Observation of Large Momentum Phononlike Modes in Glasses

C. Masciovecchio,[1] G. Ruocco,[2] F. Sette,[1] M. Krisch,[1] R. Verbeni,[1] U. Bergmann,[1] and M. Soltwisch[3]

[1]*European Synchrotron Radiation Facility, B.P. 220 F-38043 Grenoble, Cedex France*
[2]*Universitá di L'Aquila and Istituto Nazionale di Fisica della Materia, I-67100, L'Aquila, Italy*
[3]*Institut für Experimentalphysik, Freie Universität Berlin, D-14195 Berlin, Germany*

(Received 19 December 1995)

The dynamic structure factor of glycerol and LiCl:6H_2O glasses, measured by inelastic x-ray scattering, shows modes dispersing linearly with momentum in the 2–8 nm^{-1} region. This finding demonstrates that acousticlike propagating modes can exist in glasses up to wavelengths comparable to interparticle separations. It also shows that the *boson* peak, a feature systematically observed in the same energy region spanned by these excitations, must have a contribution from this propagating collective dynamics, and not only from possible localized modes. [S0031-9007(96)00115-9]

PACS numbers: 63.10.+a, 63.50.+x, 78.70.Ck

The dynamical properties of disordered systems are not well established in the intermediate, mesoscopic, time-space domain. Here, they are not properly described either by a macroscopic thermodynamical picture or by a microscopic single particle dynamics. The concept of propagating collective modes implies the existence of a simple relation between the energy and the momentum of specific excitations. This occurs as a consequence of translational invariance, and is typical in crystals and free particles. In liquids and glasses, this concept may lose its physical significance when local interparticle interactions start to dominate and the topological disorder does not allow one to derive some kind of quasiparticle and its excitation spectrum [1]. In opposition to this picture, however, one may argue that the translational invariance becomes an increasingly less important aspect at large energies and momentum transfers, because one samples particle-particle correlations on a very short time and space scale. Therefore, if local properties become dominant over long range correlations among particles, the differences in the dynamics of liquid, glass, and crystalline states may disappear. An example is provided by recent inelastic x-ray scattering measurements in water: a *propagating* collective dynamics is shown to exist in the liquid up to a momentum transfer $Q = 14\ \mathrm{nm}^{-1}$ [2], and, in the mesoscopic wavelength region from 0.5 to 3 nm, the velocity of sound of these acoustic excitations is found to be *equivalent* in the liquid and in the crystalline solid (ice Ih) [3]. In glasses, the collective dynamics at these high frequencies, and its propagating or localized nature, has not yet been established experimentally [1].

The dynamics of density fluctuations in the high momentum-frequency (Q-ω) region can be assessed by the experimental determination of the dynamic structure factor $S(Q,\omega)$. This is, traditionally, the domain of neutron spectroscopies, although these techniques, due to kinematic limitations, are not easily applied to disordered systems with a large velocity of sound. This explains the lack of experimental determinations of the $S(Q,\omega)$ in glasses at Q transfer in the nm^{-1} range, corresponding to Q values below the first maximum in the static structure factor $S(Q)$, where the medium-range order should play a relevant role [4].

Useful information on the high frequency dynamics of disordered systems is obtained by studying the density of states (DOS), with either incoherent neutron scattering or depolarized Raman scattering. With these methods, however, one cannot determine the energy-momentum dispersion relation and, therefore, the extent of the propagating nature of the dynamics. Moreover, it is not straightforward to extract the DOS. In neutron scattering, to eliminate the residual coherent scattering and the mulitphonon contributions, it is necessary to extrapolate the data to the limit of zero Q. In Raman scattering the situation is even more complex, due to the fact that the measured spectrum results from the dynamics of the system *and* the coupling mechanism of the photon field to the specific excitation. Incoherent neutron scattering [5–7] and light scattering [8–12] from glasses show a broad feature with maximum intensity typically around 2 to 10 meV, and with an almost universal shape, asymmetric towards the high energy side [13]. The intensity of this feature scales with temperature approximately according to the Bose-Einstein statistics, and for this reason is referred to as the *boson* peak. A lively debate exists on the excitations giving rise to the *boson* peak and, so far, conclusions on their vibrational (localized or propagating) or relaxational nature have not yet been reached [1].

The kinematical limitations of neutrons do not apply to inelastic x-ray scattering with meV energy resolution, and therefore this technique can be utilized to directly measure the $S(Q,\omega)$ of disordered systems [2].

In this Letter we report the $S(Q,\omega)$ measurement of two glasses, glycerol and a solution of LiCl in H_2O, in the momentum transfer region 2–8 nm^{-1}. Following Angell's definition [14], these materials are intermediate between strong and fragile glasses [15,16]. In both systems we detect inelastically scattered intensity, dispersing linearly with momentum transfer Q. The velocities of sound are 3330 ± 50 m/s in glycerol, and 3800 ± 300 m/s in

0031-9007/96/76(18)/3356(4)$10.00

LiCl:H_2O. These measurements demonstrate that, in spite of the absence of translational invariance, a *propagating* longitudinal collective dynamics can exist in glasses down to wavelengths similar to interatomic distances. Direct implications of these findings are as follows: (i) The localization of the eigenmodes of the density fluctuation spectrum does not take place in the frequency region considered here, and (ii) the origin of the *boson* peak is most likely due to these high frequency collective dynamics.

The experiment was carried out at the new very high energy resolution inelastic x-ray scattering beamline (BL21-ID16) at the European Synchrotron Radiation Facility. The undulator x-ray beam was monochromatized by a cryogenically cooled Si(111) double crystal and by a very high energy resolution Si(999) backscattering monochromator [2,17]. This beam, with an energy of 17 794 eV, had an energy resolution of 2 meV and an intensity of 10^9 photons/s. The scattered photons were collected by a spherical silicon crystal analyzer, operating as well at the Si(999) in backreflection, and in Rowland geometry. This analyzer, obtained by gluing $\approx$12 000 perfect crystals of $0.6 \times 0.6 \times 2$ mm^3 size on a spherical blank with 6150 mm radius [2,18], yielded an energy resolution of 2.9 ± 0.5 meV. The total instrumental resolution function, measured using a Plexiglas scatterer at the maximum of its static structure factor where the scattering is dominated by the elastic component, was well approximated by a Lorentzian of $2\Gamma_R = 3.7$ meV. The momentum transfer $Q = 2\,k_0\,\sin(\theta_s/2)$, where k_0 and θ_s are, respectively, the wave vector of the incident photon and the scattering angle, was selected between 1 and 22 nm^{-1} by rotating the 7 m long analyzer arm in the horizontal scattering plane. The Q resolution was set to 0.4 nm^{-1} by an aperture in front of the analyzer. Energy scans were done by varying the relative temperature between the monochromator and analyzer crystals: The analyzer was kept at 294 K, and the monochromator temperature was scanned from 294.75 to 292.8 K with a step of -0.015 K, corresponding to an energy step of 0.7 meV. Each scan took about 70 min, and each Q point was obtained by averaging 7 scans in glycerol, and 18 scans in LiCl:H_2O. The data were normalized to the intensity of the incident beam.

High purity anhydrous glycerol was contained inside a 10 mm long sealed copper cell, loaded in an argon glove box. The glass was obtained holding the cell at 145 K [19] in vacuum. The cell and vacuum chamber windows were made of 25 μm thick kapton foil. Similarly, the LiCl:H_2O glass was obtained by cooling to 80 K a 7 mm long cell containing a liquid solution of one LiCl atoms pair per 6 H_2O molecules [20]. The glass nature of the two samples was established by the similarity of the static structure factor in the glass and liquid states at temperatures just above and below the glass transition [19,20]. Empty cell measurements gave the flat electronic background of the Si diode detector of 0.6 count/min. The cell lengths were chosen to be comparable to the x-ray photoabsorption length, and to give negligible multiple scattering.

Representative inelastic x-ray scattering spectra of the two glasses, directly showing the spectral shape of the dynamic structure factor convoluted with the instrumental resolution function, are reported in Fig. 1. The glycerol spectrum at $Q = 5$ nm^{-1} is shown in Fig. 1(a), while in Fig. 1(b) we report the one of LiCl:H_2O at $Q = 6$ nm^{-1}. The experimental data are shown together with the corresponding fits and error analysis as discussed in the following. The insets show an enlargement of the spectral region where the inelastic signal is best visible. This inelastic intensity is due to collective excitations in the two glasses, and can be observed up to 7 and 8 nm^{-1}

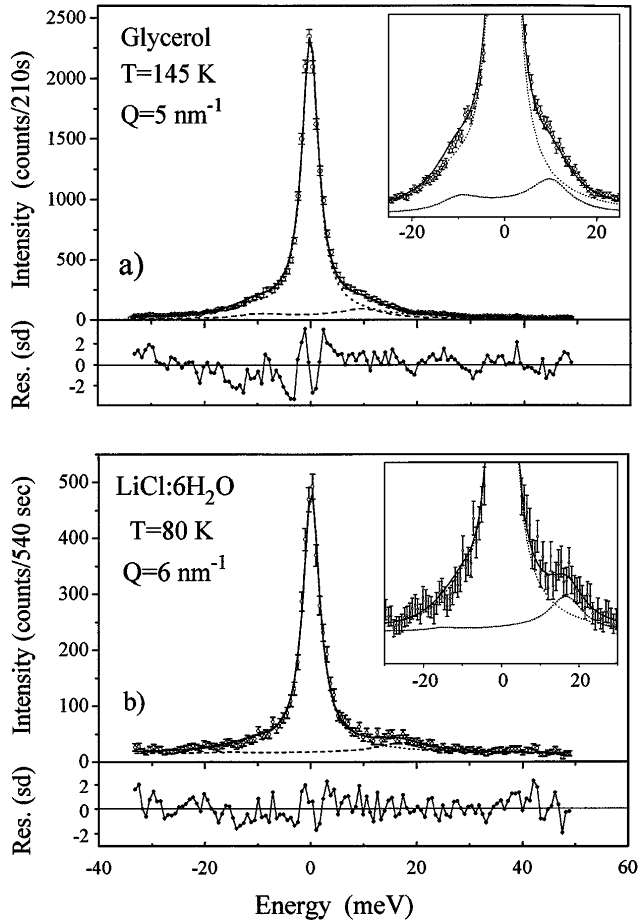

FIG. 1. Inelastic x-ray scattering spectra of glycerol (a) and LiCl:H_2O (b) glasses, measured at the indicated temperatures and Q transfers. The data (○), shown with their error bars, are superimposed to the fit (solid line) as explained in the text. The bottom panels report the difference between the data and the fit in standard deviation (sd) units for each data point. In spite of the longer counting time, the noise level in the LiCl:H_2O sample is larger than in glycerol due to the smaller scattering volume and the larger photoelectric absorption from the Cl atoms. The line under the central peaks is the resolution function, shown to emphasize the inelastic intensity on the sides of the central peak. An enlargement of the frequency region where the excitations are best visible is reported in the insets.

in glycerol and LiCl:H_2O. At larger Q, the inelastic signal is no longer visible for its increased broadening, and for the intensity of the central peak which grows approaching the maximum of the $S(Q)$. This maximum is observed at $Q \approx 14.5$ and $19\ \mathrm{nm}^{-1}$ in glycerol and LiCl:H_2O, respectively. To determine the energy position and the width of these excitations at each Q, the spectra have been modeled by the function $F(Q,\omega)$, consisting of a δ function for the elastic scattering, and a damped harmonic oscillator (DHO) model [21] for the two side peaks:

$$F(Q,\omega) = I_0(Q)\delta(\omega) + [n(\omega) + 1] \times I(Q)\frac{\omega\Gamma(Q)\Omega(Q)}{[\Omega(Q)^2 - \omega^2]^2 + \Gamma(Q)^2\omega^2}. \quad (1)$$

Here $I_0(Q)$ and $I(Q)$ are the intensities of the central peak and of the inelastic contributions, respectively, $\Omega(Q)$ is the central frequency of the side peaks, and $\Gamma(Q)$ is their energy width; $n(\omega)$ is the Bose factor.

The experimental data, after subtraction of the detector dark counts, have been fitted by the convolution of $F(Q,\omega)$ with the Lorentzian representing the resolution function. We used standard χ^2 minimization, obtaining χ^2 values always within its standard deviation. In the bottom panels of Figs. 1(a) and 1(b) we show the difference between the data and the fitting function in units of 1 standard deviation (sd) for each data point.

The choice of the DHO model in the $S(Q,\omega)$ of these glasses is arbitrary. It was used because it contains the basic features of the inelastic part of the $S(Q,\omega)$ of a disordered system, and allows one to determine the spectroscopic parameters and their Q dependence independently of specific theories [22]. Moreover, this model function has been successfully applied to describe the shape of $S(Q,\omega)$ in a simulated model glass [23].

The individual contributions to a typical fit are shown by the dashed lines in Fig. 1 for the two glasses. The contribution of the DHO model to the fit, representing the inelastic intensity in the measured spectra, is reported for selected Q transfers in Fig. 2(a) for glycerol, and in Fig. 2(b) for LiCl:H_2O. The dispersion with Q is evident, and the broadening increases with momentum transfer. The values of $\Omega(Q)$ derived from the fits are shown in Fig. 3. They follow a linear behavior with a slope corresponding to a speed of sound of 3330 ± 50 m/s in glycerol [Fig. 3(a)], and of 3800 ± 300 m/s in LiCl:H_2O [Fig. 3(b)]. Similarly, the values of $\Gamma(Q)$ for the two glasses are shown in Fig. 4. In glycerol, the width, shown in Fig. 4(a), increases with Q transfer following approximately a Q^2 dependence. In the LiCl:H_2O glass, the width, shown in Fig. 4(b), has a behavior qualitatively similar to glycerol. The larger scattering of the parameters in the fits of LiCl:H_2O compared to glycerol, and the correlation of the deviations of $\Omega(Q)$ and $\Gamma(Q)$ from the general trend, is a consequence of the worse signal to noise ratio in LiCl:H_2O.

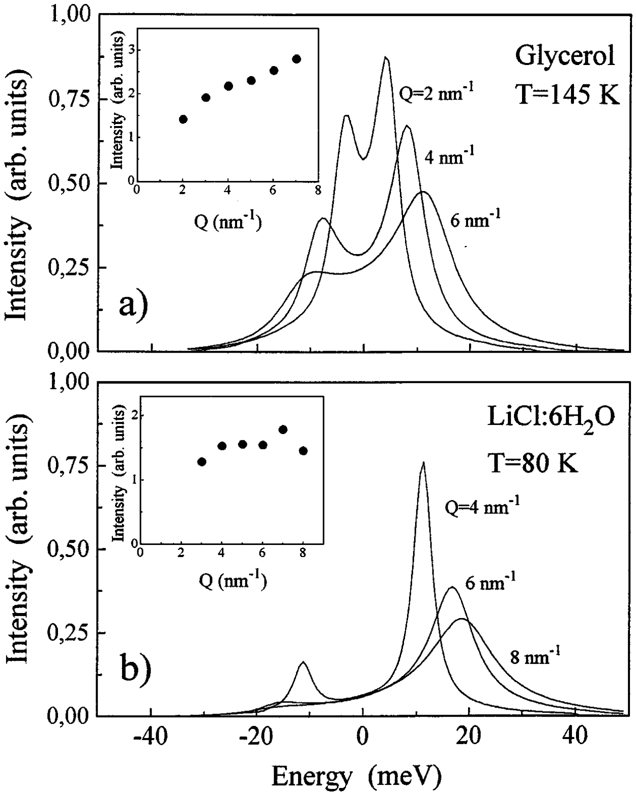

FIG. 2. The inelastic contributions to the fits are shown for glycerol (a) and LiCL:H_2O (b) at the indicated Q values. The curves have been normalized to unit area. The Q dependence of their integrated intensities are reported in the insets.

The results shown in Figs. 2 and 3 demonstrate the propagating nature of the collective excitations observed in these systems. Moreover, the similarity of the velocities of sound reported here with those of the corresponding longitudinal sound waves measured at very small Q [24,25], indicates that in these glasses, as in crystalline solids, there are no relevant relaxation processes.

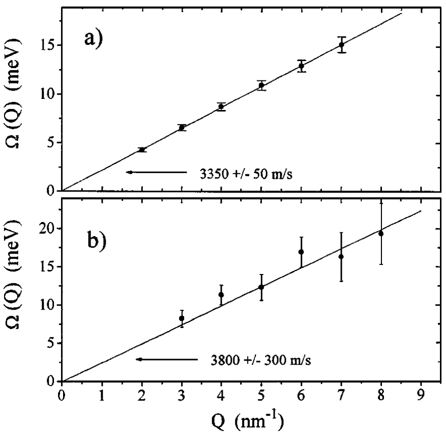

FIG. 3. Dispersion relation $\Omega(Q)$ in glycerol (a) and LiCl:H_2O (b) as obtained from the fit. In each figure, the solid line indicates the best linear fit, and the slope corresponds to the indicated speed of sound.

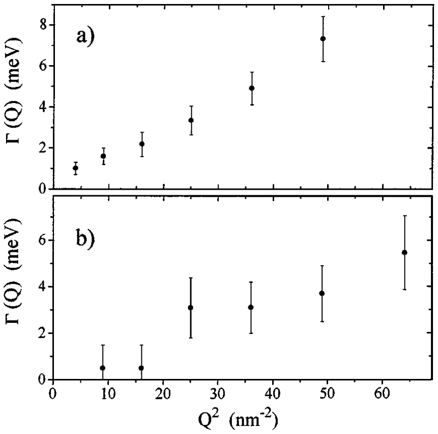

FIG. 4. Energy widths $\Gamma(Q)$ as obtained from the fits for (a) glycerol and (b) LiCl:H_2O as a function of Q^2.

Finally, the observation of propagating longitudinal modes with energies between 4 and 20 meV gives an indication on the origin of the *boson* peak. In fact, in glycerol and LiCl:H_2O glasses the *boson* peaks are centered at 5 [11] and 6 meV [16], respectively, and span an energy region up to values comparable to the highest energies of the excitations found here. We can therefore conclude that an important contribution to this peak must come from these longitudinal propagating modes. This observation, however, does not exclude the existence of other excitations (propagating or localized) contributing to the *boson* peak, which are not probed by the present experiment. Assuming their existence, however, they must have a pure transverse character and/or energies difficult to resolve with the presently available energy resolution, i.e., below $\approx$4 meV.

The results reported here apply to two intermediate glasses. It is attractive, however, to speculate on their generality, and, therefore, it is of great interest to determine whether a propagating collective dynamics at high frequencies exists also in fragile and strong glasses. Work in this specific direction is in progress.

We acknowledge O. Consorte, W. Galli, B. Gorges, K. Martel, and J.F. Ribois for their technical assistance. We also thank J.F. Legrand, V. Mazzacurati, and G. Signorelli for useful discussions.

[1] See *Proceedings of the International Workshop on Dynamics of Disordered Materials II, Grenoble, France, 1993,* edited by A.J. Dianoux, W. Petry, and D. Richter (North-Holland, Amsterdam, 1993).

[2] F. Sette, G. Ruocco, M. Krisch, U. Bergmann, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Phys. Rev. Lett. **75**, 850 (1995).

[3] G. Ruocco, F. Sette, U. Bergmann, M. Krisch, C. Masciovecchio, V. Mazzacurati, G. Signorelli, and R. Verbeni, Nature (London) **379**, 521 (1996).

[4] A.P. Sokolov, A. Kisliuk, M. Soltwisch, and D. Quitmann, Phys. Rev. Lett. **69**, 1540 (1992).

[5] U. Buchenau, M. Prager, N. Nucker, A.J. Dianoux, N. Ahmad, and W.A. Phillips, Phys. Rev. B **34**, 5665 (1986).

[6] U. Buchenau, H.M. Zhou, N. Nucker, K.S. Gilroy, and W.A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).

[7] J. Wuttke, W. Petry, G. Coddens, and F. Fujara, Phys. Rev. E **52**, 4026 (1995).

[8] G. Carini, M. Cutroni, A. Fontana, G. Mariotto, and F. Rocca, Phys. Rev. B **29**, 3567 (1984).

[9] M. Kruger, M. Soltwisch, I. Petscherizin, and D. Quitmann, J. Chem. Phys. **96**, 7352 (1992).

[10] A. Brodin, A. Fontana, L. Borjesson, G. Carini, and L. Torell, Phys. Rev. Lett. **73**, 2067 (1994).

[11] A.P. Sokolov, A. Kisliuk, D. Quitmann, A. Kudlik, and E. Rossler, J. Non-Cryst. Solids **138**, 172 (1994).

[12] P. Benassi, V. Mazzacurati, G. Monaco, G. Ruocco, and G. Signorelli, Phys. Rev. B **52**, 976 (1995).

[13] V.K. Malinovsky, V.N. Novikov, P.P. Parshin, A.P. Sokolov, and M.G. Zemlyanov, Europhys. Lett. **11**, 43 (1990).

[14] C.A. Angell, in *Relaxation in Complex Systems,* edited by K.L. Ngai and G.B. Wright (National Academy of Sciences—National Research Council, Washington, D.C., 1984), p. 3.

[15] A.P. Sokolov, E. Rossler, A. Kisliuk, and D. Quitmann, Phys. Rev. Lett. **71**, 2062 (1993).

[16] N.J. Tao, G. Li, X. Chen, W.M. Du, and H.Z. Cummins, Phys. Rev. A **44**, 6665 (1991).

[17] R. Verbeni, F. Sette, M. Krisch, U. Bergmann, B. Gorges, C. Halcoussis, K. Martel, C. Masciovecchio, J.F. Ribois, G. Ruocco, and H. Sinn, J. Synchrotron Radiat. **3**, 64 (1996).

[18] C. Masciovecchio, U. Bergmann, M. Krisch, G. Ruocco, F. Sette, and R. Verbeni (to be published).

[19] A.A. Newman, *Glycerol* (Morgan Grampian, London, 1968).

[20] A. Elarby-Aouizerat, J.F. Jal, P. Chieux, J.M. Letoffe, P. Claudy, and J. Dupuy, J. Non-Cryst. Solids **104**, 203 (1988).

[21] B. Fak and B. Dorner, Institute Laue Langevin (Grenoble, France) Report No. 92FA008S, 1992.

[22] The energy-width parameter $\Gamma(Q)$, in the present context, represents not only the energy broadening due to anharmonicity, but even more the broadening associated with the relaxed definition of Q as a good quantum number in a system without translational invariance.

[23] G. Ruocco and M. Sampoli (private communication).

[24] Y. Yan, L. Cheng, and K.A. Nelson, J. Chem. Phys. **88**, 6477 (1988).

[25] N.J. Tao, G. Li, and H.Z. Cummins, Phys. Rev. B **43**, 5815 (1991).