Atomic structure of Pd₈₁Si₁₉ glassy alloy under high pressure

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Abstract:

In situ high pressure x-ray diffraction experiments and reverse Monte Carlo simulations on Pd₈₁Si₁₉ glassy alloy were performed up to about 35 GPa. High quality structure factor data with q range up to 13.5 Å⁻¹ were obtained. The pressure dependence of relative volume of Pd₈₁Si₁₉ glassy alloy can be well described by a third-order Birch-Murnaghan equation of state with bulk modulus of $B_0=229$ GPa and a pressure derivative of $B'_0=2.7$. The continuous and monotonic change of relative volume as a function of pressure does not indicate any first-order phase transitions in Pd₈₁Si₁₉ glassy alloy in the studied pressure range. The pressure dependence of the atomic structures was systematically investigated by means of bond angle distribution, Honeycutt and Andersen index, Voronoi tessellation, total and partial coordination numbers and local chemical ordering analyses. It is found that the topological and chemical atomic structures of the Pd₈₁Si₁₉ glassy alloy do not change much upon pressure, indicating the stability of this material under pressure.

Keywords: High pressure; Glassy alloy; X-ray diffraction; Atomic structure

1. Introduction

Pressure induced phase transitions in amorphous materials is a long-standing challenge in the fields of condensed matter physics and materials science. Most remarkable findings are those observations of pressure induced polyamorphism, such as in ice [1], silicon [2], silica [3], As_2O_3 [4] and GeSe_2 [5]. The structural polyamorphic transitions from a low-density amorphous state to high-density amorphous state in these materials often result from an increase in atomic coordination numbers (CN) since they have directional bonds and low coordination number values ($\text{CN} < 6$) at ambient condition. Amorphous alloys, or glassy alloys, are a relative new class of amorphous materials with non-directional bonds and closely packed atomic structures with high coordination number values ($\text{CN} = 11-14$) at ambient condition, in which the pressure induced polyamorphism was thought to be impossible. Recently, surprising observations of pressure induced polyamorphism were reported in $[\text{La}_{0.5}\text{Ce}_{0.5}]_{64}\text{Al}_{16}\text{Ni}_5\text{Cu}_{15}$ bulk amorphous alloy [6] and $\text{Ce}_{55}\text{Al}_{45}$ amorphous alloy ribbon [7]. Further intensive studies have been carried out in a search for the polyamorphic transition phenomena and the origin for the polyamorphism in other glassy alloy systems [8-16]. But most of these studies were based on the first sharp diffraction peak position (FSDP) of x-ray diffraction (XRD) patterns with limited q range. In order to get reliable atomic structures of glassy alloys at high pressure, experimental diffraction data with large q range ($> 12 \text{ \AA}^{-1}$) are urgently needed, but they are rarely reported. Very recently, Mattern *et al.* [17] reported high pressure XRD data with q range up to $12 \text{ \AA}^{-1}$ on $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ amorphous alloy obtained using a high energy x-ray of $\sim 59.8 \text{ keV}$. This study has inspired the current work focused on

simple binary alloy $\text{Pd}_{81}\text{Si}_{19}$ investigated under high pressure at ambient temperature.

$\text{Pd}_{81}\text{Si}_{19}$ alloy can be quenched to fully amorphous balls with diameter up to 8 mm [18] which is a good glass forming binary alloy and has large plastic engineering strains of up to 82% [19]. The simple composition, but, at the same time, the excellent glass forming ability and the ability to withstand large plastic deformation make this alloy an ideal case compound to make an accurate systematic analysis of glassy atomic structure and its variation under pressure. In this work, we selected this $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy, as a prototype glassy system, performed *in situ* high pressure x-ray diffraction experiments along with reverse Monte Carlo (RMC) simulations [20]. No amorphous-to-amorphous or amorphous-to-crystalline transitions were observed in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy up to the highest pressure point of 35 GPa. Various structure analysis methods were used to identify the atomic structure evolution of the alloy upon pressure. The results reveal that the atomic structures remained almost unchanged at all pressures investigated, indicating the remarkable stability of this material up to about 35 GPa.

2. Methods

$\text{Pd}_{81}\text{Si}_{19}$ glassy alloy ribbons with a thickness of about 35 μm and a width of about 3 mm were prepared with the single-roller melt-spinning method. The sample was cut into about $30 \times 30 \mu\text{m}^2$ chip and then loaded into a symmetric diamond anvil cell (DAC) together with a ruby ball as a pressure calibrant [21] and Ar or Ne as a pressure transmitting medium. Firstly, *in situ* high pressure XRD experiments were performed at Shanghai Synchrotron Radiation Facility (SSRF) beamline BL15U1 with the wavelength of 0.6888 Å and a beam size of 5×5

μm^2 . Ar was loaded as a pressure transmitting medium in SSRF experiments. Due to the relative large x-ray wavelength and the relative small opening angle of the DAC, access to direct space was significantly limited so that only the first sharp diffraction peak of the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy could be observed in XRD patterns recorded in Shanghai. Secondly, *in situ* high pressure XRD experiments were performed at beamline P02.2 at PETRA III DESY, Hamburg, Germany, with a wavelength of 0.207 Å and a beam size of $3\times 4 \mu\text{m}^2$. Ne was loaded as a pressure transmitting medium in the DESY experiments using a gas loader from Sanchez Technology provided by the PETRA III Extreme Conditions Science Infrastructure (ECSI). For both experiments, background patterns were collected next to the sample at each pressure point for the background subtraction. The two-dimensional data were integrated with Fit2D [22], after the diffractions from the diamond and the transmitting medium were carefully masked out. The DESY data were further analyzed in the program package PDFgetX2 [23] to retrieve structure factors ($S(q)$) and pair correlation functions ($g(r)$) at different pressures. The density of the sample at ambient pressure was measured by the Archimedes method and the densities at high pressures were then estimated by the shift of the first sharp peak of XRD patterns. The same approach was also used to obtain densities which were used as starting parameters in our reverse Monte Carlo simulations performed using 20,000 atoms to simultaneously fit the experimental $S(q)$ and $g(r)$ data at three pressures recorded at DESY, *i.e.*, 2.5 GPa, 18.2 GPa and 31.4 GPa. For further local atomic structure analyses of the final converged configurations, cutoff distances, based on the first minimum in $g(r)$ curves, are used to be 3.59 Å, 3.50 Å and 3.45 Å at the pressure of 2.5 GPa, 18.2 GPa

and 31.4 GPa, respectively, which were caused by the densification of the alloy under pressure.

3. Results and discussion

3.1. Inverse FSDP positions

In situ high pressure XRD experiments up to 35.5 GPa with small pressure steps were performed at beamline BL15U1, SSRF, Shanghai. Fig. 1 shows selected high pressure x-ray diffraction patterns during compression for the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at room temperature. Due to the low x-ray energy available at beamline BL15U1, only the first sharp diffraction peak, with q range up to $3.5 \text{ \AA}^{-1}$, can be observed in these XRD patterns. With increasing pressure, the position of FSDP shifts to high q range as expected for the densification effect of pressure. Judging from the smooth broad patterns, the sample remained fully amorphous in the entire pressure range studied, which is different from pressure induced crystallization phenomenon observed at about 24 GPa in $\text{Ce}_{75}\text{Al}_{25}$ amorphous alloy ribbon [24]. Fig. 2 shows the inverse FSDP position parameter, $d_{\text{max}} = 2\pi / q_1$, and its dependence on pressure for $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy, where q_1 is the position of FSDP. The accuracy of q_1 was estimated to be about $\Delta q_1 = \pm 0.005 \text{ \AA}^{-1}$. A monotonic decrease of d_{max} is observed upon increasing pressure. The d_{max} is correlated to the volume (V) of the glass by a power law function, $(2\pi/q_1)^n$ vs V , which can be conveniently used to extract the relative volume (density) change as a function of pressure. However, the value of n is still under discussion. Indeed, it has been suggested by Jiang *et al.* [25] that $(2\pi/q_1)^3 \propto \text{volume}$, while Ma *et al.* [26] used $(2\pi/q_1)^{2.31} \propto \text{volume}$, and very recently, Zeng *et al.* [27] proposed $(2\pi/q_1)^{2.5} \propto \text{volume}$. Therefore, until now,

the exact n value for the relationship of $(2\pi/q_1)^n$ vs volume is still debated. Thus, for the time being, we only estimated relative volume change using $n=3$. The relative volume change with pressure, V_p/V_0 , is proportional to the parameter of $[d_{\max}(P)/d_{\max}(0)]^3$, where P and 0 denote the high-pressure and ambient-pressure conditions, respectively [25]. The volume-pressure dependence can be described by the equation of state of solids (EOS) in terms of a third-order Birch-Murnaghan (B-M) relation [17]:

$$P = \frac{3}{2} B_0 \left[\left(\frac{V_p}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V_p}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 - \frac{3}{4} (4 - B_0') \left[\left(\frac{V_p}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\},$$

where B_0 and B_0' are the bulk modulus and its pressure derivative at zero pressure, respectively. The inset in Fig. 2 shows the relative volume-pressure dependence and the fit to the B-M equation resulting in $B_0=229$ GPa and $B_0'=2.7$. The large value of B_0 is consistent with small compressibility of about 12% at 35.5 GPa, **which is similar to the measured bulk modulus value of 243 GPa for a similar PdCuSi glass, estimated by ultrasonic measurements [28]**. The good agreement of experimental data and calculated EOS is presented and no noticeable deviation is observed. The continuous and monotonic change of relative volume as a function of pressure does not indicate any first-order phase transitions in Pd₈₁Si₁₉ glassy alloy in the studied pressure range.

3.2. Pair correlation functions under pressure

In order to determine changes of atomic structure in Pd₈₁Si₁₉ glassy alloy under pressure, we further performed high pressure x-ray diffraction experiments at the Extreme Conditions Beamline P02.2 at PETRA III DESY with a wavelength of 0.207 Å at three different

pressures, 2.5 GPa, 18.2 GPa and 31.4 GPa. With the high energy (small wavelength) x-ray, we were able to obtain the high pressure XRD patterns with q range up to about $13.5 \text{ \AA}^{-1}$, which allows us to accurately determine the structure factor, $S(q)$, and the atomic pair correlation function, $g(r)$, at high pressures. Again, the inverse FSDP positions, $2\pi/q_1$, from the data recorded in DESY are also plotted in Fig. 2 by red stars. It is clear that these three points are located exactly in the $(2\pi/q_1)-P$ relation obtained at SSRF, indicating the consistency of the two different sets of experiments. Fig. 3a shows the atomic pair correlation function, $g(r)$, of the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at three different pressures. The shapes of these three pair correlation functions are almost the same. However, we note a shift to lower r range with increasing pressure. If we normalize the r values of $g(r_2)_{P=18.2\text{GPa}}$ and $g(r_3)_{P=31.4\text{GPa}}$ to the $g(r_1)_{P=2.5\text{GPa}}$ by multiplication with a value of 1.025 and 1.040 for $P=18.2$ GPa and 31.4 GPa, respectively, the three $g(r)$ curves become almost identical to each other (see the inset in Fig. 3a). To get more insight on the structure changes under pressure, partial $g(r)$ are shown in the Fig. 3b~3d for $g_{\text{Pd-Pd}}(r)$, $g_{\text{Pd-Si}}(r)$ and $g_{\text{Si-Si}}(r)$, respectively. For $g_{\text{Pd-Pd}}(r)$, the shape of the partial $g(r)$ for 3 different pressures are almost identical, only difference is the position shifts to the smaller r range as was the same trend in the total $g(r)$. For the $g_{\text{Pd-Si}}(r)$ and $g_{\text{Si-Si}}(r)$, the shapes changed slightly during compression. This is because the **electron distribution around Si atoms can be more easily modified than the Pd atoms**. In the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy, the proportion of $g_{\text{Pd-Pd}}(r)$, $g_{\text{Pd-Si}}(r)$ and $g_{\text{Si-Si}}(r)$ is 0.65, 0.31 and 0.04, respectively. In other word, the total $g(r)$ of $\text{Pd}_{81}\text{Si}_{19}$ is dominated by the $g_{\text{Pd-Pd}}(r)$ with the shape unchanged during compression, which is consistent with trend

observed in the total $g(r)$ in Fig. 3a. This is extra evidence that the amorphous phase of the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy does not change considerably in the studied pressure range. To get more detailed information on atomic structure at the different pressures, reverse Monte Carlo simulations were carried out for $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at three pressure points of 2.5 GPa, 18.2 GPa and 31.4 GPa by simultaneously fitting the experimental $S(q)$ and $g(r)$ data. Figs. 4a and 4b provide a comparison of the experimental (solid line) and simulated (circle) data of $S(q)$ and $g(r)$. The good agreement between the simulations and experiments at all the three pressures ensures that reliable atomic configurations for further analysis were modeled.

3.3. Bond angle distributions

Bond angle distribution (BAD) is frequently used to quantify chemical and topological orderings in liquid and amorphous structures. It is formed by a pair of vectors drawn from a reference atom to its two neighboring atoms within a cutoff distance, which is determined by the location of the first minimum of $g(r)$. It should be stressed that due to the densification effect, the location of the first minimum of $g(r)$ is shifted to left side at higher pressures. Therefore, here we use the cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å at the pressure of 2.5 GPa, 18.2 GPa and 31.4 GPa, respectively. The partial bond angle distributions of the Pd-Pd-Pd, Pd-Si-Pd, Pd-Pd-Si, Si-Pd-Si, Si-Si-Pd and Si-Si-Si triples at different pressures are illustrated in Fig. 5. Among all the 6 triples, there are two main peaks located at the angles of $\sim 58^\circ$ and $\sim 110^\circ$ for Pd-Pd-Pd (Fig. 5a), $\sim 60^\circ$ and $\sim 115^\circ$ for Pd-Si-Pd (Fig. 5b), $\sim 50^\circ$ and $\sim 103^\circ$ for Pd-Pd-Si (Fig. 5c), $\sim 40^\circ$ and $\sim 97^\circ$ for Si-Pd-Si (Fig. 5d), $\sim 50^\circ$ and $\sim 108^\circ$ for Si-Si-Pd (Fig. 5e), $\sim 36^\circ$ and $\sim 100^\circ$ for Si-Si-Si (Fig. 5f). These 6 triples can be divided into 3

groups, i.e., Pd-(Pd/Si)-Pd, Pd-(Pd/Si)-Si and Si-(Pd/Si)-Si. The positions of the two peaks of Pd-(Pd/Si)-Pd are larger than those in Pd-(Pd/Si)-Si, and the locations in Si-(Pd/Si)-Si are the smallest. The wide spread of BADs in these 3 groups indicates complexity of short range ordering in Pd₈₁Si₁₉ glassy alloy. Moreover, there is a hump located around 150° in all 6 partial triples, which is typically associated with some kind of complex polytetrahedral ordering [29]. We found that the pressure effect on the bond angle distribution in Pd₈₁Si₁₉ glassy alloy is not prominent. Only one obvious change of BAD upon pressure is detected in the Si-Pd-Si triples (Fig. 5d) between 18.2 GPa and 31.4 GPa. The first peak intensity increases from 0.5 to 0.75 and the second peak intensity decreases from 0.7 to 0.6 in the BAD during compression from 18.2 GPa to 31.4 GPa. The reason for only change was observed in Si-Pd-Si triplet is that the BAD is sensitive to the neighboring atoms as can be divided into 3 groups. Pd atoms are more stable than Si atoms during compression, so the Si-(Pd/Si)-Si group will change more obviously than the other 2 groups. Since the content of Si-Si-Si triplets is almost negligible, the most obvious changes will be in the Si-Pd-Si triplet if there is any, as observed.

3.4. HA index analysis

We further use the common-neighbor analysis by Honeycutt and Andersen (HA) index [30] to characterize the local environment surrounding each pair of bonded atoms. Four digits are used to describe the common neighbor: (i) the first digit denotes the root pair; (ii) the second digit represents the number of near neighbors shared by the root pair; (iii) the third digit stands for the number of the nearest-neighbor bonds among the shared neighbors; (iv) a

fourth index is used to distinguish configurations with the same first three indices but with a different topology. The results of an HA index analysis of the structures obtained from the RMC simulations are shown in Fig. 6, with the same cutoff distances used in the bond angle distribution analysis. In all three studied pressures, the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy structures are dominated by icosahedral (1551) and distorted icosahedral (1541 and 1431) order. In addition, there are significant amounts of hexagonal close-packed (1422) order and body-centered-cubic (1441 and 1661) crystal-like order, but relatively small amount of face-centered-cubic (1421) order. Only the 1551 bond pairs have slightly changed by about 1.8% with compression from 2.5 GPa up to 31.4 GPa, while all the other type bond pairs keep almost the same fractions during compression, i.e., less than 1% variation. This further confirms that the amorphous phase of $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy does not change much when compressed to 31.4 GPa.

3.5. Voronoi tessellation analysis

While HA index analysis provides information about the local order of the root pair atoms, it cannot differentiate whether or not the complete clusters exist. A more detailed picture of the topology of the polyhedral surrounding Pd and Si atoms is further obtained from Voronoi tessellation analysis [31], which is a more three-dimensional approach than the HA analysis since it provides a more complete geometrical construction of a central atom to its neighboring atoms. The Voronoi polyhedra (VP) are constructed from the perpendicular bisectors between a central atom and all of its neighboring atoms. The VPs are classified based on the number of edges per polyhedral face $\langle n_3, n_4, n_5, n_6, \dots, n_i \rangle$, where n_i is the number

of the i -edged sides of the polyhedron. This method can categorize neighbors as atoms having common faces of polyhedra, and also coordination numbers and bond lengths, both total and partials. Fig. 7a shows the populations of the 11 most abundant VP types from the RMC atomic configurations at three pressures. The same cutoff distances are used as in the bond angle distribution and HA index analyses, i.e., 3.59 Å, 3.50 Å and 3.45 Å for the configurations at the pressure of 2.5 GPa, 18.2 GPa and 31.4 GPa, respectively. Most of the Voronoi types show less than 1% variations under three pressures. Only 2 exceptions that show monotonic increase with increasing pressure are icosahedral $\langle 0, 0, 12, 0 \rangle$ and distorted icosahedral $\langle 0, 1, 10, 2 \rangle$. This observation is consistent with the HA index analysis in which only the 1551 pairs slightly increases while others keep almost constant. Fig. 7b shows the coordination number (CN) distribution of the VPs at different pressures. The CN=12 and CN=13 VPs dominate in all three pressures, both having the population about 30%, followed by the CN=11 and CN=14 VPs, both containing about 15%. The CN=10 and CN=15 VPs have population about 5%, while those VPs with CN<10 and CN>15 are negligible. The average coordination numbers in total, Pd-centered partial and Si-centered partial in Pd₈₁Si₁₉ glassy alloy remain almost unchanged at three studied pressures within the experimental uncertainty. They are in total CN=12.4±0.1, Pd-centered partial CN=12.7±0.1 and Si-centered partial CN=10.9±0.2 in Fig. 8a. We note that in Fig. 4 in ref. [32], changes of the average CN and the distribution of CN in La₇₅Al₂₅ glassy alloy were reported from low to high pressure, which are different from our case. However, it should be noted that the estimation of CN is very sensitive to the cutoff distances used. The average number of Pd atoms (10.6±0.1) and

Si atoms (2.1 ± 0.1) around Pd-centered VPs as well as the average number of Pd atoms (9.4 ± 0.1) and Si atoms (1.5 ± 0.2) around Si-centered VPs are shown in Fig. 8b. The patterns in both Figs. 8a and b are almost identical to each other at the three pressures studied. Pressure dependencies of Voronoi polyhedra distribution (Fig. 7) and coordination number distribution (Fig. 8) clearly indicate the absence of dramatic atomic structure changes in the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy during compression up to 31.4 GPa.

To clearly illustrate how the local chemical environment changes during compression, the coordination number of both Pd-centered VPs and Si-centered VPs are separated into m Pd atoms and n Si atoms, respectively, giving $\text{CN} = m + n$. Now, a given Voronoi polyhedron composed of m Pd atoms and n Si atoms is denoted by an index (m, n) [33]. The fractions of the different (m, n) VPs in Pd- and Si-centered Voronoi polyhedra are presented in Figs. 9a and 9b, respectively, at 2.5 GPa, 18.2 GPa and 31.4 GPa. In Pd-centered clusters, the (11, 2), (11, 1), (10, 2) and (10, 3) types are most abundant at all three pressures, while the (10, 1), (9, 1) and (9, 2) types have the leading population in Si-centered VPs. Although slight changes are observed at 31.4 GPa, the distributions for both Pd- and Si-centered VPs are almost the same at studied pressures, again indicating the similarity in the atomic structures of the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at three pressures.

The bond length gives a more straight forward view on inter-atomic distances variation with pressure. The nearest distances between the central atom and the shell atoms of the Voronoi polyhedra were statistically calculated for all the Pd- and Si-centered VPs and the results are shown in Fig. 10. It shows that Si-Si decreases quicker at higher pressure,

especially from 18.2 to 31.4 GPa. This shortening is responsible for the slight changes in bond angle distribution detected in Fig. 5d, and chemical differences detected in Fig. 9 between these two pressures. Although the structure of Pd₈₁Si₁₉ glassy alloy is very stable up to ~35 GPa, we believe that the topological environment could be altered if the material is compressed to higher pressures when r_{Pd-Pd} / r_{Si-Si} ratio reaches a critical value [34,35], such as the observation of dramatic density deviation in the Zr₅₇Nb₅Cu_{15.4}Ni_{12.6}Al₁₀ amorphous alloy in parallel plate impact experiments [8]. But this kind of topological transition is different from the polyamorphism observed in the rare-earth based glassy alloys or in the CaAl glassy alloys which was due to the electronic structure changes. It is possible that atomic size ratio change can lead to the phase transitions in glassy material systems.

4. Conclusions

In summary, we have performed *in situ* high pressure x-ray diffraction experiments and reverse Monte Carlo simulations on Pd₈₁Si₁₉ glassy alloy up to about 35 GPa. The results shows a monotonic change of the inverse FSDP position of the diffraction patterns and the real space atomic pair correlation function can be scaled with the pressure. The volume dependence of pressure can be well described by a third-order Birch-Murnaghan equation of state indicating the absence of phase transformation in the studied pressure range in Pd₈₁Si₁₉ glassy alloy. Based on the RMC simulations, detailed atomic structure analyses confirmed that the topological and chemical atomic structures of the Pd₈₁Si₁₉ glassy alloy do not change much upon compression, by the means of bond angle distribution, HA index, Voronoi tessellation, total and partial coordination numbers and local chemical ordering analyses. The

obtained results reveal that the atomic structure of $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy under pressure (up to about 35 GPa) is extremely stable. In addition, it is still possible that the instability of atomic clusters in glassy alloys occurs at even higher pressures via a big change in atomic size ratio.

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Figure Captions

FIG. 1. *In situ* x-ray diffraction patterns of $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy under high pressure obtained from SSRF. The position of the main amorphous diffraction peak shifts to the higher q range with increasing pressure as a result of densification. The sample remained amorphous nature in the entire pressure range.

FIG. 2. The inverse FSDP position dependence of pressure of $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy, showing monotonic decreasing trend without noticeable deviation. Red stars are the data obtained from DESY experiments. The inset shows the relative volume change with pressure and the third-order Birch-Murnaghan equation of state is given by the solid line. The good agreement of equation of state and experimental relative volume change does not indicate any first-order phase transitions in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy within the studied pressure range.

FIG. 3. (a) The experimental total atomic pair correlation functions, $g(r)$, of the $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at three different pressures, 2.5 GPa, 18.2 GPa and 31.4 GPa obtained from DESY. The inset is the pair correlation functions with normalized r values, i.e. $r_2^* = r_2 \times 1.025$ and $r_3^* = r_3 \times 1.040$. The partial pair correlation functions of (b) $g_{\text{Pd-Pd}}(r)$, (c) $g_{\text{Pd-Si}}(r)$ and (d) $g_{\text{Si-Si}}(r)$ are also plotted.

FIG. 4. Comparison of the experimental (solid line) and simulated (circle) data of $S(q)$ (a), and $g(r)$ (b), showing good agreement which allows us to get reliable atomic configurations for further structure analysis.

FIG. 5. Calculated bond angle distributions of $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively. (a) Pd-Pd-Pd, (b)

Pd-Si-Pd, (c) Pd-Pd-Si, (d) Si-Pd-Si, (e) Si-Si-Pd and (f) Si-Si-Si.

FIG. 6. Populations of top HA indices in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively.

FIG. 7. (a) Populations of dominant Voronoi polyhedra, (b) coordination number distribution among all the VPs in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively.

FIG. 8. (a) Total, Pd-centered partial and Si-centered partial average CNs, and (b) average atomic constituent information of Pd- and Si-centered VPs in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively.

FIG. 9. Fractions of the local chemical distribution around (a) Pd and (b) Si atoms in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively.

FIG. 10. The nearest bond distances among Pd-Pd, Si-Si, and Pd-Si pairs statistically calculated from all the Voronoi polyhedral in $\text{Pd}_{81}\text{Si}_{19}$ glassy alloy at 2.5 GPa, 18.2 GPa and 31.4 GPa, using cutoff distances of 3.59 Å, 3.50 Å and 3.45 Å, respectively.