Effect of physical aging on Johari-Goldstein relaxation in La-based bulk metallic glass

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The influence of physical aging on the β relaxation in $La_{60}Ni_{15}Al_{25}$ bulk metallic glass has been investigated by mechanical spectroscopy. The amplitude of the β relaxation ($\Delta G''$) decreases while its relaxation time (τ_β) increases during aging. We find that, as in organic glasses, the changes of $\ln(\tau_\beta)$ and $\ln(\Delta G_{max})$ are linearly correlated with $\ln(\tau_\beta) = b - a \ln(G''_{max})$. This behavior is discussed in term of the asymmetric double-well potential (ADWP) model, with U and Δ the energies characterizing the ADWP. It is suggested that during aging the ratio U/Δ remains approximately constant, with a value close to the coefficient describing the linear correlation between $\ln(\tau_\beta)$ and $\ln(G''_{max})$(U/$\Delta \sim a$). Moreover, the evolution *versus* aging time of ΔG_{max} can be described by a simple stretched exponential equation giving values of τ_{aging} consistent with $\tan(\delta)$ measurements during aging. The very similar behavior of the β relaxation during aging in metallic glasses and organic material strongly suggests a common nature for this relaxation. © *2014 AIP Publishing LLC.*
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Typically in dielectric and mechanical relaxation measurements in supercooled liquids and glassy materials are observed two relaxation processes: (i) the main (α) relaxation reflects the cooperative motion of atoms or molecules, characterized by non-Debye relaxation behavior and a non-Arrhenius temperature dependence.[1,2] The temperature dependence of the α relaxation for glassy materials is usually characterized by the Vogel-Fulcher-Tamman (VFT) equation, which can be expressed as[1,2]

$$\tau_\alpha = \tau_\infty^\alpha \exp\left(\frac{B}{T - T_0}\right), \quad (1)$$

where τ_∞^α is the relaxation time in the limit of high temperatures and T_0 is the Vogel temperature and B a parameter. The dynamic glass transition, T_g, is generally defined as $\tau_\alpha(T_g)$ = 100 s. (ii) The secondary relaxation (β relaxation, sometime resolved as a "shoulder" or excess wing[3]) usually has a smaller strength and it is detected below the glass transition temperature, where it displays an Arrhenius temperature dependence,[1,2]

$$\tau_\beta = \tau_\infty^\beta \exp\left(\frac{U_\beta}{kT}\right), \quad (2)$$

where τ_∞^β is the high temperature limit of τ_β, U_β is the activation energy, and k is the Boltzmann constant. The secondary relaxation is linked to the local motion of atoms or molecules in amorphous materials and is generally accepted to have a non-cooperative nature,[4–7] although recent results present an alternative viewpoint.[8,9] Many investigations indicate that α- and β-relaxations are both intrinsic phenomena of

glass forming materials.[2,4] This ubiquity has stimulated several experimental and theoretical efforts, interpreting the secondary relaxation as the precursor of the α relaxation in glass-forming liquids.[2,4,10,11] Strong correlation has been observed between the α- and the Johari-Goldstein (JG) β-relaxation above the glass transition temperature for several prototypical glass formers such as ortho-terphenyl, D-sorbitol, and cresolphthaleindimethylether.[12,13]

As a new-comer of the glassy family, metallic glasses (MGs) present fascinating mechanical properties as well as outstanding physical and chemical properties.[5] The relaxation behavior in the glassy state, i.e., the JG relaxation, is very important for understanding the glass transition, as well as the diffusion and mechanical properties in metallic glasses.[14] However, a relatively small number of investigations of the secondary relaxation in metallic glasses are present in the literature, addressing its dynamics[15,16] and physical origin.[17–19] Part of the reason for the limited number of investigations is that the main technique used for this investigation of MG are mechanical measurements since techniques more common for organic materials such as dielectric relaxation and light scattering cannot be used. However, previous comparisons of mechanical relaxation and dielectric have shown very similar behavior for the secondary relaxation in organic glasses.[20,21] In mechanical relaxation spectra, contrary to the case of amorphous polymers, most metallic glasses do not present a prominent JG relaxation peak, making the investigation of the JG in metallic glasses more challenging.[14] On the other hand, the microstructure of the metallic glasses is less complex than that of other glassy materials, with the absence of internal degrees of freedom. Thus, they are excellent candidates for the investigation of dynamic relaxation. For glass forming materials, the relaxation behaviors strongly depend on the cooling rates, pressure, and physical aging.[2,22–27] In particular the JG

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relaxation can be used as a "probe" to investigate the physical aging.[25] In the case of metallic glasses, only a few investigations on the aging of metallic glasses have been reported.[28,29] We have shown that the intensity of JG relaxations for metallic glasses decreases during aging.[29] Additionally, physical aging causes a decrease of the local atomic mobility in metallic glasses.[30]

In this letter, we use mechanical spectroscopy to investigate the effect of physical aging on the JG β relaxation in $La_{60}Ni_{15}Al_{25}$ bulk metallic glass; this metallic glass has the advantage of showing a prominent JG relaxation. We find that the relaxation time and relaxation strength of the JG relaxation change during aging and that these changes are linearly correlated. We show how, similarly to their organic counterpart, the behavior of the JG relaxation during aging can be interpreted using the asymmetric double-well potential (ADWP) model.[31]

The preparation of the $La_{60}Ni_{15}Al_{25}$ bulk metallic glass was described in previous literature.[16] Dynamic mechanical measurements were carried out in an inverted torsion mode using a mechanical spectrometer described by Etienne *et al.*[32] Mechanical spectroscopy experiments were carried out in a high vacuum atmosphere with the dimension of 30 mm in length × 2 mm in width × 1 mm in thickness. Mechanical measurements were performed at the measurement temperature in the frequency ranges from 10^{-2} to 2 Hz. In all the experiments the strain amplitude was lower than 10^{-4}.

The temperature behaviors of τ_α and τ_β processes obtained using this apparatus are reported in Figure 1. Additional mechanical measurements to investigate the α process in the vicinity of the glass transition were done using a torsion fixture in a Anton Parr rheometer (MCR502) measuring down to 4 × 10^{-4} Hz, in this case the sample was slowly heated from the glassy state.
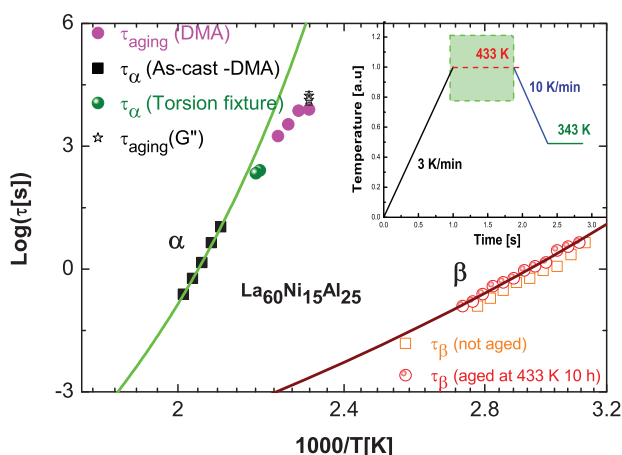

FIG. 2. Time dependence of the loss factor tanδ of $La_{60}Ni_{15}Al_{25}$ bulk metallic glass at different temperatures 433, 438, 443, and 448 K, respectively. The metallic glasses were heated to the aging temperature at a heating rate 3 K/min (frequency: 0.3 Hz) and then held isothermally in this aging temperature. Solid lines are the best fits with Eq. (3).

To characterize the aging dynamics, aging experiments were carried out measuring the time dependence of the loss factor tanδ (at fixed frequency equal to 0.3 Hz). Figure 2 show tanδ (0.3Hz) of $La_{60}Ni_{15}Al_{25}$ bulk metallic glass at four temperatures below T_g, following a rapid cooling from equilibrium. As expected the evolution from a non-equilibrium state to equilibrium is faster at higher aging temperature. The kinetics of the physical aging in amorphous materials during aging can be described using the stretched exponential [or Kohlrausch-Williams-Watts (KWW)] relaxation function. The following equation has been introduced to analyze the isothermal aging process in amorphous materials:[29,33,34]

$$\tan\delta(t_a) - \tan\delta(t_a=0) = A\{1 - \exp[-(t_a/\tau_{aging})^{\beta_{aging}}]\},$$
(3)

where A is the maximum magnitude of the dynamic mechanical relaxation and $A = \tan\delta(t_a \to \infty) - \tan\delta(t_a=0)$, τ_{aging} is the aging time, β_{aging} is the Kohlrausch exponent. The best fit of Eq. (3) to the data is shown in Figure 2 (solid line). In the fit β_{aging} was fixed as 0.56 (same value of β_{KWW} in fit to isothermal spectra of the α relaxation) to minimize the error on τ_{aging}. This can be justified by the weak temperature dependence of β_{KWW}, but this assumption is not critical since a simultaneous fit of the data in Fig. 2 with β_{aging} a variable gave smaller values of $\beta_{aging} \sim 0.48$ and τ_{aging} values with a difference smaller than the size of the symbols (i.e., log(τ_{aging}) change smaller the 3%). The τ_{aging} values are reported in the relaxation plot in Figure 1. τ_{aging} appears as a continuation of the $\tau_\alpha(T)$ behavior, as observed for amorphous polyvinylethylene (PVE).[25] There is greater deviation from the VFT behavior deeper in the glassy state.

The β process is in the accessible frequency range of our measurements only at temperatures much lower than T_g, where τ_{aging} is too long to observe any change in the β relaxation spectra. To measure the effect of aging on the β process it was therefore necessary to use a protocol where aging

FIG. 1. The relaxation map of $La_{60}Ni_{15}Al_{25}$ bulk metallic glass. The τ_β was obtained from a fit to the isothermal spectra for a sample not aged and for a sample aged for 10 h at 433 K. The best fit of τ_β with Eq. (2) gives $U_\beta = 0.83 \pm 0.03$ eV, log(τ_∞^β)= 12.5 ± 0.5 before aging and $U_\beta = 0.84 \pm 0.02$ eV, (log τ_∞^β) = 12.4 ± 0.4 after aging for 10 h. The green solid line is the best fit to the log(τ_α) data above the glass transition with the VFT equation (Eq. (1)), the best fit parameters were log(τ_∞^α) = 12(fixed), $B = -4100 \pm 120$ K, $T_0 = 340 \pm 5$ K. Inset is the schematic illustration of aging on the β process.
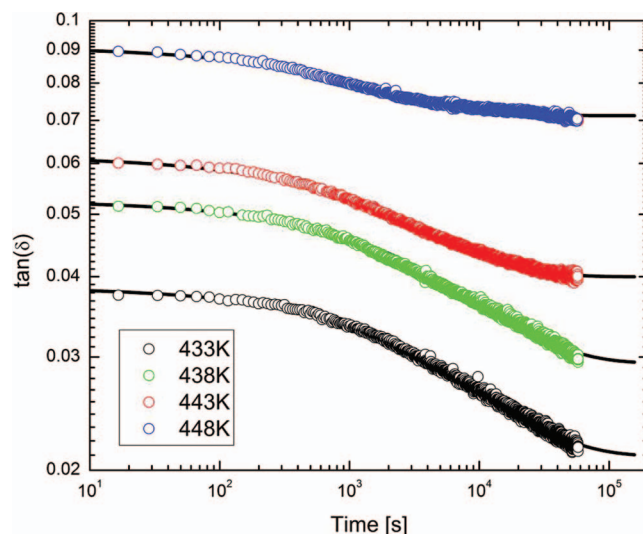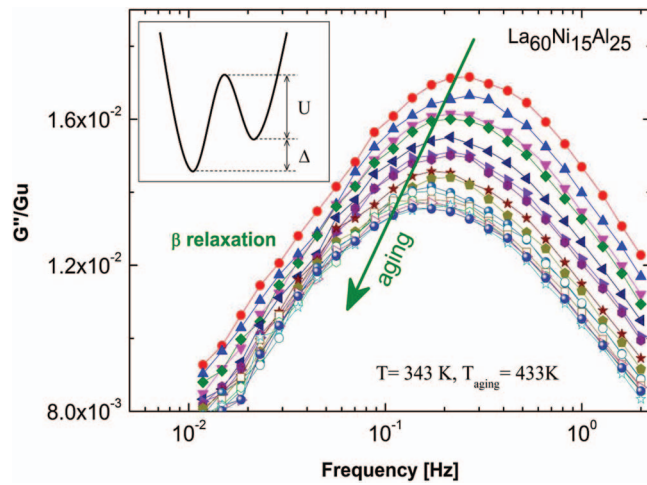
FIG. 3. Mechanical loss spectra of JG β relaxation in $La_{60}Ni_{15}Al_{25}$ bulk metallic glass aged at 433 K for 5, 10, 20, 40, 80, 160, 320, 640, 1280, 2240, 2880, 3840, 4800, 5280, 6250, 7480 min, respectively (the measurement temperature was 343 K). G_u corresponds to the unrelaxed modulus, which is assumed to be equal to storage modulus G' at room temperature. Inset: Schematic of ADWP model.

FIG. 4. Main figure: $\ln(\underline{\tau_\beta})$ vs $\ln(G''_{max}/G_U)$ for $La_{60}Ni_{15}Al_{25}$ metallic glass aged at $T = 433$ K and measured at 343 K, the solid line is the best fit with a linear function with slope $-a = -1.7 \pm 0.1$. Lower inset: G''_{max}/G_U versus time aging for the same metallic glass, the solid line is the best fit using a stretched exponential behavior as Eq. (3) with $\beta_{KWW} = 0.56$ (fixed) and $\tau_{aging} = 18 \pm 4 \times 10^3$ s. Upper inset: $\ln(\underline{\tau_\beta})$ vs aging time for the same metallic glass.

periods at an aging temperature close to T_g were followed by measurements at a temperature much lower than T_g (see inset to Fig. 1). The measuring temperature being much lower than T_g the aging during the measurements was neglected. During this aging protocol the samples were heated to the aging temperature at a constant heating rate of 3 K/min and held at the aging temperature for different aging periods, followed by cooling to the measurement temperature at a rate of 10 K/min. In our measurement of the aging effect on the JG relaxation, $La_{60}Ni_{15}Al_{25}$ metallic glass was aged at the $T = 433$ K, well below the glass transition temperature T_g (=461 K) for various time periods, and measured at 343 K.

Figure 3 shows the evolution of the JG relaxation spectra at different aging times. It is evident that the amplitude of the JG relaxation decreases with increasing aging time, while the peak maximum of the JG relaxation moves to lower frequency. Previous dielectric relaxation measurements of the JG relaxation during physical aging in polymers showed similar behavior.[25,35] But in that case the β relaxation peak shifted to higher frequency while decreasing in amplitude. But there are very few results (this is the first for MG) to say whether this is a general difference between organic and metallic glasses. Moreover, it is generally complicated to compare mechanical and dielectric data, in the former the intensity depends on the magnitude of the local strain induced by the reorientation of a particular molecule/atom, while the latter depends on its dielectric dipole.

From the time dependence of the peak maximum it is possible to measure τ_{aging}[25,35] which is in principle equivalent with the τ_{aging} determined from the tanδ measurement (Figure 2). Thus a comparison of the two values allows a check of the validity of our aging protocol. The τ_{aging} form the G'' vs aging time dependence at $T = 433$ K (best fit in lower inset to Figure 4) is reported in Figure 1, and it is in good agreement with that obtained from tanδ vs aging time, validating our aging protocol.
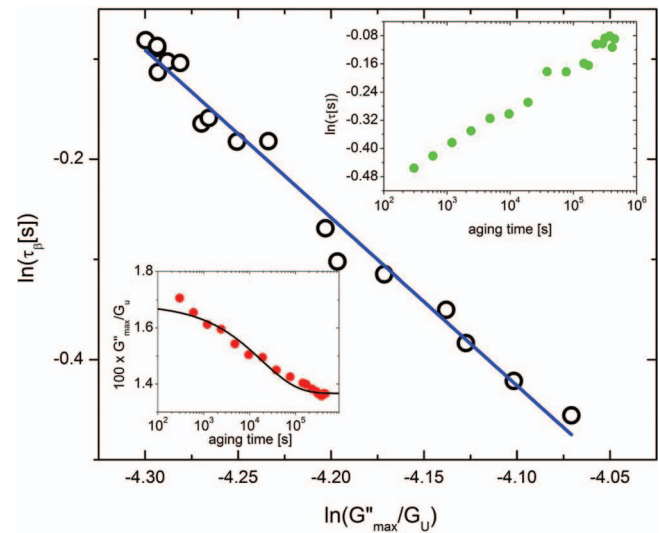
In Fig. 4, $\ln(\tau_\beta)$ versus $\ln(G''_{max})$ is shown during aging, the behavior is well described by a linear correlation (solid line). This is the first evidence of a linear correlation between $\ln(\tau_\beta)$ and $\ln(G''_{max})$ of a JG relaxation in a metallic glass. Interestingly an analogous correlation has been found for polymers[35] and small organic molecules.[36]

Dyre and Olsen found that for organic glass formers,[36] the correlation between the amplitude and relaxation time of the secondary relaxation with varying temperature, while in thermodynamic equilibrium, can be rationalized using the ADWP model. Here we show how the ADWP model can be used also to interpret the aging behavior of the beta relaxation in a metallic glass. According to the ADWP the relaxation time and maximum of the mechanical loss are given by[36]

$$\tau_\beta = \tau_0 \exp\left(\frac{2U + \Delta}{2k_B T}\right) \cosh^{-1}\left(\frac{\Delta}{2k_B T}\right),$$

$$G''_{max} = G''_0(T) \cosh^{-2}\left(\frac{\Delta}{2k_B T}\right),$$

(4)

τ_0 and G''_0 are prefactors, U and Δ are the free energies describing the ADWP model as shown in the inset to Figure 3.

Considering the linear correlation between $\ln(\tau_\beta)$ and $\ln(G''_{max})$ observed during aging, $\ln(\tau_\beta) = b - a\ln(G''_{max})$, and considering the prefactors independent of aging we obtain

$$\frac{2U + \Delta}{2kT} - \ln\left(\cosh\left(\frac{\Delta}{2kT}\right)\right) = 2a\ln\left(\cosh\left(\frac{\Delta}{2kT}\right)\right),$$

(5)

which in the approximation that $\Delta \gg 2kT$ reduces to

$$\frac{2U + \Delta}{2kT} - \frac{\Delta}{2kT} + \ln(2) = 2a\left(\frac{\Delta}{2kT} - \ln(2)\right),$$

(6)

from which follows

$$a = \frac{\frac{U}{kT} + \ln(2)}{\frac{\Delta}{kT} - 2\ln(2)}. \qquad (7)$$

For the same approximation that $\Delta \gg 2kT$, according to Eq. (4) $\tau_\beta(T)$ behavior is Arrhenius with activation energy U. Fitting the $\tau_\beta(T)$, we find $U = 0.84 \pm 0.02$ eV. Considering the best fit value $a = 1.7$, we then get from Eq. (7) $\Delta = 0.55$ eV. Thus, during aging the ratio U/Δ remains approximately constant (U/$\Delta \sim a$). We note that a value of the coefficient $a \sim 2$ was also found during other aging experiments for polymeric materials[35] and molecular dynamics simulations (MDS).[37] Analyzing the data reported by Dyre and Olsen[36] for the case of an organic glass former in thermodynamic equilibrium, we found a value of coefficient close to 2 as well; thus this behavior could potentially extend also in the liquid state.

Thus, the results herein show for the first time that the behavior of the JG relaxation during aging in a metallic glass is analogous to that observed in organic glass formers. This is consistent with the nature of the JG process in metallic glass being the same as in organic glass formers. This is remarkable since metallic glasses are very simple systems without internal degree of freedom (i.e., side chains or chemical groups with higher mobility) but yet have a JG process which is sensitive to the change of structure of the glass during physical aging like more complex systems with very different chemistry.

In conclusion, the effect of physical aging in the glass of the JG β relaxation in $La_{60}Ni_{15}Al_{25}$ bulk metallic glass was studied by mechanical spectroscopy. The amplitude of the JG relaxation decreases with aging while the relaxation time τ_β increases. Furthermore, our results show that the $\ln(\tau_\beta)$ and $\ln(\Delta G_{max})$ are linearly correlated. This behavior was analyzed in term of the ADWP model. Our results are consistent with the ratio U/Δ remaining approximately constant (U/$\Delta \sim a$) during aging. The behavior during aging is very similar to that observed in organic materials suggesting the common nature of this process and confirming that the nature of the JG process is not related to intramolecular degree of freedom.

[1] C. M. Roland, *Viscoelastic Behavior of Rubbery Materials* (Oxford, New York, 2011).

[2] K. L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer, New York, 2011).

[3] J. C. Qiao, J. M. Pelletier, and R. Casalini, "Main (α) relaxation and excess wing in $Zr_{50}Cu_{40}Al_{10}$ bulk metallic glass investigated by mechanical spectroscopy," J. Non-Cryst. Solids (in press).

[4] S. Capaccioli, M. Paluch, D. Prevosto, L. M. Wang, and K. L. Ngai, J. Phys. Chem. Lett. **3**, 735–743 (2012).

[5] W. H. Wang, Prog. Mater. Sci. **57**, 487–656 (2012).

[6] J. C. Qiao and J. M. Pelletier, J. Appl. Phys. **112**, 083528 (2012).

[7] G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[8] D. Bock, R. Kahlau, B. Micko, B. Pötzschner, G. J. Schneider, and E. A. Rössler, J. Chem. Phys. **139**, 064508 (2013).

[9] R. Kahlau, T. Dörfler, and E. A. Rössler, J. Chem. Phys. **139**, 134504 (2013).

[10] K. L. Ngai and S. Capaccioli, Phys. Rev. E **69**, 031501 (2004).

[11] K. L. Ngai, J. Chem. Phys. **109**, 6982–6994 (1998).

[12] R. Böhmer, G. Diezemann, B. Geil, G. Hinze, A. Nowaczyk, and M. Winterlich, Phys. Rev. Lett. **97**, 135701 (2006).

[13] A. Nowaczyk, B. Geil, G. Hinze, and R. Böhmer, Phys. Rev. E **74**, 041505 (2006).

[14] H. B. Yu, W. H. Wang, and K. Samwer, Mater. Today **16**, 183–191 (2013).

[15] H. B. Yu, W. H. Wang, H. Y. Bai, Y. Wu, and M. W. Chen, Phys. Rev. B **81**, 220201 (2010).

[16] Z. Wang, H. B. Yu, P. Wen, H. Y. Bai, and W. H. Wang, J. Phys.: Condens. Matter **23**, 142202 (2011).

[17] H. B. Yu, K. Samwer, Y. Wu, and W. H. Wang, Phys. Rev. Lett. **109**, 095508 (2012).

[18] Y. H. Liu, T. Fujita, D. P. B. Aji, M. Matsuura, and M. W. Chen, Nat. Commun. **5**, 3238 (2014).

[19] L. N. Hu and Y. Z. Yue, J. Phys. Chem. C **113**, 15001–15006 (2009).

[20] B. Jakobsen, K. Niss, C. Maggi, N. B. Olsen, T. Christensen, and J. C. Dyre, J. Non-Crystalline Solids **357**, 267–273 (2011).

[21] R. Casalini and C. M. Roland, Macromolecules **47**, 4087–4093 (2014).

[22] R. Casalini and C. M. Roland, Macromolecules **46**, 6364–6368 (2013).

[23] R. Casalini, D. Fragiadakis, and C. M. Roland, Macromolecules **44**, 6928–6934 (2011).

[24] S. P. Bhardwaj and R. Suryanarayanan, J. Phys. Chem. B **116**, 11728–11736 (2012).

[25] R. Casalini and C. M. Roland, Phys. Rev. Lett. **102**, 035701 (2009).

[26] P. Lunkenheimer, R. When, U. Schneider, and A. Loidi, Phys. Rev. Lett. **95**, 055702 (2005).

[27] R. Richert, P. Lunkenheimer, S. Kastner, and A. Loidl, J. Phys. Chem. B **117**, 12689–12694 (2013).

[28] J. C. Qiao, J. M. Pelletier, and R. Casalini, J. Phys. Chem. B **117**, 13658–13666 (2013).

[29] J. C. Qiao, R. Casalini, J. M. Pelletier, and H. Kato, J. Phys. Chem. B **118**, 3720–3730 (2014).

[30] J. C. Qiao, J. M. Pelletier, H. C. Kou, and X. Zhou, Intermetallics **28**, 128–137 (2012).

[31] K. S. Gilroy and W. A. Phillips, Philos. Mag. B **43**, 735–746 (1981).

[32] S. Etienne, J. Y. Cavaillé, J. Perez, R. Point, and M. Salvia, Rev. Sci. Instrum. **53**, 1261–1266 (1982).

[33] J. C. Qiao and J. M. Pelletier, Intermetallics **28**, 40–44 (2012).

[34] J. M. Pelletier, J. Non-Cryst. Solids **354**, 3666–3670 (2008).

[35] R. Casalini and C. M. Roland, J. Chem. Phys. **131**, 114501 (2009).

[36] J. C. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).

[37] D. Fragiadakis and C. M. Roland, Phys. Rev. E **88**, 042307 (2013).