

## Light-Induced Giant Softening of Network Glasses Observed near the Mean-Field Rigidity Transition

J. Gump, I. Finkler, H. Xia, and R. Sooryakumar

*Department of Physics, The Ohio State University, Columbus, Ohio 43210, USA*

W. J. Bresser and P. Boolchand

*Department of Electrical, Computer Engineering and Computer Science, University of Cincinnati, Cincinnati, Ohio 45221-0030, USA*

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The longitudinal acoustic (LA) mode of bulk  $\text{Ge}_x\text{Se}_{1-x}$  glasses is examined in Brillouin scattering (BS) over the  $0.15 < x < 1/3$  range using near band-gap radiation ( $\lambda = 647.1$  nm). The LA-mode frequency ( $\nu_{\text{LA}}$ ) softens with increasing laser power in an athermal and reversible manner by nearly 30% ( $=\Delta\nu_{\text{LA}}/\nu_{\text{LA}}$ ) near  $x = x_c = 0.19(1)$  or mean coordination number,  $r_c = 2 + 2x_c = 2.38(2)$ , close to the mean-field rigidity percolation transition ( $r_t = 2.40$ ). BS is a bulk probe of elasticity, and photsoftening is maximized here when network stress is minimized near the elastic phase transition.

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Light induced effects in chalcogenide glasses and thin films have displayed a richness of phenomenology that has attracted widespread interest [1–12] for over two decades. Some of these effects include photodarkening [2], photofluidity [3], giant photodensification [4], photochemical dissolution [5], anisotropic optomechanical response [6], photocrystallization [7], and phase change [8]. These effects have stimulated device applications, some of which have become the cornerstone of matured information storage technologies including phase change [9]—and programmable metallization cell [10]—memories and digital video disks [11].

At a basic level, two generic themes have evolved to explain the richness of these phenomena: one has emphasized aspects of local structure and the other aspects of global structure. In the former, the common theme [12] is that illumination of semiconducting glasses with near band-gap radiation produces electron-hole pairs that can produce metastable local defect configurations (such as under- and over-coordinated atoms in the neutral and charged states) in chalcogen-bearing systems. These defects localize in band tail states and alter the fundamental optical gap. With increased illumination, the concentration of defects can approach 1% of the atoms in a network. These defects can also serve to mediate rapid switching [1] of normal covalent bonds leading to atomic displacements, and in a natural way to photodiffusion [13], leading to global structural changes. Light-induced effects thus lead to a loss of medium-range structure, including photodiffusion in its early stages and photofluidity eventually.

Global structures in network glasses are characterized by their connectedness or mean coordination number  $r$  and have been classified based on their elastic response [14–17] into *floppy*, *intermediate*, and *stressed rigid phases*. Much less attention has been paid to whether

elastic response of a base glass plays a role, if any, on the way light interacts with it. In this context, it is noteworthy that photocontraction effects [4] on obliquely deposited (porous) amorphous chalcogenide thin films are optimized ( $\Delta t/t \sim 25\%$ ) in the stress-free intermediate phase, but decrease by an order of magnitude ( $\Delta t/t \sim 5\%$ ) in the stress-prone floppy and stressed-rigid phases. Photodarkening [18] in bulk Ge-Se glasses also displays a parallel behavior, suggesting that perhaps the interaction of light with a disordered network may intrinsically depend on its global connectedness or elasticity.

We have now examined bulk  $\text{Ge}_x\text{Se}_{1-x}$  glasses in Brillouin scattering (BS) using near band-gap radiation and in this Letter report evidence of a pronounced light-induced softening of the LA mode near the glass composition  $x = x_c = 0.19(1)$  or  $r_c = 2.38(2)$ . The softening is found to be *athermal* and *reversible* in nature at illumination power,  $P_r < 6$  mW. Light-induced softening of the LA mode decreases at  $x > 0.21$ , or at  $x < 0.18$ , but it is optimized close to the mean-field rigidity percolation transition of  $r_t = 2.40$ . BS is a bulk probe of elasticity with a length scale that is set by the wavelength (110 nm) of the LA mode in the glasses. Mode softening is optimized near the rigidity transition as global network stress minimizes at this ideal connectivity. These new results underscore the close connection between light-induced effects and rigidity transitions in disordered networks.

The BS measurements were performed in backscattering with a tandem six-pass Fabry-Perot interferometer [19] using a 647.1 nm laser beam focused to a 50  $\mu\text{m}$  spot size. The free spectral range and resolution were 35 and 0.1 GHz, respectively. At this excitation energy, glasses are quasitransparent, and bulk (instead of surface) properties are measured. Spectra of  $\text{Ge}_x\text{Se}_{1-x}$  glasses were examined as a function of composition in the

$0.15 < x < 1/3$  range and taken as a function of exciting laser power ( $1 \text{ mW} < P_r < 6 \text{ mW}$ ). Gaussian line shape analysis was carried out to fit both Stokes and anti-Stokes modes to extract the peak centroids and widths. Temperature increase due to laser heating was estimated through Raman Stokes/anti-Stokes measurements over a range of  $(x, P_r)$  values in a geometry similar to the one used in the BS experiments. Furthermore,  $T$ -dependent BS were undertaken to establish the thermal component of the LA-mode shift at various  $x$ . Glass samples used in the present work were characterized earlier [20,21] in Raman scattering and temperature modulated differential scanning calorimetry (MDSC) measurements, and compositional trends in glass transition temperatures  $T_g(x)$  and the nonreversing heat enthalpy at  $T_g$ ,  $\Delta H_{nr}(x)$ , were measured.

Figure 1 displays Brillouin line shapes observed at several glass compositions, all recorded at a probe power of  $P_r = 2 \text{ mW}$ . Here one observes the LA-mode frequency,  $\nu_{LA}(x)$ , to systematically blueshift with increasing  $x$ . Figure 2 shows Brillouin line shapes for a glass sample at  $x = 0.22$ , this time studied as a function of probe laser power ( $P_r$ ). These spectra reveal the LA-mode frequency ( $\nu_{LA}$ ) to redshift and the mode width ( $\Gamma_{LA}$ ) to concomitantly broaden as  $P_r$  increases to  $6 \text{ mW}$ . Furthermore, upon decreasing the power  $P_r$  to its starting value of  $2 \text{ mW}$ , one recovers the original line shape ( $\nu_{LA}, \Gamma_{LA}$ ), underscoring that changes in the observed Brillouin line shape are reversible. The nonreversing heat-flow term  $\Delta H_{nr}(x)$  deduced from the MDSC results [20,21] is included in Fig. 3(c).

Some part of the observed mode softening is of a thermal nature. This component was established in BS

on samples heated in the  $25^\circ\text{C} < T < T_g + 25^\circ\text{C}$  range. In general,  $\nu_{LA}(T)$  is found to soften as  $T$  approaches  $T_g$  and when  $x$  is less than 0.18. Typical temperature increases due to laser heating were in the  $50^\circ\text{C}$  range in our setup. For example, at  $x = 0.20$ , a temperature rise of  $57^\circ\text{C}$  was observed for the highest laser power ( $P_r = 6 \text{ mW}$ ), yielding a thermal contribution to LA-mode softening of  $0.5 \text{ GHz}$ , which represents about 10% of the observed softening of  $6 \text{ GHz}$  at this composition. The thermal changes in density and refractive index are already included in the temperature dependence of  $\nu_{LA}$  and they clearly play an insignificant role. Thermal corrections to the observed shifts were made at each glass composition, and Figs. 3(a) and 3(b) display only the light-induced softening to  $\nu_{LA}$  and broadening to  $\Gamma_{LA}$ , respectively. The central result of the present work is the giant, reversible, photoinduced softening and broadening of the LA mode localized near the glass composition  $x_c = 0.19(1)$ .

Our interpretation of the BS results is that at low probe power ( $P_r = 2 \text{ mW}$ ) the observed  $\nu_{LA}(x)$  increase with  $x$  reflects the intrinsic variation (Fig. 4) of the longitudinal bulk elastic constant  $C_{11}(x)$  of the glasses. We use the relation

$$C_{11} = [\{\rho(x)\lambda^2\nu_{LA}^2\}/(4n(x)^2)] \quad (1)$$

to obtain the elastic constant, where  $\lambda$  is taken as  $647.1 \text{ nm}$ ,  $n(x)$  represents the refractive index [22], and  $\rho(x)$  is the specific gravity of  $\text{Ge}_x\text{Se}_{1-x}$  glasses [23]. The low power ( $P_r = 2 \text{ mW}$ ) BS deduced  $C_{11}(x)$  results are in quantitative accord with those reported in ultrasonic

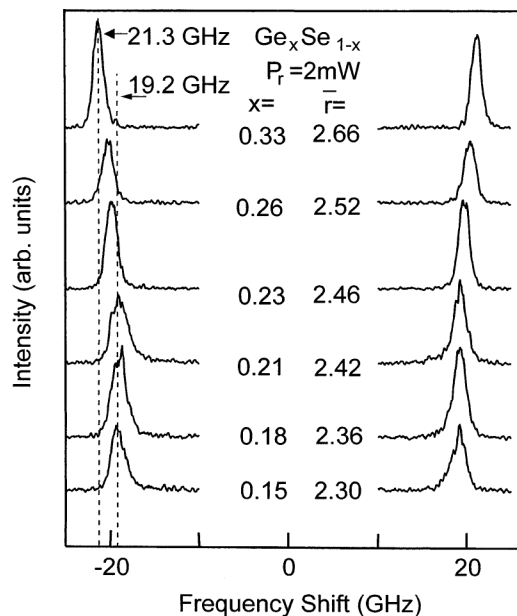


FIG. 1. Brillouin line shapes in  $\text{Ge}_x\text{Se}_{1-x}$  glasses, showing a blueshift of the LA mode with increasing  $x$ .

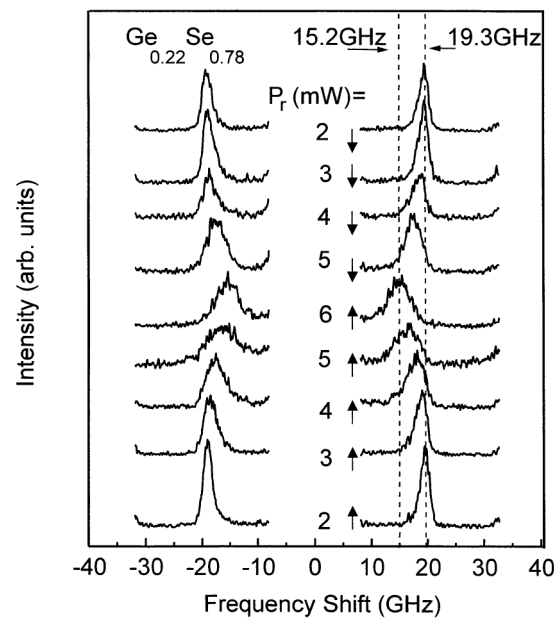


FIG. 2. Observed Brillouin line shapes in  $\text{Ge}_{0.22}\text{Se}_{0.78}$  glass as a function of laser power  $P_r$ , showing reversibility of LA mode softening.

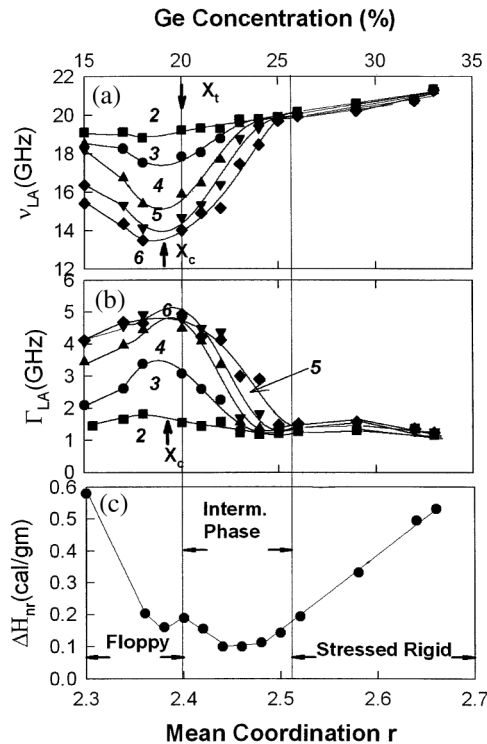


FIG. 3. Brillouin scattering in  $\text{Ge}_x\text{Se}_{1-x}$  glasses, showing compositional trends in the light-induced changes in (a) LA mode frequency  $\nu_{\text{LA}}$  and (b) mode width  $\Gamma_{\text{LA}}$ . The number appearing with each curve gives the laser power  $P_r$  used. (c) Nonreversing heat flow  $\Delta H_{\text{nr}}(x)$  from MDSC (Ref. [20]). Solid lines are guides to the eyes.

measurements [24]. Both BS and ultrasonic moduli are bulk probes of elastic response, and smearing of the rigidity transition near  $x_c = 0.19$  even at a low probe power ( $P_r = 2$  mW) in glasses is a natural consequence of the macroscopic nature of the probes, as recognized earlier [24].

On the other hand, light-induced softening of the LA mode with illumination power ( $P_r$ ) reveals the mean field rigidity transition near  $r = 2.4$  in a rather spectacular fashion [Figs. 3(a) and 4]. The count of Lagrangian constraints per atom [ $n_c = (5/2)r - 3$ ] due to bond stretching ( $r/2$ ) and bond bending ( $2r - 3$ ) forces steadily increases with  $r$  ( $= 2 + 2x$ ) to acquire a value of three when  $r = r_t = 2.4$  or  $x = x_t = 0.20$  corresponding to the mean-field rigidity predicted by Phillips and Thorpe [25]. Near this threshold concentration ( $x_t$ ), a covalently bonded network acquires a global minimum in mechanical stress ( $\sim |n_c - n_d|$ ) because the count of constraints  $n_c$  equals the degrees of freedom  $n_d$  ( $= 3$ ). Under these conditions, illumination of glasses with near band-gap light ( $E_{\text{ph}} = 1.92$  eV for  $\lambda = 647.1$  nm,  $E_g \sim 2$  eV for Ge-Se glasses), results in *facile switching* of Ge-Se and Se-Se covalent bonds. Photon energy is directly and effectively pumped into covalent bonds by a process that is thought to be mediated by the creation of transient self-

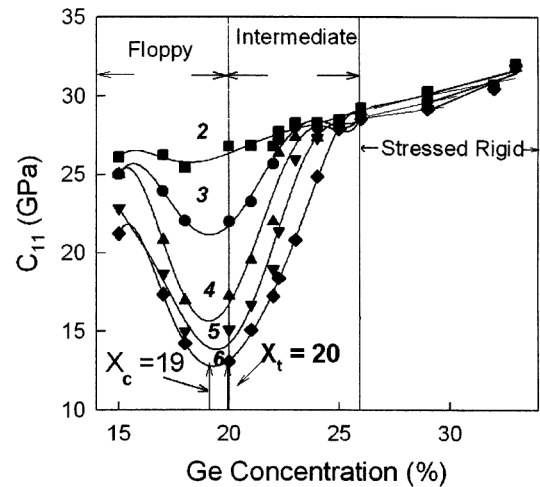


FIG. 4. Variations in longitudinal elastic constant  $C_{11}(x)$  in  $\text{Ge}_x\text{Se}_{1-x}$  glasses as a function of power  $P_r$  (indicated for each curve). Here  $x_c$  and  $x_t$  designate, respectively, the observed threshold in light-induced softening of  $C_{11}$  and the mean-field rigidity transition. The lines at  $x = 0.20$  and  $0.26$  designate, respectively, the rigidity and stress transition in the present glasses (see Ref. [21]).

trapped excitons [1] and results in large atomic displacements, i.e., photodiffusion leading to photsoftening and photobroadening. Frequency dependent relaxation (damping) in glasses has been shown [26] to lead to LA-mode broadening in the presence of mode softening. With increasing illumination power, both photsoftening and photobroadening increase proportionately. The close proximity of the observed threshold ( $x_c$ ) in photsoftening to the mean-field rigidity threshold ( $x_t$ ), and the systematic loss of the softening (Fig. 4) when  $x > x_t$  or when  $x < x_t$ , suggests that the stress-free condition of the backbone underlies the giant, athermal, and reversible light-induced softening of the LA mode. At 6 mW, we estimate the LA-mode amplitude (15 pm) to be about 5% of the nearest-neighbor bond length (270 pm), not large enough to meet Lindemann's criteria [27] of melting (12%).

The rigidity transition in Ge-Se glasses explored in the present BS experiments differs in details from that reported in Raman scattering [19,20] and MDSC [20] in one rather significant way. BS probes the *mean-field behavior* while the latter two the *non-mean-field behavior* of the rigidity transition in the present glasses. As mentioned earlier, BS is intrinsically a bulk probe [28] of network elasticity. On the other hand, Raman scattering [21] probes vibrational modes on a molecular scale; however, the blueshift in Raman frequency of corner-sharing  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra with  $x$  reflects the increased global connectivity of the glasses from which elastic power laws have been deduced [20,21]. MDSC probes the nonreversing enthalpy near  $T_g$ , and it encompasses bond rearrangements taking place at all length

scales revealing the non-mean-field intermediate phase [14–17] that separates the floppy from stressed-rigid phases. In the intermediate phase, the medium-range structural elements of interest consist of isostatic rings [14,15] containing three and/or four tetrahedral units. These structural elements are typically 1.5 nm or less in size and certainly too small to be probed in BS. Furthermore, these rings associated with self-organization effects [14–17] most likely dissociate at high illumination power, collapsing the intermediate phase as observed in earlier Raman scattering [20,21] as a function of laser exciting power. For these reasons, one does not expect to observe the intermediate phase in BS. On the other hand, in photocontraction [4] and photodarkening [18] experiments on Ge-Se thin platelets, no such length scale restrictions enter and non-mean-field effects are observed. One comes to recognize that global probes (Brillouin scattering and ultrasonic moduli) of elasticity of disordered networks provide an intrinsically different average from methods that probe elasticity of these systems at all length scales.

In summary, Brillouin scattering on binary  $\text{Ge}_x\text{Se}_{1-x}$  glasses has revealed a sensational light-induced softening of the longitudinal elastic constant ( $C_{11}$ ) by nearly 50% over a narrow compositional range centered near the mean-field rigidity transition composition of  $x_c = 0.19(1)$ . The use of increased illumination power to excite Brillouin scattering in network glasses has opened new ground; it has shown that some aspects of light-induced effects are intrinsically related to the elastic response of network glasses.

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