

Correlation between β Relaxation and Self-Diffusion of the Smallest Constituting Atoms in Metallic Glasses

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In multicomponent metallic glasses, we demonstrate that diffusion and secondary (β) relaxation are closely related. The diffusion motion of the smallest constituting atoms takes place within the temperature and time regimes where the β relaxations are activated, and, in particular, the two processes have similar activation energies. We suggest cooperative stringlike atomic motion plays an important role in both processes. This finding provides additional insights into the structural origin of the β relaxations as well as the mechanisms of diffusions in metallic glasses.

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Relaxation and diffusion are two fundamental processes in supercooled liquids and glasses. They constitute long-standing issues in condensed matter physics [1–6]. At sufficiently high temperature, a liquid shows only one relaxation mode, and diffusions of different components are coupled, and the two processes are usually connected by the Stokes-Einstein relation [1–6]. While in a supercooled liquid, the relaxation splits into primary (α) and secondary (β) relaxations [2,3]. The α relaxation is the central challenge in glassy physics and is being actively discussed [1–6]. As the α relaxation disappears below the glass transition temperature T_g , the β relaxation, which continues below T_g , is the principal source of the dynamics in glassy state and is of practical significance to many properties of glassy solids [7–11]. Diffusion of different components in supercooled liquids is usually decoupled, and the Stokes-Einstein relation breaks down [4–12].

Recent theoretical work [13] and simulations [14–17] have indicated that atomic size disparity has critical effects on relaxation and diffusion in supercooled liquids and glasses. Several investigations [13–17] suggest that glass transition (α relaxation) is mainly controlled by the slowing down of diffusions of large constituting particles, whereas diffusions of small particles persist into deep glassy states. Metallic glasses (MGs) and their forming liquids represent the ideal systems for verifying these suggestions because of their large size difference in constituting atoms [18,19], and their relatively simple atomic structures without the complex intramolecular effects in polymeric glasses [8–11,20–26]. In a $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ MG, Bartsch *et al* revealed that the diffusive motion of the largest Pd atoms and the α relaxations are indeed correlated [26]. They found for the Pd atoms the Stokes-Einstein relation holds in the whole temperature range investigated, from melting temperature down to T_g , while for other smaller atoms the Stokes-Einstein relation breaks down. These results lead to an interesting question: are

there any connections between the decoupling of diffusion of different components and the split of the relaxation modes in supercooled liquids and glasses? Or, to a lesser extent, are β relaxations related to the atomic size disparity as well?

In this work, we compare the dynamics of β relaxations with the self-diffusions of the smallest constituting atoms in MGs and we show these two processes are closely correlated. In a wide range of MGs, the diffusive atomic motions of the smallest constituting atoms take place within the temperature and time regime where the β relaxations are activated, and, in particular, they have the similar activation energies. Our findings suggest a connection between the decoupling of diffusions of different components and the splits of the relaxation modes in MGs and their forming supercooled liquids. The implications of this result for understanding the structural origins of β relaxation as well as the mechanisms of diffusion in MGs are discussed.

Two typical MGs were selected for experiments— $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (vit4) and $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ (the compositions are in atomic percent)—because of their excellent glass-forming ability and different relaxation behaviors [8,9]. Their glassy nature was ascertained by x-ray diffraction (MAC Mo3 XHF diffractometer with Cu K_α radiation), differential scanning calorimeter (PerkinElmer DSC-7 and DSC-5). The dynamical mechanical spectroscopies (DMS) of these MGs were measured on a TA Q800 dynamical mechanical analyzer by single-cantilever bending method with a heating rate of 2 K/min, strain amplitude about 0.1% and varied testing frequency f . The temperature dependent atomic (diffusive) hopping rates of P atoms in $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and Be atoms in vit4 MGs had been measured by nuclear magnetic resonance (NMR). Specially, a spin alignment echo technique (SAE) was used in these NMR measurements, which had been found suitable for studying the diffusive atomic

motions of the smallest constituting atoms in MGs [27–29]. The SAE technique is based on the Jeener-Broekaert sequence $90^\circ_x - \tau_1 - 45^\circ_y - \tau - 45^\circ - \tau_2$, where 90° and 45° are the tipping angles of the radio-frequency pulses, x and y are the phases of the pulses, and τ_1 , τ_2 , and τ_3 are delays between pulses. Further details can be found elsewhere [27–29].

Figure 1(a) shows temperature dependent loss modulus E'' of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ MG measured by DMS with discrete f ranging from 1 to 16 Hz. Besides the α relaxation peaks around the glass transition temperature $T_g \sim 580$ K, broad humps around 450–550 K can also be observed. We identified these broad humps as the β relaxation peaks superimposed on the tails of the α relaxations. Figure 1(b) shows the f dependence of the onset and peak temperature of the β relaxations, respectively, and fitted by the Arrhenius relation $f = f_\infty \exp(-E_\beta/RT)$, where f_∞ the prefactor, E_β the activation energy of β relaxation, and T temperature. The E_β is determined to

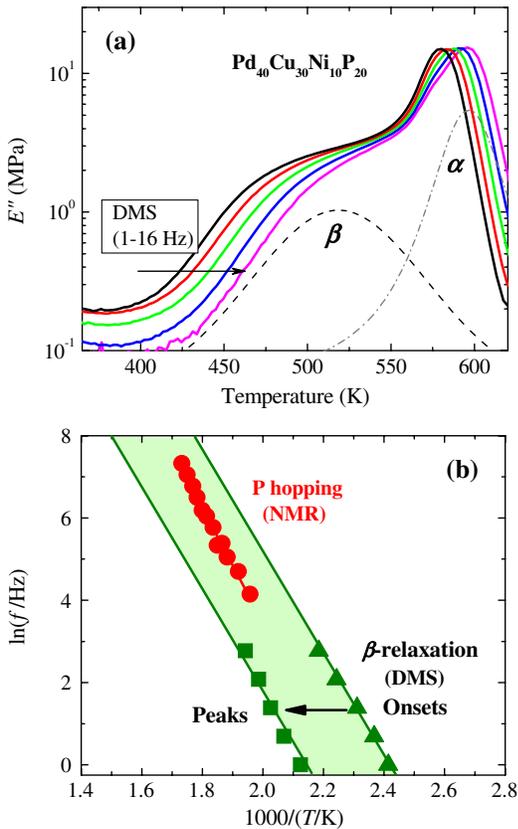


FIG. 1 (color online). (a) Temperature dependence of the loss modulus E'' of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ MG, the frequencies f used are 1, 2, 4, 8, and 16 Hz from left to right, respectively. The dashed curves are the double-peak fits of the E'' curve with $f = 16$ Hz, showing there are two distinct relaxations (α and β relaxations). (b) The f dependence of the onset (triangle symbols) and peak (square symbols) temperature of the β relaxations and fitted with Arrhenius relations (lines). The circle symbols stand for the P atomic diffusive hopping rates measured by NMR.

be 128 ± 10 kJ/mol from the Arrhenius plot. The value $E_\beta/RT_g = 25 \pm 2$ is consistent with the empirical relationship $E_\beta/RT_g \approx 26$ found in various MGs and non-metallic glasses [9,30].

Figure 1(b) also includes the data of the temperature-dependent hopping rates of P atoms measured by NMR of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ MG (the red circle symbols [27]). It is remarkable that the NMR data fall in the temperature and frequency range defined by the β relaxations. What is more, the activation energy for the P atomic hopping is about 125 ± 15 kJ/mol which is very similar to the activation energy of the β relaxations (128 ± 10 kJ/mol) of the MG. It is noted that the relaxation processes of supercooled liquids and glasses are dependent on the experimental techniques, and the frequency or temperature of β relaxations (as well as other relaxation processes) are not identical but with small differences when measured by different techniques [3,31]. Taking this effect into account, Fig. 1(b) strongly suggests the β relaxations (measured by DMS) and the hopping motions of P atoms (probed by NMR) take place in the same temperature and frequency range with the same activation energy. Compared with other constituting elements in the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ MG, P has the smallest atomic radius (100 pm for P atoms, while 140, 135, and 135 pm for Pd, Ni, and Cu atoms, respectively [32]). This comparison suggests that β relaxations in MGs and the motions of the smallest constituting atoms could be connected.

To further verify the above findings, Fig. 2 plots the E'' curves of the vit4 MG together with the temperature dependent Be atomic hopping rates measured by NMR (as shown by the dashed vertical lines) [28,29]. The β relaxation of the vit4 MG is not as evident as that of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ MG. It is manifested as the faint relaxation hump or excess

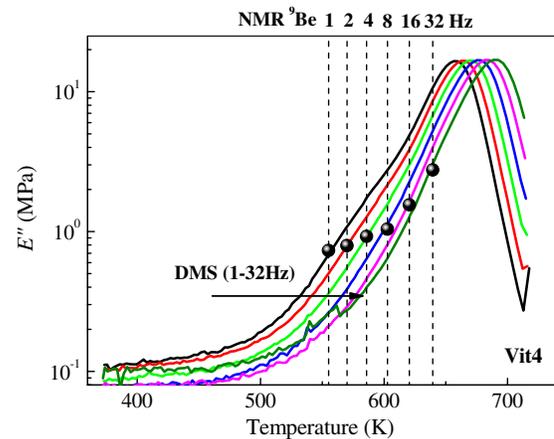


FIG. 2 (color online). Temperature dependence of E'' of the vit4MG, the frequencies f used are 1, 2, 4, 8, 16 and 32 Hz from left to right, respectively. The dashed lines are the NMR probed P atomic diffusive hopping rate (as indicated on top) at the corresponding temperature. The ball symbols indicate the intersecting E'' curves and lines have the same frequencies.

TABLE I. Summary of the data of the glass transition temperature T_g , the activation energy of β relaxation E_β , and diffusion activation energy Q_{sd} of the smallest constituting atom in different MGs.

BMG	Probed Atom	T_g (K)	E_β (kJ/mol)	$Q_{s.d}$ (kJ/mol)
Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5} (vit1) [28,29,34]	Be	614	128 ± 10	115 ± 15
Zr _{46.75} Ti _{8.25} Cu _{7.5} Ni ₁₀ Be _{27.5} (vit4) [28,29,34]	Be	621	118 ± 10	115 ± 15
Pd ₄₀ Ni ₄₀ P ₂₀ [27]	P	602	130 ± 10	125 ± 10
Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀ [27]	P	593	128 ± 10	125 ± 10
Pd ₄₃ Cu ₂₇ Ni ₁₀ P ₂₀ [27]	P	592	128 ± 10	125 ± 10
Pd ₄₇ Cu ₂₅ Ni ₉ P ₁₉ [27]	P	594	125 ± 10	125 ± 10
Pd _{41.75} Cu _{41.75} P _{16.5} [27]	P	578	102 ± 15	88 ± 20
Fe ₇₅ Zr ₂₅ [35]	Fe	540	117 ± 15 ^a	116 ± 30
Co ₈₉ Zr ₁₁ [4]	Co	670	145 ± 10 ^a	135 ± 10
Ni ₅₀ Zr ₅₀ [4]	Ni	730	155 ± 10 ^a	140 ± 15
Fe ₉₁ Zr ₉ [4]	Fe	695	150 ± 10 ^a	142 ± 10

^aEstimated by $E_\beta \approx (26 \pm 2)RT_g$.

wing, which has been proved to be the flank of β relaxation submerged under the much stronger α relaxation [1,33]. Nevertheless, one can see that the hopping motions of the Be atoms take place within the temperature and time regime where the β relaxation is activated in the vit4 MG. The activation energy of Be atomic hopping determined from the NMR data is about 115 ± 15 kJ/mol and the E_β for the same MG is about 118 ± 10 kJ/mol [9], they are equivalent within errors. Again, the Be atoms have the smallest atomic radius (105 pm) compared other constituting elements in vit4 (Zr 155 pm, Ti 140 pm, Cu and Ni 135 pm, respectively [32]). Since the relaxation behaviors of vit4 and Pd₄₀Ni₁₀Cu₃₀P₂₀ MGs are very different and are representative for most known MGs [8,9], it appears to be universal that β relaxation and the motions of the smallest constituting atoms are correlated in MGs (and see below).

As the NMR probed atomic hopping motion is a kind of short-range diffusion [27–29], and its activation energy has been shown to be consistent with those measured by other techniques such as tracing atoms and elastic back scattering [27–29], therefore, if the above correlation is universal, an equivalent between E_β and the activation energy of self-diffusion of the smallest constituting atoms Q_{sd} is expected to hold in MGs. Table I lists the available data of Q_{sd} and E_β for 11 different MGs, which are taken from literature [4,27–29,34,35]. Figure 3 shows the plot of E_β against Q_{sd} . The data reveals nearly a one-to-one correspondence between E_β and Q_{sd} , and remarkably, a linear relationship $y = x$ can well fit the data within the error bars, indicating $E_\beta \approx Q_{sd}$. We emphasize that the equivalence between E_β and Q_{sd} is obeyed only for the diffusions of the *smallest* constituting atoms in *glassy* states (at temperatures below T_g). For larger constituting atoms, their diffusion activation energy is much larger than E_β , for instance, the activation energy of Ni atoms diffusion in vit4 MG is about 220 kJ/mol which is about 2 times larger than E_β and the activation energy of the Be atoms diffusion [4]. For temperatures above T_g , (i.e., in the supercooled liquid states), the

diffusion coefficients often changes significantly, resulting in an increase of the activation energy (e.g., see Ref. [4]). Additionally, it is interesting to note that small atoms are indispensable for improving the glass-forming ability in MGs, especially for the formations of bulk MGs [19].

The above results clearly demonstrate that the β relaxations in MGs and the diffusive motions of the smallest constituting atoms are correlated, as both of the processes take place in the same temperature and frequency range and have the similar activation energies. Our findings thus connect the two fundamental processes in MGs [36,37]. It also implies one can study the mechanisms of β relaxation in MGs from the perspective of diffusions, and the vice versa.

There are many studies demonstrating β relaxation and diffusion in MGs are both cooperative processes [4,9,36–43]. Especially, by molecular dynamics simulation of a real DMS experiment, Cohen *et al.* recently show that randomly pinning only a small fraction of atoms (about 2%, not allowing them to participate in the relaxation dynamics)

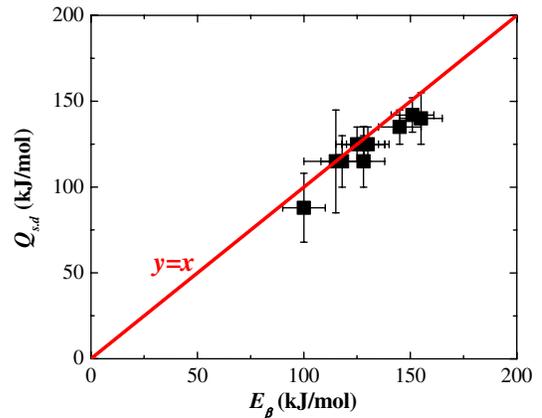


FIG. 3 (color online). Comparison between the activation energy of β relaxation E_β , and the activation energy of the self-diffusions of the smallest constituting atoms Q_{sd} , in different MGs. A linear relation $y = x$ (the line) can well fit the data.

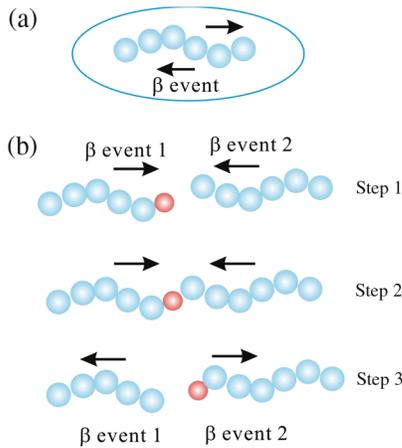


FIG. 4 (color online). (a) Schematic draw of the atomic configurations and motions of a β event in MGs. The ellipse represents the confinement of elastic matrix. The two arrows represent the atoms move back-and-forth reversibly. (b) Schematic draw about the relationship between β events and diffusions. The smaller red circle indicates a diffusing atom.

can strongly suppress the β relaxations in a model Lennard-Jones glass [44]. Such a result provides convincing evidence that β relaxation is related to the motions of stringlike configurations [41–43]. Mechanistically, as schematics shown in Fig. 4(a) and 4(b), we suggest the following picture to explain the correlations between β relaxation and self-diffusion of the smallest constituting atoms. As suggested by theoretical work and simulations [39–43], a β event is considered as a string of atoms that moves back and forth reversibly and cooperatively within the confinement of a surrounding elastic matrix [Fig. 4(a)]. When two strings of atoms move toward each other and get close enough [as indicated by step 1 in Fig. 4(b)], the small atom at the end of one string could be attracted and taken over by another string of atoms [step 2 in Fig. 4(b)], then the two strings of atoms move in the opposite direction [step 3 in Fig. 4(b)], as they move back and forth separately. The net result of this process is the atom at the end of one string diffuses a small distance. The process means a “bottle-neck” that determines the excitation energy for diffusion and β relaxation. As a consequence, the β relaxation and diffusions of the smallest constituting atoms are intimately related and the smallest constituting atoms act as the “tracing” atoms in probing β relaxation in MGs. In addition, we note the process shown in Fig. 4 is different from the models in literature [4,42,43]. Especially, it suggests that the diffusion of the smallest constituting atoms is a consequence of several β events. This suggestion could have implications for understanding the decoupling of diffusions of different constituting atoms and the breakdown of the Stokes-Einstein relation in MG-forming liquids [26].

A long-standing controversial question about the β relaxation is whether it involves all the atoms or only small fractions [36,38,45]. Based on the above results, we can

infer the latter case (at least in MGs). If all the smallest constituting atoms were to undergo diffusive type motions associated with β relaxations, the application of an external stress would induce the viscous flow at the temperature and time scale of the β relaxations, which has not been observed in any kind of glasses so far. What observed in metallic glasses is that the transition of deformation modes (from brittle to ductile in tension) is coincident with the temperature and time scale of β relaxations [8]. It implies only a small fraction of materials take part in the motions of β relaxations and consistent with the fact that mechanical properties are sensitive to minor structural defects. Presumably, only in the loosely packed regions (or weak bonded regions) could β relaxations and the diffusions of the smallest constituting atoms take place, in agreement with observations that MGs with pronounced β relaxations often have nanoscale density fluctuations [8,46].

In summary, we have shown that in multicomponent metallic glasses the β relaxations are closely related to the self-diffusion of the smallest constituting atoms. The diffusive motions of the smallest constituting atoms take place within the temperature and time regime where the β relaxations are activated, and they have the similar activation energies. We suggest cooperative stringlike atomic motions play an important role in both processes. This correlation is anticipated to provide new insights into the structural origin of the β relaxations as well as the mechanism of diffusions in metallic glasses.

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