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A connection between the structural α-relaxation and the β-relaxation found in bulk metallic glass-formers

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New metallic glasses containing La or Ce have been introduced having dynamic properties bordering on two extremes of conventional metallic glasses. This provides opportunity to test if the trends or correlations established before in molecular and polymeric glass-formers also exist in the broader family of metallic glasses. Due to the drastically different chemical and physical structures of metallic glass-formers than soft matter, there is no guarantee that any correlation found in the latter will hold in the former. If the trends and correlations are found, the result brings metallic glasses closer to the much wider classes of glass-formers in the similarity of properties. In non-metallic glass-formers, a general and fundamental connection has been established between the non-exponentiality parameter of the structural α-relaxation and the separation between its relaxation time τ_α and the β-relaxation time τ_β. In this paper, we explore the experimental data of metallic glass-formers and show the correlation applies. An explanation of this correlation is given by the Coupling Model. The establishment of the correlation may facilitate the understanding of the roles played by the β-relaxation in macroscopic properties of metallic glasses including the relations to shear transformation zone, ductile-brittle transition in deformation, crystallization, and diffusion. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4812281]

I. INTRODUCTION

Metallic glass-forming materials are unusual in their chemical and physical structures composed of multi-atomic particles, in stark contrast to covalent bonded molecules in molecular and polymeric glass-formers.[1–6] The interaction potential in metallic glass-formers[7] is also very different from the van der Waals interaction with or without the complication due to the presence of hydrogen bonds and ionic interaction. Naturally the following question arises. Beyond glass-forming ability, do metallic glasses share any of the outstanding and general dynamic property established before in the much more abundant class of molecular and polymeric glass-formers. Whether the answer is positive or negative, the answer would be interesting and could have far reaching implications.

In non-metallic glass-formers, there is a secondary relaxation with strong connection to the structural α-relaxation manifested in various properties of dynamics.[8–11] This secondary relaxation involves the motion of the entire molecule or the entire monomer in the case of polymer. Its properties as well as its universal presence in all glass-formers are suggested in analogy to the primitive relaxation of the Coupling Model (CM). The single secondary relaxation found decades ago by Johari and Goldstein[12] in totally rigid molecular glass-formers such as chlorobenzene certainly involves the motion of the entire molecule. For this reason, the term Johari-Goldstein (JG) β-relaxation has been used to distinguish the secondary relaxation belonging to this important class from the other secondary relaxation of intramolecular nature and having no connection to the structural α-relaxation.[8–11] The multi-particle structure of the metallic glass-formers can pose a challenge to the universal presence of the JG β-relaxation for three different reasons. First, it is unclear if secondary relaxation exists in metallic glass-formers. Second, even if it exists, its nature is unclear. Third, it remains to be shown if the secondary relaxation exhibit any connection to the α-relaxation in any of the dynamic properties. Notwithstanding, secondary relaxation in different metallic glasses is either resolved[13] or unresolved but present as the excess loss[14] in isochronal and isothermal mechanical relaxation measurements,[15–17] and hence its existence seems assured, but still unclear whether it belongs to the class of the JG β-relaxation. Recent synchrotron X-ray study of $Zr_{55}Cu_{30}Ni_5Al_{10}$ alloy has shown the secondary relaxation originates from a short-range collective rearrangement of atoms,[18] implying that it involves motion of all atoms, and satisfying one major criterion of being the JG β-relaxation.[9] Still remains to be shown is any connection it may have to the α-relaxation in dynamic properties, before the conclusion can be made.

The purpose of the study reported in this paper is to provide a connection between the JG β-relaxation and the α-relaxation analogous to that found in non-metallic glass-formers. At any temperature T and pressure P, there is a general relation between the α-relaxation time $\tau_\alpha(T, P)$ and the JG β-relaxation times $\tau_\beta(T, P)$. The relation is between $\log[\tau_\alpha(T, P)/\tau_\beta(T, P)]$ and $n(T, P)$, where $n(T, P)$ is the

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[a)] Author to whom correspondence should be addressed. Electronic mail: ngai@df.unipi.it complement of the stretch exponent, $\beta_{KWW} \equiv (1-n)$, of the Kohlrausch correlation function of the α-relaxation

$$\varphi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \quad (1)$$

For metallic glass-formers, the mechanical relaxation is performed at ambient pressure, and at temperatures not far above the glass transition temperature T_g. Therefore, in metallic glass-formers we shall limit ourselves to testing the correlation between $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ and $n(T_g)$ at $T = T_g$ and ambient pressure. If successful, like in non-metallic glass-formers, the correlation leads to the conclusion that the secondary relaxation is the JG β-relaxation, and it has fundamental importance when considering the dynamics of glass transition and macroscopic properties including shear transformation zone, ductile-brittle transition in deformation, crystallization, and diffusion.

II. CORRELATION OF $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ WITH $n(T_g)$: METALLIC GLASS-FORMERS

To find out if the aforementioned correlation exists in metallic glass-formers, the two quantities, $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ and $n(T_g)$, have to be determined. This is not an easy task for any metallic glass-former. Although T_g can be determined by calorimetry, and $\tau_\alpha(T_g)$ estimated from the scanning rate, the difficulty lies in acquiring $\tau_\beta(T_g)$ and $n(T_g)$. For molecular glass-formers, several experimental techniques including dielectric relaxation, mechanical relaxation, light scattering, and nuclear magnetic resonance are at disposal to obtain these two quantities, but mainly mechanical relaxation is applicable to metallic glass-formers. The limited frequency range and lower resolution of mechanical relaxation make determination of $\tau_\beta(T)$ difficult at any temperature. Isothermal mechanical relaxation over many decades of frequencies are prerequisite for characterizing the structural α-relaxation and determining $n(T_g)$. At the present time, isothermal mechanical relaxation had been carried out on a few metallic glass-formers, and not all were able to resolve the β-relaxation. More customary are isochronal mechanical measurements, but $\tau_\beta(T_g)$ and $n(T_g)$ were obtained less directly with assumptions introduced to fit the temperature dependence of the isochronal mechanical loss data. Due to the limitations of mechanical data of metallic glass-formers, larger errors accompany the values of $\tau_\beta(T_g)$ and $n(T_g)$ obtained. Therefore, if it exists in metallic glass-formers, the correlation is not expected to be as precise as that found in small molecular and polymeric glass-formers.[8–11] This point has to be borne in mind when judging the correlation to be obtained within the family of metallic glass-formers.

A. Experimental results from metallic glass-formers

The isochronal shear loss modulus G'' measurement of the metallic glass-former, $Zr_{65}Al_{7.5}Cu_{27.5}$ at 5.4 kHz by Rösner *et al.*[14] is perhaps the first that enabled deduction of $\tau_\beta(T_g)$ and $n(T_g)$ from the data, as demonstrated by Ngai in Ref. 19. From the Vogel-Fulcher-Tammann (VFT) temperature dependence of the α-relaxation time τ_α of $Zr_{65}Al_{7.5}Cu_{27.5}$ (ZrAlCu) obtained by Rösner *et al.*,[14] values of T_g defined operationally by either $\tau_\alpha(T_g) = 100$ s or 1000 s were determined. The data of Rösner *et al.*[14] had been used by Ngai[19] to extract the characteristics of the dynamics of the α-relaxation, which led to the $n(T_g) = 0.40$. Also determined is the JG β-relaxation time at T_g given in logarithmic scale by $\log[\tau_\beta(T_g)/s] = -3.28$ and -3.88 for T_g defined by $\tau_\alpha(T_g) = 100$ s and 1000 s, respectively.[19] In the following, we present the data of two recently studied metallic glass-formers, $La_{70}Ni_{15}Al_{15}$ (LaNiAl) and $Cu_{45}Zr_{45}Ag_{10}$ (CuZrAg), and the analyses that give the estimates of $\tau_\beta(T_g)$ and $n(T_g)$ for each of them.

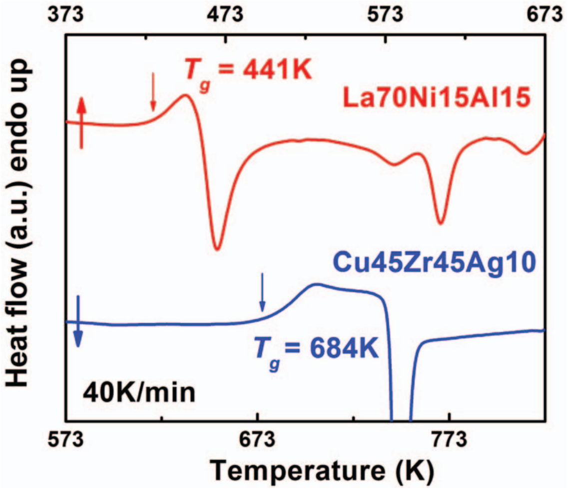

FIG. 1. The DSC traces of $La_{70}Ni_{15}Al_{15}$ (red curve) and $Cu_{45}Zr_{45}Ag_{10}$ (blue curve) measured at 40 K/min.

The differential scanning calorimetry (DSC) data of LaNiAl and CuZrAg at heating rate of 40 K/min are presented in Fig. 1. From the data, T_g of LaNiAl and CuZrAg are 441 and 684 K, respectively. Isochronal loss modulus E'' data from 1 to 16 Hz of LaNiAl and CuZrAg are shown in Figs. 2 and 3, respectively. The shifts of the lower temperature β-loss peak of LaNiAl and the excess loss of CuZrAg with frequency are given in the insets of Figs. 4 and 5. From the shifts, the activation energy E_β of the β-relaxation is estimated to be 90 kJ/mol for LaNiAl, and 205 kJ/mol for CuZrAg. The isochronal spectra at 1 Hz had been fitted globally with the contributions from the α- and β-relaxation assumed to be

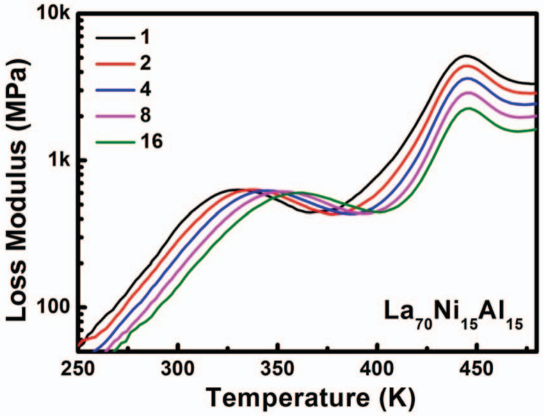

FIG. 2. Temperature dependence of the loss modulus for a $La_{70}Ni_{15}Al_{15}$ MG, measured with frequency from 1 to 16 Hz, at the heating rate of 3 K/min.

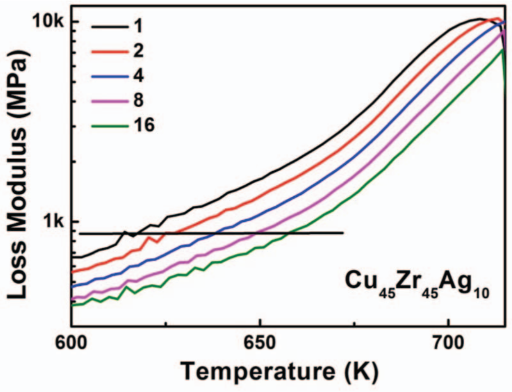

FIG. 3. Temperature dependence of the loss modulus for a $Cu_{45}Zr_{45}Ag_{10}$ MG, measured with frequency from 1 to 16 Hz, at the heating rate of 3 K/min.

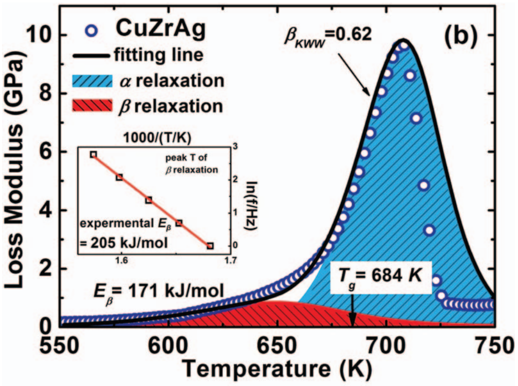

FIG. 5. Temperature dependence of loss modulus of $Cu_{45}Zr_{45}Ag_{10}$ measured at 1 Hz. The colored regions represent the KWW fit. The inset is a plot of log *f* against $1000/T_p$, where T_p is the peak temperature of the β-relaxation.

additive. The correlation function of the α-relaxation is assumed to be given by the Kohlrausch function, and the temperature dependence of $\tau_\alpha(T)$ has the VFT form. The fits have been carried out before,[20] and are reproduced in Figs. 4 and 5. The VFT temperature dependence of $\tau_\alpha(T)$ and the Arrhenius *T*-dependence of $\tau_\beta(T)$ for $T < T_g$ have been determined by the fit. For LaNiAl, the global fit gives the activation energy $E_\beta = 87$ kJ/mol slightly smaller than 90 kJ/mol obtained from the shift with frequency. The value of $E_\beta = 171$ kJ/mol from the global fit for CuZrAg is significantly smaller than 205 kJ/mol determined from the shift with frequency. The larger discrepancy of E_β from the two methods is due to the fact that the β-relaxation of CuZrAg is not resolved, and larger uncertainty of its activation energy is involved in the fit. All parameters relevant to test the correlation including $n(T_g) \equiv (1 - \beta_{KWW}(T_g))$ were determined from the global fits, and are listed in Table I for LaNiAl and CuZrAg. The values of $\beta_{KWW}(T_g)$ are 0.42 and 0.62 for LaNiAl and CuZrAg, respectively. The parameters for $Zr_{65}Al_{7.5}Cu_{27.5}$ (ZrAlCu) deduced from the data of Rösner *et al.*[14] are also given there.

Isochronal shear loss modulus G'' of $Ce_{70}Al_{10}Cu_{20}$ was measured at the frequencies of 0.5, 1, 2, and 5 Hz by Liu *et al.*[16] The low temperature loss show no feature that can be identified with the presence of the β-relaxation. Essentially the same fitting procedure as described above was used to fit exclusively the α-loss peak with the combination of the Kohlrausch function for the time dependence and VFT equation for $\tau_\alpha(T)$.[16] The value of $\beta_{KWW} = 0.8$ was obtained from the fit. In addition to isochronal measurements, Liu *et al.*[16] made isothermal shear modulus measurements. Their data at several temperatures together with the fits by the Fourier transform of the Kohlrausch function are reproduced in Fig. 6. Remarkably, the same value of $\beta_{KWW} = 0.8$ fits the isothermal data. The excess wing of $G''(f)$ on the high frequency side is evident from the deviation of the experimental data over and above the Kohlrasuch fit. The location of the arrows indicate the primitive relaxation frequencies at 343 and 353 K calculated from the coupling model equation to be discussed in Subsection II B later.

There are a few other metallic glass-formers which had been studied by isothermal mechanical relaxation, and $n(T_g)$ determined directly by the fit to the Fourier transform of the Kohlrausch stretched exponential function.[15,21,22] However, not all of them have complementary data to determine

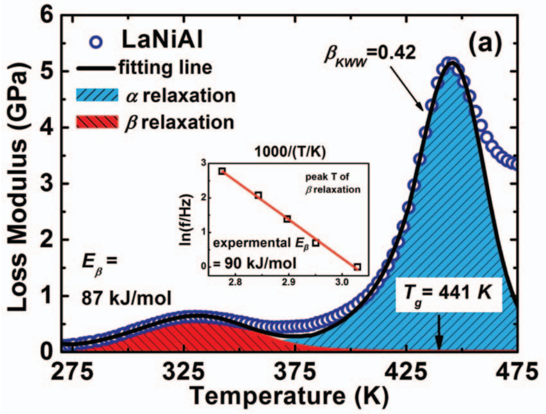

FIG. 4. Temperature dependence of loss modulus of $La_{70}Ni_{15}Al_{15}$ measured at 1 Hz. The colored regions represent the KWW fit. The inset is a plot of log *f* against $1000/T_p$, where T_p is the peak temperature of the β-relaxation.

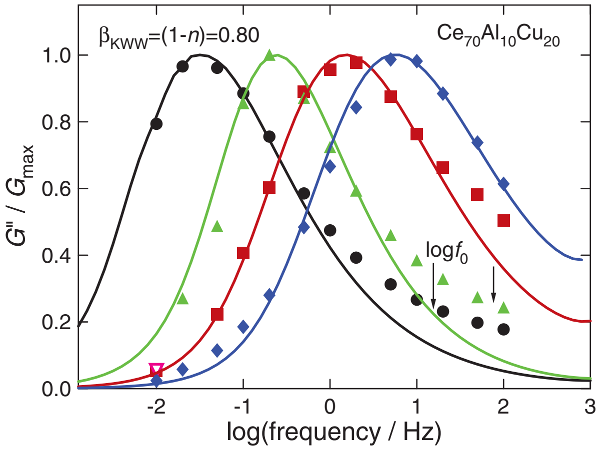

FIG. 6. The frequency dependence of the normalized loss modulus of $Ce_{70}Al_{10}Cu_{20}$ determined at temperatures of 343, 353, 363, and 373 K (from left to right). The solid lines are the fits by the combination of the KWW function with $\beta_{KWW} \equiv (1 - n) = 0.80$, and the VFT equation. The arrows indicate the logarithm of the primitive frequencies, $\log f_o$, calculated from the CM equation.

TABLE I. The values of the relevant parameters, $\tau_\beta(T_g)$, $n(T_g)$, and T_g defined by $\tau_\alpha(T_g) = 10^3$ s of the six metallic glass-formers considered. Fits to the isothermal mechanical relaxation data of $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ and $Ce_{70}Al_{10}Cu_{20}$ by the Fourier transform of the KWW function make possible determination of $n(T_g)$ within the error of ±0.02 (indicated by *), albeit two different values of $n(T_g)$, 0.43 snf 0.50, in the case of $Pd_{40}Ni_{10}Cu_{30}P_{20}$ were given in two references. Determination of $n(T_g)$ from fits to isochronal mechanical relaxation data involves larger errors of about ±0.04 (indicated by **). The uncertainty of $\log[\tau_\beta(T_g)/\mathrm{s}]$ is also estimated and given. N/A: not available.

Metallic glass-former	T_g (K)	$\log[\tau_\beta(T_g)/\mathrm{s}]$	$n(T_g)$	E_a/RT_g
$Zr_{65}Al_{7.5}Cu_{27.5}$[14,19]	606	-3.28 ± 0.5	0.40 ± 0.04**	N/A
$Cu_{45}Zr_{45}Ag_{10}$,[20] and this study	684	-1.93 ± 0.5	0.38 ± 0.04**	30.1 ± 5.3
$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$[15]	620	-3.3 ± 0.3	0.50 ± 0.02*	26.8
$Pd_{40}Ni_{10}Cu_{30}P_{20}$[21]	593	-3.64 ± 0.3	0.43[21]	26.1
		-3.64 ± 0.3	0.50[22]	
$Ce_{70}Al_{10}Cu_{20}$[16]	343	N/A	0.20 ± 0.02*	N/A
$La_{70}Ni_{15}Al_{15}$[20] and this study	441	-4.7 ± 0.5	0.58 ± 0.04**	23.8

$\tau_\beta(T)$ for $T \le T_g$, and hence they cannot be used to test the correlation. The only cases we find that can be used for our purpose are $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vit4),[15] and $Pd_{40}Ni_{10}Cu_{30}P_{20}$.[21] The value of $\tau_\beta(T_g)$ is obtained by extrapolating the experimentally determined Arrhenius T-dependence of $\tau_\beta(T)$ for $T < T_g$ to T_g. The relevant parameters, $\tau_\beta(T_g)$, $n(T_g)$, and T_g defined by $\tau_\alpha(T_g) = 10^3$ s of these metallic glass-formers are entered into Table I. The uncertainties of $\tau_\beta(T_g)$ and $n(T_g)$ are estimated for each metallic glass-former and given in the table. The uncertainty is statistically sufficiently low such that the values of these quantities determined are valid. The conclusion of this paper is the same whether T_g defined by either $\tau_\alpha(T_g) = 10^3$ s or $\tau_\alpha(T_g) = 10^2$ s.

Putting the results obtained for the six metallic glass-formers altogether in a plot of $\tau_\beta(T_g)$ versus $n(T_g)$, the correlation between these two quantities can be tested. The plot is presented in Fig. 7. The data of $Ce_{70}Al_{10}Cu_{20}$ are not sufficient to determine $\tau_\beta(T_g)$, and the point representing it in Fig. 7 is the primitive relaxation time, $\tau_0(T_g)$, of the CM to be introduced in Sec. II B.

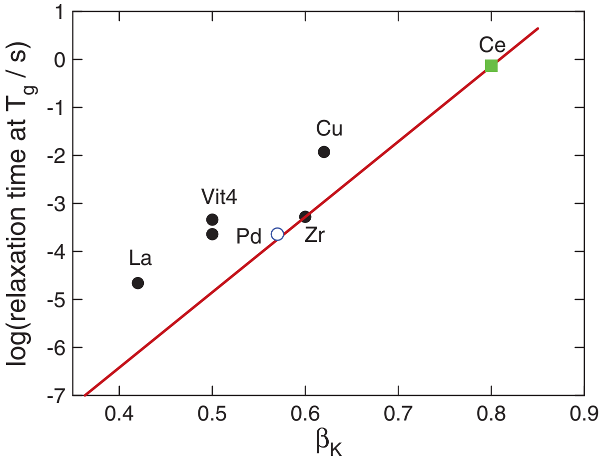

FIG. 7. Plot of $\log[\tau_\beta(T_g)]$ at $T = T_g$ against $\beta_{KWW} \equiv (1 - n)$, of the Kohlrausch-Williams-Watts correlation function used to characterize the frequency dispersion of the α-relaxation. La stands for $La_{70}Ni_{15}Al_{15}$, Cu stands for $Cu_{45}Zr_{45}Ag_{10}$, Ce stands for $Ce_{70}Al_{10}Cu_{20}$, and Pd stands for $Pd_{40}Ni_{10}Cu_{30}P_{20}$. The two points for Pd correspond to the two values of β_{KWW} given in the literature by different authors. For more details, see text.

The shear mechanical relaxation data of three other La metallic glass-formers, $La_{68.5}Ni_{16}Al_{14}Co_{1.5}$, $La_{60}Ni_{15}Al_{25}$, and $La_{57.5}Ni_{12.5}Al_{17.5}Cu_{12.5}$, and $Zr_{55}Cu_{30}Ni_5Al_{10}$ published by Qiao and Pelletier[17] are helpful to show the correlation. It can be seen from the normalized frequency dependence of the loss modulus $G''(f/f_{max})/G_{max}$ that higher the La content in the metallic glass-former, the larger the full-width at half-maximum of the α-loss peak, and larger is the separation between the β- and the α-loss peaks or equivalently between $\log \tau_\alpha$ and $\log \tau_\beta$.

B. Explanation from the CM, and generality

Conceptually, the primitive relaxation of the CM and the JG β-relaxation are equivalent in the sense that both are independent relaxation acting as the precursor of the structural α-relaxation. Their properties are similar, especially those demonstrating the strong connection to the α-relaxation such as the pressure dependence.[8–11] Furthermore, τ_{JG} is approximately the same as the primitive relaxation time τ_0 at any temperature T and pressure P in the supercooled liquid state of many glass-formers,[8–11] i.e.,

$$\tau_\beta(T, P) \approx \tau_0(T, P). \qquad (2)$$

According to the CM, τ_0 can be calculated from the parameters, τ_α and n, of the α-relaxation appearing in the Kohlrausch correlation function given by Eq. (1) via the relation

$$\tau_\alpha = \left[t_c^{-n}\tau_0\right]^{\frac{1}{1-n}}. \qquad (3)$$

In Eq. (3), t_c is the temperature insensitive crossover time from primitive relaxation with time dependence, $\exp(-t/\tau_0)$, to cooperative α-relaxation with the Kohlrausch stretched exponential time dependence. In the context of the CM, n is the coupling parameter, characterizing the heterogeneous and cooperative dynamics. The value of t_c is about 1–2 ps for soft molecular glass-formers and polymers as determined by quasielastic neutron scattering experiments and molecular dynamics simulations.[11] It is shorter for metallic systems with $t_c \approx 0.2$ ps from simulations,[23,24] which is reasonable as inferred from the stronger metallic bonds compared with van der Waals interaction in soft matter, and is also exemplified by the much higher shear modulus of bulk metallic glasses (BMG) than molecular glasses.[25,26]

From the CM equations (2) and (3), the separation between τ_α and τ_β (all quantities in seconds) is given by

$$[\log_{10}\tau_\alpha - \log_{10}\tau_\beta] \approx n(\log_{10}\tau_\alpha - \log_{10}t_c), \qquad (4)$$

and it is proportional to n. This explains the empirical relation between the separation and n found generally in molecular and polymeric glass-formers, and could also be applicable to the six metallic glass-formers in Table I. At $T = T_g$ defined by $\tau_\alpha(T_g) = 10^3$ s, Eq. (4) has the simplified form of

$$\begin{aligned}\log_{10}\tau_\beta(T_g) &= (1-n)\log_{10}\tau_\alpha(T_g) + n\log_{10}t_c\\ &= 3\,(1-n) - 12.7n, \qquad (5)\end{aligned}$$

which is represented by the red line in Fig. 7. The trend in the dependence of $\tau_\beta(T_g)$ on $n(T_g)$ is in accord with that from Eq. (5). However, $\tau_\beta(T_g)$ of three of the six metallic glass-formers (LaNiAl, CuZrAg, and Vit4) are longer than that predicted value by about one and half decade. Discrepancy of this order of magnitude is not unexpected because of the uncertainty introduced to obtain $\tau_\beta(T_g)$ on $n(T_g)$ in LaNiAl and CuZrAg from the fits to the isochronal loss data. Taking the errors into consideration, we can conclude that the correlation of $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ with $n(T_g)$ is obeyed by metallic glass-formers in the same manner as found generally in molecular, polymeric, and even inorganic glass-formers.[6]

C. Correlation of $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ with $m(T_g)$

While the frequency dispersion and hence $n(T_g)$ of metallic glass-formers is hard to obtain, more accessible from experiments is the fragility or steepness index, $m = d\log\tau_\alpha(T_g/T)/d(T_g/T)$ evaluated at $T_g/T = 1$.[27] On the other hand, by plotting the isochronal mechanical loss against T/T_g, a qualitative measure of the separation between τ_α and τ_β can be deduced. This was done by Yu *et al.*[28] in their study of the family of $(\mathrm{Ce}_x\mathrm{La}_{1-x})_{68}\mathrm{Al}_{10}\mathrm{Cu}_{20}\mathrm{Co}_2$ for $0 \le x \le 1$, They found Ce-richer member has smaller value of m and the β-relaxation is closer to the α-relaxation and shows up as an excess wing. La-richer member has larger m and its β-relaxation is more separated from the α-relaxation and becomes resolved either as a shoulder or peak. In this manner, Yu *et al.*[28] found correlation between fragility m and a property of the β-relaxation, namely, the degree of separation between τ_α and τ_β in the metallic glass-formers. However, one should be mindful that this very correlation breaks down in some molecular glass-formers. A well-known example is propylene carbonate which has a large $m = 104$[27] but the β-relaxation is too close to the α-relaxation and appears as an excess wing.[29] In contrast, the correlation between $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ with $n(T_g)$ remains valid.

It is true that when restricting the glass-formers considered to a special class, correlation between properties with m holds, as found by Yu *et al.*[28] in the family of $(\mathrm{Ce}_x\mathrm{La}_{1-x})_{68}\mathrm{Al}_{10}\mathrm{Cu}_{20}\mathrm{Co}_2$ for $0 \le x \le 1$. Notwithstanding, it remains a nontrivial task to derive any observed correlation with m. Here, we provide a derivation of the correlation between $\log[\tau_\alpha(T_g)/\tau_\beta(T_g)]$ with m found in metallic glass-formers. Established from the studies of many different metallic glass-formers is that in the glassy state the activation energy of β-relaxation is related to T_g by $E_\beta = 26(\pm 2)RT_g$.[30] Hence, in a plot against T_g-scaled reciprocal temperature, T_g/T, $\log_{10}\tau_\beta(T_g/T)$ has the same slope of $26/2.303 = 11.3$ (but not necessarily the same magnitude) for all metallic glass-formers with different values of $n(T_g)$ or Kohlrausch exponent $\beta_{\mathrm{KWW}}(T_g) \equiv (1-n(T_g))$. The fact that the variation of $\log_{10}\tau_\beta(T_g/T)$ with T_g/T for $T_g/T > 1$ is the same for all the metallic glasses considered is remarkable, and it implies that this holds also for $T_g/T < 1$ as well. This is shown by applying the CM Eqs. (2) and (3), from which we have for all T_g/T the relation

$$\tau_\alpha\left(\frac{T_g}{T}\right) = \left[(t_c)^{-n}\,\tau_0\left(\frac{T_g}{T}\right)\right]^{\frac{1}{1-n}} \approx \left[(t_c)^{-n}\,\tau_\beta\left(\frac{T_g}{T}\right)\right]^{\frac{1}{1-n}}. \qquad (6)$$

To satisfy this relation, the dependence of the magnitude of $\tau_0(T_g/T)$ or $\tau_\beta(T_g/T)$ as well as $\tau_\alpha(T_g/T)$ on the metallic glass-former through n becomes clear. It is easy to see from Eq. (6) that at $T_g/T = 1$ where $\tau_\alpha(T_g/T) = 10^3$ s, $\log_{10}\tau_0(T_g/T)$ or $\log_{10}\tau_\beta(T_g/T) = [3(1-n) - (12.7)n]$. This dependence of $\log_{10}\tau_0(T_g/T)$ on n at $T_g/T = 1$ is demonstrated for $n = 0.2$, 0.3, 0.4, and 0.5 in Fig. 8, and also shown are the parallel shifts of $\log_{10}\tau_0(T_g/T)$ with T_g/T for $T_g/T > 1$ and $T_g/T < 1$. In the final step, we calculate $\tau_\alpha(T_g/T)$ for all the four chosen values of n.

The results shown in Fig. 8 clearly demonstrate larger n engenders steeper rise of $\tau_\alpha(T_g/T)$ or more fragile behavior. The fragility index m has been calculated, and the values are

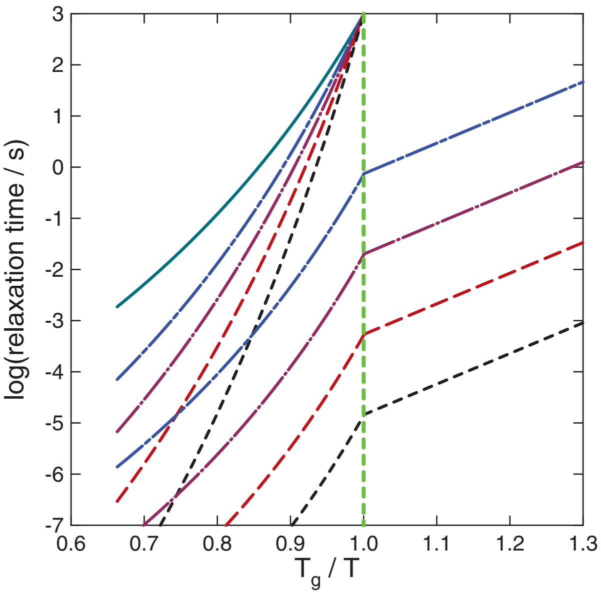

FIG. 8. The parallel lines for $T_g/T \geq 1$ from top to bottom represent the $\log[\tau_\beta(T)]$ of metallic glasses with increasing values, 0.2, 0.3, 0.4, and 0.5, of the coupling parameters $n \equiv (1-\beta_{\mathrm{KWW}})$. Here, T_g is defined by $\log[\tau_\alpha(T_g)] = 3$. The location of $\log[\tau_\beta(T_g)]$ at $T = T_g$ for each value of n is determined by Eq. (6). The dependence of τ_β on T_g/T for $T_g/T < 1$ is taken to be the same for all n, as suggested by the case for $T_g/T > 1$. The lines for $T_g/T < 1$ are $\log[\tau_\alpha(T_g/T)]$ calculated from $\tau_\beta(T_g/T)$ by Eq. (6) for the values of $n = 0.0$, 0.2, 0.3, 0.4, and 0.5. The same color and style of the lines are used for $\tau_\alpha(T_g/T)$ and $\tau_\beta(T_g/T)$ for each n value.

25, 31.3, 35.7, 41.7, and 50, respectively, for $n = 0.0$, 0.2, 0.3, 0.4, and 0.5. Thus, the correlation between fragility index m and the degree of separation between τ_α and τ_β observed experimentally in metallic glass-formers[28] is now derived from the CM.

III. CONCLUSION

Some universal properties of the secondary β-relaxation of the Johari-Goldstein kind have been well established in soft glass-formers including molecular and polymeric substances. Among them is the relation of the JG β-relaxation to the structural α-relaxation determined by the fractional exponent, $\beta_{\mathrm{KWW}} \equiv (1-n)$, of the Kohlrausch correlation function used to characterize the frequency dispersion of the α-relaxation. Specifically, the separation between τ_α and τ_β measured by [log $\tau_\alpha(T_\mathrm{g})$ − log $\tau_\beta(T_\mathrm{g})$] at $T = T_g$ not only correlates with $n(T_\mathrm{g})$ as found empirically by experiments, but also can be explained quantitatively by the coupling model.

Metallic glass-former differs drastically in chemical and physical structures than soft matter. Composed of a collection of atoms, it is not obvious that the β-relaxation exists in metallic glass-former. Interestingly, β-relaxation exists in metallic glasses. Although the β-relaxation exists in metallic glass-formers, it is not clear if the correlation will hold. Despite the difficulty in obtaining both quantities, $\tau_\beta(T_\mathrm{g})$ and $n(T_\mathrm{g})$, in metallic glass-formers, we have found [log $\tau_\alpha(T_\mathrm{g})$ − log $\tau_\beta(T_\mathrm{g})$] correlates with $n(T_\mathrm{g})$ at $T = T_g$. Taking into consideration the uncertainties of these parameters deduced by fitting experimental data, the correlation found is quantitatively consistent with the CM prediction. The establishment of the same connection to the structural α-relaxation as found in soft glass-formers indicates that the β-relaxation is the JG β-relaxation. Thus, it plays not only a fundamental role in glass transition,[31] but also in macroscopic properties such as the shear transformation zones, ductile-brittle transition in deformation, crystallization, and diffusion in shear bands of deformed metallic glasses.[32]

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