Supplementary Materials for

Geometric Frustration of Icosahedron in Metallic Glasses


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1. Materials and Methods

1-1. Sample preparation and TEM experiment

$\text{Zr}_{80}\text{Pt}_{20}$ metallic glass ribbons were made by a single-roll rapid quenching technique with the roll speed of 60 m/sec. The TEM samples were prepared by ion-milling (Fischione, Model 1010) with a liquid nitrogen cooled stage. ABED patterns were taken by using a JEM-2100F TEM/STEM with double spherical aberration (Cs) correctors (operated at 200kV) and recorded by a TV-rate CCD camera (Gatan, ES500W Erlangshen). A nearly parallel coherent electron beam produced by a specially-designed small condenser aperture with a diameter of 5 μm is utilized as an Angstrom-sized electron probe. By using the Cs corrected STEM, the coherent electron beam can be accurately aligned and focused to a diameter as small as 0.3 ~ 0.4 nm and the instrumental parameters (spherical aberration coefficient, defocus, astigmatism etc.) can be precisely measured using a Ronchigram method. (35)

1-2. Molecular dynamics calculations and ABED simulations

$\textit{Ab-initio}$ molecular dynamics (MD) simulation was carried out using the Vienna $\textit{ab-initio}$ simulation package (VASP) (36). The projector augmented wave method (37) and the generalized gradient approximation were used to describe electron-ion interactions (38). A cubic super-cell with a periodic boundary condition and containing 160 Zr atoms and 40 Pt atoms was initially constructed according to the experimental density. The ensemble was melted and equilibrated at a high temperature of 2500 K for 2000 timesteps with the each timestep of 5 fs. Subsequently, the systems were quenched to 300 K with a cooling rate of $4 \times 10^{13}$ K / sec at 1000 time steps per 200 K. All the
calculations were carried out within a canonical ensemble NVT (constant number, volume, temperature) by using a Nosé thermostat for temperature control.

Since a cooling rate of \textit{ab-initio} MD simulation is too high, we also conducted classical MD simulations using embedded atom method (EAM) potentials that were created on the basis of the \textit{ab-initio} calculations. A 12000 atom ensemble with the composition of Zr\textsubscript{80}Pt\textsubscript{20} was melted at 2500 K for 0.1 ns (with a time step of 5 fs) and then cooled to 300 K at a cooling rate of $1.7 \times 10^{10}$ K/sec.

ABED simulations of the simulated atomic structure were carried out using a conventional multislice method (39). To understand the local atomic environments, we applied Voronoi polyhedral analysis to elucidate possible polyhedra, generally recognized as short range order (SRO), in the metallic glass (Fig. S1A).

2. Supplementary Text

2-1. Voronoi analysis for the MD model

In order to interpret the experimental ABED patterns, we investigated the structural model of the glassy Zr\textsubscript{80}Pt\textsubscript{20} produced by the \textit{ab-initio} MD simulations and classical MD simulations and applied Voronoi polyhedral analysis to elucidate prevailing polyhedra in the metallic glass. Icosahedron-like polyhedra ($<0 1 10 2>$) centered by Zr atoms are the dominant SRO and $<0 0 12 0>$ icosahedra are frequently formed around Pt atoms. Figure S1B shows the overall structural model of the \textit{ab-initio} MD simulations, where the central atoms of $<0 2 8 1>$, $<0 0 12 0>$, and $<0 1 10 2>$ polyhedra are shown in color. The connections between the colored central atoms indicate the presence of networks consisting of icosahedra and icosahedron-like
polyhedra. Since 167 atoms (total 200 atoms) belong to these three polyhedra, icosahedra and icosahedron-like clusters are apparently the main building blocks of the structural model.

To avoid possible confusion, in this study we define the ideal (or perfect) icosahedron as a $<0\ 0\ 1\ 2\ 0>$ cluster with perfect icosahedral symmetry. If the positions of 12-coordinated atoms in a $<0\ 0\ 1\ 2\ 0>$ cluster are displaced from those in an ideal icosahedron, we call the clusters as a “distorted” icosahedron. Atomic clusters similar to $<0\ 0\ 1\ 2\ 0>$ icosahedra, such as $<0\ 2\ 8\ 1>$ or $<0\ 1\ 10\ 2>$, which partially contain icosahedral symmetry, are called “icosahedron-like” clusters.

2-2. Total energy calculation of individual atomic clusters

We noticed that the distorted icosahedron observed experimentally is partially analogous to both of the icosahedral and fcc clusters as shown in Fig. 3. To confirm this from the energetic viewpoint, *ab-initio* calculations were performed to estimate the total energies of three types of 11Zr-2Pt and 12Zr-1Pt clusters: ideal icosahedron, distorted icosahedron, and fcc cluster. All the calculations were carried out by using VASP with the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation parameterizations was applied. Only the $\Gamma$ point in Brillouin zone and a supercell with edge length of 16Å were used in the calculations and the energy cutoff is 300eV. The total energies were converged within $10^{-4}$ eV and both structures of the ideal icosahedron and the fcc cluster were relaxed prior to the total energy calculations. The total energy of distorted-icosahedral was directly calculated from the structure obtained by the MD simulations.
2-3. Features of atomic clusters other than the <0 0 12 0> icosahedron

In addition to the <0 0 12 0> icosahedron, we also investigated the prevailing atomic clusters with indices of <0 3 6 1>, <0 2 8 0>, <0 2 8 1>, and <0 1 10 2> in the metallic glasses using ABED. Fig. S6A shows atomic models of the four clusters from two different directions. All the icosahedron-like clusters can be detected in the glass and the corresponding ABED patterns are shown in Fig. S6B and S6C. The experimental diffraction patterns are well consistent with the ones derived from the MD models. As shown in Fig. S6B, the icosahedron-like clusters (<0 2 8 1> and <0 1 10 2>) have very similar ABED patterns to that of the <0 0 12 0> distorted icosahedron. But, the structural difference can be well identified from the ABED patterns. Interestingly all the patterns partially keep the fivefold symmetry whereas only a pair of spots is deviated from fivefold position. Note that the deviated spots consequently make the fcc [110]-like pattern together with the other two pairs of spots. Therefore, both icosahedron- and fcc-like structural features can be identified from the prevailing clusters with indices of <0 3 6 1>, <0 2 8 0>, <0 2 8 1>, and <0 1 10 2>. The concept of geometric frustration can thus be applied to these atomic clusters too, analogous to the <0 0 12 0> distorted icosahedron.

2-4. ABED patterns of non-icosahedral clusters in the metallic glass

The ABED patterns from non-icosahedral clusters such as <0 4 6 3> and <0 3 6 3> were also checked as shown in Fig. S4. The zone-axis patterns obtained from the fivefold-like axes (normal to pentagonal atomic arrangements) are clearly different from the pattern of icosahedra or icosahedron-like clusters. Even by rotating these clusters to
all the possible zone-axis directions, it was impossible to find symmetric patterns similar to the ones obtained from icosahedra.

2-5. Topology analysis of atomic clusters in the metallic glass

In order to survey the manner of distortion of each atomic cluster determined by ABED, we employed a mathematical tool to abstract essence of geometric relations, called “homology group”. Homology groups are defined for geometrical objects called “simplicial complexes” or “cubical complexes”, which are consist of a finite number of simple geometrical objects called n-dimensional simplices (points, segments, triangles, etc.) or cubes (points, segments, squares, etc.), respectively. For given such a complex $X$ and each integer $n$, the homology group $H_n(X)$ provides the topological feature of $X$ in terms of “n-dimensional holes”. n-dimensional holes may be heuristically thought of as connected components, tunnels and cavities for $n=0,1,2$, respectively. The homology group $H_n(X)$ can be identified with a $b_n$-dimensional vector space (or a finitely generated module with $b_n$-dimensional free component in algebra). The integer $b_n$ expresses a count of n-dimensional holes in $X$ and is called the $n$-th Betti number of $X$, which can be often applied to characterizing the topology of $X$. For details of the mathematical theory, one can find in the references (29 and 40).

Here we analyze the homology for each atomic cluster in the metallic glass, determined by ABED and MD simulations. The MD model we used in this study consists of 200 atoms, indicating the presence of 200 atomic clusters. For computing homological quantities, we need first to construct three-dimensional objects with voxels (three-dimensional pixels) for the 200 atomic clusters. The voxel dimension is $0.005 \times 0.005 \times 0.005$ nm$^3$. In the case of atoms in metallic glasses, hard sphere model is
basically acceptable. The corresponding cubical complex can be constructed for computing homological quantities. For each atom position in a targeted cluster, we prepared spherical objects with given atomic radii which can be a variable in this analysis. For the computation, we utilized a CHomP (Computational Homology Project) software package available at http://chomp.rutgers.edu/. The CHomP software can provide information of homology, in particular, the Betti numbers, of cubical complexes made by input data such as voxel objects. We here focus especially on the 0-th Betti number $b_0$ which represents the number of connected components in the objects. In the Homology analysis, we always keep the constant inter-atomic distances in the clusters determined by ABED and/or MD simulations while changing the virtual sizes of constituent atoms simultaneously according to their real atomic size ratio, as shown in Fig. S7. For the Zr-Pt binary system, we first determine standard values of atomic sizes which are exactly same as metallic bond radii ($R_A$: 0.16025 nm for Zr; $R_B$: 0.13870 nm for Pt) and always keep the atomic size ratio ($R_A/R_B$) during changing $R_A$ and $R_B$. In this analysis, we use normalized atomic radii that are the virtual atomic radii divided by $R_A$ or $R_B$. The normalized atomic radii of real (or original) atoms are always 1 and the virtual atom size can be larger or smaller than 1. With this simple treatment, we do not need to consider the true atomic sizes during the Homology analysis. Then we can topologically characterize three-dimensional atomic arrangement in the clusters only by one Betti number $b_0$. By changing normalized atomic radii, i.e. monitoring the territory of each atomic coordinate, this method enables us to understand distortion manner for each atomic cluster.

The geometric frustration discussed in this study can also be quantified in terms of its Homology group. The 0-th Betti number $b_0$ can provide the number of
non-connected features in the atomic clusters being analyzed. As shown in Fig. S8, by
increasing the atomic radii, the connectivity of the ideal <0 0 12 0> icosahedron
changes dramatically from the Betti number 13 (total atom number in the cluster) to 1.
Apparently, the distortion caused merely by the atomic size disparity of constituent
elements (Pt and Zr) is trivial (Fig. S8). In contrast, the distorted <0 0 12 0> icosahedra
determined by ABED show continuous decrease of Betti number from 13 to 1,
indicating large variation of inter-atomic distances in the clusters. All the <0 0 12 0>
icosahedra in the glass are distorted in the same topological manner and clearly different
from the ideal icosahedron. We can scale up the homology analysis from individual
atomic clusters to the global structure of the glass to investigate the inherent correlation
between local atomic configurations and long-range disordered packing. When we
plotted the Betti number variation of the entire MD dataset by counting all the
component atoms as centers of polyhedra, we found that the Betti number distribution is
consistent with that of the distorted icosahedron and icosahedron-like clusters revealed
by ABED. This demonstrates that the connectivity of the distorted icosahedra or
icosahedron-like clusters is compatible with the long-range disorder of the metallic
glass. Therefore, the homology analysis may provide a simple way to understand the
atomic structure of disordered metallic glasses from the topological view.

2-6. Detection capability of ABED technique

Since most TEM specimens are essentially three-dimensional with certain
thickness, the volume interrogated by a small electron probe may contain too many
atoms to identify the local structure because the sample is too thick. Therefore, for
ABED samples, the thinner is better. However, for the TEM samples prepared by ion
milling or electrochemical polishing, the thinnest edge is usually thicker than ~2 - 3 nm. For example, the metallic glass sample used in this ABED study has a thickness of ~3 - 5 nm determined by electron energy loss spectroscopy (EELS). However, even 3 - 5 nm, it is still much thicker compared with the size of individual coordination polyhedra (atomic clusters). We therefore estimated atom numbers inside the column in which electron beam passes thorough by assuming average atomic radii of 0.30 nm and packing density of 0.7. Fig. S9 shows the plots of atom numbers in the column for three different thicknesses (3 and 5 nm). When the beam diameter is focused down to 0.3 ~ 0.4 nm, the atom number is reduced to about 15 ~ 30 atoms, corresponding to 2 ~ 3 atomic clusters. Since the beam diameter is the FWHM value of Gaussian distribution, the actual area that contributes to total ABED intensity is expected to be ~0.5 nm. Nevertheless the atom number is still less than 25 ~ 60 (= 2 ~ 5 atomic clusters) even for the 0.5 nm probe size. Because the ABED intensity strongly depends on the orientation of atomic clusters, it becomes much more realistic to detect a single atomic cluster experimentally using the present ABED technique. We actually checked an effect of the cluster overlapping for the total ABED intensity using the structural models shown in Fig. S10. The simulated ABED pattern is almost unchanged by increasing the number of off-axis cluster. This means only on-axis cluster shows the strong diffraction intensity and gives the main contribution to the total ABED intensity.

We also examined the sensitivity of ABED to the cluster distortion. Fig. S11 shows simulated ABED patterns for both the ideal and distorted icosahedra. The beam incidence direction is slightly tilted from the exact fivefold axis of the clusters. From the exact fivefold axis, the ideal icosahedron only shows a very broad ring (see Fig. 1). Even if the cluster is slightly tilted, the pattern still keeps the broadness, clearly different
from the distorted cluster. Moreover, the degree of distortion of icosahedron and icosahedron-like clusters can be determined by ABED. As shown in Fig. S6B, two pairs of diffraction vectors keep at the fivefold positions, but a pair of spots is heavily deviated. The deviation is directly related to the distortion of the clusters. Therefore, using the ABED technique, we can roughly estimate a degree of distortion from the feature of the diffraction patterns.

2-7. Atomic structure simulated by a classical MD method (slow cooling)

Figure S12 shows the results of Voronoi polyhedral analysis from the slowly cooled MD model. The indices of <0 2 8 1>, <0 0 12 0>, <0 2 8 0>, <0 1 10 2>, and <0 2 8 2> are frequently found in the lists. This result is consistent well with the model obtained by our ab-initio MD simulation (Fig. S1A). Additionally both of our results are also consistent with the analysis by a reverse Monte Carlo simulation of the identical Zr$_{80}$Pt$_{20}$ glass (25). We also conducted bond orientational order analysis for the classical MD model as shown in Fig. 3C. Although the statistics of the plot looks much better than that of the ab-initio MD model, most of the atomic clusters are situated between ideal icosahedron and fcc.
3. Figures

Fig. S1 (A) Voronoi polyhedral analysis of the Zr$_{80}$Pt$_{20}$ MD structural model. Icosahedra (<0 0 12 0>) and icosahedron-like clusters (<0 1 10 2>, <0 2 8 1>) are frequently observed in the model. The cut-off value for Voronoi analysis is 0.38 nm. (B) Structural model of glassy Zr$_{80}$Pt$_{20}$ produced by *ab-initio* MD simulation. Colored atoms denote central atoms of icosahedron or icosahedron-like polyhedra. The corresponding Voronoi indices are shown in the inset.
Fig. S2 TEM micrographs of the Zr$_{80}$Pt$_{20}$ metallic glass. (A) A typical SAED pattern and low-magnification bright-field TEM image; and (B) Spherical aberration-corrected HRTEM image showing the amorphous nature of the sample.
Fig. S3 Angular values between two diffraction vectors expected from the ideal and distorted icosahedral clusters. The ranges of the distorted icosahedron are estimated by measuring the angles in several 5-, 3-, and 2-fold patterns obtained from the distorted \(<0\ 0\ 12\ 0>\) icosahedral clusters in the MD model. The experimental values shown in Fig. 1C are within the ranges determined from MD models.
Fig. S4 Simulated ABED patterns from $<0\ 3\ 6\ 3>$ and $<0\ 4\ 6\ 3>$ clusters (non-icosahedral clusters). Although it is difficult to define the fivefold axis in the non-icosahedral clusters, pentagon-like atomic arrangements are roughly normal to the beam incidence in this analysis. The fcc-like pattern seen in the icosahedron cannot be observed in these non-icosahedral clusters.
Fig. S5 Structure difference between ideal icosahedrons and the distorted icosahedron detected by the ABED and MD simulations. It can be seen that a pentagon in the ideal icosahedron can turn to be a fcc-like configuration by slight atom shift.
Fig. S6 (A) Atomic models of four icosahedron-like clusters that are frequently observed in the metallic glass. Both icosahedron-like fivefold and fcc-like cubic configurations can be recognized from the clusters. (B) Simulated and experimental ABED patterns taken from the distorted icosahedron and icosahedron-like clusters. The beam incidence directions are slightly tilted from the exact fivefold axis. All the patterns partially keep the fivefold symmetry. The diffraction from the distorted portions exhibits a two-fold symmetry, similar to that of the <110> pattern of the fcc cluster. (C) Experimental ABED patterns showing a nearly threefold symmetry, together with the simulated ABED patterns from low-coordination number clusters (<0 2 8 0> and <0 3 6 1>). The simulated patterns are consistent well with the experimental ones.
Fig. S7 Schematic diagram of the homology analysis. The atom size ratio (R_A/R_B) keeps a constant in the analysis (in (A)), while the atom positions are always fixed (in (B)). By changing the virtual atomic radii, we can monitor the change of the Betti number $b_0$ (number of connected components) to characterize the distortion manner of the clusters. If coordinates of each atom center are exactly identical for some atomic configurations, the size of constituent atoms affects the Betti numbers as shown in (C).
Fig. S8 Topology analysis for the distorted icosahedra (<0 0 12 0>) determined by ABED. Both ideal and distorted icosahedra are Pt centered polyhedra with 12 Zr surrounding atoms (12Zr-Pt). Error bars indicate the variation ranges of the Betti number of the distorted icosahedra. The histogram of all atomic clusters (200 clusters) in the Zr-Pt MD model is also shown. The color bar indicates the frequency of Betti number $b_0$ for each normalized atomic radii.
Fig. S9 Relationship between the electron beam size and the number of atoms in the columns where an electron beam passes through. The sample thicknesses are set to 3 and 5 nm, respectively. The average bond distance and packing density used in calculation are 0.30 nm and 0.7.
Fig. S10 Effect of the sample thickness on ABED. On-axis cluster gives the strongest intensity in the ABED patterns, whereas off-axis clusters do not contribute to the total intensity.
Fig. S11 Simulated ABED patterns from ideal and distorted icosahedra. The beam incidence direction is slightly tilted from the exact fivefold axes. The ideal icosahedron gives quite broad intensity, whereas the distorted one has a symmetric pattern with well-defined spots.
Fig. S12 Voronoi polyhedral analysis for the Zr$_{80}$Pt$_{20}$ taken from 12,000 atom model obtained by the classical MD simulation at the cooling rate of $1.7 \times 10^{10}$ K/sec.


