Molecular dynamics study on the physical properties of gold and silver alloys

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Abstract: In order to describe the physical properties of δ-Pu from the microscopic scale, we perform molecular dynamics calculation using the analogy material Ag-Au alloy. The melting point, volume heat capacity and linear expansion coefficient of Ag-Au alloys with different doping levels were calculated by the interatomic potentials based on the embedded atomic method (EAM). The results show that the melting points of Ag-Au alloy within all doping levels are around 1400 K, indicating that the doping level has little effect on its melting point. The volume of heat capacity increases with the increasing of the atomic weight of gold, however it is around 2.5 $J \cdot cm^{-3} \cdot K^{-1}$, and the trend of change is gradually accelerated. The coefficient of linear expansion decreases with the increasing of the atomic weight of gold, and the trend of change gradually slow down.

Introduction

Plutonium is located in the middle of the periodic table of actinides, and its valence electrons are between delocalized and local states, which is susceptible to temperature, pressure and bonding, so plutonium exhibits an exotic nature, and is considered the most complex elements in the periodic table [1-2]. Because plutonium has strong radioactivity, extreme toxicity and strong chemical properties, the experimental work on plutonium is relatively scarce. A large number of studies have shown that the self-irradiated damage effect of plutonium is directly related to the crystal structure and mass density [3, 4]. Therefore, it is a gradually good idea to carry out research using a simulated material with the same crystal structure and mass density as δ-Pu.

At the end of the last century, the Michael team at the Los Alamos National Laboratory in the United States proposed to use Ag-Au alloys which has the same face-centered cubic structure (FCC) to replace δ-Pu [2], and used the Laser-Driven Mini-Flyer experiment methods to study the damage behavior of Ag-Au alloy and δ-Pu. It was found that the Ag-Au alloy was able to reproduce the properties of δ-Pu. Zhu *et al.* [5] studied the point defect of Helium in Ag-Au alloy using the first-principles based on density functional theory. Dang *et al.* [6] simulated the alloying behavior of Ag-Au nanoparticles with core-shell structure on the basis of molecular dynamics method and improved analytical embedded potential function. Recently, there are no reports about the physical properties of Ag-Au alloy with molecular dynamics methods. Therefore, we plan to calculate the melting point, volume heat capacity and linear expansion coefficient of Ag-Au alloy with doping level at 7:1, 3:1, 5:3, 1:1, 3:5, 1:3, 1:7 with the molecular dynamics method based on the potential of embedded atoms.

Calculation methods and models

In this paper, the interaction between atoms is described by the embedded atomic method (EAM) proposed by Daw and Baskes *et al.* [7, 8]. According to the EAM model theory, the energy composition of each atom is shown as Eq.1

$$E_i = F(r_i) + \frac{1}{2}\sum_{j \neq i} f(r_{ij}) \tag{1}$$

In the Eq.1, $F(\rho_i)$ is the embedding energy term, which is determined by the electron density superposition of the other atoms embedded in the atom at the embedded atom. $\varphi(r_{ij})$ is the interaction potential between the two atoms, which is determined by the distance between atoms. In this paper, the EAM model parameters between Au-Au and Ag-Ag are calculated by Foiles [9], and the EAM model parameters between Ag-Au alloys are determined by fitting the corresponding lattice constant, formation energy of single vacancy, elastic modulus and other basic physical properties.

The molecular dynamics code used in this paper is LAMMPS [10] which is an open source program, and uses predictive-corrective method and periodic boundary condition. The ensemble, the simulation time and the amount of simulated temperature change are set according to the specific physical quantity. Silver and gold are face-centered cubic structures with lattice constants of 4.09 Å and 4.08 Å. First, A simulated box of 2×2×2 and 32 atoms is constructed to arrange the atomic position of silver and gold atoms, such that the doping level is 7:1, 3:1, 5:3, 1:1, 3:5, 1:3, 1:7, marked by *a*, *b*, *c*, *d*, *e*, *f*, *g*, respectively. Finally, this box is extended to 20×20×20 containing 32,000 atoms. The calculation model of *a*, *b*, *c* and *d* is based on the lattice constant 4.09 Å of silver. The calculation model of *e*, *f* and *g* is based on the lattice constant 4.08 Å of gold. Some simulated models are shown in Fig. 1.

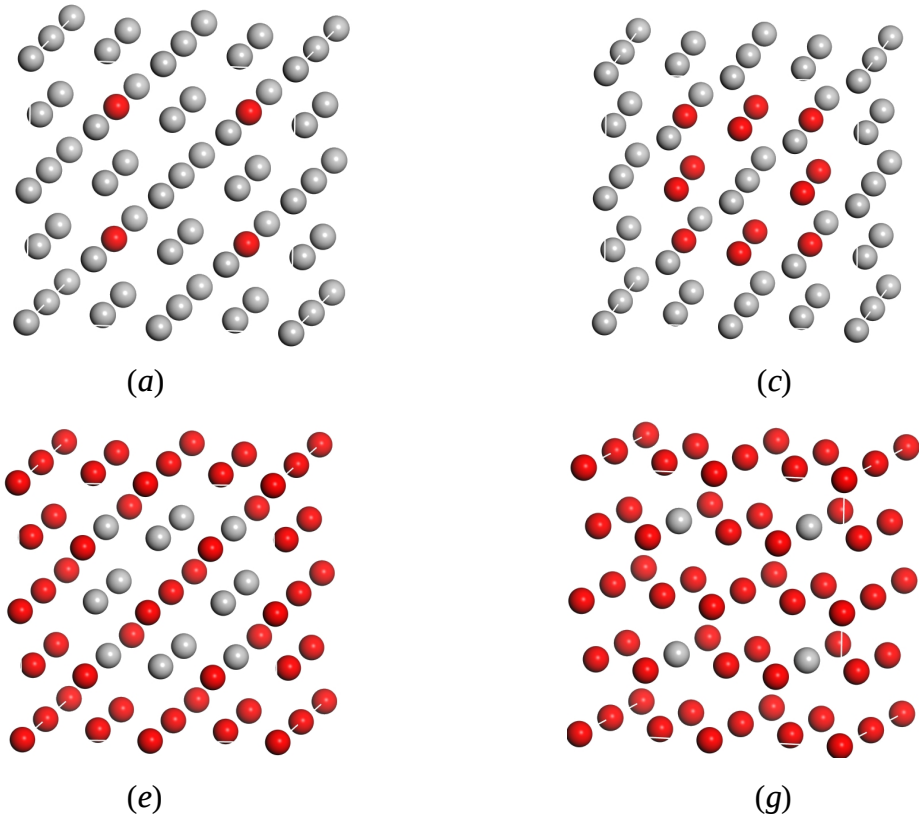

Fig. 1 Simulated models of Ag-Au alloys whose doping level is *a*, *c*, *e*, *g* .
Gray spheres denote silver atoms, red for gold atoms, respectively.

Results and discussion

volume heat capacity

Volumetric heat capacity (VHC), also termed as volume-specific heat capacity, describes the ability of a given volume of a substance to store internal energy while undergoing a given temperature change, but without undergoing a phase change. [11]

According to the above definition, the volume heat capacity can be given by

$$C_V = \frac{\Delta E}{\Delta T \times V} \tag{2}$$

According to the Eq. 2, the volume remains fixed during the simulation, and then the energy of the system is taken into account with the temperature changes, so we choose NVT ensemble. The simulated temperature is changed from 2.5 K to 2000 K with the Nosé-Hoover thermostat [12]. The time step is 0.001 ps and the total simulation time is 1200 ps. According to total energy of the corresponding systems at different temperatures, we plot the *E-T* curve, obtain the curve slope ($\Delta E/\Delta T$) by linear fitting, and calculate the corresponding C_V value. *E-T* curves at different temperatures are shown in Fig. 2, $\Delta E/\Delta T$ and C_V are listed in Table 1.

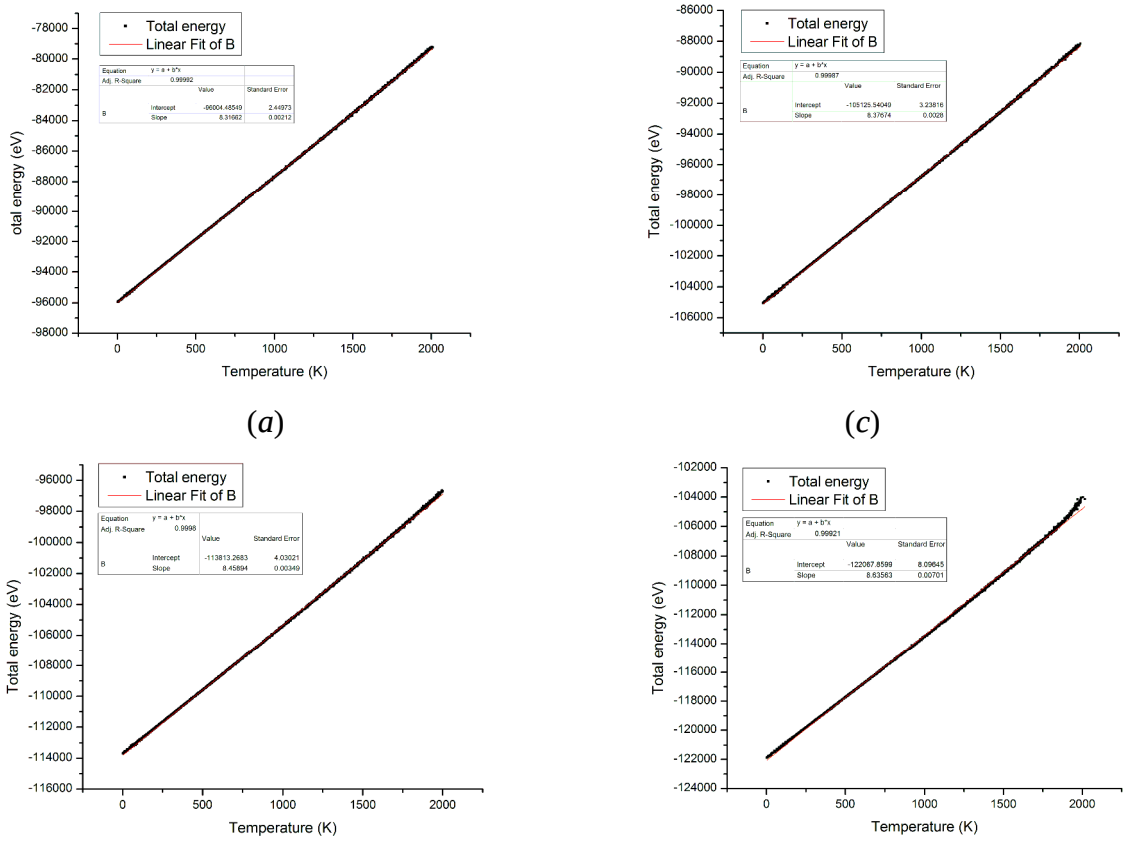

Fig. 2 *E-T* curves of Ag-Au alloys whose doping level is *a*, *c*, *e*, *g*

In Table 1, it can be seen that the volume heat capacity of Ag-Au alloy increases with the increasing of the atomic weight of gold, and the change trend is accelerated, which means that under the certain circumstances, the more doping level of Au in the Ag-Au alloy, the more energy is required to reach the same temperature, therefore the heat absorption capacity. A possible reason is that with the increasing of Au atomic weight, the mass of Ag-Au alloy will increase with fixed atomic numbers, the overall number of electrons will increase, and interaction between atoms will

be strengthened, resulting in increasing of volumetric heat capacity and heat absorption capacity.

Table 1 volume thermal capacity value of various Ag-Au alloys

	a	*b*	*c*	*d*	*e*	*f*	*g*
Volume [10^{-24}·cm^{-3}]		547343.432				543338.496	
$\Delta E/\Delta T$ [eV·K^{-1}]	8.317	8.340	8.377	8.397	8.459	8.527	8.636
C_V [J·cm^{-3}·K^{-1}]	2.435	2.441	2.452	2.458	2.494	2.514	2.547

Linear expansion coefficient

The coefficient of thermal expansion represents the volume change of matter relative to temperature, and there are two kinds of bulk expansion coefficient and linear expansion coefficient [13, 14]. By definition, the coefficient of linear expansion can be calculated by

$$a = \frac{\Delta L}{\Delta T \times L} \tag{3}$$

As can be seen from Eq. 3, the volume in the simulation process is variable, so using the NPT system. The simulated temperature is raised from 200 K to 1 200 K at NPT ensemble at an interval of 50 K, The system is equilibrated at each temperature using NVT. We calculate the lattice parameters (L) of the alloy at different temperatures. The slope of the L-T curve ($\Delta L/\Delta T$) is obtained by linear fitting. Finally, the corresponding linear expansion is calculated from the initial lattice constant coefficient. L-T curves are shown in Fig. 3, $\Delta L/\Delta T$ and α are presented in Table 2.

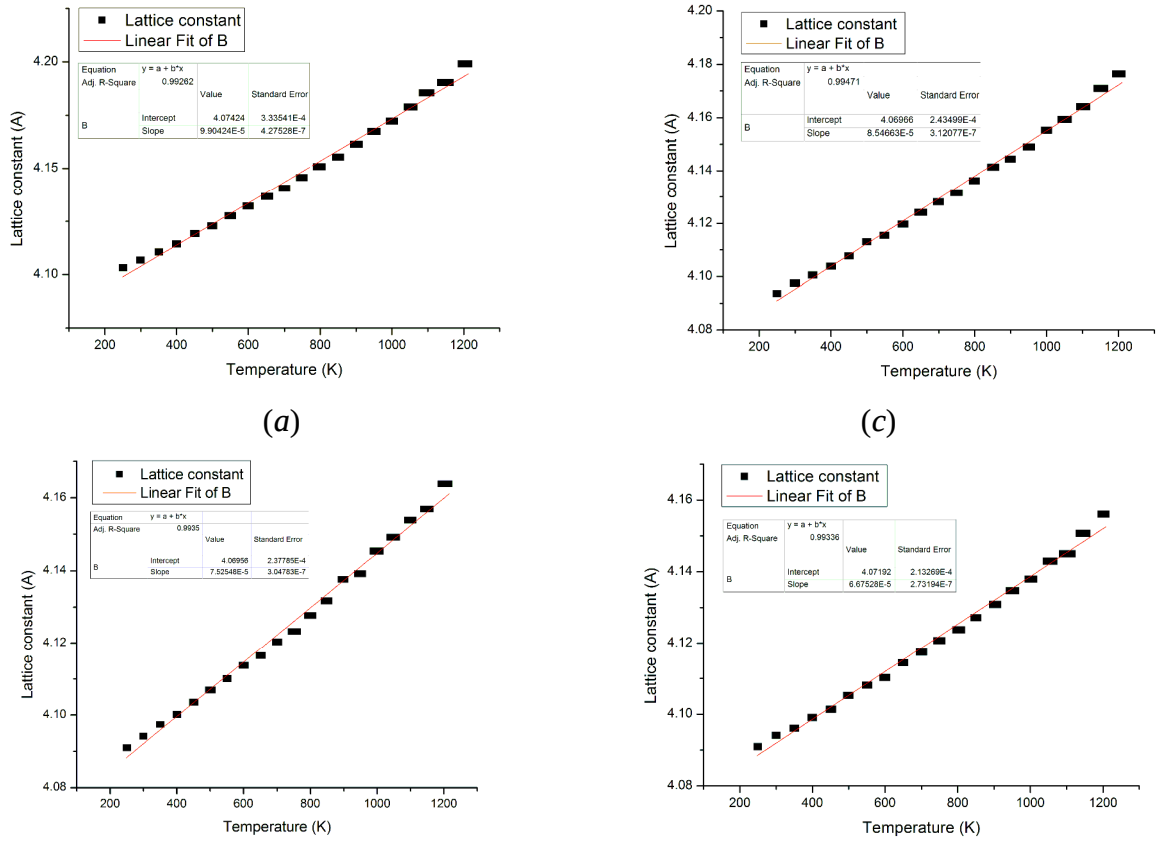

Fig. 3 L-T curves of Ag-Au alloys whose doping level is *a*, *c*, *e*, *g*

It can be seen from the data in Table 2 is that the linear expansion coefficient of Ag-Au alloy

decreases with the increasing of the atomic weight of gold, and the change trend gradually decreases, which indicates that with the gold doping proportion increasing in the Ag-Au alloy, in the case of increasing the same temperature, the volume change of the alloy is smaller, which indicate that the alloy structure is more stable and less affected by the temperature change. In the case of the total number of atoms are unchanged, with the number of Au atoms increasing, Ag-Au alloy contains the number of electrons increasing, the interaction between atoms increasing, making the alloy structure is more stable.

Table 2 volume heat capacity value of various Ag-Au alloys

	a	*b*	*c*	*d*	*e*	*f*	*g*
Lattice constant [10^{-1}·nm]	4.09					4.08	
$\Delta L/\Delta T$ [10^{-6}·nm·K^{-1}]	9.904	9.183	8.547	7.889	7.525	7.082	6.675
α [10^{-6}·K^{-1}]	24.22	22.45	20.9	19.29	18.44	17.36	16.63

Melting point

The melting point is the temperature at which the solid state changes its state into liquid state. Therefore, the melting point of the Ag-Au alloy is determined by the temperature of the primary phase transition. The simulation temperature is from 2.5K to 2000K, time step is 0.005 ps, and total simulated time is 6000 ps. The results are shown in Fig. 4.

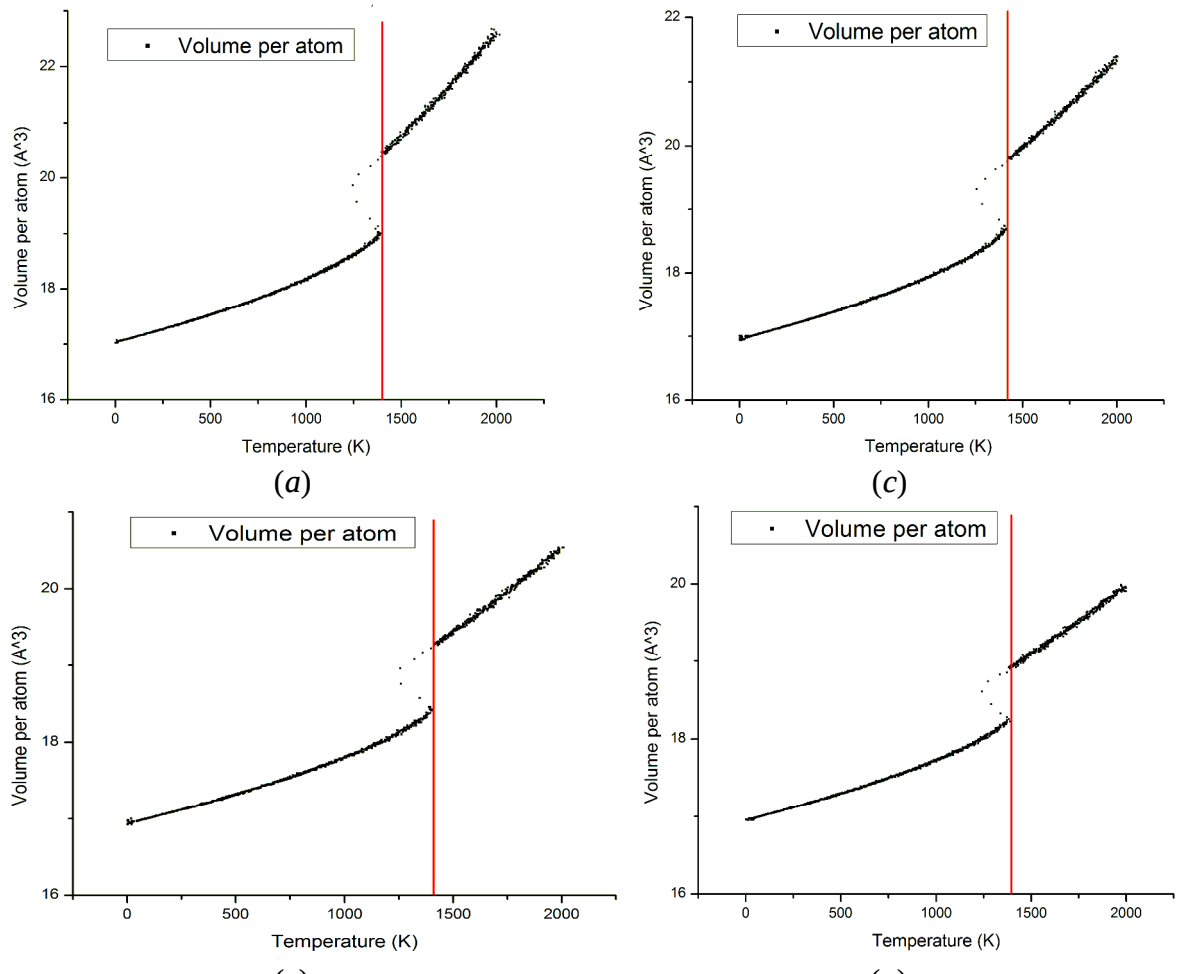

Fig. 4 *E-T* curves of Ag-Au alloys whose doping level is *a*, *c*, *e*, *g*

It can be concluded from Fig. 4 that the melting point of Ag-Au alloy in all doping ratios is

around 1400 K, indicating that the doping ratio of Ag-Au alloy has little effect on its melting point, Ag and Au have the same spatial structure, And the influence of the doping ratio on the melting point of the alloy is weak. At the same time, with the increase of the atomic ratio of Au, the unit atomic volume is getting smaller, which shows that with the gold ratio of Ag-Au alloy increasing, the structure of the alloy is more stable, which is consistent with the previous conclusion.

Conclusions

In this paper, the melting point, volume heat capacity and linear expansion coefficient of Ag-Au alloys with seven kinds of doping ratios were calculated by molecular dynamics method based on embedded atomic force. Results show that the melting point of Ag-Au alloy in all doping ratios is around 1400 K, which means that the doping ratio of Ag-Au alloy has little effect on its melting point. The volume of heat capacity increases with the increase of the atomic proportion of gold, and the trend of change is gradually accelerated. The coefficient of linear expansion decreases with the increase of the atomic proportion of gold, and the trend of change gradually slows down.

With the increase of the gold doping ratio, the endothermic capacity increases and the alloy structure is more stable. The results are consistent with the experimental data and other theoretical studies. In this paper, the physical properties of Ag-Au alloys with different doping levels were studied. The influence of the doping ratio on the physical properties of Ag-Au alloys was studied and analyzed. Moreover, the research method can be extended to self-radiation damage in δ-Pu, and further our understanding for effects of helium and other decay products on this complex metal and its alloys.

Acknowledgements

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References

[1] N.G. Cooper: *Challenges in plutonium science* [M]. USA: Los Alamos Laboratory, 2000.
[2] R.C. Albers: Nature. Vol. 410 (2001), p. 759-761
[3] J. A. Brinkman: J. Appl. Phys. Vol. 25 (1954), p. 961-970
[4] M.W. Thompson: *Defects and Radiation Damage in Metals* [M]. Cambridge University Press in Chinese, (1974), in press
[5] Z. Q. Zhu: *Ab initio Study of He Point Defects in fcc Ag-Au Alloys* [D]. Chengdu: University of Electronic Science and Technology of China, 2013.
[6] M. Dang, S. F. Xiao, H. Q. Deng. Rare Metal Materials and Engineering in Chinese. Vol. 42(2013), p. 2321-2325.
[7] M.S. Daw, S.M. Baskes. Phys. Rev. B. Vol. 29(1984), p.6443
[8] M.S. Daw, S.M. Baskes. Phys. Rev. Lett. Vol. 50(1983), p.1285
[9] S. M. Foiles, M.S. Daw and S.M. Baskes. Phys. Rev. Vol. 33(1986), p.7983-7990
[10] P. Steven, C. Paul: LAMMPS Users Manual LAMMPS Documentation [EB/OL]. http:/LAMMPS.sandia.gov /.
[11] Z. Tan, G. W. Guo: *The thermal property of industrial alloy*[M]. Metallurqical Industry Press in Chinese, (1994), in press
[12] S. Nosé. Chem. Phys. Vol. 81(1984), p. 511
[13] R. A. Johnson. Phys. Rev. Vol. 39(1989), p. 12554-2559
[14] Z. Q. Li, J. S. Tse. Phys. Rev. Vol. 61(2000), p. 14531-14536