Invariance of the relation between α relaxation and β relaxation in metallic glasses to variations of pressure and temperature

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(Received 28 June 2020; revised 13 August 2020; accepted 14 September 2020; published 28 September 2020)

Dielectric relaxation experiments performed at ambient and elevated pressures P in molecular, ionic, and polymeric glass formers have established that the relation of the Johari-Goldstein (JG) β-relaxation time $\tau_\beta(T, P)$ to the α-relaxation time $\tau_\alpha(T, P)$ is invariant to changes of T and P while the latter is kept constant. This property of the JG β relaxation is remarkable despite the fact that the invariance of the ratio $\tau_\beta(T, P)/\tau_\alpha(T, P)$ from experiment is sometimes approximate because the β relaxation is composed of a distribution of processes, and the $\tau_\beta(T, P)$ determined can be arbitrary. The property indicates the fundamental importance of the JG β relaxation and it cannot be neglected whenever the α relaxation is considered. Notwithstanding, the property has not been checked on whether it applies to metallic glasses. Conventional experiment techniques cannot fulfill the task, and the alternative is molecular dynamics simulations. In this paper we report the results of molecular dynamics simulations of dynamical mechanical spectroscopy performed on two very different metallic glasses, $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$, at different pressures P. The JG β relaxation appears as an excess wing on the low-temperature side of the α loss peak at $T_{\alpha,P}$ in the isochronal loss modulus spectra $E_P''(T)$. On the other hand, the isochronal non-Gaussian parameter $\alpha 2_P(T)$ peaks at the temperature $T_{\alpha 2,P}$ different from $T_{\alpha,P}$ of $E''_P(T)$. From the fact that $T_{\alpha 2,P}$ is significantly lower than $T_{\alpha,P}$, we identified the peak temperature $T_{\alpha 2,P}$ of $\alpha 2_P(T)$ with the JG β relaxation, and hence the JG β relaxation is fully resolved by studying the isochronal non-Gaussian parameter $\alpha 2_P(T)$. After scaling temperature by $T_{\alpha,P}$, the normalized $E_P''(T/T_{\alpha,P})$ and $\alpha 2_P(T/T_{\alpha,P})$ both show superposition of data taken at various pressures for all $T/T_{\alpha,P}$ covering the JG β relaxation and the α relaxation. Moreover the ratio $T_{\alpha 2,P}/T_{\alpha,P}$ is invariant to changes of T and P while $\tau_\alpha(T, P)$ is maintained constant. Thus we have verified for two different metallic glasses, $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$, that $\tau_\alpha(T, P)/\tau_\beta(T, P)$ is invariant to changes of T and P at constant $\tau_\alpha(T, P)$, as found in soft matter.

DOI: 10.1103/PhysRevB.102.094205

I. INTRODUCTION

Chronologically the dynamics of glass formers starts at short times when all basic units, atomic, molecular, or particles, are mutually caged via the intermolecular potential. According to the coupling model [1–4] the caged dynamics is not a relaxation process. Manifesting in susceptibility as the nearly constant loss (NCL) the caged dynamics has no characteristic time, and it persists until the cages decay first by the local and independent relaxation with primitive relaxation time τ_0 [1–5]. The caged dynamics in the coupling model (CM) is different from that in the mode coupling theory of Götze [6]. The latter does not have the NCL but instead a susceptibility minimum generated by the sum of two power laws. The onset of cage decay in the CM is followed in time by relaxations of an increasing number of units and stochastically at locations with overlap [1–5] before arriving at the structural α relaxation. The collection of these relaxation processes with a distribution of relaxation times is defined [1–6] effectively as the Johari-Goldstein (JG) β relaxation [7,8], which does not contribute to viscosity η or diffusion constant D. Notwithstanding, the β relaxation is indispensable for the onset of the structural α relaxation. In Fig. 1 we utilize the isochronal loss modulus $G''(T)$ of $Zr_{65}Al_{7.5}Cu_{27.5}$ measured by Rösner *et al.* [9] to show the NCL of caged dynamics and termination by the JG β relaxation which acts as the precursor of the α relaxation. The complementary Fig. S1 in the Supplemental Material (SM) [10] shows the relationship of NCL, JG β relaxation, and the α relaxation in a hypothetical isothermal dielectric loss spectrum. This view of how the dynamics evolve with time is supported by the time-resolved all-particles motion data of colloidal particles by confocal microscopy [11,12], the MD simulations results of binary Lennard-Jones particles [13] and related model systems [14,15], ions in glasses [16,17], a polymer [18], binary metallic alloys $Zr_{50}Cu_{50}$ [19,20] and $Ni_{80}P_{20}$ [21,22], and experiment [23]. It was envisaged by theoretical models [1–4,24]. Some of the examples given are in the liquid state while the metallic glasses we studied in this paper are glasses. Notwithstanding, the relations between the caged dynamics, JG β relaxation, and the α relaxation are the same in the liquid or in the glassy state.

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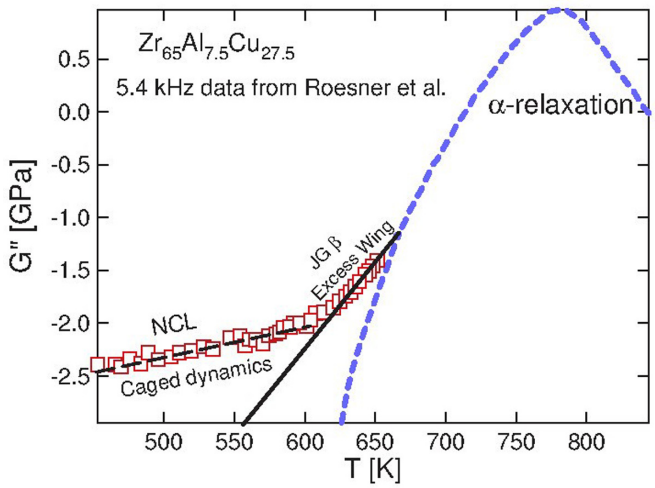

FIG. 1. The loss modulus $G''(T)$ of $Zr_{65}Al_{7.5}Cu_{27.5}$ measured by Rösner *et al.* [9] (open squares), and the calculated the isochronal shear loss modulus at 5.4 kHz contributed by the dominant α relaxation, $G''_{\alpha}(T)$ (dashed line). The JG relaxation is not resolved as a loss peak and instead appears as an excess wing. The most probable temperature of the JG relaxation at 5.4 kHz is estimated to lie between $T_{\rm JG} = 647$ and $T_{\rm JG} = 635$ K.

The fact that the JG β relaxation is dynamically heterogeneous and distributed is not only obvious from some the papers cited in the above, but also this property was anticipated in the island of mobility model [7,25,26] and in the CM [27]. It was verified in metallic glasses by experiments [28–30] and simulations [19–22]. In molecular glass formers it was found by deuteron NMR experiment [31]. Despite the heterogeneous nature of the JG β relaxation, a single relaxation time τ_β determined from fit to the susceptibility frequency spectrum by some empirical function is often used to stand for the distribution of relaxation times.

The caged dynamics and the JG β relaxation are not independent and instead are linked. This property was verified in many glass formers by the termination of the caged dynamics regime by the onset of the JG β relaxation observed in the susceptibility spectra [1,2,5], or by the change in temperature dependence of the caged dynamics at the secondary glass transition temperature $T_{g\beta}$ in molecular [32,33] and polymeric [34] glass formers, and also in metallic glasses [35]. In turn, the JG β relaxation is strongly linked to the onset of structural α relaxation by various properties [3,36,37], and also in metallic glasses [21,22]. The property we emphasize in this paper is the approximate invariance of the relation between the JG β and the α relaxation times, $\tau_\beta(T,P)$ and $\tau_\alpha(T,P)$, to changes of temperature T and pressure P while keeping $\tau_\alpha(T,P)$ constant. This is a general property observed in various glass formers [3–5,36–46]. It is fundamentally important because it implies that the α relaxation is strongly linked to and inseparable from the JG β relaxation. It even implies that the dependence of τ_α on specific volume and entropy actually originates from τ_β [36,38–42], and therefore no glass transition theory is complete without considering the role of the JG β relaxation. Although this fundamentally important property had been verified in many different glass formers, it has not been investigated before on whether it applies to metallic glasses. Conventional experimental measurements at elevated pressure would be difficult if not impossible to use because the material is metallic and is in the glassy state. Nevertheless, molecular dynamic simulations when combined with the dynamic mechanical spectroscopy (MD-DMS) method [19–22] possibly can give an answer to this question. In metallic glasses, usually the isochronal mechanical loss moduli E'' is obtained as a function of temperature by dynamic mechanical spectroscopy at low frequencies around 1 Hz and corresponding long times t_p of the order of 0.1 s. On the other hand, combined with the dynamic mechanical spectroscopy method (MD-DMS), molecular dynamics simulations make it possible to study the relaxation of metallic glasses at elevated pressures [19–22].

In this paper, we study the relation of the JG β relaxation and the caged dynamics to the α relaxation through the MD-DMS method. By calculating the loss modulus $E_P''(T)$ and the dynamic heterogeneity $\alpha 2_P(T)$, we find that the relation of the JG β-relaxation time $\tau_\beta(T,P)$ and the caged dynamics to the α-relaxation time $\tau_\alpha(T,P)$ is insensitive to changes of T and P while $\tau_\alpha(T,P)$ is kept constant. These are verified by superposition of the data after normalizing $E_P''(T)$ by the peak height $E_{P,\max}''$ and scaling T by $T_{\alpha,P}$ for the metallic glasses $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$. Furthermore, we show after scaling the temperature dependence of $\alpha 2_P(T)$ by $T_{\alpha,P}$ that the normalized $\alpha 2_P(T/T_{\alpha,P})/\alpha 2_{P,\max}(T/T_{\alpha,P})$ has approximately the same shape, and the ratio of the two peak temperatures, $T_{\alpha 2,P}/T_{\alpha,P}$, is independent of P. The reason is that the $\alpha 2_P(T)$ data encompass both the caged dynamics regime and the JG β-relaxation spectral range, and the peak is dominated by the latter and its heterogeneous dynamics. It is the isochronal analog of the approximate invariance of the ratio $\tau_\alpha(T,P)/\tau_\beta(T,P)$ to variations of T and P while $\tau_\alpha(T,P)$ is maintained constant, which was found in many nonmetallic glass formers [3–5,36–46]. Thus, we can conclude that the relation of the caged dynamics and the JG β relaxation to the α relaxation in the two metallic glasses is invariant to a change of pressure at constant $\tau_\alpha(T_{a,P},P) = t_p$ for all P. This result for metallic glasses is remarkable because high pressure causes marked changes to the local structure, medium range order, and density of metallic glasses, as can be inferred from the change in the total radial distribution functions [19,20]. The paper is organized as follows. In Sec. II the models of the two metallic glasses $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ and the methods of simulation are given. The simulations are described and the results presented in Sec. III. The results are discussed and conclusions are drawn in Sec. IV.

II. MODELS AND METHODS

In order to ensure our results and conclusions are general, we performed the DMS simulations with different loading frequencies in two distinct model metallic glass systems (metal-metal $Zr_{50}Cu_{50}$ and metal-metalloid $Ni_{50}P_{50}$ systems) with various thermal histories.

A. Model systems

Molecular dynamics (MD) simulations were performed by the open source code LAMMPS [47]. A series of simulations based on $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ were performed by the embedded atom method potential [48–50], for

system size $N_{Zr_{50}Cu_{50}} = 8000$ (5.2 nm × 5.2 nm × 5.2 nm) and $N_{Ni80P20} = 32\,000$ (7.5 nm × 7.5 nm × 7.5 nm) respectively. Samples were prepared under different external pressures for comparing the results at different pressures.

The $Zr_{50}Cu_{50}$ samples were equilibrated at 1900 K with constant number, pressure (0 and 15 GPa) and temperature (*NPT*) ensembles for 10 ns. Next, the samples were quenched down to 50 K, step by step with the step size of 50 K at a rate of 0.1 K/ps with the corresponding *NPT* ensembles. At the end we obtained the samples under external pressures of 0 and 15 GPa at the cooling rate of 0.1 K/ps at different temperatures. To confirm the validity of the following results, the samples with external pressures, 0 and 15 GPa, at a different rate of 10 K/ps were prepared using the same method.

The $Ni_{80}P_{20}$ samples were prepared by quenching a liquid from 1000 to 200 K at a rate of 0.1 K/ns (10^8K/s). Such a slow cooling rate is about two to three orders of magnitude slower than most of the MD simulations of MGs conducted thus far. *NPT* ensembles were used during the quenching. The external pressure was adjusted to five different values of $P = -10, -4, 0, 5$, and 10 GPa.

During the quenching process, configurations of each sample at the temperatures of interest were collected for further study by dynamical mechanical spectroscopy (DMS). All simulations were applied under periodic boundary condition in all three directions. The temperature is maintained by the Nosé-Hoover thermostat [51] and the time step is 2 fs.

B. Molecular dynamics simulation of dynamical mechanical spectroscopy

In the MD-DMS method, we apply ten full cycles of sinusoidal strain $\varepsilon(t) = \varepsilon_A \sin(2\pi t/t_p)$ to the $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ metallic glasses (MGs). For the $Zr_{50}Cu_{50}$ samples, the sinusoidal strain is along the xy direction, where t_p is set at 100 ps and ε_A at 2%. For the $Ni_{80}P_{20}$ samples, the sinusoidal strain is along the x direction, where t_p is set at 100 ns and ε_A at 0.71%. The two values of ε_A are in the linear elastic region to ensure the deformations do not change the structure of the MGs. To make possible the statistical analysis of the results and to avoid the dependence on the initial state, we perform 50 independent MD-DMS loadings for the $Zr_{50}Cu_{50}$ samples, at every temperature of interest, which all started from the same initial configuration but with momenta randomly assigned from the Maxwell-Boltzmann distribution at the specific temperature. Then the mean resultant stress obtained from the 50 independent MD-DMS loading processes were fitted by the formula $\sigma(t) = \sigma_0 + \sigma_A \sin(2\pi t/t_p + \delta)$, where σ_A is maximum stress and δ is the phase shift between strain and stress. Finally, the formulas $E'' = (\sigma_A/\varepsilon_A) * \sin(\delta)$ and $E' = (\sigma_A/\varepsilon_A) * \cos(\delta)$ were used to calculate the loss and storage modulus respectively. All the MD-DMS loading processes were performed under the condition of constant number, volume, and temperature (*NVT*) ensemble.

III. RESULTS

A. $Zr_{50}Cu_{50}$

The glassy samples were prepared by different cooling rates at either zero pressure or under elevated pressures as described. The procedure used to tune the state of metallic glasses by the cooling rate and pressure during the quenching process as well as the characterization of the structures by the total radial distribution functions has been given in Refs. [19,20]. Prominent changes in the local structure, medium-range order, and density were found by pressure elevated to 15 GPa.

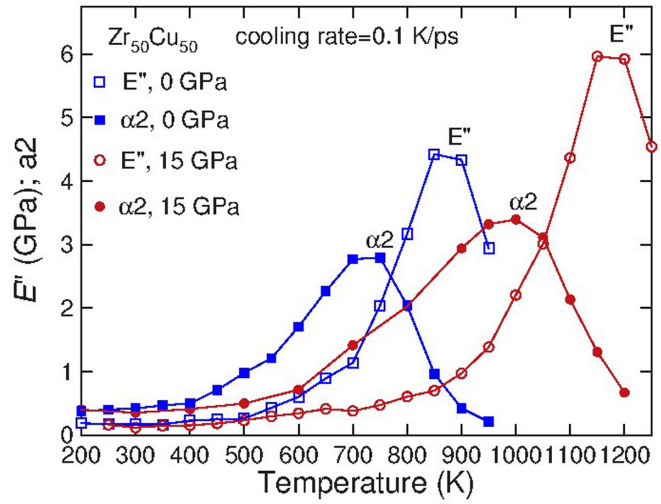

FIG. 2. The loss modulus $E_P''(T)$ and the non-Gaussian parameter $\alpha 2_P(T)$ at $P = 0$ and 15 GPa of $Zr_{50}Cu_{50}$ metallic glass prepared by the cooling rate of 0.1 K/ps.

By using the MD-DMS simulations method described before, the loss moduli $E_P''(T)$ were obtained as a function of T for samples of $Zr_{50}Cu_{50}$ prepared at two different cooling rates and pressures, $P = 0$ and 15 GPa, with the choice of $t_p = 100$ ps. The results are shown in Figs. 2 and 3 for cooling rates of 0.1 and 10 K/ps respectively. The loss modulus $E_P''(T)$ shows a peak contributed by the α relaxation, which is accompanied by a broad shoulder contributed by the not fully resolved β relaxation at lower temperatures than the peak. At

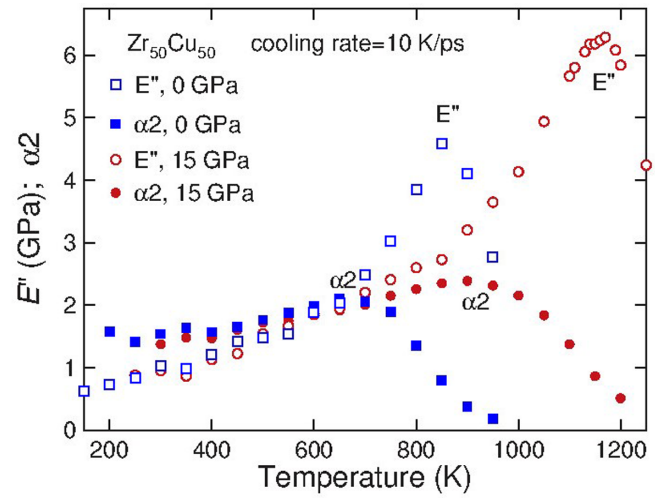

FIG. 3. The loss modulus $E_P''(T)$ and the non-Gaussian parameter $\alpha 2_P(T)$ at $P = 0$ and 15 GPa of $Zr_{50}Cu_{50}$ metallic glass prepared by the cooling rate of 10 K/ps.

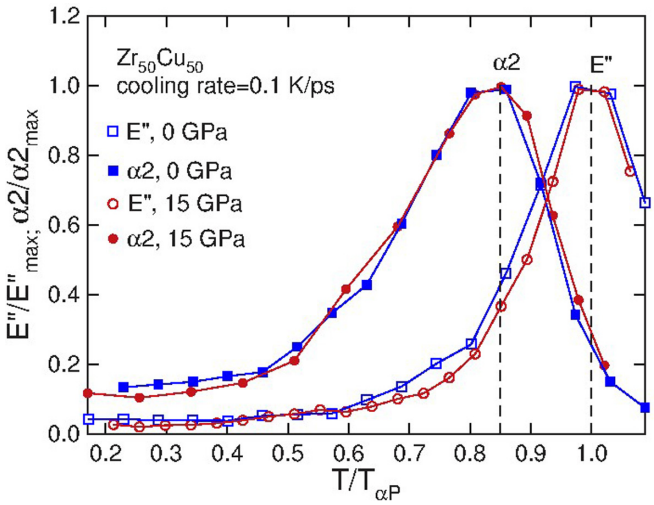

FIG. 4. The data of $E_P''(T)$ and $\alpha 2_P(T)$ at $P = 0$ and 15 GPa from Fig. 1 are normalized by the respective peak values. Temperature is scaled by $T_{\alpha,P}$. The broken line on the left indicates the value of $T_{\alpha 2,P}/T_{\alpha,P}$, which is independent of P.

the α-loss peak temperature $T = T_{\alpha,P}$, the α-relaxation time is equal to t_p, i.e.,

$$\tau_\alpha(T_{\alpha,P}, P) = t_p, \tag{1}$$

for all P. At temperature lower than $T_{\alpha,P}$, the loss modulus $E_P''(T)$ is contributed by the JG β relaxation and the caged dynamics at even lower temperatures, as found in dynamic mechanical measurements [9,24,35] (see Fig. 1). If the relation of the JG β-relaxation time $\tau_\beta(T, P)$ and the caged dynamics to the α-relaxation time $\tau_\alpha(T, P)$ are insensitive to changes of T and P while $\tau_\alpha(T, P)$ is kept constant, it can be verified by superposition of the data after normalizing $E_P''(T)$ by the peak height $E_{P,\max}''$ and scaling T by $T_{\alpha,P}$. As shown in Figs. 4 and 5, good superposition of the normalized and scaled $E_P''(T/T_{\alpha,P})$ data of $Zr_{50}Cu_{50}$ at zero and 15 GPa pressures

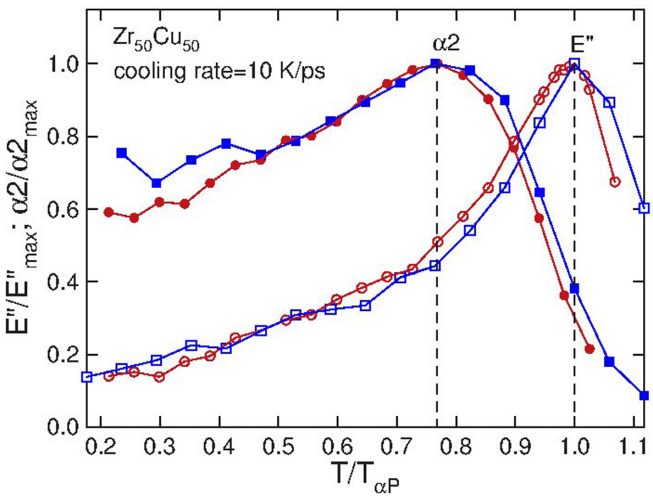

FIG. 5. The data of $E_P''(T)$ and $\alpha 2_P(T)$ at $P = 0$ and 15 GPa from Fig. 2 are normalized by the respective peak values. Temperature is scaled by $T_{\alpha,P}$. The broken line on the left indicates the value of $T_{\alpha 2,P}/T_{\alpha,P}$, which is independent of P.

was obtained for the entire range of $T/T_{\alpha,P}$ covering the α-loss peak and the JG β relaxation. In the scaled $E_P''(T/T_{\alpha,P})$ data of $Zr_{50}Cu_{50}$, although the JG β relaxation is not fully resolved, its presence is suggested by the excess loss shown by the broad shoulder on the low-temperature side of the α-loss peak at $T/T_{\alpha,P} = 1$.

As an assist to $E_P''(T)$ in our study of the β relaxation in $Zr_{50}Cu_{50}$, we examine additionally the non-Gaussian parameter

$$\alpha_2(t) = 3\langle r^4(t)\rangle/5\langle r^2(t)^2\rangle - 1. \tag{2}$$

It is the indicator of the dynamical heterogeneity of all processes including the caged dynamics, the β relaxation, and the α relaxation. For each metallic glass $Zr_{50}Cu_{50}$ prepared under pressure P, we computed $\alpha_2(t)$ at $t = t_p$ as a function of temperature over broad temperature range from way below $T_{\alpha,P}$ to above $T_{\alpha,P}$ at which $\tau_\alpha(T, P)$ is equal to t_p. Denoted by $\alpha 2_P(T)$ as shown in Figs. 2 and 3, the result shows it increases with increasing temperature to exhibit a peak at $T_{\alpha 2,P}$. Since $T_{\alpha 2,P}$ lies far below $T_{\alpha,P}$, the $\alpha 2_P(T)$ peak at $T_{\alpha 2,P}$ cannot be associated with the α relaxation. It has to be identified with the β relaxation, even though it is not resolved in $E_P''(T)$. This association is also suggested by the results obtained before at ambient pressure and shown in Figs. 1(a) and 1(b) in Ref. [19]. It is made clearer by the illustrations of data from samples prepared at ambient pressure for three different cooling rates in Fig. S2 in the Supplemental Material [10]. At $T_{\alpha 2,P}$, the characteristic β-relaxation time $\tau_\beta(T_{\alpha 2,P}, P)$ is equal to t_p. Thus like Eq. (1) for $\tau_\alpha(T_{\alpha,P}, P)$, we also have

$$\tau_\beta(T_{a2,P}, P) = t_p. \tag{3}$$

In order to see via $\alpha 2_P(T)$ if the relation between the JG β relaxation and the α relaxation is invariant to changes of P and T at constant τ_α, temperature is scaled by $T_{\alpha,P}$. Furthermore, $\alpha 2_P(T/T_{\alpha,P})$ are normalized by the respective peak heights $\alpha 2_{P,\max}$. The $T_{\alpha,P}$-scaled and normalized $\alpha 2_P(T/T_{\alpha,P})/\alpha 2_{P,\max}$ for $Zr_{50}Cu_{50}$ at cooling rates of 0.1 and 10 K/ps are presented in Figs. 4 and 5 respectively. It is made clearer by the illustrations of data obtained from samples under different conditions in Fig. 6. By inspection of the figures, it is clear that the ratio $T_{\alpha 2,P}/T_{\alpha,P}$, as well as the $T_{\alpha,P}$-scaled temperature dependence of $\alpha 2_P(T/T_{\alpha,P})$ covering both the α and the JG β relaxations, is invariant to change of pressure at constant $\tau_\alpha(T_{\alpha,P}, P) = t_p$ for all P. These results derived by isochronal considerations are equivalent to having verified that the ratio $\tau_\alpha(T, P)/\tau_\beta(T, P)$ is invariant to P and T at constant $\tau_\alpha(T, P)$ as found generally in soft matter.

The $T_{\alpha,P}$-scaled and normalized data of $E_P''(T)$ are shown in Figs. 4 and 5. Although $E_P''(T/T_{\alpha,P})/E_{P,\max}''$ shows the JG β relaxation as a broad shoulder and not a resolved peak, this isochronal spectrum covering both the α and the JG β relaxations is invariant to change of pressure at constant $\tau_\alpha(T_{\alpha,P}, P) = t_p$ for all P. Therefore $E_P''(T/T_{\alpha,P})/E_{P,\max}''$ also verifies the invariance property in $Zr_{50}Cu_{50}$. To clarify the correlation between the loss modulus and the non-Gaussian parameter, we plot the data of E'' as a function of $\alpha 2_{P,\max}$ in Fig. 7(a) and the scaled data in Fig. 7(b); the collapse of the data indicates the intrinsic correlation between the loss modulus and the non-Gaussian parameter which had been proposed in Ref. [20].

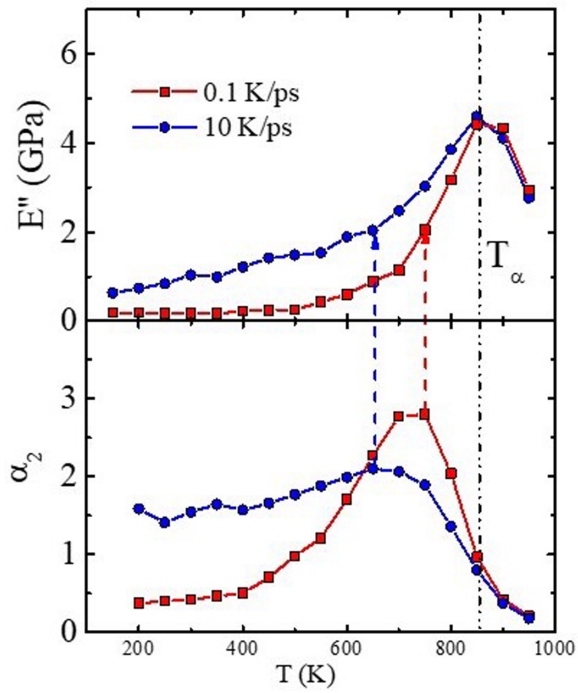

FIG. 6. The panel on top shows the loss modulus E'' as a function of temperature T for samples prepared at different cooling rates of 0.1, and 10 K/ps respectively. The bottom panel shows the non-Gaussian parameter $\alpha 2$ vs temperature T for samples prepared at the different cooling rates as in the upper panel.

The results collected in Figs. 4 and 5 showing the invariance property are important because invariance holds despite pronounced changes of atomic structure and density on varying pressure. Thus, the finding from this study in metallic glasses is the strong connection of the JG β relaxation to the structural α relaxation independent of P and T, like that found generally in molecular glass formers [3,4,36–46].

B. $Ni_{80}P_{20}$

In support of the results from $Zr_{50}Cu_{50}$ obtained and reported in the previous subsection are general, we performed MD simulations and MD-DMS independently to obtain $E_P''(T)$ and $\alpha 2_P(T)$ of a different metallic glass, $Ni_{80}P_{20}$, where the JG β relaxation exhibits a more prominent broad shoulder on the low-temperature side of the α-loss peak than that of $Zr_{50}Cu_{50}$. The samples of $Ni_{80}P_{20}$ were prepared at drastically different cooling rates than those of $Zr_{50}Cu_{50}$ and t_p is set at 100 ns instead of 100 ps. The loss modulus $E_P''(T)$ and the non-Gaussian parameter $\alpha 2_P(T)$ were calculated for several samples all cooled at 0.1 ns/K at five different pressures $P = -10$, -4, 0, 5, and 10 GPa. The results of $E_P''(T)$ presented in Fig. 8 show α-loss peaks at temperatures $T_{\alpha,P}$, which increases with P. The β relaxation is not resolved but its presence is indeed suggested by the broad shoulder on the low-temperature side of the α-loss peak. After $E_P''(T)$ is normalized by the α-loss peak value $E''_{P,\max}$ and temperature is scaled by $T_{\alpha,P}$, the result $E_P''(T/T_{a,P})/E''_{P,\max}$ as a function of $T/T_{\alpha,P}$ is shown in Fig. 9. Despite some scattering of the data, the shoulder representing the β relaxation in $E_P''(T/T_{a,P})/E''_{P,\max}$ seems unchanged for different pressures like that found in Figs. 4 and 5 for $Zr_{50}Cu_{50}$.

The $\alpha 2_P(T)$ data of $Ni_{80}P_{20}$ in Fig. 10(a) exhibit a peak at $T = T_{\alpha 2,P}$. From the fact that $T_{\alpha 2,P}$ is appreciably lower than $T_{\alpha,P}$, it follows the $\alpha 2_P(T)$ peak at $T = T_{\alpha 2,P}$ is associated with the JG β relaxation. Like $T_{\alpha,P}$, the value of $T_{\alpha 2,P}$ also increases with P. In Fig. 10(b), the $\alpha 2_P(T)$ data were normalized by the peak heights and temperature was scaled by $T_{\alpha 2,P}$ to show that the shape is independent of P and T within the scatters of the data. The link of $\alpha 2_P(T)$ to $E_P''(T)$ is demonstrated in Fig. 11, where temperature of all the data in Figs. 8 and 10(a) were scaled by $T_{\alpha,P}$ of the α relaxation. Found again in the figure is invariance of the ratio, $T_{\alpha 2,P}/T_{\alpha,P}$ to changes of pressure as well as the $T_{\alpha,P}$-scaled temperature dependence of $\alpha 2_P(T/T_{\alpha,P})$ covering both the α and the β relaxations.

Done independently and differently, the results of MD simulations of dynamical mechanical spectroscopy of $Ni_{80}P_{20}$ confirms those of $Zr_{50}Cu_{50}$. The scaled $E_P''(T/T_{\alpha,P})$ data of $Ni_{80}P_{20}$ in Fig. 11, exhibit a shoulder on the low-temperature side of the α-loss peak, which can be identified as the contribution from the JG β relaxation. The location on the $T/T_{\alpha,P}$ axis of the shoulder does not depend on pressure. This result from $E_P''(T/T_{\alpha,P})$ also can be taken as direct evidence of

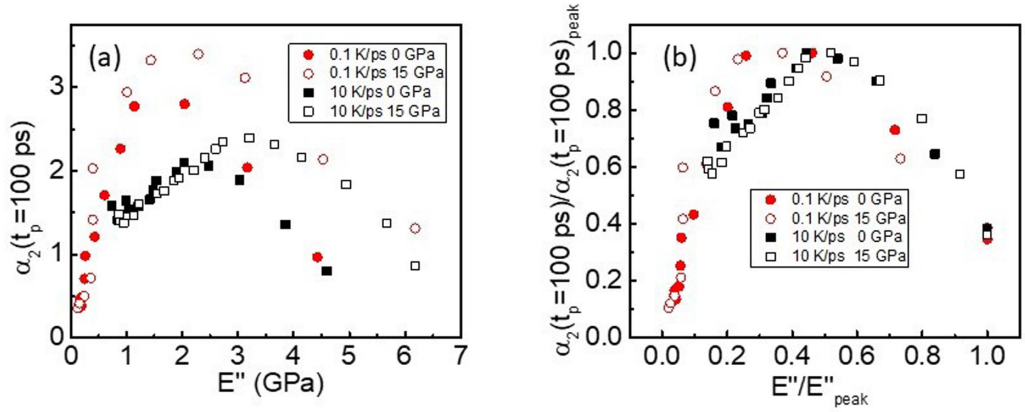

FIG. 7. (a) The data of $\alpha 2_P(T)$ vs $E_P''(T)$ for $Zr_{50}Cu_{50}$ metallic glass. (b) The normalized $\alpha 2_P(T)$ vs normalized $E_P''(T)$ for $Zr_{50}Cu_{50}$ metallic glass.

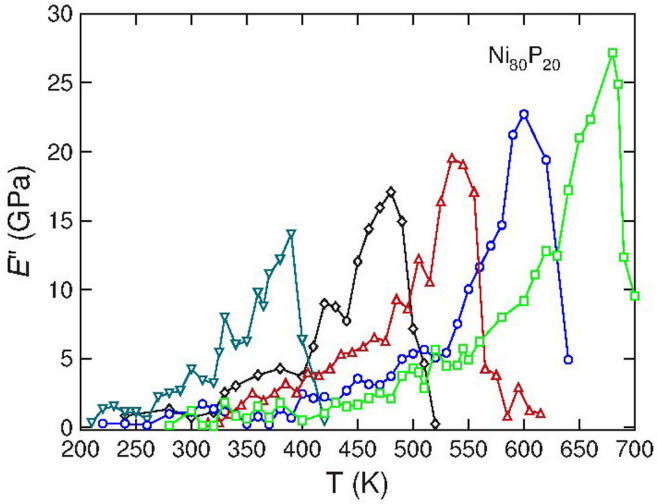

FIG. 8. The loss modulus $E_P''(T)$ at five different pressures of $P = -10$, -4, 0, 5, and 10 GPa of $Ni_{80}P_{20}$ metallic glass prepared by the cooling rate of 0.1 K/ns.

invariance of the relation between $T_{\beta,P}$ and $T_{\alpha,P}$, the JG β and α relaxation temperatures, in the metallic glasses.

IV. DISCUSSION AND CONCLUSION

In the sections presented above we report the results of MD simulations of dynamical mechanical spectroscopy (MD-DMS) in two different metallic glasses $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ performed independently on samples prepared under different conditions. The $Zr_{50}Cu_{50}$ is composed of two metallic elements, while $Ni_{80}P_{20}$ is formed from a metal and a metalloid. The objective of the work is to investigate whether the JG β relaxation in metallic glasses is strongly related to the α-relaxation in properties, like the invariance of $\tau_\alpha(T,P)/\tau_\beta(T,P)$ to P and T at constant $\tau_\alpha(T,P)$ found in other molecular and polymeric glass formers [3,4,36–46]. The JG β relaxation of $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ is not fully

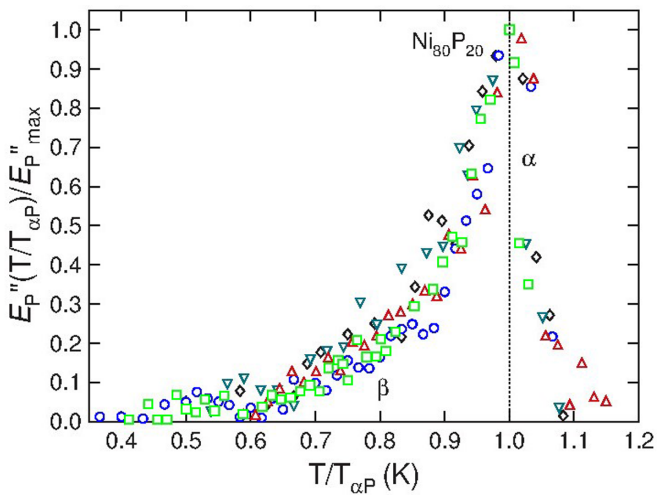

FIG. 9. The data of $E_P''(T)$ at $P = -10$, -4, 0, 5, and 10 GPa of $Ni_{80}P_{20}$ metallic glass from Fig. 5 are normalized by the respective peak values. Temperature is scaled by $T_{\alpha,P}$.

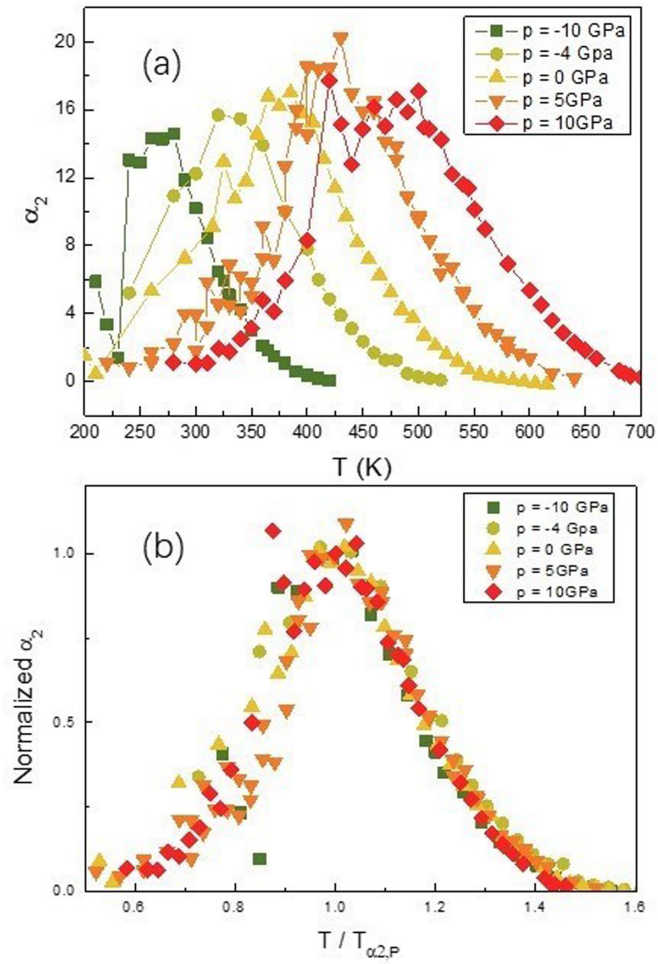

FIG. 10. (a) The non-Gaussian parameter $\alpha 2_P(T)$ at $P = -10$, -4, 0, 5, and 10 GPa of $Ni_{80}P_{20}$ metallic glass. (b) The data of $\alpha 2_P(T)$ from (a) are normalized by the respective peak values. Temperature is scaled by $T_{\alpha 2,P}$.

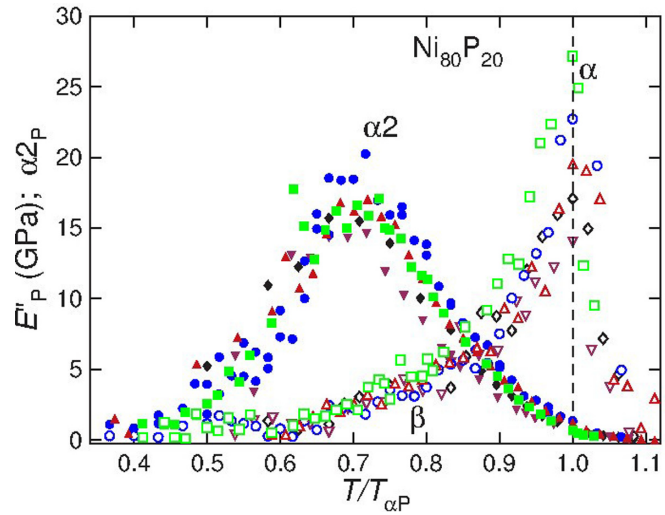

FIG. 11. The temperature dependence of $E_P''(T)$ and $\alpha 2_P(T)$ at $P = -10$, -4, 0, 5, and 10 GPa of $Ni_{80}P_{20}$ metallic glass is scaled by $T_{\alpha,P}$.

resolved in the isochronal loss modulus $E_P''(T)$ and appears as a shoulder. The isochronal $E_P''(T)$ data alone at different pressures do support that the relation between the JG β relaxation to the α relaxation is invariant to change in thermodynamic condition. Notwithstanding we study also the isochronal non-Gaussian parameter $\alpha 2_P(T)$ in which the JG β relaxation is fully resolved to appear as a peak at $T_{\alpha 2,P}$. The fact that $T_{\alpha 2,P}$ is much lower than $T_{\alpha,P}$ is testimony that the peak of $\alpha 2_P(T)$ is contributed by the JG β relaxation.

The link of the non-Gaussian parameter to the JG β relaxation is general and shared by nonmetallic glass formers. An example is the study of colloidal particles by confocal microscopy [1]. Elucidated in Fig. S3 of the Supplemental Material [10], $\alpha_2(t)$ computed from the mean-square displacement exhibits a broad peak covering the entire time range from caged dynamics, JG β relaxation, and α relaxation. The peak of $\alpha_2(t)$ occurs in the β-relaxation regimes at time t_{x2} somewhat longer than the primitive relaxation time τ_0 of the coupling model, which is approximately equal to τ_β [4]. This is illustrated in Fig. S3 by collecting several sets of data of colloidal particles suspension at volume fraction $\phi = 0.56$ from confocal microscopy [10]. The value of t_{x2} in Fig. S3 is no more than a factor of 2 longer than $\tau_0 = 500$ s, and hence the relation between t_{x2} and τ_0 is like the approximate relation between τ_0 and the β-relaxation time τ_β found in many glass formers [3,4,36–46]. It is written as $t_{x2} \approx \tau_\beta$ to stand for this fact. The same results from colloidal particles suspension [10] was found by simulation in other systems including binary Lennard-Jones particles [12], and Li ions in the metasilicate glass Li_2SiO_3 [52]. Therefore, the peak time t_{x2} of $\alpha_2(t)$ in isothermal data or alternatively the peak temperature $T_{\alpha 2,P}$ of $\alpha_2(t)$ in isochronal data of $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ can be taken as associated with the JG β-relaxation time τ_β.

In the glassy state of $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$ under isochronal condition, e.g., $t_p = 100$ ps and 100 ns, respectively, we can see clearly from Figs. 2–11 and Fig. S2 in the SM that the $\alpha 2_P(T)$ peaks at the temperature $T_{\alpha 2,P}$ lower than $T_{\alpha,P}$. From the discussion given above, $T_{\alpha 2,P}$ is identifiable with the temperature of the isochronal β-relaxation time $\tau_\beta(T_{\alpha 2,p}, P)$. Additional support of this identification comes from the fact that $T_{\alpha 2,P}$ falls inside the temperature range of excess loss of $E_P''(T)$ of $Zr_{50}Cu_{50}$ on the low-temperature side of the α-loss peak, and is contributed by the β relaxation. The latter is even clearer in the case of $Ni_{80}P_{20}$, where the more prominent shoulder of $E_P''(T)$ represents that the not fully resolved β-relaxation is overlapping the $\alpha 2_P(T)$ peak. Thus we are led to the conclusion that the $\alpha 2_P(T)$ peak pertains to the JG β relaxation, and the invariance of $T_{\alpha 2,P}/T_{\alpha,P}$ to pressure reflects the invariance of $T_{\beta,P}/T_{\alpha,P}$ in isochronal spectrum to change of pressure, despite changes in atomic structure, and density. We have shown that the ratio of the two peak temperatures, $T_{\alpha 2,P}/T_{\alpha,P}$, is independent of P, and obtained the important result of metallic glasses that the relation of the caged dynamics and the JG β relaxation to the α relaxation in the two metallic glasses is also invariant to change of pressure at constant $\tau_\alpha(T_{\alpha,P}, P) = t_p$ for all P. This property from isochronal data is the analog of the invariance of the ratio, $\tau_\alpha(T, P)/\tau_\beta(T, P)$, to changes of T and P while $\tau_\alpha(T, P)$ is kept constant found in many molecular and polymeric glass formers. The fundamental importance of the JG β relaxation has been clearly brought out by the property in molecular and polymeric glass formers. From the results presented in this paper, we show that the property applies also to metallic glasses.

The two binary metallic glasses chosen to study, $Zr_{50}Cu_{50}$ and $Ni_{80}P_{20}$, all have the JG β relaxation not fully resolved as a peak in the isochronal loss modulus $E_P''(T)$. Naturally one can ask why we did not choose metallic glasses having fully resolved JG β relaxation such as $Pd_{40}Cu_{30}Ni_{10}P_{20}$ [53] and $La_{60}Ni_{15}Al_{25}$ [35]. The answer is that application of the MD simulations and MD-DMS to the multicomponent metallic glasses becomes more difficult than binary metallic glasses, and the results can be less clear. Notwithstanding, studies of the JG β and α relaxations in multicomponent metallic glasses by MD simulations and MD-DMS will be the next challenge for anyone to undertake.

ACKNOWLEDGMENTS

B.W. was supported by Fundamental Research Funds for the Central Universities (Grant No. G2018KY0317). We acknowledge Beijing Computational Science Research Center (CSRC) for computational support.

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