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Correlations of the nonexponentiality and state dependence of mechanical relaxations with bond connectivity in Ge-As-Se supercooled liquids

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We have studied the mechanical responses of supercooled Ge-As-Se liquids to flexural strains and temperature steps. The departures from exponential relaxation correlate well with the variations in connectivity. The structural state dependence of the mechanical relaxation, detected in pure and weakly cross-linked Se, is suppressed completely at the rigidity percolation threshold $\langle r_c \rangle$, where the liquid fragility is a minimum. The shapes of the decay functions of samples with the same $\langle r_c \rangle$ but different compositions are not universal at T_g probably because of chemical effects near the binary edges of the ternary system.

By setting off the number of degrees of freedom in a covalently bonded network glass against the number of its bonding constraints, Phillips[1] predicted a threshold of mechanical stability at average coordination numbers of $\langle r_c \rangle = 2.4$. These considerations stimulated a number of ultrasonic experiments in binary[2-5] and ternary[6] chalcogenide systems. However, no evidence for anomalous elastic behavior at $\langle r_c \rangle$ could be obtained. Later on, Thorpe[7] recognized that the qualitative Phillips theory can be formulated rigorously as a problem of rigidity percolation. Several refined analytical and numerical calculations based on these topological ideas suggested that below $\langle r_c \rangle$ an increasing number of floppy modes should be detectable.[8] Experimental results from vibrational,[9] neutron,[10] and Mössbauer[11] spectroscopies seemed to confirm this prediction.

It was also shown that topological effects rather than chemical ones must be considered to explain the energetic relaxations among glassy configurations in Ge-As-Se chalcogenides as probed by infrared hole burning at cryogenic temperatures.[12] The relevance of the concept of connectivity has also been explored in the *liquid* state.[13,14] A recent study[14] of ternary chalcogenide alloys provided evidence for a correlation between the rigidity percolation, the strength of the entropy crisis near their glass transition, and the departure from Arrhenius behavior, i.e., the fragility. This raises the question of whether the other two key aspects of the vitrification process, viz., the relaxation following external perturbations and nonlinear effects found when relaxation occurs far from thermal equilibrium, also show systematic composition dependences in this model system.

There have been experimental[15,16] and theoretical[17] indications that fragile glass formers relax less exponentially than strong ones, i.e., those for which the mean relaxation times or viscosities follow simple Arrhenius laws in the whole range. On the other hand, there are several examples which seem in conflict with any such simple generalization.[18,19]

To obtain additional systematic data on this question, we have studied the time-dependent stress relaxation of $Ge_aAs_bSe_c$ glass formers. Our samples were taken from batches which had been prepared previously.[14] We specify their composition by the average coordination number $\langle r \rangle = 4a + 3b + 2c$ and the fraction $y = a/(a+b)$. Practically all measurements were taken on bar samples cut to identical sizes ($1 \times 1 \times 5$ mm^3).[20] The tensile stress relaxation was recorded automatically[21] in the flexural conformation. Since the relaxation time for a supercooled liquid usually depends on its fictive[22] as well as the actual temperature, we have repeated the runs after various equilibration times both to ensure equilibration is reached and to acquire data on this structural relaxation phenomenon.

Figure 1 shows typical results for an equilibrated $Ge_{10}As_{10}Se_{80}$ sample ($\langle r \rangle = 2.3$, $y = 0.5$) in its glass transformation range. With increasing temperature T, the stress relaxation curves shift to smaller times and their maximum steepness increases; i.e., the mechanical relaxa-

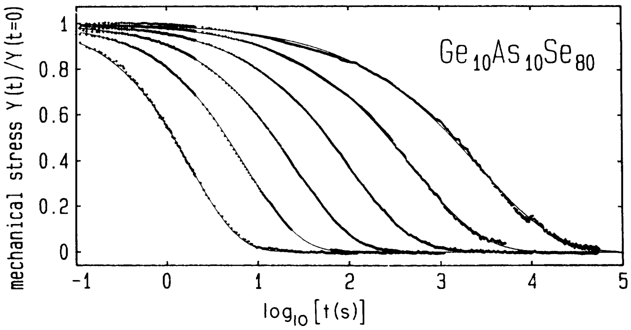

FIG. 1. Stress relaxation $Y(t)/Y(t=0)$ for Ge_{10} $As_{10}Se_{80}$ ($\langle r \rangle = 2.3$, $y = 0.5$) recorded at the temperatures (from left to right) 433.4, 422.6, 413.3, 403.7, 394.5, and 385.3 K. The lines are fits using Eq. (1), and the parameters displayed in Figs. 2 and 3.

tion is the closer to exponential the higher T is. Similar data was obtained for six other compositions at constant $y \approx 0.5$ and for two at $\langle r \rangle = 2.4$ but $y \neq 0.5$. A good quantitative description of these data was achieved using the stretched-exponential function[23]

$$Y(t) = Y(t=0)\exp[-(t/\tau)^{\beta}] \ . \qquad (1)$$

Here β characterizes the broadening and $\langle \tau \rangle_Y = \tau\Gamma(1+1/\beta)$ the average relaxation time of the tensile stress autocorrelation function. Although other fitting procedures are usually also applicable to this type of relaxation function,[24,25] Fig. 1 shows that a three-parameter expression is sufficient to provide an excellent fit to our data. High quality fits with Eq. (1) were obtained for all viscoelastic decay functions of the samples with $\langle r \rangle > 2.1$, i.e., except for pure and weakly cross-linked amorphous selenium (a-Se) where additional short-time processes show up.[26] However, for these compounds the slower relaxations could be parametrized satisfactorily using Eq. (1).

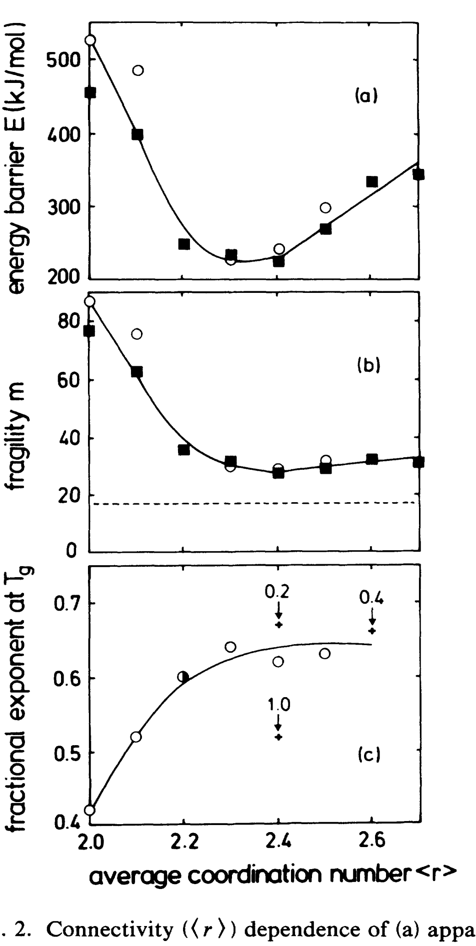

FIG. 2. Connectivity ($\langle r \rangle$) dependence of (a) apparent energy barriers E, (b) fragilities m, and (c) fractional exponents β as determined at the glass transition temperatures T_g. The squares represent results from measurements of the viscosity on samples with $y = 0.5$ (taken from Ref. 14). The present stress relaxation experiments yielded data on alloys with $y = 0.5$ (circles) and off that pseudobinary cut with y given near the plusses. The fractional exponent at $\langle r \rangle = 2.2$ was extrapolated (Ref. 20) from a measurement of a thicker ($2.5 \times 2.5 \times 5$ mm^3) sample. The dashed line indicates the minimum fragility. The solid lines are guides to the eye only.

The temperature dependences of $\langle \tau \rangle_Y$ from all our samples within experimental uncertainty were found to comply with the Arrhenius law $\langle \tau \rangle_Y = \tau_0 \exp(E/RT)$, but with unphysical τ_0. In Fig. 2(a) the connectivity dependence of the apparent energy barriers E_Y from these fits is shown together with that determined from viscosity measurements[14] (E_η) on the same samples. Near $\langle r \rangle = 2.4$ a well-defined minimum shows up for both sets of results. For $\langle r \rangle \leq 2.1$ the activation energies E_Y (for the slow processes) are substantially higher than E_η. We note, however, that for a-Se the energy barrier of the short-time process within experimental error agrees with E_η,[14] raising the possibility that the "constant-velocity" condition used in the viscosity determination may have been located in the initial relaxation regime. The Arrhenius law when plotted as $\log_{10}\langle \tau \rangle$ versus T_g/T and with $T_g = T(\langle \tau \rangle = \tau_g)$ exhibits a slope

$$\begin{aligned} m &= d \log_{10}\langle \tau \rangle / d(T_g/T) \\ &= E/[\ln(10)RT_g] = \log_{10}(\tau_g/\tau_0) \ . \end{aligned} \qquad (2)$$

The latter equality is simply a rewriting of the Arrhenius law for $T = T_g$. The quantity m has been called variously the "fragility"[27] and more recently the "steepness index."[17]

In calorimetric experiments T_g is usually determined by heating or cooling the specimens with rates of 10 K/min, thereby defining the relaxation time $\tau_{g,\text{cal}}$ to be 200 s.[22] By adopting this convention for τ_g, we have calculated the slopes m for the various $\langle r \rangle$ numbers from the present data and plotted them in Fig. 2(b). This plot demonstrates that the fragility of the Se-rich alloys decreases with increasing cross-linking. The minimum of m at $\langle r_c \rangle = 2.4$ is very shallow, however, and the increase of this figure is very slight at large $\langle r \rangle$. This is because, beyond the rigidity percolation threshold $\langle r_c \rangle$, the increase in the apparent activation energies is compensated by increases in T_g.[14] Note that the minimum value m can reasonably have with the above definition of τ_g is when τ_0 is the inverse of a vibration frequency, whence $m \approx 16$.

Several samples with $\langle r \rangle = 2.4$ but different compositions ($y = 0.2$, 0.5, and 1.0) were investigated. For these, $m = 29 \pm 2$ was found to be constant. From the viscosity data of Ref. 14 for As_2Se_3 $\langle r \rangle = 2.4$, $y = 0$), a larger slope ($m = 37$) was calculated. This higher fragility, which is also reflected by a relative large calorimetric anomaly at T_g, is probably due to nonrandom bonding distributions in this compound.[14]

In Fig. 2(c) we present the variations of β with $\langle r \rangle$ as determined at T_g. The relaxation of a-Se is the most nonexponential ($\beta = 0.42$). With increasing cross-linking, β assumes larger values and for $\langle r \rangle \geq 2.3$ is roughly constant at 0.63. By comparing Figs. 2(b) and 2(c), it is clear that the increase in the fragility m is accompanied by a decrease in nonexponentiality. Figure 2(c) also shows that $\beta(T_g)$ for several compositions at a constant

$\langle r \rangle = 2.4$ is not universal. Chemical effects probably play an important role for compositions close to the binary As-Se and Ge-Se edges, i.e., for samples with $y \approx 0$ (as discussed above[28]) and $y = 1$. Several authors have pointed out that a nanoscale (50 Å) phase separation (into Se chains and $GeSe_2$ "outrigger rafts") may take place in the germanium-selenium system at $\langle r \rangle = 2.4$.[9,29]

In Fig. 3 we have plotted the scaled exponents $\beta(T)/\beta(T_g)$ versus T/T_g for samples with constant $y = 0.5$ [Fig. 3(a)] and $\langle r \rangle = 2.4$ [Fig. 3(b)]. Although thermorheological simplicity [$\beta(T) =$ const] is an often used assumption, a T dependence of β is usually expected since in the low-viscosity liquid state the relaxation should be close to exponential. On the other hand, it has been shown for the entropy relaxation of several organic liquids[16,30] that $\beta(T)$ extrapolates to zero at temperatures T_0, at which $\tau(T)$ asymptotically diverges. The ratio of T_g to the Vogel-Fulcher temperature T_0 decreases with increasing fragility according to [Eq. (8) in Ref. 26]

$$T_g/T_0 = (1 - 16/m)^{-1} . \tag{3}$$

Hence, for the strong glass formers, the degree of nonexponentiality should not be very (if at all) T dependent. Similar conclusions have been drawn more rigorously by Ngai, Rendell, and Plazek, who used arguments based on the Adam-Gibbs equation and a coupling scheme.[31] Consistent with these ideas, we find that the fractional exponent of our strongest case, $Ge_{15}As_{15}Se_{70}$ (with $\langle r \rangle = 2.4$ and $y = 0.5$), exhibits the weakest T dependence as compared with other samples along both the $\langle r \rangle = 2.4$ and $y = 0.5$ pseudobinary cuts (see Fig. 3).

By extrapolating the β values of Fig. 3 linearly (on T or $1/T$ scales) to smaller values, we have determined that the temperatures $T_{\beta \to 0}$ are roughly 1.5 times larger than the T_0's as calculated from the data given in Fig. 2 using Eqs. (2) and (3). We suspect that this lack of coincidence of T_0 and $T_{\beta \to 0}$ is at least partly due to the fact that any T dependence of β as determined from the tensile mechanical response near T_g will appear to be more pronounced than those obtained from measurements of the (simpler and possibly more fundamental) shear relaxations.[26]

The results presented so far have been taken on structurally equilibrated samples. We now discuss the evolution of the average *nonequilibrium* stress relaxation times $\langle \tau_n \rangle_Y$ recorded during the isothermal stabilization of freshly quenched samples with $\langle r \rangle = 2.1$ and 2.4. For the latter sample, no change of $\langle \tau_n \rangle_Y$ could be detected while annealing at $T_a = 426$ K ($\log_{10}[\langle \tau(T_a) \rangle] = 3.55$) for more than 15 h (not shown[32]). Note that in these experiments it is not possible to record the structural relaxation which occurs before the stabilization of the final temperature (about 15 min) is complete. The absence of changes during the annealing of the strong $\langle r \rangle = 2.4$ liquid is compatible with its weak calorimetric anomaly at T_g.[14] In the fragile $\langle r \rangle = 2.1$ sample, large changes in $\langle \tau_n \rangle_Y$ were observed. However, in contrast to the $\langle r \rangle = 2.0$ case,[26] the structural equilibration, surprisingly, now proceeds faster than the relaxation following a bending strain.

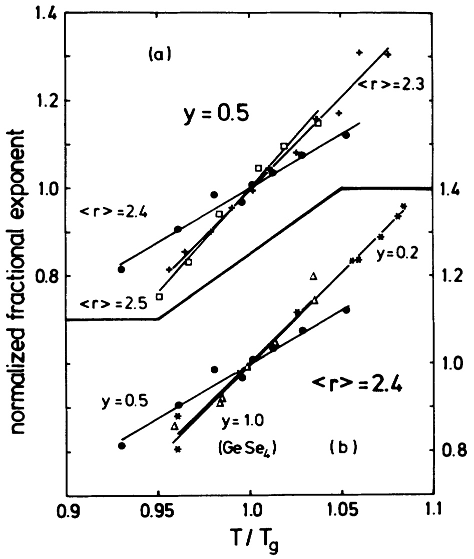

FIG. 3. Scaled Kohlrausch exponents $\beta(T)/\beta(T_g)$ vs scaled temperatures T/T_g for constant (a) y (=0.5) and (b) $\langle r \rangle$ (= 2.4). The straight lines represent linear least-squares fits.

To summarize, we have shown that Ge-As-Se compositions with low connectivity, typical of fragile liquids, show very nonexponential and state-dependent mechanical stress relaxations. Conversely, at the rigidity percolation threshold $\langle r_c \rangle$, the nonexponentiality is small and also weakly temperature dependent, and a state dependence cannot be detected. In overconstrained conditions the temperature dependence of β, like the larger excess heat capacity,[14] returns. However, at $\langle r_c \rangle$, β is not solely determined by $\langle r \rangle$, probably because bonding is nonrandom for high, or low, Ge/Se ratios.

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[1] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1979).

[2] K. S. Gilroy and W. A. Phillips, Philos. Mag. B **47**, 655 (1983).

[3] J. Y. Duquesne and G. Bellessa, Europhys. Lett. **9**, 453 (1989).

[4] S. S. Yun *et al.*, Phys. Rev. B **39**, 8702 (1989).

[5] S. Etienne, J. Perez, S. Peytavin, and M. Ribes, J. Solid State Chem. **92**, 27 (1991).

[6] B. L. Halfpap and S. M. Lindsay, Phys. Rev. Lett. **57**, 847 (1986).

[7] M. F. Thorpe, J. Non-Cryst. Solids **57**, 355 (1983).

[8] J. C. Phillips and M. F. Thorpe, Solid State Commun. **53**, 699

(1985); H. He and M. F. Thorpe, Phys. Rev. Lett. **54**, 2107 (1985).

[9] For a review, see J. C. Phillips, Phys. Rev. B **31**, 8157 (1985).

[10] P. Boolchand *et al.*, Solid State Ionics **39**, 81 (1990); W. A. Kamitakahara *et al.*, Phys. Rev. B **44**, 94 (1991); for pure Se, see W. A. Phillips *et al.*, Phys. Rev. Lett. **63**, 2381 (1989).

[11] W. Bresser, P. Boolchand, and P. Suranyi, Phys. Rev. Lett. **56**, 2493 (1986).

[12] S. P. Love *et al.*, Phys. Rev. Lett. **65**, 1792 (1990).

[13] Y. Tsuchiya, J. Non-Cryst. Solids **122**, 205 (1990).

[14] M. Tatsumisago *et al.*, Phys. Rev. Lett. **64**, 1549 (1990).

[15] C. A. Angell, in *Relaxations in Complex Systems,* edited by K. L. Ngai and G. B. Wright (Naval Research Laboratory, Washington, D.C., 1984), pp. 3–11.

[16] P. K. Dixon and S. R. Nagel, Phys. Rev. Lett. **61**, 341 (1988).

[17] D. J. Plazek and K. L. Ngai, Macromolecules **24**, 1222 (1991).

[18] K. L. Ngai, J. Non-Cryst. Solids **95&96**, 969 (1987).

[19] L. M. Torrell, L. Börjesson, and M. Elmroth, J. Phys. **2**, SA207 (1990).

[20] From one glass ingot, four samples were cut with identical lengths, but with cross sections varying by factors of up to 14. As a preliminary result, we find at a given T that $Y(t)$ in the thicker samples was slower and more exponential. Detailed investigations of this sample-size effect are currently underway. Unusual geometry effects in bending experiments have also been found by E. Suhir and C. R. Kurkjian (unpublished).

[21] R. Böhmer, H. Senapati, and C. A. Angell, J. Non-Cryst. Solids **131-133**, 182 (1991).

[22] C. T. Moynihan *et al.*, Ann. N.Y. Acad. Sci. **276**, 15 (1976).

[23] F. Kohlrausch, Pogg. Ann. Phys. **199**, 337 (1863).

[24] R. V. Chamberlin and D. N. Haines, Phys. Rev. Lett. **65**, 2197 (1990).

[25] S. M. Rekhson, in *Glass Science and Technology,* edited by D. R. Uhlmann and N. J. Kreidl (Academic, Orlando, FL, 1986), Vol. 3, Chap. 1.

[26] R. Böhmer and C. A. Angell, Phys. Rev. B (to be published).

[27] M. Tatsumisago and C. A. Angell (unpublished).

[28] Because of the larger fragility of As_2Se_3, one would probably have expected a smaller β for samples close to this composition. We note, however, that β from the enthalpy relaxation of As_2Se_3 is 0.67 (Ref. 22). This is another example of the danger of generalizations concerning the relation of β and fragility.

[29] A. Feltz, H. Aust, and A. Blayer, J. Non-Cryst. Solids **55**, 179 (1983).

[30] M. Oguni, H. Hikawa, and H. Suga, Thermochim. Acta **158**, 143 (1990); P. K. Dixon, Phys. Rev. B **42**, 8179 (1990).

[31] K. L. Ngai, R. W. Rendell, and D. J. Plazek, J. Chem. Phys. **94**, 3018 (1991).

[32] A more detailed account of the annealing experiments is given in: R. Böhmer and C. A. Angell, in Proceedings of the Sixth European Conference on Internal Friction and Ultrasonic Attenuation in Solids, edited by L. B. Magalas (Trans. Tech, Aedermannsdorf/Switzerland, 1992), in press.