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Signature of viscous flow units in apparent elastic regime of metallic glasses

Z. Wang, P. Wen, L. S. Huo, H. Y. Bai, and W. H. Wang[a)]
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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We characterize and identify the flow units in two typical metallic glasses (MGs), which have markedly different β-relaxation behaviors and mechanical properties. The viscoelastic hysteresis loops are found in the cyclic deformation in the nominal elastic regime of the metallic glasses. We show that the hysteresis loops are related to the activation of the flow units in metallic glasses, and a model is proposed to describe the flow units. We demonstrate that the flow units are both the deformation units of the anelastic and plastic deformation behaviors and the structural origin of the β-relaxation in metallic glasses. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4753813]

The structural origins of elastic and plastic deformations and relaxations of metallic glasses (MGs) has been the research focus of material science and condensed matter physics for decades.[1–7] Several models have been proposed to describe the mechanisms of the deformation and the relaxations.[8–14] The shear transformation zone (STZ),[9] which were hypothesized as the "plastic units" containing tens of atoms confined within elastic medium, is a widely accepted model for the plastic deformation in MGs. Previous studies especially computer simulation results reveal that the actual deformation can be interpreted based on the assumption.[11,15–18] In colloidal glasses, soft spots which resemble the flow units in MGs have been experimentally observed.[19,20] Recently, experimental observations reveal that the MGs are intrinsic structural inhomogeneous.[5–7] The MGs were found to be elastic heterogeneous in nano-scale,[6,7,14] which implies the relationship between the plastic units and the heterogeneous "defects" in MGs. However, more experimental evidences for existence of the flow units as well as their relationships with macroscopic mechanical properties are still lacking.

The β-relaxation is viewed as locally initiated and reversible process in glasses.[21,22] The β-relaxation can be detected through a method of the dynamic mechanical spectroscopy, which is highly sensitive to "defects" in solids including polycrystalline metals[23] and polymers.[22] Recently, the activation of STZs is found to associate with the β-relaxation.[24] Yu *et al*. experimentally confirmed that the activation energy of the deformation units and β-relaxations in MGs are nearly equivalent.[25] However, the features and the activation process of the flow units, the roles of the flow units in the plastic deformation, and relaxations in MGs are still unclear. It is anticipated that the flow units in MGs could be verified and characterized through dynamic mechanical approach. However, the β-relaxation behavior of most MGs is too obscure to be distinguished from the α-relaxation.[26] This makes the detection of the flow units through the dynamic mechanical spectra difficult.

In this Letter, we developed a $La_{70}Ni_{15}Al_{15}$ MG with a pronounced β-relaxation. We use the MG and a $Cu_{45}Zr_{45}Ag_{10}$ MG (for comparison) as model systems to study the activation and features of the flow units in MGs using the dynamic tensile tests and the dynamical mechanical analyzer (DMA). The influence of the flow units on the relaxation and the plastic deformation is studied to clarify the structural origins of the plastic deformation and the β-relaxations in MGs.

The $La_{70}Ni_{15}Al_{15}$ and $Cu_{45}Zr_{45}Ag_{10}$ MG in bulk and ribbon forms were prepared by melt casting and melt spinning, respectively. The glassy nature was ascertained by X-ray diffraction and differential scanning calorimetry. The dynamical mechanical behaviors were tested on a TA Q800 DMA. The MG rods were measured through temperature ramp mode at a heating rate of 3 K/min, and dynamic and quasi-static tensile tests of MG ribbons were carried out in DMA machine.

The temperature dependences of the loss modulus E'' of two model MGs measured at 1 Hz are shown in Fig. 1. The $La_{70}Ni_{15}Al_{15}$ (Fig. 1(a)) and $Cu_{45}Zr_{45}Ag_{10}$ (Fig. 1(b)) have distinctly different β-relaxation behaviors. For $La_{70}Ni_{15}Al_{15}$ MG, a pronounced β-relaxation peak separated from α-relaxation can be clearly observed. The $Cu_{45}Zr_{45}Ag_{10}$ MG only has a weak β-relaxation hump overlapped with the broad α-relaxation peak. The difference in β-relaxation mode reflects the different characteristics of the flow units in the two MGs.[22] We fit the whole relaxation curve by coupling two Kohlrausch–Williams–Watts (KWW) equations in the Fourier transforms of $d\{\Delta E \exp[-(t/\tau)^{\beta_{KWW}}]\}$, which can characterize the heterogeneity of glass-forming liquids. Here, $\Delta E = E(f=\infty) - E(f=0)$, β_{KWW} is a nonexponential parameter related to the dynamic heterogeneity, and τ is average relaxation time. The loss modulus E'' can be fitted well using an appropriate β_{KWW} with a given temperature dependent τ. For α-relaxation, the temperature dependence of τ_α is described by the Vogel–Fulcher–Tammann (VFT) equation $\tau_\alpha = \tau_{\alpha 0}\exp\left(\frac{DT_0}{T-T_0}\right)$, the τ_β of β-relaxation has the form of the Arrhenius process $\tau_\beta = \tau_{\beta 0}\exp\left(\frac{E_\beta}{RT}\right)$. The prefactors for the two metallic supercooled liquids are $\tau_{\alpha 0} \sim 10^{-13}$ and $\tau_{\beta 0} \sim 10^{-15}$, which correlate with the translational atomic motions and are consistent with privious work.[10] The blue and the red regions in Fig. 1 represent the fit of α- and β-relaxations, respectively. The black bold line is the superposition of the two fitting processes. Due to the low thermal stability, the crystallization occurs above T_g, and the fit of α-relaxation of $Cu_{45}Zr_{45}Ag_{10}$ is conducted only in the low temperature side. Except for the blemish, the fitting curves agree with experimental data for the MGs. The key

[a)]Author to whom correspondence should be addressed. Electronic mail: whw@aphy.iphy.ac.cn.

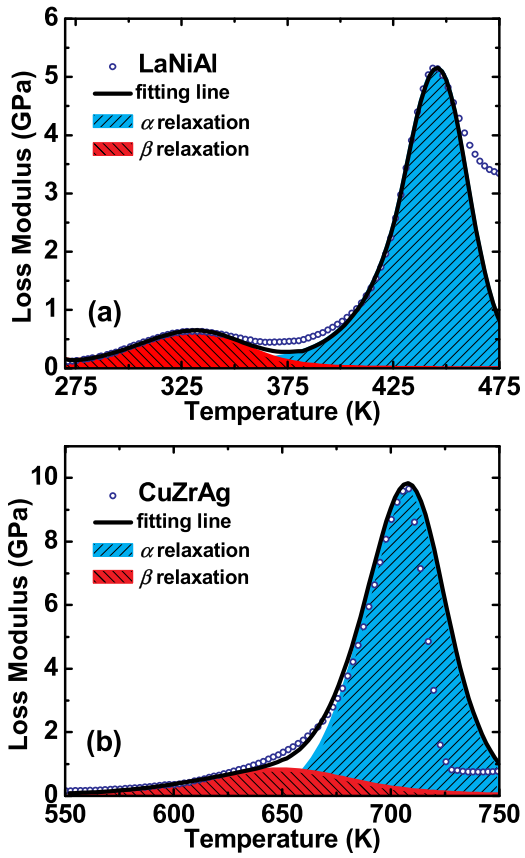

FIG. 1. Temperature-dependent loss modulus E'' of (a) $La_{70}Ni_{15}Al_{15}$ and (b) $Cu_{45}Zr_{45}Ag_{10}$ measured at 1 Hz. The blue region represents the KWW fit of α-relaxation while the red region represents the fit of β-relaxation, and the black bold line is the superposition of the two fitting processes. The ratio of the relaxation strength (the height of the relaxation peak) of these two relaxations represents the flow unit density.

parameters of D, β_{KWW}, and E_β obtained from the fits are listed in Table I, which are consistent with the data previously reported.[25–28]

The obtained fitting parameters of D and β_{KWW} can distinguish the features of the flow units in the two MGs. The broader distribution with the decrease of β_{KWW} indicates that the faster relaxation domains correlate with the potential flow units in glass state existing in supercooled liquids.[29] The smaller values of D and β_{KWW} indicate that the La-based MG is more fragile and has highly structural inhomogeneous compared with that of $Cu_{45}Zr_{45}Ag_{10}$ MG. The fraction of the defects is found to be proportional to the intensity of the internal friction peak or the relaxation strength of the loss modulus peak.[23,30] The relaxation strength ratios of $La_{70}Ni_{15}Al_{15}$ and $Cu_{45}Zr_{45}Ag_{10}$ in Fig. 1 are about 12% and 8%, respectively. The results indicate that the fraction of the potential flow unit regions in La-based MG is about 30%

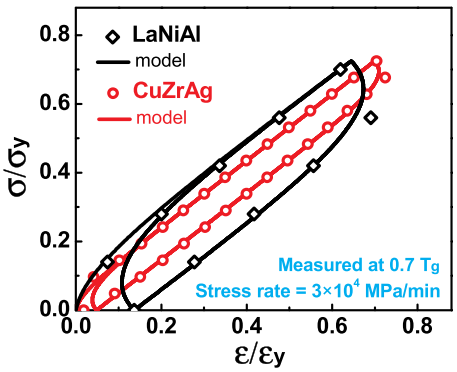

FIG. 2. The experimental and simulation results of dynamic tensile test at 0.7 T_g and stress rate 3×10^4 MPa/min (ε_y and σ_y are yield strain and stress, respectively). The open diamonds or circles represent the experimental data, while the solid lines are the best simulation results. $La_{70}Ni_{15}Al_{15}$ and $Cu_{45}Zr_{45}Ag_{10}$ are represented by dark and light colors, respectively.

higher than that in $Cu_{45}Zr_{45}Ag_{10}$. This result is roughly consistent to the previous predictions.[31] The large difference in fraction of the flow units confirms the large difference in heterogeneity in the MGs. The activation energy E_β of the β-relaxations of the MGs, determined from the frequency dependent peak temperature, is listed in Table I.

To identify whether the β-relaxation and deformation zones stem from the flow units and to estimate the viscosity of the flow units, the dynamic tensile tests on the MGs are conducted. Figure 2 presents the stress-strain curve in the apparent elastic regimes of the two MGs at 0.7 T_g. The $La_{70}Ni_{15}Al_{15}$ ribbon was tested at about room temperature (303 K ≈ 0.7 T_g), and $Cu_{45}Zr_{45}Ag_{10}$ was measured at equivalent temperature 473 K (also 0.7 T_g) to eliminate the impact of the diverse T_g. We applied stress to the maximum stress of ~0.7σ_y (σ_y is yield strength of the MGs) and then gradually unloaded to zero stress with a stress rate of 3×10^4 MPa/min for 10 iterations. The first cycle is presented here for clarity due to the minor change for each cycle. We observed obvious mechanical hysteresis loop in the apparent elastic regime of the MGs. The loops confirm the existence of soft flow units, and the deformation in the elastic regimes of the MGs is viscoelastic. The activated flow units contribute to the viscoelasticity and the mechanical hysteresis loop of the MGs.[6,14] Figure 2 also shows that the two MGs have markedly different viscoelastic behavior under such stress level and rate. The hysteresis loop of $La_{70}Ni_{15}Al_{15}$ is obviously larger than that of $Cu_{45}Zr_{45}Ag_{10}$, confirming that the fraction and viscosity (see details later) of the flow units are different in the MGs.

To understand the activation process of the flow units and the viscoelastic behavior of the MGs, we simulate the viscoelastic process by using a three-parameter viscoelastic

TABLE I. The fitting parameters of KWW fit and obtained parameters of E_1, E_2, and viscosity of the flow units from three-parameter viscoelastic model fit for the MGs.

MGs	T_g [K]	β_{KWW}	D	E_β [kJ/mol]	E_β/T_g [kJ/mol·K]	E_1 [GPa]	E_1/T_g [GPa/K]	E_2 [GPa]	E_2/T_g [GPa/K]	η [GPa s]	η/T_g [GPa s/K]
$La_{70}Ni_{15}Al_{15}$	441 ± 1	0.42 ± 0.03	18 ± 2	87 ± 5	0.197	16.5 ± 2	0.037	108.5 ± 10	0.246	1.5 ± 0.2	0.0034
$Cu_{45}Zr_{45}Ag_{10}$	684 ± 1	0.62 ± 0.05	22 ± 2	171.5 ± 30	0.251	59 ± 5	0.086	331 ± 30	0.484	4 ± 0.5	0.0058

model.[32] The MGs can be considered as the combination of elasticity and vicoelasticity when stress is applied,[2] and the flow units represent the vicoelastic portions surrounded by elastic matrix as illustrated in Fig. 3(a). The proposed three-parameter model based on the Voigt model contains a spring (represents the elastic matrix) parallel connected with the combine of a dashpot (represents the flow unit) and another spring (represents the shell of flow unit) in series as shown in Fig. 3(b). The governing equation of the model is expressed as

$$E_2\sigma + \eta\frac{d\sigma}{dt} = E_1E_2\varepsilon + (E_1 + E_2)\eta\frac{d\varepsilon}{dt}, \quad (1)$$

where the σ is applied stress and the ε is obtained strain; the E_1, E_2, and η denote, respectively, the modulus of the matrix, the modulus of flow unit shell, and the average viscosity of flow units. Note that the models constructed of three basic elements (two springs and a dashpot) are equivalent regardless of how these elements are placed.

As shown in Fig. 2(a), the three-parameter model fits the experimental data fairly well. The fitting parameters of E_1, E_2, and η are listed in Table I. The unreasonable high value of E_2 (>100 GPa) implies that the flow unit is directly connected to the elastic matrix,[33] and a more simplified two-parameter Voigt model can describe the behavior of the flow units. The obtained average viscosity of the flow units in $La_{70}Ni_{15}Al_{15}$ and $Cu_{45}Zr_{45}Ag_{10}$ are ~1.5 and ~4 GPa, respectively. The viscosity data are close to that of supercooled liquids and similar to previously reported results.[14] The distinct viscosity difference, which is one of reasons for the obviously different hysteresis loop of the MGs, indicates that the flow units in CuZr-based MG have much higher activation energy. This is agreement with the flow units activation energy determined by DMA for $Cu_{45}Zr_{45}Ag_{10}$ (~2 eV), which is indeed much larger than that of $La_{70}Ni_{15}Al_{15}$ (~1 eV). The relaxation spectrum of the two MGs also confirms the results. For La-based MG, a clear beta-relaxation peak is found at 0.7 T_g (303 K), while for CuZr-based MG, no peak or shoulder can be detected even at 600 K (>0.7 T_g). This means much fewer flow units are activated in CuZr-based MG. The flow units in the two MGs have different characteristics. The flow units in La-based MG have smaller viscosity and lower activation energy and larger volume fraction; On the contrary, the flow units in CuZr-based MG have higher viscosity and activation energy and much smaller volume fraction.

The different characteristics of the flow units result in different mechanical properties in the two MGs. A quasi-static tension tests are performed on these two MGs at 0.75 T_g (323 K for $La_{70}Ni_{15}Al_{15}$ and 513 K for $Cu_{45}Zr_{45}Ag_{10}$) with the same strain rate (1×10^{-5} s^{-1}). Figure 4 shows the engineering stress-strain curves for the two MGs. In contrast to pure brittle fracture in $Cu_{45}Zr_{45}Ag_{10}$, clear yielding and notable tensile plasticity can be observed in $La_{70}Ni_{15}Al_{15}$. The ductility in tension at 0.75 T_g achieved in the La-based MG is due to the activation of high density of flow units.[34] In contrast, the flow units with high activation energy and high viscosity in $Cu_{45}Zr_{45}Ag_{10}$ have been not activated even at 550 K, and the CuZr-based MG then exhibits brittle behavior at 0.75 T_g. This result indicates that the mechanical behavior and ductility of MGs is governed by the activation of the fundamental flow units, and the activation energy and density of the flow units play a crucial role in the viscoelasticity and plasticity of MGs.

Next, we show that the flow units are the initiation units of glass transition. We assume that the applied varying strain is in the form of the mathematically convenient complex notation of $\varepsilon = \varepsilon_0 e^{i\omega t}$, and responding stress is then: $\sigma = \sigma_0 e^{i(\omega t-\phi)} = (\sigma' - i\sigma'')e^{i\omega t}$ (ϕ is the phase lag between strain and stress) according to the linear theory of anelasticity.[32] The expression of loss modulus in three-parameter model can be easily resolved as, $E'' = E_2^* \frac{\omega\tau}{1+\omega^2\tau^2}$, where $\tau = \eta/E_2^* = \frac{\eta_0 \exp\left(\frac{\Delta E}{RT}\right)}{E_2^*}$ for Newtonian liquids.[32] The value of E_2 is not equal to E_2^* because of nonlinear correlation at such

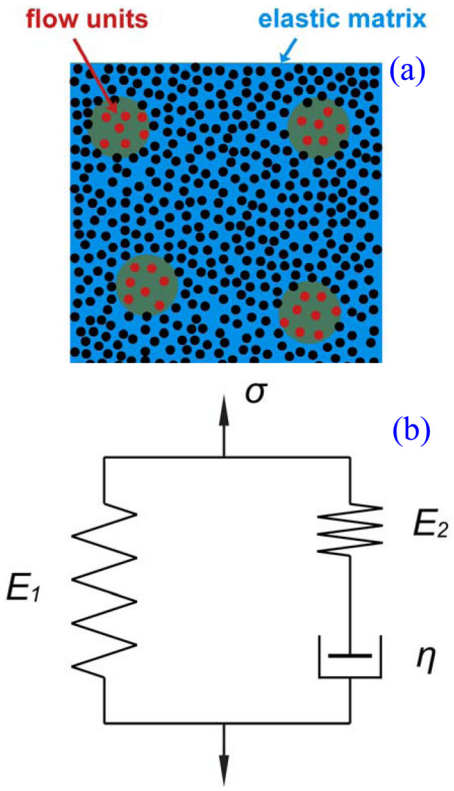

FIG. 3. Schematic illustrations of (a) the metallic glasses with flow units embedded in the elastic matrix and (b) three-parameter viscoelastic model for the MGs.

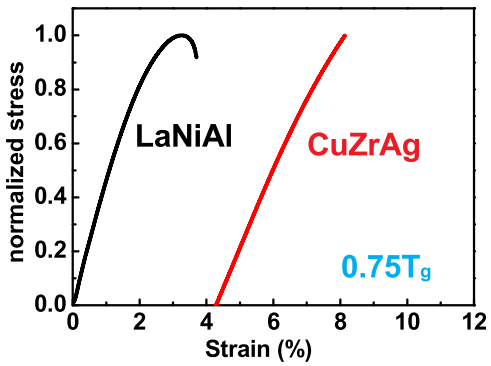

FIG. 4. Quasi-static tension tests at about 0.75 T_g for the two MGs. The stress σ and strain ε results are normalized by yielding stress σ_y and strain ε_y (2%) for comparison.

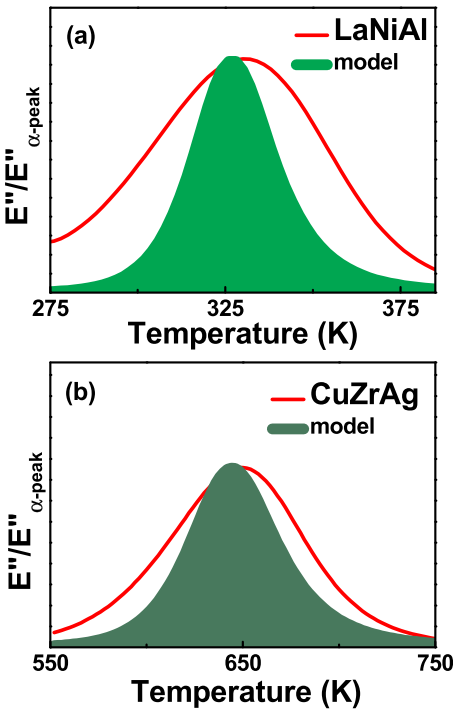

FIG. 5. Loss modulus E″ spectra of (a) $La_{70}Ni_{15}Al_{15}$ and (b) $Cu_{45}Zr_{45}Ag_{10}$ MGs obtained from DMA experiment (red line) and fitted from three-parameter model (green region).

high stress.[32] It is generally believed that both the viscosity and the relaxation time follow the Arrhenius equation,[10,13] and thence the E'' peak caused by flow units can be deducted as a function of temperature. Figure 5 shows the E'' as function of temperature deduced from the viscoselstic three-parameter model for the two MGs. A clear E'' peak can be seen, and the peak denotes the β-relaxation and is comparable to the experimental β-relaxation peak in DMA curves. Therefore, it can be deduced that the features of the activated flow units are similar with that of the supercooled liquid, and the activation of flow units are the precursor of the glass transition.

In summary, the existence of the flow units is experimentally verified in typical metallic glasses. We show that the flow units are the common structural origin of the β-relaxation and the initial deformation zone, and are also responsible for the observed viscoelastic behavior in glasses. The results provide insight into the plastic mechanism and the relaxations in metallic glasses.

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[1]W. Klement, R. H. Willens, and P. Duwez, Nature (London) **187**, 869 (1960).
[2]W. Dmowski, T. Iwashita, C. P. Chuang, J. Almer, and T. Egami, Phys. Rev. Lett. **105**, 205502 (2010).
[3]W. H. Wang, Prog. Mater. Sci. **57**, 487 (2012).
[4]M. L. Falk and J. S. Langer, Ann. Rev. Condens. Matter Phys. **2**, 353 (2011).
[5]Y. H. Liu, G. Wang, R. J. Wang, and W. H. Wang, Science **315**, 1385 (2007).
[6]H. Wagner, D. Bedorf, S. Küchemann, M. Schwabe, B. Zhang, W. Arnold, and K. Samwer, Nature Mater. **10**, 439 (2011).
[7]Y. H. Liu, D. Wang, K. Nakajima, W. Zhang, A. Hirata, T. Nishi, A. Inoue, and M. W. Chen, Phys. Rev. Lett. **106**, 125504 (2011).
[8]F. Spaepen, Acta Metall. Mater **25**, 407 (1977).
[9]A. S. Argon, Acta Metall. Mater **27**, 47 (1979).
[10]C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).
[11]M. L. Falk and J. S. Langer, Phys. Rev. E **57**, 7192 (1998).
[12]P. Guan, M. Chen, and T. Egami, Phys. Rev. Lett. **104**, 205701 (2010).
[13]J. C. Dyre, Rev. Mod. Phys. **78**, 953 (2006).
[14]J. C. Ye, J. Lu, C. T. Liu, Q. Wang, and Y. Yang, Nature Mater. **9**, 619 (2010).
[15]C. A. Schuh and A. C. Lund, Nature Mater. **2**, 449 (2003).
[16]F. Delogu, Phys. Rev. Lett. **100**, 255901 (2008).
[17]C. E. Packard, L. M. Witmer, and C. A. Schuh, Appl. Phys. Lett. **92**, 171911 (2008).
[18]A. B. El-Shabasya and J. J. Lewandowski, Scr. Mater. **62**, 481 (2010).
[19]P. Schall, D. A. Weitz, and F. Spaepen, Science **318**, 1895 (2007).
[20]C. Ke, M. L. Manning, P. J. Yunker, W. G. Ellenbroek, Z. Zexin, A. J. Liu, and A. G. Yodh, Phys. Rev. Lett. **107**, 108301 (2011).
[21]P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
[22]K. L. Ngai and M. Paluch, J. Chem. Phys. **120**, 857 (2004).
[23]W. B. Jiang, P. Cui, Q. P. Kong, and M. Winning, Phys. Rev. B **72**, 174118 (2005).
[24]W. L. Johnson and K. Samwer, Phys. Rev. Lett. **95**, 195501 (2005).
[25]H. B. Yu, W. H. Wang, H. Y. Bai, Y. Wu, and M. W. Chen, Phys. Rev. B **81**, 220201 (2010).
[26]J. M. Pelletier, D. V. Louzguine-Luzgin, S. Li, and A. Inoue, Acta Mater. **59**, 2797 (2011).
[27]T. Fujita, K. Konno, W. Zhang, V. Kumar, M. Matsuura, A. Inoue, T. Sakurai, and M. W. Chen, Phys. Rev. Lett. **103**, 075502 (2009).
[28]Z. F. Zhao, P. Wen, C. H. Shek, and W. H. Wang, Phys. Rev. B **75**, 174201 (2007).
[29]M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
[30]T. A. Read, Phys. Rev. **58**, 371 (1940).
[31]D. B. Miracle, T. Egami, K. M. Flores, and K. F. Kelton, MRS Bull. **32**, 629 (2007).
[32]A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, 1972).
[33]Y. Yang, J. F. Zeng, J. C. Ye, and J. Lu, Appl. Phys. Lett. **97**, 261905 (2010).
[34]H. B. Yu, X. Shen, Z. Wang, L. Gu, W. H. Wang, and H. Y. Bai, Phys. Rev. Lett. **108**, 015504 (2012).