Crystal-Like Nature of Acoustic Excitations in Glassy Ethanol

A. Matic,[1] C. Masciovecchio,[2] D. Engberg,[1] G. Monaco,[3] L. Börjesson,[1] S. C. Santucci,[2] and R. Verbeni[3]

[1]*Department of Applied Physics, Chalmers University of Technology, SE-41296 Göteborg, Sweden*
[2]*Sincrotrone Trieste, I-34012 Basovizza, Trieste, Italy*
[3]*European Synchrotron Radiation Facility, BP-220, F-38043 Grenoble, France*

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We report on inelastic x-ray scattering experiments on crystalline and glassy phases of ethanol in order to directly compare the influence of disorder on high frequency acoustic excitations. We find that both the dispersion and the line-width of the longitudinal acoustic excitations in the glass are the same as in the polycrystal in the reciprocal space portion covering the 1st and 2nd Brillouin zones. The structural disorder is found to play little role apart from an intrinsic angular averaging, and the nature of these excitations must essentially be the same in both glass and poly crystal.

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The understanding of acoustic excitations in glasses is far from the level reached for crystalline solids. From a theoretical point of view the absence of periodicity prevents the simplified descriptions of collective dynamics through Bloch formalism. In the long-wavelength limit a glass, as well as a crystal, has the response of an elastic medium to an acoustic excitation, and the excitation can be assigned a wave vector and an energy. However, when the wavelength decreases and approaches the typical length scale where the disorder becomes important in a glass (, i.e., normally in the 5-20 Å range), it is no longer obvious how to uniquely define an excitation by its momentum transfer and energy. The breakdown of the long-wavelength scenario is for glasses expected to occur in this mesoscopic regime, i.e., at wave vectors in the nm^{-1} and energies in the meV range. Acoustic excitations in this region have also been linked to the anomalies in thermal properties and the so called Boson peak, the excess in the vibrational density of states compared to the Debye behavior of crystals [1]. Several different models have been proposed to explain these anomalies, with quite contrasting implications on the nature of the high frequency acoustic excitations in the glassy state and on the interpretation of experimental data [2–8].

From an experimental point of view, investigations of high frequency acoustic excitations in glasses have been hampered by the kinematic limitations of the standard tool, inelastic neutron scattering. For glasses of normal sound velocity (1000-5000 m/s) the acoustic branch falls outside the experimentally accessible momentum and energy transfer range, whereas in a crystal the experiment can always be performed in a higher order Brillouin zone. However, in recent years there has been considerable progress in the understanding of high frequency acoustic excitations in disordered systems mainly due to the development of the high resolution inelastic x-ray scattering (IXS) technique [7], enabling direct observations of longitudinal collective excitations in the region of the first Brillouin zone, and advances in computer simulations [9–14]. In IXS the dynamic structure factor, $S(Q, \omega)$ is directly probed in the relevant dynamical range (nm^{-1} and meV). The common findings from the IXS experiments on glasses, performed so far, is a linear dispersion of the acoustic modes at small wave vectors, with a slope of the dispersion corresponding to the longitudinal low frequency sound velocity, and a Q^2 dependence of the linewidth of the excitations [7,15–17]. An explanation for the general Q^2 broadening has so far been lacking, but it was shown to be of nondynamic origin [15]. However, the extent of the region where the acoustic excitations are propagating, and theQ^2 behavior, is found to strongly depend on the mesoscopic structure and topology of the specific glass [17]. It has also been suggested, from IXS experiments, that in the vicinity of the crossover from a propagating to nonpropagating regime there should be a Q^4 dependence of the linewidth marking a rapid decrease of the lifetime of the excitations [3,5].

In order to address the influence of structural disorder on the nature of acoustic excitations and their link to dynamical anomalies, we have investigated the crystalline and glassy phases of ethanol at wave vectors corresponding to the 1st and 2nd Brillouin zone of the crystal using inelastic x-ray scattering. We present the first quantitative comparison of high frequency acoustic excitations in the glass and crystal phases of the same substance at the same temperature. We find that the dispersion as well as the experimental linewidth of the acoustic excitations is the same in the glass as in the polycrystal over the whole probed momentum transfer region covering the 1st and 2nd Brillouin zones. The disorder plays little role apart from an intrinsic angular averaging, thus the nature of the excitations must be essentially the same in the crystal and the glass.

Ethanol is one of a few polymorphic systems where the different phases can be investigated at the same temperature, enabling a direct comparison of the structural influence on the dynamical properties. For ethanol four solid phases exist; monoclinic crystal, plastic crystal, rotationally disordered crystal and true topological glass. The monoclinic crystal, the rotationally disordered crystal

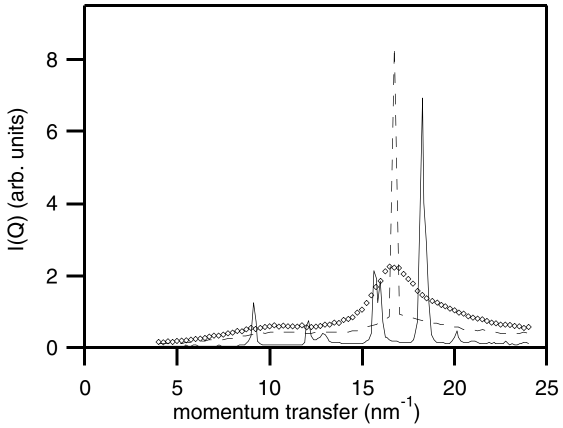

FIG. 1. Diffracted intensity from the three solid phases of ethanol. The dotted line represents monoclinic crystal, the dashed line the rotationally disordered bcc crystal and the symbols the topological glass. The maximum of the static structure factor for the topological glass is located at 16 nm^{-1}, whereas the main Bragg peak is found at 16 nm^{-1} and 18 nm^{-1} for the rotationally disordered and monoclinic crystals, respectively.

and the glass phases are all stable below 95 K and are obtained by applying proper thermal treatment to the sample [18]. During recent years considerable attention has been paid to the structure and dynamics of solid ethanol [18–23]. It has been found that the glass phase of ethanol shows a clear excess in the vibrational density of states (VDOS) around 3 meV, a Boson peak, as well as an excess in specific heat compared to the crystal phase [18]. These anomalies are also observed in the rotationally disordered bcc crystal and the orientational disorder accounts for up to 90% of the excess in the VDOS and specific heat in the case of ethanol [18,21].

The IXS experiment was performed using the high resolution spectrometer at beamline ID16 of the European Synchrotron Radiation Facility, Grenoble, France [7]. The different phases were prepared *in situ* in the cryostat using the same sample and all the measurements were performed at the same temperature, $T = 86$ K. Figure 1 shows the diffracted intensity, *I(Q)*, for the three phases, recorded simultaneously with the inelastic experiments. The two crystalline phases show, as expected, distinct Bragg peaks, whereas the topological glass shows a smooth pattern characteristic of an amorphous solid. IXS spectra were recorded in the Q-region 1-15 nm^{-1}.

In Fig. 2 the experimental IXS data at two different momentum transfers are displayed. At low momentum transfers one observes well defined inelastic peaks, whereas at high momentum transfers the inelastic component is broad and the peaks are ill defined. In order to quantitatively follow the evolution of the dynamic structure factor as a function of momentum transfer the spectra were fitted with a convolution of the resolution function and a damped harmonic oscillator for the inelastic contribution and a delta function for the elastic scattering [16,17] according to

$$S(Q,\omega) = I_0(Q)\delta(\omega) + I(Q)\frac{\Omega(Q)^2\Gamma(Q)}{[\omega^2 - \Omega(Q)^2]^2 + \omega^2\Gamma(Q)^2} \times \frac{\omega/k_BT}{1 - \exp(\omega/k_BT)}. \qquad (1)$$

where $\Omega(Q)$ and $\Gamma(Q)$ represent the position and width of the excitation, respectively. Apart from a large difference

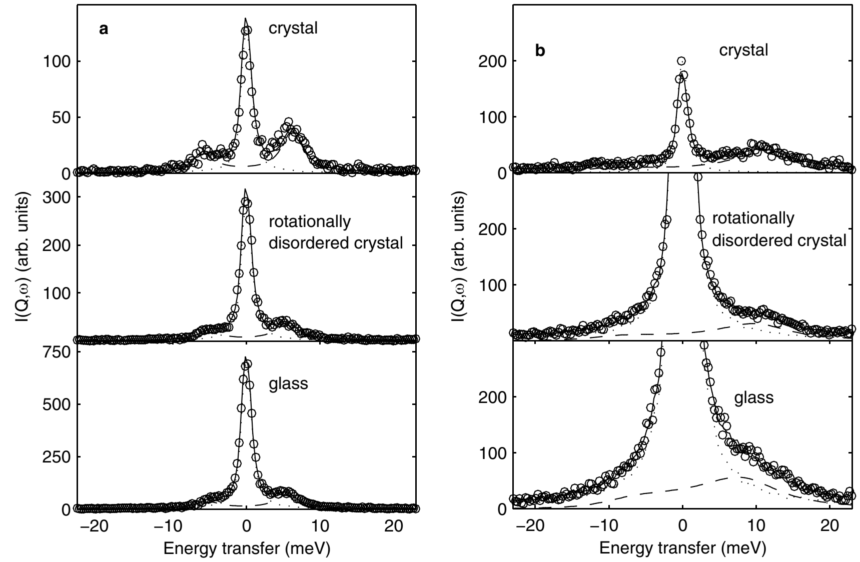

FIG. 2. Spectra from IXS experiments at two different momentum transfers $Q = 3$ nm^{-1} (a) and $Q = 7$ nm^{-1} (b) for the monoclinic crystal, the rotationally disordered crystal and the topological glass. The symbols represent the experimental data, the full line the fit of the spectra, the dashed line the convoluted inelastic contribution and the dotted line the experimental resolution.

in the elastic contribution, the glass showing a much higher elastic intensity, the results from the different phases are remarkably similar. They reveal an almost linear dispersion for momentum transfers up to $Q \approx$ 8-9 nm^{-1} in all three phases, see Fig. 3, and a linewidth which is the same within experimental accuracy. At momentum transfers above $Q \approx$ 8-9 nm^{-1}, the position of the excitation actually decreases in energy for all three phases.

For a crystalline sample this behavior is not surprising and can be understood in the well known terms of Brillouin zones and phonon dispersion curves. In a polycrystalline sample, as the monoclinic and rotationally disordered bcc phases, the measured dynamic structure factor will be averaged over all crystalline directions [24]. The dispersion observed in the first Brillouin zone in figure three thus represents the average of the dispersion relations in the different crystalline directions, with the slope of the dispersion relation related to an average longitudinal sound velocity. The end of this average LA branch is found at a momentum transfer around $Q =$ 8-9 nm^{-1}, the average Brillouin zone boundary. At larger momentum transfers, in the second zone, the energy of the excitation decreases, as expected. Here, the spectrum may also contain contributions from transverse excitations through umklapp processes with a lattice vector, G. That this is indeed the case is evident when one considers the total inelastic intensity as a function of momentum transfer, Fig. 3, where the inelastic intensity shows a very rapid increase for $Q > 8\ \text{nm}^{-1}$, i. e., beyond the first Brillouin zone.

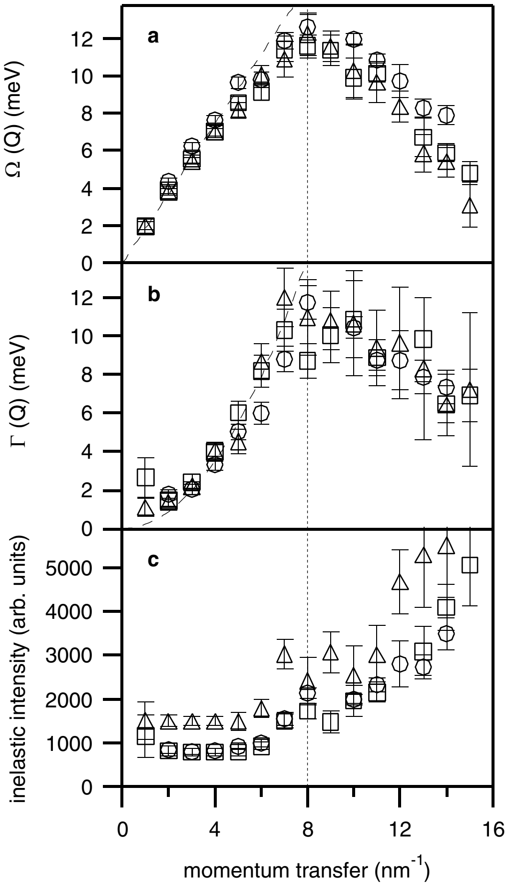

FIG. 3. Results from the quantitative analysis of the IXS spectra of ethanol in the monclinic crystal (circles), rotationally disordered bcc crystal (squares) and glass (triangles) phases. Momentum transfer dependence of the position, $\Omega(Q)$, width, $\Gamma(Q)$ and total inelastic intensity are shown in the figures (a)-(c). The dashed line in panel (a) shows the linear dispersion corresponding to the low frequency sound velocity for the glass, $v_L = 2850$ m/s [20]. The average high frequency sound velocity for the rotationally disordered bcc crystal is the same as for the glass, whereas it is 14% higher in the monoclinic crystal. The dashed line in panel (b) indicates a Q^2 behavior of the width at low momentum transfers. The vertical dotted line in the panels (a)-(c) schematically marks the position of an average Brillouin zone.

Conversely, the results for the glass are surprising. Even though the material lacks translational order we observe a crystal-like dispersion curve, see Fig. 3. The slope of this dispersion for the glass agrees well with the low frequency longitudinal sound velocity determined by Brillouin light scattering [20], showing that the inelastic contribution observed in the experiment is indeed related to the longitudinal acoustic excitation. The maximum of the dispersion curve occurs around $Q = 8\ \text{nm}^{-1}$, i.e., at $Q = Q_p/2$ where Q_p is the main peak of the static structure factor, *S(Q)*, and the dispersion curve goes towards a minimum at Q_p. This crystal-like behavior provides evidence that also in the glass we have phononlike excitations with wavelengths approaching the interparticle distance in the material. The Q-value of the main peak in *S(Q)* acts as a reciprocal lattice point for the glass defining a pseudo-Brillouin zone for $Q < \text{Q}_\text{P}/2$. Such a behavior has actually been suggested from computer simulations on both model systems such as Lennard-Jones glasses [25] as well as more realistic models of metallic glasses [26], and is here clearly experimentally shown. We note that also for the glass there is a rapid increase in the inelastic intensity around and after the pseudo-Brillouin zone boundary. This may be a contribution of transverse modes, contributing through umklapp-like scattering with the reciprocal lattice vector corresponding to the principle peak in *S(Q)* [6]. We note that previously reported results from IXS experiments on crystalline and amorphous high density phases of ice are in agreement with our findings [27,28].

The lack of influence of the structural disorder on the dispersion of the longitudinal acoustic excitations shows that they are essentially of the same nature in the glass and in the poly crystal, in the energy region of the excess in the VDOS. Thus, the origin of the dynamical anomalies in the glass cannot be directly related to any significant changes in the nature of these excitations. This is underlined when considering the origin of the experimental linewidth of the high frequency acoustic excitations in glasses. In the region of the first Brillouin zone we observe a progressive increase of the width of the inelastic features following an approximate Q^2 dependence. Within the accuracy of the present experiment the width is the same in all three phases indicating a common origin.

In the crystalline phases the increase of the width can be understood as a result of the increasing energy spread of the phonon branches in different crystalline directions, due to differences in sound velocity. Thus the observed width of the inelastic component is a result of averaging over different local structural orientations in the glass, and cannot be linked to the lifetime, or damping, of a single excitation, nor to the lack of short range order. In the glass the averaging is intrinsic as a result of the structural disorder. The fact that the experimental linewidth is a result of inhomogenous effects, rather than related to the lifetime, is underpinned by the previously observed temperature independence [15].

To conclude, here we report on the first quantitative comparison between longitudinal high frequency acoustic excitations in glass and crystal phases prepared from the same sample. We find that the dispersion as well as the line-width in the glass is the same as in the polycrystal in the 1st and 2nd Brillouin zones . Thus the nature of the excitations is essentially the same and no significant change can be directly linked to the origin of dynamical anomalies observed in the glass phase of ethanol. We also show that in the glass the wave vector of the main peak in the static structure factor acts as a reciprocal lattice point defining a pseudo-Brillouin zone boundary at $Q_p/2$. This fact provides support for the existence of umklapplike scattering processes of acoustic excitations in glasses, suggested from inelastic neutron scattering experiments [6]. From our results we can also offer an explanation of the universal Q^2 dependence of the linewidth in IXS experiments, as resulting from an angular averaging over different local structures in the glass in analogy with the averaging over different crystalline directions in a polycrystal.

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[1] E.W. A. Philips, *Amorphous Solids: Low Temperature Properties* (Springer-Verlag, Berlin, 1981).

[2] U. Buchenau *et al.*, Phys. Rev. Lett. **60**, 1318 (1988).

[3] M. Foret *et al.*, Phys. Rev. Lett. **77**, 3831 (1996).

[4] A. P. Sokolov *et al.*, Phys. Rev. Lett. **78**, 2405 (1997).

[5] E. Rat *et al.*, Phys. Rev. Lett. **83**, 1355 (1999).

[6] D. Engberg *et al.*, Phys. Rev. B **58**, 9087 (1998).

[7] F. Sette, M. H. Krish, C. Masciovecchio, G. Ruocco, and G. Monaco, Science **280**, 1550 (1998).

[8] E. Duval and A. Mermet, Phys. Rev. B **58**, 8159 (1998).

[9] R. Fernandez-Perea, F. J. Bermejo, and E. Enciso, Phys. Rev. B **53**, 6215 (1996).

[10] M. C. C. Ribeiro, M. Wilson, and P. A. Madden, J. Chem. Phys. **108**, 9027 (1998).

[11] G. Ruocco, F. Sette, R. Di Leonardo, G. Monaco, M. Sampoli, T. Scopigno, and G. Viliani, Phys. Rev. Lett. **84**, 5788 (2000).

[12] W. Götze and M. R. Mayr, Phys. Rev. E **61**, 587 (2000).

[13] J. Horbach, W. Kob, and K. Binder, Eur. Phys. J. B **19**, 531 (2001).

[14] T. Grigera, V. Martin-Myor, G. Parisi, and P. Verocchio, Nature (London) **422**, 289 (2003).

[15] G. Ruocco, F. Sette, R. Di Leonardo, D. Fioretto, M. Krisch, M. Lorenzen, C. Masciovecchio, G. Monaco, F. Pignon, and T. Scopigno, Phys. Rev. Lett. **83**, 5583 (1999).

[16] A. Matic *et al.*, Phys. Rev. Lett. **86**, 3803 (2001).

[17] A. Matic *et al.*, Europhys. Lett. **54**, 77 (2001).

[18] M. A. Ramos *et al.*, Phys. Rev. Lett. **78**, 82 (1997).

[19] A. Srinivasan *et al.*, Phys. Rev. B **53**, 8172 (1996).

[20] A. Srinivasan, F. J. Bermejo, and A. De Bernabe, Mol. Phys. **87**, 1439 (1996).

[21] C. Talon *et al.*, Phys. Rev. B **58**, 745 (1998).

[22] M. A. Gonzalez, E. Enciso, F. J. Bermejo, and M. Bee, Phys. Rev. B **61**, 6654 (2000).

[23] A. Criado *et al.*, Phys. Rev. B **61**, 8778 (2000).

[24] F.W. de Wette and A. Rahman, Phys. Rev. **176**, 784 (1968).

[25] G. S. Grest, S. R. Nagel, and A. Rahman, Phys. Rev. Lett. **49**, 1271 (1982).

[26] J. Hafner and M. Krajci, J. Phys. Condens. Matter **6**, 4631 (1994).

[27] M. Koza *et al.*, Phys. Rev. B **69**, 024204 (2004).

[28] H. Schober, M. M. Koza, A. Tölle, C. Masciovecchio, F. Sette, and F. Fujara, Phys. Rev. Lett. **85**, 4100 (2000).