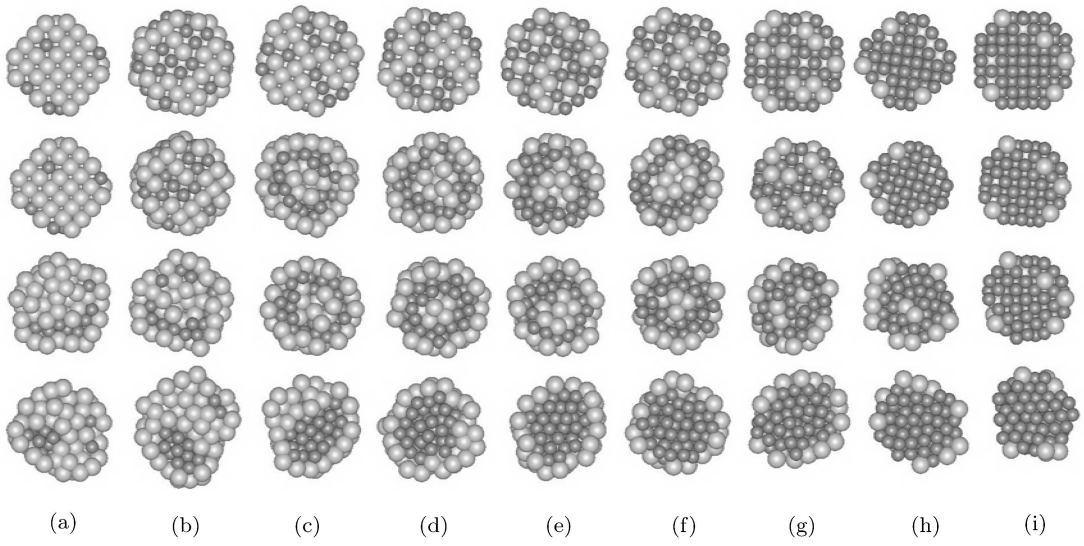


Fig.2. Cross sections of $(AgCo)_{201}$ clusters with different Co concentrations after relaxing for 1 ns under different conditions. The upper row shows the initial ideal configurations, the middle row shows the configurations at 200 K, the lower row is the configurations at 500 K, and the lowest row is the configurations at 1000 K. (a) 10% Co, (b) 20% Co, (c) 30% Co, (d) 40% Co, (e) 50% Co, (f) 60% Co, (g) 70% Co, (h) 80% Co, and (i) 90% Co.

For the clusters with 10% and 20% Co, the Co atoms segregate at the subsurface layer because Co atoms are not numerous enough to form an entire subsurface layer. Onion-like configurations are not obvious for the clusters with 70% and 80% Co since there are not enough Ag atoms in the core layer. When the temperature is 1000 K, the configuration evolutions are obviously different from those clusters at 200 K and 500 K. The Ag atoms segregate at the surface of the clusters to form core-shell configurations for the clusters with 40%, 50%, 60%, and 70% Co. For the clusters with 80% and 90% Co, since there are not enough Ag atoms, they cannot cap the surface entirely in spite of the Ag atoms also segregating to the surface. For the cluster with 30% Co, Co atoms assemble together at one side of the clusters. The Co atoms segregate at the subsurface layer for the clusters with 10% and 20% Co, which are similar to those clusters at 500 K, but many more Co atoms assemble together. From the configuration evolution under different conditions, it is reasonable to conclude that the variations of the configurations of $(AgCo)_{201}$ clusters are related to both temperature and concentration.

The above-mentioned evolution of the configurations as Co atoms segregate at the subsurface layer are similar to the results of Kim *et al* [11] especially for the clusters when Co concentrations are lower than 30%. They found that all Pd atoms preferentially segregated at the subsurface layer in spite of the fact that the most stable positions for Pd atoms were in the central site. This is because of an energy barrier at the subsurface layer. In order to characterize the energies of Ag clusters with Co atoms at different layers, $Ag_{200}Co_1$ clusters were constructed. A single Co atom was buried in the central plane of an Ag cluster, as shown in Fig.3. The detailed positions are shown with 1, 2, 3, and 4, which are used to describe the Co atom at the surface layer, the subsurface layer, the middle layer, and the core layer, respectively. These clusters relaxed for 0.2 ns at 0 K to make the clusters reach a steady state. The energy per atom was obtained by averaging the potential energy of the steady state. As shown in Fig.3, when the temperature is 0 K, the lowest energy position of Co atom is the subsurface layer, viz., the most stable position for the Co atom at 0 K is the subsurface layer. The energy per atom increases with the increase of temperature. The energy per atom at 100 K is similar to that at 0 K, the most stable position for the Co atom at 100 K is still the subsurface layer. The position changes to the core layer at 200 K since the energy of the core layer is lower than those of other positions. But the difference of the energies between the subsurface layer and core layer is very small. Furthermore, an energy barrier in the middle layer should be overcome for Co atoms penetrating to the core layer. Therefore, Co atoms will segregate at the subsurface layer if the obtained energy of Co atoms cannot overcome the energy barrier of the middle layer. Since the position of the Co atom changes with the increase of temperature, the energy per atom with a Co atom embedded in different layers cannot be used to define the energy as a function of the different layers. The dependence of energy on the positions of Co atoms is extrapolated from the results of low temperature. The most stable position for Co atoms is the subsurface layer at low temperature. The position changes to the core layer with the increase of temperature, but there is an energy barrier in the middle layer, which makes Ag–Co cluster form an Ag–Co–Ag three-shell onion-like structure. When the temperature is high enough, the Co atoms can obtain enough energy to overcome the energy barrier, therefore, the clusters form an Ag–Co core-shell structure.

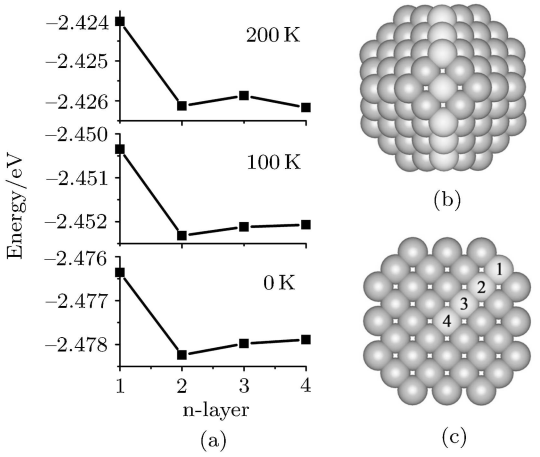


Fig.3. (a) Energy per atom of $Ag_{200}Co_1$ clusters with Co atoms at different layers. (b) Central plane (light spheres) buried Co atom. (c) 1, 2, 3, and 4 are the buried positions of the Co atom, which are used to describe the Co atom at the surface layer, the subsurface layer, the middle layer, and the core layer, respectively.

The Ag concentration in the core of the cluster changes with the increase of temperature. The cluster with 50% Co was selected as the calculated object because the surface of this cluster is almost composed of Ag atoms except for some defects on the surface. Therefore, by removing the Ag atoms capping the surface, the distribution of Co atoms in the sub-

surface layer can be reflected correctly by using the Ag concentration in the core. Figure 4 illustrates the variations of Ag concentrations in the core with the change of temperatures and the corresponding cross sections of clusters at different temperatures. The Ag concentration of the cluster at 0 K is near 50% and decreases with the increase of temperature. This indicates that higher temperature can make Co atoms obtain larger energy to overcome the energy barrier, which easily leads to more Co atoms penetrating to the core layer. When the temperature is 800 K, there is no Ag atom in the core layer and the cluster forms a core-shell structure. The temperature range for the transformation from the onion-like structure to the core-shell structure is between 700 K and 800 K. Dorfbauer *et al* [12] found that the freezing structure of Ag–Co from 1300 K to 100 K was core-shell and not onion-like. This indicated that the formation of the core-shell structure occurred at higher temperatures. Therefore, it can be concluded that higher temperatures can make Co atoms obtain adequate energy to overcome the energy barrier and make the cluster form a core-shell structure.

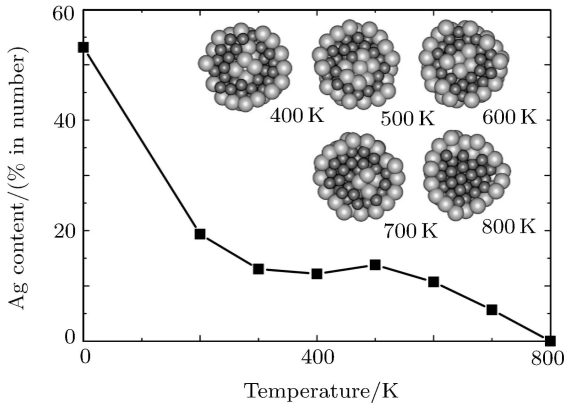


Fig.4. Variations of Ag concentrations in the core after relaxing for 1 ns for the cluster with 50% Co as a function of the temperatures and the cross sections of the clusters at different temperatures.

The excess energy was used to define the variation of the energy during the structural evolution process. The excess energy ΔE_{C} of a cluster at a given temperature was defined as follows:[10,13]

$$\Delta E_{\mathrm{C}} = E_{\mathrm{C}} - E_{\mathrm{C}}^{\mathrm{Id}}, \quad (1)$$

where E_{C} is the energy per atom in the cluster, $E_{\mathrm{C}}^{\mathrm{Id}}$ is the energy per atom of an infinite ideal solution with the same concentration, which is given by

$$E_{\mathrm{C}}^{\mathrm{Id}} = \frac{1}{N_{\mathrm{Ag}} + N_{\mathrm{Co}}}[N_{\mathrm{Ag}} E_{\mathrm{C}}(\mathrm{Ag}) + N_{\mathrm{Co}} E_{\mathrm{C}}(\mathrm{Co})], \quad (2)$$

where $E_{\mathrm{C}}(\mathrm{Ag})$ and $E_{\mathrm{C}}(\mathrm{Co})$ are the energy per atom of Ag and Co bulk at a given temperature, respectively. The energy per atom can be obtained by averaging the potential energy of the steady state. Their values at the temperatures of 0 K, 200 K, and 500 K are given in Table 1. In the current study, the bulk system was setup by using a cubic periodic super cell with FCC structure including 500 atoms. Then, the bulk relaxed for 1 ns at the given temperature. N_{Ag} and N_{Co} are the numbers of Ag atoms and Co atoms, respectively.

Table 1. Values of $E_{\mathrm{C}}(\mathrm{Ag})$ and $E_{\mathrm{C}}(\mathrm{Co})$, which are the energy per atom for Ag and Co bulk, respectively.

eV/atom	0 K	200 K	500 K
$E_{\mathrm{C}}(\mathrm{Ag})$	–2.849998	–2.797977	–2.718626
$E_{\mathrm{C}}(\mathrm{Co})$	–4.402624	–4.351143	–4.273592

Substituting the above-mentioned values in Table 1 into Eqs.(1) and (2), we can obtain the dependence of the excess energy on the Co concentrations at 0 K, 200 K, and 500 K, as shown in Fig.5. Clearly, all the excess energies are positive since there is a surface energy in the clusters. When the temperature is 0 K, the excess energy of the element Ag is lower than that of the element Co, indicating that the segregation of Ag to the surface of the $(\mathrm{AgCo})_{201}$ cluster is energetically favourable. The Ag–Co interface increases with the increase of Co concentration, leading to the increase of the excess energy. The excess energy reaches a maximum value when Co concentration is between 60% and 70%. Then, the excess energy decreases with the increase of Co concentration due to the decrease of Ag–Co interfaces. When the clusters relax for 1 ns at 200 K, comparing with the excess energies at 0 K, we find no changes for the clusters with 10%, 20%, 70%, 80%, and 90% Co while the excess energies decrease for the clusters with 30%, 40%, 50%, and 60% Co. The decrease of the excess energies of the clusters is consistent with those of the structural variations. This indicates that the structural variations of the clusters are induced by the release of the excess energy. When the temperature is 500 K, the excess energies decrease except for the cluster with 90% Co comparing with those at 0 K, the structural variations of the clusters occur for the clusters with the decrease of the excess energy. This is similar to the results of 200 K. Therefore, the structural evolution of the clusters is induced by the release of the excess energy.

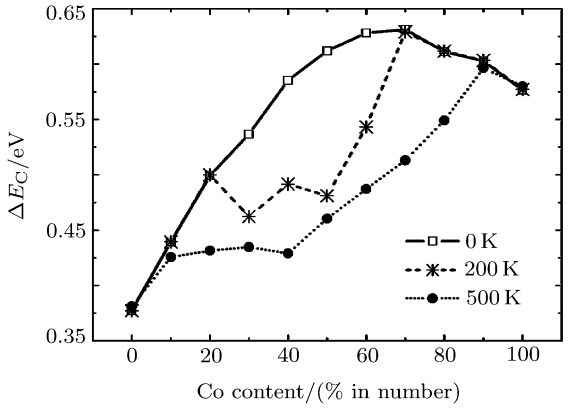


Fig.5. Excess energies of $(AgCo)_{201}$ clusters with different Co concentrations at the temperatures of 0 K, 200 K, and 500 K, respectively.

After relaxing the $(AgCo)_{201}$ clusters for 1 ns at 200 K and 500 K, the pair distribution function was employed to analyse their structural types. As shown in Fig.6, at 200 K, the peaks of clusters with 10%, 20%, 70%, 80%, and 90% Co appear, which coincide with those of the nearest neighbours of FCC that can be calculated by using $\sqrt{2n}a_0/2$ (where n is the nth nearest neighbour, a_0 is lattice constant). This suggests that the clusters are in an FCC structure. However, the intensities of the FCC peaks of the clusters with 70% and 80% Co decrease slightly due to the deformation of the surface of the cluster. There is a short range order of atomic arrangement existing for the clusters with 30%, 40%, 50%, and 60% Co. Since the temperatures are lower than the melting points of the clusters, the amorphous structures are solid disorder, which are similar to the amorphous structures. For the final structures at 500 K, only the cluster with 90% Co exhibits FCC peaks, the others form disorder structures. Detailed observation shows that no polyhedron with amorphous structure forms in the clusters at 200 K and 500 K. The calculation of the melting of the Co–Ag core-shell cluster indicated that amorphization was induced by the Co core.[13] An amorphous aggregate formed during the freezing of the Al_3Ni clusters because the surface segregation inhibited nucleation to an ordered structure.[5] Since a large mismatch exists between the Ag and Co equilibrium lattice distances, therefore, a large lattice misfit is caused by the forming of Ag–Co shells. It is reasonable to conclude that the amorphous structure is induced by the large lattice misfit at the Ag–Co interfaces.

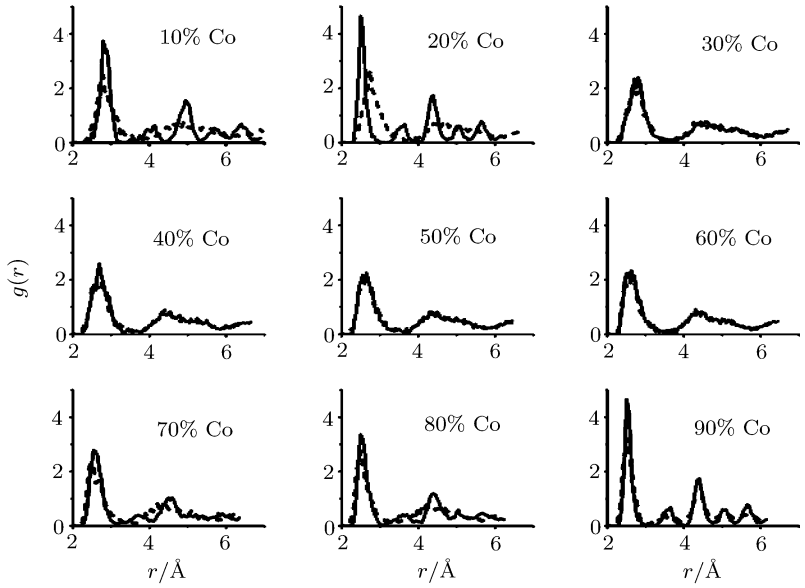


Fig.6. Pair distribution functions of $(AgCo)_{201}$ clusters with different Co concentrations after cluster relaxing for 1 ns at 200 K (solid line) and 500 K (dashed line).

4. Conclusions

The structural evolution of $(AgCo)_{201}$ clusters with different Co concentrations under various temperature conditions was studied by using MD with EAM. The temperature-dependent energies of the clusters change with Co atoms embedded in different layers of Ag cluster. The most stable position for the Co atoms is the subsurface layer at lower temperature. The position changes to the core layer with the

increase of temperature, but there is an energy barrier in the middle layer, which makes the Ag–Co cluster form an Ag–Co–Ag three-shell onion-like structure. The Co atoms can obtain enough energy to overcome the energy barrier with the increase of temperature, this leads to the cluster forming an Ag–Co core-shell structure. Amorphization for the onion-like and core-shell clusters is induced by the large lattice misfit at the Ag–Co interfaces. The structural evolution in the Ag–Co cluster are related to the release of the excess energy.

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