Structural and Dynamical Properties of Liquid Ag₇₄Ge₂₆ Alloy Studied by Experiments and *ab initio* Molecular Dynamics Simulation

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Abstract

The structures and dynamics of liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures were investigated by high-energy X-ray diffraction and *ab initio* molecular dynamics simulation. The calculated structure factors agree remarkably well with the experimental data. Local atomic structure orders have been characterized by angular distribution functions, Honeycutt-Andersen index, Voronoi tessellation and the atomic cluster alignment. We reveal that (i) $\langle 0,3,6,4,0 \rangle$, $\langle 0,2,8,4,0 \rangle$, $\langle 0,3,6,5,0 \rangle$, and $\langle 1,3,4,5,1 \rangle$ polyhedral dominate in the undercooled $\text{Ag}_{74}\text{Ge}_{26}$ liquid. (ii) The icosahedral-like short-range order is enhanced as the temperature decreases while $\langle 0,3,6,4,0 \rangle$, $\langle 0,2,8,4,0 \rangle$, $\langle 0,3,6,5,0 \rangle$, and $\langle 0,1,10,2,0 \rangle$ polyhedral become the major short-range orders at low temperature. (iii) The medium-range order which was formed for amorphous phase at ambient temperature persists in the undercooled liquid. In addition, it is found that the diffusion constant of Ag is lower than that of Ge over the studied temperature range. Our findings elucidate that highly dominated short-range order associated with nearest-neighbors shell could empower the development of medium-range order and the formation of metallic glasses.

Keywords: $\text{Ag}_{74}\text{Ge}_{26}$ Alloy, liquid structure, *ab initio* molecular dynamics, X-ray diffraction

I. Introduction

What are the intrinsic structure of metallic liquids and the relationship between local structure and thermodynamic properties in liquids have been the fundamental questions in the past decades [1-5]. According to classic solidification theory, metallic liquids usually undergo nucleation and growth processes of crystal(s) during solidification. Using different cooling rates, liquids could form diverse crystal phases, which consequently have distinctly dynamical and mechanical properties. By rapid quenching, the metallic liquids could also transform into a glassy state with a critical cooling rate bypassing the crystal nucleation and growth [6, 7]. Debates have been raised on the glass-forming ability from different viewpoints [8-10]. One factor, which affects the glass-forming ability, is the atomic structure and the structure evolution of metallic liquids during solidification.

Due to many reasons, e.g., high temperature and oxidation, atomic structures of metallic liquids during solidification process are less studied as compared to the solid metals, and still not well understood. Noble metals (Au, Ag, etc.) and semiconductors (Si, Ge, etc) are commonly used in the electronic and optoelectronic devices for information technology applications. Their binary alloys own a deep eutectic point and exhibit good glass-forming ability. Unlike the high melting point of 1235 K and 1211 K for pure Ag and Ge, respectively, the melting temperature of their eutectic alloy $\text{Ag}_{74}\text{Ge}_{26}$ [11], decreases to 924 K. Benefiting from its deep eutectic, high electrical and thermal conductivity, AgGe alloys have been considered as the potential metallic glasses and candidates for high power electronic device application [12]. Since silver crystallizes in the face-centered cubic (fcc) structure and germanium crystallizes in the diamond structure [13], crystallographic characteristics of the liquid eutectic alloy are still missing. Recently, *ab initio* molecular dynamics simulations provide abundant results, remarkably consisting with experimental data [14], and reveal structural evolution in the atomic scale during solidification of metallic liquids [15-17]. Therefore, the combination between experimental and theoretical studies could reveal

temperature-dependent liquid structure in the $\text{Ag}_{74}\text{Ge}_{26}$ eutectic alloy. In our previous study [18], it was found that the $\text{Ag}_{74}\text{Ge}_{26}$ eutectic alloy could form a glassy structure with strong icosahedral short-range order and Bergman-type medium-range order after rapid cooling. In this work, two questions are addressed, *i.e.*, (i) Could the medium-range order persists at higher temperatures and descend into amorphous state? (ii) What are the motifs in liquid and the nature of atomic evolution of liquid eutectic alloy? Here high-energy X-ray diffraction and *ab initio* molecular calculations of $\text{Ag}_{74}\text{Ge}_{26}$ eutectic alloy above the melting point have been carried out. Both the experimental and simulation data are distinctly consistent. The atomic configurations obtained from *ab initio* molecular dynamics simulations have been statistically analyzed by angular distribution functions, Honeycutt-Andersen index, Voronoi tessellation and the atomic cluster alignment to address these two questions mentioned above.

II. Experimental and computational details

The molten alloy with the composition of $\text{Ag}_{74}\text{Ge}_{26}$ were investigated at three temperatures, 1123, 1073, and 1023 K, using high-energy synchrotron X-ray diffraction (HEXRD) measured at Shanghai Synchrotron Radiation Facility with a wavelength (λ) of 0.1783 Å. In order to obtain the diffraction data, high-purity Ag (99.999%) and Ge (99.999%) were melted more than 5 times to form parent $\text{Ag}_{74}\text{Ge}_{26}$ ingots, and slices cut from parent ingots were sealed in thin-walled quartz capillary with the diameter of 1 mm after pumped to a vacuum of 10^{-3} Pa. The samples were uniformly heated using a cylindrical Pt-Rh wound resistance furnace, which has low temperature gradient. We observed no reaction between the sample and the container below about 1300 K here. Currently, it is difficult to collect high quality diffraction data without crystallization for undercooled liquid of $\text{Ag}_{74}\text{Ge}_{26}$ alloy using this furnace and we then focus on the high-energy X-ray diffraction measurements at temperatures above the melting point. The diffraction data were collected in transmission using a MAR345 image plate detector. The diffracted intensity as a function of q was

obtained by integrating around the Debye rings of the exposed image plate. The required geometric corrections for misalignment of the detector relative to the beam normal were performed using FIT2D [19]. The data were then converted to the total structure function, $S(q)$, using standard procedures in PDFgetX2 [20]. An acquisition time of 300 s was provided high quality data with large signal to noise.

Molecular dynamics simulations of the liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy were achieved by *ab initio* calculation based on density function theory (DFT), using Vienna *ab initio* simulation package (VASP) [21, 22]. The interaction between electrons and ions was described by Projector Augmented-Wave (PAW) method [23]. The general gradient approximation (GGA) in the form by Perdew-Burke-Ernzerhof (PBE) [24] is used for the exchange-correlation energy functional. An energy cutoff of 249.85 eV is used to expand the wave function. The MD simulations were performed in a NVT (*i.e.* constant atom number, volume, and temperature) ensemble with Nosé-Hoover thermostat and a time step of 3 fs [25]. The equilibrium volume at different temperatures was established by monitoring the pressure of system, in a criterion within 0.0 ± 1.0 kbar. The initial supercell containing 200 atoms (148 Ag atoms and 52 Ge atoms) randomly distributed in a cubic box, and the system was heated to 1200 K and simulated for 4000 MD steps in order to remove the memory effects from the initial configuration and allow the system to reach the equilibrium liquid state at this temperature. Then the temperature was lowered to 1123, 1073, 1023, 976, 873, and 773 K by stages, at a uniform cooling rate of 0.1 K/step. Each stage was relaxed more than 4000 steps, ensuring the persuasion for the equilibrium of system and reliability of simulations. Last 2000 steps were selected for statistical analyses. The structure factor, pair-correlation function, coordination numbers (CN), bond-angle distribution, Honeycutt and Andersen (HA) indices, Voronoi tessellation method and atomic cluster alignment method, were performed to analyze the atomic configurations.

III. Results and discussion

3.1 Structure factor and pair-correlation function

The structure factor, $S(q)$, which is an important physical quantity for describing the property of liquid, can be directly measured from scattering experiments. The simulated structure factor $S(q)$ is obtained from the three partial structure factors $S_{ij}(q)$, atomic concentration of the elements c_i and c_j , and the scattering factors f_i and f_j in the alloys:

$$S(q) - 1 = \frac{c_i^2 f_i^2 (S_{ii} - 1) + 2c_i c_j f_i f_j (S_{ij} - 1) + c_j^2 f_j^2 (S_{jj} - 1)}{(c_i f_i + c_j f_j)^2} \quad (1)$$

The scattering factors f_i and f_j are obtained from tabulated data [26]. The partial structure factors, $S_{ij}(q)$, are related to the partial pair correlation functions $g_{ij}(r)$ by

$$S_{ij}(q) = \delta_{ij} + 4\pi\rho_{ij} \int_0^\infty [g_{ij}(r) - 1] \frac{\sin(qr)}{qr} r^2 dr \quad (2)$$

where the $g_{ij}(r)$ is the partial pair-correlation function, which can be calculated using the following equation:

$$g_{ij}(r) = \rho_{ij}^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(r_i) \delta(r_j - r) \right\rangle \quad (3)$$

where $\rho_{ij} = \rho_0 \sqrt{a_i a_j}$, a_i and a_j are number concentrations for Ag and Ge atoms, respectively. ρ_0 is the number density of the system. In this work, the initial atomic number densities ρ of $\text{Ag}_{74}\text{Cu}_{26}$ was obtained by $\rho = 0.74\rho_{\text{Ag}} + 0.26\rho_{\text{Ge}}$. The density of the system was then adjusted to approximately keep internal pressure close to zero at each temperature.

Fig. 1 shows the temperature dependence of total and partial structure factors $S(q)$ of liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy. The solid lines represent the calculated $S(q)$, and the results of XRD experiments at 1023, 1073, and 1123 K are indicated by open circles. The calculated values are in good agreement with experiments, which validate simulated atomic configurations. The first peaks of the $S(q)$ shrink and their amplitudes become higher as the temperature is decreased. At 1200 K, the spectra are smooth, while some structure details emerge at 773 K

with a peak appears in the valley between the first and second peaks. The second peak also begins to split. All of these features suggest that some short-range order and/or medium-range order are developing upon cooling. Later we address the local evolution in details using various methods.

The calculated pair-correlation functions (PCFs) are plotted in Fig. 2. The first peak of total PCFs in Fig. 2(a) locates at 2.82 ± 0.03 Å and its position increases slightly from 1123 K to 773 K and its amplitude increases noticeably, indicating local structure order strengthening. The second and third peaks enhance obviously while the temperature cools from 1123 K to 773 K. However, the second peak seems to split at 773 K, especially in Ag-Ag pairs of Fig. 2(b). Similarly, in our previous study, the second peak of Ag-Ag pairs has a distinct split at 300 K, which Ag-dominant icosahedral core consists in the Bergman-type medium range order [18]. These results indicate that local structure evolves continuously and short-range order is strengthened upon cooling. The interactions among short-range-order local clusters lead to the development of medium-range order in the undercooled liquid. The coordination number (CN) is also calculated based on the pair-correlation functions in Fig. 3, in which the cutoff distance is determined by the minimum between the first and second peaks in pair-correlation functions. The results show that the coordination numbers increased slightly from 12.22 to 12.65 as the temperature changes from 1123 K to 773 K. The coordination numbers of Ag-centered shell and Ge-centered shell increase by 3.97% and 2.98% when cooling from 1123 K to 773 K. It could be concluded that Ag atoms aggregate around Ag-centered and Ge-centered cores and leads to the formation of the medium-range ordering.

3.2 Chemical short-range order and bond-angle distributions

The Warren-Cowley parameter defined in Eq. (4) below is commonly used to measure the chemical short-range order (CSRO) [27]:

$$a_{ij} = 1 - (N_{ij}/c_j N_{\text{tot}}) \quad (4)$$

where N_{ij} is the coordination number of j type atoms around i type atoms, c_j is the concentration of j type atoms, N_{tot} is the total coordination number. The temperature dependence of the CSRO parameters is shown in Fig. 4. The negative value of the CSRO parameter represents attraction, while the positive value indicates repulsion. The CSRO parameters of Ge-Ge are positive, and that of Ag-Ag and Ge-Ag are negative. Therefore, there is a weak attraction between Ag atom and Ag or Ge atoms, yet a stronger repulsion between Ge atoms in the liquid. It seems that Ge atoms disperse into the system surrounding Ag-centered clusters to form the short-range order and tight connections after the liquid enters undercooled state, which contribute to the formation of medium range order in amorphous state.

The bond-angle distributions, $g_3(\theta)$, characterize the local structure in a higher-order correlation, *i.e.*, triple-atom correlations in liquid alloys [28]. Fig. 5 shows the calculated results for the partial bond-angle distributions. All triple atoms are taken into account as long as the two-atoms sharing the same vertex atom are within the cutoff distance which is set to be distance corresponding to the first minimum in pair-correlation functions. The partial bond-angle distributions of Ag-Ag-Ag, Ag-Ag-Ge, Ag-Ge-Ag and Ge-Ge-Ag exhibit two main peaks at 55° and 110° . Both peaks become sharper as the temperature is decreased, indicating more order structure at lower temperature. Besides, the peak at 55° exhibits an upward shift for about 2° as the temperature decreases from 1123 K to 773K. Note that for body-centered cubic (bcc) structure, bond-angle distribution has a high probability at 53° , while the bond angles of face-centered cubic (fcc), hexagonal close packed (hcp) and icos are 60° or larger. The upward shift of the peak around 55° can be regarded as the development of fcc, hcp or icos short-range-order (SRO) is faster than the bcc-type SRO upon cooling. The peaks at 110° reflect the different shift as one of the main maximum values, since bond-angle distribution of bcc and other structures are similar in the vicinity of 110° . The formation of the quasi-flat around 150° reveals a rise of the local order from some complex tetrahedral

structures [29]. The two main peaks of the partial bond-angle distributions of Ge-Ag-Ge and Ge-Ge-Ge locate at 50° and 100° , both of which are smaller than that of the rest four triples. The two main peaks in these triples here deviate from the characteristic values of bcc, fcc, hcp and icos. Again, it is obvious that the local structure in liquid $\text{Ag}_{74}\text{Ge}_{26}$ eutectic alloy is occupied by the icosahedral short-range order and descends to later amorphous phase during cooling [18].

3.3 Short range order analyzed by HA index, Voronoi tessellation and Atomic cluster alignment

HA index is introduced to characterize the common neighbors of an atom pair, offering more detail information about the SRO in the liquid alloys. Three digits are used to describe the common neighbors [30]. The first digit is fixed at 1 for the atom couples with atom distance less than the cutoff radius, which is the same value in the calculation of coordination number. The second digit interprets the number of common atoms around the reference pair, and the third digit indicates how many bonds formed among the common neighbor atoms. Fig. 6 shows the statistical results of several prevalent HA indices in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures. A slight increase in the sum of 144, 166, describing the structure unit of bcc clusters, was also observed. It can be regarded as competitions between icos and bcc SRO in the cooling process of liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy. The development of bcc-type pairs is slower than that of icos-type pairs, which is consistent with results from the bond-angle distribution analyses. Interestingly, 155 pairs, the standard index for icosahedral (icos) structure, together with 154, 143 pairs, considered as approximate icos indices, are found to be the dominant structure motifs in the liquid in all temperature range studied here. Upon cooling, 155 pairs increase significantly and soar up to 22.4% at 773 K, finally 35.0% at 300 K [18]. Again, it seems that the undercooled liquid shares a continuous icosahedral-like atomic surroundings and a tight connection to amorphous state.

Voronoi index $\langle n_3, n_4, n_5 \dots n_i \rangle$, in which n_i is the number of i -edged polygon, offers another effective perspective to analyze local atomic orders [31]. The standard Voronoi indices of bcc, fcc, and icos are $\langle 0, 6, 0, 8, 0 \rangle$, $\langle 0, 12, 0, 0, 0 \rangle$ and $\langle 0, 0, 12, 0, 0 \rangle$, respectively. Fig. 7 shows the top 15 most populated Voronoi indices in $\text{Ag}_{74}\text{Ge}_{26}$ liquid at various temperatures. It can be seen that two groups of Voronoi polyhedral (VP) account for the most VPs in the analysis. One group is the icosahedral $\langle 0, 0, 12, 0, 0 \rangle$ and its distorted variances of $\langle 0, 1, 10, 2, 0 \rangle$ and $\langle 0, 2, 8, 2, 0 \rangle$, whereas the other group is composed of a deformed fcc polyhedral $\langle 0, 3, 6, 4, 0 \rangle$, $\langle 0, 3, 6, 5, 0 \rangle$, and $\langle 0, 4, 4, 6, 0 \rangle$. Therefore, the fcc and icos short-range order (ISRO) play dominant roles in the liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy according to the Voronoi index analysis. The top 5 Voronoi polyhedral at 773 K are $\langle 0, 3, 6, 4, 0 \rangle$, $\langle 0, 2, 8, 4, 0 \rangle$, $\langle 0, 3, 6, 5, 0 \rangle$, $\langle 0, 1, 10, 2, 0 \rangle$ and $\langle 0, 4, 4, 6, 0 \rangle$. While at 1123 K the distribution of top 3 VPs is uniform, the fraction of distorted icos increased when the temperature decreased. The population of most VPs increases when the temperature decreases, indicating the order strengthening upon cooling. It is remarkable that icos-like clusters, including $\langle 0, 0, 12, 0, 0 \rangle$, $\langle 0, 1, 10, 2, 0 \rangle$ and $\langle 0, 2, 8, 2, 0 \rangle$, rise up from 2.9% at 1123 K to 4.3% at 773 K. Unanimously, the top 5 VPs account for the local clusters in the amorphous state, which reveals similarity of atomic surroundings in undercooled liquid and amorphous state [18]. These results are consistent with the HA index analysis, suggesting that ISRO is the most abundant in the undercooled liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy and has a direct contribution to the formation of the amorphous state.

To provide a more robust visual picture about the SRO and MRO in the liquid, atomic cluster alignment analysis has been performed [32]. At each temperature, 2000 Ag-centered clusters and 2000 Ge-centered clusters, each containing 16 atoms, are randomly collected from the MD simulation trajectories. Then these clusters are translated to align the center atoms and rotated to achieve the minimum mismatch between the clusters by the collective alignment method described in Ref. 32. As shown in Fig. 8, the spatially resolved distribution

functions obtained from the collective alignment analysis provide averaged atomic structure of the SRO in the supercooled $\text{Ag}_{74}\text{Ge}_{26}$ liquid. When reducing the temperature from 1123 K to 773 K, the development of ISRO can be clearly seen in Fig. 8, which is similar to the amorphous state. The results from the cluster alignment analysis are well consistent with HA index and Voronoi tessellation analyses discussed above. In order to get a more quantitative measure of the degrees of various SROs in the liquid, the atomic distribution obtained from the collective alignment is further aligned with bcc, fcc, hcp and icos templates of various bond lengths. The extent of the alignment is described in terms of “energy”. The lower the energy is, the better the alignment. As shown in Fig. 9, Ge-centered icos template reaches its minimum energy around -2.2×10^5 with a bond length of 2.9 Å at 1123 K, distinctly lower than that of other three templates. Similar results are also found in Ag-centered template alignment, which give us a visualized version of atomic surroundings and quantify different local structures. It confirms that icos clusters dominate in the $\text{Ag}_{74}\text{Ge}_{26}$ liquid, well consistent with the conclusion in the HA index and Voronoi tessellation analyses.

3.4 Dynamics properties

Self-diffusion coefficient (D) can be derived from the mean square displacement (MSD) as the function of time based on the Einstein equation:

$$D = \lim_{t \rightarrow \infty} \langle R_{i\alpha}^2(t) \rangle / 6t \quad (5)$$

Since the atoms in the liquid will increase their motility with increasing temperature, the calculated self-diffusion coefficients show an approximate linear increase with temperature as shown in Fig. 10. For Ag atoms, the calculated self-diffusion constant ranges from 1.39×10^{-5} at 773 K to $2.96 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1123 K. As mentioned before, Ge atoms disperse in the liquid higher than Ag atoms, whose self-diffusion constant increases $1.59 \times 10^{-5} \text{ cm}^2/\text{s}$ at 773 K to $3.9 \times 10^{-5} \text{ cm}^2/\text{s}$ at 1123 K. It seems that the faster motility and repulsiveness of Ge atoms in $\text{Ag}_{74}\text{Ge}_{26}$ liquid might reduce the probability of the formation of bcc-, fcc-, and hcp-clusters

and favor the ISRO.

IV. Summary

Eutectic $\text{Ag}_{74}\text{Ge}_{26}$ liquid alloy was studied by high-energy X-ray diffraction and *ab initio* MD simulation in the temperature range from 1123K to 773 K. The calculated structure factors of the $\text{Ag}_{74}\text{Ge}_{26}$ liquid agree well with HEXRD experiments. The HA indices and Voronoi tessellation analysis indicate that a strong ISRO emerges as the temperature decreases. Icosahedral-type atom bonding clearly observed from liquid state to undercooled liquid by atomic cluster alignment method. $\langle 0,3,6,4,0 \rangle$, $\langle 0,2,8,4,0 \rangle$, $\langle 0,3,6,5,0 \rangle$, and $\langle 1,3,4,5,1 \rangle$ polyhedral dominate in the $\text{Ag}_{74}\text{Ge}_{26}$ liquid at high temperature while $\langle 0,3,6,4,0 \rangle$, $\langle 0,2,8,4,0 \rangle$, $\langle 0,3,6,5,0 \rangle$, and $\langle 0,1,10,2,0 \rangle$ polyhedral become the major short-range orders at low temperature. The medium-range order which was formed for amorphous phase at ambient temperature persists in the undercooled liquid. Self-diffusion constants are also calculated via mean square displacement, the diffusion constants of Ag are consistently lower than that of Ge over the studied temperature range. Our results unveil that the highly dominated short-range order could interact and connect beyond the nearest neighbors between clusters to facilitate the development of medium-range and longer orders upon cooling. Our results provide a deeper understanding of metallic liquid on the atomic scale. More research to understand the correlation between the local structure orders and the electrical/mechanical properties in the undercooled metallic liquids and metallic glasses would be very interesting.

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Figure Captions

Figure 1. Temperature dependence of total and partial structure factors $S(q)$ of liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy. The solid lines and open circles represent calculated and experimental $S(q)$, respectively. The curves are shifted vertically as indicated by the figures in parentheses.

Figure 2. Total and partial pair-correlation functions of liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 3. Total and partial coordination numbers in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 4. CSRO parameters in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 5. Calculated partial bond-angle distribution functions in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures. (a) Ag-Ag-Ag, (b) Ag-Ag-Ge, (c) Ge-Ag-Ge, (d) Ge-Ge-Ge, (e) Ge-Ge-Ag, and (f) Ag-Ge-Ag.

Figure 6. HA indices in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 7. Voronoi indices in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 8. Atomic-density contour plot of the final configuration of collective alignment in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.

Figure 9. Attractive potential energies as the function of bond-length curves for fcc, hcp, and icosahedral type of short-range orders in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at two temperatures.

Figure 10. Self-diffusion coefficients in liquid $\text{Ag}_{74}\text{Ge}_{26}$ alloy at different temperatures.