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Compositional origin of unusual β-relaxation properties in La-Ni-Al metallic glasses

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The β-relaxation of metallic glasses (MGs) bears nontrivial connections to their microscopic and macroscopic properties. In an effort to elucidate the mechanism of the β-relaxation, we studied by dynamical mechanical measurements the change of its properties on varying the composition of $La_{60}Ni_{15}Al_{25}$ in various ways. The properties of the β-relaxation turn out to be very sensitive to the composition. It is found that the isochronal loss peak temperature of β-relaxation, $T_{\beta,peak}$, is effectively determined by the total (La + Ni) content. When Cu is added into the alloy to replace either La, Ni, or Al, the $T_{\beta,peak}$ increases with decrease of the (La + Ni) content. The trend is in accordance with data of binary and ternary MGs formed from La, Ni, Al, and Cu. Binary La-Ni MGs have pronounced β-relaxation loss peaks, well separated from the α-relaxation. In contrast, the β-relaxation is not resolved in La-Al and La-Cu MGs, showing up as an excess wing. For the ternary La-Ni-Al MGs, increase of La or Ni content is crucial to lower the $T_{\beta,peak}$. Keeping the Al content fixed, increase of La content lowers the $T_{\beta,peak}$ further, indicating the more important role La plays in lowering $T_{\beta,peak}$ than Ni. The observed effects on changing the composition of $La_{60}Ni_{15}Al_{25}$ lead to the conclusion that the properties of the β-relaxation are mainly determined by the interaction between the largest solvent element, La, and the smallest element, Ni. From our data, it is further deduced that La and Ni have high mobility in the MGs, and this explains why the β-relaxation in this La-based MGs is prominent and well resolved from the α-relaxation as opposed to Pd- and Zr-based MGs where the solvent and largest atoms, Pd and Zr, are the least mobile. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4893954]

I. INTRODUCTION

The secondary or β-relaxation, which persists on cooling down to the glassy state where the structural α-relaxation was fully arrested, has recently become an active research area.[1–3] This research trend in non-metallic glass-formers is due to the fact that the β-relaxation in a special class has a strong connection to the α-relaxation in properties. For molecular glass-formers, a requirement for the β-relaxation to belong to this special class is involvement of the entire molecule. The β-relaxation found by Johari and Goldstein[4] in totally rigid glass-formers automatically satisfies the condition. Metallic glasses (MGs) are composed of individual atoms and some can be treated as randomly packed hard spheres without complex inter- and intra-molecular interactions.[5] Despite the difference in chemical composition and physical structure from molecular glass-formers, the β-relaxation in MGs has also been observed by dynamical mechanical spectroscopy (DMS),[3,6–11] although its microscopic origin is unclear.[5,12–16] To meet the requirement of β-relaxation, all constituent atoms, solvent and solute, larger and smaller atoms, should participate in the β-relaxation for MGs. This has support from the observations of the involvement of the smaller and solute P atom in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ MG,[13] and the larger and solvent Zr atom in $Zr_{55}Cu_{30}Ni_{5}Al_{10}$ MG[5] in the β-relaxation. Among the MGs investigated up to now, a La-based La-Ni-Al MG system, such as $La_{60}Ni_{15}Al_{25}$, is known to be different from other MGs in having a very pronounced β-relaxation well separated from the α-relaxation.[6,7,11,12,17,18] The β-relaxation in MGs are linked to important properties including flow units for deformations,[12] brittle to ductile transition,[19] crystallization,[20,21] shear transformation zone,[22] and Poisson's ratio,[23] etc. The pronounced β-relaxation peak in this La-based MG can even lead to special mechanical properties, such as the tensile plasticity.[19] As a result, the question of what makes the β-relaxation of this La-Ni-Al MG[6,7,11] so special is an interesting one. The answer to this question can enhance the understanding of the nature of the β-relaxation, and its role in crystallization and the mechanical properties of MGs.

The addition of minor elements, or microalloying, is well practiced in the research of MGs to tailor the properties,[24,25] such as the glass forming ability (GFA),[26] and mechanical properties,[27]etc. Motivated by the simulation work on the pinning effect on the β-relaxation behavior of amorphous solids, in which a small fraction of pinned particles are sufficient to suppress the β-relaxation,[28] a typical La-based MG, $La_{60}Ni_{15}Al_{25}$, with pronounced β-relaxation was selected as the model material to

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[a)] Author to whom correspondence should be addressed. Electronic mail: whw@aphy.iphy.ac.cn investigate the compositional dependence of the properties of the β-relaxation.

We report the changes of the β-relaxation on varying the composition of $La_{60}Ni_{15}Al_{25}$ in several different directions in an effort to further understand the nature of the β-relaxation of this alloy system. First, Cu was added into the alloy to substitute either La, Ni, or Al to form various quaternary MGs. Then we fabricated binary MGs, La-Ni, La-Al, and La-Cu and also ternary MGs composed of La, Ni, and Al with the content of one constituent kept fixed. The observed trends of changes with composition are considered altogether to gain insight into the nature of the β-relaxation. The results indicate the high mobility of the solvent La atoms and the smallest Ni atoms and also the interaction between them are crucial for $La_{60}Ni_{15}Al_{25}$ to possess the unusual properties of β-relaxation. The root cause of the unique dynamics and mechanical properties of the La-based MGs can be traced to the fact that the La solvent atoms constitute the fast component in the La-based MGs while the Pd and Zr solvent atoms are the slowest component in Pd- and Zr-based MGs.[29,30]

II. EXPERIMENTAL PROCEDURES

The ingots of the alloys studied in this work were prepared by arc melting the constituent elements in a Ti-gettered Argon atmosphere. Each ingot was remelted at least five times to ensure chemical homogeneity. For the ternary and quaternary alloys, cylinder samples with the diameter of 2 mm were fabricated by copper mould casting method. For the binary alloys ($La_{62}Ni_{38}$, $La_{65}Ni_{35}$, $La_{68}Ni_{32}$, $La_{65}Al_{35}$, and $La_{70}Cu_{30}$) which cannot be cast into bulk form due to their poor GFA, glassy ribbons with thickness of about 20 μm were fabricated by the single-roll melt-spinning in an Argon atmosphere. The amorphous structure of the samples was verified by X-ray diffraction (XRD) using Cu K_α radiation.

The thermal behaviors of the MGs were analyzed by the Perkin Elmer DSC 7 and 8000 at a heating rate of 20 K/min. The melting temperature, T_m, and liquidus temperature, T_L, were analyzed by the Netzsch DSC at a heating rate of 20 K/min. The dynamical mechanical properties of the MGs were measured on a TA Q800 dynamical mechanical analyzer (DMA). For the quaternary La-Ni-Al-Cu and ternary $La_{60}Ni_{15}Al_{25}$ cylindrical samples, single-cantilever bending method was used in an isochronal mode with a heating rate of 3 K/min, strain amplitude of 5 μm and discrete testing frequency of 1, 2, 4, 8, and 16 Hz. For the ternary samples, single-cantilever bending method was used in an isothermal mode with a temperature step of 3 K and discrete testing frequency of 1, 2, 4, 8, and 16 Hz. For the binary ribbon samples, tension mode was used in an isothermal mode with a temperature step of 3 K and discrete testing frequency of 0.2, 0.4, 0.8, 1.6, and 3.2 Hz.

III. RESULTS

A. Quaternary La-Ni-Al-Cu MGs

1. Isochronal dynamical mechanical measurements

The Cu was added into the $La_{60}Ni_{15}Al_{25}$ MG for partial substitution of either La, Ni, or Al. The glassy structures of the ternary, $La_{60}Ni_{15}Al_{25}$, and quaternary $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ ($x = 0$, 1, 2, 5, 8, and 10, with Cu replacing La), $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$ ($x = 0$, 1, 2, and 5, with Cu replacing Ni), and $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ ($x = 0$, 1, 2, 5, 8, 10, and 15, with Cu replacing Al) MGs were checked by XRD and thermal analysis. In Table I, the parameters of the thermal properties of the MGs are listed. The variations of the supercooled liquid region, ΔT ($\Delta T = T_{x1} - T_g$, in which T_{x1} is the onset temperature of the first crystallization event and T_g is the glass transition temperature), the reduced glass transition temperature, T_{rg} ($T_{rg} = T_g/T_l$, where T_l is the liquidus temperature), and the γ parameter ($\gamma = T_{x1}/(T_g + T_l)$, defined in Ref. 31), are calculated. There is a trend that the width of the supercooled liquid region ΔT and the γ parameter first increase to reach a maximum value and then decrease. The width of the supercooled liquid region is a measure of the supercooled

TABLE I. Thermal properties of the La-Al-Ni-Cu MGs.

Alloy composition (at.%)	T_g (K)	T_{x1} (K)	ΔT (K)	T_m (K)	T_L (K)	T_g/T_L	γ
$La_{60}Ni_{15}Al_{25}$	455	507	52	702	829	0.549	0.395
$La_{59}Ni_{15}Al_{25}Cu_1$	454	508	54	695	827	0.549	0.397
$La_{58}Ni_{15}Al_{25}Cu_2$	454	509	55	691	836	0.543	0.395
$La_{55}Ni_{15}Al_{25}Cu_5$	457	538	81	678	875	0.522	0.404
$La_{52}Ni_{15}Al_{25}Cu_8$	459	535	76	671	904	0.508	0.393
$La_{50}Ni_{15}Al_{25}Cu_{10}$	464	537	73	671	892	0.520	0.396
$La_{60}Ni_{15}Al_{25}$	455	507	52	702	829	0.549	0.395
$La_{60}Ni_{14}Al_{25}Cu_1$	454	510	56	695	820	0.554	0.400
$La_{60}Ni_{13}Al_{25}Cu_2$	449	499	50	689	816	0.550	0.394
$La_{60}Ni_{10}Al_{25}Cu_5$	442	493	51	663	850	0.520	0.382
$La_{60}Ni_{15}Al_{25}$	455	507	52	702	829	0.549	0.395
$La_{60}Ni_{15}Al_{24}Cu_1$	449	519	70	697	821	0.547	0.409
$La_{60}Ni_{15}Al_{23}Cu_2$	443	509	66	692	813	0.545	0.405
$La_{60}Ni_{15}Al_{20}Cu_5$	426	514	88	668	790	0.539	0.423
$La_{60}Ni_{15}Al_{17}Cu_8$	416	485	69	664	769	0.541	0.409
$La_{60}Ni_{15}Al_{15}Cu_{10}$	412	464	52	670	770	0.535	0.393
$La_{60}Ni_{15}Al_{10}Cu_{15}$	401	434	33	676	769	0.521	0.371

liquid stability against crystallization and correlates with the GFA to some extent.[24,32] The present result is in accordance with a recent research on the Ni-based MGs, in which GFA is shown to be a piecewise continuous function formed by intersecting compositional subsurfaces, each associated with a nucleation pathway for a specific crystalline phase, and the GFA varies exponentially with composition, whereas exponential cusps are observed from one crystallization pathway to another. And the overall GFA is shown to a peak at multiple exponential hypercusps that are interconnected by ridges, so there exists an optimized content of minor alloying element for GFA of the alloy.[33]

In Figs. 1(a)–1(c), we present the temperature dependences of loss modulus G'' at 1 Hz of the series of MGs of $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$, $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$, and $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs. G'' has been scaled by the maximum loss modulus, G''_{max}, of the α-relaxation peak. It can be seen that when La or Ni is partially replaced by Cu, the β-relaxation shifts to higher temperatures, but it is almost unchanged when Al is partially substituted by Cu. The insets of Figs. 1(a)–1(c) show the temperature dependence of G'' of the $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$, $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$, and $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$, respectively, where T and G'' have been scaled by the peak temperature of α-relaxation, $T_{\alpha,peak}$, and the maximum α-loss modulus, G''_{max}. It can be seen from the insets that the addition of the Cu into $La_{60}Ni_{15}Al_{25}$ to replace either La, Ni, or Al, the β-relaxation moves closer to the α-relaxation. Consequently, the increasing overlap of the β- and α-relaxations makes the β-relaxation peak less evident, and eventually transform from a peak to a shoulder.

To investigate the specific factors of the relationship between the β- and α-relaxations, the $T_{\beta,peak}$ was obtained from the isochronal experimental data quantitatively. For MGs with well resolved β-relaxation peak, $T_{\beta,peak}$ was directly obtained from the experimental results, while for those whose β-relaxation exhibits a shoulder form, the values were determined by fitting with the procedure described in Ref. 12. The results are collectively shown in Table II. The dependencies of the separation between the β- and α-relaxations, $\Delta T_{\alpha,\beta}$ ($\Delta T_{\alpha,\beta} = T_{\alpha,peak} - T_{\beta,peak}$), on the Cu content in $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$, $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$, and $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ are presented in Fig. 2(a). The plots show $\Delta T_{\alpha,\beta}$ invariably decreases with the addition of Cu to substitute either La, Ni, or Al. The dependencies of $T_{\beta,peak}$ on the total Cu and (La + Ni) content are presented in Figs. 2(b) and 2(c), respectively. The lines in Fig. 2 represent the best linear fit to the data obtained. It can be seen from Fig. 2(b) that when La or Ni is substituted by Cu, $T_{\beta,peak}$ increases almost linearly and when Al is substituted by Cu, the $T_{\beta,peak}$ is almost unchanged. These results indicate that $T_{\beta,peak}$ is effectively determined by the (La + Ni) content in the La-Ni-Al-Cu MGs. When the content of (La + Ni) decreases with the addition of Cu, the $T_{\beta,peak}$ increases linearly as shown in Fig. 2(c).

Therefore, although the β-relaxation appears to move towards the α-relaxation with Cu replacement in all three cases in the insets of Figs. 1(a)–1(c), where the temperature is normalized by the $T_{\alpha,peak}$, the specifics of the relation between β- and α-relaxations are different.

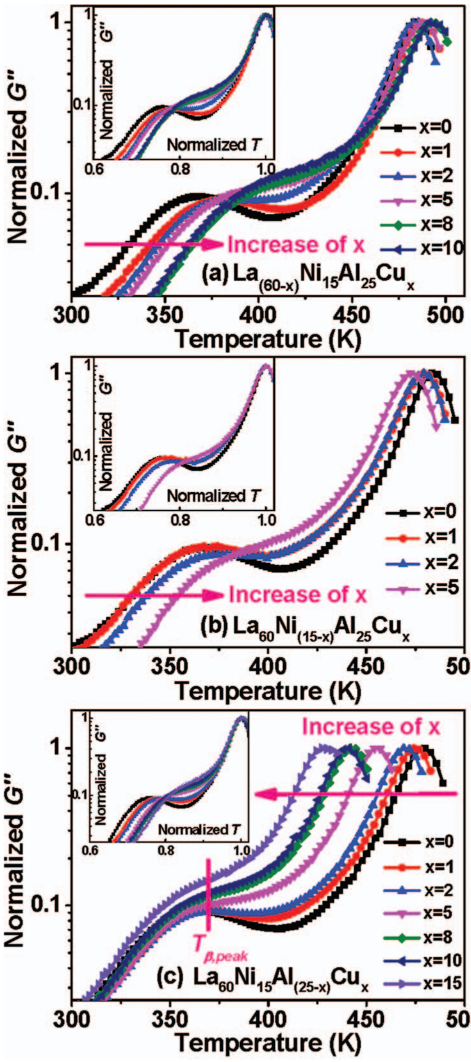

FIG. 1. Temperature dependence of the loss modulus G'' for the (a) $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ (x = 0, 1, 2, 5, 8, and 10), (b) $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$ (x = 0, 1, 2, and 5) and (c) $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ (x = 0, 1, 2, 5, 8, 10, and 15) MGs. The loss modulus G'' is normalized by the loss modulus at the peak temperature of the α-relaxation, $T_{\alpha,peak}$. The insets show the temperature dependence of the loss modulus G'' for the (a) $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ (x = 0, 1, 2, 5, 8, and 10), (b) $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$ (x = 0, 1, 2, and 5) and (c) $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ (x = 0, 1, 2, 5, 8, 10, and 15) MGs, where the temperature is normalized by the peak temperature of the α-relaxation, $T_{\alpha,peak}$, and the loss modulus G'' is normalized by loss modulus at the peak temperature of the α-relaxation, $T_{\alpha',peak}$. Arrows represent the direction of the increase of Cu content. The $T_{\beta',peak}$ of $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs is indicated by the vertical line.

(i) For the case of substitution of La by Cu, both $T_{\beta,peak}$ and $T_{\alpha,peak}$ increase, but the increase of $T_{\alpha,peak}$ is far less than compared with $T_{\beta,peak}$. Taking $La_{60}Ni_{15}Al_{25}$ and $La_{50}Ni_{15}Al_{25}Cu_{10}$ MGs as examples, the increase of $T_{\beta,peak}$ is almost 46 K, while the increase of $T_{\alpha,peak}$ is only about 9 K. Hence the change in relation between the β- and α-relaxations is mainly due to the increase of $T_{\beta,peak}$. The slope of change of $T_{\beta,peak}$ with the substitution of La by Cu is about 4.52 K per 1% change in La content.

(ii) In the case of substitution of Ni by Cu, the β-relaxation shifts to higher temperatures as well. Meanwhile, the α-relaxation moves to lower temperatures. Both effects are responsible for the decrease of separation between the

TABLE II. The peak temperatures of β- and α-relaxations for the La-Al-Ni-Cu MGs.

Alloy composition (at.%)	$T_{\beta,peak}$ (K)	$T_{\alpha,peak}$ (K)	$\Delta T = T_{\alpha,peak} - T_{\beta,peak}$ (K)
$La_{60}Ni_{15}Al_{25}$	367 ± 1	483	116 ± 1
$La_{59}Ni_{15}Al_{25}Cu_1$	380 ± 1	487	107 ± 1
$La_{58}Ni_{15}Al_{25}Cu_2$	387 ± 1	485	98 ± 1
$La_{55}Ni_{15}Al_{25}Cu_5$	390 ± 2	487	97 ± 2
$La_{52}Ni_{15}Al_{25}Cu_8$	407 ± 3	492	85 ± 3
$La_{50}Ni_{15}Al_{25}Cu_{10}$	414 ± 3	491	77 ± 3
$La_{60}Ni_{15}Al_{25}$	367 ± 1	483	116 ± 1
$La_{60}Ni_{14}Al_{25}Cu_1$	370 ± 2	479	109 ± 2
$La_{60}Ni_{13}Al_{25}Cu_2$	376 ± 2	479	103 ± 2
$La_{60}Ni_{10}Al_{25}Cu_5$	382 ± 2	472	90 ± 2
$La_{60}Ni_{15}Al_{25}$	365 ± 1	479	114 ± 1
$La_{60}Ni_{15}Al_{24}Cu_1$	367 ± 2	474	107 ± 2
$La_{60}Ni_{15}Al_{23}Cu_2$	372 ± 2	469	97 ± 2
$La_{60}Ni_{15}Al_{20}Cu_5$	371 ± 3	454	83 ± 3
$La_{60}Ni_{15}Al_{17}Cu_8$	370 ± 2	441	71 ± 2
$La_{60}Ni_{15}Al_{25}Cu_{10}$	373 ± 2	441	68 ± 2
$La_{60}Ni_{15}Al_{10}Cu_{15}$	370 ± 2	427	57 ± 2

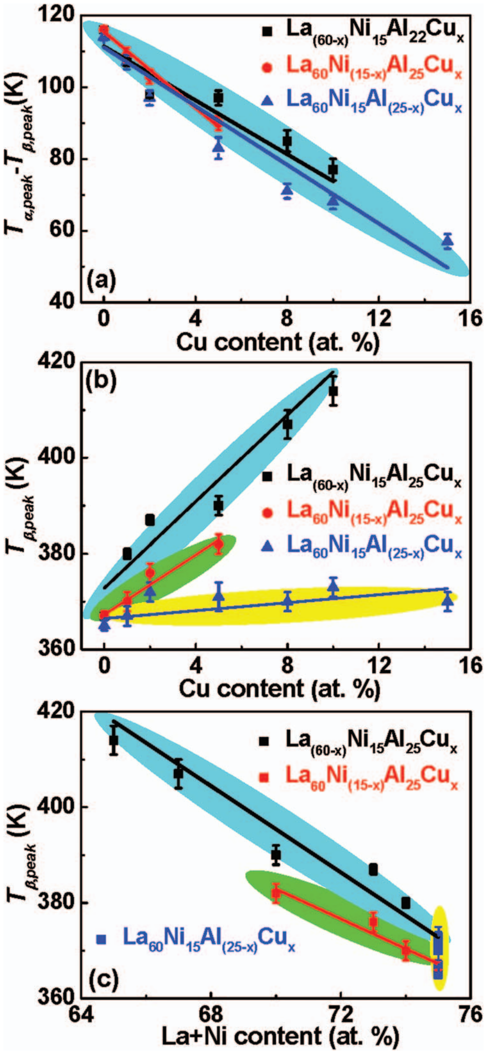

FIG. 2. (a) The width between the β- and α-relaxation, $\Delta T_{\alpha,\beta}$ ($\Delta T_{\alpha,\beta} = T_{\alpha,peak} - T_{\beta,peak}$), as a function of the content of Cu. (b) The peak temperature of β-relaxation, $T_{\beta,peak,}$ as a function of the content of Cu. (c) The peak temperature of β-relaxation as a function of (La + Ni) content for the $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$, $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$, and $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs, respectively. The line represents the best linear fit to the data. The shadow ellipse areas are used to guide the eye.

β- and α-relaxations. The slope of change of $T_{\beta,peak}$ with the substitution of Ni by Cu is about 3.12 K per 1% change in Ni content.

(iii) For the case of Al being substituted by Cu, the change in the separation of the β-relaxation from the α-relaxation is mainly due to the large decrease of the $T_{\alpha,peak}$, while the low temperature flank of the β-loss peak as well as $T_{\beta,peak}$ remains almost unchanged. The fact that $T_{\beta,peak}$ is practically unchanged, while the contents of La and Ni remain the same is an indication that the dynamics of the β-relaxation is principally determined by the La and Ni atoms, and the interaction between them. It is possible that the slower Al atoms participate in the β-relaxation but the relaxation strength is weak and the contribution is not evident in $La_{60}Ni_{15}Al_{25}$ or $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs. On the other hand, $T_{\alpha,peak}$ decreases by about 54 K when the Cu content reaches 15% to replace Al. This together with no change in $T_{\beta,peak}$ suggest that Al atoms contribute mainly in the α-relaxation, although they participate in the β-relaxation, albeit not detected in all the La-based MGs.

Based on the above experimental results, it can be concluded that La and Ni play a crucial role in determining the $T_{\beta,peak}$, and the $T_{\beta,peak}$ is more sensitive to the La content than that of the Ni, since the slope of change of $T_{\beta,peak}$ as a function of La content is larger compared with the case of Ni.

2. Isothermal dynamical mechanical measurements

The frequency dispersion of the α- and β-relaxations can only be obtained directly by the isothermal dynamical mechanical measurements. To further confirm the variation of β-relaxation in $La_{60}Ni_{15}Al_{25}$ with the Cu substitution, the frequency dependent isothermal mechanical relaxation spectra of $G''(f)$ of $La_{60}Ni_{15}Al_{25}$, $La_{50}Ni_{15}Al_{25}Cu_{10}$, $La_{60}Ni_{10}Al_{25}Cu_5$, and $La_{60}Ni_{15}Al_{17}Cu_8$ have been measured within the experimental frequency window of $3 \times 10^{-2} \leq f \leq 15$ Hz. Figure 3(a) shows the isothermal data for the $La_{60}Ni_{15}Al_{25}$ obtained over a wide range of temperatures, which show the α- and β-relaxations separately at different temperature regions. To clearly identify the β-relaxation, Fig. 3(b) presents the spectra at the temperature near the β-relaxation region, where the pronounced β-relaxation peak can be observed. The data taken at lower temperatures are shifted to superpose the one taken at the highest temperature. Satisfactory superposition of all the data shown in Fig. 3(c) enables determination of the frequency dispersion of the α-relaxation, and the fit by the Fourier transform of the Kohlrausch-Williams-Watts (KWW) stretched exponential function,[3,9]

$$\phi(t) = \exp[-(t/\tau\alpha)^{1-n}], \tag{1}$$

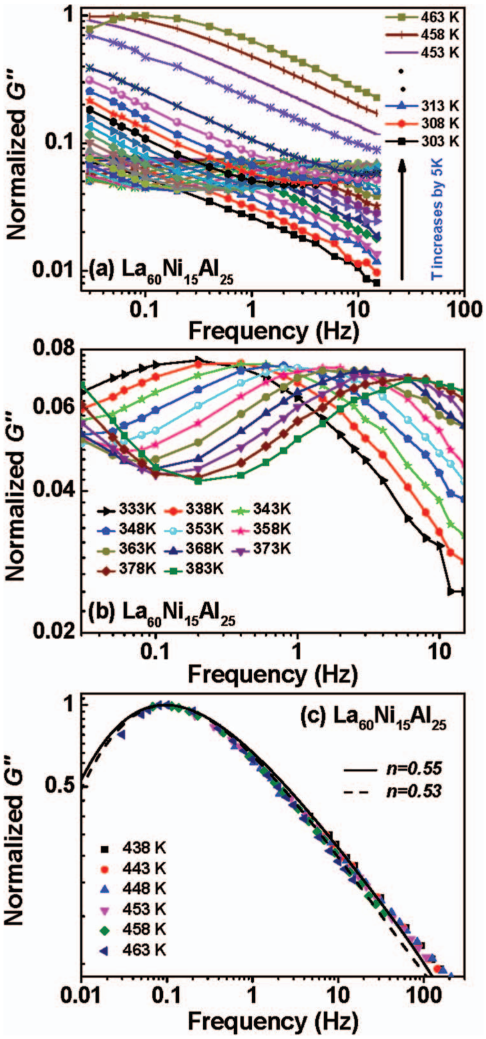

FIG. 3. (a) The normalized loss modulus G'' of $La_{60}Ni_{15}Al_{25}$ MG as a function of frequency at different temperatures. (b) Frequency dependence of the normalized loss modulus G'' of $La_{60}Ni_{15}Al_{25}$ MG at the lower temperatures. (c) Master curves of $La_{60}Ni_{15}Al_{25}$ MG (438–463 K) of DMA measurement. The solid and dashed lines represent KWW fit to the master curve.

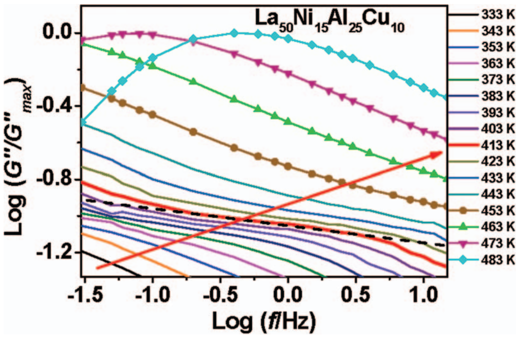

FIG. 4. (a) The normalized loss modulus G'' of $La_{50}Ni_{15}Al_{25}Cu_{10}$ MG as a function of frequency at temperatures from 333 K to 483 K. The red arrow indicates that the β-relaxation increases in strength and shifts to higher frequency with increase of the temperature. The red thick curve shows the frequency dependence of the normalized loss modulus G'' at 413 K. The dashed black line shows that the intermediate weak frequency dependence of $G''(f)$ can be described approximately by a power law, Af^{-c} with $c \approx 0.1$.

where n is the complement of the stretched exponent, $n = 1 - \beta$. The fits with two values of $n = 0.53$ and 0.55 are shown. Due to significant scatters of the data, these values are rough estimates of the actual value. The large separation between the α- and β-relaxations in frequencies is indicated by almost hundred degrees difference in the temperature range for the α- and β-relaxations to appear in the same experimental frequency window.

One reason to show the isothermal spectra of $La_{60}Ni_{15}Al_{25}$ in Figs. 3(a)–3(c) is to make a contrast with $La_{50}Ni_{15}Al_{25}Cu_{10}$. We have already seen from the isochronal spectra in Fig. 1(a) that the replacement of 10% La by Cu transforms the resolved β-loss peak to a shoulder, and moving it closer to the α-relaxation. The isothermal $G''(f)$ spectra of $La_{50}Ni_{15}Al_{25}Cu_{10}$ from 333 to 483 K are presented in Fig. 4. The β-relaxation is not resolved as a peak at all temperatures investigated. Only seen is the increase of its relaxation strength and shift to higher frequencies to overlap with the α-relaxation with increase of temperature. The trend is suggested by the arrow in Fig. 4. Thus the α-loss peak is broadened by the overlap, and the resultant shape does not reflect the actual frequency dispersion of the α-relaxation of $La_{50}Ni_{15}Al_{25}Cu_{10}$ MG. The difference in isothermal spectra of the two La-based MGs here is similar to that between Pd-based MGs,[34] $Pd_{40}Ni_{10}Cu_{30}P_{20}$, $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ (containing Cu), and $Pd_{40}Ni_{40}P_{20}$, $Pd_{30}Ni_{50}P_{20}$ (without Cu). The two Pd-based MGs containing Cu have resolved β-loss peak in the isothermal spectra well separated from the α-relaxation, and the observed frequency dispersion of the slow process is truly that of the α-relaxation, as in the case of $La_{60}Ni_{15}Al_{25}$. However, we hasten to point out that the resolved β-loss peak is much more prominent in $La_{60}Ni_{15}Al_{25}$ than in the two Pd-based MGs containing Cu. This difference in relaxation strength of the β-relaxation of $La_{60}Ni_{15}Al_{25}$ compared with that of the two Pd-based MGs containing Cu has the consequence that the β-relaxation of the former remains well resolved but not evident for the latter in the master curves constructed by superposition of isothermal data taken over a range of temperatures to be discussed in Subsection III A 3. On the other hand, the two Pd-based MGs without Cu have no resolved β-relaxation because the two processes are not well separated from each other. Like the case of $La_{50}Ni_{15}Al_{25}Cu_{10}$, the α-relaxation is broadened by the overlapping β-relaxation, and the observed frequency dispersion does not reflect that of the α-relaxation, as shown by the data of $Pd_{30}Ni_{50}P_{20}$ in Fig. 3(b) in Ref. 34. Therefore, it is meaningless to compare the observed frequency dispersion of the Pd-based MGs containing Cu with that of the Pd-based MGs without Cu. They appear to have the same shape as shown in the inset of Fig. 5 in Ref. 34 and imply the same fractional exponent, (1-n), when fitted by the Fourier transform of the KWW function (Eq. (1)), but the origins of the shape are entirely different. This difference is important when applying the Coupling Model (CM) to explain the approximate relation between τ_β and τ_α given by[1,2,23,35]

$$\tau\alpha \approx [tc^{-n}\tau\beta]^{1/(1-n)}, \qquad (2)$$

which is obtained via the CM equation,

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

Together with the approximate equality,

$$\tau_\beta \approx \tau_0, \tag{4}$$

where τ_0 is the primitive relaxation time in the context of CM. In Eqs. (2) and (3), t_c is the temperature insensitive crossover time from primitive (or non-cooperative) relaxation with time dependence, $\exp(-t/\tau_0)$, to cooperative α-relaxation with the Kohlrasuch stretched exponential time dependence of Eq. (1). The quantity n is the coupling parameter of the α-relaxation, characterizing the heterogeneous and cooperative α-relaxation dynamics, and has the same value as n appearing in the exponent, $(1 - n)$, in Eq. (1). 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.[1] It is shorter for metallic systems with $t_c \approx 0.2$ ps from simulations,[36,37] which is reasonable from the CM[1] in view of 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 MG than molecular glasses.[24,38] The approximate relation (3) is conceptually based on the primitive relaxation of the CM and the 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. Experimental dielectric and mechanical relaxation data of many glass-formers, where τ_0 was calculated from Eq. (3) and τ_β obtained from experiment, have verified this approximate relation.[1,2,39–42]

Equation (2) applies to $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$, and also to $La_{60}Ni_{15}Al_{25}$ MGs because n from the fit is truly the coupling parameter n_α of the α-relaxation in the CM. In contrast, Eq. (2) does not apply to $Pd_{40}Ni_{40}P_{20}$, $Pd_{30}Ni_{50}P_{20}$, and $La_{50}Ni_{15}Al_{25}Cu_{10}$, since the frequency dispersion is determined not only by the actually smaller coupling parameter n of the α-relaxation than n from the fit, but also by the extra broadening from the overlap with the β-relaxation. The cautionary remark applies to other MGs with unresolved β-relaxation not well separated from the α-relaxation.

3. Master curves

Assuming the time-temperature superposition (TTS) principle is valid for the MGs, the master curve of $La_{50}Ni_{15}Al_{25}Cu_{10}$ was obtained from the isothermal spectra taken over the entire temperature range, and is presented in Fig. 5(a). On the high frequency side of the intense α-relaxation peak appears a shoulder, which can be taken as the presence of an unresolved β-relaxation. The master curves of other Cu-containing La-based MGs presented in Fig. 5(b) show similar β-relaxation properties, but differently for $La_{60}Ni_{15}Al_{25}$ which has a resolved β-loss peak well separated from the α-loss peak. It should be pointed out that TTS strictly does not hold when both the α- and β-relaxations are considered, because the two processes have different temperature dependence. Hence, the master curves are only approximate representations of the overall dynamics at the reference temperature. Nevertheless, the master curves in Fig. 5(b) give another demonstration of the change in the relation between the α- and the β-relaxations by the substitution of La by Cu, in accordance with the isochronal experiment.

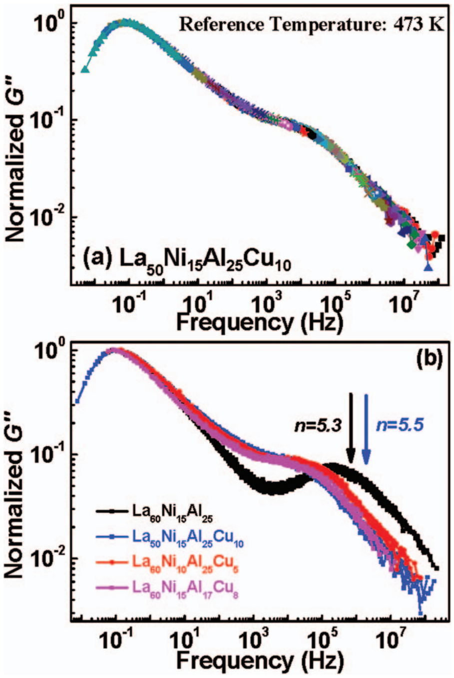

FIG. 5. (a) The master curve of the $La_{50}Ni_{15}Al_{25}Cu_{10}$ MG. The reference temperature is 473 K. (b) Comparison of master curves of $La_{60}Ni_{15}Al_{25}$, $La_{50}Ni_{15}Al_{25}Cu_{10}$, $La_{60}Ni_{10}Al_{25}Cu_5$, and $La_{60}Ni_{15}Al_{17}Cu_8$, respectively. The reference temperature for them are 453 K, 473 K, 443 K, and 413 K, respectively.

It is worthwhile to compare the master curves of the La-based MGs in Fig. 5(b) with those of the Pd-based MGs obtained in Ref. 34. The master curves of all the Pd-based MGs in Fig. 5 of Ref. 34 exhibit a shoulder but no resolved β-loss peak, and the results resemble those of our Cu-containing La-based MGs. The master curve of $La_{60}Ni_{15}Al_{25}$ in Fig. 5(b) distinguished itself from the rest of the other MGs in having a resolved β-loss peak is another manifestation of the unusual dynamic properties of the La-Ni-Al systems.

B. Binary La-Ni, La-Al, and La-Cu MGs

The DMA data of quaternary La-Ni-Al-Cu MGs and the trends found in varying the composition point to the crucial role played by La and Ni in determining the properties of the β-relaxation. To further confirm their role as well as that of the constituent elements, the ribbons of the binary $La_{65}Ni_{35}$, $La_{65}Al_{35}$, and $La_{70}Cu_{30}$ MGs were prepared. The glassy nature of the binary MG ribbons was confirmed by the XRD and DSC. Figure 6 shows the temperature dependences of loss modulus G'' of the binary MGs measured in ribbons with thickness of about 20 μm at a frequency of 0.2 Hz. Due to their instability towards crystallization at higher temperatures, the α-relaxation peak cannot be observed directly, and the β- and α-relaxations were fitted with the procedure described in Ref. 12. The results for $La_{65}Ni_{35}$, $La_{65}Al_{35}$, and $La_{70}Cu_{30}$ are presented in Figs. 6(a)–6(c). It can be seen that the properties of the β-relaxation depend strongly on the

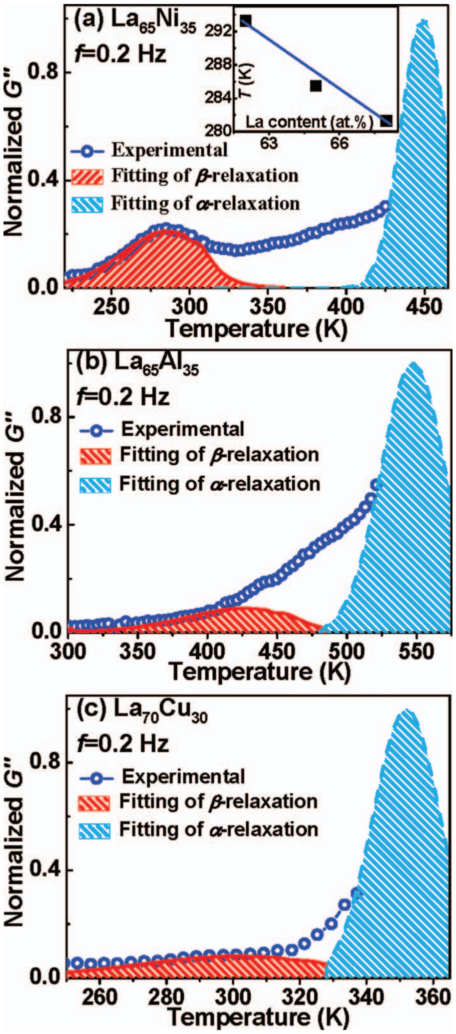

FIG. 6. Temperature dependence of the normalized loss modulus G'' for the (a) $La_{65}Ni_{35}$, (b) $La_{65}Al_{35}$, and (c) $La_{70}Cu_{30}$ MG ribbons at a frequency of 0.2 Hz. The inset shows the temperature dependence of $T_{\beta,peak}$ on the La content of La-Ni binary MGs. The blue regions represent the KWW fit of α-relaxation, while the red regions represent the KWW fit of the β-relaxation.

composition. For $La_{65}Ni_{35}$, a pronounced β-relaxation peak was observed at $T_{\beta,peak} \approx 285$ K. For $La_{65}Al_{35}$, only an excess wing is found. For $La_{70}Cu_{30}$, the excess wing is weak, and the temperature dependence of the loss at lower temperatures becomes so weak that the process resembles nearly constant loss in molecular glass-formers and in a metallic glass.[43] The drastic change of the β-relaxation found by replacement of Ni in $La_{65}Ni_{35}$ by Cu is consistent with the same effect found in the quaternary MGs shown before in Fig. 1(b). The inset of Fig. 6(a) shows the temperature dependence of $T_{\beta,peak}$ on the La content for all three binary La-Ni MGs measured. It is found that the $T_{\beta,peak}$ decreases with increase of La content. This further indicates that La plays a more important role to lower $T_{\beta,peak}$. From the collection of data of the binary MGs we can independently conclude that La and Ni are indeed crucial to the unique β-relaxation properties found in $La_{60}Ni_{15}Al_{25}$, in concert with the experimental results of quaternary La-Ni-Al-Cu MGs.

C. Ternary La-Ni-Al MGs

We also studied other members of the family of ternary La-Ni-Al MGs based on $La_{60}Ni_{15}Al_{25}$ but varying the contents of the two constituents while keeping the content of one element constant. The glassy nature of the ternary MGs was confirmed by the XRD. Figure 7(a) presents the normalized temperature dependence of G'' of the ternary $La_{(60\text{-}x)}Ni_{(15+x)}Al_{25}$ MGs, and the inset of Fig. 7(a) shows the $T_{\beta,peak}$, as a function of La content. On replacing Ni by La while keeping Al content fixed, the $T_{\beta,peak}$ decreases. The line in the inset represents the best linear fit to the data and slope is about -3 K per 1% change of La. The concomitant reduction of $T_{\alpha,peak}$ is possibly due to increase of La content as well. Figures 7(b) and 7(c) present the normalized temperature dependence of G'' of the $La_{(60\text{-}x)}Ni_{15}Al_{(25+x)}$, and $La_{60}Ni_{(15\text{-}x)}Al_{(25+x)}$ MGs and the insets of Figs. 7(b) and 7(c) show the $T_{\beta,peak}$ as a function of La or Ni content when Ni

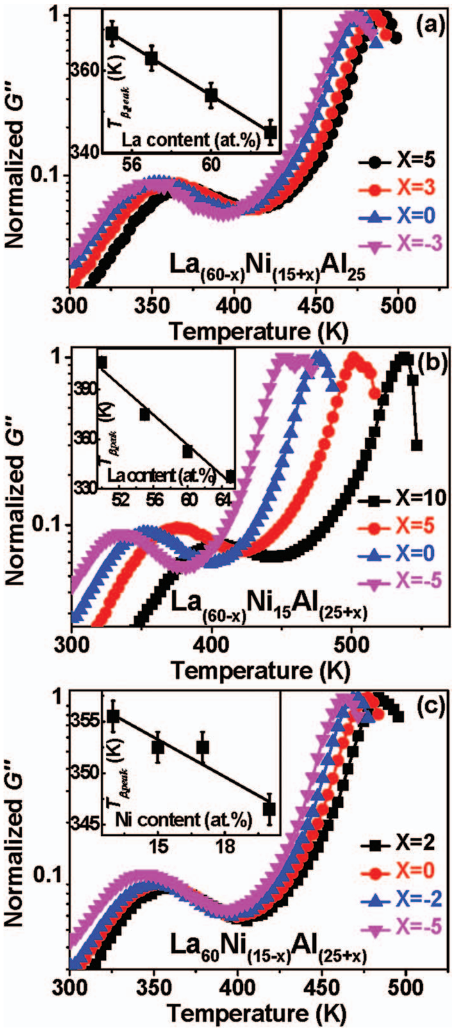

FIG. 7. Temperature dependence of the loss modulus G'' for the (a) $La_{(60\text{-}x)}Ni_{(15+x)}Al_{25}$, (b) $La_{(60\text{-}x)}Ni_{15}Al_{(25+x)}$, and (c) $La_{60}Ni_{(15\text{-}x)}Al_{(25+x)}$ MGs, respectively. The loss modulus G'' is normalized by loss modulus at the peak temperature of the α relaxation, $T_{\alpha',peak}$. The inserts in (a) and (b) show the peak temperature of β-relaxation as a function of La content when the content of Ni or Al is fixed. The insert in (c) shows the peak temperature of β-relaxation as a function of Ni content when the content of La is fixed. The line in the inset represents the best linear fit to the data.

or La content is fixed, respectively. Both show the increase of $T_{\beta,peak}$ on replacing the La and Ni by Al, which indicates that both La and Ni are important to lower $T_{\beta,peak}$. The lines in the insets of Figs. 7(b) and 7(c) represent the best linear fit to the data and the slopes are -4.59 K and -1.21 K per 1% atomic change of La and Ni, respectively. Thus, the data of the ternary MGs further confirm the important role of La in lowering $T_{\beta,peak}$. The trends seen in the ternary MGs are in accordance with those found in the quaternary and binary MGs.

IV. DISCUSSIONS

A. Fragility of $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MGs

Based on the above isochronal and isothermal experimental results, it is found that for the quaternary $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MGs, with the substitution of La by Cu, the β-relaxation transforms from a peak to a shoulder. To explain the evolution of the β-relaxation, the fragility introduced by Angell,[44] which describes the temperature dependence of viscosity or relaxation time of the supercooled liquid region, is measured. The fragility has been found to correlate with the evolution of the β-relaxation in a LaCe-based MG system[45] and in a series of neat polyalcohols.[46] In both cases, more fragile glasses exhibit more pronounced β-relaxation, though the correlation between fragility and β-relaxation in glasses still remains controversial.[47] Here, the $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MG systems were selected to investigate the correlation between fragility and β-relaxation. The method to estimate the fragility is interpreted in details in Ref. 48. The dependence of T_g on the heating rate is shown in Fig. 8(a). For each heating rate, q_H, a particular average structural relaxation time, τ, can be obtained,

$$\tau = \frac{\Delta T g}{q H}, \tag{5}$$

where $\Delta Tg = T_g{}^{end} – T_g{}^{onset}$ is the width of the glass transition held constant at 30 K, which is a good approximation for ΔTg at all constant heating rates. The ΔTg was also found to be kept at 25 K for all constant heating rates in Ref. 49. The structural relaxation time, τ, was fitted by the Vogel-Fulcher-Tammann (VFT) equation,

$$\tau = \tau_\infty \exp\left(\frac{DT_0}{T - T_0}\right), \tag{6}$$

where τ_∞ is the value of the relaxation time at infinite temperature, and is kept constant with the value of 1×10^{-14} s. D is the fragility parameter and T_0 is the VFT temperature. The fragility parameters fitted by Eq. (6) are shown in Fig. 8(b). Compared with the ternary $La_{60}Ni_{15}Al_{25}$ MG, the substitution of La by Cu increases D slightly to make the glasses stronger. For the ternary $La_{60}Ni_{15}Al_{25}$ MG, the fragility parameter D is about 21.1, while for the quaternary $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MGs, the fragility parameter D is about between 24 and 26. This is in accordance with the finding[49] that the MGs become stronger with the increase of number of components. It is rationalized by pronounced size mismatches between the components in the multicomponent systems, and the existence of higher packing densities with smaller free volume and higher degree of order. However, the fragility of the quaternary MGs does not change or slightly changes with content of Cu from 1% to 10%. On the other hand, the β-relaxation and its relation with the α-relaxation changes significantly and monotonically as can be seen from Fig. 1(a). So there is no direct relationship between the fragility and β-relaxation for this $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MG system. Also noted here is the width of the supercooled liquid region, ΔT, and the γ parameter first increase and then decrease, and hence the GFA may be optimized only at an intermediate substitution. So the gradual and monotonic variation of β-relaxation may indicate that for this La-Ni-Al-Cu MGs, there is no direct relationship between the GFA and β-relaxation.

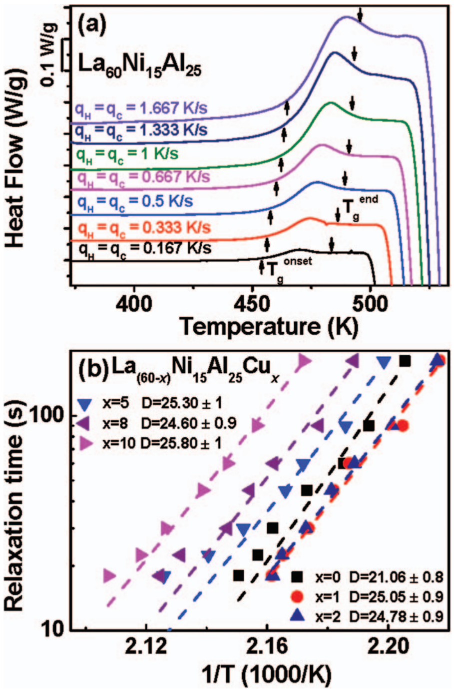

FIG. 8. (a) DSC heat flow curves of the $La_{60}Ni_{15}Al_{25}$ showing the glass transition shift for the same heating and cooling rates, q_H and q_C, respectively. $T_g{}^{onset}$ and $T_g{}^{end}$ represent the onset and end of the glass transition, respectively. (b) The fragility parameter, D, calculated from fitting the relaxation time data using Eq. (6). The dashed lines are the VFT fits to the measured values of $T_g{}^{onset}$.

B. Mixing enthalpy

Mixing enthalpy principle has been used to explain the different manifestations of the β-relaxation in MGs.[14] Prominent β-relaxation is associated with systems where all atomic pairs have large similar negative values of mixing enthalpy, whereas positive or significant fluctuations in mixing enthalpy suppress β-relaxation. The data of mixing enthalpy of constituent atomic pairs are derived from Ref. 50 and are presented in the inset of Fig. 9. The addition of Cu makes the fluctuation of mixing enthalpy between atomic pairs larger. Since the mixing enthalpy between Cu-Ni and Cu-Al are $+4$ and -1 kJ/mol, respectively, while the mixing enthalpy for the La-Ni, La-Al, and Ni-Al are $+27$, -38, and -22 kJ/mol.

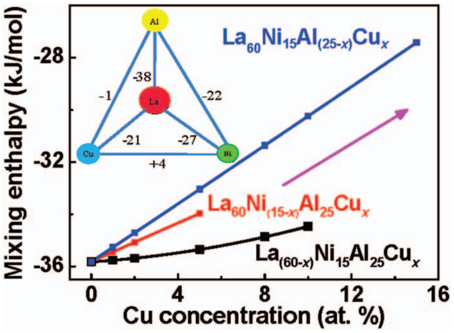

FIG. 9. Mixing enthalpy for the La-Ni-Al-Cu MGs. The inset shows the mixing enthalpy of the constituent pairs in La-Ni-Al-Cu MG. The symbol represents the alloys prepared in this work. The direction of the arrow indicates the decrease of separation between the β- and α-relaxations with the increase of Cu content.

Using the empirical models for ΔH_{mix}, the mixing enthalpy for the La-Ni-Al-Cu quaternary MGs is shown in Fig. 9. The direction of the arrow indicates the decrease of separation between the β- and α-relaxations with the increase of Cu content. It can be seen that with the addition of Cu, the mixing enthalpy becomes weaker (less negative). According to Ref. 14, this should make the β-relaxation less pronounced. The present experimental DMA results of the quaternary La-Ni-Al-Cu MGs are in accordance with this rule. For the binary La-Ni, La-Al, and La-Cu, it is found that the $La_{65}Ni_{35}$ MG with less negative mixing enthalpy ($\Delta H_{mix} = -24.57$ kJ/mol) shows a more pronounced β-relaxation than $La_{65}Al_{35}$ whose mixing enthalpy is more negative ($\Delta H_{mix} = -34.58$ kJ/mol). As a result, the mixing enthalpy principle fails to explain the trend of the β-relaxation for the binary La-Ni and La-Al MG systems. However, as cautioned in Ref. 14, the mixing enthalpy principle does not consider the interactions between the same kinds of atoms, which could be important for binary or monatomic systems.

C. Coupling model explanation

Mention has been made of the CM[1] in Sec. III, and the key Eqs. (1)–(4) have been applied to various problems related to the β-relaxation in MGs.[23,35,42,51,52] The primitive relaxation time, τ_0, of the CM is related to τ_α exactly by Eq. (3). The difference between Eqs. (2) and (3) originates from $\tau_0 \approx \tau_\beta$, the fact that the two relaxations are only approximately the same. If n is known from the fit of the frequency dispersion of the α-relaxation by the Fourier transform of Eq. (1) and t_c is known from experiment, then Eq. (3) can be used to calculate τ_0. The calculated value of τ_0 turns out to be approximately the same as τ_β when applying this CM prediction to many different glass-formers.[2,39–42,51–53] The value of n for $La_{60}Ni_{15}Al_{25}$ is estimated to be about 0.53 or 0.55 by fitting the isothermal $G''(f)$ in Fig. 3(c). These values of n are consistent with the values of 0.58 ± 0.04 obtained from fit to the isochronal spectra.[42] We apply Eq. (3) with $t_c = 0.2$ ps to calculate τ_0 from τ_α of the $G''(f)$ master curve in Fig. 5(b) by taking into account that the actual value of α-loss peak is at about 0.1 Hz or $f_{max} = 0.1$ Hz. For $n = 0.55$, we obtain $\log(\tau_0/\text{s}) = -6.9$ or $\log(f_0/\text{Hz}) = 6.1$ and $\log(f_0/f_{max}) = 7.1$ shown by the blue arrow in Fig. 5(b). For $n = 0.53$, we obtain $\log(f_0/\text{Hz}) = 5.8$ and $\log(f_0/f_{max}) = 6.8$, indicated by the black arrow. The approximate agreement of the calculated $\log(f_0/f_{max})$ with the experimental $\log(f_\beta/f_{max})$ is indication of applicability of the CM to $La_{60}Ni_{15}Al_{25}$ MG, because the α-relaxation is well separated from the β-relaxation, and hence its dispersion truly reflects that from intermolecular cooperativity and the coupling parameter of the α-relaxation. It has been applied with similar success to the master curve of $Pd_{40}Ni_{10}Cu_{30}P_{20}$, which has the dispersion of the α-relaxation not broadened by the β-relaxation.[18] However, the above should not be applied to $La_{50}Ni_{15}Al_{25}Cu_{10}$ and $Pd_{30}Ni_{50}P_{20}$,[34] with the value of n determined by the fit to the α-loss peak using the Fourier transform of the KWW function. This is because, as elucidated by Fig. 4 herein and Fig. 3(b) in Ref. 34, the nearby β-relaxation overlaps and broadens the α-relaxation of $La_{50}Ni_{15}Al_{25}Cu_{10}$ and $Pd_{30}Ni_{50}P_{20}$ MGs. Therefore, the value of n from the fit is larger than the actual value of the intermolecular coupling for these two MGs. Incidentally, the extra broadening of the α-loss peak in $Pd_{30}Ni_{50}P_{20}$ make its width not too different from that of $Pd_{40}Ni_{10}Cu_{30}P_{20}$.[34] This implies the actual coupling parameter of $Pd_{30}Ni_{50}P_{20}$ is smaller than that of $Pd_{40}Ni_{10}Cu_{30}P_{20}$, and this explains qualitatively the smaller separation of the β-relaxation from the α-relaxation in the former than in the latter.

D. Possible origins from the diffusion perspective

The La-based MGs similar to $La_{60}Ni_{15}Al_{25}$ are unique in having a prominent, fast, and well resolved β-relaxation loss peak, which is well separated from the α-relaxation peak. This is unlike the spectra of most other MGs, which show the existence of the β-relaxation by the presence of excess loss or shoulder of the α-relaxation peak in isochronal spectra.[17,18] As a result, what makes the La-based MGs so special is an interesting question. In a previous research on a $La_{55}Al_{25}Ni_{20}$ MG,[6] according to the approximate equivalence of activation energy between the β-relaxation and the diffusion coefficient for Al and Ni in Al, it was concluded that the low temperature relaxation was associated with the short-range order of Al-Al or Al-Ni atomic pairs. For the present case of $La_{60}Ni_{15}Al_{25}$, we have three key experimental results to make our own deductions. First, the β-relaxation is almost unchanged, while the α-relaxation shifts to lower temperatures on replacing Al by Cu in the $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs. The observed effects indicate the La-Ni atomic pairs are mainly responsible for the β-relaxation. Second, the β-relaxation shifts to higher temperature side when La or Ni is replaced by Cu in the $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ and $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$ MGs. Third, a pronounced β-relaxation peak well separated from the α-peak exists in the binary La-Ni MGs, while the β-relaxation weakens to become an excess wing in the binary La-Al and La-Cu MGs. These two latter experimental facts support the first one, and all lead to the conclusion that the solvent La atoms and its interaction with Ni atoms may play a crucial role to determine the β-relaxation. According to a very recent research in a Au-based MG,[16] the distinct atomic rearrangements occurring at the onset of slow β-relaxation temperature regime are mainly confined to the short-range order. As a result, the observed pronounced β-relaxation peak in the $La_{60}Ni_{15}Al_{25}$ MG may arise from the La-Ni atomic pairs at short range.

MGs usually exhibit a single secondary or β-relaxation, however, molecular and polymeric glass-formers often have more than one secondary relaxations. The studies of past years[2] have found secondary relaxation satisfying some criteria is fundamentally important in the sense that it is the precursor of the α-relaxation by exhibiting properties that are connected to or inseparable from the α-relaxation, and hence related to glass transition. One criterion for small molecular glass-former is that the secondary relaxation involves the entire molecule.[1,2,47,54] If this criterion is applicable to MGs, then it means the all components must be involved in the β-relaxation. Based on the above experimental results, it is deduced that for this La-based La-Ni-Al MG, La-Ni atomic pairs are the mobile units, while the Al atoms is slower compared with the La and Ni atoms.

The β-relaxation in $La_{65}Ni_{35}$ is prominent and fast, but it becomes weak and slow in $La_{70}Cu_{30}$. This change suggests that Cu atoms in the quaternary $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ and $La_{60}Ni_{(15\text{-}x)}Al_{25}Cu_x$ MGs are slow compared with La and Ni as contributors to the β-relaxation, and may slow down the remaining La and Ni atoms by their presence. The slower motion of Cu atoms in the $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MG is in contrast with the faster motion of Cu in a Au-based MG, in which Cu in combination with the presence of Si accelerate the low-temperature kinetic phenomenon and enhance the dynamical heterogeneity in the glassy state.[16] Evidence of the disparity in the time scales of contributions from Cu and (La + Ni) can be found in the peculiar shape of the unresolved β-relaxation in the isothermal $G''(f)$ spectra of $La_{50}Ni_{15}Al_{25}Cu_{10}$ in Fig. 4. The high frequency part of the thick red curve for example in the figure looks like the high frequency flank of a β-relaxation contributed by (La + Ni) but assumes a very weak frequency dependence at lower frequencies for some decades before rising again. The intermediate weak frequency dependence of $G''(f)$ can be described approximately by a power law, Af^{-c} with $c \approx 0.1$, as illustrated by the dashed black line in Fig. 4, which can be interpreted as the loss, while the slower Cu atoms remain caged. Also it appears as the rather flat dispersion on the high frequency side of the shoulder in the master curve of $G''(f)$ in Fig. 5(a). The final rise of $G''(f)$ at lower frequencies is the contribution to the β-relaxation from the slower Cu atoms no longer being caged. These evidences of caged Cu dynamics in $La_{50}Ni_{15}Al_{25}Cu_{10}$ are not found in the isothermal and isochronal spectra of $La_{60}Ni_{15}Al_{25}$. This is unsurprising because of the absence of the slower Cu in $La_{60}Ni_{15}Al_{25}$, and the La and Ni atoms contribute in concert together to the fast β-relaxation, resulting in a well resolved loss peak isochronically (Fig. 1) or isothermally [Figs. 3(a) and 3(b)]. Notwithstanding, La and Ni will be caged at higher frequencies and lower temperatures than the ranges covered in the present experiment.

Such power law, Af^{-c} with $c \approx 0.1$, is found in the susceptibility molecular glass-formers at frequencies higher than the β-relaxation in isothermal spectra, and interpreted satisfactorily as the loss when the molecules are caged.[51,55–60] Its counterpart in isochronal spectra appears as a loss with weak temperature dependence at temperatures lower than the β-relaxation,[1] which was also found in $Zr_{65}Al_{7.5}Cu_{27.5}$ at 5.4 kHz by Samwer and co-workers[43,61] and interpreted as nearly constant loss of caged dynamics by Ngai.[51]

From the various experimental results shown in this paper, we have deduced that La and Ni in $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MGs, is faster than Al and Cu and principally responsible for the β-relaxation. Since La is the largest compared with the other components, this is unusual because in Pd- and Zr-based MGs, the solvent atoms Pd and Zr are larger than the other components and have the lowest mobility. For example, tracer diffusion measurements have shown that Pd is the slowest of all components in $Pd_{43}Cu_{27}Ni_{10}P_{20}$[29] and so is Zr in $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ (Vitreloy 4)[30] as well as from the simulation of $Zr_{50}Ni_{50}$.[62] The smaller atoms, P and Ni in $Pd_{43}Cu_{27}Ni_{10}P_{20}$ and Be and Ni in Vitreloy 4, have higher mobility, and hence are the faster contributors to the β-relaxation, while the solvent atoms, Pd and Zr, are the slower contributors.[29,30] The situation in the Pd- and Zr-based MGs is opposite to $La_{(60\text{-}x)}Ni_{15}Al_{25}Cu_x$ MGs, whereby we can expect the β-relaxation in the Pd- and Zr-based MGs is initiated by the motion of the P, Ni and Be, Ni, respectively at shorter times/higher frequencies in the isothermal spectra and lower temperatures in the isochronal spectra. The slower solvent atoms, Pd and Zr, will be caged for some time thereafter, and show up later as the low frequency part of the β-relaxation at longer times/lower frequencies isothermally, and at higher temperatures isochronically. To support this expectation, we have replotted some of the isothermal mechanical loss data of $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ published by Qiao *et al.*[34] in Fig. 10. The plot of $\log G''(f)$ vs. $\log f$ over a range of temperatures reveals similar characteristics as in Fig. 4 for $La_{50}Ni_{15}Al_{25}Cu_{10}$. The onset of β-relaxation is followed at intermediate frequencies by a power law, Af^{-c} with $c < 0.1$, or $c \approx 0$. The thicker black line with black symbols on it shows nearly a flat plateau. The eventual rise of $\log G''(f)$ above the plateau at higher temperature is the contribution to the β-relaxation from the slow Pd atoms. The master curve of $\log G''(f)$ constructed from the data assuming TTS also exhibits a long plateau on the low frequency side of the shoulder (see Fig. 4 of Ref. 34). It is remarkable that the properties of the

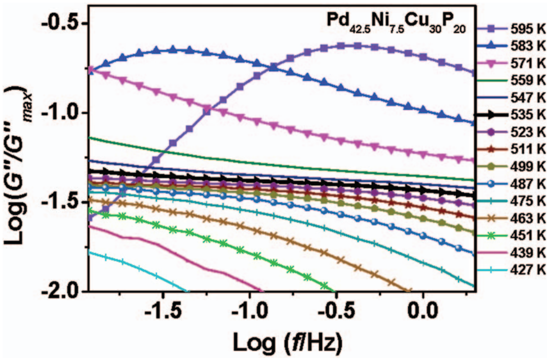

FIG. 10. The normalized loss modulus G'' of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ MG as a function of frequency at temperatures from 427 K to 595 K. The thick black line with black symbols on it shows nearly a flat plateau of the frequency dependence of the normalized loss modulus G'' [Ref. 34].

β-relaxation in the Pd-based glasses are similar to the La-based glasses containing Cu, while the slower atoms are the majority solvent Pd in the former, and are the minority Al and Cu atoms in the latter. We have chosen $Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}$ to compare with $La_{50}Ni_{15}Al_{25}Cu_{10}$ because the separations in frequency of the α-peak from the β-shoulder in their master curves, Fig. 5 in Ref. 34 and Fig. 5(a) herein, are comparable. On the other hand, the separation is much smaller in $Pd_{40}Ni_{40}P_{20}$ and $Pd_{30}Ni_{50}P_{20}$ (see Fig. 5 in Ref. 34). Since within this short frequency interval the contribution from the faster P and Ni atoms to the β-relaxation is followed before long by the contribution from the slower Pd atoms, and thus the caged Pd regime cannot be observed either as a plateau-like region in the master curve (see Fig. 5 in Ref. 34, or as a power law, Af^{-c} with $c < 0.1$ in the isothermal spectra (see Fig. 3(b) in Ref. 34).

In molecular glass-formers the basic unit is a single molecule, and the β-relaxation of molecular glass-formers is simply the rotation/translation of the entire molecule, whereas the basic unit of MGs is composed of more than one atom. The component atoms can differ in local mobility, especially the larger solvent atoms and the smaller solute atoms, and hence they contribute to the β-relaxation at different times/frequencies. Thus the nature of β-relaxation in MGs is different from the molecular glass-formers and polymers, and recognition of this difference is crucial to arrive at correct interpretation of the data. The special characters of the β-relaxation in MGs pointed out in our current paper has support from synchrotron X-ray investigations of ultra-quenched $Zr_{55}Cu_{30}Ni_5Al_{10}$ metallic glass by Liu *et al.*[5] The authors demonstrated that the β-relaxation involves short-range collective rearrangements of the large solvent atoms, but they also admitted the participation of the smaller atoms with higher mobility which is Cu in their case. Thanks to the structure characterization experiment of Liu *et al.*,[5] which reveals the atomic configuration changes caused by β-relaxation and brings out the involvement of the large solvent atom. The onset of the β-relaxation usually originates from the small atoms with higher mobility. It is observed as the leading edge of a shoulder at high frequencies for isothermal data, and low temperatures for isochronal data of the usually unresolved β-relaxation. The change of this characteristic of the unresolved β-relaxation with temperature is routinely used to determine its activation energy. This is the reason why the activation energy of the β-relaxation obtained this way is nearly the same as that of the diffusion of the small atom.

Our experimental investigations indicate that the larger solvent La and smaller Ni atom are the more mobile constituents in the $La_{60}Ni_{15}Al_{(25\text{-}x)}Cu_x$ MGs. Thus, measurement of the diffusion coefficients of La and Ni in these La-based MGs should have approximately the same activation energy as that of the β-relaxation. Measurements of diffusion of La and Ni in these La-based MGs will be crucial.

V. CONCLUSIONS

By modifying the composition of $La_{60}Ni_{15}Al_{25}$ in various ways including alteration of the composition of this ternary metallic glass, replacement of any of the components by Cu, and reduction to binary alloys, we find the changes in the characteristics and properties of the β-relaxation and its relation to the α-relaxation. From the trends of the changes the origin of the unusually pronounced and fast β-relaxation in $La_{60}Ni_{15}Al_{25}$ arises from the high local mobility of La and Ni, acting in concert together. The β-relaxation is effectively determined by the interaction between La and Ni, which is further confirmed by the existence of pronounced β-relaxation peak for La-Ni binary MGs, but not in the La-Cu and La-Al binaries. The collection of these experimental evidences indicate the exceptional high mobility of the majority or solvent La atoms as well as Ni can readily explain why the β-relaxation in La-based MGs is strong, fast and well resolved from the α-relaxation. The replacement of the fast La atoms by the slow Cu atoms change the characteristics of the β-relaxation, and its relation with the α-relaxation. The role of Cu in La-based MG is in contrast to a Au-based MG,[16] where Cu plays a role in the rapid relaxation behavior at low temperature. The faster La-Ni atoms give rise to the onset of the β-relaxation to be followed by an intermediate time/frequency regime where the slower Cu atoms are caged, until later when the cage decays and Cu atoms finally contribute to the low frequency part of the β-relaxation. Thus, in the presence of slow and fast atoms, the β-relaxation is composed of different processes spreading over some range of frequencies. The majority or solvent atoms, Pd and Zr, in Pd- and Zr-based MGs are the slowest components, opposite to the La-based MGs studied in this work. In these cases, the onset of the β-relaxation comes from the smaller and faster solute atoms. The slower Pd and Zr solvent atoms are caged in an intermediate time/frequency regime following the onset, and eventually contribute to the low frequency part of the β-relaxation. The remarkable similarity of the isothermal and isochronal spectra of the Cu-containing La-based and the Pd-based MGs is rationalized by this interpretation.

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