

Origin of the boson peak in a network glass B_2O_3

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We report coherent inelastic neutron-scattering spectra for the network glass former B_2O_3 measured at temperatures from 100 to 1300 K ($T_g \sim 525$ K). At the first sharp diffraction peak, which stems from the van der Waals packing of layerlike units, one finds a correlated in-phase motion of these units at low frequency, and in addition a quasi-incoherent contribution for all temperatures. The contribution of the in-phase motion in the frequency range of the boson peak and the fast relaxations is significantly higher than the one expected for the sound waves. [S0163-1829(99)06605-9]

An important issue concerning the dynamics of disordered solids is to unravel the nature of the modes in the frequency range between the macroscopic long-wavelength motion and the atomic motion on a microscopic level. Obviously, the long-wavelength sound waves are universal, because at long wavelengths one deals with an elastic or viscoelastic medium for any glass former independent of the microscopic characteristics. The microscopic dynamics, however, is dominated by the weakest atomic springs, so it must be system specific by definition. At the crossover, between those extremes, one finds excess modes over the Debye sound wave expectation, giving rise to the broad boson peak in Raman and neutron scattering. The boson peak is a universal characteristic feature of disordered materials and its nature is not well understood, however presently much debated.¹⁻¹³ It is observed at an energy of a few meV in most kinds of glasses^{2,8-11} polymers,¹² and orientational glasses.¹⁴ For a number of glasses it has been shown that the excess vibrational modes observed as the boson peak are the origin of the anomalous thermal properties of glasses in the range 1–20 K.^{2,15}

Up to now, there has been only little information on the microscopic motion at the boson peak. In vitreous silica, the neutron scattering spectra in the frequency range of the boson peak were interpreted as a sum of sound waves and coupled librations of the corner-connected SiO_4 tetrahedra.¹⁵ These modes in silica are at present the subject of a large number of numerical investigations.^{7,16-18}

Another well-studied example is a computer glass,^{19,20} soft spheres with a repulsive $1/r^6$ potential between the at-

oms and held together by external pressure. There, one finds a chainlike eigenvector for both the low-frequency vibrations and the low-barrier relaxations. The chain is formed by nearest-neighbor atoms which move in phase parallel to the direction of the chain. Such a motion will not stress the strong springs between nearest neighbors. A similar motion was also reported in a molecular-dynamics simulation of the network glass former B_2O_3 .¹ In the present paper, we identify this motion experimentally in the real system B_2O_3 by coherent inelastic neutron scattering.

B_2O_3 is one of the classical covalent glass formers, with an important advantage for the study of the puzzling fast picosecond dynamics of glasses: the flow process remains slow up to very high temperatures, much higher than the glass transition temperature $T_g = 523$ K. In consequence, one finds practically undamped transverse sound waves in the Brillouin scattering frequency range around 10 GHz up to temperatures of 1500 K.^{21,22} Thus one can study the picosecond dynamics up to high temperatures in the liquid without having to separate slow and fast processes. At these high temperatures, one obtains strong inelastic neutron signals which provide detailed microscopic information on the atomic motion.

The samples contained isotopically pure ^{11}B in order to avoid the strong neutron absorption of the natural isotope mixture. Neutron-scattering spectra were measured using the cold neutron time-of-flight spectrometer IN6 at the Institute Laue-Langevin, Grenoble, with an incoming wavelength of 4.1 Å. The neutron data were corrected for the empty con-

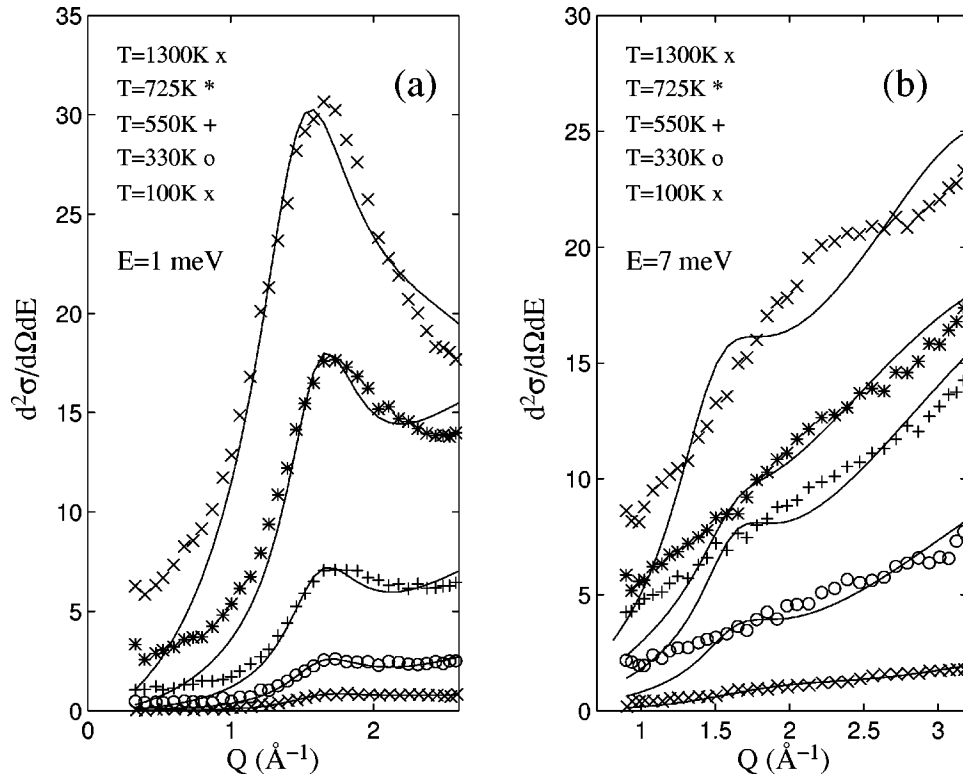


FIG. 1. Q dependence of the inelastic scattering in B_2O_3 at different temperatures (a) at 1 meV (b) at 7 meV. The lines show the result of the analysis.

tainer signal, the tails of the elastic line and for the multiple scattering, assuming the latter to be independent of the momentum transfer Q . Figure 1 shows the Q dependence of the corrected inelastic scattering for two energy transfers, 1 meV in Fig. 1(a) and 7 meV in Fig. 1(b). One notes that the first sharp diffraction peak around 1.6 \AA^{-1} is reflected in the inelastic data at 1 meV, but not at the higher frequency. The data corroborate an earlier room-temperature measurement.²³ The finding is similar to results in polybutadiene.²⁴ In that case, however, the analysis was more difficult because then the slow and fast processes already merged at temperatures only slightly above the glass transition temperature.

The coherent neutron-scattering spectra suggest the presence of two kinds of low-frequency motion: an in-phase motion reproducing the first sharp diffraction peak in $S(Q)$, and an uncorrelated motion of atoms. A quantitative analysis can be performed by decomposing the inelastic scattering into two components, proportional to $Q^2 S(Q, 0)$ (Ref. 25) and $Q^2 e^{-2W}$,²⁴ respectively. That analysis can even be carried out at elevated temperatures, describing the multiphonon scattering to a reasonable approximation in terms of an effective frequency-dependent Debye-Waller exponent.^{26,27} The continuous lines in Fig. 1 show the result of such a fit. Note that the description is by no means perfect: At higher temperatures there is an unexplained component of the scattering at small Q for both frequencies, and the general Q dependence is only poorly fitted at 7 meV. Nevertheless, such a simple approach describes surprisingly well the temperature and momentum transfer of the spectra. In particular, it gives a rough description of the disappearance of the sharp diffraction peak in the inelastic scattering with increasing frequency, giving a quantitative fit of the main feature.

Such an analysis yields two partial densities of states: an in-phase part $g_{in}(\omega)$ corresponding to the $Q^2 S(Q, 0)$ part, and a quasi-incoherent part $g_{inc}(\omega)$ corresponding to the $Q^2 e^{-2W}$ part. The total density of states is then the sum of the two. In Fig. 2 we present the results for the density of states corresponding to the in-phase and the quasi-incoherent motions, respectively, for temperatures from 100 to 1300 K. The total density of states is not shown. However, it is easy to anticipate the boson peak at 2.5 meV as the sum of the two contributions at low temperature.

The data in Fig. 2 are presented as $g(E)/E^2$ versus the energy transfer $E = \hbar\omega$. In such a diagram, the Debye sound wave density of states appears as a constant, which can be calculated from the density and the sound velocities.²¹ The wavelength of a transverse sound wave at an energy transfer of 2 meV is still 40 \AA , much longer than the distance of 4 \AA between the atomic neighbors responsible for the first sharp diffraction peak. Thus the sound waves, at least those at the boson peak and below, have to be counted as part of the in-phase density of states.²⁵

The results in Fig. 2 show almost no change in $g(E)$ up to T_g , whereas both the in-phase and the quasi-incoherent contributions increase between 550 and 925 K. In the same temperature range there is a strong decrease of the sound velocities,²¹ which leads to an increase of the sound wave density of states by a factor of 5–6. Figure 2, however, demonstrates that the sound waves alone are not enough to explain the full in-phase density of states. At low temperatures the in-phase part extrapolates to the Debye limit given by the Brillouin sound velocities at low frequency,²¹ but between zero frequency and boson peak there is a peak of the in-phase density of states exceeding the limiting Debye value

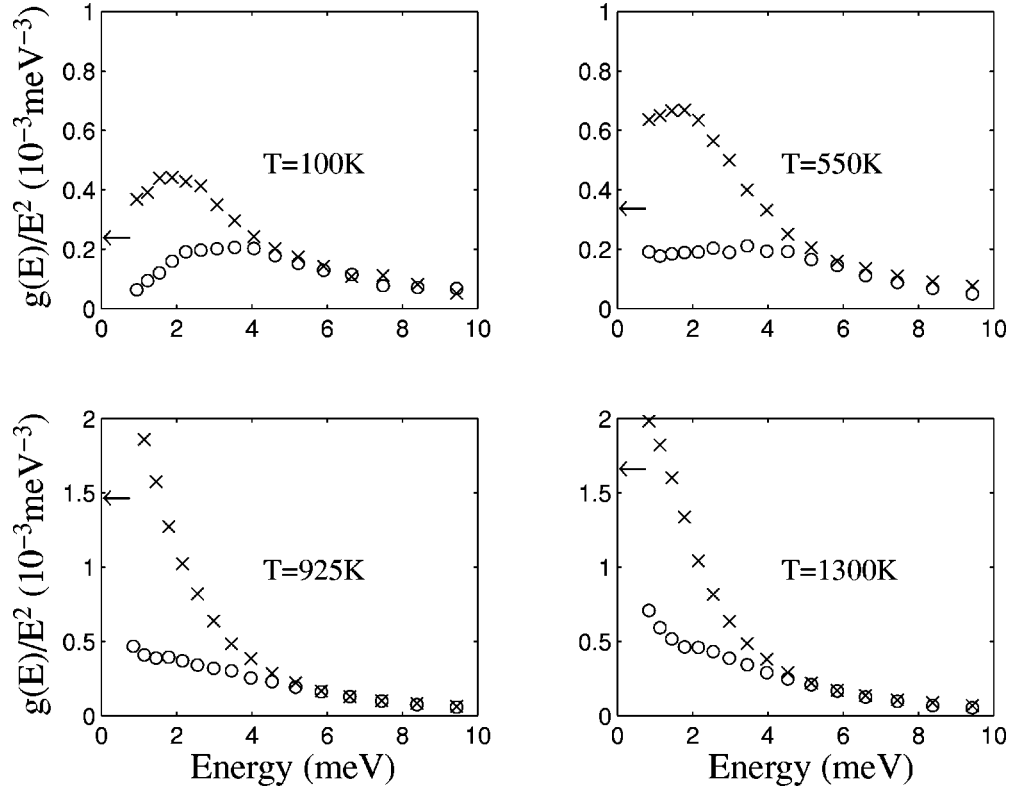


FIG. 2. Fit results in terms of a total effective density of states decomposed into in-phase (cross) and quasi-incoherent (rings) excitation parts (note the different scales). Arrows indicate Debye values.

by a factor of 2. Above the glass transition temperature $T_g = 523$ K, one even finds a clear excess over the Debye limit at the low-frequency end of the measurement (and in the extrapolation to zero frequency).

This shows that both the excess modes of the boson peak as well as the fast relaxational picosecond motion above T_g have a sizable in-phase component in their motion. This is the main result of the present paper, much clearer shown than in the similar polybutadiene case.²⁴ In the following, we discuss the significance of the result on a microscopic level.

Let us first recall that the appearance of diffraction peaks is due to atomic pair correlations. In order to include the atomic motion into the pair-correlation scheme, the simplest way is to consider a single pair of atoms at a distance d . We neglect Debye-Waller factors, and assume the scattering lengths to be identical. The first atom is situated at $+d/2$ and the second one at $-d/2$ in the z direction. Let θ be the angle between the momentum transfer \mathbf{Q} and the z direction. Then the directional average over the elastic scattering per atom in all possible directions of \mathbf{Q} is given by

$$\begin{aligned} & \frac{1}{4} \int_0^\pi d\theta \sin \theta |e^{i(Qd \cos \theta)/2} + e^{-i(Qd \cos \theta)/2}|^2 \\ & = 1 + \frac{\sin(Qd)}{Qd}. \end{aligned} \quad (1)$$

The diffraction peak of that correlation appears at $Qd \approx 5\pi/2$.

Now we turn to the inelastic scattering. We consider a mode in which the first atom has an amplitude \mathbf{u}_1 and the

second an amplitude \mathbf{u}_2 . Then the inelastic scattering from that mode at the mode frequency in the one-phonon approximation is proportional to

$$\begin{aligned} & \frac{1}{2} |(\mathbf{Q}\mathbf{u}_1)e^{i(Qd \cos \theta)/2} + (\mathbf{Q}\mathbf{u}_2)e^{-i(Qd \cos \theta)/2}|^2 \\ & = 2(\mathbf{Q}\mathbf{u}_i)^2 \cos^2 \frac{Qd \cos \theta}{2} + 2(\mathbf{Q}\mathbf{u}_a)^2 \sin^2 \frac{Qd \cos \theta}{2} \end{aligned} \quad (2)$$

where

$$\mathbf{u}_i = \frac{\mathbf{u}_1 + \mathbf{u}_2}{2}, \quad \mathbf{u}_a = \frac{\mathbf{u}_1 - \mathbf{u}_2}{2} \quad (3)$$

are the in-phase and antiphase parts of the motion in the mode, respectively.

The result shows that the two contributions decouple, i.e., one can calculate the inelastic intensity for in-phase and antiphase motion separately, and then add the results together. The same holds for motions parallel and perpendicular to the z direction, at least after the orientational average. The motion parallel to z enters with a $\cos \theta$ factor and the motion perpendicular to z with a $\sin \theta$ factor, so the cross-terms cancel in the averaging.

In consequence, it suffices to calculate the four pure cases, in-phase and antiphase motion parallel and perpendicular to the line connecting the two atoms. The first and most important is the motion of both atoms in phase along the connecting line. For that case, the orientational average yields

$$\begin{aligned}
Q^2 u_i^2 \int_0^\pi d\theta \sin\theta \cos^2\theta \cos^2\frac{Qd \cos\theta}{2} \\
= \frac{Q^2 u_i^2}{3} \left(1 + \frac{3 \sin(Qd)}{Qd} + \frac{6 \cos(Qd)}{Q^2 d^2} - \frac{6 \sin(Qd)}{Q^3 d^3} \right).
\end{aligned}
\tag{4}$$

At and above the first sharp diffraction peak at $Qd \approx 5\pi/2$, the last two terms on the right-hand side of this equation play no large role. The main interference pattern is contained in the $\sin(Qd)/Qd$ term, which reproduces the elastic peak. In the inelastic signal, however, its relative weight is a factor of 3 higher than in the elastic scattering. That shows that the inelastic scattering is highly sensitive to this particular kind of motional correlation.

The same holds if the two atoms move against each other along the line connecting them. One obtains the result of Eq. (4) with a change of sign for all the trigonometric functions on the right-hand side. Where the in-phase inelastic scattering has a peak, the antiphase scattering has a minimum, and vice versa. Looking at Fig. 1(b), one has the impression that the data exhibit such an antiphase component, though not as strong as the in-phase peak at lower frequency in Fig. 1(a).

For motion perpendicular to the line connecting the two atoms, be it in phase or antiphase, the $\sin(Qd)/Qd$ term cancels, and one is only left with the smaller oscillation of the additional terms. Thus most of the interference pattern in the inelastic scattering comes from correlated motions along the line connecting atomic neighbors.

With this result in mind, we again look at the results in Fig. 2. The in-phase $Q^2 S(Q)$ component at low frequencies appears to be significantly higher than the expected Debye-like sound wave part of the motion. Obviously the atoms responsible for the first sharp diffraction peak move in phase along the line connecting them not only in the sound waves, but also in the excess modes, at least for frequencies lower than the boson peak frequency.

As pointed out above, that tendency has been seen before both in numerical simulations of B_2O_3 (Ref. 1) and simulations of a quite different glass former, a soft sphere model glass,^{19,20} where the low-frequency resonant vibrational

modes and the low barrier relaxational modes had a chainlike eigenvector, with the chain direction along the displacement direction of the atoms.

In principle, such a behavior is physically plausible: A mode with a large mean-square displacement is only possible if the restoring force constants are small. This means that the stretching of the strong longitudinal springs between atoms should be small. That requirement is fulfilled if the atoms move together along the connecting line. It seems to be fulfilled even in B_2O_3 , where the first sharp diffraction peak comes from atom pairs bonded only by the weak van der Waals forces.

We now return to the question of the separability of the sound waves and the additional modes. At low frequency, we are used to think in terms of long-wavelength hydrodynamic modes which interact with the microscopic motion. It is not clear whether the same concept is still a good basis at the boson peak frequency. Numerical simulations are beginning to explore that question, but are still hampered by the limited cell size.^{28,29} Recent x-ray Brillouin scattering data^{4,5,30} seem to support the hydrodynamic concept. They still show recognizable longitudinal sound waves, though strongly damped, above the boson peak. On the other hand, in our present results in Fig. 2 the in-phase density of states as well as the total density of states fall below the Debye value at relatively low frequency, in particular at higher temperatures. What is the reason for this marked decay of both contributions at higher frequencies?

There are at least two possible answers to this question. The first is that the sound waves and other modes in this frequency range are strongly damped. As a result their response shifts to lower frequencies giving, in particular, the excess over the Debye level density of the ‘‘in-phase’’ motion. This agrees with the results of inelastic x-ray scattering which show a strong broadening of the longitudinal modes above the boson peak frequency⁵ and with ideas presented in Ref. 2. The second possibility is a positive dispersion of the transverse sound waves, which account for 90% of the sound wave density of states. Such a positive dispersion is indeed known for crystals having a layer structure like graphite³¹ or a linear structure like polyethylene³² (B_2O_3 is believed to have a layerlike structure, at least locally). Our present data, however, do not allow to decide that question unequivocally.

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