Frank-Kasper Z16 local structures in Cu-Zr metallic glasses

Anh Khoa Augustin Lu ^{*}

MathAM-OIL, AIST, 980–8577 Sendai, Japan

Kengo Nishio [†]

*CD-FMat, AIST, 305–8568 Tsukuba, Japan
and MathAM-OIL, AIST, 980–8577 Sendai, Japan*

Tetsuya Morishita

*CD-FMat, AIST, 305–8568 Tsukuba, Japan
and MathAM-OIL, AIST, 980–8577 Sendai, Japan*

Koji Ohara

SPRING-8, JASRI, Hyogo 679-5198, Japan

Zhen Lu

MathAM-OIL, AIST, 980–8577 Sendai, Japan

Akihiko Hirata

*Waseda University, 169–8555 Tokyo, Japan
and MathAM-OIL, AIST, 980–8577 Sendai, Japan*

(Received 10 June 2020; accepted 27 October 2020; published 30 November 2020)

Although previous molecular dynamics studies proposed the existence of Zr-centered Frank-Kasper Z16 structures in Cu-Zr metallic glasses, it cannot be concluded yet, owing to the degeneracy problem of the Voronoi index and the artifact in sets of potentials for Cu-Zr systems. We solve both problems by combining a recently developed Finnis-Sinclair potentials to generate realistic atomic structures and the p_3 code to properly differentiate local structures. In previous studies, the Voronoi index $\langle 0, 0, 12, 4 \rangle$ was typically associated with Frank-Kasper Z16 local structures. However, we demonstrate that this index includes two types of polyhedra, only one of which is associated with the Frank-Kasper Z16 structures. We reveal that the Z16 structures are more frequent than the other structures and that the two have different behaviors. The tendency of Zr-centered Z16 local structures to be neighbors of Cu-centered icosahedral local structures is also confirmed. Our findings illustrate the importance of properly differentiating local structures in order to elucidate the behavior of metallic glasses at the atomic scale.

DOI: [10.1103/PhysRevB.102.184201](https://doi.org/10.1103/PhysRevB.102.184201)

I. INTRODUCTION

Glasses are ubiquitous materials that have been present for millennia in human history. They have disordered atomic structures like liquids but behave mechanically like solids [1,2]. In the last decades, metallic glasses have become one of the major subjects of interest in the materials science community because of their unique mechanical properties,

which enable a wide range of potential applications [3]. Since the first experimental realization of $\text{Au}_{75}\text{Si}_{25}$ metallic glass in 1960 by Klement *et al.* [4], a broad range of bulk metallic glasses have been experimentally demonstrated. For example, CuZr-based binary or ternary alloys ($\text{Cu}_{64}\text{Zr}_{36}$ [5,6], $\text{Cu}_{45}\text{Zr}_{45}\text{Ag}_{10}$ [7]), Ti-based, transition metal-based, and rare earth based metallic glasses have a wide range of adjustable glass-forming ability (GFA). While a large number of metallic glasses has been demonstrated, the relationship between their atomic structure and their GFA remains unclear.

Over the last decades, the atomic structure of metallic glasses has been intensively studied by using various theoretical methods [8–13] and experimental techniques [14,15], with a particular focus on their local structures. Molecular dynamics studies of Cu-Zr metallic glasses have revealed the predominance of Cu-centered local icosahedral structures and underlined the possible role of the local icosahedral structures

^{*}augustin.lu@aist.go.jp; augustinlu@gmail.com

[†]k-nishio@aist.go.jp

FIG. 1. Visual representations of (a) $@5^3(65)^35^66$ (Z16) and (b) $@5^5(656)^25^5$ (O16), the two types of local structures associated with the Voronoi index $\langle 0, 0, 12, 4 \rangle$. Cu and Zr atoms are colored in red and green, respectively. Schlegel projections of the corresponding Voronoi polyhedra are shown on the right side. The polygons are colored according to the number of edges (pentagons in cyan and hexagons in yellow).

on the increase in viscosity observed in supercooled Cu-Zr metallic liquid in the glass transition regime [10]. To study the structure of metallic glasses beyond the short-range order, the so-called *medium-range order* (MRO), the spatial distribution of icosahedral local structures has been studied, as well as the way they are connected to each other [16,17]. It has been suggested that networks of interpenetrating icosahedral local structures have a significant impact on their mechanical properties [18,19].

A molecular dynamics study of $\text{Cu}_{64}\text{Zr}_{36}$ using embedded-atom model (EAM) potentials has shown that the population

of both Cu-centered local structures with Voronoi index $\langle 0, 0, 12, 0 \rangle$ and Zr-centered local structures with Voronoi index $\langle 0, 0, 12, 4 \rangle$ increase when the system is annealed for a long time at 800 K [20]. As the Voronoi index $\langle 0, 0, 12, 4 \rangle$ is typically been associated with the Frank-Kasper Z16 structure, the correlation between Cu-centered icosahedral and Zr-centered Frank-Kasper Z16 local structures has been proposed. The same authors have also shown that Cu-centered $\langle 0, 0, 12, 0 \rangle$ local structures tend to be neighbors of Zr-centered $\langle 0, 0, 12, 4 \rangle$ local structures. A later study by Zemp *et al.* suggested that Cu_2Zr Laves phase combining icosahedra

(a) Local rearrangement

FIG. 2. Schlegel diagrams representing one possible transformation from Z16 to O16 by two local rearrangements. Quadrilaterals, pentagons, and hexagons are colored in green, cyan, and yellow, respectively. (a) Schematic representation of a local rearrangement in a local structure. Circles represent the atoms. Red solid lines represent edges of the Voronoi polyhedron. (b) Z16 polyhedron and edges selected (colored in red), (c) first rearrangement, (d) edges selected (colored in blue) for second rearrangement, (e) O16 polyhedron.

FIG. 3. Classification of the Zr-centered local structures by frequency of occurrence in $\text{Cu}_{65}\text{Zr}_{35}$, obtained with a cooling rate of 10^9 K/s: (a) the 15 most frequent Voronoi indices and (b) the 15 most frequent $@p_3$ local structures. The Voronoi index corresponding to each $@p_3$ codeword is indicated on the right of each bar. The bars for local structures corresponding to Voronoi index $\langle 0, 0, 12, 4 \rangle$ are colored in red.

and Z16 Frank-Kasper polyhedra could lead to an increase in strength and Young's modulus, and a stronger localized shear band [21]. However, it was not possible to state a conclusion about Z16 itself, owing to two fundamental problems, one mathematical and one physical.

The first problem is the degeneracy of the Voronoi index [22]. Although it is known that $\langle 0, 0, 12, 0 \rangle$ properly indicates the icosahedral local structures, there is a possibility that local structures different from the Z16 ones contribute to the frequency of occurrence of the Voronoi index $\langle 0, 0, 12, 4 \rangle$. Indeed, previous works have shown that several Voronoi indices include more than one type of local structures (for examples: $\langle 0, 2, 8, 2 \rangle$ [23] or $\langle 0, 3, 6, 4 \rangle$ [24]). The second problem is an artifact of some sets of EAM and Finnis-Sinclair (FS) potentials. Indeed, recent studies have shown that some of the most popular sets of potentials overestimate the stability of Laves phases, in which Cu-centered icosahedral local structures are adjacent to Zr-centered Z16 structures [21,25,26]. As a result, crystallization into Laves phases was observed in molecular dynamics simulations using these empirical potentials, even

though such structures are not observed experimentally in Cu-Zr systems at room temperature [27]. Therefore, there is a possibility that the positive correlation between icosahedral and Z16 local structures is only an artifact of the empirical potentials in use. To assess the existence of Z16 local structures and the correlation between icosahedral and Z16 local structures in Cu-Zr metallic glasses, a reliable potential as well as a method to properly describe local structures are necessary. Therefore, in this work we will answer the following two questions: Do Frank-Kasper Z16 structures really exist in Cu-Zr metallic glasses? Is the relationship between Cu-centered

FIG. 4. Schlegel diagrams of (a) the Z16 and (b) the first-ranked Zr-centered local structures. Quadrilaterals, pentagons, and hexagons are colored in green, cyan, and yellow, respectively. The local structures can be obtained from each other by a local rearrangement of the atoms, symbolized by the red edges.

TABLE I. First-neighbor correlation index with icosahedral local structures in $\text{Cu}_{50}\text{Zr}_{50}$ at 300 K.

Local structure	MD model	RMC model
Icosahedral	0.79	0.87
@456 ³ 5 ⁷ 65 ² (0, 1, 10, 4)	0.35	0.44
Z16	0.91	1.01
O16	0.39	0.37

FIG. 5. Classification of the Cu-centered local structures (referred by their @ p_3 codewords) in $\text{Cu}_{65}\text{Zr}_{35}$. The sample was obtained with a cooling rate of 10^9 K/s. For comparison purpose, the fraction of corresponding Voronoi indices are shown in pink. The ranks of each local structure (blue) and each Voronoi index (pink) are written between brackets on the left of the corresponding labels.

icosahedral local structures and Z16 local structures merely an artifact?

In this work, we aim at solving both problems by using the recently developed FS potentials based on EAM potentials for Cu and Zr by Mendelev *et al.* [28] to generate reasonable atomic structures and using the p_3 code to study the local structures [29,30]. In our simulations, no crystallization was observed even when the liquid $\text{Cu}_{65}\text{Zr}_{35}$ was cooled at a very slow (in terms of simulations) cooling rate $Q = 10^9$ K/s. In our $\text{Cu}_{65}\text{Zr}_{35}$ models, we demonstrate that the Voronoi index $\langle 0, 0, 12, 4 \rangle$ includes two types of polyhedra, one of which is the Z16 Frank-Kasper polyhedron [31]. For convenience, the other structure is denoted by O16. Z16 has a positive

FIG. 6. First-neighbor correlation matrix for the five most frequent Cu-centered and five most frequent Zr-centered local structures in $\text{Cu}_{65}\text{Zr}_{35}$, obtained with a cooling rate of 10^9 K/s. The matrix is represented as a heat map from blue (negative correlation) to red (positive correlation).

FIG. 7. Visual representation of a medium-range order cluster made of an icosahedral (left) and a Frank-Kasper Z16 (right) local structures sharing a common face. Central atoms are colored in red, shared atoms are colored in teal and other first neighbors are colored in gray. The Voronoi polyhedra are delimited by solid blue lines.

correlation (i.e., tend to be neighbor) with icosahedral local structures in $\text{Cu}_{65}\text{Zr}_{35}$, which is higher than that of O16. This demonstrates the importance of properly differentiating each type of local structure. Our results suggest that medium-range structures combining icosahedral and Z16 structures are formed during the glass formation. We further show that the positive correlation holds in the whole range of cooling rates (10^9 – 10^{13} K/s) and atomic compositions ($0.3 < x < 0.8$) studied in the present work. These results are supported by RMC calculations based on an experimental sample of $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass, where the positive correlation between icosahedral and Z16 local structures is also observed.

II. METHODOLOGY

In order to carefully describe the short- and medium-range order in Cu-Zr metallic glasses, we used the following methodology. Firstly, since we are focusing on the Frank-Kasper Z16 structures, we used a new set of FS potentials that

FIG. 8. Evolution of the fraction of Zr-centered local structures with the Voronoi index $\langle 0, 0, 12, 4 \rangle$ in $\text{Cu}_{65}\text{Zr}_{35}$ with respect to the cooling rate.

FIG. 9. Evolution of the correlation index between Cu-centered icosahedral local structures with Z16, O16 and most frequent Zr-centered local structures in $\text{Cu}_{65}\text{Zr}_{35}$ with respect to the cooling rate.

solves the problem of overstabilization of Laves phases, which combine icosahedral and Z16 local structures in a periodic structure. Secondly, we used the p_3 code to classify the local structures in the atomic structures generated by molecular dynamics simulations. Thirdly, we calculated first-neighbor correlation indices in order to determine how some types of local structures favor (or not) other ones in their vicinity. Finally, molecular dynamics results are compared with experimental x-ray diffraction measurements using reverse Monte Carlo (RMC).

A. Molecular dynamics

Molecular dynamics simulations were performed using the LAMMPS software with GPU acceleration [32–34]. To reproduce the inter-atomic interactions in Cu-Zr systems, FS potentials [35–37] were used. Recent works highlighted artificial crystallization into Laves phases near the $\text{Cu}_{64}\text{Zr}_{36}$ atomic composition as a result of overstabilization of Laves phases when using some of the most popular potentials for Cu-Zr [21,25,26]. Thus, in this study, we used a new set

FIG. 10. Example of a network of interpenetrating icosahedral and Z16 local structures found in $\text{Cu}_{65}\text{Zr}_{35}$. Small (resp. large) spheres represent Cu (resp. Zr) atoms. Red and blue color show centers of icosahedral and Z16 local structures, respectively. Pale red and pale blue depict the first neighbors of the central atoms.

of FS potentials recently developed by Mendelev *et al.* to address the overstabilization problem [28]. Starting from an initial crystalline configuration, the temperature was increased from 300 K to 2500 K. The resulting liquid was cooled to 300 K with a constant cooling rate Q between 10^9 K/s and 10^{13} K/s. Simulations were performed with periodic boundary conditions. The time step was set to 2 fs. The pressure and temperature were controlled throughout the calculation (NPT ensemble) using Nose-Hoover style non-Hamiltonian equations of motions [38,39]. All calculations were performed under zero-pressure condition. Models of glasses with different atomic compositions (i.e., $\text{Cu}_{30}\text{Zr}_{70}$, $\text{Cu}_{35}\text{Zr}_{65}$, ..., $\text{Cu}_{80}\text{Zr}_{20}$) were generated. Each sample contained 50 000 atoms.

B. p_3 analysis

To study the local structures, Voronoi tessellation was performed, where the atomic structure was divided in a set of polyhedra, each one containing exactly one atom. Since Cu and Zr have different atomic radii (1.26 Å and 1.58 Å, respectively [2]), the radical plane was used to define the polyhedra [40]. The traditional way of characterizing the polyhedra is to attribute to each atom k a so-called *Voronoi index* $\bar{v}_k = \langle n_3, n_4, n_5, \dots \rangle$, where n_3 is the number of triangles, n_4 is the number of quadrilaterals, n_5 is the number of pentagons, etc.

Although this method successfully isolated particular types of local structures such as the icosahedral ones corresponding to the Voronoi index $\langle 0, 0, 12, 0 \rangle$, it has serious shortcomings. In fact, how the different polygons of each polyhedron are arranged is ignored. As a result, in many cases, different types of polyhedra share the same Voronoi index [22,24]. The degeneracy problem has been addressed by using the recently developed p_3 code [23,29,30].

In this method, each Voronoi polyhedron is described by a unique codeword p_3 . The local structure composed of the atom in a Voronoi polyhedron and its nearest neighbors is described by $@p_3$. For instance, @555555555555, which contains twelve “5” ($\equiv$ pentagons), describes the icosahedral local structure, which is also the only structure associated with the Voronoi index $\langle 0, 0, 12, 0 \rangle$. @555656565555556, which contains twelve “5” ($\equiv$ pentagonal faces) and four “6” ($\equiv$ hexagonal faces) for a total of 16 faces, describes the Z16 Frank-Kasper structure [31,41]. The associated Voronoi index is $\langle 0, 0, 12, 4 \rangle$. However, another type of local structure, @5555565656555555 (hereafter referred to as O16), is also associated with this Voronoi index. But, as illustrated by Fig. 1, the arrangement of its faces is different. Indeed, in the Z16 structure, the four hexagonal faces are separated from each other by pentagonal faces while in the O16 structure, there are two pairs of contiguous hexagonal faces. One can obtain an O16 structure by performing two local rearrangements of a Z16 structure, as shown in Fig. 2. Therefore, it is important to properly differentiate the local structures, and this is why we used the p_3 code to analyze them in this work.

To shorten the codewords and improve their readability, superscripts were used to express the number of occurrences of consecutive identical digits (or series of digits). For example, @555555555555 was rewritten as $@5^{12}$, which reads *At, five, twelve times*, and @555656565555556 was rewritten as

(a) Zr-centered local structures

(b) Cu-centered local structures

FIG. 11. Distribution of the dominant (a) Zr-centered and (b) Cu-centered local structures in $\text{Cu}_x\text{Zr}_{1-x}$ samples, with respect to the Cu fraction x . The samples were obtained with a cooling rate of 10^9 K/s.

FIG. 12. Evolution of the correlation indices in samples obtained with a cooling rate of $Q = 10^9$ K/s.

@ $5^3(65)^35^66$, which reads *At five, three times; six five, three times; five, six times; six*. Similarly, @5555565665655555 was rewritten as @ $5^5(656)^25^5$.

This method has proven successful in demonstrating that entropy-driven docosahedral local structures are dominant in simple liquids and glasses by properly differentiating their local structures [24]. Furthermore, it has been successfully applied in a recent study which revealed the reason why body-centered-cubic (BCC) metals tend to have a better GFA than face-centered-cubic (FCC) ones [42].

C. Nearest-neighbor correlation matrix

Since they have a high fraction, icosahedral local structures are expected to play an important role in the glass transition of Cu-Zr liquids. However, little is known about the arrangement of local structures with respect to each other, i.e., beyond the short-range order. In order to better understand how the short-range order evolves towards a medium-range order, one has to understand whether one type of polyhedron is favored or unfavored in the vicinity of another one, or in other words, how different local structures tend to be interpenetrating each other. In that respect, we calculated the

FIG. 13. Relation between the frequencies of occurrences of icosahedral and Z16 local structures in $\text{Cu}_x\text{Zr}_{1-x}$ samples.

FIG. 14. Structure factor of $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass at 300 K for the experimental sample, compared with MD and RMC models.

FIG. 15. The five Zr-centered local structures with the highest fraction for $\text{Cu}_{50}\text{Zr}_{50}$. For each local structure, the fraction of the corresponding Voronoi index is also shown in red.

nearest-neighbor correlation matrix between pairs of $@p_3s$, which is a generalization of the method introduced by Li *et al.* [43]. The nearest-neighbor correlation between each pair of types of local structures was calculated as follows.

Let V_i be the Voronoi polyhedron of the atom i , C_i be the local structure composed of the atom i and its neighbors. When V_i and V_j share a common face, the atoms i and j are bonded. In other words, the associated local structures C_i and C_j are interpenetrating. Let B_{total} be the total number of bonds in the system. b_{XY} is the number of bonds linking the central atom of a local structure of type X and the central atom of a local structure of type Y . For example, $b_{@5^{12}@5^3(65)^3 5^6}$ is the number of bonds connecting the center of an icosahedral ($X = @5^{12}$) local structure and that of a Z16 local structure [$Y = @5^3(65)^3 5^6$]. The probability p_{XY} to find a pair XY (i.e., a bond connecting a local structure of type X to a local structure of type Y) is given by Eq. (1).

$$p_{XY} = \frac{b_{XY}}{B_{\text{total}}} \quad (1)$$

Let n_X (resp. n_Y) be the number of X (resp. Y) local structures in the system and N the total number of atoms in the system. If local structures X and Y were uncorrelated, the probability p_{XY} would be given by Eq. (2).

$$p_{XY}^0 = \frac{n_X(n_Y - 1)}{N(N - 1)} (X = Y)$$

$$p_{XY}^0 = \frac{2n_X n_Y}{N(N - 1)} (X \neq Y) \quad (2)$$

Finally, the nearest-neighbor correlation index C_{XY} is defined in Eq. (3).

$$C_{XY} = \frac{p_{XY}}{p_{XY}^0} - 1 \quad (3)$$

The C_{XY} reveal the following properties.

(i) If the system is *completely uncorrelated*, then $p_{XY} = p_{XY}^0$ and $C_{XY} = 0$.

(ii) If the local structure Y is *favoured* in the vicinity of the local structure X , then $p_{XY} > p_{XY}^0$ and $C_{XY} > 0$.

(iii) If the local structure Y is *unfavoured* in the vicinity of the local structure X , then $p_{XY} < p_{XY}^0$ and $C_{XY} < 0$.

The correlation index C_{XY} thus indicates how likely two types of local structures X and Y interpenetrate each other, in

other words, the central atom of local structure X is one of the atoms of local structure Y and vice versa. This matrix is helpful in developing the understanding of the medium-range order.

D. Experimental characterization

A metallic ingot with a nominal composition of $\text{Cu}_{50}\text{Zr}_{50}$ was prepared by arc melting from commercial pure metallic elements. A $\text{Cu}_{50}\text{Zr}_{50}$ metallic glass ribbon with a thickness of 50 μm was prepared by melt-spinning method using a Cu wheel at a tangential velocity of around 25 m/s in vacuum. High-energy x-ray diffraction measurements (HEXRD) were performed on the $\text{Cu}_{50}\text{Zr}_{50}$ ribbon sample at room temperature by using the BL04B2 beamline of SPring-8 [44]. The detector of the first generation was an intrinsic germanium (Ge) and that of the second generation is a triple-cadmium telluride (CdTe) detector. The incident x-ray energy was 61 keV, as obtained from a Si(220) crystal monochromator. Diffraction patterns of the samples, placed in a silica glass tube, were measured in a transmission geometry. The collected data was corrected by using a standard program. The error bars on the experimental structure factor $S(q)$ are less than 1% in the low-angle region with strong scattering intensity and about 3% in the high-angle region due to the weak scattering.

E. Reverse Monte Carlo

To reproduce the experimental structure factor $S(q)$, we modified the MD structures by using the reverse Monte Carlo (RMC) program (RMCA code) [45]. Note that the MD-RMC simulation presented in the present work is totally different from the normal RMC simulation. First, we input the MD structure model (Mendelev FS potential [28] and cooling rate of 10^9 K/s) as an initial configuration for RMC. We then moved atoms with a maximum movement of 0.01 $\text{\AA}$ to fit the experimental structure factor. The minimum bond length, which keeps the separation of atoms, was set to avoid producing unrealistic atomic configurations. Finally, the atomic configuration, whose structure factor is consistent with the experimental structure factor, was obtained after more than 7 000 000 atomic movements. The mean square displacement during RMC is 0.020 $\text{\AA}^2$. The distribution of atomic dis-

placements is also shown in Appendix B. Thus, the final model was produced by modifying the MD model with small atomic displacements using the RMC program, not by the pure RMC. While the obtained atomic models are strictly speaking MD+RMC models, they will be simply referred to as RMC models for simplicity.

III. RESULTS AND DISCUSSION

A. $\text{Cu}_{65}\text{Zr}_{35}$

$\text{Cu}_{65}\text{Zr}_{35}$ metallic glass atomic configurations are generated with cooling rates between 10^9 K/s and 10^{13} K/s. We verified that no crystallization occurred in any of the samples. Firstly, the radial distribution profiles show little change with respect to the cooling rate. Secondly, by verifying the distribution of local structures associated with Cu_2Zr , Cu_8Zr_3 , $\text{Cu}_{51}\text{Zr}_{14}$, and $\text{Cu}_{10}\text{Zr}_7$ crystals (details can be found in the Appendix), we confirmed that no crystallization occurred. This contrasts with previous studies in which crystallization into Laves phases was observed due to an artifact of the sets of EAM potentials used [26].

First focusing on Zr-centered Z16 local structures, we point out that the Voronoi index $\langle 0, 0, 12, 4 \rangle$ ranks sixth among Zr-centered polyhedra [5.1%, Fig. 3(a)]. As shown in Fig. 1, this Voronoi index includes two types of local structures, Z16 and O16. Our study based on the p_3 code reveals that these Z16 and O16 local structures are ranked fourth (3.8%) and 13th (1.2%), respectively. Therefore, considering Z16 and Voronoi index $\langle 0, 0, 12, 4 \rangle$ as being the same leads to overestimating the fraction of Z16 (5.3% instead of 3.8%) while underestimating its rank (sixth instead of fourth) thus, leading to an inaccurate description.

The most frequent Zr-centered local structure is $@456^3565^86$, one of the local structures corresponding to Voronoi index $\langle 0, 1, 10, 5 \rangle$, in agreement with previous studies based on Voronoi indices [25,46]. Note that the fraction of Zr atoms that are centers of polyhedra having the Voronoi index $\langle 0, 1, 10, 5 \rangle$ (13.2%) is different from the fraction of Zr atoms that are centers of $@456^3565^86$ local structures (12.2%). Indeed, we found that five types of local structures share the Voronoi index $\langle 0, 1, 10, 5 \rangle$, namely $@456^3565^86$ (12.2%, first), $@456^35^2(65^3)^25$ (0.5%, 31st), $@45(56^2)^25^265^5$ (0.4%, 36th), $@4(56)^55^5$ (0.1%, 98th), and $@45^36^55^7$ (less than 0.1%, outside top 100). We focus on $@456^3565^86$ since it is overwhelmingly dominant among local structures with Voronoi index $\langle 0, 1, 10, 5 \rangle$. A $@456^3565^86$ local structure can be obtained by a local atomic rearrangement of the atoms of the Z16 structure, as illustrated in Fig. 4. We note that $@456^3565^86$ local structures are absent from the crystal phases of Cu-Zr systems near $\text{Cu}_{65}\text{Zr}_{35}$ (see Appendix, Table II). In fact, most of the Voronoi indices regroup more than one type of local structures. For example, the second-ranked Voronoi index $\langle 0, 2, 8, 6 \rangle$ [8.1%, Fig. 3(a)] includes 17 types of local structures, including sixth-ranked $@456^3565^26465^4$ (2.6%) and seventh-ranked $@456^3565^56465$ (2.4%), as shown in Fig. 3(b).

The three most common Zr-centered local structures are present in none of the Cu-Zr crystal phases (detailed distributions in the Appendix). We note that among the other Zr-centered local structures presented in Fig. 3(a), Z16

(fourth) are present in Cu_2Zr Laves phases, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$, $@456^3565^56465$ (seventh) are found in $\text{Cu}_{10}\text{Zr}_7$ and $@5^4(665)^25^66$ (11th) are found in Cu_8Zr_3 . O16 structures do not correspond to any of the crystal structures studied. Our findings suggest that $\text{Cu}_{65}\text{Zr}_{35}$ glasses share several local structures with Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$, but little with $\text{Cu}_{10}\text{Zr}_7$. A similar trend is also found in Cu-centered local structures as described below.

For Cu atoms, the most frequent type of local structure observed in our simulations is the icosahedral local structure $@5^{12}$ (27.4%, Fig. 5), in good agreement with previous studies [10,46]. They are present in Cu_2Zr Laves phases, Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$. The second one is $@45^26^25^445^2$ (12.7%), one of the two local structures having the Voronoi index $\langle 0, 2, 8, 2 \rangle$, the other one being $@45^3(655)^254$ (1.7%, ranked ninth). Note that $@45^26^25^445^2$ local structures are found in Cu_8Zr_3 . The local structures associated with $\langle 0, 2, 8, 2 \rangle$ are often called *distorted icosahedra*. However, this is not reasonable. By etymology, the icosahedron is a polyhedron with twenty faces. Since the local structures associated with $\langle 0, 2, 8, 2 \rangle$ have twenty faces, they are icosahedra but not distorted icosahedra. However, the arrangements of the faces of the icosahedral $@45^26^25^445^2$ and $@45^3(655)^254$ are different from that of the icosahedral $@5^{12}$. Regular icosahedral local structures belong to $@5^{12}$. Hereafter, by the term *icosahedral local structure*, we mean $@5^{12}$. The third most frequent local structure is the dicosahedral structure $@4(56)^25^8$ (10.5%), the most frequent in simple glasses [42], which is found in Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$. Also, we note that the fourth-ranked local structure ($@45^365^445$) is found in Cu_8Zr_3 and the sixth-ranked local structure ($@45^26^2565^24645$) is found in $\text{Cu}_{51}\text{Zr}_{14}$.

So far, icosahedra are believed to be linked to the high GFA of Cu-Zr metallic glasses in the Cu-rich composition [47–49]. However, in recent years, there have been studies questioning the importance of icosahedra in defining the GFA [21,25]. Nevertheless, their conclusion suffers from the artificial crystallization into Laves phase due to the set of EAM potential used. Here, we note that icosahedra are also present in crystalline phases with a composition close to $\text{Cu}_{65}\text{Zr}_{35}$, namely Cu_8Zr_3 , $\text{Cu}_{51}\text{Zr}_{14}$, in addition to Cu_2Zr Laves phases (details in the Appendix, Table II). Cu_8Zr_3 and $\text{Cu}_{51}\text{Zr}_{14}$ are known crystalline phases from the phase diagram of Cu-Zr [50] that are observed experimentally [51]. Therefore, icosahedra alone should not be directly linked to a high GFA.

To extend our knowledge beyond the short-range order, the first-neighbor correlation matrix is represented in Fig. 6. It can be seen that the correlation index between Cu-centered icosahedral and Zr-centered Z16 local structures is highly positive (red color). Among the top 15 Zr-centered and Cu-centered local structures, Z16 are the ones that have the highest correlation index with icosahedral local structures (not shown). This shows the tendency of icosahedral local structures to be neighbors of Frank-Kasper Z16 local structures and form medium-range structures as illustrated in Fig. 7. In our sample, out of the 50 000 atoms, 41 821 (or 83.6%) are part of an icosahedral or a Z16 local structure (either the central atom or a first neighbor of the central atom), which is a significant fraction.

FIG. 16. The five Cu-centered local structures with the highest fraction for $\text{Cu}_{50}\text{Zr}_{50}$. For each local structure, the fraction of the corresponding Voronoi index is also shown in red.

Thus, by using the p_3 code and the recently developed EAM potentials, the existence of Z16 structures and the positive correlation between icosahedral and Z16 structures in a $\text{Cu}_{65}\text{Zr}_{35}$ metallic glasses are fully confirmed. We note that among the top 15 Cu-centered local structures, only icosahedral and docosahedral [$@4(56)^2 5^8$] ones show a positive correlation index with icosahedral local structures (not shown).

To show the importance of differentiating the Z16 and O16 local structures, the evolution of their fractions is studied with respect to the cooling rate used to produce the metallic glass atomic structures. Although both local structures have the same Voronoi index, only the fraction of Z16 local structures increases when the cooling rate is reduced (Fig. 8). In addition, as can be seen in Fig. 9, the correlation index between icosahedral and Z16 local structures is always higher than the correlation index between icosahedral and O16 local structures over the whole range of cooling rates. Therefore, it is important to properly differentiate Z16 and O16 local structures.

The high correlation index between Cu-centered icosahedral and Zr-centered Z16 local structures suggests the formation of networks of interpenetrating icosahedral and Z16 local structures. Since both icosahedral and Z16 local structures are stabilized over cooldown, it is reasonable to consider them as basic clusters (icosahedral for Cu, Z16 for Zr), instead of considering only Cu-centered icosahedral ones as in previous studies [18,19]. Such networks are observed in our atomic configurations and one of them is illustrated in Fig. 10. In this network, the Z16 local structure connects networks of icosahedral local structures. The nature and the impact of such networks on the mechanical properties shall be investigated in a future study.

B. $\text{Cu}_x\text{Zr}_{1-x}$

We examine the correlation between icosahedral and Z16 local structures in $\text{Cu}_x\text{Zr}_{1-x}$ systems ($0.3 \leq x \leq 0.8$). None of the sample crystallized in the cooling range studied (10^9 – 10^{13} K/s). We note that atomic compositions in the 60–75% range maximize the fractions of icosahedral, Z16, and $@456^3 565^8 6$ local structures (Fig. 11). The first-neighbor correlation matrix shows that the positive correlation

between icosahedral and Z16 local structures, observed in the previous section for $\text{Cu}_{65}\text{Zr}_{35}$ (see Fig. 9), occurs over the whole range of atomic compositions independently of the atomic composition (Fig. 12). Again, the correlation index between icosahedral and Z16 local structures consistently remains higher than the correlation index between icosahedral and O16 local structures. Therefore, the positive correlation between icosahedral and Z16 local structures is a universal feature in Cu-Zr metallic glasses. Figure 13 illustrates the relation between the fractions of Cu-centered icosahedral and Zr-centered Z16 local structures on the whole range of atomic compositions and cooling rates. It can be seen that the fractions of these two types of local structures are clearly connected.

For reference, the results for $@456^3 565^8 6$ ($\langle 0, 1, 10, 5 \rangle$) and $@456^3 5^7 65^2$ ($\langle 0, 1, 10, 4 \rangle$) are also included in Fig. 11(a). The former is the most frequent Zr-centered local structures for $x \geq 0.55$ while the latter is the most frequent one for $x \leq 0.5$. In Fig. 11(b), the results for $@45^2 6^2 5^4 45^2$, $@4(56)^2 5^8$ (docosahedral) and $@45^3 6^3 5^4 45$ are also included. While $@5^{12}$ is the most frequent for $x \geq 0.5$, $@45^2 6^2 5^4 45^2$ is the most frequent at $x = 0.45$ and $@45^3 6^3 5^4 45$ is the most frequent for $x < 0.45$. With increasing Cu concentration, the fraction of docosahedral local structures increases. This is because the system becomes closer to a simple metal system, where docosahedral local structures are dominant [42].

C. Comparison with experimental $\text{Cu}_{50}\text{Zr}_{50}$

Finally, we compare the distribution of local structures in $\text{Cu}_{50}\text{Zr}_{50}$ metallic glasses. In order to build a relation between the theoretical atomic configuration from MD with experimental samples, we performed RMC simulations to fit the structure factor $S(q)$ measured by x-ray measurements, starting from the atomic structure obtained from MD with a cooling rate of 10^9 K/s. As can be seen in Fig. 14, the RMC model corrects the discrepancy in the structure factor between the MD model and experimental measurements, particularly in the height of the first peak and the splitting of the second peak.

The five most common local structures are presented by type of center in Fig. 15 and Fig. 16. There is a fairly good agreement in local structure distributions between MD and

TABLE II. Local structures of the crystalline phases of Cu-Zr systems with atomic composition close to Cu₂Zr Laves phases.

Phase	Cu-centered local structures	Fraction	Zr-centered local structures	Fraction
Cu ₂ Zr (Laves)	@5 ¹² (icosahedral)	100%	@5 ³ (65) ³ 5 ⁶ 6 (Z16)	100%
Cu ₅₁ Zr ₁₄	@5 ¹² (icosahedral)	23.5%	@46 ⁴ 465 ⁵ 64656	42.9%
	@45 ² 6 ² 565 ² 4645	23.5%	@456 ⁵ 465 ⁵ (65) ²	21.4%
	@45 ² 6 ² 5 ² (654) ²	12.8%	@456 ³ 56 ² 5 ³ 6 ² 546 ² 46	21.4%
	@4(56) ² 5 ⁸ (docosahedral)	11.8%	@5 ³ (65) ³ 5 ⁶ 6 (Z16)	14.3%
	@45 ² 6 ² 5 ⁴ 45 ²	11.8%		
	@36 ³ (56) ² 464 ²	7.8%		
	@45 ² 6 ³ 56545 ² 4	5.9%		
	@4 ² 6 ³ (644) ²	3.9%		
Cu ₈ Zr ₃	@4(56) ² 5 ⁸ (docosahedral)	50.0%	@5 ³ (65) ³ 5 ⁶ 6 (Z16)	66.7%
	@5 ¹² (icosahedral)	37.5%	@5 ⁴ (665) ² 5 ⁶ 6	33.3%
	@45 ³ 65 ⁴ 45	12.5%		
Cu ₁₀ Zr ₇	@4 ² 656 ² 45 ² 45	70.0%	@46 ⁴ 5 ⁹ 656	28.6%
	@45658(46) ² (45) ² 6	15.0%	@456 ³ 565 ⁵ 6465	28.6%
	@36 ² 745 ² 64 ² 64	10.0%	@4568(65) ² (46) ² 4565 ²	21.4%
	@36 ² 84656(45) ² 64	5.0%	@46 ⁵ (46) ⁴ 6 ³ 4	7.1%
			@456 ² 8465 ³ (46) ² 565	7.1%
			@367 ² (64) ² 65646 ⁴ 4 ²	7.1%

RMC results. It should be noted that the fraction of each local structure is slightly lower in the RMC model compared to MD. There is an excellent agreement in terms of rankings (identical top five) for both Zr-centered (Fig. 15) and Cu-centered (Fig. 16) local structures. Overall, the MD and RMC models show a good agreement.

To extend further the analysis, we also compare the first-neighbor correlation indices in Table I. It can be seen that the correlation indices are higher in the RMC model than in the MD one, except for the icosahedron-O16 correlation index. More importantly, the most positive correlation between icosahedral and Z16 local structures is also observed in the RMC model. As the RMC model is designed to reproduce features of the experimental sample, this observation suggests that the positive correlation between Cu-centered icosahedral and Zr-centered Z16 local structures is a realistic feature.

IV. CONCLUSIONS

Owing to the degeneracy problem of the Voronoi index and the artifact in sets of EAM potentials for Cu-Zr, the existence of Zr-centered Frank-Kasper Z16 structures in Cu-Zr metallic glasses has not been fully confirmed yet. In this work, by using the p_3 code and the recently developed EAM potential, we have concluded that Zr-centered Z16 structures exist in Cu-Zr metallic glasses. We have shown that two different types of local structures, Z16 and O16, have the same Voronoi index $\langle 0, 0, 12, 4 \rangle$ but behave differently. Indeed, in Cu₆₅Zr₃₅, only the fraction of Z16 increases when the cooling rate decreases while the fraction of O16 does not change significantly. Moreover, Z16 has a higher (positive) correlation with icosahedral local structures than O16. Our findings indicate the formation of medium-order clusters combining interpenetrating icosahedral and Z16 local structures. A thorough study of the local structures shows that our model shares similar features with

Cu₈Zr₃, Laves Cu₂Zr and Cu₅₁Zr₁₄. The positive correlation is observed over a large range of atomic composition of Cu_xZr_{1-x} ($0.3 \leq x \leq 0.8$) glasses and over a large range of cooling rates (10^9 – 10^{13} K/s). These results are supported by RMC calculations which fit the experimental structure factor. The p_3 analysis, combined with the nearest-neighbor correlation matrix, constitute a powerful methodology improve the understanding of the short- and medium-range order in metallic glasses.

ACKNOWLEDGMENT

The high-energy x-ray diffraction measurement was carried out at SPring-8 under the Proposal 2019B2091.

FIG. 17. Distribution of the atomic displacements generated by the RMC simulation.

APPENDIX A: LOCAL STRUCTURES IN CRYSTAL PHASES OF Cu-Zr SYSTEMS

Table II summarizes the distribution of local structures found in crystalline phases of Cu-Zr systems near the Cu₂Zr composition, including Laves phases.

APPENDIX B: ATOMIC DISPLACEMENT DURING RMC

Figure 17 shows the distribution of the atomic displacements in the MD structure after the RMC simulation. The displacements, which range from 0 to 0.35 Å, are much smaller than the bond distances.

-
- [1] P. G. Debenedetti and F. H. Stillinger, Supercooled liquids and the glass transition, *Nature (London)* **410**, 259 (2001).
 - [2] D. B. Miracle, D. V. Louzguine-Luzgin, L. V. Louzguina-Luzgina, and A. Inoue, An assessment of binary metallic glasses: Correlations between structure, glass forming ability and stability, *Int. Mater. Rev.* **55**, 218 (2010).
 - [3] C. Schuh, T. Hufnagel, and U. Ramamurty, Mechanical behavior of amorphous alloys, *Acta Mater.* **55**, 4067 (2007).
 - [4] W. Klement, R. H. Willens, and P. Duwez, Non-crystalline structure in solidified gold-silicon alloys, *Nature (London)* **187**, 869 (1960).
 - [5] D. Wang, Y. Li, B. B. Sun, M. L. Sui, K. Lu, and E. Ma, Bulk metallic glass formation in the binary Cu–Zr system, *Appl. Phys. Lett.* **84**, 4029 (2004).
 - [6] D. Xu, B. Lohwongwatana, G. Duan, W. L. Johnson, and C. Garland, Bulk metallic glass formation in binary cu-rich alloy series – Cu_{100–x}Zr_x ($x = 34, 36, 38.2, 40$ at.%) and mechanical properties of bulk Cu₆₄Zr₃₆ glass, *Acta Mater.* **52**, 2621 (2004).
 - [7] T. Fujita, K. Konno, W. Zhang, V. Kumar, M. Matsuura, A. Inoue, T. Sakurai, and M. W. Chen, Atomic-Scale Heterogeneity of A Multicomponent Bulk Metallic Glass with Excellent Glass Forming Ability, *Phys. Rev. Lett.* **103**, 075502 (2009).
 - [8] J. D. Bernal, A geometrical approach to the structure of liquids, *Nature (London)* **183**, 141 (1959).
 - [9] R. L. McGreevy, Reverse monte carlo modelling, *J. Phys.: Condens. Matter* **13**, R877 (2001).
 - [10] Y. Q. Cheng, E. Ma, and H. W. Sheng, Atomic Level Structure in Multicomponent Bulk Metallic Glass, *Phys. Rev. Lett.* **102**, 245501 (2009).
 - [11] M. I. Mendelev, D. J. Sordelet, and M. J. Kramer, Using atomistic computer simulations to analyze x-ray diffraction data from metallic glasses, *J. Appl. Phys.* **102**, 043501 (2007).
 - [12] M. Mendelev, M. Kramer, R. Ott, D. Sordelet, D. Yagodin, and P. Popel, Development of suitable interatomic potentials for simulation of liquid and amorphous Cu–Zr alloys, *Philos. Mag.* **89**, 967 (2009).
 - [13] V. Borovikov, M. I. Mendelev, and A. H. King, Effects of stable and unstable stacking fault energy on dislocation nucleation in nano-crystalline metals, *Modell. Simul. Mater. Sci. Eng.* **24**, 085017 (2016).
 - [14] A. Hirata, P. Guan, T. Fujita, Y. Hirotsu, A. Inoue, A. R. Yavari, T. Sakurai, and M. Chen, Direct observation of local atomic order in a metallic glass, *Nat. Mater.* **10**, 28 (2010).
 - [15] A. Hirata, L. J. Kang, T. Fujita, B. Klumov, K. Matsue, M. Kotani, A. R. Yavari, and M. W. Chen, Geometric frustration of icosahedron in metallic glasses, *Science* **341**, 376 (2013).
 - [16] R. Soklaski, Z. Nussinov, Z. Markow, K. F. Kelton, and L. Yang, Connectivity of icosahedral network and a dramatically growing static length scale in Cu-Zr binary metallic glasses, *Phys. Rev. B* **87**, 184203 (2013).
 - [17] M. Ghaemi, R. Tavakoli, and A. Foroughi, Comparing short-range and medium-range ordering in Cu Zr and ni Zr metallic glasses – correlation between structure and glass form ability, *J. Non-Cryst. Solids* **499**, 227 (2018).
 - [18] M. Wakeda and Y. Shibutani, Icosahedral clustering with medium-range order and local elastic properties of amorphous metals, *Acta Mater.* **58**, 3963 (2010).
 - [19] M. Lee, C.-M. Lee, K.-R. Lee, E. Ma, and J.-C. Lee, Networked interpenetrating connections of icosahedra: Effects on shear transformations in metallic glass, *Acta Mater.* **59**, 159 (2011).
 - [20] J. Ding, Y.-Q. Cheng, and E. Ma, Full icosahedra dominate local order in cu₆₄zr₃₄ metallic glass and supercooled liquid, *Acta Mater.* **69**, 343 (2014).
 - [21] J. Zemp, M. Celino, B. Schönfeld, and J. F. Löffler, Crystal-Like Rearrangements of Icosahedra in Simulated Copper-Zirconium Metallic Glasses and their Effect on Mechanical Properties, *Phys. Rev. Lett.* **115**, 165501 (2015).
 - [22] F. Yonezawa, Glass transition and relaxation of disordered structures, in *Solid State Physics* (Elsevier, San Diego, 1991), pp. 179–254.
 - [23] K. Nishio and T. Miyazaki, Polyhedron and polychoron codes for describing atomic arrangements, in *Nanoinformatics* (Springer, Singapore, 2018), pp. 97–130.
 - [24] K. Nishio, A. K. A. Lu, and T. Miyazaki, Entropy-driven dicosahedral short-range order in simple liquids and glasses, *Phys. Rev. E* **99**, 022121 (2019).
 - [25] X. X. Yue, C. T. Liu, S. Y. Pan, A. Inoue, P. K. Liaw, and C. Fan, Effect of concentration on the structure of isothermally-annealed CuZr metallic glasses, *Mater. Sci. Technol.* **34**, 2287 (2018).
 - [26] R. E. Ryltsev, B. A. Klumov, N. M. Chchelkatchev, and K. Y. Shunyaev, Nucleation instability in supercooled Cu–Zr–al glass-forming liquids, *J. Chem. Phys.* **149**, 164502 (2018).
 - [27] H. Okamoto, Cu-Zr (copper-zirconium), *J. Phase Equilib. Diffus.* **33**, 417 (2012).
 - [28] M. I. Mendelev, Y. Sun, F. Zhang, C. Z. Wang, and K. M. Ho, Development of a semi-empirical potential suitable for molecular dynamics simulation of vitrification in Cu-Zr alloys, *J. Chem. Phys.* **151**, 214502 (2019).
 - [29] K. Nishio and T. Miyazaki, How to describe disordered structures, *Sci. Rep.* **6**, 23455 (2016).
 - [30] K. Nishio and T. Miyazaki, Describing polyhedral tilings and higher dimensional polytopes by sequence of their two-dimensional components, *Sci. Rep.* **7**, 40269 (2017).
 - [31] F. C. Frank and J. S. Kasper, Complex alloy structures regarded as sphere packings. i. definitions and basic principles, *Acta Crystallogr.* **11**, 184 (1958).
 - [32] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.* **117**, 1 (1995).

- [33] W. M. Brown, P. Wang, S. J. Plimpton, and A. N. Tharrington, Implementing molecular dynamics on hybrid high performance computers – short range forces, *Comput. Phys. Commun.* **182**, 898 (2011).
- [34] W. M. Brown, A. Kohlmeyer, S. J. Plimpton, and A. N. Tharrington, Implementing molecular dynamics on hybrid high performance computers – particle–particle particle-mesh, *Comput. Phys. Commun.* **183**, 449 (2012).
- [35] M. W. Finnis and J. E. Sinclair, A simple empirical N-body potential for transition metals, *Philos. Mag. A* **50**, 45 (1984).
- [36] M. S. Daw and M. I. Baskes, Semiempirical, Quantum Mechanical Calculation of Hydrogen Embrittlement in Metals, *Phys. Rev. Lett.* **50**, 1285 (1983).
- [37] M. S. Daw and M. I. Baskes, Embedded-atom method: Derivation and application to impurities, surfaces, and other defects in metals, *Phys. Rev. B* **29**, 6443 (1984).
- [38] G. J. Martyna, D. J. Tobias, and M. L. Klein, Constant pressure molecular dynamics algorithms, *J. Chem. Phys.* **101**, 4177 (1994).
- [39] W. Shinoda, M. Shiga, and M. Mikami, Rapid estimation of elastic constants by molecular dynamics simulation under constant stress, *Phys. Rev. B* **69**, 134103 (2004).
- [40] B. J. Gellatly and J. L. Finney, Characterisation of models of multicomponent amorphous metals: The radical alternative to the voronoi polyhedron, *J. Non-Cryst. Solids* **50**, 313 (1982).
- [41] J. P. K. Doye and D. J. Wales, The effect of the range of the potential on the structure and stability of simple liquids: From clusters to bulk, from sodium to C₆₀, *J. Phys. B: At. Mol. Opt. Phys.* **29**, 4859 (1996).
- [42] K. Nishio, A. K. A. Lu, and T. Miyazaki, Universal short-range order and material dependent glass-forming ability of liquid metals., *Phys. Rev. Research* **1**, 012013 (2019).
- [43] M. Li, C. Z. Wang, S. G. Hao, M. J. Kramer, and K. M. Ho, Structural heterogeneity and medium-range order in Zr_xCu_{100-x} metallic glasses, *Phys. Rev. B* **80**, 184201 (2009).
- [44] K. Ohara, Y. Onodera, S. Kohara, C. Koyama, A. Masuno, A. Mizuno, J. T. Okada, S. Tahara, Y. Watanabe, O. D. A. Hirohisa, Y. Nakata, H. Tamaru, T. Ishikawa, and O. Sakata, Accurate synchrotron hard x-ray diffraction measurements on high-temperature liquid oxides, *International Journal of Microgravity Science and Application* **37**, 370202 (2020).
- [45] R. L. McGreevy and L. Pusztai, Reverse monte carlo simulation: A new technique for the determination of disordered structures, *Mol. Simul.* **1**, 359 (1988).
- [46] L. Ward, D. Miracle, W. Windl, O. N. Senkov, and K. Flores, Structural evolution and kinetics in Cu-Zr metallic liquids from molecular dynamics simulations, *Phys. Rev. B* **88**, 134205 (2013).
- [47] F. C. Frank, Supercooling of liquids, *Proc. R. Soc. London A* **215**, 43 (1952).
- [48] L. Yang, J. H. Xia, Q. Wang, C. Dong, L. Y. Chen, X. Ou, J. F. Liu, J. Z. Jiang, K. Klementiev, K. Saks, H. Franz, J. R. Schneider, and L. Gerward, Design of Cu₈Zr₅-based bulk metallic glasses, *Appl. Phys. Lett.* **88**, 241913 (2006).
- [49] Y. Cheng and E. Ma, Atomic-level structure and structure–property relationship in metallic glasses, *Prog. Mater. Sci.* **56**, 379 (2011).
- [50] D. Arias and J. P. Abriata, Cu-Zr (copper-zirconium), *J. Phase Equilib.* **11**, 452 (1990).
- [51] X. Cui, Q. D. Zhang, X. Y. Li, and F. Q. Zu, On crystallization behavior and thermal stability of Cu₆₄Zr₃₆ metallic glass by controlling the melt temperature, *J. Non-Cryst. Solids* **452**, 336 (2016).