Hand in Hand Evolution of Boson Heat Capacity Anomaly and Slow

β -relaxation in La-based Metallic Glasses

B. Huang^{a,*}, Z.G. Zhu^a, T.P. Ge^a, H.Y. Bai^a, B.A. Sun^b, Y. Yang^b, C.T. Liu^b, and W.H.

Wang^{a,*}

^a*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, , People's*

Republic of China

^b*Centre for Advanced Structural Materials, Department of Mechanical and*

Biomedical Engineering, City University of Hong Kong, Tat Chee Avenue,

Kowloon Tong, Kowloon, Hong Kong, People's Republic of China

Abstract

Glassy materials lacking the periodicity of crystals possess varieties of dynamic behaviors. Boson peak and slow β -relaxation (or Johari-Goldstein β -relaxation) preceding the α -relaxation are the two intrinsic and markedly different dynamic behaviors of glasses, and their structural origins are long-standing issues. Through alloying a model La-based metallic glass (MG) with different types of elements we find that the low-temperature boson heat capacity anomaly evolves hand in hand with high-temperature slow β -relaxation associated with free volume. With the free volume model and the generalized Maxwell model describing the heterogeneous structure, we demonstrate that the slow β -relaxation of MGs is a series of localized microscopic flows, which naturally develops from defective regions where boson peak arises. The

coupling of boson peak and slow β -relaxation indicates their common structural origin of localized loosely packed regions in MGs.

Keywords: Metallic glass; Low-temperature heat capacity; Relaxation; Heterogeneity

Corresponding authors. *E-mail addresses: bohuang617@gmail.com (B. Huang) and whw@iphy.ac.cn (W.H. Wang).

1. Introduction

All types of glasses display excess specific heats below about 40 Kelvin caused by excess low-energy excitations which markedly differ from their crystalline counterparts [1]. The quasilinear temperature (T) dependence of specific heat below about 1 K is ascribed to two-level tunneling systems (TLS), and the broad maximum in T^3 reduced specific heat at higher temperatures is dominated by the boson peak (BP) vibrational modes over Debye contribution [1]. As a prominent feature of glasses, BP has been explained by various theoretical approaches such as soft potential model (SPM) [2, 3], fluctuation of force constants on a cubic lattice [4], interstitialcy theory [5, 6] and vibrational instability of weakly interacting modes [7, 8]. However, the origin of BP remains a matter of fierce controversies [9, 10]. Recent experiments and theories show that BP may associate with the “defective” loosely packed structure or weakly bonded regions in glasses [11-17]. For example, the localized modes of guest atoms in binary borate glasses overlap with BPs [13]; the progressive decrease of poorly packed boroxol rings caused by pressure leads to reduction of BP for vitreous

1 B₂O₃ [15]; with a broadband version of picosecond photo-acoustics technique, BP is
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3 related to marginally stable regions in glasses [16]; severely deformed metallic
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5 glasses (MGs) show intensified BPs related to the increase of highly localized
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7 nano-scaled shear transformed zones [17]; theoretical work identifies BP to be
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9 hybridized modes between transverse acoustic modes and local librational vibrations
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11 in loosely packed nano-regions [11, 14]. With Maxwell's theory of viscoelasticity
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13 based on the assumption of spatially fluctuating local viscoelastic coefficients,
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15 Schirmacher *et. al.* combine the BP and low-temperature asymmetric α -relaxation
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17 anomaly for different types of glasses [18].
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25 At the high temperatures approaching the glass transition temperature (T_g), a slow
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27 secondary or β -relaxation (also called Johari-Goldstein β -relaxation) preceding
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29 α -relaxation emerges [19]. Regarded as the elementary process of glass transition, the
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31 β -relaxation is commonly found in wider classes of amorphous materials such as
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33 polymers, pharmaceuticals, proteins and so on [19]. Many experiments support that
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35 the β -relaxation is a process of localized motions of a small number of molecules
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37 confined in loosely packed regions, i. e., the so-called "islands of mobility" [20]. But
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39 the nature of the molecular motion involved in the relaxation varies greatly from one
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41 system to another. For instance, the β -relaxation in polymer involves restricted
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43 rotation of the bonded repeat unit [21], while in water the process relates to rotation
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45 and translation [22]. Experiments reveal that the β -relaxations of MGs with simple
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47 atomic structures are associated with diffusion of small atoms [23], short-range
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49 collective rearrangements of large solvent atoms [24], cooperative movement of La
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and Ni [25]. The pronounced β -relaxation peak of LaNiAl MG is connected with the large mixing enthalpies of constituting elements [23]. Despite of the intensive studies, the structural origin and mechanism of slow β -relaxation of MGs are controversial. Recently it is reported that the obvious β -relaxations of LaNiAl relate to large excess free volume [26] and localized hidden flows in the nanoscale liquid-like regions detected by stress relaxation spectra [27]. Since both BP and slow β -relaxation seem to relate with the soft regions in MGs and glass transition, it is intriguing to explore if and how the two localized dynamic modes, having markedly difference in activation energies and features, connect with each other, and their structural origins.

In this article, we select the nonmagnetic $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ MG as a model system to study the relationship of BP and slow β -relaxation through varying the two dynamic modes by substituting solvent La with different types of elements. We show the connection between BP and slow β -relaxation exists. The correlation of BP and slow β -relaxation is discussed with the MGs' structural model with defective loosely packed regions.

2. Experimental

Cylindrical amorphous rods of $\text{La}_{70-x}\text{Ni}_{15}\text{Al}_{15}\text{Cu}_x$ ($x=0, 2, 5, 8$), $\text{La}_{70-x}\text{Ni}_{15}\text{Al}_{15}\text{Pd}_x$ ($x=2, 5$), $\text{La}_{70-x}\text{Ni}_{15}\text{Al}_{15}\text{Ti}_x$ ($x=2, 5$), $\text{La}_{68}\text{Ni}_{15}\text{Al}_{15}\text{Si}_2$, $\text{La}_{68}\text{Ni}_{15}\text{Al}_{15}\text{Sn}_2$ and $\text{La}_{60}\text{Ni}_{15}\text{Al}_{15+x}\text{Cu}_{10-x}$ ($x=0, 5, 8, 10$) MGs (2 mm in diameter) were fabricated with the copper mold casting method in argon atmosphere ($\text{La}_{70-x}\text{Al}_{15}\text{Ni}_{15}\text{M}_x$ and $\text{La}_{60}\text{Al}_{15+x}\text{Ni}_{15}\text{Cu}_{10-x}$ MGs are labeled as M_x and $\text{Al}_x\text{Cu}_{10-x}$ in the following text,

1 tables and figures). La was substituted by Cu, Pd, Ti, Si, Sn and Al as these elements
2
3 have different atomic radiuses, mixing enthalpies (ΔH^{mix}) and bonding tendencies
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5 with La. Rectangular plates of $\text{La}_{70-x}\text{Ni}_{15}\text{Al}_{15}\text{Cu}_x$ ($x=0, 2, 5, 8$) (2 mm in thickness)
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8 were fabricated with the copper mold casting method to detect the elastic properties.
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10 The glassy nature of the samples was ascertained by X-ray diffraction (a MAC Mo3
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12 XHF diffractometer with $\text{Cu K}\alpha$ radiation).
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17 Samples with the masses between 15 mg and 20 mg were cut from the glassy
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19 rods. The heat capacity C_p ($C_p \approx C_v$, error < 2%) of the samples were measured in a
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21 physical property measurement system (PPMS 6000) of Quantum Design from 2.0 K
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23 to 101 K with the thermal relaxation method. Dynamic mechanical spectrum (DMS)
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25 between 270 K and 500 K was measured on a TA Q800 dynamical mechanical
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27 analyzer using the glassy rods. The temperature ramp mode at a heating rate of 3
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29 K/min was used with the single-cantilever bending method. The strain amplitude was
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31 5 μm , and testing frequencies are 1 Hz, 4 Hz, 4 Hz, 8 Hz and 16 Hz (Only the 1 Hz
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33 data are shown in the main article). The heat flows of Cu-alloyed MGs between 350 K
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35 and 480 K during the heating process were measured under a purified argon
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37 atmosphere in a Perkin Elmer DSC-7 with a heating rate of 20 K/min.
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47 The densities ρ of Cu-alloyed La-based MGs were measured at room temperature
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49 with the Archimedes principle using the 2 mm $\times$ 2 mm $\times$ 10 mm samples cut from the
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51 rectangular plates. The room temperature sound velocities and elastic properties were
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53 measured with the Resonant Ultrasound Spectrometer (RUSpec) of Magnaflux
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55 Quasar Systems with 2 mm $\times$ 2 mm $\times$ 2 mm cubic samples cut from the rectangular
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plates.

3. Results

3.1 The low-temperature boson heat capacity anomaly for Cu-alloyed MGs

The specific heats C_p of Cu-alloyed MGs between 2.0 K and 101 K are shown in the inset of Fig. 1(a). No specific heat anomaly can be observed directly. The T^2 dependent C_p/T of Cu-alloyed MGs in the temperature range of $4.0 \text{ K}^2 \leq T^2 \leq 41 \text{ K}^2$ are shown in Fig.1(a). The sharp peaks of C_p/T appear below 10 K^2 caused by superconducting transitions. The dashed line is the fitting line of the C_p/T of Cu8 in the temperature range of $6.6 \text{ K}^2 \leq T^2 \leq 11 \text{ K}^2$ with

$$C_p/T = \gamma T + A_D T^3, \quad (1)$$

where γT is mainly contributed by free electrons, and $A_D T^3$ is the contribution of disordered atoms with the Debye elastic approximation. The T^2 dependent C_p/T increases faster than the fitting line above 14 K^2 due to the BP. According to SPM [2], the density of state of excess modes $g_{\text{ex}}(\omega)$ is proportional to ω^4 at the low energy side of BP and the corresponding excess specific heat $C_{p,\text{ex}}$ is proportional to T^5 . We fit the C_p/T of Cu-alloyed MGs between the square of superconducting temperatures and about 25 K^2 with the equation

$$C_p = A_{\text{el}} T + A_{\text{TLS}} T + A_D T^3 + A_{\text{sm}} T^5 = \gamma T + A_D T^3 + A_{\text{sm}} T^5, \quad (2)$$

where $A_{\text{el}} T$, $A_{\text{TLS}} T$, $A_D T^3$ and $A_{\text{sm}} T^5$ represents the contributions of electrons, TLS, Debye elastic vibrations and excess vibrational modes, respectively (Fitting parameters are list in Table 1 of Ref. [28]) [29, 30]. Compared with the fit of Eq. (1),

the low-temperature C_p/T can be well fitted in a larger temperature range [the solid lines in Fig. 1(a)].

With the subtraction of the linear term Eq. (2), the specific heats $(C_p - \gamma T)/T^3$ of Cu-alloyed MGs contributed by the vibrations of disordered atoms are obtained [see Fig. 1(b)] (The following specific heats $(C_p - \gamma T)/T^3$ of other La-based MGs are all obtained with this method, and the fitting parameters of Eq. (2) are listed in Table 1 of Ref. [28]). With increasing temperature, $(C_p - \gamma T)/T^3$ increases more slowly than the fitting line of SPM (the dashed lines) above about 5 K. Broad boson heat capacity peaks appear above Debye levels of elastic medium (Debye levels are flat in the BP region) whose mechanism is highly controversial [3, 6, 31, 32]. With the increase of Cu concentration the $(C_p - \gamma T)/T^3$ peak moves to a higher temperature with a lower intensity.

3.2 The high-temperature dynamic mechanical behavior for Cu-alloyed MGs

DMSs of Cu-alloyed MGs with a frequency of 1 Hz between 290 K and 460 K are shown in Fig. 2(a). A broad slow β -relaxation peak well resolved from α -relaxation appears for Cu0. With the addition of Cu, the β -relaxation peak gradually moves to higher temperature and merges into the α -relaxation peak. The α -relaxation peak seems to change slightly with Cu addition.

We fit both of the slow β -relaxation and the left part of α -relaxation of Cu0 with the Kohlrausch-Williams-Watts (KWW) equation in the Fourier transforms (The fits of slow β -relaxation and α -relaxation in the storage modulus E' are in Fig. 2 of Ref.

[28] represented by the red and blue shaded regions in Fig. 2(a). The yellow shaded gap region beyond the fit relates to the cooperative movement of groups of atoms and the coupling of β - and α -relaxations [27, 33]. We subtract the α -relaxation region and the gap region of Cu0 from the total DMSs to obtain separated β -relaxation peaks for Cu-alloyed MGs. The obtained slow β -relaxation peaks are shown in Fig. 2(b). It can be clearly seen that the β -relaxation peak gradually moves to high temperature with its intensity decreasing with Cu addition. The change tendency of the β -relaxation peak coincides with that of the $(C_p - \gamma T)/T^3$ peak indicating the connection of BP and slow β -relaxation.

3.3 The high-temperature thermal behavior for Cu-alloyed MGs

The differential scanning calorimetric (DSC) curves of Cu-alloyed MGs between 357 K and 480 K are shown in Fig. 3(a). With 8 at.% Cu addition, the glass transition temperature T_g of Cu0 decreases from 420 K to 413 K. The onset primary crystallization temperature $T_{x,onset}$ of Cu0 increases to 454 K. A distinct sub- T_g exothermic heat flow peak appears for each MG as shown in Fig. 3(b). With the increase of Cu concentration, the onset temperature $T_{rel,onset}$ of the relaxation peak gradually increases. The area of the peak region (the region surrounded by the dashed line and the DSC curve), i. e., the enthalpy change $-\Delta H_{rel}$, decreases.

$T_{x,onset}$, T_g and $T_{rel,onset}$ of Cu8 are marked on its DMS curve in Fig. 2(a) to elucidate the structural change in the heating process. The α -relaxation peak appears above T_g where the whole sample starts to change into the liquid-like state. $T_{rel,onset}$

lies in the temperature range of cooperative movements of flows. DSC does not have the sensitivity to pick up the slow β -relaxation response as a small amount of atoms or clusters are involved. Thus, almost no anomaly can be found in DSC curves below $T_{\text{rel,onset}}$. However, from the sub- T_g exothermic heat flow peak reflecting the release of excess remnant enthalpy, we can get information of free volume in MGs [34, 35]. The Cu concentration dependent $T_{\text{rel,onset}}$ is shown in Fig. 4(a). With the increase of Cu concentration, $T_{\text{rel,onset}}$ increases implying the increase of activation energy of the structural relaxation consuming the free volume. The $(C_p - \gamma T)/T^3$ peak temperature T_{max} and β -relaxation peak temperature $T_{\beta,\text{peak}}$ also increase with the addition of Cu [Fig. 4(a)]. The Cu concentration c_{Cu} dependent $-\Delta H_{\text{rel}}$, heat capacity peak intensity $[(C_p - \gamma T)/T^3]_{\text{max}}$ and β -relaxation peak intensity $E''_{\beta,\text{peak}}$ are shown in Fig. 4(b). $-\Delta H_{\text{rel}}$ is nearly proportional to the free volume concentration in the MGs microalloyed with Cu. With the increase of Cu, $-\Delta H_{\text{rel}}$ decreases suggesting the decrease of free volume concentration. $[(C_p - \gamma T)/T^3]_{\text{max}}$ and $E''_{\beta,\text{peak}}$ also decrease with the addition of Cu. Our result suggests both of the boson heat capacity anomaly and slow β -relaxation are influenced by free volume which is consistent with recent experimental results [26, 36].

3.4 More experimental evidences on the connection between boson heat capacity anomaly and slow β -relaxation

Free volume in MGs is defined as that part of excess volume quenched from melting liquids which can be redistributed without energy change [37, 38].

Experiments and simulations have shown that the amount of excess volume in an alloy is determined by the size ratio of composing atoms, the concentrations of different elements and their interactions [39-41]. Therefore, we can change the free volume in La-based MGs by alloying elements with different atomic sizes, concentrations, ΔH^{mix} and bonding tendencies with La to tune boson heat capacity anomaly and slow β -relaxation and demonstrate their connection. Another miscible addition of Pd (ΔH^{mix} of Pd and La is -82 kJ/mol [42]), with an atom radius (1.37 Å) larger than that of Cu (1.28 Å) but still smaller than that of La (1.87 Å), is investigated. With the substitution of La with 2% Pd, the $(C_p - \gamma T)/T^3$ peak of La₇₀Al₁₅Ni₁₅ MG moves to higher temperature with the intensity decreasing slightly, and the position of β -relaxation peak also slightly moves to higher temperature as shown in Fig. 5(a). With 5% Pd addition, the change of the $(C_p - \gamma T)/T^3$ peak and β -relaxation is much more obvious. Compared with the same amount of substitution of Cu (*e.g.* 2% or 5%), the substitution effect on the $(C_p - \gamma T)/T^3$ peak and β -relaxation is weaker. Unlike the addition of Cu (ΔH^{mix} of Cu and La is -21 kJ/mol [42]), the α -relaxation significantly varies. For the demixing condition, the addition of Ti with an atomic radius of 1.47 Å showing a relatively small positive ΔH^{mix} (+20 kJ/mol) with La is investigated [42]. As shown in Fig. 5(b), two outstanding different phenomena exist comparing with the miscible situation. The first difference is the non-monotonic behavior of the $(C_p - \gamma T)/T^3$ peak and β -relaxation upon this minor substitution. The intensity of the $(C_p - \gamma T)/T^3$ peak degenerates significantly with 2% addition of Ti, but recovers with 5% addition of Ti. At the same time, the positions of the $(C_p - \gamma T)/T^3$ peak and β -relaxation

peak move to higher temperatures, and then rebound. The second difference is the sluggish change of β -relaxation peak temperature compared to that of $(C_p-\gamma T)/T^3$ peak. The α -relaxation almost does not change. Results for the covalent bonding additions of Si and Sn with atomic radiuses of 1.11 Å and 1.40 Å in the same group of the periodical table are shown in Fig. 5(c). The intensities of the $(C_p-\gamma T)/T^3$ and β -relaxation peaks decrease, and the positions move to high temperatures. The α -relaxation also apparently moves to high temperatures. Fig. 5(d) shows the $(C_p-\gamma T)/T^3$ peaks and high temperature relaxations of the La-based MGs with 10% La substituted by Cu and Al (ΔH^{mix} of Al and La is -38 kJ/mol [42]). With the increase of Al, both the $(C_p-\gamma T)/T^3$ peak and β -relaxation intensities decrease slightly, while their positions do not change. The independence of the $(C_p-\gamma T)/T^3$ peak position on Al concentration in LaNiAl MGs indicates that the excess soft modes of BP could also be associated with some particular structure constructed by La and Ni similarly to the slow β -relaxation [25]. With this alloying, the α -relaxation moves to higher temperatures.

In the above alloying, only for the addition of the element strongly interacting with La (having large negative ΔH^{mix} with La, like Pd and Al, or tending to form covalent bonds, like Si and Sn) is the α -relaxation expected to be changed. Whereas for all the conditions the slow β -relaxation is altered and evolves hand in hand with the $(C_p-\gamma T)/T^3$ peak, albeit the change is slower for the Ti addition. The substitution of La with smaller atoms (larger atomic size disparity) tends to move the $(C_p-\gamma T)/T^3$ peak and β -relaxation to higher temperatures with lower intensities. Different from the

addition of elements with negative ΔH^{mix} with La or showing covalent bonding tendency, the addition of large amount of demixing Ti moves the $(C_p - \gamma T)/T^3$ peak and β -relaxation to lower temperatures with higher intensities. The packing is more efficient, and less excess volume exists in a mixture of big and small hard spheres than in a system of equally sized hard spheres as small particles fit into the cavities between the big ones [39, 40, 43]. Strongly mixing systems show a negative excess volume, while immiscible systems tend to exhibit a positive excess volume [40, 41]. Therefore, the above alloying phenomena just suggest that less excess volume in La-based MGs tends to move the $(C_p - \gamma T)/T^3$ peak and β -relaxation to high temperatures and decrease their intensities (For Al addition the peak temperatures do not change), and *vice versa*.

To quantify the correlation of the boson heat capacity anomaly and slow β -relaxation, we separate the β -relaxation region from the total DMS for all other MGs with the same method for Cu-alloyed MGs. Fig. 6(a) shows $T_{\beta, \text{peak}}$ vs. T_{max} for all the La-based MGs (Similar T_{max} -dependent activation energy of slow β -relaxation (E_β) is shown in Fig. 3 of Ref. [28]). $T_{\beta, \text{peak}}$ increases with T_{max} , and a linear relation appears except for Ti addition. The intercept and slope of the fitting line (the black line) are 149 ± 18 K and 27 ± 3 , respectively. The smaller slope for Ti addition (the dashed line) corresponds to the minor change of β -relaxation position in Fig. 5(b). Figure 6(b) shows $E''_{\beta, \text{peak}}$ vs. $[(C_p - \gamma T)/T^3]_{\text{max}}$ for all the La-based MGs. An increasing trend of $E''_{\beta, \text{peak}}$ appears with the increase of $[(C_p - \gamma T)/T^3]_{\text{max}}$ except for Al-, Si- and Sn-alloyed MGs. As shown in Fig. 5(c) and (d), for Al-alloyed MGs, α -relaxation

peaks are strong, and for Si- and Sn-alloyed MGs α -relaxation peaks are obviously weak. The relatively large $E''_{\beta, \text{peak}}$ for Al-alloyed MGs at high temperatures and small $E''_{\beta, \text{peak}}$ for Si- and Sn-alloyed MGs could be caused by the coupling of α - and β -relaxations. The T_{max} , $[(C_p - \gamma T)/T^3]_{\text{max}}$, $T_{\beta, \text{peak}}$ and $E''_{\beta, \text{peak}}$ of all the La-based MGs are listed in Table 2 in Ref. [28].

Apart from compositional effect, ageing influence on the slow β -relaxation of $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ MG, i. e., Cu0, has been studied by Wang, *et. al.* [26]. With annealing the β -relaxation moves to high temperature and the intensity decreases which is correlated with the decreasing size of subatomic cavities. We annealed the as quenched Cu0 at 473 K and measured its low-temperature heat capacity. With annealing the intensity of the $(C_p - \gamma T)/T^3$ peak decreases from 0.990 mJ/mol K⁴ to 0.722 mJ/mol K⁴, and the peak temperature moves from 6.8 K to 10.0 K (see Fig. 4 in Ref. [28]). The effect is similar to the Cu alloying effect and the annealing effect on the boson heat capacity anomaly of Vit105 [36]. These results provide more evidences for the close connection of BP and slow β -relaxation, which is associated with localized loosely packed regions containing free volume.

4. Discussion

4.1 Theoretical explanation of the connection of boson heat capacity anomaly and slow β -relaxation

. Since free volume seems essential to both boson heat capacity anomaly and slow β -relaxation in the La-based MGs, we try to explain our experimental results

with free volume model, which accepts the existence of loose atoms or clusters in the defective regions of MGs surrounded with quenched free volume. The potential

energy of a loose atom or cluster vibrates with a small distance δ from the equilibrium position r can be expressed as

$$u(r + \delta) = u(r) + u'(r)\delta + \frac{1}{2!}u''(r)\delta^2 + \frac{1}{3!}u'''(r)\delta^3 + \frac{1}{4!}u''''(r)\delta^4, \quad (3)$$

where $u(r)=u'(r)=0$. In SPM, the coefficients of the last three terms in Eq. (3) are considered, and the minimum in the C_p/T^3 (Here, C_p is only contributed by disordered atomic structure) plot is explained as the crossover of the contributions of anharmonic and harmonic states [2, 44]. In the boson heat capacity peak region, $k_B T \gg W$ (W is the characteristic crossover energy of SPM). Thus, we simply neglect the last two terms in Eq. (3) and propose the boson heat capacity anomaly of MGs is contributed by harmonic vibrations of loose atoms or clusters in single potential wells, i. e., the resonance modes of "defects" with the character of interstitials in crystals [5, 13, 45, 46].

The potential energy of an atom or a cluster at the equilibrium position r in a metal can be expressed as $u(r) = -[(\alpha' + 1)Nz^2 e^2 / 4\pi\epsilon_0 r](1 - \rho/r) \approx -[(\alpha' + 1)Nz^2 e^2 / 4\pi\epsilon_0 r] = -\alpha/r$, where α' reflects the interacting contribution of atoms outside the neighboring atoms, N is the number of neighboring atoms, z is the number of valence electrons, ϵ_0 is the vacuum dielectric constant, ρ reflects the coulomb repulsive interaction which can be neglected and $\alpha = (\alpha' + 1)Nz^2 e^2 / (4\pi\epsilon_0)$ [47]. With Eq. (3) and the harmonic approximation, the potential energy of the vibrating loose atom or cluster can be expressed as $u(r + \delta) = -\alpha\delta^2/r^3$. The restoring force on the loose atom or cluster is

$F = -du(r+\delta)/d\delta = 2\alpha\delta/r^3$. Thus, the vibrational energy is

$$E_{ex} = \hbar\omega = k_B\theta_E = \hbar\left(\frac{2\alpha}{mr^3}\right)^{1/2}, \quad (4)$$

where $\hbar$ is reduced Plank constant, ω is the frequency of the harmonic vibration, θ_E is Einstein temperature and m is the mass of the loose atom or cluster.

The distribution of free volume size v in the defective regions causes the fluctuations of r and E_{ex} . Thus, the total heat capacity C_p can be described as [48]

$$C_p = \gamma T + n_D C_D + 3R \int_0^\infty \left(\frac{E_{ex}}{2k_B T}\right)^2 \sinh^{-2}\left(\frac{E_{ex}}{2k_B T}\right) [n_{ex} \cdot \chi_{vib}(E_{ex})] dE_{ex}, \quad (5)$$

where n_D and n_{ex} represent the fractions of Debye and excess modes ($n_D + n_{ex} = 1$), respectively. The Debye term $n_D C_D$ is contributed by elastic matrix, and the last term

is contributed by the loose atoms or clusters. $C_D = 9R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^\xi}{(e^\xi - 1)^2} d\xi$, and

the Debye temperature θ_D can be determined by the acoustic velocities and the density at room temperature. $\chi_{vib}(E_{ex})$ is the distribution function of E_{ex} , i. e., the density of

states of excess vibrational modes. Similarly to the case of Vit105 [36] and glass formers like orthoterphenyl [46], the boson heat capacity peak for the Cu-alloyed

MGs can also be fitted with a Gaussian form of $\chi_{vib}(E_{ex})$, i. e.,

$$\chi_{vib}(E_{ex}) = \frac{1}{\sigma_{ex} \sqrt{2\pi}} e^{-\frac{(E_{ex} - \bar{E}_{ex})^2}{2\sigma_{ex}^2}} \quad [\text{as shown by the solid lines in Fig. 1(b)}] \quad (\text{Fitting}$$

parameters can be found in **Table 3 of Ref. [28]**). The Debye contributions are marked by dash-dotted lines. The Gaussian distribution of E_{ex} suggests the topologically diverse form of the excess excitations which randomly occur without interactions.

According to Eq. (4), the vibrational energy of the loose atom or cluster with a

radius of a (the occupied space is about $8a^3$) surrounded by excess free volume of the size v can be approximately expressed as $E_{ex} = \hbar[16\alpha/m(8a^3 + v)]^{1/2}$. So, the distribution of free volume size v is

$$p(v) = \frac{\hbar}{16} \left(\frac{2\alpha}{m} \right)^{1/2} (a^3 + v/8)^{-3/2} \chi_{vib}(E_{ex}). \quad (6)$$

Eq. (5) and (6) indicate that boson heat capacity anomaly is associated with the distribution of free volume. Firstly, we analyze the data of Cu-alloyed MGs to show how free volume influences boson heat capacity anomaly. The average atomic radius $\bar{a}$ and atomic mass $\bar{m}$ are calculated for the Cu0. We set $\alpha' = 0$, $N=1$, $z=1$, and simply suppose the excess modes are contributed by only one type of loose clusters with a radius of $5^{1/3}\bar{a}$ and a mass of $5\bar{m}$ (Too small or large loose clusters will induce unreasonable free volume concentration). With the assumptions and the fitting results of the boson heat capacity peaks, the v_s (the size of loose clusters, *i. e.*, $4\pi a^3/3$) scaled free volume distributions $p(v/v_s)$ of Cu-alloyed MGs are calculated and shown in Fig. 7(a). Free volume concentration x_f equals to $n_{ex} \int_{-8a^3}^{\infty} v p(v) dv / v_s$. The calculated x_f for Cu-alloyed MGs is shown in the inset of Fig. 7(a). With the increase of Cu concentration, the distribution of free volume changes, and the concentration decreases from 0.083 to 0.015 which is consistent with the above DSC result and other experimental results [49]. So the decrease of the boson heat capacity anomaly and the increase of its activation energy are caused by the reducing concentration and size of free volume.

Next, we will show the free volume change affects the high-temperature slow β -relaxation. According to the free volume theory [50], the viscosity η of the defective

region under a small shear stress can be expressed as

$$\eta = \frac{k_B T}{\Delta f P v_D v_s} \exp\left(\frac{\Delta G^m}{k_B T}\right), \quad (7)$$

where $\Delta f \ll 1$ for inhomogeneous flow, v_D is the Debye frequency and $v_D = k_B \theta_D / h$, ΔG^m is the energy barrier of the states before and after jumping without stress. P is the probability of the existence of enough space for a cluster to jump and equals to $P = \int_{v_s}^{\infty} p(v) dv$. We use the Maxwell model represented by a purely viscous dashpot with a viscosity η and a purely elastic spring with an elastic modulus E connected in series to describe the slow β -relaxation of MGs. Under a dynamic stress of frequency ω_s we obtain (see [Supplementary Note A](#))

$$E''(\omega_s) = \frac{(\Delta f P v_D v_s / \omega_s k_B T) \exp\left(\frac{\Delta G^m}{k_B T}\right)}{(1/E)^2 + \left[(\Delta f P v_D v_s / \omega_s k_B T) \exp\left(\frac{\Delta G^m}{k_B T}\right)\right]^2}. \quad (8)$$

For Cu0, $E = 3.45$ GPa and $v_D = 3.25 \times 10^{12}$ Hz which are calculated with the room temperature velocities of ultrasonic sound waves with the frequency in the order of 10^5 Hz (see [Table 4 in \[28\]](#)). The slow β -relaxation peak of Cu0 at 1 Hz is fitted as shown in Fig. 2(b) (the dashed black line). The fitting peak is much narrower than the β -relaxation peak.

Actually, the energy barriers ΔG_{local}^m at different local defective regions should be different. The narrow fitting peak is caused by the assumption of only one value of ΔG^m in the simple Maxwell model. Elastic models like the shoving model of Dyre, *et al.* [51, 52] give that the activation energy ΔE of viscous liquids is proportional to the instantaneous shear modulus G_∞ . It is easy to obtain that $\Delta G_{local}^m \approx \Delta E_{local}$ (ΔE_{local} is the

local activation energy of viscous liquids) from the known data and the expression for
 the viscosity $\eta = [h/(2a)^3] \exp(\Delta E/T)$ [52], which indicates the equivalence of the free
 volume model to elastic models connecting slow and fast dynamics. With the
 independent harmonic approximation of vibrations of the loose atom or cluster in the
 soft region, $G_{\infty,local} \approx \lambda m E_{ex}^2 / (2a \hbar^2)$ where the constant λ reflects the average effect
 of transverse and longitudinal sounds [52]. Thus, we have the distribution of $G_{\infty,local}/\lambda$
 in the boson peak temperature range (~ 10 K)
 $p(G_{\infty,local}/\lambda) \approx (\hbar/2)(2a/m)^{1/2} (G_{\infty,local}/\lambda)^{-1/2} \chi_{vib}(E_{ex})$. The calculated $p(G_{\infty,local}/\lambda)$ of
 the Cu-alloyed La-based MGs are shown Fig. 7(b). $p(G_{\infty,local}/\lambda)$ is similar to the
 Gaussian distribution in consistent with simulations of various glasses [18, 53-55] (If
 we set $p(G_{\infty,local}/\lambda)$ as a Gaussian function, the boson heat capacity anomaly can also
 be fitted but slightly worse than setting $\chi_{vib}(E_{ex})$ as a Gaussian function as shown in
 Fig. S1). In the slow β -relaxation temperature range, the distribution of $G_{\infty,local}/\lambda$ will
 induce the fluctuations of ΔG_{local}^m . In sufficiently small local defective regions, Δf_{local}
 $=1$ and $P_{local}=1$. From Eq. (7), we see that the fluctuations of ΔG_{local}^m will lead to a
 distribution of local viscosities η_{local} . Therefore, MGs in the slow β -relaxation
 temperature range should be regarded as the patchwork of elastic matrix and localized
 liquid-like regions with distributed η_{local} evolved from the loosely packed regions as
 shown Fig. 8(a). Instead of using the Maxwell model we use the generalized Maxwell
 model, i. e., a series of Maxwell units with the same elastic modulus E_{local} ($E_{local}=E$)
 and different viscosities η_{local} and one purely elastic spring with an elastic modulus E
 connected in parallel to describe the heterogeneous structure and slow β -relaxation of

MGs as shown in Fig. 8(b) (In the figure, $\eta_{\text{local}} = \eta_1, \eta_2, \dots, \eta_i, \dots$). One Maxwell unit represents one localized defective liquid-like region, and the parallel elastic spring represents the elastic matrix of MGs.

As discussed above and with respect to the isolated flows of slow β -relaxation occurring independently and randomly like the excitation of excess vibrational modes [27], a simple Gaussian distribution of $\Delta G_{\text{local}}^m$ with an average value of $\overline{\Delta G_{\text{local}}^m}$ and a standard deviation of $\sigma_{\Delta G_{\text{local}}^m}$ should be a good choice for the fit of slow β -relaxation peak. With the generalized Maxwell structural model, the slow β -relaxation peak can be described by the following equation (see Supplementary Note B),

$$E_{\beta}'' = \int_0^{\infty} \frac{n_{\beta} P(v_D v_s / \omega_s k_B T) \exp\left(-\frac{\Delta G_{\text{local}}^m}{k_B T}\right)}{(1/E)^2 + \left[(v_D v_s / \omega_s k_B T) \exp\left(-\frac{\Delta G_{\text{local}}^m}{k_B T}\right)\right]^2} \chi_{re}(\Delta G_{\text{local}}^m, \overline{\Delta G_{\text{local}}^m}, \sigma_{\Delta G_{\text{local}}^m}) d(\Delta G_{\text{local}}^m), \quad (9)$$

where $n_{\beta}P$ reflects the concentration of the defective flow unit regions. A better fitting line of CuO with Eq. (9) is shown in Fig. 2(b) (the black line) (The fit of the storage modulus E' is in Fig. 2 of Ref. [28]). The wide distribution of $\Delta G_{\text{local}}^m$ is consistent with the small nonexponential parameter $\beta_{\text{KWW},\beta}$ ($\beta_{\text{KWW},\beta}=0.42$) of KWW fit implying the strongly disordered structure [33] (see Table 5 of Ref. [28]). The corresponding distributed η_{local} 's are shown in the inset of Fig. 8(a). The slow β -relaxation peaks of other Cu-alloyed MGs are also well fitted with Eq. (9) as shown in Fig. 2(b) (the solid lines). The calculated P and fitting parameters are listed in Table 1.

With Cu addition, the free volume size and concentration decrease as implied by the boson heat capacity peak evolution. P , i. e., the jumping probability of the of

loose clusters, decreases. The concentration of localized flow regions decreases as suggested by the reduction of $n_{\beta}P$. $p(G_{\infty,local}/\lambda)$ corresponding to $\chi_{vib}(E_{ex})$ moves to higher energies with smaller peak values and slightly larger widths [as shown in Fig. 7(b)], resulting in the increase of ΔG_{local}^m , $\sigma_{\Delta G_{local}^m}$ and η_{local} . Consequently, $E''_{\beta,peak}$ decreases and $T_{\beta,peak}$ increases. The width of slow β -relaxation increases quite slightly due to the slightly wider distribution of E_{ex} and broader boson peak. Therefore, the connection of boson heat capacity anomaly and slow β -relaxation of Cu-alloyed La-based MGs can be qualitatively interpreted.

The boson heat capacity anomaly and slow β -relaxation for other La-based MGs can also be analyzed similarly to that for the Cu-alloyed MGs. The higher concentration of small atoms and larger atomic size disparity decrease the free volume concentration and size, and $\chi_{vib}(E_{ex})$ and $p(G_{\infty,local}/\lambda)$ move to higher energies leading to the less pronounced boson heat capacity anomaly and slow β -relaxation at higher temperatures. The addition of demixing Ti by 5% increases free volume and causes the inverse change of boson heat capacity anomaly and slow β -relaxation. The quick decrease of boson heat capacity anomaly and slow β -relaxation with 2% Ti addition [Fig. 5 (b)] and the relatively sluggish change of $T_{\beta,peak}$ [the dashed line in Fig. 6 (a)] could be associated with the structural heterogeneity or asymmetry like the case for some ideal glasses [56, 57], which is caused by phase separation due to the positive ΔH^{mix} of Ti and La [58]. The possible structural heterogeneity or asymmetry of Ti-system changes Poisson ratios in the local defective regions and affect λ . Thus, the dependence $G_{\infty,local}$ on E_{ex} changes which will evidently result in the different

dependence of $T_{\beta,\text{peak}}$ on T_{max} .

A diagram on the relation between the boson heat capacity peak and slow β -relaxation of MGs within experimental time window is constructed based on the loosely packed regions as illustrated in Fig. 9. The boson heat capacity peak, slow β -relaxation and α -relaxation peaks appear with increasing temperatures [9]. The BP is mainly associated with the quasilocalized vibrations of atoms or clusters (blue balls) in the defective loose packed regions containing free volume surrounded by elastic matrix, corresponding to the change of the state in the shallow basin in the potential energy landscape (PEL). The distribution of free volume induces the fluctuations of E_{ex} in the loosely packed regions resulting in the broad boson heat capacity peak at low temperatures (from several K to 20-30 K). Under a dynamic stress, when the temperature approaches around T_g (with sufficient thermal energies) the loose atoms/clusters will move reversibly with a large scale and the weak bonds break in the regions with small $G_{\infty,\text{local}}$. The loose fragments diffuse or jump to the large enough free volume space with a probability represented by the red shaded region in the up-left diagram in Fig. 9. The β -events composing β -relaxation, i. e., the localized flows in the defective regions, occur (the cross of the shadow basin in the PEL) [27, 59]. When the free volume sizes are smaller caused by alloying or thermal treatment, the anomalous heat capacity peak becomes weak and moves to a higher temperature due to larger E_{ex} of the loose atoms or clusters. $G_{\infty,\text{local}}$ increases and more energies are needed to break the bonds. The probability of the existence of sufficient jump space is also smaller. Thus the activation of slow β -relaxation also occurs at higher

temperature, and its intensity becomes smaller. *Vice versa*. For Al alloying, perhaps only the concentration of the defective regions decreases inducing only the decrease of the boson heat capacity and β -relaxation peak intensities. When the temperature continue rising, the elastic matrix around the weakly bonded regions becomes soft, and the hidden flows act cooperatively [27]. Meanwhile, the excess free volume gradually disappearing as indicated by the DSC curves in Fig 3(b). The whole sample becomes liquid-like and α -relaxation occur when the temperature reaches T_g (the cross of the largescale crater in the PEL).

4.2 The connection of boson heat capacity anomaly, slow β -relaxation in other glassy materials

The two dynamic modes of other types of glasses like polymers have been studied. However, usually they are not studied simultaneously for the same specimen. It is reported that the aging of a slightly cross-linked poly(methyl methacrylate) (PMMA) by annealing at 10 K below T_g has no effect on BP. By methanol assisted aging at room temperature a significant decrease of BP is observed. Similar change of β -relaxation peak from DMS is also found, while the high-temperature β -relaxation tail in the α -relaxation region varies differently [60]. Pérez-Castañeda *et. al.* report the height of the C_p/T^3 boson peak of the ultrastable amber aged for 110 million years decreases 22% from the standard rejuvenated glass [61]. Suppression of about 70% of the β -relaxation intensity is also discovered in the vapor-deposited ultrastable toluene with the glassy state proximate to "ideal glass" [62]. The much more relaxed glass

state of these ultrastable glasses corresponds to the inherent structure with the lowest potential energy, i. e., the deepest basin in PEL. The large intrabasin vibrational energy and interbasin energy barrier connect the boson heat capacity anomaly and slow β -relaxation. The intercept and the slope of the fitting line of the $[(C_p - \gamma T)/T^3]_{\max}$ dependent $E''_{\beta, \text{peak}}$ for Cu-, Pd-, Ti-alloyed La-based MGs in Fig. 6(b) are -0.22 ± 0.16 GPa and 0.85 ± 0.18 GPa mol K⁴/mJ. When the defective regions of La-based MG totally disappear and the β -relaxation is totally suppressed in its ideal state, $[(C_p - \gamma T)/T^3]_{\max}$ approaches about 0.26 mJ/mol K⁴ which is only contributed by elastic medium [56] (see Fig. S2).

4.3 The connection of boson heat capacity anomaly, slow β -relaxation with fragility and other relaxation processes

Fragility is a qualitative concept classifying glassy materials through addressing the deviation of liquid relaxation times from Arrhenius behavior above T_g [63]. It is generally regarded that the more fragile glassy material will show smaller excess specific heat scaled by Debye contribution [64-66] and more pronounced slow β -relaxation separated from α -relaxation [23, 63, 67]. However, the breakdown of the empirical correlation of fragility and slow β -relaxation has been discovered in La-based MGs as mentioned in several papers [23, 25, 68], which indicates more complex mechanisms of slow β -relaxation and the diversity of the temperature-dependent behavior of relaxation times above T_g .

In LaNiAl MGs, the fragility first decreases slightly and then stays almost

constant with the replacement of La by Cu [25]. Meanwhile, the slow β -relaxation merges into the α -relaxation peak and becomes less pronounced gradually and significantly. The excess specific heat intensity scaled by Debye contribution $[(C_p - \gamma T - n_D C_D)/n_D C_D]_{\max}$ decreases as listed in Table 1. Thus, the general relations of the fragility to boson peak and slow β -relaxation both fail in the LaNiAl MGs at least for the Cu-alloying condition. Actually, we can find from Fig. 1(b), Fig. 2(a) and Fig. 5 that α -relaxation couples with boson peak and slow β -relaxation weakly especially for the Cu-, Ti- and Al-alloyed La-based MGs. Since fragility describes the growth rate of the correlated regions of α -process, it is not surprising that no obvious and universal relation of fragility to boson peak and slow β -relaxation can be found in the La-based MGs.

Recently a unusual fast secondary relaxation is discovered in a La-based MG. The authors propose that this type of relaxation is the activation of individual "defect" and more fundamental than slow β -relaxation as its activation energy is closer to those of deformation units obtained from simulations and nanoindentation [69]. The connection of BP and the fast secondary relaxation could be stronger.

5. Conclusions

In summary, we reveal the connection between the low-temperature boson heat capacity anomaly and high-temperature slow β -relaxation in MGs by alloying of different types of elements and annealing experiments. The slow β -relaxation peak temperature is proportional to the anomalous heat capacity peak temperature, and its

peak intensity increases with the peak intensity. Both the boson heat capacity anomaly and slow β -relaxation are sensitive to excess free volume in MGs. We regard the slow β -relaxation is series of isolated flows developed at high temperatures in loose packed regions where BP arises. Our results shed light on the structural origin and mechanisms of BP and slow β -relaxation, and indicate the strong relation between fast BP dynamics and slow structural relaxation in MGs.

Acknowledgements

We are grateful for the experimental assistance or discussions of H. L. Peng, Q. Wang, D. Q. Zhao, D. W. Ding and S. K. Su. The financial supports of the NSF of China (No. 51271195, 51461165101), the MOST 973 Program (No. 2015CB856800), the GRF of Hong Kong (No. CityU9042066 and No. CityU9041863) are appreciated.

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Figure captions

Figure. 1 (a) The T^2 dependent C_p/T with the inset showing the T dependent C_p for
Cu-alloy MGs. (b) The T dependent $(C_p - \gamma T)/T^3$ in a semilogarithmic scale
for Cu-alloy MGs. The dashed and solid lines are the fitting results. The
dash-dotted lines are Debye contributions.

Figure. 2 (a) The T dependent loss modulus E'' between 290 K and 460 K. The red
and cyan shaded regions are the β - and α -relaxation regions obtained with
KWW fit. The yellow shaded region is beyond KWW fit. (b) The
separated β -relaxation peak for Cu-alloy MGs. The dashed and solid lines
are fitting results.

Figure. 3 The DSC curves (a) between 357 K and 480 K, (b) near T_g for Cu-alloy
MGs. Dashed-dotted lines are tangents of DSC curves to show the
determination of T_g , $T_{x,onset}$ and $T_{rel,onset}$. The dashed lines are
extrapolations of linear parts at low temperatures.

Figure. 4 The Cu concentration c_{Cu} dependent (a) $T_{\text{rel,onset}}$, T_{max} , $T_{\beta,\text{peak}}$ (b) $-\Delta H_{\text{rel}}$,

$[(C_p-\gamma T)/T^3]_{\text{max}}$ and $E''_{\beta,\text{peak}}$ for Cu-alloy MGs.

Figure. 5 Left part of each figure: T dependent $(C_p-\gamma T)/T^3$ below 100 K in a semilogarithmic scale for (a) Pd-, (b) Ti-, (c) Si- and Sn-, (d) Al-alloyed La-based MGs. Right part of each figure shows corresponding T -dependent loss modulus E'' with 1 Hz at high temperatures.

Figure. 6 (a) The T_{max} dependent $T_{\beta,\text{peak}}$, and (b) $[(C_p-\gamma T)/T^3]_{\text{max}}$ dependent $E''_{\beta,\text{peak}}$ for La-based MGs alloyed with Cu, Pd, Ti, Si, Sn and Al. The solid line is fitting line. The dashed line is the guide to eyes.

Figure. 7 (a) The reduced free volume v/v_s distribution with the inset showing Cu concentration c_{Cu} dependent free volume concentration x_f , (b) $G_{\infty,\text{local}}/\lambda$ distribution in the local defective regions.

Figure. 8 (a) Schematic illustration of MG composed of elastic matrix and defective liquid-like regions with the inset showing the local viscosity η_{local} distribution of defective regions. (b) Generalized Maxwell model: a series of Maxwell units with the same elastic modulus E and different viscosities η_{local} ($\eta_{\text{local}}=\eta_1, \eta_2, \dots \eta_i, \dots$) and one purely elastic spring with an elastic

modulus E connected in parallel. The purely elastic spring and Maxwell units represent elastic matrix and defective liquid-like regions, respectively.

Figure. 9 T -dependent glassy dynamics with the upper left diagram showing free volume distribution. The diagrams under the boson heat capacity peak, β - and α -relaxation peaks depict localized movements of defective region with increasing temperature. Related potential energy landscapes are shown above the peaks.

Figureg

Figure-1, Huang, *et al.*

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Table 1 The jump probability P , flow unit concentration $n_{\beta}P$, $\overline{\Delta G^m_{local}}$, $\sigma_{\Delta G^m_{local}}$, excess specific heat intensity scaled by Debye contribution $[(C_p-\gamma T-n_D C_D)/n_D C_D]_{\max}$ of Cu-alloyed La-based MGs.

MG	P	$n_{\beta}P$	$\overline{\Delta G^m_{local}}$ (eV)	$\sigma_{\Delta G^m_{local}}$ (eV)	$[(C_p-\gamma T-n_D C_D)/n_D C_D]_{\max}$
Cu0	0.0543	0.071	0.956	0.055	1.448
Cu2	0.0508	0.068	0.971	0.062	1.441
Cu5	0.0455	0.063	0.995	0.064	1.432
Cu8	0.0413	0.061	1.072	0.067	1.412