Bergman-type medium range order in amorphous Zr$_{77}$Rh$_{23}$ alloy studied by ab initio molecular dynamics simulations

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Abstract
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Keywords
Zr77Rh23 alloy, Metallic glass, Short-range order, Medium-range order, ab initio molecular dynamics

Disciplines
Metallurgy | Physics

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Bergman-type medium range order in amorphous Zr$_{77}$Rh$_{23}$ alloy
studied by ab initio molecular dynamics simulations

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ABSTRACT

In recent years, some arguments about the existence of medium-range order (MRO) in the Zr-Rh system have been put forward. However, research on the structural features of the Zr-Rh binary alloy at the atomic level is still lacking. This study uses ab initio molecular dynamics simulations to systematically study the local structures of Zr$_{77}$Rh$_{23}$ from the liquid to the glassy states. Pair correlation function (PCF), coordination number (CN), Honeycutt–Anderson(HA) index, bond-angle distribution functions, and the Voronoi tessellation method are used to reveal a clear icosahedral-like configuration in the amorphous Zr$_{77}$Rh$_{23}$ alloy. It is noteworthy that the splitting in the second peak
of the partial PDF implies the existence of a medium range order (MRO) in the Zr$_{77}$Rh$_{23}$ system. We obtain the local order in three-dimensional atomic density distributions by using a new atomistic cluster alignment (ACA) method. Interestingly, a Bergman-type MRO is observed in the glassy Zr$_{77}$Rh$_{23}$. Furthermore, the spatial distribution and connections of icosahedral-like clusters are shown to further demonstrate the MRO network. Our findings shed light on the nature of atomic local structures of amorphous Zr$_{77}$Rh$_{23}$ alloy and have important implications to understanding the formation of various MROs in metallic glasses.

**Keywords:** Zr$_{77}$Rh$_{23}$ alloy, metallic glass, short-range order, medium-range order, ab initio molecular dynamics.
I. Introduction

Metallic glasses (MGs) are novel amorphous engineering alloys. Due to the absence of the dislocations of crystalline defects, MGs not only have great flexibility, but are also much stronger (3-4 times or more) than their crystalline counterparts. In addition, MGs have higher thermal stability and lower stiffness. These advantages offer great potential for applications of MGs [1, 2]. Notably, Zr-rich alloys are important MGs due to their strong glass forming ability [3] and outstanding mechanical properties, such as high Young’s modulus [4], fracture toughness [5] and elasticity [6]. The superconducting properties of the Zr-Rh system was proposed in 1955, and has subsequently attracted widespread interest [7]. The Zr-Rh phase system has been studied experimentally [8, 9], and many new metastable phases of the Zr-Rh alloy have been discovered by rapid quenching [10]. Although much experimental research has been devoted to the mechanical properties, electronic properties, and metastable phases of Zr-Rh compounds, we still lack a complete understanding of the short-range order (SRO) and medium-range order (MRO) from liquid to glassy state at the atomic level [11-13].

For the pair correlation function (PCF) of amorphous materials, SRO is usually constituted by the atoms of the nearest-neighbor shell, while the MRO is manifested by the second nearest-neighbor atoms [14]. The splitting in the second peak of the PCF or a pre-peak in the total structure factor are identifying characteristics of MRO. However, the diverse mechanisms of such splitting and pre-peaks have been debated for many years [15-18]. A Bergman-type cluster is one of the MROs in MGs, and is an icosahedral-based cluster which, moving outward from the center atom, forms an icosahedron, dodecahedron, and a larger icosahedron [19, 20]. The Bergman-type MRO seems to be related to splitting in the second peak of the PDF in a Cu-Zr system [18, 21] and an Ag$_{0.74}$Ge$_{0.26}$ alloy [22]. The positions of the two sub-peaks formed by the splitting of the second peak are the same as the maxima of the corresponding distribution of the second and third shells of the Bergman-type cluster.

In recent years, arguments about the existence of a MRO in the Zr-Rh system
have been advanced. Mauro et al. [23] pointed out that despite the lack of the pre-peak in the structure factor, the Zr-Rh system should also contain an MRO like other similar solute-solute correlation Zr-rich systems which have MROs, such as Zr-Pt and Zr-Ir. The reason for absence of a pre-peak in the Zr-Rh system structure factor may be ascribed to the smaller value of Faber-Ziman coefficients in Zr-Rh than those in either the Zr-Pt or Zr-Ir systems. However, Johnson et al. [24] argues that the ratio of Faber-Ziman coefficients is not the only factor responsible for the absence of a pre-peak, and reveals Zr$_{77}$Rh$_{23}$ has a strong chemical SRO but weaker size-induced MRO. To date, whether the MRO is established in the Zr-Rh system or, if it exists, how these MRO clusters are formed, remains to be solved.

In this work, a Bergman-type MRO was first found in the amorphous Zr$_{77}$Rh$_{23}$ metallic glass from ab initio molecular dynamics (MD) simulations with extremely high cooling rates. The PCFs, coordination number (CN), bond-angle distribution functions, and Voronoi tessellation method are used to characterize the Zr$_{77}$Rh$_{23}$ alloy SRO during rapid cooling. The atomistic cluster alignment (ACA) method is utilized to further explore the MRO of the Zr$_{77}$Rh$_{23}$ alloy in a glassy state. Thus, we use the computational method to obtain a detailed structure of the Zr$_{77}$Rh$_{23}$ system at an atomistic level, which will be beneficial to the understanding of the local structure Zr$_{77}$Rh$_{23}$ alloy.

II. Computation details

The ab initio MD simulations of Zr$_{77}$Rh$_{23}$ were performed by using the Vienna ab initio simulation package (VASP) code based on the density functional theory (DFT) [25, 26]. For the exchange-correlation energy functional, the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form was used [27], while the projector augmented-wave (PAW) method [28, 29] was utilized to describe the electron-ion interaction. An NVT canonical ensemble (constant-number of particles, constant-temperature, constant-volume) with a Nosé-Hoover thermostat was used to control the temperature [30, 31]. Only the Γ point in the Brillouin zone was applied.
The initial configuration of the simulation was a cubic supercell consisting of 200 atoms (154 Zirconium atoms and 46 Rhodium atoms) with random distribution, and periodic boundary conditions were used. First, the cubic supercell was thermally equilibrated at 2000 K (the melting point of Zr$_{77}$Rh$_{23}$ is 1334 K [32]) in order to avoid any memory effect of the random initial configuration. Then, the system was cooled from the liquid state at 1389 K to the glassy state at 300 K with a constant cooling rate of 33.3 K/ps. The time step was 3 fs in this work. At each temperature, the average pressure inside the supercell tended to zero (within 0.0±0.5 kBar) by adjusting the size of the simulation box. When cooled to a certain temperature, the supercell was operated at 6000 time steps to put the system in equilibrium, and last 4000 trajectories were collected for the statistical analyses of the structural properties. The PCF, HA index, and ACA method[33] were calculated by using the collected MD trajectories to investigate the local order of Zr$_{77}$Rh$_{23}$ at different temperatures.

III. Results and discussion

A. Pair correlation function.

PCF is an important structural parameter in real space describing the possibility of finding another atom in the range from $r$ to $r + \Delta r$ from average center atom. The total structure factor $S(q)$ were obtained from the three partial structure factors $S_{\alpha \beta}(q)$, atomic concentration of the elements $\chi_{\alpha}$ and $\chi_{\beta}$ and the scattering factors $f_{\alpha}$ and $f_{\beta}$ in the alloys:

$$S(q)=1+\frac{\chi_{\alpha}^2 f_{\alpha}^2 (S_{aa}(q)-1)+2 \chi_{\alpha} \chi_{\beta} f_{\alpha} f_{\beta} (S_{ab}(q)-1)+\chi_{\beta}^2 f_{\beta}^2 (S_{bb}(q)-1)}{(\chi_{\alpha} f_{\alpha} + \chi_{\beta} f_{\beta})^2}$$

(1)

The scattering factors $f_{\alpha}$ and $f_{\beta}$ are obtained from tabulated data [34] he partial structure factors, $S_{\alpha \beta}(q)$, are related to the partial pair correlation functions $g_{\alpha \beta}(r)$ by

$$S_{\alpha \beta}(q) = \delta_{\alpha \beta} + 4 \pi \rho_{\alpha \beta} \int_{0}^{\infty} g_{\alpha \beta}(r) - 1 \frac{\sin(qr)}{qr} r^2 dr$$

(2)

where, the $g_{\alpha \beta}(r)$ can be calculated by the Eq. (3)
Due to a limited number of the experimental data for glassy state of Zr$_{77}$Rh$_{23}$ until now, the calculated total structure factors $S(q)$ of Zr$_{77}$Rh$_{23}$ at 1389 K are compared with the neutron scattering data of liquid Zr$_{77}$Rh$_{23}$ at 1389 K in experiment [24], as shown in Fig.1 (a). The simulation and the experimental results are in good agreement, which indicate that our simulation is reasonable. Total and partial PCF ($g(r)$) of Zr$_{77}$Rh$_{23}$ from 1389 K to 300 K are plotted in Fig. 1 (b). The first peaks of total PCFs become sharper with the decrease in temperature, indicating that the SRO becomes well-defined upon cooling. The PCF between different atoms is called partial PCF (PPCF), which can be expressed as:

$$g_{\alpha\beta}(r) = \rho_{\alpha\beta}^{-2} \left( \sum_i \sum_{j \neq i} \delta(r - r) \delta(r_i - r_j) \right)$$

(3)

where $\rho_{\alpha\beta} = \rho_0 \chi_{\alpha} \chi_{\beta}$ is the corresponding partial density, and $\rho_0$ is the atomic density of the liquid, $\chi_{\alpha}$ and $\chi_{\beta}$ are the atomic concentration of the corresponding elements in the liquid, respectively. The space range of $r$ was extended to 1.5 times of box length for the calculation of $g_{\alpha\beta}(r)$. The correlation between Zr and Rh atoms can be directly reflected from the PPCFs in Fig.1 (b). It is found that the first peak of $g_{\text{Zr-Zr}}(r)$ and $g_{\text{Zr-Rh}}(r)$ are clearly higher than $g_{\text{Rh-Rh}}(r)$ from the PPCFs, demonstrating that the interaction between Zr-Zr and Zr-Rh are stronger than that in the Rh-Rh atoms. However, the second peak of $g_{\text{Rh-Rh}}(r)$ is quite high, indicating that the interaction of Rh-Rh atoms is very weak and is pushed to the second nearest-neighbor layer. In PPCFs, the height of the first and second peaks becomes sharper as the temperature decreases, indicating the interaction between different atoms tends to cluster together with decreasing temperature. Remarkably, there is an obvious split in the second peak of the total PCF and PPCFs for Zr-Zr and Zr-Rh as the temperature drops to 300 K, which highlighted in the insets of Fig. 1 (b). Recently, it has been shown that the global structural feature of PCFs for MGs at the MRO scale can be demonstrated by spherical-periodic order (SPO) and local translational symmetry (LTS) [16]. For the total PCF of Zr$_{77}$Rh$_{23}$ at 300 K, the ratios of $R_1/R_1 = 1.00$, $R_2/R_1 =$
$R_3/R_1 = 1.95$, $R_4/R_1 = 2.53$ are in excellent accord with characteristic values $\sqrt{1}$ (1.00), $\sqrt{3}$ (1.73), $\sqrt{4}$ (2.00), $\sqrt{7}$ (2.64) in Ref. 16, showing that the glassy state of Zr$_{77}$Rh$_{23}$ possesses a global structural feature. Therefore, we surmise that there may be an MRO in the Zr$_{77}$Rh$_{23}$ system.

Fig. 1. (a). Comparisons of calculated total structure factors $S(q)$ of liquid Zr$_{77}$Rh$_{23}$ at 1389 K (solid blue line) and measured neutron scattering data (solid red circles) from Ref. 24. (b). Total and partial pair-correlation functions of Zr$_{77}$Rh$_{23}$ at different
temperatures. The insets show total PCF and PPCFs of Zr-Zr and Zr-Rh at 300 K. The red circles mark the splitting of the second peaks. The peak values of $R_1$, $R_2$, $R_3$, and $R_4$ in total PCF at 300 K are 3.16, 5.50, 6.15 and 8.00 Å, respectively.

B. Local structure order

The local structure order of liquid and amorphous materials is often determined by coordination number (CN), bond-angle distribution functions, HA index and Voronoi tessellation methods. CN is one of the fundamental means of describing the SRO of amorphous materials. By integrating PPCFs to the distance corresponding to first minimum in the PPCFs obtained above, the CNs of a central atom can be calculated. The total and partial CNs of Zr$_{77}$Rh$_{23}$ at different temperatures are shown in Fig 2. It is interesting to note that the CNs of Zr-Zr/Rh and Rh-Zr/Rh change very little with the decrease in temperature, indicating that the order of the first nearest-neighbor for Zr$_{77}$Rh$_{23}$ from liquid to glassy state is very stable. The CN of Zr-centered configurations remain almost unchanged at 14, while the CN of the Rh-centered configurations range from 10.4 to 10.9 upon fast cooling. Moreover, we select the first minimum as well as the left and the right second maximum of total PCF as cutoff values to determine the total number of atoms of Zr$_{77}$Rh$_{23}$ at 300 K, which correspond to the number of atoms in first, second and third shells, respectively (see Table 1). Significantly, the total number of atoms of the Zr$_{77}$Rh$_{23}$ system agrees with the number of atoms of three shells for a Bergman-type MRO cluster, which is defined as a one center atom (1 atom)-icosahedral (12 atoms)-dodecahedral (20 atoms)-icosahedral (12 atoms) arrangement. Previous studies have pointed out that the splitting in the second peak of the PCF in metallic glass can be ascribed to the Bergman-type MRO. The dodecahedral formation in the second shells of Bergman clusters corresponds to the left peak position of splitting, and the right-shoulder of the second peak can be ascribed to the third shells with defective icosahedra. Accordingly, we speculate that the Zr$_{77}$Rh$_{23}$ system has a Bergman-type MRO structure at 300 K.
Fig. 2. CN of Zr\textsubscript{77}Rh\textsubscript{23} at different temperatures. Lines labelled as A-B are partial CNs, representing the A atom as the centered atom and the B atom as the coordination atom. The cutoff distance is close to the first minimum in the total PCF.

Table 1. Total number of atoms by integrating the different cutoff distances corresponding to first minimum, as well as the left and the right second maxima in total PCF at 300 K. The value in parenthesis is the total number of atoms of ideal Bergman-type MRO cluster in first, second and third layers.

<table>
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<th>Second-max-left</th>
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<tr>
<td>Cutoff (Å)</td>
<td>4.12</td>
<td>5.50</td>
<td>6.15</td>
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<tr>
<td>number of atoms</td>
<td>13.48 (12)</td>
<td>31.77 (32)</td>
<td>47.45 (44)</td>
</tr>
</tbody>
</table>

To further study the local structure order information of the Zr\textsubscript{77}Rh\textsubscript{23}, bond-angle distribution functions at different temperatures are shown in Fig. 3, which can characterize the angular distribution of bonding between Zr and Rh atoms. We divide bond-angle distribution functions of Zr\textsubscript{77}Rh\textsubscript{23} into two groups: Zr-centered in Fig. 3 (a)-(c) and Rh-centered in Fig. 3 (d)-(f). For the Rh-centered group, it is noteworthy that the main peaks for Zr-Rh-Zr are located at around 64° and 117°, respectively, corresponding to the two characteristic peaks of the bond angular distribution function for standard icosahedron-symmetric structures. For the Zr-centered group, the peaks in
Zr-Zr-Zr indicate a slight shift, located at about 58° and 110°, respectively, while those in the Zr-Zr-Rh also show a shift located at 51° and 103°. This indicates more distorted icosahedral geometries exist in the Zr$_{77}$Rh$_{23}$ system. However, the curves in Rh-Rh-Rh are rather cluttered, with no obvious peaks. Consequently, there are many perfect icosahedral and distorted icosahedral geometries in the Zr$_{77}$Rh$_{23}$ alloy.

Fig. 3. The calculated partial bond-angle distribution functions of Zr$_{77}$Rh$_{23}$ at different temperatures.

In order to further analyze the types and characteristics of the local structure ordering of the system, the HA-index method is used, which is represented by a set of three numbers [35]. Figure 4 gives the six main configurations of HA index results for Zr$_{77}$Rh$_{23}$. Various configurations can be characterized by different HA indexes. For example, a perfect icosahedron could be represented by 155, with 154 and 143 usually regarded as distorted icosahedral configurations. The fraction of 155 makes up a great part of the system, and clearly increases with a decrease of temperature, demonstrating that the number of perfect icosahedrons increases in Zr$_{77}$Rh$_{23}$. At 300K, the fraction of 155 is as high as 41%, with the content of 154 and 143 decreasing slightly with the
decrease in temperature. Thus, it can be seen that the icosahedral-like configuration stands out in Zr$_{77}$Rh$_{23}$. In addition, 144 and 166 usually represents body-centered cubic, with those two fractions of HA indices being relatively low and varying very little with temperature. The fraction of 166 fluctuates at around 10%, and that of 144 fluctuates at around 7%.

Fig. 4. The distribution of HA indexes with error bar for Zr$_{77}$Rh$_{23}$ at different temperatures.

To clearly present the structure of various types of atomic clusters, the distribution of polyhedral clusters in the system is further investigated by the Voronoi tessellation method. The Voronoi index can be defined as $<n_3, n_4, n_5, \ldots, n_i, \ldots>$, where $n_i$ is the number of $i$-edged faces of the Voronoi polyhedra (VP) and the sum of $n_i$ is the total CN. Figure 5 illustrates the percentage of the top ten Voronoi tessellation indexes in the Zr$_{77}$Rh$_{23}$ alloy, varying with temperature. The Voronoi index $<0, 0, 12, 0>$ represents a perfect icosahedron while $<0, 1, 10, 2>, <0, 2, 8, 1>, <0, 2, 8, 2>, <0, 3, 6, 3>$ and $<0, 3, 6, 4>$ represent distorted icosahedrons. From Fig. 5, the Voronoi indexes can be divided into two groups, icosahedron-like and others. Many distorted icosahedrons are apparent with large CNs (CN = 12-14) in the Zr$_{77}$Rh$_{23}$ system. The
fraction of distorted icosahedron <0, 1, 10, 2> is the highest among these Voronoi indexes, most of which are Zr-centered clusters. HA analysis shows that the perfect icosahedron 155 index is the highest fraction. This is due to the fact that the formation of a perfect icosahedron requires twelve bonds with 155 indices; however, distorted icosahedrons with a combination of 155, 154 and 143 indices are relatively easier to form [36].

Fig. 5. Calculated populations of Voronoi tessellation indexes for Zr77Rh23 at different temperatures. The percentage of the top ten Voronoi tessellation indexes with error bar are listed.

The atomistic cluster alignment (ACA) method [33] is an effective analysis method, which not only provides a direct three-dimension visualization of the average local SRO, but also further explores the MRO structures for liquid and amorphous systems [37-39]. In this study, 2000 clusters for each type of central atoms are randomly selected from the MD simulation trajectories at 300 K and 1389 K, respectively. In Fig. 6 (a)-(b), each cluster is made up of 16 atoms. All those clusters overlap their central atoms. Then the collective alignment is carried out by applying rigid rotation and translational operations to the clusters until the overall mean-square distance among all the clusters is minimized. After the collective alignment, three-dimensional atomic
density distributions smoothed with Gaussian smearing are obtained. The results of this alignment will reveal the common structural motif characterizing the local environment of a given chemical constituent. As shown in Fig. 6 (a)-(b), the whole Zr\textsubscript{77}Rh\textsubscript{23} system exhibits defective icosahedral-like geometry at 300 K and 1389 K. However, at 1389 K, although the upper half parts of both Zr- and Rh-centered patterns shows icosahedral-like five-fold symmetry, the lower half parts lack such symmetry, representing the weaker icosahedral SRO exists in the system. The missing part indicates that the atoms failed to find a common structural order in the collective alignment process. Nevertheless, it can be concluded that Zr\textsubscript{77}Rh\textsubscript{23} possesses a very strong icosahedral-like geometric local structure in the nearest-neighbor shell from the liquid state to glassy states. The SRO in liquid Zr\textsubscript{77}Rh\textsubscript{23} is also quite strong, which is consistent with the CN results.

Analysis of PCF and total CNs at 300 K in this work have revealed that MRO may be formed in the Zr\textsubscript{77}Rh\textsubscript{23} system upon cooling. To verify this, we investigate the second and third nearest-neighbor layers of Zr\textsubscript{77}Rh\textsubscript{23} at the glassy state using the ACA collective alignment. A little difference in collective alignment is that each cluster is expanded to the 35 atoms in Fig. 6 (c), while the 15 nearest neighboring atoms from thirty-second to forty-sixth, representing third nearest neighbor, are simulated in Fig. 6 (d). In Fig. 6 (c), the whole Zr\textsubscript{77}Rh\textsubscript{23} system at 300 K clearly shows that an icosahedral geometry is wrapped outside a dodecahedral geometry, and in Fig. 6(d), the nearest-neighbor third layers illustrate a defective icosahedral pattern. By using collective alignment of three shells of Zr\textsubscript{77}Rh\textsubscript{23}, we prove the whole system forms the Bergman-type MRO structure (icosahedral-dodecahedral-icosahedral arrangement) at the glassy state. Furthermore, we infer that as the temperature is reduced to 300 K, the SRO of the Zr\textsubscript{77}Rh\textsubscript{23} system is further strengthened to form Bergman-type MRO.
Fig. 6. The collective alignment results of Zr$_{77}$Rh$_{23}$ at 1389 K (a) and 300 K (b) for nearest-neighbor shells, as well as the nearest-neighbor and second-nearest-neighbor shell (c), and the third nearest-neighbor shell (d) at 300 K. In order to see the icosahedral more clearly, we have connected it with black lines in (d). The red clusters at the left stand for the whole ones in a Zr$_{77}$Rh$_{23}$ system. The cyan and green clusters represent Zr-centered and Rh-centered ones, respectively. The isovalue is set at $0.15 \text{Å}^{-3}$ and $0.1 \text{Å}^{-3}$ in (a)-(b) and (c), respectively. In (d), the isovalue is set at $0.106 \text{Å}^{-3}$, $0.132 \text{Å}^{-3}$ and $0.11 \text{Å}^{-3}$ for all, Zr-centered and Rh-centered patterns, respectively.

In order to investigate the topological packing of the distorted icosahedral clusters, we identify the distorted icosahedral clusters in a snapshot at 300 K by using the individual cluster-template alignment scheme of the ACA method. The template is chosen as the icosahedral cluster, consisting of 13 atoms obtained from the collective alignment. Each cluster extracted from the glass sample is aligned against a standard
template. The structural similarity is described by the square of the distance between the cluster and template atoms. If the alignment score is less than 0.16, in this work the cluster is assigned as an icosahedral cluster. The spatial distribution and connections of these clusters in Zr$_{77}$Rh$_{23}$ in the glass sample is reflected in Fig. 7 (a). It is clear that these aligned distorted icosahedral clusters connect with each other to form MRO. The central atoms of these clusters are labelled as red.

Based on the spatial distribution of clusters in Fig. 7(a), Fig. 7(b) shows four different connection schemes of distorted icosahedral clusters in Zr$_{77}$Rh$_{23}$: vertex sharing (VS), edge sharing (ES), face sharing (FS) and interpenetrating sharing (IS). Previous work has revealed that the splitting of the second PCF peak originating from an uneven contribution of cluster connections—that is, the intensities of contribution for 1-atom and 3-atom connections—are much stronger than that of 2-atom and 4-atom connections [40]. According to the degree of connection distortion of two icosahedral clusters, three representative connection types for FS are illustrated in Fig. 7(b). IS1 displays two distorted interpenetrated icosahedral clusters and IS2 displays three interpenetrated distorted icosahedral clusters. Table 2 shows the distance between the central atoms of distorted icosahedrons for different connection schemes corresponding to Fig. 7(b). In Table 2, the distances for VS and ES schemes are relatively large, while the distances for the IS scheme are relatively small, around 3 Å. Note that different degrees of distortion for the FS scheme in Fig. 7(b) result in large range distances (3.82-4.98 Å) between two icosahedral clusters.

In order to understand correlations between different icosahedrons and better understand how the MRO is constructed in the Zr$_{77}$Rh$_{23}$ glass system, we calculate the pair correlation function among the different icosahedrons defined above using the coordinates of the center atoms in each icosahedron. The result is shown in Fig. 8. In order to obtain the distance relation of these centered atoms more accurately, the alignment score is set to a larger value of 0.25. Based on Table 2, the blue region in 2-3 Å corresponding to the IS connection scheme which confirms that the IS scheme is dominant in Zr$_{77}$Rh$_{23}$. The second peak is located around 4.4 Å (green region) which
is mainly occupied by the FS connection at different distortions, while the proportion of ES may be relatively small. The purple region around 6-7 Å demarcates contributions by the VS scheme. It can be seen that the difference of distance among those four connection schemes are relatively large. Additionally, contributions for IS and FS are much stronger than that of ES and VS schemes in glassy state of Zr$_{77}$Rh$_{23}$. Thus, the reason for the splitting of the second PCF peak in Zr-Zr and Zr-Rh could be inferred to be a result of, on one hand, a Bergman-type MRO in the Zr$_{77}$Rh$_{23}$ system in the glassy state. On the other hand, it can be attributed to the difference of the contribution of the connection schemes.

Fig. 7. (a) Spatial distribution of distorted icosahedron clusters (light purple atoms) in Zr$_{77}$Rh$_{23}$ at 300 K. Central atoms are labelled in red. (b) Schematic diagrams for the connection schemes (VS, ES, FS, and IS) for different distorted icosahedral clusters in Fig. 7 (a). The red and blue spheres represent different clusters, and the green are the sharing atoms.

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</tbody>
</table>
In our studies, the glassy state of Zr$_{77}$Rh$_{23}$ is quenched from the liquid at the constant cooling rate of 33.3 K/ps. However, previous researches have revealed that the degree and extent of SRO and MRO may depend on the cooling rate, in which different cooling rates have certain effects on the local structure of glassy state [41-43]. Hence, in the future work, we can try to simulate the effect of cooling rate on the structure in the glassy state with thousands of atoms by using a new simulation technique, such as the deep potential for molecular dynamics (DeePMD) [44, 45] based on machine learning that serves as the interface between deep neural network models and molecular simulation tools, such as LAMMPS [46] and path-integral MD packages like i-PI[47].

IV. Conclusions

In summary, the local structure of a Zr$_{77}$Rh$_{23}$ system after cooling has been studied through ab initio molecular dynamics simulations. As the temperature drops to 300 K, an obvious split is found in the second peak of the PCF for Zr-Zr and Zr-Rh, respectively, implying that there may be an MRO in the amorphous Zr$_{77}$Rh$_{23}$ system.
The analysis of CN, bond-angle distribution functions, HA index, and the Voronoi tessellation index demonstrate that this Zr\textsubscript{77}Rh\textsubscript{23} system exhibits strong icosahedral-like SRO from liquid to glassy state. CN results reveal that the order of the first nearest-neighbor for Zr\textsubscript{77}Rh\textsubscript{23} from liquid to glassy state is very strong. In addition, when the temperature drops to 300 K, the SRO of the Zr\textsubscript{77}Rh\textsubscript{23} system is further strengthened and the Bergman-type MRO structure is formed. Bergman-type MRO structure is likely the main factor for the splitting of PCF at 300K. The network formed by icosahedral-like clusters in the glassy state of Zr\textsubscript{77}Rh\textsubscript{23} are obtained by the ACA method, and the different contributions for the four main connection schemes of those distorted icosahedral clusters are presented, which may also be the cause of the PCF splitting. These interesting insights are helpful for broadening understanding of both SRO and MRO in the Zr-Rh alloy.

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