Floppy modes and the Boson peak in crystalline and amorphous silicates: an inelastic neutron scattering study

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ABSTRACT

We present the results of an inelastic neutron scattering study of a crystalline polymorph of SiO_2 (α-quartz), and a number of silicate glasses (pure silica, SiO_2, and three glasses in the alkali silicate series $(K,Li)_2Si_2O_5$). We demonstrate the presence of the Boson peak in the inelastic spectra of both the crystalline and amorphous materials and argue that it arises simply from the dispersion characteristics of transverse acoustic modes. Furthermore, we investigate the role of the lower-energy floppy modes in the inelastic spectra, and show that they are controlled by chemical effects.

KEYWORDS: floppy modes, Boson peak, silicates, neutron scattering, inelastic spectra.

Introduction

So many amorphous materials display low-temperature anomalies in their specific heats that they are generally regarded as being universal properties of the glassy state. These anomalies are usually of two kinds. The first concerns the observation that, while many crystals obey the Debye law $C \propto T^3$ for temperatures less than say, 1 K, glasses with the same chemistry frequently display the law $C \propto T$ at correspondingly low temperatures (Phillips, 1987). In addition, glasses such as silica, SiO_2, contain an excess specific heat over crystalline phases in a higher temperature regime, where $T \approx 10$ K. This second observation is tied in with the appearance of the ubiquitous Boson peak in inelastic neutron and Raman spectra (Buchenau *et al.*, 1988). The name 'Boson peak' refers to the fact that the temperature dependence of its intensity scales roughly with the Bose-Einstein distribution.

Until recently, the two anomalies were rather poorly understood at the microscopic level. It was known that both must be reflected in the structure of the vibrational density of states of the glassy state. Dove *et al.*, (1997) demonstrated that the Boson peak arises largely from a flattening of the dispersion of the transverse acoustic modes, in a manner similar to that which occurs in a crystalline material at its Brillouin zone boundary. This idea is not new, being originally suggested by Leadbetter (1969), and recently developed further by Elliott (1996) and Taraskin and Elliott (1997*a,b*). What was new was that further experimental support for this model was provided by the demonstration that the presence of floppy modes can alter significantly the inelastic spectrum. This explained why certain glasses (particularly alkali silicate glasses, which are necessarily more fragile than silica) appear not to contain a Boson peak. The Boson peak is still there, but masked by the large numbers of low-energy floppy modes.

Floppy modes are low-energy deformations of a structure composed of a network of relatively rigid structural units, such as silicate tetrahedra. These units can rotate against each other without distortion, such that the overall structure undergoes a type of low-energy flexing motion. In this paper, we will develop these arguments further,

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by investigating the inelastic scattering in a further number of materials, and particularly the effect of doping alkali silicates with different cations.

Experimental details

Our inelastic neutron scattering data were obtained using the PRISMA time-of-flight neutron spectrometer at the ISIS Facility. Approximately 20 g of each sample were ground up to a fine powder and placed in a vanadium can. PRISMA is an indirect geometry machine, with five sets of double-bounce analyser/detector arms spaced at $10°2θ$. All analysers were set to an analysing energy of 12.7 meV, and pyrolytic graphite filters were used to reduce contamination from higher-order analyser reflections. Two settings of the whole detector arm were measured for each sample, so that the measured range in wavevector was from ~2 to 6 Å^{-1}, with a range in energy transfer from -8 to 30 meV. The energy resolution was ~0.8 meV (FWHM). The spectra were normalized against standard vanadium scans and corrected using in-house software. The signals from the background and empty can were subtracted and the data were corrected for the effects of multiple scattering and normalized against the different masses of the samples. The resultant spectra were then divided through by the detailed balance factor, $n(E)+1$.

The data were analysed further in two different ways. First, we obtained the neutron scattering function $S(E)$ by integrating the spectra over all Q values accessed in this experiment. Note that $S(E) \propto g(E)/E^2$, where $g(E)$ is the vibrational density of states. Second, we plotted contour maps of the inelastic scattering cross-section $d\sigma/d\Omega dE$ as a function of the wavevector transfer, Q, and energy transfer, E.

Experimental results

The neutron scattering function, S(E), and the density of states

In Fig. 1 we show the inelastic spectra, $S(E)$, of vitreous silica measured at temperatures of 300 and 873 K. The most obvious feature in the spectra is a strong peak at an energy transfer of ~5 meV. This is the Boson peak, which, as we have discussed in the introduction, is due to a flattening-off of the transverse acoustic modes around a quasi-Brillouin zone boundary. Note that
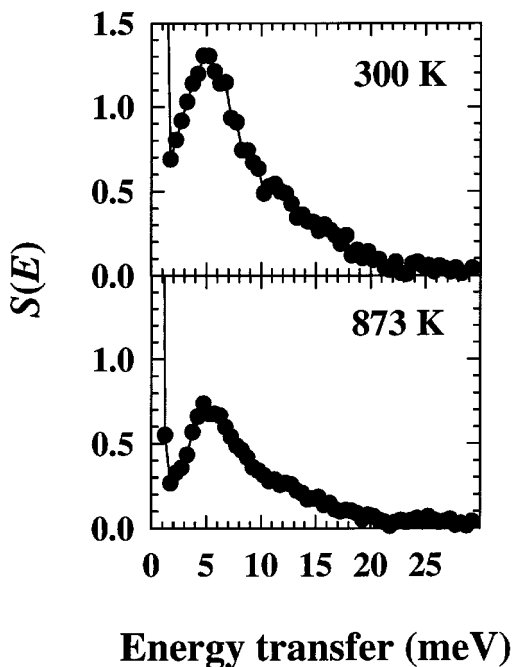

FIG. 1. The inelastic neutron scattering function, $S(E)$, for vitreous silica measured at temperatures of 300 and 873 K.

the detailed balance factor has been divided out of these spectra. On heating, the Boson peak decreases in intensity, which is perhaps due to the effect of the Debye – Waller factor for the transverse acoustic modes. What is perhaps less obvious in both spectra is that there is a small amount of scattering at lower energies than the Boson peak, which becomes clear when the data are compared with the spectrum for α-cristobalite, as was done by Dove *et al.* (1997). This low energy scattering was demonstrated as being due to floppy modes.

For comparison with the glass spectra, in Fig. 2 we show the inelastic spectrum, $S(E)$, of crystalline α-quartz, measured at 300 K. The sharp peak at ~8 meV is the effective Boson peak, which again is due to the dispersion of the transverse acoustic modes, the lowest branch of which flattens-off at ~8 – 10 meV, a higher energy than those in α-cristobalite (Dove *et al.,* 1997). In Fig. 3, we show spectra of three alkali silicate glasses, measured at 300 K. The data scatter in these spectra is greater than those in Figures 1 and 2, but the general trends are clear: in $Li_2Si_2O_5$, the Boson peak is apparent at an energy of ~6 meV,
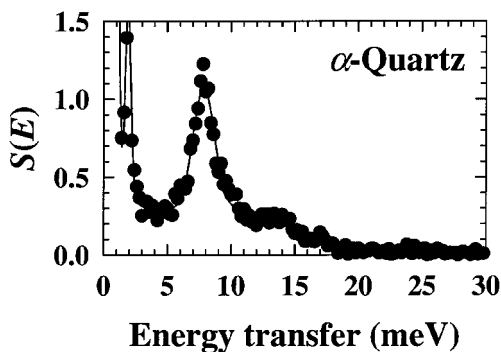
FIG. 2. The inelastic neutron scattering function, $S(E)$, for crystalline α-quartz, measured at a temperature of 300 K.

with a number of floppy modes present at lower energies, partially filling the gap between the Boson peak and the elastic line. As K^+ ions are added to the structure, the floppy modes become stronger, so that in the mixed $LiKSi_2O_5$ glass and the pure $K_2Si_2O_5$ glass, the Boson peak is completely hidden beneath the large numbers of floppy modes. Note that there is no discernible difference between the spectra for $LiKSi_2O_5$ and $K_2Si_2O_5$.

Contour maps of the inelastic neutron scattering

We now go on to discuss the contour maps of the inelastic scattering. In Fig. 4 we show the (Q,E) map of the inelastic scattering from vitreous SiO_2 at 300 K. The dominant feature of the spectrum is the line of intensity at a roughly constant energy transfer of ~5 meV (together with its effective mirror image at −5 meV), peaking around $Q = 3$ Å^{-1} and extending continuously to higher wavevectors. The intensity increases as the wavevector is increased, scaling roughly with Q^2. This feature has been studied previously by Buchenau *et al.* (1988), and is of course, the Boson peak. As the wavevector increases, and the inelastic scattering becomes stronger and stronger, intensity appears at higher energies as well, extending out to ~20 meV. This scattering is presumably from the longitudinal acoustic mode and the optic modes.

In Fig. 5 we show the contour map of the inelastic scattering from K-disilicate glass ($K_2Si_2O_5$) at a temperature of 300 K. The scattering takes on a rather different form from that in vitreous SiO_2: while there is clearly
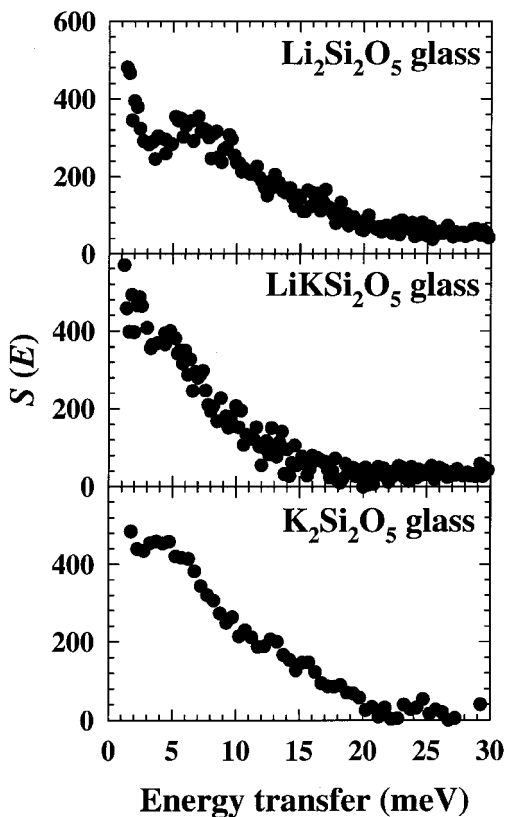

FIG. 3. Inelastic neutron scattering function, $S(E)$, for three alkali silicate glasses measured at 300 K.

scattering at energies of ~5 meV extending from $Q \approx 3$ Å^{-1} to higher wavevectors, the bulk of the scattering appears more localized in Q, around 3 Å^{-1} and 5 Å^{-1}.

Discussion

First of all, we will discuss the effect of changing the alkali ion from Li^+ to K^+ in the alkali disilicate glasses, whose spectra are illustrated in Fig. 3. The main point is that the floppy modes increase as Li^+ is substituted by K^+. This is readily understood when one considers that the oxygen environment of the Li^+ ion in Li-disilicate is known to be tetrahedral and reasonably well-defined (Hannon *et al.*, 1992), with a Li−O bond length of ~2.0 Å. On the other hand, in K-disilicate glass, the K^+ environment is rather more poorly defined, with a coordination number between 4 and 7, and an approximate K−O bond
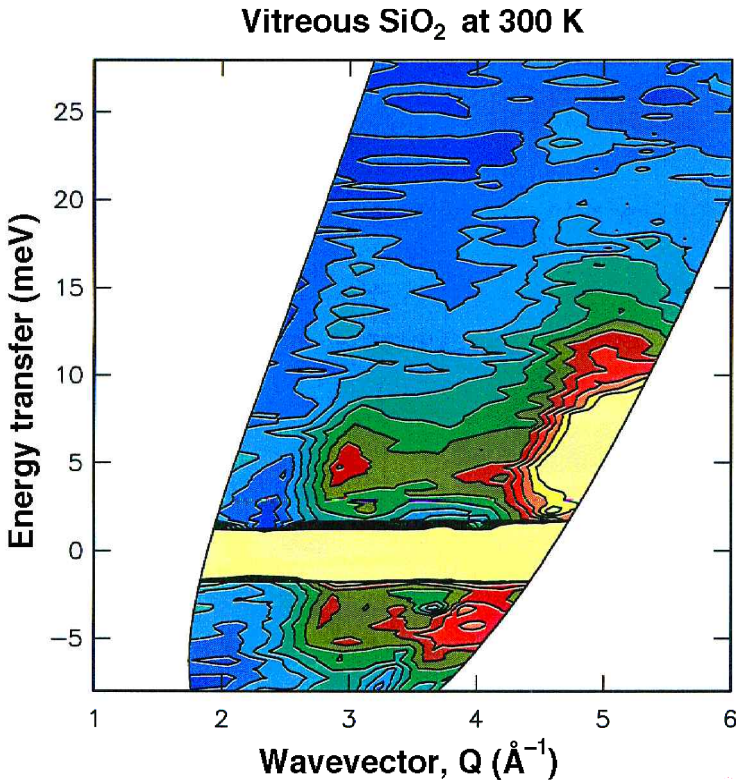
Vitreous SiO$_2$ at 300 K

Fig. 4. A contour map of the neutron scattering cross section, dσ/dΩdE, for vitreous silica at a temperature of 300 K.

length of 2.7 Å. The result is that the cavities in the silicate network which contain the alkali ions are larger and more irregular in K-disilicate than in Li-disilicate, so that there are more locally floppy regions. Consequently, K-disilicate contains considerably more floppy modes than Li-disilicate. We note that a simple mode-counting argument (as used in Dove *et al.,* 1997) predicts that both Li-disilicate and K-disilicate should contain the same number of floppy modes, because it does not take account of the different ionic radii and bonding character-istics of the alkali ions.

We now turn to the contour maps of the inelastic scattering shown in Figs 4 and 5, beginning with vitreous silica (Fig. 4). It is straightforward to show that the scattering from the transverse acoustic modes in a polycrystalline sample will take on the form of a line of scattering spread out in **Q**, but centred on the zone boundary energy. The intensity of the scattering should peak at **Q** positions corresponding to the two strong

Bragg peaks in the diffraction pattern. The crucial point is that there will be a gap between zero energy and the line of scattering. Looking at Fig. 4, this is exactly what happens in vitreous silica. The Boson peak is apparent as the line of scattering at a roughly constant energy transfer of 5 meV which, as we have already suggested, corresponds to the energy where the dispersion of the transverse acoustic modes must flatten off. The first peak in the intensity of this line of scattering is at $Q = 3$ Å^{-1}, which corresponds to a strong peak in the elastic structure factor of vitreous silica (e.g. Buchenau *et al.,* 1988). We therefore consider that this may be taken as a quasi-Bragg peak, and so is very closely related to the spectrum of a crystal. We believe that this argument demonstrates clearly that the Boson peak is due to the transverse acoustic modes.

In contrast, the spectrum of vitreous K-disilicate shown in Fig. 5 shows no obvious line of scattering representing the Boson peak. Instead, the scattering is rather more localized in
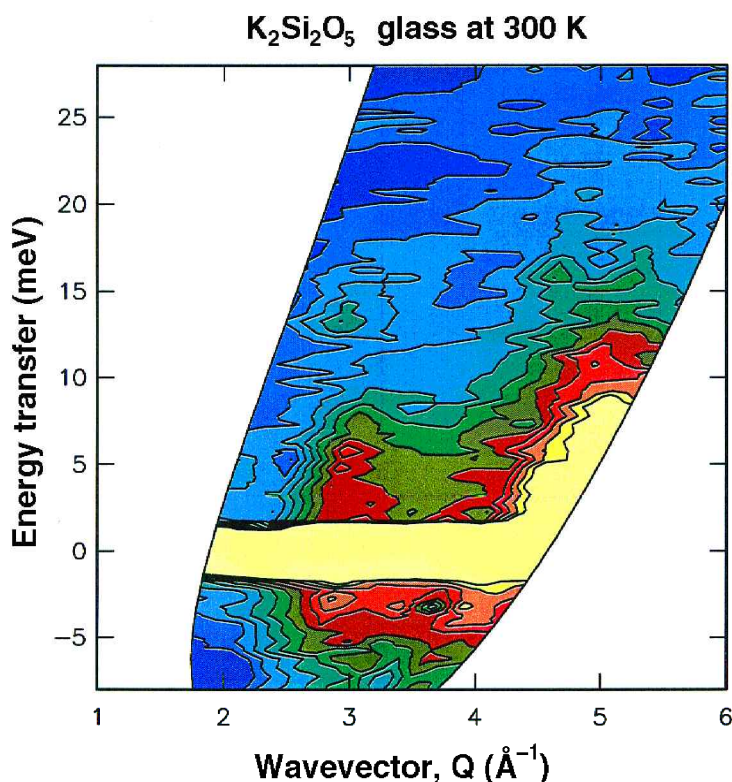
$K_2Si_2O_5$ glass at 300 K

FIG. 5. The neutron scattering cross section for amorphous $K_2Si_2O_5$ at a temperature of 300 K.

Q. Note in particular, the strong scattering in the 300 K spectrum which extends from the diffraction peak at $Q = 3 \text{ Å}^{-1}$ up to the Boson peak energy of 5 meV. This scattering is largely due to the floppy modes, which we suggest represent a whole series of rather flat acoustic branches fanning out from the strong peak of elastic scattering at $Q = 3 \text{ Å}^{-1}$.

Conclusions

We have presented inelastic neutron results from a study of the Boson peak and floppy modes in a number of silica glasses. The data provide strong support for earlier suggestions that the Boson peak arises from the dispersion characteristics of the transverse acoustic modes. The role of floppy modes in alkali silicate glasses has also been investigated, and unlike the Boson peak, which is due to relatively well-defined transverse acoustic modes, the floppy modes are spread out over a wide energy range. Furthermore, the alkali cations

Li^+ and K^+ are shown to produce qualitatively different inelastic spectra, related to the relative sizes of the cavities introduced into the silicate network to accommodate them.

Acknowledgements

References

Buchenau, U., Zhou, H.M., Nucker, N., Gilroy, K.S. and Phillips, W.A. (1987) Structural relaxation in vitreous silica. *Phys. Rev. Lett.,* **60**, 1318–21.

Dove, M.T., Harris, M.J., Hannon, A.C., Parker, J.M., Swanson, I.P. and Gambhir, M. (1997) Floppy modes in crystalline and amorphous silicates. *Phys. Rev. Lett.,* **78**, 1070–3.

Elliott, S.R. (1996) Comment on 'Phonons in glasses:

Numerical simulations and phenomenological theory'. *Phys. Rev. Lett.,* **77**, 4105.

Hannon, A.C., Vessal, B. and Parker, J.M. (1992) The structure of alkali silicate glasses. *J. Non-Cryst. Solids*, **150**, 97–102.

Leadbetter, A.J. (1969) Inelastic cold neutron scattering from different forms of silica. *J. Chem. Phys*., **51**, 779.

Phillips, W.A. (1987) Two-level states in glasses. *Rep. Prog. Phys*., **50**, 1657–1708.

Taraskin, S.N. and Elliot, S.R. (1997*a*) Phonons in vitreous silica: dispersion and localization. *Europhys. Lett.*, **39**, 37–42.

Taraskin, S.N. and Elliot, S.R. (1997*b*) Nature of vibrational excitations in vitreous silica. *Phys. Rev. B*, **56**, 8605–22.