

## Shear Waves through the Glass-Liquid Transformation

M. Grimsditch and R. Bhadra

*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

L. M. Torell

*Department of Technology, Uppsala University, Box 534, S-75121 Uppsala, Sweden*

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The temperature dependences of hypersonic longitudinal and transverse sound waves in "strong" ( $B_2O_3$ ) and "fragile" [ $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ ] glass-forming systems have been probed using Brillouin scattering. In the latter material the transverse modes become masked by a central component in the spectrum which broadens as the temperature is raised through the liquidus temperature; in  $B_2O_3$ , on the other hand, well-defined (undamped) transverse modes are observed above the melting temperature of crystalline  $B_2O_3$  ( $\sim 723$  K) all the way to 1300 K.

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The presence of shear waves in liquids is not a novel concept. Relaxation theories<sup>1</sup> predict that, provided the frequency of the phonon is higher than the reciprocal of relaxation times ( $\tau$ ), propagating ("undamped") shear modes exist. Ultrasonic measurements have shown this to be true in certain viscous systems where close to melting ( $\Delta T \approx 10$  K), propagating shear elastic modes do exist.<sup>2</sup> We are aware of only two ultrasonic investigations where shear waves, albeit highly damped, were observed well above the melting temperature, in an alkali-borosilicate mixture<sup>3</sup> and in pure  $B_2O_3$ .<sup>4</sup> The relatively few studies of this nature are due to the usually very short relaxation times above melting so that probe frequencies higher than those in ultrasonics are often needed, and also because it is extremely difficult to perform shear ultrasonic measurements at high temperatures.<sup>3,4</sup> For this type of investigation Brillouin scattering offers considerable advantages: The frequencies involved are considerably higher than typical ultrasonic ones ( $\sim 5$  GHz versus  $\sim 50$  MHz) and the technique can be adapted to measurements at elevated temperatures relatively easily.

In spite of the above advantages not many<sup>5-13</sup> investigations of "shearlike" excitations in liquids have been reported to date using Brillouin scattering. In Ref. 5 a large number of liquids were investigated; many exhibited broad central features in their spectra which were interpreted as overdamped shear waves, and a few showed evidence of propagating shear waves but only very close to the melting temperature. The transition from solid to liquid in noncrystalline materials has been investigated in Refs. 6 and 7: A clear distinction was observed in the behavior above (normal liquid) and below (supercooled liquid) the melting temperature ( $T_m$ ) of the corresponding crystalline materials; the region close to  $T_m$ , however, was not covered in detail and no propagating shear modes were observed above  $T_m$ . These findings are consistent with the results of Ref. 8 where the crystalline

material was investigated by the same technique and the shear modes were shown to vanish abruptly at  $T_m$ . The Brillouin technique has also been used to study a material as a function of pressure,<sup>9</sup> showing the evolution of shear modes as the density is increased. Although other reports of propagating shear modes in the supercooled region can be found in the literature,<sup>10,11</sup> the only observations of this phenomenon above  $T_m$  are in Refs. 12 and 13. In Ref. 12 propagating shear waves are reported 20 K above the melting temperature in pentachlorobiphenyl; in Ref. 13 it is mentioned that in  $ZnCl_2$  undamped shear modes were observed 27 K above  $T_m$ : No spectra or analysis was presented.

Here we have chosen to study the behavior of shear modes through the transition from a supercooled to a normal liquid in two of the most widely investigated glass-forming systems:  $B_2O_3$  and  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  (representative, but incomplete, lists of references for each material are Refs. 4 and 14-21 and Refs. 10 and 22-26, respectively). The two systems were chosen because they represent opposite extremes of structural behavior.  $B_2O_3$  on the one hand is well known to form a network and can therefore be classified as "strong" following a recent classification of glass-forming liquids.<sup>27</sup> Other characteristics of strong glass formers are small changes in the heat capacity ( $C_p$ ) and expansion coefficient ( $\alpha$ ) as the structure becomes arrested at the glass transition  $T_g$ .  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ , on the other hand, represents the opposite behavior and is denoted in the classification as an extremely "fragile" liquid. Typically non-network systems like the ionic and molecular glass formers belong to this group; they usually show large changes of  $C_p$  and  $\alpha$  at the glass transition.

The intention of the present study of two extreme cases of glass-forming liquids is to investigate the differences in shear-mode propagation which arise due to their different structural characteristics. Figure 1 shows Brillouin spectra of  $B_2O_3$  recorded in a  $90^\circ$  scattering

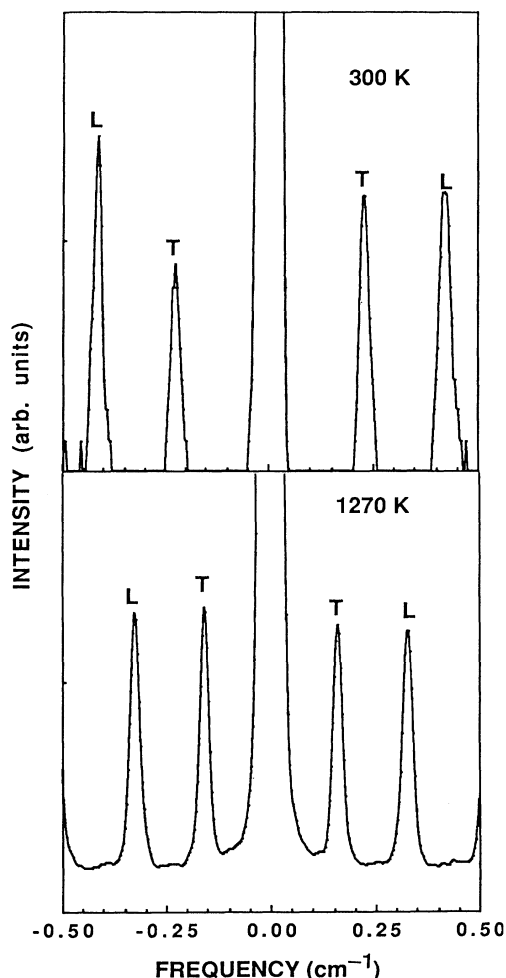


FIG. 1. Brillouin spectra from  $B_2O_3$  showing the existence of undamped shear modes below, as well as above, the melting temperature 723 K. L and T indicate longitudinal and transverse modes, respectively.

geometry with the incident light polarized in the scattering plane and no analyzer in the scattered beam. The upper portion was taken at room temperature (below the melting temperature 723 K of crystalline  $B_2O_3$ ) and the lower one was recorded at 1270 K. In these spectra L and T denote longitudinal and transverse modes, respectively, which were identified by their polarization characteristics; the noteworthy feature is that at 1270 K (almost twice the melting temperature) the transverse modes are still sharp indicating that no appreciable damping has taken place. The velocities of the two modes as a function of temperature are shown by the circles in Fig. 2; up to  $T_m$  they agree with those of Refs. 18, 20, and 21 (in the calculation of velocities we have taken the room-temperature refractive index to be 1.46 and scaled it according to the Clausius-Mossotti relation at higher temperatures). A feature to note in Fig. 2 is that the velocities are influenced by the structural changes

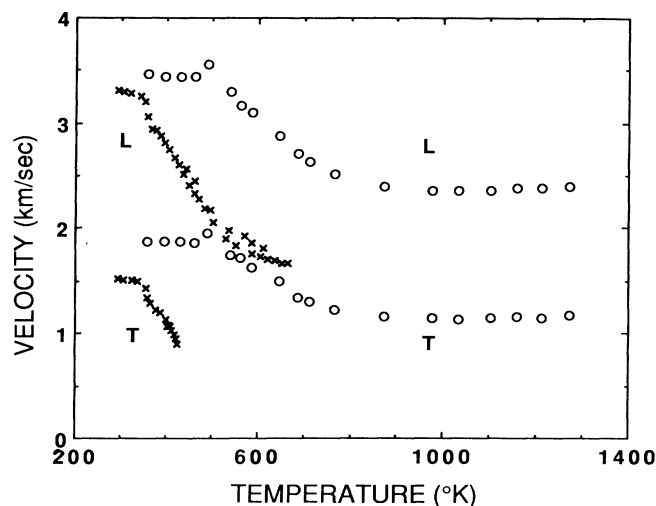


FIG. 2. Sound velocities of transverse and longitudinal waves in  $B_2O_3$  (circles) and  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  (crosses) as a function of temperature.

which occur between the glass transition temperature ( $T_g = 526$  K) and melting ( $T_m = 723$  K) but are essentially unchanged above  $T_m$ . The shear modulus obtained from our results at 1300 K is  $(2.10 \pm 0.05) \times 10^{10}$  dyn/cm<sup>2</sup> and should be compared with the value extrapolated from 820 K in Ref. 4 which yielded  $2.33 \times 10^{10}$  dyn/cm<sup>2</sup>. Although the existence of shear modes in liquid  $B_2O_3$  may seem surprising, our results are consistent with the shear relaxation times ( $\tau_s$ ) reported in Ref. 4; at 1300 K they find  $\tau_s^{-1} = 0.25$  GHz which is still well below the frequency (4.5 GHz) of the shear mode measured in our experiments. By extrapolating the data of Ref. 4 to higher temperatures we find  $\tau_s^{-1} = 4.5$  GHz at  $T \cong 2300$  K; this implies that in our experiment the shear modes should not become damped until this temperature is reached. Preliminary experiments up to 1700 K have been hampered by the chemical reaction of  $B_2O_3$  with the  $SiO_2$  container.

In contrast to  $B_2O_3$ , spectra from the "fragile" glass former  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  are shown in Fig. 3. These spectra were also recorded in the  $90^\circ$  scattering geometry, but an analyzer was placed in the scattered beam to eliminate contributions from the longitudinal modes and from the polarized central peak. In this case shear modes are observed in the supercooled region between  $T_g = 333$  K and  $T_m = 438$  K but not above  $T_m$  as was found in  $B_2O_3$ . The width of the longitudinal Brillouin peak in  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  was found to go through a maximum at  $\sim 500$  K indicating that the relaxation times at this temperature are  $\sim 2 \times 10^{-11}$  sec. The sound velocities as a function of temperature are shown by the crosses in Fig. 2. (The refractive index used to obtain these velocities was taken from Ref. 28.)

It is interesting to note in Fig. 3 that the disappearance of the transverse modes in  $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$  is not

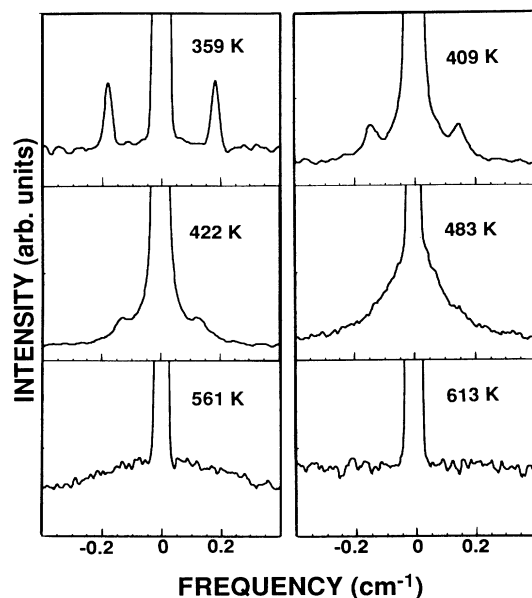


FIG. 3. Depolarized Brillouin spectra from  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$  at various temperatures close to melting, 438 K.

predominantly a broadening (i.e., damping) of the peaks to the point that they become overdamped and merge with the zero-frequency central component; rather, it is a central component which broadens as the temperature is raised till it envelops the shear-mode peaks. This depolarized central component, which is indicative of molecular reorientations, is due to rotational motion of the  $\text{NO}_3$  ions. The intermediate- and high-temperature spectra in Fig. 3 are very similar to those obtained for many polar liquids in Ref. 5. There, by fitting the data with models which assume one relaxation time, the broad central component was interpreted as a superposition of shear waves and molecular rotations. We believe, however, that the results presented here are the first to show the complete evolution of the spectra across the melting temperature. With reference to Fig. 3 it can be seen that in the high-temperature (low-viscosity) regime there is coupling between the reorientational motions and propagating shear modes which can be described by the same average relaxation time.<sup>5</sup> As the temperature decreases the two processes become decoupled and a single-relaxation-time theory can no longer be applied. It is interesting to note that there is another type of decoupling which is observed in the intermediate-viscosity range in  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ , namely, the decoupling of the electrically conducting modes from the viscosity modes.<sup>29</sup> There are also indications that the shear and the longitudinal relaxation processes, which can be represented by the same average relaxation times in the low- and intermediate-viscosity range, show slightly divergent average relaxation times in the temperature range close to the glass transition.<sup>30</sup>

In conclusion, we demonstrate the existence of transverse modes in a liquid at temperatures far above the melting temperature. This phenomenon was detected in the "strong" glass-forming liquid  $\text{B}_2\text{O}_3$  in which the coordinated network maintains the intermediate-range order to high temperatures. In contrast, in the "fragile" system  $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ , as the temperature is raised, the lack of directional character in the bonding and the high configurational degeneracy lead to a rapid degradation of the intermediate-range order and the consequent disappearance of the shear modes. At intermediate temperatures, evidence of decoupling of the  $\text{NO}_3$ -reorientational relaxation from the shear relaxation is observed. This may be the first one in a series of decouplings which subsequently occur for various relaxation processes as the temperature is lowered and the average relaxation times become longer. The observation may be general for "fragile" systems and it may explain the broader distribution of relaxation times compared to that found in "strong" liquids such as  $\text{B}_2\text{O}_3$ .

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