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# Measurements of slow $\beta$-relaxations in metallic glasses and supercooled liquids

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Dynamic mechanical measurements were performed on a series of strong and fragile metallic glass-forming liquids in isochronous and isothermal routes. Our results indicate that slow $\beta$-relaxation mode is ubiquitous in metallic glass-forming systems though it may manifest as an excess wing in strong glasses due to strong coupling with the $\alpha$-relaxation. Furthermore, we find that the degree of coupling between $\alpha$-relaxation and slow $\beta$-relaxation correlates with the fragility of these glass-forming liquids. The possible mechanism and the connections between $\alpha$-relaxation and slow $\beta$-relaxation are discussed.

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## I. INTRODUCTION

The dramatical slowdown of the relaxation processes in liquids on cooling toward the glass transition temperature $T_g$ is one of the most intriguing questions in condensed matter physics.[1–8] Usually, there are multiple relaxation processes in the relaxation spectra of glasses, among which the most prominent is $\alpha$-relaxation, which plays a critical role in the glass transition. There are also secondary relaxations above and below $T_g$. Among them, the process known as the Johari-Goldstein (JG) relaxation has attracted the most interest.[2] Being a process that precedes $\alpha$-relaxation in time, the JG relaxation plays a key role in pursuing the origin of universal relaxations in glass-forming liquids and, further, in resolving the mystery of glass transition.

In frequency domain, in contrast to the occurrence of a distinct slow $\beta$-relaxation, some materials show the excess wing (EW) on the high-frequency flank of the $\alpha$-relaxation. The relationship between $\alpha$-relaxation, slow $\beta$-relaxation, and EW is one of the most debated issues in this field.[8–10] The intensive studies hitherto on the $\beta$-relaxation and EW are mostly in polymer and organic glasses. While the origin of the secondary relaxation remains unclear, it usually was related to different motions such as intermolecular motion, intramolecular motion, or small or large angle jumps.

Metallic liquid is the simplest liquid with atoms as its structural units. Its structure is close to a dense random packing of spheres without the complex intramolecular effect, rotational degree of freedom, or angle jump. The liquids offer an opportunity to understand the mechanism of complex relaxations of supercooled liquids. However, metallic supercooled liquids are normally quite unstable with respect to crystallization. By careful selection of composition, their stability can approach that of conventional oxide glasses, and bulk metallic glasses (BMGs) can be cast at low cooling rates.[11] The availability of these alloys offers wide experimental temperature and time windows for investigating the dynamical relaxation characteristics in metallic liquids. Quasielastic neutron-scattering experiments exhibited that at high $T$, the relaxations would be separated at a crossover temperature $T_c$.[12] Li *et al.*[13] directly observed that certain local atomic motion in a Pd-based liquid had an obvious change at its crossover range. These results imply that the relaxation below $T_c$ of metallic supercooled liquids may be different from that above $T_c$, and motivate us to investigate whether the JG relaxations can universally exist in metallic glasses. On the other hand, the intrinsic properties depicted by fragility are closely linked with the relaxations and the relationship between different relaxation modes.[10,14] Thus it is interesting to study the relationship between the characteristic relaxation and the fragility in metallic glasses.

In this paper, we systematically investigated the dynamic mechanical relaxation in a series of BMGs and their corresponding supercooled liquids with marked difference in fragility. The results indicate that slow $\beta$-relaxation mode is ubiquitous in bulk metallic glass-forming systems and manifests itself as an excess wing in strong glasses due to strong coupling with the $\alpha$-relaxation. It is found that the degree of coupling between $\alpha$-relaxation and slow $\beta$-relaxation correlates with the fragility of these glass-forming liquids. We have discussed the possible mechanism and the connections between $\alpha$-relaxation and slow $\beta$-relaxations.

## II. EXPERIMENT

These BMGs were prepared by Cu-mold casting method. The preparation and structural information of these BMGs can be found in Ref. 11. All dynamic mechanical measurements were performed on TA2980 dynamic mechanical analyzer by single-cantilever bending method. A sinusoidal strain was applied during continuous heating and frequency sweep measurements. The Young's modulus (the storage Young's modulus $E'$ and loss Young's modulus $E''$), dependent on frequency and temperature, can be determined by the measurements. Before dynamic-mechanical analysis (DMA) measurements, a pretreatment was processed for each as-cast sample; i.e., all samples were heated into respective supercooled liquid region and cooled at constant rate ($\leqslant 40$ K/min) to room temperature in order to prevent the formation of the as-cast samples from interfering. The dynamic mechanical spectra show shoulderlike $\beta$-relaxation and EW in the fragile and strong liquids, respectively. The observations provide direct evidence for the views that the EW is the high-frequency flank of the $\beta$-relaxation. The difference between the characteristic average relaxation time $\tau$ of $\alpha$- and $\beta$-relaxations, which decides whether the

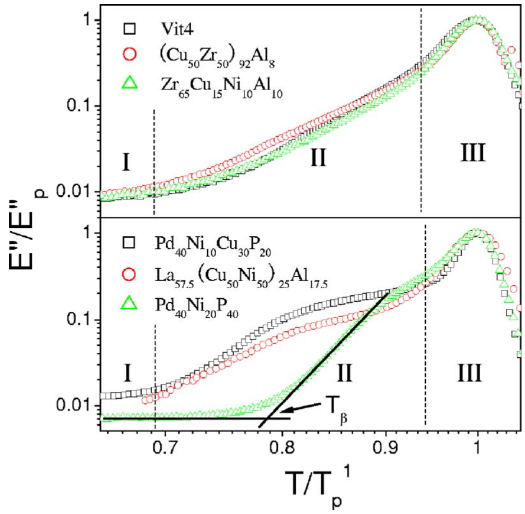

FIG. 1. (Color online) The temperature dependence of the reduced loss modulus $E''/E''_p$ measured at 1 Hz on different metallic glass-forming liquids in ramp mode (3 K/min). The $T$ scale was normalized to the $T_p^1$ for comparison.

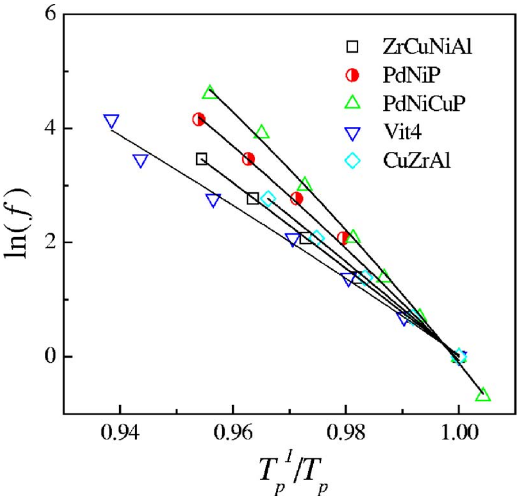

FIG. 2. (Color online) The frequency dependence of the reduced loss peak temperature $T_p^1/T_p$ for various BMGs obtained under ramp mode (3 K/min) in DMA measurements. The solid lines are the best fits to the VFT equation $f=f_0\exp[-B/(T_P-T_0)]$.

$\beta$-relaxation behaves as a shoulder or EW, changes with the intrinsic properties of the liquids as indicated by their fragilities.

## III. RESULTS AND DISCUSSIONS

Figure 1 shows the reduced loss modulus $E''/E''_p$ of the six BMG systems in the temperature domain measured at 1 Hz at the heating rate of 3 K/min. $E''_p$ is the loss modulus at the peak, and the temperature $T$ is also scaled by the peak temperature $T_p^1$ determined at 1 Hz. The values of $T_p^1$ are 652±1, 675±1, 728±1, 580±1, 596±1, and 443±1 K for $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4), $Zr_{65}Cu_{15}Ni_{10}Al_{10}$, $(Cu_{50}Zr_{50})_{92}Al_8$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pd_{40}Ni_{40}P_{20}$, and $La_{57.5}(Cu_{50}Ni_{50})_{25}Al_{17.5}$, respectively. Common characteristics can be found in these temperature dependence of $E''$ curves. That is, all these curves can be divided into three regions. Region I is the low-temperature range where $E''$ is nearly independent of temperature. Region II has a characteristic shoulder that is formed in the glassy state. Such shoulder has been affirmed to be related to the slow-$\beta$ relaxation.[15] So the slow $\beta$-relaxation is universal for these BMGs. Region III is the one where the $E''$ peak can be found. The peak is a typical characteristic of supercooled liquid (SL) and is related to the $\alpha$-relaxation of SL. However, the three regions have more or less individual characteristics. The individuality depends on the dynamical characteristic of the different BMG systems.

The frequency dependence of the $E''$ peak in region III represents the dynamical characteristic of the SL. Figure 2 plots the frequency applied in continuous heating DMA measurement (3 K/min) vs the reduced loss peak temperature $T_p^1/T_p$ for various BMGs. The error of the $T_p$ is less than 1 K, controlled by the probing time and the heating rate in the DMA measurement. It is well known that the dynamical characteristic of a glass former in the temperature domain is usually described well by the Vogel-Fulcher-Tammann (VFT) equation: $f=f_0\exp[-B/(T_P-T_0)]$. The solid lines in Fig. 2 are the best fits to the VFT equation of experimental data, and the parameters of the best fits are listed in Table I. Accordingly, the fragility $m$ depicting the dynamical charac-

TABLE I. The activation energy and onset temperature for the slow $\beta$-relaxation $E_\beta$, $T_\beta$ (1 Hz), liquidus temperature $T_l$, fragility $m$ $[m=(DT_gT_0)/(T_g-T_0)^2/\ln 10]$, and the parameters used in VFT fit for various metallic glass-forming systems.

| BMGs | $f_0$ | $B$ | $T_0$ (K) | $m$ | $E_\beta$ (kJ/mol) | $T_\beta$ (K) | $T_l$ (K) |
|---|---|---|---|---|---|---|---|
| Vit4 (Ref. 26) | $1.1\times10^{14}$ | 9954.7 | 345±10 | 34.4 | 138.4 | 478 | 1050 |
| $Zr_{65}Cu_{15}Ni_{10}Al_{10}$ | $7.5\times10^{20}$ | 20016.1 | 258±10 | 36 | 130.8 | 491 | 872 |
| $(Cu_{50}Zr_{50})_{92}Al_8$ (Ref. 27) | $7.3\times10^{18}$ | 16222.5 | 354±10 | 41 | 174.1 | 505 | 1155 |
| $Pd_{40}Ni_{40}P_{20}$ (Ref. 28) | $1.6\times10^{13}$ | 5380.7 | 419±10 | 53 | 178.1 | 440 | 973 |
| $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (Ref. 29) | $5.6\times10^{12}$ | 4062.5 | 442±10 | 57.7 | 128.9 | 397 | 823 |
| $La_{57.5}(Cu_{50}Ni_{50})_{25}Al_{17.5}$ (Ref. 30) | $7.1\times10^{7}$ | 1548.7 | 356±10 | 60 | 92.4 | 308 | 783 |

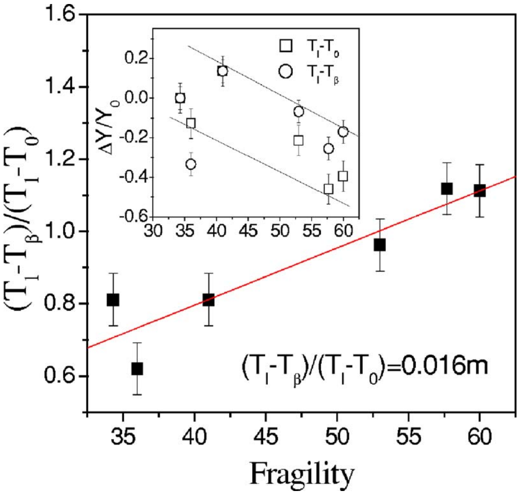

FIG. 3. (Color online) Relationship between the onset temperature of slow $\beta$-relaxation $T_\beta$ and fragility $m$ in various BMGs. The solid line is drawn by the linear fit with $(T_l - T_\beta)/(T_l - T_0) = 0.016m$. The relative change $[\Delta Y/Y_0 = (Y_i - Y_0)/Y_0$, where $Y_0$ is the value for Vit4] of $T_l - T_\beta$ and $T_l - T_0$ to that of Vit4 were shown in the inset.

teristic of SL can be calculated from these parameters by means of the equation $m = \log_{10} e[BT_g/(T_g - T_0)^2]$ (the values of $T_g$ at 20 K/min were used).[16] It is noted that the values of $m$ from our calculation are consistent with that from other researchers.[16]

For the six BMG systems studied in this work, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pd_{40}Ni_{40}P_{20}$, and $La_{57.5}(Cu_{50}Ni_{50})_{25}Al_{17.5}$ SLs have larger fragilities, meaning that their SLs are more fragile. On the other hand, the other three metallic SLs are rather strong with small $m$. It is worth noting that the individuality of region II in the reduced $E''-T$ curves corresponds to the fragility index $m$; i.e., the larger $m$ the BMG has, the more obvious its region II is. This can be qualitatively explained as follows: for strong liquids, if the size of the cooperative rearrangement region does not change significantly during $T$ changes,[10] the relaxation times of the primary and secondary relaxations do not differ a lot. Accordingly, only an inconspicuous bump below $T_g$ can be discerned in the strong glass-forming liquids. On the contrary, the slow $\beta$-relaxation could evolve into an obvious shoulder in fragile glass-forming liquids.

A relationship between a scaled parameter related to $\beta$-relaxation in the form $(T_l - T_\beta)/(T_l - T_0)$ and fragility of BMGs is established in Fig. 3. Here $T_\beta$ is the onset temperature of the secondary relaxation (see Fig. 1). $T_l - T_\beta$ was scaled to $T_l - T_0$ to diminish the large difference among various BMGs, where $T_l$ is the liquidus temperature above which an alloy is completely molten and $T_0$ is the VFT temperature. It is believed that above $T_l$, the effects of cooperativity can be omitted and the temperature dependence of the relaxation time conforms to the Arrhenius equation.[17] $T_0$ is the hypothetical kinetic instability point and is regarded as the low limit of $T_g$. In most cases, $T_0$ is close to the Kauzmann temperature.[3,18] Thus, it might be reasonable to take $T_0$ as the temperature where a unique, noncrystalline state of lowest energy—the ideal glass state—is obtained approximately.

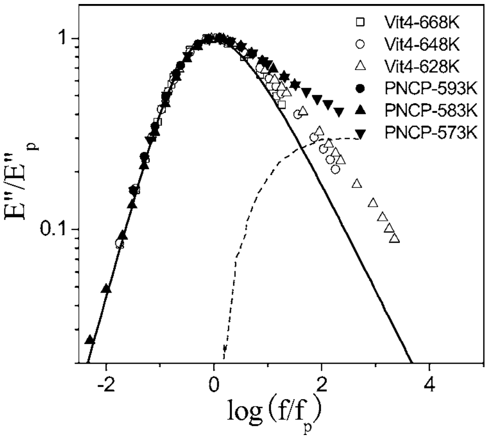

FIG. 4. Master curves for Vit4 (628–668 K) and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (573–593 K) BMGs of DMA measurements. The solid line is the KWW fit to the master curve of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ with $\beta = 0.57$. The dashed line indicates the possible contribution from slow $\beta$-relaxation mode by subtracting the KWW fit from the master curve. Logarithmic scales are chosen for the reduced loss modulus $E''/E''_p$.

Accordingly, the value of $(T_l - T_\beta)/(T_l - T_0)$ could be used to evaluate the degree of coupling between $\beta$ and structural relaxations. For metallic liquids, $(T_l - T_\beta)/(T_l - T_0)$ shows an increasing trend with increasing fragility although relative change $[\Delta Y/Y_0 = (Y_i - Y_0)/Y_0$, where $Y_0$ is the value for Vit4] of $T_l - T_\beta$ and $T_l - T_0$ to that of Vit4 tends to decrease with fragility (inset in Fig. 3). A linear fit produces a quantitative relationship: $(T_l - T_\beta)/(T_l - T_0) = 0.016m$. A decrease of $T_l - T_0$ relative to that of Vit4 (up to $-39\%$) with increasing fragility is qualitatively consistent with the prediction of two order parameter (TOP) model.[17] The distance between $T_l$ and $T_\beta$ also decrease with increasing fragility (up to $-17\%$), which means that the absolute distance between $T_l$ and $T_\beta$ is larger for strong system. But the $(T_l - T_\beta)/(T_l - T_0)$ increases with fragility ($\sim 37\%$), which indicates an obvious correlation between the degree of coupling between $\alpha$-relaxation and slow $\beta$-relaxation modes and the intrinsic dynamic characteristic of the BMG systems indicated by their fragilities.

Frequency sweeps were conducted on $Pd_{40}Ni_{10}Cu_{30}P_{20}$ (573–593 K) and Vit4 (628–668 K) samples, and their respective master curves are shown in Fig. 4. Both glasses show a prominent $\alpha$-relaxation peak in frequency domain. On the low-frequency side of the loss peak, these two systems behave in the same way within experimental error, but they differ significantly at high frequencies. After bifurcation at about 1 decade frequency, the spectra of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ possess a larger value of normalized $E''$ and the difference tends to increase with frequency. As marked excess wing is observed in Vit4, this difference provides another evidence of the existence of slow $\beta$-relaxation in $Pd_{40}Ni_{10}Cu_{30}P_{20}$. A Kohlrauschi-Williams-Watts (KWW) fit to the experimental spectra of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ with $\beta = 0.57$ (Ref. 15) (solid line) is plotted in Fig. 4, and the dashed line is the result of subtracting the fit curve from the experimental data to indicate the possible contribution from the underlying $\beta$-relaxation. It is worth noting that the shape parameter $\beta$ of

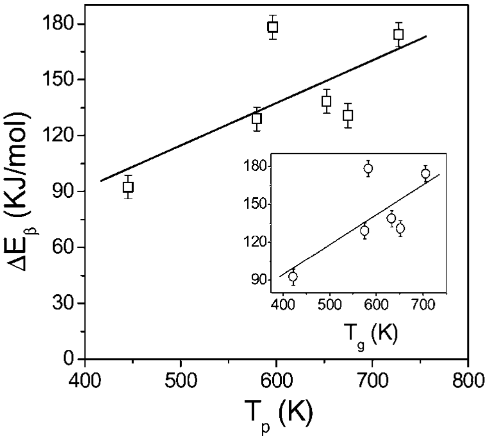

FIG. 5. The relationship between $E_\beta$ and dynamic $T_p$ determined at 1 Hz for various metallic glass-forming systems. The solid line is produced by the linear fit and its slope is 27.5*R*. The relation between $E_\beta$ and calorimetric $T_g$ is depicted in the inset, and the slope of the solid line produced by the linear fit is 28.4*R*.

strong liquid Vit4 has a stronger *T* dependency than the fragile one—$Pd_{40}Ni_{10}Cu_{30}P_{20}$. This could be partially ascribed to the *T* dependence of the relaxation time $\tau$ for the $\beta$-process in Vit4, of which the low-frequency part is fully obscured by the dominant $\alpha$ peak. That is to say, when approaching the crossover temperature $T_c$, $\tau$ for the two relaxations come progressively closer and the distributions of $\tau$ become narrower at higher *T*. Similar phenomena are also observed in $(Cu_{50}Zr_{50})_{92}Al_8$ and $Pd_{40}Ni_{40}P_{20}$ liquids.

The *T* dependence of $\tau$ for slow $\beta$-relaxation conforms to the Arrhenius equation: $\tau=\tau_0 \exp(E_\beta/RT)$, where $\tau_0$ is a prefactor, *R* the gas constant, and $E_\beta$ the activation enthalpy. An empirical relationship between $E_\beta$ and $T_g$: $E_\beta \approx 24RT_g$ was found in nonmetallic glass formers.[19,20] We herein determined the $E_\beta$ by an alternative method due to the fact that no well-separated secondary relaxation peak could be discerned from the dynamic measurements performed in ramp mode of BMGs. A line parallel to the *T* coordinate was drawn, and it intersects with the experimental data obtained under different frequencies. The data of these intersections were used to calculate $E_\beta$ instead of the peak data. The determined $E_\beta$ agrees well with those reported before.[21,22] Figure 5 shows the relationship between $E_\beta$, $T_p$, and $T_g$ (inset) for these BMGs. The slope of the solid line from linear fit is 27.5*R* for the $E_\beta \sim T_p$ plot and 28.4*R* for $E_\beta \sim T_g$, respectively. The empirical relationship further confirms the universality of the origin of the JG relaxation and its connection with the glass transition in different glasses. The deviation of the slope from 24*R* could arise from the bonding difference between BMGs and nonmetallic glasses.

The origin of the slow $\beta$-relaxation mode in metallic glasses should be ascribed to certain local motion of some structural unit other than rotational degree of freedom or angle jump although many questions still remain unsolved.[3,16,23,24] It is generally accepted that there is dynamic heterogeneity in glasses and supercooled liquids. We can imagine that there are many islandlike clusters, whose size has a wide distribution below a few nanometers, in metallic supercooled liquids. The interaction between atoms is strong within clusters, or we can say, this region is denser. Between these clusters, that is the loser region, i.e., the interaction in this region is relatively weak. When temperature goes down below $T_g$, the collective motions in these clusters are kinetically frozen. However, the motions in the loser regions are still active and will be kinetically frozen at lower temperature. This local motion, comprising only the atoms in the loser regions, is the slow $\beta$-relaxation mode in metallic glasses. With respect to the kinetically strong metallic liquids, more constraints are put on moving particles[25] even in the loser region. Thus the *T* dependence of the number of local structures in the strong liquid will be weaker than that for the fragile one, and this finally results in a smaller difference in the average relaxation time for the cooperative structural relaxation and local secondary relaxation. As mentioned above, in the glass formed by a strong liquid, more constraints are put on moving particles in the loser region. Thus the activation energy of slow $\beta$-relaxations in such system will be larger. And as the precursor of structural relaxation, the slow $\beta$-relaxations must be activated before the glass transition process. Thus a larger $E_\beta$ should correspond to a higher $T_g$.

## IV. CONCLUSIONS

We confirm the universal existence of the slow $\beta$-relaxations in bulk metallic amorphous systems by dynamic mechanical measurements. Our results show that the degree of coupling between $\alpha$-relaxation and slow $\beta$-relaxation correlates with the fragility of the glass-forming liquids in the following way: $(T_l-T_\beta)/(T_l-T_0)=0.016m$ in typical BMGs. The empirical relationship between $E_\beta$ and $T_g$: $E_\beta \sim kRT_g$ has been proved valid in metallic systems though the constant *k* (27–29) is a little larger than that (~24) in nonmetallic glass formers. We believe that this arises from the difference in bond type between nonmetallic glasses and BMGs.

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