Evolution of the atomic structure of a supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid

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Abstract:

Structural data from the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ ternary alloy liquid were collected *in-situ* in the temperature range from 1172K to 953 K during continuous cooling using the high-energy synchrotron X-ray Advanced Photon Source. The lowest-r peaks of the pair distribution functions (PDFs) sharpened, becoming higher and narrower, with decreasing temperature. The experimental data are in good agreement with the results of *ab-initio* molecular dynamics (AIMD) simulations. Quantitative analyses of the simulated structures (clusters, interconnecting zones and free volume) in the supercooled liquid were made based on the tight-bond cluster model. The significance of Al additions on the increase in glass forming ability (GFA) was estimated from the simulated structures and their electronic structure analysis.

1. Introduction

Metallic glasses were originally synthesized in 1960 by rapidly quenching the liquid phase [1]. Much effort has been since devoted to the study of metallic glasses due to their unique properties such as high elastic limit, high strength, high corrosion resistance and good soft magnetic properties [2-4]. The structure of the supercooled liquid [5], which exists in the temperature range between the melting temperature and the glass transition temperature, is believed to have a significant influence on the glass forming ability (GFA) and almost all physical and mechanical properties of the metallic glasses. Because such a structure, lacking in long-range order, is extremely

complex at the atomic scale [6], the precise atomic configurations have not been well understood. In spite of this complexity, significant breakthroughs have been achieved in recent years with new developments in the technology of structure detection and computer simulation technology. Kelton et al. argued that the local atomic structures in terms of the Honeycutt-Andersen indices indicated a high degree of icosahedron and distorted icosahedral order for many supercooled liquid metals (Ti, Ni, Zr and Al) [7-9], and pointed out that the chemical and topological ordering were in agreement with the prediction of the rapid development of chemical as well as topological ordering of icosahedral clusters in a supercooled $Zr_{54}Cu_{46}$ liquid [10]. The analysis of the structural investigations using molecular dynamics (MD) simulations on the $Zr_{50}Cu_{50}$, $Zr_{36}Cu_{64}$, $Zr_{65}Cu_{35}$, and $Zr_{35}Cu_{65}$ metallic glasses suggested that icosahedron and distorted icosahedron were the basic short range order in these glasses [11-15].

Comparing with Zr-Cu binary alloy system, Zr-Cu-Al ternary alloys own better GFA and other mechanical properties due to the addition of Al. Many research works have been conducted on these alloys [16-22]. Cheng proposed that icosahedral clusters were identified as the basic local structural motifs in $Zr_{47}Cu_{46}Al_7$ ternary bulk metallic glasses and that the addition of Al increased the population of icosahedron [16]. Kim et al. reported that the addition of Al to $Zr_{50}Cu_{50}$ increased the population of icosahedron and thus enhanced the GFA and strength of $Cu_{47.5}Zr_{47.5}Al_5$, however, Al-centered clusters and its medium-range structures were structurally less stable, making them more susceptible to disorder [17]. Liu proposed an expression formulated from *ab-initio* molecular dynamics simulations (AIMD) to predict the

trend of GFA and it was successfully applied to the $(\text{Zr}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Al}_x$ ternary alloy system [18, 19]. Ho et al. showed that slight composition difference resulted in a diverse distribution of icosahedron and distorted icosahedron by comparing the local atomic structure between $\text{Zr}_{50}\text{Cu}_{45}\text{Al}_5$ and $\text{Zr}_{45}\text{Cu}_{50}\text{Al}_5$ based on the AIMD simulations [20].

The above-mentioned experimental studies suggest that the formation of icosahedral short-range order can be regarded as a feature of the change in the atomic structure of many supercooled metallic liquids. Different from these, in this paper the tight-bond cluster model is introduced to describe the structural evolution because of its advantages in understanding the relationship between the atomic structure and the physical phenomenon as well as in considering the properties of different elements in the alloys [23]. In our work, a Zr-based ternary alloy $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ was chosen for analysis, of considerable interest due to its good GFA and mechanical properties. In addition to structural evolution in the supercooled liquid, the influence of Al on the GFA to Zr-Cu binary alloy was also studied. We further investigated the electronic structure reflecting the bonding properties by calculating the density of states (DOSs) [24]. This paper aims to clarify the subtle changes in the structural evolution in the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid by combining the experimental data with AIMD simulations.

2. Experimental procedure and results

A master alloy ingot of $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ was prepared by arc melting the mixture of pure Zr (99.97%), Cu (99.999%) and Al (99.999%) multiple times to ensure a homogenous composition. Spherical samples with a diameter of 2-3 mm were melted and then cooled in vacuum using the Washington University beamline electrostatic levitation (BESL) facility [25,26] for X-ray scattering studies at the Advanced Photon Source (APS, station 6-ID-D). During cooling, the scattering intensity, $I(Q)$, was collected *in-situ* over a wide momentum transfer (Q) range at different temperatures in the supercooled liquid using the high-energy synchrotron X-ray source. $I(Q)$ was corrected by masking bad pixels in the GE area detector, applying a pixel efficiency gain map, and subtracting the appropriate detector dark current and scattering background. The data were then corrected for oblique incidence, absorption, multiple scattering, fluorescence, polarization, sample geometry and Compton scattering contributions. The total structure factor, $S(Q)$, was constructed from the corrected $I(Q)$ data using an in-house analysis package written in LabViewTM. Six heating-cooling cycles are performed on the same sample and the total static structure factors at different temperatures during cooling were collected. When comparing their total static structure factors at the temperatures near the $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ melting temperature for different cycles shown in Fig. 1, it is found that the $S(Q)$ curves present similar plateau, and the first and second peak positions remains nearly unchanged at $2.58 \pm 0.02 \text{ \AA}^{-1}$ and $4.64 \pm 0.02 \text{ \AA}^{-1}$ for all of the six cycles. Here, we show detailed results of the structural evolution from the fifth cooling process. The measured x-ray total static structure factors for temperatures from 1172 K to 953 K, which are lower than the

melting temperature (1173K), are shown in Fig. 2. Three peaks are clearly visible and the peak becomes wider and lower quickly as Q increases. With temperature decreasing, the first peak intensity increases and the first peak position shifts slightly towards higher Q , indicating that the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid become more ordered. In addition, the presence of a shoulder on the second peak is observed and it becomes more obvious with decreasing temperatures, which also reflects a further ordered liquid structure.

The pair distribution function (PDF), $g(r)$, which gives the probability of finding atoms in a spherical shell of radius of r from a given atom and the thickness of Δr is obtained by a Fourier transform of $S(Q)$ using

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{1}{2\pi^2\rho_0} \int (S(Q) - 1) \frac{\sin(Qr)}{Qr} Q^2 dQ. \quad (1)$$

Fig. 3(a) shows PDFs for the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid for temperatures from 1172 K to 953 K. The peaks of the PDFs decrease in amplitude quickly as r increases, and contain no sharp peaks, which is the characteristic of an amorphous system. Furthermore, the first peak, especially the second and third peaks do not split into multiple sub-peaks, as the feature of a liquid, indicating that the sample measured is in the supercooled liquid state.

The structural information of the supercooled liquid mainly lies in the first peak of the PDF. Fig. 4(a) shows the first peaks of the PDFs at different temperatures in the supercooled liquid. The first peaks of the PDFs become higher and narrower with

decreasing temperature, which indicates increased structural order, although the change is small. The first peak intensities and positions of the PDFs for all temperatures are summarized in Table I. Over the temperature range of the supercooled liquid, the first peak position remains nearly unchanged at $3.00 \pm 0.02 \text{ \AA}$, but the intensity increases from 2.19 at 1172 K to 2.30 at 953 K. The effect of thermal vibration contributes to the variation. As the temperature decreases, the average amplitude of the thermal vibrations decreases. Then it becomes more likely to find atoms near their fixed positions. On the other hand, for liquids atomic diffusion also occurs during the cooling process, allowing the atomic structure to evolve.

3. Simulation methods and results

3.1. Simulation methods

To quantitatively describe the structural evolution and obtain more information about the clusters within the first shell in the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid, *ab-initio* molecular dynamics (AIMD) simulations, which are based on the density-function theory (DFT) [27], are an important technique of computational material science and have been used to simulate the structural evolution in the supercooled liquid. The Vienna *ab-initio* simulation package (VASP) [28], based on first principles, is a computer program for atomic scale simulation. VASP uses a plane-wave basis with the projector augmented plane wave (PAW) pseudopotential describing ion-valence electrons interactions and the generalized gradient

approximation (GGA) accounting for the exchange correlation interaction between electrons with the PW91 function developed by Perdew and Wang [29-31]. The Verlet algorithm is applied to solve the equations of atomic motion. In this work, the cutoff energy of the plane-wave basis is 273.2 eV.

As an initial structure, a crystal structure of $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$, which is made up of 250 atoms of $5 \times 5 \times 5$ bcc cells, is placed in a cubic box. Periodic boundary conditions are imposed on this supercell. The process is carried out in the NVT ensemble with a Nose thermostat for temperature control [32]. The time step is 2 fs. The average cooling rate is about 3.3×10^{13} K/s. The simulation steps are as follows:

- (1) heating up and equilibrating for 1000 time steps at 3000 K (well above the melting temperature 1173 K) for breaking the initial crystal structure and obtaining the liquid state,
- (2) quenching down to 1200 K, which is above the melting temperature of the 1173 K, and holding at 1200 K for 1000 time steps to obtain the experimental molten state,
- (3) cooling to 300 K and holding at the temperatures of 1100 K, 1000 K, 900 K, 800 K, 700 K, 600 K and 500 K for 1000 time steps, respectively, to obtain the corresponding configurations.

3.2. *Pair-distribution function*

As for the experimental data, the pair distribution function is one of the most important characteristic methods to interpret the short-range order. It can be obtained by the following equation:

$$g_{(r)} = \frac{V}{N} \left\langle \frac{n(r, \Delta r)}{4\pi r^2 \Delta r} \right\rangle. \quad (2)$$

where V is the total volume, N is the number of atoms in the simulation system, and $n(r, \Delta r)$ is the number of the atoms in a spherical shell whose distance away from a central atom is between r and $r + \Delta r$; The term of $\langle \rangle$ implies the average of molecular dynamics. Fig. 3(b) presents the PDFs calculated from eq. (2). Although the temperature range of the simulated PDFs is different from that from the ones obtained experimentally (Fig. 3(a)), they are all characteristic of the supercooled liquid. Fig. 5 shows the comparison between the experimental PDF at 1005 K and the simulated PDF at 1000 K. Considering the ultrahigh simulation cooling rate, which is several orders of magnitude higher than the experimental cooling rate, and the quite small simulation size, it could be realized that the two PDF curves match quite well, only showing a small difference on intensity and position in the first peak, justifying the reliability of the simulated data. An enlarged view of the first peak in the PDFs is presented in Fig. 4(a) and Fig. 4(b) to highlight structural details in the first coordination shell. It can be seen that the intensity of the first peaks increases both in the simulation and the experimental data with decreasing the temperature. As illustrated in the Table I, the first peak positions are near 2.95 ± 0.02 Å and the intensity increases from 2.23 to 2.51 in the wider temperature range from 1200 K to

600 K in the simulations. It is found that the first peak intensity increasing rate is about 5.0% per 100 K in the experiment while the first peak intensity increasing rate is about 4.7% per 100K in the simulation during the cooling, indicating that the simulation is in close agreement with the experimental results. However, the peak intensity variation in the simulation is less homogeneous than that in the experiment. Especially, there is a jump in the peak intensity in cooling from 1100 K to 1000 K and again from 900 K to 800 K, and the peak intensity increase value is 0.07 and 0.06 respectively. The variation can be attributed to the very limited simulation box size, which only contains several hundred atoms.

3.3. *Cluster, interconnecting-zone and free volume*

The tight-bond cluster model for amorphous alloys proposed by ref. [23] consists of clusters, interconnecting-zones (i-zones) and regions of free volume. The clusters are formed from atoms with short and strong directional bonding; the regions of free volume are between the clusters and have liquid-like loose bonding; the interconnecting zones connect the cluster and free volume with bonds that are shorter than the free volume bonds and longer than the bonds in the structure of the corresponding crystallized structure. The three components of the model are quantified by comparing the pair distribution functions (PDFs) and radial distribution functions (RDFs) for the nearest atom pairs for the as-cast $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ bulk metallic glass and its completely crystallized counterpart [33]. The radii of Zr, Al and Cu are 1.62 Å, 1.43 Å and 1.28 Å, respectively, which are obtained according to the periodic

table of chemical elements. The Zr-Zr has the largest atom pair distance with the characteristic value 3.24 Å. Beyond 3.33 Å, which is 2.8% larger than 3.24 Å, there are almost no Zr-Zr nearest atom pairs existing within the PDF for the crystallized counterpart. As a result, the initial distances for the i-zone atom pairs are set at least 2.8% greater than their characteristic atomic radii. The initial distances for the atomic pairs in the free volume region are set at 9.6% larger than their characteristic atomic radii because the free volume regions do not exist in the crystallized counterpart and the terminal of the RDF for the crystallized counterpart is 9.6% greater than the Zr-Zr characteristic atomic radius. The end of the first peaks in the RDF for the as-cast bulk metallic glass is about 20% greater than the Zr-Zr characteristic atomic radius. So the final atom distances for the free volume atom pairs are 120% of their characteristic atomic radii [33].

Fig. 6 shows the relative fractions of cluster, i-zone and free volume atom pairs compared to their summation as a function of temperature. It can be seen that their relative fractions change linearly over the whole temperature range. The fraction of free volume atom pairs becomes smaller, while the fractions of both cluster and i-zone atom pairs increases as the temperature decreases in the supercooled liquid. The first peak positions are near 2.95 Å, which corresponds to the cluster atom pair distances for Zr-Zr, Zr-Cu, Zr-Al and i-zone atom pair distances for Al-Al and Al-Cu. The increase in the fractions of cluster and i-zone atom pairs accounts for the increase of the first peak intensity as the temperature decreases. Atoms are bonded mainly in the form of cluster atom pairs (accounting for about 60%), and about 40% of atom pairs

belongs to the i-zone and free volume atom pairs. To determine the effect of different elements, the quantities of atom pairs containing Al, Zr and Cu are calculated. It can be seen in Fig. 7 that the fraction of Al cluster atom pairs is the largest, while that of the free volume atom pairs is the smallest among the three elements at different temperatures, indicating that it is easier to form short bonds with Al atoms even if the radius of Al is not the smallest. The Al content is the least in the ternary alloy, but the fraction of Al cluster atom pairs is the largest, indicating that the bonding between Al and Zr or Cu tend to be strong. Furthermore, the variation in Al atom pairs with decreasing temperature is the most dramatic, increasing from 0.6245 to 0.6763 for cluster atom pairs and decreasing from 0.1624 to 0.1183 for free volume atom pairs. Obviously, during cooling, a portion of the Al free volume atom pairs transforms into cluster atom pairs, resulting in more dense clusters in the first shell. If we look at free volume atom pairs, it is found that about 85% of the free volume atom pairs are related to Zr atom pairs (Zr-Zr, Zr-Cu and Zr-Al), suggesting that the bonds between Zr atom pairs tend to be weaker, especially for Zr-Zr and Zr-Cu.

It is well known that the addition of Al to Zr-Cu binary alloys stabilizes the structure and leads to the improvement of GFA [34]. Compared with Zr and Cu atoms, Al atoms prefer to form short bonds with other atoms and the number of Al cluster atom pairs increases significantly as the temperature decreases in the supercooled liquid, leading to a reduction of the internal energy and an increase in the packing density of Al-centered clusters. Figs. 8(a), (b) and (c) show the first shell clusters at 700 K where Zr, Cu and Al respectively occupy the cluster centers. It is recognized

that the Al-centered cluster is the most densely packed because there are more cluster atom pairs than those for the Zr- and Cu-centered clusters. The average distances between the central atom and the shell atoms of the three clusters are calculated by taking the radii of the three elements into consideration. From this it is confirmed that the Al-centered cluster has the closest packing among the three kinds of clusters. As a result, in terms of energy, it is difficult for the Al-centered cluster to transform into a crystal structure because of the highest energy required to break the bonds in the Zr-, Cu- and Al-centered clusters. By integrating through the first peak of the partial PDF, it is found that the average coordination number of Al is 12.30 at 1200 K, which is larger than that for the closest-packed crystal. From the viewpoint of structure, as the temperature decreases the Al-centered clusters in the first shell become more tightly packed and the difference in packing density becomes larger relative to that in the crystal structure.

3.4. DOS analysis

In order to probe the effect of different elements on the bonding properties and the significance of Al on the GFA in the $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ ternary alloy, the Al-centered clusters within the first shell are chosen for the calculations of the DOSs with VASP. Two clusters with the same centered Al atom in Figs. 9(a) and (b), obtained at 1100 K and 700 K, are selected for comparison. The self-consistent computation is conducted first. Then an $8 \times 8 \times 8$ grid for the Monkhorst-Pack scheme of k-point sampling is used and the cut off energy is set at 400 eV for the calculation of DOSs.

Fig. 9(b) shows the deviation from the Al-centered cluster presented in Fig. 9(a). One Zr shell atom breaks away from the first shell and the remaining shell atoms approach the core-Al atom, resulting in the stronger bonding between the atoms with the decrease of the free volume atom pairs and the increase of the i-zone and cluster atom pairs. As a result, the Al-centered cluster in Fig. 9(b) has a tighter packing.

The calculation of electronic structure provides us with their bonding characteristics. The DOS represents the contribution to the energy state of coupling all atomic orbits, while the PDOS shows that different atomic orbits contribute to different energy states. Fig. 10 and Fig. 11 show the calculated PDOSs and DOSs of the Al-centered clusters. It is found in Fig. 10 that the energy state in the range from -6 eV to -4.5 eV is dominant because of the Cu *d*-electrons and that the Zr *d*-electrons mainly contribute in the range from -4 eV to -2eV. The low energy state is mainly attributed to Al *sp*-electrons. It is in good agreement with the distribution of the relative fractions of the cluster, the i-zone and the free volume atom pairs of Al, Cu and Zr respectively. The fraction of Al cluster atom pairs is the largest among the three elements and the free volume atom pairs are mainly attributed to Zr atom pairs. Furthermore, the *sp-d* coupling between Al and Zr or Cu is observable near the Fermi level, leading to the strong bonding and the stability of the Al-centered clusters [24]. It is noticed in Fig. 11 that at low temperature the energy state shifts towards lower energies, implying that the electronic cloud in bonded atoms has larger overlap and the bonds length becomes shorter. This is in line with the increase of cluster atom pairs as the temperature decreases.

4. Conclusions

The structural evolution in the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid was studied by employing *in-situ* high-temperature, high-energy, synchrotron X-ray experiments and AIMD simulations. The pair distribution functions obtained from both the experiments and the simulations reveal that the structure in the supercooled liquid is different from that of the crystal and glass. The first peaks become narrower and higher as the temperature decreases. By quantitatively analyzing the cluster, i-zone and free volume atom pairs in the tight-bond cluster model, it is found that the relative fraction of the cluster atom pairs increases linearly and that of the free volume atom pairs decreases linearly with decreasing temperature. The distribution and variation of the Al atom pairs with different bond length in the supercooled liquid elucidate the effect of Al on the GFA. In addition, the DOSs and PDOSs related to the electronic structure within the Al-centered clusters were also calculated to clarify the bonding characteristics.

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Table Caption:

TABLE I. The first peak intensities and positions of PDFs for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid in the experiments and simulations.

Figure Captions:

FIG. 1. The x-ray static structure factors, $S(Q)$, for the temperatures near the melting temperature of $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ (1173 K) for the six heating-cooling cycles. For better comparison, curves are vertically offset.

FIG. 2. (a) The x-ray static structure factors, $S(Q)$, for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K. For better comparison, curves are vertically offset. (b) The first and second peaks of the $S(Q)$ for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K.

FIG. 3. (a) PDFs for the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K in the experiments. (b) PDFs for the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid for temperatures from 1200 K to 600 K in AIMD simulations. For better comparison, curves are vertically offset.

FIG. 4. (a) The first peaks of PDFs for temperatures from 1172 K to 953 K in the experiments. (b) The first peaks of PDFs for temperatures from 1200 K to 600 K in AIMD simulations.

FIG. 5. Comparison between the experimental PDF at 1005 K and the simulated PDF at 1000 K.

FIG. 6. Changes of the relative fractions of cluster, i-zone, free volume atom pairs as a function of temperature from 1200 K to 500 K in AIMD simulations.

FIG. 7. Changes of the relative fractions of Al, Cu and Zr cluster, i-zone, free volume atom pairs as a function of temperature from 1200 K to 500 K in AIMD simulations.

FIG. 8. (a), (b) and (c) represent the Zr-, Cu- and Al-centered clusters within the first shell, which are obtained at 700 K. Blue for Zr, pink for Cu and yellow for Al. Cluster bonding in black color, i-zone bonding in red color, and free volume bonding in green color.

FIG. 9. (a) and (b) show the Al-centered clusters within the first shell, which are obtained at 1100 K and 700 K respectively. Blue for Zr, pink for Cu and yellow for Al. Cluster bonding in black color, i-zone bonding in red color, and free volume bonding in green color.

FIG. 10. The calculated PDOSs of the Al-centered clusters which are obtained at 1100 K and 700 K in Fig. 9(a) and (b). The Fermi levels are indicated by the violet dotted lines.

FIG. 11. Comparison between the DOSs of the Al-centered clusters which are obtained at 1100 K and 700 K in Fig. 9(a) and (b).

TABLE I. The first peak intensities and positions of PDFs for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid in the experiments and simulations.

temperature(K)	the first peak intensity	the first peak position($\text{\AA}$)	
1172	2.19	2.98	
1118	2.21	3.00	
1073	2.23	3.00	
1037	2.25	3.00	experiment
1005	2.27	3.00	
977	2.28	3.00	
953	2.30	3.00	
1200	2.23	2.93	
1100	2.26	2.95	
1000	2.33	2.95	
900	2.37	2.93	simulation
800	2.43	2.95	
700	2.47	2.93	
600	2.51	2.95

FIG. 1. (Color online) The x-ray static structure factors, $S(Q)$, for the temperatures near the melting temperature of $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ (1173 K) for the six heating-cooling cycles. For better comparison, curves are vertically offset.

FIG. 2. (Color online) (a) The x-ray static structure factors, $S(Q)$, for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K. For better comparison, curves are vertically offset. (b) The first and second peaks of the $S(Q)$ for for supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K.

FIG. 3. (Color online) (a) PDFs for the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid at temperatures from 1172 K to 953 K in the experiments. (b) PDFs for the supercooled $\text{Zr}_{55}\text{Cu}_{35}\text{Al}_{10}$ liquid for temperatures from 1200 K to 600 K in AIMD simulations. For better comparison, curves are vertically offset.

FIG. 4. (Color online) (a) The first peaks of PDFs for temperatures from 1172 K to 953 K in the experiments. (b) The first peaks of PDFs for temperatures from 1200 K to 600 K in AIMD simulations.

FIG. 5. (Color online) Comparison between the experimental PDF at 1005 K and the simulated PDF at 1000 K.

FIG. 6. (Color online) Changes of the relative fractions of cluster, i-zone, free volume atom pairs as a function of temperature from 1200 K to 500 K in AIMD simulations.

FIG. 7. (Color online) Changes of the relative fractions of Al, Cu and Zr cluster, i-zone, free volume atom pairs as a function of temperature from 1200 K to 500 K in AIMD simulations.

FIG. 8. (Color online) (a), (b) and (c) represent the Zr-, Cu- and Al-centered clusters within the first shell, which are obtained at 700 K. Blue for Zr, pink for Cu and yellow for Al. Cluster bonding in black color, i-zone bonding in red color, and free volume bonding in green color.

FIG. 9. (Color online) (a) and (b) show the Al-centered clusters within the first shell, which are obtained at 1100 K and 700 K respectively. Blue for Zr, pink for Cu and yellow for Al. Cluster bonding in black color, i-zone bonding in red color, and free volume bonding in green color.

FIG. 10. (Color online) The calculated PDOSs of the Al-centered clusters which are obtained at 1100 K and 700 K in Fig. 9(a) and (b). The Fermi levels are indicated by the violet dotted lines.

FIG. 11. (Color online) Comparison between the DOSs of the Al-centered clusters which are obtained at 1100 K and 700 K in Fig. 9(a) and (b).