Exploration of the atomic-level structures of the icosahedral clusters in Cu–Zr–Al ternary metallic glasses via first-principles theory

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Abstract

The atomic-level structures of the icosahedral clusters in Cu–Zr–Al ternary metallic glasses were studied via the first-principles theory. The rules of icosahedra stability were determined. Icosahedra with a better chemical order or with a better symmetry exhibited a better stability. The strong connectivity between Al atom and Cu and Zr atoms was observed as demonstrated by the obvious degree of ‘bond shortening’. The Al atom contributed more to the structural stability when used as the central atom than the other atoms. Therefore, the addition of even a small amount of Al atom to the Cu–Zr binary system remarkably improved the stability of the icosahedron structures. The continued addition of Al atoms had a lower contribution to the improvement to the glass-forming ability of the Cu–Zr–Al alloys.

1. Introduction

As a kind of novel materials, metallic glasses (MGs) have many unique properties and are widely used in many fields [1]. However, without long-range order, accurately characterizing their microstructure is difficult. Thus, the microstructure of MGs must be explored. Owing to their excellent physical, chemical, and mechanical properties, Cu–Zr-based MGs have attracted increased attention [2–6]. Cu–Zr binary MGs are an early system studied in the field of bulk metallic glasses (BMGs). They have a good glass-forming ability (GFA) within a wide range of compositions with a critical size of up to 2 mm [7–12]. Cu–Zr–Al ternary MGs, which are also produced via the copper mold casting method, have better mechanical properties, better thermal stability, lower production costs, and higher practical application value [13–19].

Cu–Zr–Al ternary MGs have been studied for a long time. Inoue et al [20] were the first to report that Zr₆₅Cu₂₇₅Al₇₅ alloy has a very wide supercooled liquid region. Subsequent studies successfully prepared, ternary Cu–Zr–Al MGs with a better GFA under different compositions [4, 7, 21–24]. Zhou et al [4] fabricated Cu–Zr–Al MGs with a critical size greater than 10–15 mm by using various ingredients. The influence of the introduction of Al atoms into the Cu–Zr binary system on GFA has attracted wide attention [9, 22, 25, 26]. The static and dynamic atomic structures of Cu–Zr(-Al) MGs have been intensively studied through computer simulations [18, 27, 28], and the icosahedral short-range order structure is found to be closely related to GFA [29–33]. The Cu–Zr-based MGs are considered by numerous studies to be composed of clusters, most of which are touching each other and/or interpenetrating [34, 35]. These clusters may have different structures and compositions, depending on the stoichiometry of the system. In addition, a fundamental understanding of the bonding preferences of these clusters is key to understanding and improving the GFA of MGs. This necessity is confirmed by the experimental results, which show that small additions of some elements, such as Al, improve the GFA effectively [4, 7, 9, 21–26, 29]. The addition of Al atoms may promote the formation of icosahedral
clusters, thereby enhancing GFA [29]. Unlike the Cu–Zr binary system, the addition of Al atoms substantially improves the GFA. Several experimental studies on the internal mechanism of the constituent elements of the best glass formers determined that they have a specific atomic ratio. If the chemical composition of the best glass formers can be explained and predicted, then this information would have a high relevance to the preparation of more effective BMGs. However, this microalloying effect needs to be further studied, and how the introduction of Al atoms affects the icosahedral structure is unclear. The stability rules of Cu–Zr–Al ternary icosahedral structures are also unknown.

For Cu–Zr binary and Cu–Zr–Al ternary MGs, the dramatic enhancement of GFA provides a good model for exploring the relationship between microstructure and GFA [36]. Moreover, research on this topic will provide a reference for the study of other metallic glasses with similar microstructure systems. We investigated Cu–Zr–Al icosahedral structure via density functional theory (DFT) calculations to determine bonding alterations induced by the substitution of Al atoms. Several icosahedral structures of the Cu–Zr–Al ternary system with Cu and Al atoms as the central atoms were constructed. The stability rule within the Cu–Zr–Al ternary icosahedral structures was explored via geometric optimization and energy calculation in accordance with the first-principles theory. Finally, the influence of the introduction of Al atoms on the structural stability of the icosahedron was analyzed.

2. Method

Previous studies showed that the icosahedron structures in Cu–Zr–Al have Cu and Al atoms as the central atoms [29, 30]. Compared with the Zr atom, the Cu and Al atom has a stronger ability to form an icosahedron as the central atom. The energy of all Cu-centered Cu–Zr binary icosahedral isomers was calculated (Figure S1 (available online at stacks.iop.org/MRX/9/065203/mmedia)). Ternary icosahedron structures with Cu and Al atoms as the central atoms were constructed. The content of Cu atoms in the Cu–Zr–Al ternary MGs with good GFA was about 25%–60%, whereas that of Al atoms was less than 16% [4, 20, 22]. Every icosahedral cluster with a central atom consisted of 13 atoms and involved five-fold symmetry. The atomic numbers of Cu and Al atoms in the icosahedra were about 3–8 and 1–2, respectively. The structures with the lowest energy among the Cu–Zr binary icosahedral isomers of different components were used as the initial structures to construct the ternary structures. Cu–Zr–Al ternary icosahedron structures with one and two Al atoms under several specific components were constructed (figure 1). First, icosahedrons with a component ranging from Cu₉Zr₆Al₂ to Cu₅Zr₆Al₂ were constructed (Figure S2). This study involved two construction processes: replacing the Cu atom in the center or replacing the Cu or Zr atom in the shell with the Al atom (figures 1(a) and (b)). Cu and Zr atoms have similar contents among Cu–Zr–Al ternary amorphous alloys with good GFA, such as Cu₄₇.₅Zr₄₅.₁Al₇.₄ [32, 37]. Therefore, ternary icosahedron structures with two Al atoms were studied only two components (Figure S3): Cu₃Zr₆Al₂ and Cu₅Zr₅Al₂ contain two Al atoms and have similar compositions of Cu and Zr atoms. The new structures were obtained by replacing the Cu or Zr atom in the shell of the initial structure (the most stable structure containing one Al atom) with Al atom (figure 1(c)).

The calculations were performed within the framework of DFT applied in CASTEP code [38]. Exchange and correlation functional was treated by the generalized gradient approximation in the formulation of Perdew, Burke, and Ernzerhof [39]. The Kohn–Sham wave functions of valence electrons were expanded to the basis set of plane waves within the specified cutoff energy (E_cut) of 500 eV. The Vanderbilt-type nonlocal ultrasoft pseudopotential [40] was used herein to describe valence electrons. Pseudo wave functions, the smooth part of charge density, and potential were represented on a fast Fourier transform grid of 20 × 20 × 20, which was sufficient for the cutoff energies. The Brillouin zone was sampled by a 3 × 3 × 3 Monkhorst–Pack mesh of k-points with an actual spacing of 0.02 Å⁻¹. We tested the vacuum space and found that the dimension of the cubic supercell that was 2.5-fold larger than the diameter of the Cu₆Al₆Zr₄icosahedron was sufficient to eliminate particle–particle interactions. The Cu₆Al₆Zr₄icosahedron was placed at the center of the supercell. The positions of Cu, Zr, and Al atoms were relaxed during structural optimization until the self-consistent field convergence criteria, i.e., the energy per atom, the tolerance for total energy, the root-mean-square displacement of atoms, the rms force on atoms, and the rms stress tensor were less than 5 × 10⁻⁷ eV, 5 × 10⁻⁶ eV, 5 × 10⁻³ Å, 0.01 eV Å, and 0.02 GPa, respectively.

3. Results

3.1. Effects of chemical order on structural stability

3.1.1. Al-centered structures

The chemical orders of the isomer structures of three components, namely, Cu₆Zr₆Al₄, Cu₅Zr₇Al₄, and Cu₅Zr₆Al₂, were investigated. All ternary isomer structures were obtained by replacing the Cu atom in the center
with the Al atom of Cu₅Zr₈, Cu₆Zr₇ and Cu₇Zr₆ binary icosahedral clusters. The higher the content of Cu–Zr bonds was in an icosahedral structure of the same chemical composition, the lower the tendency was for homogeneous atoms to be interconnected. The contents of the Cu–Zr bond between different isomers and the results are shown in figure 2. ΔE is the energy difference between the initial configuration and the new configuration after the replacement of other atoms by Al atoms.

The content of the Cu–Zr bonds gradually increased as the structural energy between isomers in different components increased, especially in Cu₄Zr₄Al₁ (figures 2(a)) and Cu₅Zr₅Al₁ (figure 2(c)). This result meant that when the icosahedron was unstable, the content of the Cu–Zr bond increased and the chemical order weakened. Therefore, the structural stability with a higher chemical order was better in the Al-centered ternary icosahedral clusters. Cu₆Zr₆Al₁ was used as an example herein to observe and compare directly the structures of different isomers. The content of the Cu–Cu and Zr–Zr bonds was substantially higher as the structure tended to stabilize (figure 3).

In the component of Cu₅Zr₇Al₁, as the energy difference between isomers increased, the content of the Cu–Zr bond displayed an abnormal ‘downward’ trend at points A to B (figure 2(b)). But structure A was more stable than structure B. The spatial configuration of the two structures was compared: the structures corresponding to point A and B are shown in figure 4. Structure A had an obvious fivefold symmetry, which is the unique local symmetry of Cu–Zr-based MGs [41–46]. Intuitively icosahedron is a local cluster with full five-fold symmetry, while it can be distorted in multicomponent systems. The structure A with a better symmetry and less distortion was more stable. Therefore, both chemical order and symmetry affected the stability of the structure, and the stable structure had a better chemical order and topological order than the unstable structure.

The chemical order of icosahedral structures with two Al atoms with the components of Cu₅Zr₆Al₂ and Cu₆Zr₅Al₂ were also investigated (figure 5). The ternary icosahedron with two Al atoms were obtained by replacing the Cu or Zr atom in the shell of Al-centered Cu₅Zr₅Al₁ (the most stable structure of Al-centered Cu₅Zr₅Al₁ icosahedral) with Al atom. As the energy difference between isomers increased, the content of the Cu–Zr bond increased and the chemical order weakened. Therefore, stable structures with two Al atoms also had a better chemical order. Direct observation and comparison of different isomer structures revealed that the content of the Cu–Cu and Zr–Zr bonds was substantially higher as energy tended to stabilize.
3.1.2 Cu-centered structures

A comparison of the isomer structures with different stabilities under the components of Cu\textsubscript{3}Zr\textsubscript{9}Al\textsubscript{1}, Cu\textsubscript{4}Zr\textsubscript{8}Al\textsubscript{1}, Cu\textsubscript{5}Zr\textsubscript{7}Al\textsubscript{1}, Cu\textsubscript{6}Zr\textsubscript{6}Al\textsubscript{1}, Cu\textsubscript{7}Zr\textsubscript{5}Al\textsubscript{1} and Cu\textsubscript{8}Zr\textsubscript{4}Al\textsubscript{1} in Cu-centered ternary icosahedron structures revealed that the atoms of the same type tended to connect with each other (figure 6). All ternary isomer structures were obtained by replacing the Cu or Zr atom in the shell of Cu\textsubscript{3}Zr\textsubscript{10}, Cu\textsubscript{4}Zr\textsubscript{9}, Cu\textsubscript{5}Zr\textsubscript{8}, Cu\textsubscript{6}Zr\textsubscript{7}, Cu\textsubscript{7}Zr\textsubscript{6}, Cu\textsubscript{8}Zr\textsubscript{5} and Cu\textsubscript{9}Zr\textsubscript{4} binary icosahedral (the most stable structure of Cu-centered binary clusters icosahedral) with Al atom. The contents of the Cu–Zr bonds of both stable and unstable structures under different components were compared (figure 6(b)). The stable structures had a lesser content of the Cu–Zr bond than the unstable structures. This result combined with the energy difference described in figure 6(a) indicated that the difference in the content of the Cu–Zr bond between Cu\textsubscript{6}Zr\textsubscript{6}Al\textsubscript{1} and Cu\textsubscript{7}Zr\textsubscript{5}Al\textsubscript{1} was large. The trend of the corresponding energy difference was also the same, indicating that chemical order contributed to structural stability.

The relationship between the content of the Cu–Zr bond and the structural energy of both the stable and unstable structures of Cu\textsubscript{5}Zr\textsubscript{6}Al\textsubscript{2} and Cu\textsubscript{6}Zr\textsubscript{5}Al\textsubscript{2} centered on Cu atom was explored (figure 7). The ternary icosahedron with two Al atoms were obtained by replacing the Cu or Zr atom in the shell of Cu\textsubscript{5}Zr\textsubscript{7}Al\textsubscript{1}, Cu\textsubscript{6}Zr\textsubscript{6}Al\textsubscript{1} and Cu\textsubscript{7}Zr\textsubscript{5}Al\textsubscript{1} (the most stable structure of Cu-centered Cu\textsubscript{5}Zr\textsubscript{7}Al\textsubscript{1}, Cu\textsubscript{6}Zr\textsubscript{6}Al\textsubscript{1} and Cu\textsubscript{7}Zr\textsubscript{5}Al\textsubscript{1} icosahedral) with Al atom. When exploring Cu-centered icosahedron structures with two Al atoms, the description of phase separation varied depending on the presence or absence of Al–Al bonds in the structure. In figure 7, A and B represent the icosahedron structure with or without Al–Al bonds, respectively. Direct comparison of the structures of the isomers showed that, among the icosahedral structures of Cu\textsubscript{5}Zr\textsubscript{7}Al\textsubscript{1} and Cu\textsubscript{6}Zr\textsubscript{6}Al\textsubscript{1}, homogeneous atoms were observed to tend to connect with each other in the stable structures. A comparison of the trend of the content of the Cu–Zr bond in both the stable and unstable structures showed that...
the former had fewer Cu–Zr bonds than the latter. Moreover, this trend was observed in structures with or without Al–Al bonds. Thus, the stable structures centered on the Cu atom still had better chemical order.

3.2. Analysis of average bond length
The structural energy of all isomers was determined via energy calculations. The energies of the most stable structures centered on Cu and Al atoms under the same component with one Al atom were compared. Results showed that Al-centered structures were more stable (figure 8). The bond parameters of the most stable structures with two different central atoms were compared and analyzed (figure 9).
The contents of chemical bonds were compared (figure 9(a)). The contents of Al–Zr and Al–Cu bonds were higher in the Al-centered structures than in the Cu-centered structures. The strength of the interaction of the Al–Cu and Al–Zr bonds was further confirmed by comparing the average bond lengths of different chemical bonds (figure 9(b)). In the Cu–Cu, Cu–Zr, and Zr–Zr bonds, the average bond length of the Cu-centered structure was shorter than Al-centered structure with the same composition. In the Al-centered icosahedral structures, the average bond length of the Al–Cu and Al–Zr bonds shorting was more pronounced than that of the other chemical bonds.

The bond shortening ratio of the Al–Cu and Al–Zr bonds was calculated under different components (figure 10). An obvious ‘bond shortening’ phenomenon was observed in Al–Cu and Al–Zr when the actual bond length was compared with the theoretical bond length, which was calculated from the radius of Cu, Zr, and Al atoms. The apparent trend of bond length shortening means that atoms were more tightly connected. Results showed stronger interactions between Al-centered atom and Cu/Zr atoms, which were beneficial to the formation of a more stable cluster structure.

In the Al-centered structures, the Cu–Al and Zr–Al bonds had a large trend of bond shortening. The bond shortening ratio of the Cu–Al bond increased with the increase in the content of Cu atoms. The same phenomenon of bond shortening was observed in Cu-centered structures, but the degree of bond shortening was weakened. Thus, the connection between the Al atom and the Cu and Zr atoms was more stable in the Al-centered structures. Similar trends of chemical bond content and bond shortening were observed in Cu5Zr6Al2 and Cu6Zr5Al2 with two Al atoms (figure 11).

4. Discussion

In general, different central atoms have an obvious influence on the interaction between atoms in icosahedral structures. In this study, when Al atoms were used as central atoms, they were more closely connected to Cu atoms and Zr atoms, and the contents of the Al–Cu and Al–Zr bonds were also higher. Fernando Pignanelli et al...
predicted that more symmetrical local structures with a shorter Cu–Al distance in Cu–Zr–Al metallic glasses becomes more stable. These results explain the contribution of the introduction of Al atoms to the stability of the icosahedral structure relative to the Cu–Zr binary icosahedral structure. These phenomena contribute to our understanding of the effects of microalloying experimentally observed in many metallic glasses. The binding energy ($E_b$) has been used to evaluate the stability of the clusters. A lower binding energy represents a more stable structure, concerning icosahedron structure formation. The binding energy ($E_b$) per atom is expressed by the following relationship:

\[
E_b = \frac{[E(Cu_{x}Al_{y}Zr_{13-x-y}) - xE(Cu) - yE(Al) - (13 - x - y)E(Zr)]}{13}
\]  

(1)

Figure 7. (a) Relationship between the content of the Cu–Zr bond and the structural energy in two different isomers centered on Cu atom. A and B represent the icosahedron structure with or without Al–Al bonds, respectively. (b) Comparison of stable and unstable structures of Cu$_{5}$Zr$_{6}$Al$_{2}$ and Cu$_{6}$Zr$_{5}$Al$_{2}$ with (A) and without (B) Al–Al bonds centered on Cu atom. Orange, cyan, and pink atoms represent Cu, Zr, and Al atoms, respectively.

Figure 8. Comparison of structural energy centered on Cu and Al atoms in structures with the same chemical composition ($\Delta E = E_{\text{Cu-centered}} - E_{\text{Al-centered}}$).
where \( E(Cu, Al, Zr_{13-x-y}) \) is the total energy of the icosahedral clusters, and \( E(Cu) \), \( E(Al) \) and \( E(Zr) \) are the total energies of single gaseous \( Cu \), \( Al \) and \( Zr \) atoms, respectively. The partial results of the binding energy of the most stable icosahedral clusters are shown in table 1. All binding energies were less than 0 eV/atom. It means that these icosahedral clusters are thermodynamic stability, in principle, can be synthesized. The lower the binding energy is, the better is the stability. This result indicated that the \( E_b \) decreased with increasing \( Al \) atoms. In addition, evident \( E_b \) differences were observed in the \( Cu-Zr-Al \) icosahedral clusters with the same chemical composition, which was attributed to the change in the relative positions of \( Al \) atom. A previous study discovered the contribution of the introduction of \( Al \) atoms to the structural stability relative to the \( Cu-Zr \) binary icosahedral structure [22, 25, 50]. However, the relationship between the positions of \( Al \) atoms and their contribution to structural stability is unclear. Accordingly, the bond shortening ratio of the icosahedral structures containing two \( Al \) atoms and their initial structures were compared in this study (table 2).

Among these compositions, \( Cu_5Zr_7Al_1 \) was obtained by replacing the \( Zr \) atom and the \( Cu \) atom of \( Cu_5Zr_7Al_1 \) and \( Cu_6Zr_6Al_1 \), respectively. The corresponding initial components of \( Cu_5Zr_7Al_1 \) were \( Cu_6Zr_6Al_1 \) and...
Figure 11. (a) Comparison of the chemical bond contents of the most stable structures with different central atoms in Cu$_5$Zr$_6$Al$_2$ and Cu$_6$Zr$_5$Al$_2$. (b) Comparison of bond lengths of the most stable chemical structure with different central atoms in Cu$_5$Zr$_6$Al$_2$ and Cu$_6$Zr$_5$Al$_2$. (c) Bond shortening in the most stable structures with different central atoms in Cu$_5$Zr$_6$Al$_2$ and Cu$_6$Zr$_5$Al$_2$.

Table 1. The binding energy ($E_b$) per atom of the icosahedral clusters. A and B represent the icosahedron structure with or without Al–Al bonds, respectively.

| Composition | Central atom | $E_b$ (eV/atom) |
|-------------|--------------|-----------------|
| Cu$_5$Zr$_6$ | Cu           | −3.8750         |
| Cu$_6$Zr$_6$Al$_1$ | Cu     | −3.9406         |
| Cu$_5$Zr$_6$Al$_1$ | Al     | −3.9780         |
| Cu$_5$Zr$_6$Al$_2$ | Al     | −4.0360         |
| Cu$_5$Zr$_6$Al$_2$-A | Cu     | −3.9980         |
| Cu$_5$Zr$_6$Al$_2$-B | Cu     | −3.9865         |

Table 2. Comparison of the bond shortening ratio of Al–Cu and Al–Zr bonds in the most stable structures centered on Al atom under five different components.

| Composition | Ratio of bond shorting of Cu–Al (%) (without/with shell Al atom bonds) | Ratio of bond shorting of Zr–Al (%) (without/with shell Al atom bonds) |
|-------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Cu$_5$Zr$_7$Al$_1$ | 7.646/10.113                                                              | 10.113                                                                   |
| Cu$_6$Zr$_6$Al$_1$ | 9.444                                                                     | 8.148                                                                    |
| Cu$_5$Zr$_6$Al$_1$ | 9.828                                                                     | 8.427                                                                    |
| Cu$_5$Zr$_6$Al$_2$ | 9.075/7.303                                                               | 9.043/7.334                                                              |
| Cu$_5$Zr$_6$Al$_2$ | 9.845/8.497                                                               | 8.619/6.467                                                              |
Cu$_7$Zr$_5$Al$_1$. The bond shortening degree of the icosahedral structure containing two Al atoms was similar to the initial structure when only the bonding of central Al atoms was considered. However, when the bonding of Al atoms in the shell was considered, the degree of bond shortening was considerably reduced, indicating that the bonding ability between the Al atoms and the Cu and Zr atoms in the shell were weaker than that of the central Al atoms.

To quantify symmetry on the cluster stability at the atomic level, we introduce the average atomic local shear strain $\bar{\gamma}$ for each atom $i$. Calculation of the atomic local shear strain $\eta^i_{\text{Mises}}$ requires two atomic configurations, one current, and one reference. The ideal icosahedron was taken as the reference atom configuration. We can then compute atom $i$’s local shear invariant as [51]:

$$\eta^i_{\text{Mises}} = \sqrt{\eta^i_{xx} + \eta^i_{yy} + \eta^i_{zz} + (\eta^i_{xy} - \eta^i_{yz})^2 + (\eta^i_{xz} - \eta^i_{yx})^2 + (\eta^i_{yz} - \eta^i_{xy})^2}$$

(2) The average atomic local shear strain was as follows:

$$\bar{\gamma} = \frac{\sum_{i=1}^{13} \eta^i_{\text{Mises}}}{13}$$

(3) $\eta^i_{\text{Mises}}$ is a good measure of local inelastic deformation. The average atomic local shear strain $\bar{\gamma}$ of Cu$_7$Zr$_5$Al$_1$A and Cu$_7$Zr$_5$Al$_1$B is 0.780 and 0.808, respectively. The smaller $\bar{\gamma}$ value is, the more symmetry the icosahedral will be. The structure Cu$_7$Zr$_5$Al$_1$A with a better symmetry and less distortion was more stable. The average atomic local shear strain $\bar{\gamma}$ of the low energy and high energy structures centered on Al atom under the same component were compared in table 3. The first and fourth configurations with the same composition in figures 3 and 5 were used to calculate the average atomic local shear strain. Results showed that stable structures were more symmetry.

A previous study proved that the contribution of Al atoms to the stability of icosahedral structures is mainly due to the strong interaction between Cu–Al and Zr–Al atoms. The electronic densities of states (DOSs) were investigated to establish a correlation between Al alloying and the origin of GFA. The total density of states (TDOSs) and partial density of states (PDOSs) near the Fermi level ($E_F$) of Cu-centered Cu$_7$Zr$_5$Al$_1$, Al-centered Cu$_7$Zr$_5$Al$_1$, Cu-centered Cu$_7$Zr$_5$Al$_1$, and Al-centered Cu$_7$Zr$_5$Al$_1$ are shown in figure 12. The electronic contribution of the cluster at the $E_F$ mainly resulted from the Zr-shell atoms mainly due to the larger number of $d$-valence electrons in Zr atoms. The left part of the TDOS (below $E_F$) is mainly contributed to the Cu-shell $d$-electrons and Zr-shell $d$-electrons, while the right part mainly comes from the Zr-shell atoms, especially Zr-shell $p$-electrons and $d$-electrons. The substitution of the Cu-shell atom by Al results in modification of the energy states, primarily those located below $−5$ eV and $E_F$. By comparing the DOS plots of the Al-centered Cu$_7$Zr$_5$Al$_2$ and Al-centered Cu$_7$Zr$_5$Al$_1$ (or Cu-centered Cu$_7$Zr$_5$Al$_6$ and Cu-centered Cu$_7$Zr$_5$Al$_1$) icosahedral, the energy range below the $E_F$ of DOS of Al-centered Cu$_7$Zr$_5$Al$_2$ (or Cu-centered Cu$_7$Zr$_5$Al$_1$) is widened. These results reveal that the main effect of shell Al atom is to spread the range of the DOSs. The energy range of Cu–Zr–Al icosahedral clusters are lower than Cu$_7$Zr$_5$ icosahedral cluster. The lowest energy state is now near at $−6$ eV and is due to the Al-shell atoms, which forms strong $s$-bonds with Cu atoms. The electronic stability of icosahedral clusters was determined by their electronic states at the $E_F$. The $E_F$ of Cu-centered Cu$_7$Zr$_5$Al$_1$ is at the peak of DOSs, then this icosahedral cluster had an insufficient number of available bonding electrons. The structure was in an unstable state and had a clear tendency to transform into another state to minimize their energy. However, the DOSs at the $E_F$ of Cu-centered Cu$_7$Zr$_5$Al$_1$ and Al-centered Cu$_7$Zr$_5$Al$_1$ icosahedral clusters were near a trough. It is also worth noting that there are minor differences between the stages around $E_F$ of Cu-centered Cu$_7$Zr$_5$Al$_1$ and Al-centered Cu$_7$Zr$_5$Al$_1$ icosahedral clusters. Thus, these two icosahedral clusters were in a relatively stable state. Therefore, a small amount of Al alloying played a fundamental role in obtaining a good GFA for the alloy [31]. Findings of Lekka et al are in keeping with the results in figure 12 (b). Lekka et al [35] pointed out that the substitution of the Cu–Zr binary icosahedral structure central atom by Al results in modification of the energy state due to Al core–Cu shell $sd$ and $pd$ hybridization. These Al bonds have covalent character, which explains the observed increase in glass-forming ability of these ternary alloys. Moreover, this interaction is more obvious when Al atoms are used as the central atoms. Given that the icosahedron has only one central atom, the addition

| Composition   | Low energy structure | High energy structure |
|---------------|----------------------|-----------------------|
| Cu$_7$Zr$_5$Al$_1$ | 0.890                | 1.009                 |
| Cu$_7$Zr$_5$Al$_2$ | 0.787                | 0.828                 |
| Cu$_7$Zr$_5$Al$_1$ | 0.902                | 0.908                 |
of just a central Al atom can notably improve the stability of the structure. However, further addition of Al atoms did not considerably enhance the interaction between Al–Cu and Al–Zr atoms. Therefore, only just a small amount of Al doping can remarkably enhance the formation ability of icosahedron and GFA. At this point, the substitution of a cluster’s atom by Al corresponds to an Al content of the order of 7.7%, a concentration that is within the range reported by previous experiments [32, 37, 52].

5. Conclusion

In summary, the structural rules in Cu–Zr–Al ternary metallic glasses were determined. The stability of icosahedral structures was determined by topological order and chemical order. In the Cu–Zr–Al ternary system with one Al atom, the Al-centered icosahedron was more stable than the Cu-centered icosahedron. The average bond lengths of the Al–Cu and Al–Zr bonds were considerably shorter than the theoretical value, indicating the strong connectivity between the Al atom and the Cu and Zr atoms. The bond shortening degree of the Al–Cu and Al–Zr bonds was similar, indicating that the connection ability between the Al atom and the Cu and Zr atoms was similar.

The contribution of the Al atom to structural stability was greater when it was used as the central atom. Therefore, adding only a small amount of Al can remarkably improve the stability of the icosahedral structures of the Cu–Zr–Al ternary system, thereby promoting the formation of icosahedral structures and improving GFA. However, further addition of Al atoms had a lower effect on structural stability.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Author contributions

Wenfei Lu: Investigation, Simulation, Writing—original draft.
Zhilue Wang: Investigation, Simulation, Writing—original draft.
Hongping Xiang: Formal analysis, Software, Methodology, Reviewing and Editing, Supervision.
Aihan Feng: Reviewing and Editing, Supervision.
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