



# The $\beta$ relaxation in metallic glasses: an overview

Hai-Bin Yu<sup>1,\*</sup>, Wei-Hua Wang<sup>2</sup> and Konrad Samwer<sup>1</sup>

<sup>1</sup>Physikalisches Institut, Universität Göttingen, D-37077 Göttingen, Germany

<sup>2</sup>Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

**Metallic glasses, combining metallic bonding and disordered atomic structures, are at the cutting edge of metallic materials research. Recent advances in this field have revealed that many key questions in glassy physics are inherently connected to one important relaxation mode: the so-called secondary ( $\beta$ ) relaxation. Here, in metallic glasses, we review the features of  $\beta$  relaxations and their relations to other processes and properties. Special emphasis is put on their current roles and future promise in understanding the glass transition phenomenon, mechanical properties and mechanisms of plastic deformation, diffusion, physical aging, as well as the stability and crystallization of metallic glasses.**

## Introduction

Metallic glasses (MGs) are currently the focus of intense research in the international metals community [1,2]. Due to the lack of long-range order and the absence of traditional defects such as dislocations and grain boundaries, MGs have many fascinating physical [3], chemical and mechanical properties [4,5], and therefore, the potential to revolutionize the field of materials science and engineering [6]. Meanwhile, because of their simpler atomic structures compared to other glasses [7,8] (e.g. polymer and covalent glasses) and wide adjustable compositions [9], MGs offer a particularly good testing ground for many fundamental issues in condensed matter physics [1,10].

Research on MGs (as well as other glasses) is closely related to the forming of supercooled liquids [6,11]. As first recognized by Johari *et al.* [12], glasses and the forming of supercooled liquids have two main relaxation processes: primary ( $\alpha$ ) and secondary ( $\beta$ ) relaxations. Specifically, the  $\alpha$  relaxation is responsible for vitrification, and its arrest (i.e. the glass transition phenomenon) represents a major challenge in glassy physics [11,13–17]. However, as the  $\alpha$  relaxation disappears below the glass transition temperature  $T_g$  [11], the  $\beta$  relaxation, which initiates at high temperature and continues below  $T_g$ , is the principal source of dynamics in the glassy state [15,17]. In the past two decades, substantial findings

have revealed that  $\beta$  relaxation is of practical significance to many of the properties of glass-forming materials [17]. For instance, the  $\beta$  relaxation determines the features of  $\alpha$  relaxation, acting as a precursor to the glass transition [17]. The  $\beta$  relaxation affects mechanical properties of glassy solids and connects to the underlying mechanisms of plastic deformation [18–21] (which is an important issue in materials science); the  $\beta$  relaxation is also crucial to protein dynamics and the preservation of foodstuffs, and the crystallization of amorphous pharmaceuticals and biomaterials [22,23]. The discovery of the  $\beta$  relaxation in MGs [18,19,24–34], as well as their clear correlations with other processes and properties [18,19,32,34], makes it a promising route to understand many fundamental issues in glassy physics and materials science [18,19,32,34]. This article presents an overview of the current roles and future promise of  $\beta$  relaxation in studies of the glass transition, the mechanical properties and the mechanisms of plastic deformation, diffusion, physical aging, and the stability and crystallization of MGs.

A note is due here. In some molecular and polymer glasses, there is more than one secondary relaxation; but some of them arise from the intra-molecular degree of freedom (and thus lack fundamental significance). Only intermolecular secondary relaxations are considered of fundamental importance and are called Johari-Goldstein  $\beta$  relaxations [15,17]. Because there is no intra-molecular degree of freedom in MGs,  $\beta$  relaxation in MGs is therefore

\*Corresponding author: Yu, H.-B. (hyu1@gwdg.de)

the analog of Johari–Goldstein  $\beta$  relaxation in non-metallic glasses.

### Measurements and features of $\beta$ relaxation in MGs

Because MGs are good conductors, dielectric spectroscopy [35], which is a standard tool for studying the relaxation dynamics in non-conductive materials [36], is not feasible. Methods, such as dynamical mechanical analysis (DMA) [18,19,24–30], internal friction [31], differential scanning calorimetry [37,38], and recently scanning tunneling microscopy [39,40] are employed in efforts to study  $\beta$  relaxation in MGs. Among them, DMA is commonly used because of its wide applicability and high sensitivity in detecting atomic rearrangements associated with defects in solids [19].

As a typical example, Fig. 1 presents a set of DMA measurements on a  $\text{La}_{68.5}\text{Ni}_{16}\text{Al}_{14}\text{Co}_{1.5}$  MG [19]. Fig. 1a shows the temperature dependence of the storage modulus  $E'$  and the loss modulus  $E''$ , with a single testing frequency  $f = 1$  Hz. The following features can be observed (i) the  $E''$  curve shows two distinct peaks: the one at higher temperature (440 K) is due to the  $\alpha$  relaxation while the one at lower temperature (330 K) is identified as the  $\beta$  relaxation [19]; (ii) the intensity of the  $\beta$  relaxation is much lower than that of the  $\alpha$  relaxation, usually by about 10%; (iii) parallel to the change of  $E''$ ,  $E'$  shows a large and a relatively small (but noticeable) drop at the temperatures corresponding to the  $\alpha$  and  $\beta$  relaxations, respectively. Fig. 1b,c focus on the dynamical properties of the  $\beta$  peaks, showing that the peak temperature/frequency of  $E''$  increases markedly with testing frequency/temperature during isochronous/isothermal routes, while peak intensity increases only slightly (see the inset of Fig. 1b). Fig. 1d shows the frequency dependent peak temperature  $T_p$  in Fig. 1b, as well as the tempera-

ture dependent peak frequency  $f_p$  in Fig. 1c. These data can be fitted by a unique Arrhenius relation,  $f = f_\infty \exp(-E_\beta/RT)$ , where  $f_\infty$  is the prefactor,  $E_\beta$  is the activation energy of the  $\beta$  relaxation, and  $T$  the temperature. The Arrhenius relation is a general property of  $\beta$  relaxation in glassy states, however, whether it stands above  $T_g$  is not clear in MGs [41]. Actually, this question is of relevance to some theoretical explanations of the origin of  $\beta$  relaxations [15,17]. Nevertheless, we stress that in glassy states  $E_\beta$  is an important parameter in obtaining some quantitative insights.

Fig. 2a compares the  $\beta$  relaxations of some more MGs in a normalized plot, which covers most of the known typical compositions with different values of  $T_g$  as well as other properties. Intriguingly, the  $\beta$  relaxations in different MGs can exhibit as either  $E''$  peaks [19,30,33] or broad humps [18,24,29], or even excess wings that almost merge into  $\alpha$  relaxations [25–29,34,42,43] (see Table 1 for a comparison). Determining the  $E_\beta$  of MGs with excess wings is not as straightforward as Fig. 1d; however, some strategies and indirect methods can be found elsewhere [18,37,38]. In addition, the behavior of the  $\beta$  relaxation in MGs is sensitive to chemical compositions [19,29,34]. For example, as shown in Fig. 2b, the replacement of a small amount of Ni by Cu in a  $\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$  MG results in a dramatic change in the appearance of the  $\beta$  relaxations. The underlying reasons for the micro-alloying effects are not yet completely clear; nevertheless, an important clue is that the  $\beta$  relaxations in some MGs with similar chemical compositions correlate with the properties of their corresponding supercooled liquids, such as fragility [34,44] (see next section). Here, fragility defined as  $m = d \log(\tau_\alpha)/(dT_g/T)|_{T=T_g}$ , where  $\tau_\alpha$  is the characteristic time of  $\alpha$  relaxation [45,46]. Liquids with large  $m$  values are often termed “fragile”; otherwise “strong”.

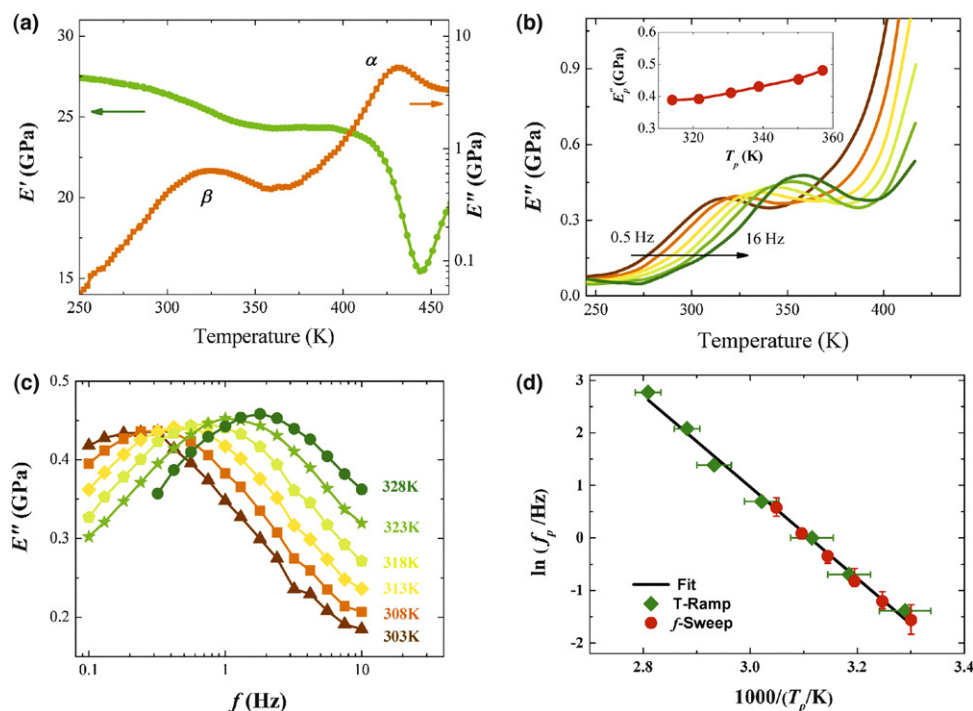


FIGURE 1

Typical DMA measurements for a La-MG [19]. (a) The temperature dependent  $E'$  (left axis) and  $E''$  (right axis) at testing frequency 1 Hz. (b) Temperature dependent  $E''$  at different frequencies, from left to right: 0.5, 1, 2, 4, 8, and 16 Hz; the inset is the intensity of  $E''$  of  $\beta$  relaxation. (c) Frequency dependent  $E''$  at temperatures as indicated. (d) The Arrhenius plot of the peak temperature and frequency corresponding to  $\beta$  relaxation.

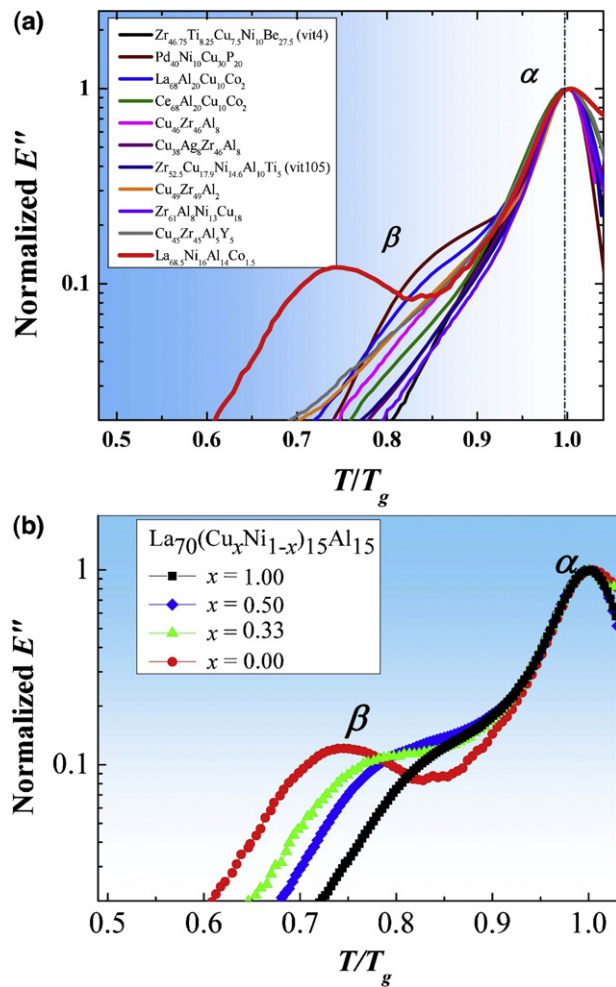


FIGURE 2

Comparisons of  $\beta$  relaxations of different MGs in a normalized plot: the temperature is scaled by  $T_g$  and  $E''$  (1 Hz) is normalized by the corresponding maximum (at  $T_g$ ). (a) The normalized plot of  $E''$  of 11 typical MGs, as labeled [19]. (b) The normalized plot of  $E''$  of  $\text{La}_{70}(\text{Cu}_x\text{Ni}_{1-x})_{15}\text{Al}_{15}$  MGs with 4 different  $x$  values, as indicated (H.B. Yu et al., to be published).

### Correlation between $\beta$ relaxation and $\alpha$ relaxation in MGs

An example of the correlation between fragility and the behavior of the  $\beta$  relaxation was obtained in a systematic study of  $(\text{Ce}_x\text{La}_{1-x})_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_2$  (where  $0 \leq x \leq 1$ ) MGs [34], as displayed in Fig. 3a–d. In this system, the Ce-rich MGs have small values of fragility (i.e. strong liquids) and show  $\beta$  relaxations as excess wings, while the La-rich ones have larger fragilities (fragile) and show  $\beta$  relaxations as pronounced humps, and both of the trends ( $\beta$  relaxations and fragilities) change systematically with  $x$ . As fragility is an important parameter of  $\alpha$  transitions, this result clearly demonstrates  $\beta$  relaxation and  $\alpha$  relaxation are correlated. In addition, an interesting observation in Fig. 3b and d is that the changes of behavior of the  $\beta$  relaxation and fragilities with composition adjustments are neither gradual nor linear, but sigmoidal showing a clear transition. This may be a sign that the structures of the MGs change drastically with alloying. However, a clear relation between atomic structures and  $\beta$  relaxations in MGs is still lacking [37,47]. Besides, we caution that the correlation between fragility and the behaviors of  $\beta$  relaxation is not necessarily held when cross

TABLE 1

Typical metallic glasses systems and examples of different manifestations of  $\beta$  relaxation as detected by DMA.

$\beta$ relaxation (from DMA measurement)	MG systems	Examples
Peak	RE–Ni/Co–Al (RE: rare earth metal)	$\text{La}_{70}\text{Ni}_{15}\text{Al}_{15}$ $\text{La}_{60}\text{Al}_{25}\text{Ni}_{15}$ $\text{Ce}_{60}\text{Ni}_{25}\text{Al}_{15}$ $\text{La}_{60}\text{Co}_{25}\text{Al}_{15}$ $\text{Pr}_{60}\text{Ni}_{25}\text{Al}_{15}$
Broad hump	RE–Cu–Al Al–Cu/Ni–La/Ce Pd–Ni/Cu–P Pd–Cu–Si	$\text{La}_{55}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_{10}\text{Co}_{10}$ $\text{La}_{70}\text{Al}_{15}\text{Ni}_{10}\text{Cu}_5$ $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$ $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$ $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$
Excess wing	Ce–Cu–Al Cu–Zr–Al Zr–Cu–Ni–Al Zr–Ti–Cu–Ni–Be	$\text{Ce}_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_2$ $\text{Cu}_{50}\text{Zr}_{50}$ $(\text{Cu}_{50}\text{Zr}_{50})_{96}\text{Al}_4$ $(\text{Cu}_{50}\text{Zr}_{50})_{92}\text{Al}_8$ $\text{Zr}_{65}\text{Cu}_{20}\text{Ni}_{15}\text{Al}_{10}$ $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$

comparisons are made for materials with totally different chemical properties. For example, some Zr based MGs have a large fragility but show  $\beta$  relaxation as excess wings [43].

Over the past decade, the  $E_\beta$  of a lot of MGs has been determined by different authors [18,19,29–33,38]. An approximately linear relationship between  $E_\beta$  and  $T_g$  was obtained [18,38]:  $E_\beta = 26(\pm 2)RT_g$  (see Fig. 4). As  $T_g$  is the characteristic temperature that signals the arrest of the  $\alpha$  transition, this relation can be considered as further evidence of the correlation between  $\beta$  and  $\alpha$  relaxations or glass transitions.

As proposed by Ngai *et al.*, the correlation between  $\beta$  relaxation and  $\alpha$  relaxation has implications for the studies of glass transitions [15,17]. This is because traditionally  $\alpha$  relaxation has been believed to mainly be responsible for the glass transition phenomenon, whereas the  $\beta$  relaxations that occur at shorter times or lower temperatures are thought to play no role in glass transitions. However, many recent findings in different glasses show  $\beta$  relaxations are connected to  $\alpha$  relaxations or glass transitions [17]. This topic is now being actively discussed in organic glasses, ionic glasses and plastic crystals and explained by a coupling model [15,17]. The developments of bulk metallic glasses [48,49] in recent years with excellent thermal stability are expected to open a new avenue to this topic for future studies.

### The $\beta$ relaxation and the mechanism of plastic deformation of MGs

The mechanical properties of MGs are of great interest in the community of materials science [4,49,50]. MGs have relatively low elastic moduli [51], high strength and hardness [8], low internal friction [52], and enhanced fatigue durability [53]. These mechanical properties make MGs potential high performance engineering and functional materials [3,5]. What is more, the mechanics of MGs are of fundamental scientific interest for their contrast with conventional crystalline metals and alloys [4,50]. At

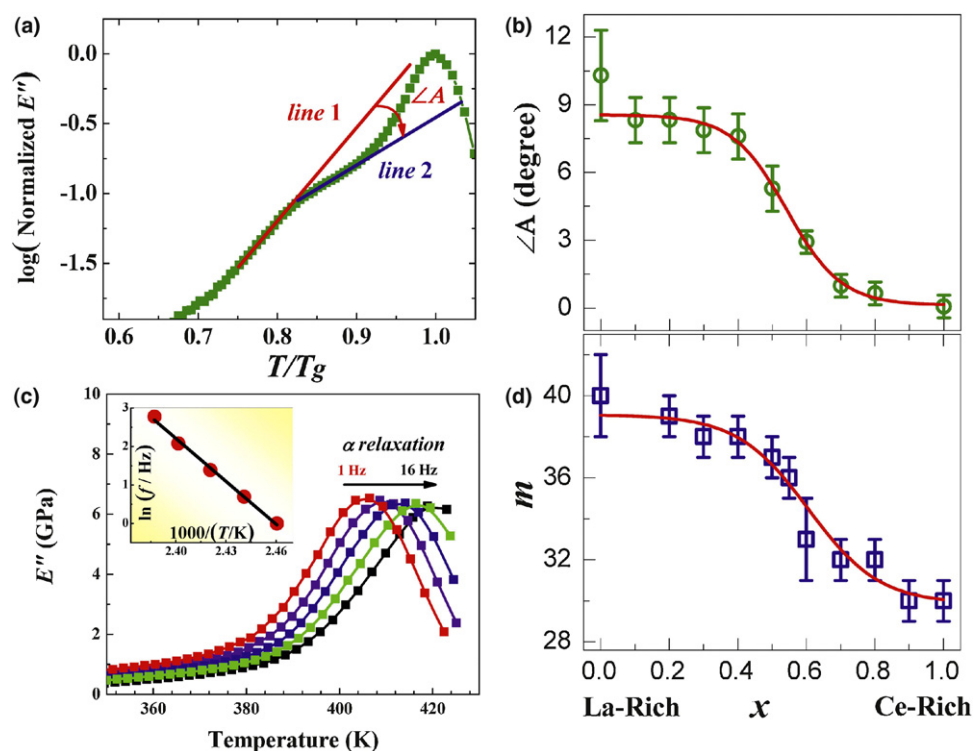


FIGURE 3

Correlation between  $\beta$  relaxation and fragility in  $(\text{Ce}_x\text{La}_{1-x})_{68}\text{Al}_{10}\text{Cu}_{20}\text{Co}_2$  MGs [34]. (a) The definition of  $\angle A$  that makes the  $\beta$  relaxation humps clear, using  $x = 0.2$  as an example. (b) The dependence of  $\angle A$  on  $x$ . (c) The  $\alpha$  relaxation from  $E''$  at testing frequencies are 1, 2, 4, 8, and 16 Hz (from left to right), with  $x = 0.2$ , the inset is an Arrhenius plot of  $\alpha$  relaxation peaks of the MG, fragility  $m$  can be extracted from it. (d) The dependence of  $m$  on  $x$ .

present, the underlying deformation mechanisms that govern the strength and ductility of MGs remain poorly understood and represent an outstanding challenge [50].

Microscopically, the deformation of MGs is proposed to be accommodated by plastic rearrangements of atomic regions involving several tens or hundreds of atoms, termed shear transformation zones (STZs)[54]. The STZ, as observed in computer simulations [55] or colloid glasses [56,57] is essentially a group of atoms within a relatively loosely packed region that undergoes a plastic distortion from one configuration to another, crossing an

energy barrier. However, such an apparently simple definition hides a considerable complexity, and various fundamental questions on STZs are still open [54–60].

Theoretically, on the basis of the Frenkel's analysis on shear strength for a dislocation free solid, Johnson and Samwer proposed a cooperative shear model (CSM) to study the STZ-oriented deformation mechanisms [61,62]. The CSM was originally introduced to elucidate the temperature dependence of yield strength [61], yet it has also been shown to provide an effective interpretation of a variety of mechanical behaviors of MGs [62]. Especially, in CSM the potential energy barrier of an STZ is given as [61]:  $W = (8/\pi^2)G\gamma_c^2\zeta\Omega$  where,  $G$  is the shear modulus,  $\Omega$  is the average volume of an STZ,  $\gamma_c$  is the average elastic limit, and  $\zeta$  is a correction factor arising from the matrix confinement of an STZ.

From the measured values of  $G$  and estimated values of  $\Omega$  of more than 40 kinds of MGs, the molar potential energy barrier of STZ,  $W_{\text{STZ}}$ , has been estimated by Yu *et al.* [18]. A remarkable finding is that, as shown in Fig. 5a,  $W_{\text{STZ}}$  and  $E_\beta$  are almost equivalent to each other in all known MGs, that is,  $W_{\text{STZ}} = E_\beta$ . This relation was also implied from a simulation of Rodney and Schuh [63]. Clearly, this relation connects two fundamental issues in glassy physics: the deformation mechanisms and relaxation dynamics.

Because STZs are considered as the basic structural units of deformation in glassy solids, it is of practical importance to see how the properties of STZs affect the mechanical properties of MGs [58]. Poisson's ratio, when plotted against  $W_{\text{STZ}} = E_\beta$  for many MGs in Fig. 5b, demonstrates yet another modest correlation between these quantities (exceptions to this correlation in some BMGs that

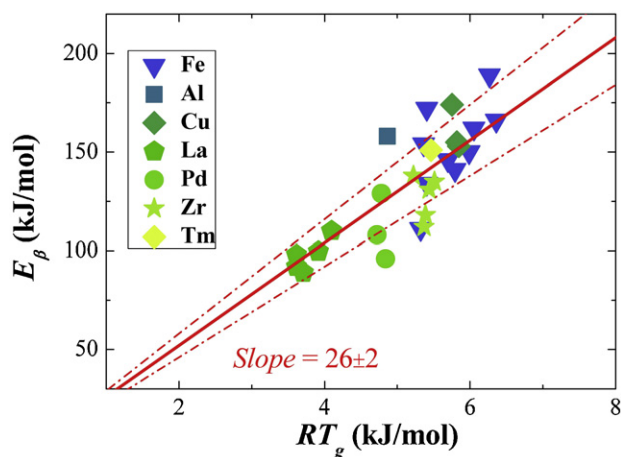


FIGURE 4

Relationship between  $E_\beta$  and  $RT_g$  for different MGs, the lines are least square linear fits [18].

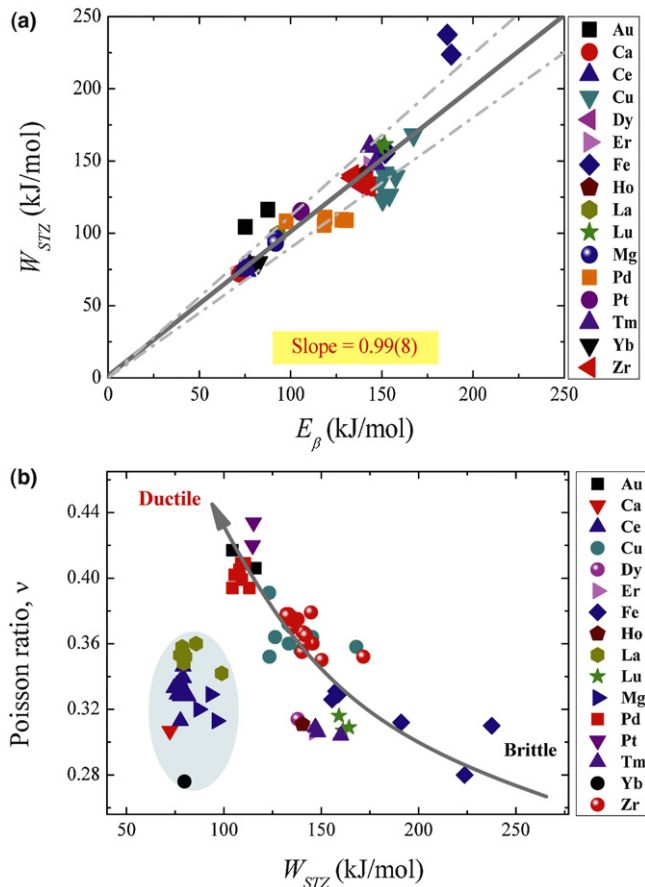


FIGURE 5

(a) Relationship between  $E_\beta$  and  $W_{STZ}$ . (b) Correlation between  $W_{STZ}$  and the Poisson ratio [18].

indicated as shaded ellipse in Fig. 5b are due to extrinsic factors [18], as confirmed by recent work of Madge *et al.* [64]. As Poisson's ratio is an indicator of ductility in MGs [65,66], this correlation suggests that  $\beta$  relaxations like the STZs are fundamental to considerations of the ductility of MGs. A lower  $W_{STZ}$  means STZs are more easily activated and thus the MG has a better ductility [18]. The correlations between  $E_\beta$  and  $W_{STZ}$  and Poisson's ratio have made the  $\beta$  relaxation a center of attention in improving the mechanical properties of MGs (see the next section).

### Achieving tensile ductility in MGs by activation of $\beta$ relaxations

A serious drawback to MGs is their brittleness [4,49]. Although some MGs show considerable plastic strain under constrained deformations such as compression and bending [67], the unconstrained tensile plasticity of MGs is almost zero [68]. This dilemma hinders the widespread engineering applications of MGs as well as some fundamental studies. Substantial efforts have been made to enhance the tensile ductility of MGs [69]. Recently the insights from the correlation between  $\beta$  relaxation and STZs [18] have been utilized in mitigating the brittleness of MGs [19,33]. The idea is straightforward: as  $\beta$  relaxation is closely related to the activation of deformation units (i.e. STZs), one can expect that MGs with pronounced  $\beta$  relaxations at relatively low temperatures might be macroscopically ductile [19]. The La-based MG shown in Fig. 1 is

such a candidate. In this MG macroscopic tensile plasticity has been achieved at and near room temperature by the activation of the  $\beta$  relaxation [19]. As shown in Fig. 6a, the temperature–strain rate deformation map reveals a clear ductile-to-brittle transition (DBT), and remarkably the  $\beta$  relaxation and DBT follow similar temperature–frequency dependencies in an Arrhenius plot, as shown in Fig. 6b. Furthermore, the deformation and fracture morphologies, as shown in Fig. 6c and d, confirm the ductile nature of the MG when the  $\beta$  relaxation is activated. These results demonstrate that  $\beta$  relaxation and DBT have the same dynamical properties, and the activation of  $\beta$  relaxations is a necessary condition of achieving tensile plasticity of the MG. It also suggests the mechanical properties can be understood and even predicted from the perspective of  $\beta$  relaxations [19].

The relationship between  $\beta$  relaxation and DBT, as shown in Fig. 6b, might be suggestive to some fundamental aspects of deformation mechanisms of MGs. It is noted in a wide range of crystalline materials, the apparent activation energy of DBT is equal to the activation energy for dislocation glide (known as the Peierls stress), which clearly reveals the underlying mechanism of DBT is controlled by the mobility of dislocations [70]. From the similar values of activation energy, one can infer that the DBT of the MG is closely related to the activation of STZs as well as the  $\beta$  relaxations [19].

Admittedly, the strength ( $\sim 400$  MPa) of the La-MG in Ref. [19] is relatively low compared to typical Zr-MGs with strength on the order of 1500 MPa [4]. Obviously, this is due to the low  $T_g$  (about 440 K) of the MG, which originates from the specific chemical composition [71]. Nevertheless, Refs [18,19] provide a novel guideline for further investigations to develop MGs with optimized high strength and tensile ductility through the control of  $\beta$  relaxations.

It is worthwhile pointing out a similar connection between  $\beta$  relaxation and mechanical properties in polymer glasses [20]. For example, transitions of impact toughness, yield strength and failure mode are often correlated with  $\beta$  relaxations [20]. Polymers with pronounced  $\beta$  relaxations often possess good ductility and vice versa. The similar connection between mechanical properties and  $\beta$  relaxations in different glasses suggests there must be some underlying universal physics yet to be discovered [72].

### The $\beta$ relaxation, diffusion, and the breakdown of Stokes–Einstein relation in MGs

Besides their technological attractions, MGs are also prototype materials for scientific study of some fundamental problems. During the past few years, diffusion in glasses and supercooled liquids has been a subject of considerable interest [73–79]. In particular, the relationship between diffusion and relaxation is an important topic and has been being actively discussed in various glass-forming liquids [73–79]. At sufficiently high temperatures,  $\alpha$  and  $\beta$  relaxations merge into a single relaxation, and diffusions of different components are coupled, and relaxation and diffusion are usually connected by the Stokes–Einstein relation, which predicts  $D\tau_\alpha/T$  should be temperature independent, here  $D$  is diffusion coefficient [6,75]. However, in almost all kinds of glass-forming liquids below approximately  $1.2T_g$  there occurs a decoupling between  $D$  and  $\tau_\alpha$ , as well as a decoupling of diffusion of different components. In some fragile organic glasses, near  $T_g$  diffusive motions are faster than expected based on their  $\tau_\alpha$  by as

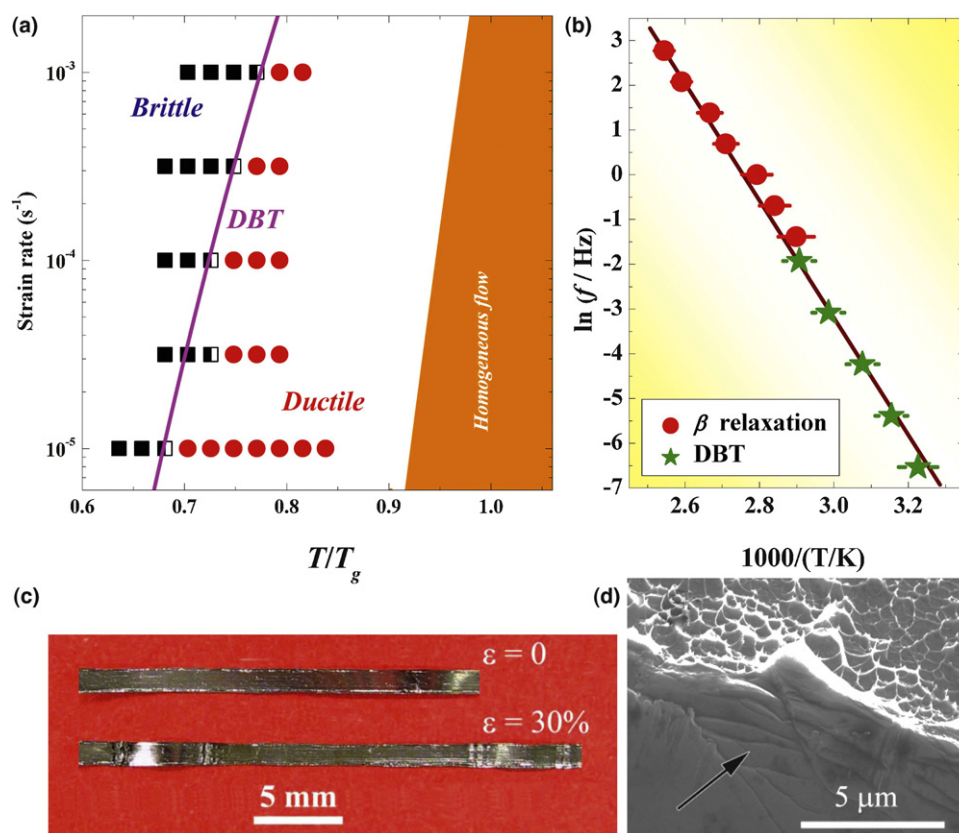


FIGURE 6

(a) The deformation mode map summarizing the tension tests at different temperature and strain rates, see Ref. [19] for the meanings of the symbols. (b) The Arrhenius plot of DBT and the  $\beta$  relaxation of the MG. (c) The photograph of the MG before and after tension. (d) SEM image of a ductile fracture surface of the La-MG [19].

much as two orders of magnitude [6,75]. The origin of the breakdown of the Stokes–Einstein relation constitutes an outstanding issue in glassy physics [6,75,78,79].

Recent results in MGs revealed intriguing connections between the decoupling of diffusion of different components and splitting of the relaxation modes, and provided fresh insights to the breakdown of Stokes–Einstein relation. On one hand, in a Pd<sub>43</sub>Ni<sub>10</sub>Cu<sub>27</sub>P<sub>20</sub> MG, Bartsch *et al.* [80] found that the diffusive motion of the largest constituting atoms (Pd atoms in this MG) and the  $\alpha$  relaxation are correlated [Fig. 7a]. For the Pd atoms the Stokes–Einstein relation holds in the whole temperature range investigated, from temperatures far above melting point down to  $T_g$ ; while for other smaller atoms, they diffuse faster than the Pd atoms, and the Stokes–Einstein relation breaks down. On the other hand, in a wide range of MGs Yu *et al.* [32] found the diffusions of the smallest constituting atoms and  $\beta$  relaxation are correlated. They demonstrated the diffusive motions of the smallest constituting atoms take place within the temperature and time regimes where the  $\beta$  relaxations are activated (see Fig. 7b for an example), and the two processes have similar activation energies (Fig. 7c). The results of Bartsch *et al.* [80] and Yu *et al.* [32] are complementary to each other. Together, they 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 [32]. It also implies that  $\beta$  relaxation could be responsible for the

enhanced diffusivity and the break-down of the Stokes–Einstein relation, as first suggested by Richert and Samwer [81]. Recently a theoretical consideration of the results in Refs [32,80] from the coupling mode has been given [82].

The above results [32,80] are also of interest within the general concept of dynamic asymmetry and its relation to size disparity [83]. For instance, theoretical work [84] and simulations [85–87] have suggested that the glass transition (the arrest of the  $\alpha$  relaxation) is mainly controlled by the slowing down of diffusions of large constituting particles, whereas diffusions of small particles persist into deep glassy states. MGs and their forming liquids represent ideal systems for verifying these suggestions because of their large size difference in constituent atoms [88], and their relatively simple atomic structures. Research along this line is expected to provide important insights into the relaxation and diffusion mechanisms in supercooled liquids and the mechanisms of the breakdown of the Stokes–Einstein relation [82].

### The $\beta$ relaxation and the mechanisms of physical aging

Metallic glasses exist in a non-equilibrium state, and the slow relaxation toward equilibrium is commonly referred to as physical aging [89]. It is accompanied by the changes in almost all physical properties, and is an important concern in many applications. The effects of physical aging can be erased by heating above  $T_g$ , indicating a close connection between aging and the glass transition [89,90]. Interestingly, a special kind of physical aging in MGs

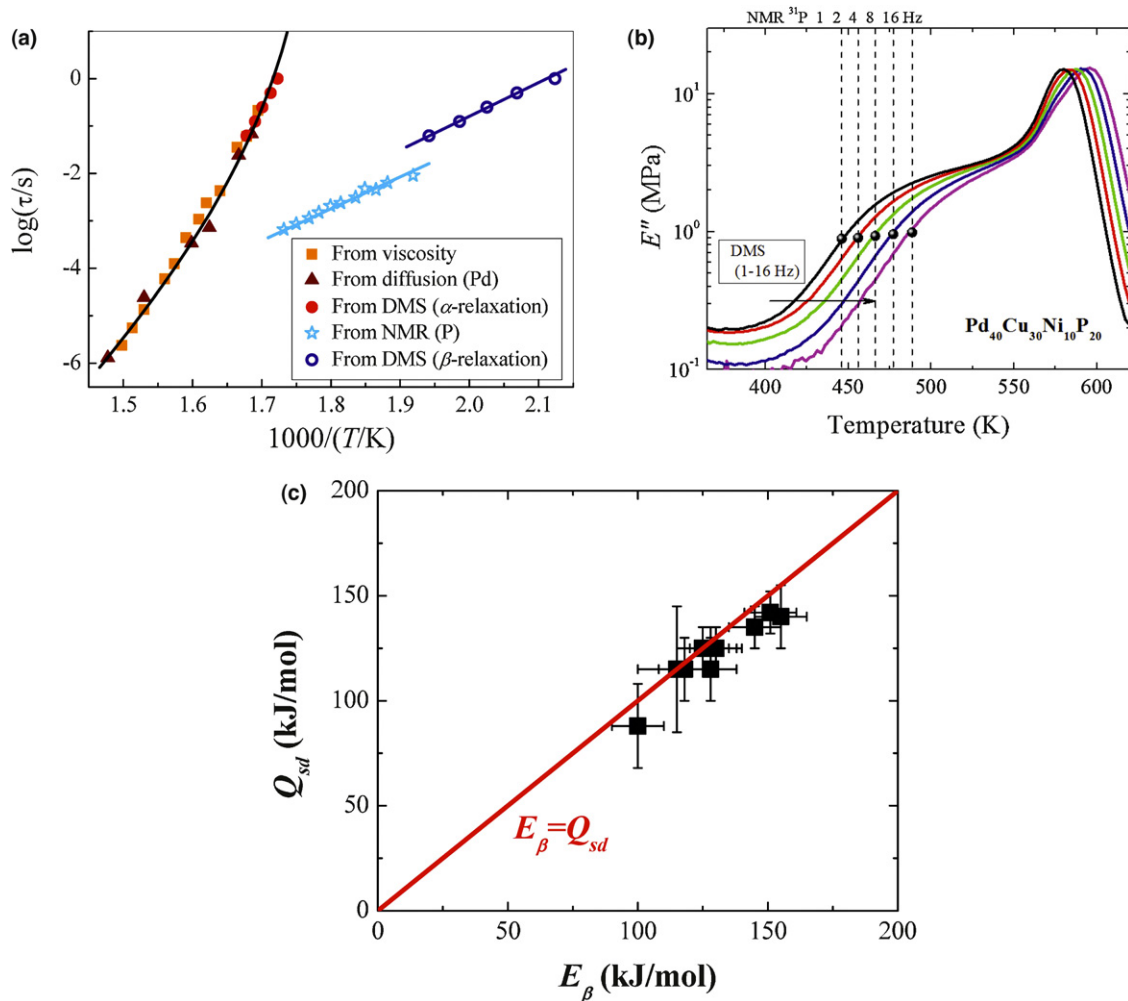


FIGURE 7

(a) Arrhenius plot of the relaxation time of  $\alpha$  and  $\beta$  relaxations of  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  MG [32]. Viscosity data from Ref. [80] is converted into relaxation time by Maxwell equation [11]. Diffusion data of Pd from Ref. [80] is converted by the Stokes–Einstein relation. (b) Temperature dependent of  $E''$  of the  $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$  MG, the frequencies are 1, 2, 4, 8 and 16 from left to right, respectively. The dashed lines are the NMR probed atomic diffusive hopping rates (as indicated on top) at the corresponding temperatures [32]. (c) Comparison between  $E_{\beta}$  and the activation energy of the self-diffusions of the smallest constituting atoms  $Q_{sd}$  in different MGs [32].

has been disclosed to correlate with  $\beta$  relaxations [91]. In contrast to common metals and alloys, whose elastic modulus decreases linearly with increasing temperature (the slope of which is called the Debye–Grüneisen constant), the rapid solidified MGs become much stiffer before the onset of glass transition, which apparently resembles the behavior of rubber and protein like materials. One remarkable feature of the stiffening phenomenon is the heating rate and thermodynamic path dependence [91,92]. Hachenberg *et al.* [91] first noticed that this stiffening phenomenon is incompatible with the typical picture of physical aging regarding the structures of the MGs, and they suggested  $\beta$  relaxation must be involved.

However, the stiffening phenomenon could also be related to the continuous densification of MGs during heat treatments and it remains to be clarified whether this densification is actually induced by the activation of  $\beta$  relaxations.

### The $\beta$ relaxation and crystallization in MGs

The crystallization of MGs is important for several aspects and has been extensively reviewed [9]; especially for those MGs where

partial crystallization might result in novel microstructures and enhanced mechanical or magnetic properties [93–95].

Usually, crystallization of MGs occurs after the glass transition, however, there are at least two conditions under which crystallization takes place before the glass transition [96,97]: (i) perturbations from some external periodic fields can markedly accelerate crystallization and promote crystallizations below  $T_g$ ; (ii) in some less stable MGs, the glass transition cannot be detected before crystallization by conventional DSC measurements, which implies crystallization precedes before the glass transition under these heating rates. Both of these conditions are considered to be correlated with  $\beta$  relaxations. As an example of the former situation, crystallization of a Pd-based MG by ultrasonic annealing at 10 K below  $T_g$  was found by Ichitsubo *et al.* [96] to be caused by the accumulation of atomic jumps associated with  $\beta$  relaxations being stochastically resonant with the supersonic vibrations, which eventually leads to crystallization. Another important conclusion of Ichitsubo *et al.* [96] was that MGs are mechanically inhomogeneous at the nanoscale, and  $\beta$  relaxation might relate to it. Ichitsubo *et al.* [97] further proposed that  $\beta$  relaxation is also

responsible for the crystallization before  $T_g$  even for less stable MGs (the second situation, as discussed above). It is also worth noting that the relationship between crystallization and  $\beta$  relaxation is also being actively discussed in molecular glasses; see Refs [98–100] for example.

### The nature and mechanism of $\beta$ relaxation in MGs

The underlying mechanism of  $\beta$  relaxation was originally suggested by Johari to indicate local diffusions in loosely packed isolated regions [12]. These regions were referred to as ‘islands of mobility’ or ‘defects’, in a mechanically rigid glass structure. However, recently, a random first order transition theory predicted that  $\beta$  relaxations are governed by ramified, string-like or quadrupolar-like clusters of particles, while  $\alpha$  relaxation takes place through activated events involving compact regions [101]. The string-like motion of  $\beta$  events is supported by a recent molecular dynamic simulation [102]. Furthermore, the correlations between  $\beta$  relaxations and other processes and properties of MGs provide some additional support to this suggestion [32,103]. However, it should note that despite the long history of research, there has been no agreement on the microscopic origin of the  $\beta$  relaxation and therefore it is still an open question [15–19,104–106].

### Summary and outlook

The  $\beta$  relaxation in MGs provides considerable potential for the understanding of many crucial unresolved issues in glassy physics and material sciences: this ranges from glass transitions, deformation mechanisms, to diffusion and the breakdown of the Stokes–Einstein relation; as well as the crystallization and stability of glasses. These correlations also provide practical guidelines to surmount the problem of mechanical brittleness of MGs. Yet, studies of  $\beta$  relaxations in MGs are far from complete; in particular, the nature and mechanism of the  $\beta$  relaxation are not clear. In addition to the questions outlined in the text, future studies of the  $\beta$  relaxation in MGs (for example in terms of the atomic and electronic structures [107]) are expected to lead to more fundamental insights.

### Further information

K.L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer, New York, 2011). The chapter 2 of this book contains an extensive literature review of  $\beta$  relaxations in other types of glasses up to the year of 2010.

### Acknowledgements

H.B. Yu acknowledges the Alexander von Humboldt Foundation for support with a post-doctoral fellowship. K. Samwer acknowledges the supports from the German Science Foundation (DFG). W.H. Wang acknowledges the supports from the NSF of China. Discussions with Prof. Hai-Yang Bai are appreciated.

### References

- [1] A.L. Greer, *Mater. Today* 12 (2009) 14.
- [2] A.L. Greer, E. Ma, *MRS Bull.* 32 (2007) 611.
- [3] W.H. Wang, *Adv. Mater.* 21 (2009) 4524.
- [4] C. Schuh, et al. *Acta Mater.* 55 (2007) 4067.
- [5] M.F. Ashby, A.L. Greer, *Scr. Mater.* 54 (2006) 321.
- [6] M.D. Ediger, P. Harrowell, *J. Chem. Phys.* 137 (2012) 080901.
- [7] D.B. Miracle, *Nat. Mater.* 3 (2004) 697.
- [8] H.W. Sheng, et al. *Nature* 439 (2006) 419.
- [9] W.H. Wang, et al. *Mater. Sci. Eng. R* 44 (2004) 45.
- [10] H.B. Yu, et al. *Appl. Phys. Lett.* 96 (2010) 081902.
- [11] J.C. Dyre, *Rev. Mod. Phys.* 78 (2006) 953.
- [12] G.P. Johari, M. Goldstein, *J. Chem. Phys.* 53 (1970) 2372.
- [13] C.A. Angell, et al. *J. Appl. Phys.* 88 (2000) 3113.
- [14] H. Tanaka, et al. *Nat. Mater.* 9 (2010) 324.
- [15] K.L. Ngai, M. Paluch, *J. Chem. Phys.* 120 (2004) 857.
- [16] M. Goldstein, *J. Non-Cryst. Solids* 357 (2011) 249.
- [17] S. Capaccioli, et al. *J. Phys. Chem. Lett.* 3 (2012) 735.
- [18] H.B. Yu, et al. *Phys. Rev. B* 81 (2010) 220201.
- [19] H.B. Yu, et al. *Phys. Rev. Lett.* 108 (2012) 015504.
- [20] C. Xiao, et al. *Macromolecules* 27 (1994) 2761.
- [21] Y. Liu, J.A. Donovan, *Polym. Eng. Sci.* 36 (1996) 2345.
- [22] K.L. Ngai, et al. *Philos. Mag.* 91 (2011) 1809.
- [23] M.T. Cicerone, J.F. Douglas, *Soft Matter* 8 (2012) 2983.
- [24] J.M. Pelletier, et al. *Mater. Sci. Eng. A* 336 (2002) 190.
- [25] P. Rosner, et al. *Europhys. Lett.* 68 (2004) 226.
- [26] K.L. Ngai, *J. Non-Cryst. Solids* 352 (2006) 404.
- [27] J. Hachenberg, K. Samwer, *J. Non-Cryst. Solids* 352 (2006) 5110.
- [28] P. Wen, et al. *Appl. Phys. Lett.* 84 (2004) 2790.
- [29] Z.F. Zhao, et al. *Phys. Rev. B* 75 (2007) 174201.
- [30] Z. Wang, et al. *J. Phys.: Condens. Matter* 23 (2011) 142202.
- [31] L. Guo, et al. *J. Appl. Phys.* 109 (2011) 113524.
- [32] H.B. Yu, et al. *Phys. Rev. Lett.* 109 (2012) 095508.
- [33] Z. Wang, et al. *Appl. Phys. Lett.* 101 (2012) 121906.
- [34] H.B. Yu, et al. *J. Non-Cryst. Solids* 358 (2012) 869.
- [35] L.M. Wang, et al. *J. Chem. Phys.* 125 (2006) 074505.
- [36] P. Lunkenheimer, et al. *Contemp. Phys.* 41 (2000) 15.
- [37] L. Hu, et al. *Appl. Phys. Lett.* 96 (2010) 221908.
- [38] L. Hu, Y. Yue, *J. Phys. Chem. C* 113 (2009) 15001.
- [39] S. Ashtekar, et al. *Phys. Rev. Lett.* 106 (2011) 235501.
- [40] S. Ashtekar, et al. *J. Phys. Chem. Lett.* 1 (2010) 1941.
- [41] M. Paluch, et al. *Phys. Rev. Lett.* 91 (2003) 115701.
- [42] W.H. Wang, et al. *J. Non-Cryst. Solids* 352 (2006) 5103.
- [43] J.C. Qiao, J.M. Pelletier, *J. Appl. Phys.* 112 (2012) 033518.
- [44] A. Döb, et al. *Phys. Rev. Lett.* 88 (2002) 095701.
- [45] R. Böhmer, et al. *J. Chem. Phys.* 99 (1993) 4201.
- [46] C.A. Angell, et al. *Science* 267 (1995) 1924.
- [47] J. Hwang, et al. *Phys. Rev. Lett.* 108 (2012) 195505.
- [48] J. Schroers, *Phys. Today* 66 (2013) 32.
- [49] M.W. Chen, *NPG Asia Mater.* 3 (2011) 82.
- [50] M.W. Chen, *Ann. Rev. Mater. Res.* 38 (2008) 445.
- [51] W.H. Wang, *Prog. Mater. Sci.* 57 (2012) 487.
- [52] D. Bedorf, et al. *Europhys. Lett.* 80 (2011) 325.
- [53] W.H. Peter, et al. *Intermetallics* 10 (2002) 1125.
- [54] M.L. Falk, J.S. Langer, *Annu. Rev. Condens. Mater. Phys.* 2 (2011) 353.
- [55] M.L. Falk, J.S. Langer, *Phys. Rev. E* 57 (1998) 7192.
- [56] P. Schall, et al. *Science* 318 (2007) 1895.
- [57] V. Chikkadi, et al. *Phys. Rev. Lett.* 107 (2011) 198303.
- [58] D. Pan, et al. *Proc. Natl. Acad. Sci. U. S. A.* 105 (2008) 14769.
- [59] M. Schwabe, et al. *J. Non-Cryst. Solids* 357 (2011) 490.
- [60] H. Wagner, et al. *Nat. Mater.* 10 (2011) 439.
- [61] W.L. Johnson, K. Samwer, *Phys. Rev. Lett.* 95 (2005) 195501.
- [62] J.S. Harmon, et al. *Phys. Rev. Lett.* 99 (2007) 135502.
- [63] D. Rodney, C.A. Schuh, *Phys. Rev. Lett.* 102 (2009) 235503.
- [64] S.V. Madge, et al. *Acta Mater.* 60 (2012) 4800.
- [65] J.J. Lewandowski, et al. *Philos. Mag. Lett.* 85 (2005) 77.
- [66] G.N. Greaves, et al. *Nat. Mater.* 10 (2011) 823.
- [67] J. Schroers, W.L. Johnson, *Phys. Rev. Lett.* 93 (2004) 255506.
- [68] Z.F. Zhang, et al. *Acta Mater.* 51 (2003) 1167.
- [69] D.C. Hofmann, et al. *Nature* 451 (2008) 1085.
- [70] P. Gumbsch, et al. *Science* 282 (1998) 1293.
- [71] H.B. Yu, et al. *Appl. Phys. Lett.* 92 (2008) 141906.
- [72] H.N. Lee, et al. *Science* 323 (2009) 231.
- [73] F. Faupel, et al. *Rev. Mod. Phys.* 75 (2003) 237.
- [74] X.P. Tang, et al. *Nature* 402 (1999) 160.
- [75] M.D. Ediger, *Annu. Rev. Phys. Chem.* 51 (2000) 99.
- [76] S.M. Chathoth, K. Samwer, *Appl. Phys. Lett.* 97 (2010) 221910.
- [77] L. Xu, et al. *Nat. Phys.* 5 (2009) 565.
- [78] K.L. Ngai, *J. Phys. Chem. B* 103 (1999) 10684.
- [79] K.L. Ngai, *Philos. Mag.* 87 (2007) 357.
- [80] A. Bartsch, et al. *Phys. Rev. Lett.* 104 (2010) 195901.



- [81] R. Richert, K. Samwer, *New J. Phys.* 9 (2007) 36.  
[82] K.L. Ngai, S. Capaccioli, *J. Chem. Phys.* 138 (2013) 094504.  
[83] T. Voigtmann, J. Horbach, *Phys. Rev. Lett.* 103 (2009) 205901.  
[84] J. Bosse, Y. Kaneko, *Phys. Rev. Lett.* 74 (1995) 4023.  
[85] R. Kurita, E.R. Weeks, *Phys. Rev. E* 82 (2010) 041402.  
[86] T. Voigtmann, *Europhys. Lett.* 96 (2011) 36006.  
[87] A.J. Moreno, J. Colmenero, *Phys. Rev. E* 74 (2006) 021409.  
[88] A. Inoue, *Acta Mater.* 48 (2000) 279.  
[89] I.M. Hodge, *Science* 267 (1995) 1945.  
[90] R. Casalini, C.M. Roland, *Phys. Rev. Lett.* 102 (2009) 035701.  
[91] J. Hachenberg, et al. *Appl. Phys. Lett.* 92 (2008) 131911.  
[92] A. Kahl, et al. *Appl. Phys. Lett.* 95 (2009) 201903.  
[93] W.H. Wang, *Prog. Mater. Sci.* 52 (2007) 540.  
[94] L. Yang, et al. *Adv. Mater.* 21 (2009) 305.  
[95] M.W. Chen, et al. *Phys. Rev. Lett.* 96 (2006) 245502.  
[96] T. Ichitsubo, et al. *Phys. Rev. Lett.* 95 (2005) 245501.  
[97] T. Ichitsubo, et al. *J. Chem. Phys.* 125 (2006) 154502.  
[98] T. Hikima, et al. *J. Non-Cryst. Solids* 235 (1998) 539.  
[99] Z. Wojnarowska, et al. *J. Phys. Chem. B* 113 (2009) 12536.  
[100] Y. Sun, et al. *AAPS J.* 14 (2012) 380.  
[101] J.D. Stevenson, P.G. Wolynes, *Nat. Phys.* 6 (2009) 62.  
[102] Y. Cohen, et al. *Europhys. Lett.* 100 (2012) 36003.  
[103] D. Bedorf, K. Samwer, *J. Non-Cryst. Solids* 356 (2010) 340.  
[104] J.C. Dyre, N.B. Olsen, *Phys. Rev. Lett.* 91 (2003) 155703.  
[105] G. Williams, *Adv. Polym. Sci.* 33 (1979) 59.  
[106] H. Tanaka, *Phys. Rev. E* 69 (2004) 021502.  
[107] Y.Q. Cheng, E. Ma, *Prog. Mater. Sci.* 56 (2011) 379.