



Acoustic nature of the boson peak in vitreous silica

C. MASCIOVECCHIO†, V. MAZZACURATI‡, G. MONACO‡, G. RUOCCO‡,
T. SCOPIGNO‡, F. SETTE†, P. BENASSI‡, A. CUNSOLO†, A. FONTANA§¶,
M. KRISCH†, A. MERMET†, M. MONTAGNA§, F. ROSSI§, M. SAMPOLI||,
G. SIGNORELLI‡ and R. VERBENI†

† European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, Cedex, France

‡ Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università dell' Aquila, I-67100 L'Aquila, Italy

§ Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Trento, I-38100 Trento, Italy

|| Dipartimento di Energetica and Istituto Nazionale per la Fisica della Materia, Università di Firenze, I-50139 Firenze, Italy

ABSTRACT

New temperature-dependent inelastic X-ray scattering (IXS) and Raman scattering (RS) data are compared with each other and with existing inelastic neutron scattering (INS) data in vitreous silica, in the 300–1775 K region. The IXS data show collective propagating excitations up to $Q = 3.5 \text{ nm}^{-1}$. The temperature behaviour of the excitations at $Q = 1.6 \text{ nm}^{-1}$ matches that of the boson peak found in INS and RS. This supports the fact that the acoustic origin of the excess of vibrational states gives rise to the boson peak in this glass.

A peculiar characteristic of disordered solids, not present in their crystalline counterpart (Phillips 1981), is an excess of low-frequency states with respect to the predictions of the Debye theory. Inelastic neutron scattering (INS) studies on the density of states $g(\omega)$ reveal, in fact, a broad peak (the boson peak (BP)) in the quantity $g(\omega)/\omega^2$ (Buchenau *et al.* 1986, 1988, Sokolov *et al.* 1995) at energies 2–10 meV ($15\text{--}80 \text{ cm}^{-1}$), where the Debye theory would predict a constant. This excess is responsible for the presence, in any glass studied so far, of a bump in the temperature dependence of C_p/T^3 (Sokolov *et al.* 1993, Brodin *et al.* 1994).

The broad BP feature is also observed in the Raman scattering (RS) spectra. This can be understood by considering that the first-order RS intensity $I(\omega)$ in the harmonic approximation is connected to $g(\omega)$ (Galeneer and Sen 1978): $I(\omega) = C(\omega)g(\omega)[n(\omega, T) + 1]/\omega$. Here $n(\omega, T)$ is the Bose population factor and $C(\omega)$ is the photon excitation coupling function, assumed to have a smooth behaviour in the considered energy region (Fontana *et al.* 1987, 1997).

The nature of this excess of states is still subject to speculation and, at present, there are two different prevailing hypotheses (for example Fontana and Viliani (1995)). In the first hypothesis, the excess of states is explained by the localization of the high-energy vibrational modes induced by the static disorder in the glass. In

¶ Email: afontana@science.unitn.it.

the second case, collective propagating modes are thought to persist at high frequencies, and the BP reflects their density of states. In the first view the BP energy corresponds to the energy of the high-Q excitations, while in the second case the excitations are expected to propagate at energies above the BP energy.

Information on the character of the excitations contributing to the boson peak can be obtained from measurements of the dynamic structure factor $S(Q, \omega)$. Using inelastic X-ray scattering (IXS) (Sette *et al.* 1995), it has been possible to measure the $S(Q, \omega)$ values for different glasses in the momentum–energy region of the BP, and to support the hypothesis of the acoustic-like character of the collective modes and therefore of the peak itself (Masciovecchio *et al.* 1996c, 1999). In the specific case of vitreous silica ($v\text{-SiO}_2$), however, the IXS data have been alternatively interpreted either with the phonon localization model (Foret *et al.* 1997) or as propagating excitations (Benassi *et al.* 1997, Masciovecchio *et al.* 1997).

A better insight into the relation between the excitations seen in $S(Q, \omega)$ and the BP could be gained by comparing the temperature dependences of their energies. The basic idea is to utilize the observation that in $v\text{-SiO}_2$, in contrast with the majority of glasses, the low-frequency sound velocity, measured by Brillouin light scattering (BLS) (Vacher and Pelous 1976) and the boson peak energy (Wischniewski *et al.* 1998) shift towards higher values with increasing temperature and, more importantly, the rates of change reported in the two cases are different. It is not the aim of this work to account for these peculiarities, which are probably due to the specific shape of the interatomic potential in silica. Rather, one can utilize the different temperature dependences of excitations with different Q , as seen by IXS, INS, RS and BLS, to establish a link between specific vibrational states and the features of the density of states. In particular, one can assess whether the excitations observed by IXS at energies comparable with the BP energy have either a temperature behaviour similar to that of the BP, or to that of the low- Q excitations measured by BLS, or even another dependence.

In this paper we report temperature-dependent IXS and RS data of $v\text{-SiO}_2$. In the IXS spectra, propagating collective excitations are found at $T \approx 1400$ K, thus confirming that the high frequency longitudinal dynamics have an acoustic-like nature in the whole temperature region below melting, and up to a momentum transfer $Q = 3.5 \text{ nm}^{-1}$, corresponding to energies more than twice the BP energy ($E_{\text{BP}} \approx 4 \text{ meV}$ at room temperature). More importantly, we find the same temperature shift for the BP energy and for the energy $\Omega(Q)$, of the modes at $Q^* = 1.6 \text{ nm}^{-1}$ ($\Omega(Q^*) \approx E_{\text{BP}}$). This supports the argument that the acoustic modes, probed by the IXS, give a significant contribution to the BP.

The IXS experiment was carried out at the very-high-energy-resolution IXS beam line (BL21/ID16) at the European Synchrotron Radiation Facility. The total resolution function, measured using a Plexiglas scatterer at the maximum of its static structure factor ($Q = 10 \text{ nm}^{-1}$), has a full width at half-maximum (FWHM) of $1.5 \pm 0.1 \text{ meV}$. The Q values were selected between 0.75 and 4 nm^{-1} , and the Q resolution was set to 0.2 nm^{-1} FWHM. Energy scans were performed by varying the relative temperature between the monochromator and the analyser crystals by $\pm 0.45 \text{ K}$ with a step of 0.0075 K . Each scan took about 200 min, and each Q value was obtained by averaging five scans (the total integration time was 500 s per point). The data were normalized to the intensity of the incident beam. Further details on the IXS beam line have been reported elsewhere (Masciovecchio *et al.* 1996a,b,c, Verbeni *et al.* 1996). The RS measurements were performed using a standard Raman

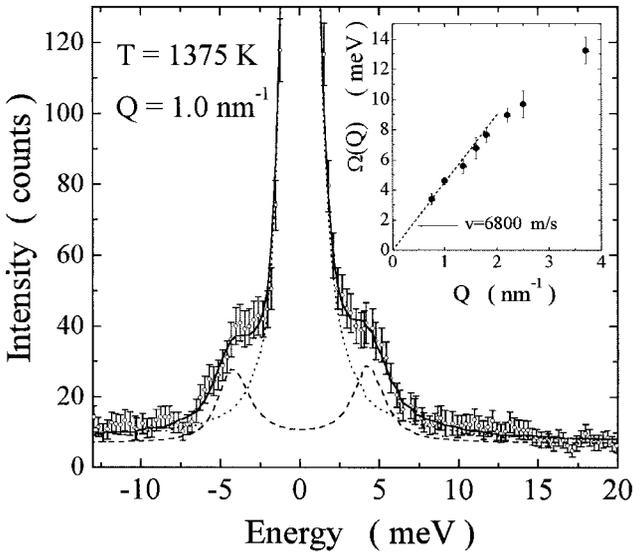


Figure 1. IXS spectrum of v -SiO₂ at $T = 1375$ K and $Q = 1 \text{ nm}^{-1}$ (○): (—), best fit to the data as discussed in the text; (---), elastic contribution to the fit; (·····), inelastic contribution to the fit. The inset reports the energy of the excitations as derived from the fits: (- - - -), linear extrapolation to small Q , and its slope corresponds to 6800 ms^{-1} .

laser system. Depolarized spectra were collected in the -300 to $+2000 \text{ cm}^{-1}$ frequency range with 1 cm^{-1} frequency resolution. The SiO₂ Suprasil sample, purchased from Goodfellow, was the same rod of 2 mm diameter used by Benassi *et al.* (1997) and Masciovecchio *et al.* (1997).

From the linear dispersion curve determined by a first set of IXS spectra taken at $T = 1375$ K, it was possible to establish that the excitations have the same propagating nature as that previously observed in the 300–1000 K region. In figure 1, we report as an example the IXS spectrum taken at $Q = 1 \text{ nm}^{-1}$, together with the fitting function. As in previous work, the IXS spectra were fitted by the experimentally determined resolution function convoluted with a δ function for the elastic peak and a damped harmonic oscillator (DHO) model (Fak and Dorner 1992) for the inelastic signal. The excitation energies are reported in the inset. The data show an acoustic-like behaviour, linearly extrapolating at small Q with a slope $v = 6800 \pm 200 \text{ ms}^{-1}$. This value, which is larger than the sound velocity measured by BLS (Vacher and Pelous 1976), implies a deformation of the acoustic branch not recognized before; this will provide an interesting subject for further investigations. The dispersion relation covers the whole BP energy region (approximately 5–7 meV) and reaches energies as high as 15–20 meV. These observations, as in previous lower-temperature measurements, show that, even at temperatures approaching T_g , an acoustic-like propagating mode exists up to energies that lie well above E_{BP} .

A second set of IXS measurements was performed as a function of temperature at the fixed value $Q^* = 1.6 \text{ nm}^{-1}$, which was chosen since $\Omega(Q^*)$ is in the range of E_{BP} at room temperature. The IXS data and the corresponding fits are shown in figure 2. It is possible to observe directly from the raw data that the intensity and energy of the inelastic excitation increase with increasing T . This is emphasized in the

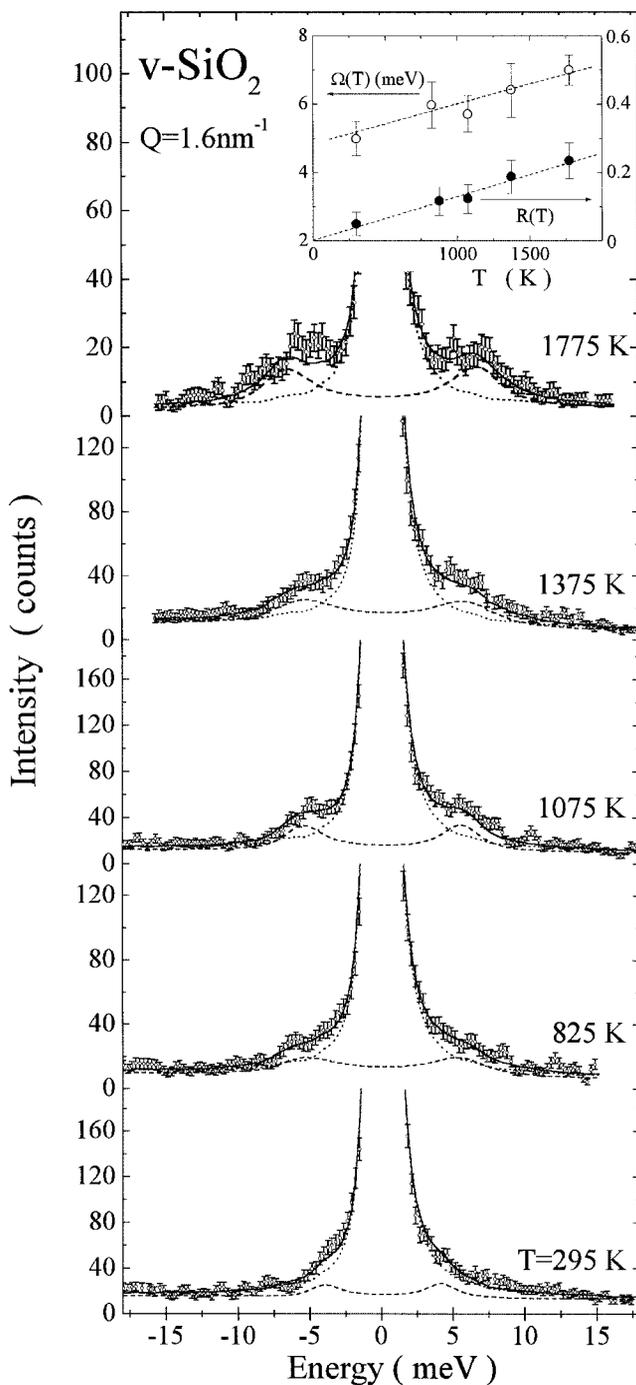


Figure 2. X-ray spectra of v-SiO₂ at $Q = 1.6 \text{ nm}^{-1}$ taken at different temperatures. The data are shown together with their best fits (—) and the individual contributions to the fitting function: elastic peak (·····) and inelastic components (---). In the inset are reported firstly the inelastic-to-elastic intensity ratio $R(T)$ (●), which follows the expected linear behaviour, and secondly the excitation energy $\Omega(T)$ (○) derived from the DHO model: (—), their linear fits.

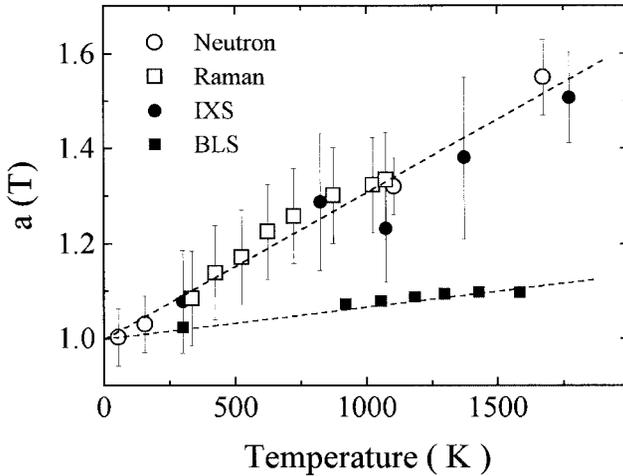


Figure 3. Temperature dependence of the scaling factor $a(T)$, normalized to $a(0) = 1$, for the different spectra: open symbols refer to *incoherent* measurements of the BP INS (○) and RS (□); full symbols are the scaling factors for the excitation energies determined from the dynamic structure factor $S(Q, \omega)$ measured at $Q = 1.6 \text{ nm}^{-1}$ by IXS (●) and at $Q = 0.036 \text{ nm}^{-1}$ by BLS (■); (---), linear guides to the eye to emphasize the differences and similarities between the temperature behaviours of the four data sets.

inset of figure 2, where the T dependence of the inelastic-to-elastic intensity ratio $R(T)$ and the excitation energy $\Omega(Q^*, T)$ are reported.

To compare the T dependence of $\Omega(Q^*, T)$ with that of other spectroscopic features, we define the scaling factor $a_{\text{IXS}}(T)$ as $\Omega(Q^*, T)/\Omega(Q^*, T = 0 \text{ K})$. Here $\Omega(Q^*, T = 0 \text{ K})$ is the $T = 0 \text{ K}$ extrapolation of the measured $\Omega(Q^*, T)$. The values of $a_{\text{IXS}}(T)$ are reported in figure 3, together with the scaling factor $a(T)_{\text{BLS}}$ for the low- Q ($Q \approx 0.036 \text{ nm}^{-1}$) excitation energy determined by BLS (Scopigno 1997). The difference between the T dependences of the low- and high- Q excitations indicates again that the acoustic modes dispersion relation is deformed from a simple linear law. This behaviour was hidden in the error bars in previous IXS and BLS studies (Benassi *et al.* 1997, Masciovecchio *et al.* 1997) and is evidenced here because of increased sensitivity and temperature range. It is not the aim of the present work to discuss the origin of the observed deformation of the dispersion relation[†].

This non-trivial T dependence can help us to assess the origin of the BP by study of the temperature dependence of its energy. In figure 3 we report, in fact, the scaling factor $a_{\text{INS}}(T)$ of the BP energy maximum, as determined from existing INS measurements (Wischniewski *et al.* 1998). The striking similarity between $a_{\text{INS}}(T)$ and $a_{\text{IXS}}(T)$ provides a first strong indication that the states probed by IXS contribute to the BP. This similarity is further confirmed by the temperature dependence of the BP energy as measured by RS in the 300–1100 K region. In figure 4 we report $I(\omega)/C(\omega)/[\ln(\omega, T) + 1]$, which corresponds directly to $g(\omega)/\omega^2$. We used the coupling coefficient $C(\omega)$ derived from the ratio of the INS (Wischniewski *et al.* 1998) and RS (this work) data measured in $v\text{-SiO}_2$ at room temperature; this $C(\omega)$

[†] This effect could, for example, be ascribed to the presence of a positive fourth-order anharmonicity in the next-nearest-neighbour interaction potentials (Scopigno 1997) or to a relaxation process active in the glass.

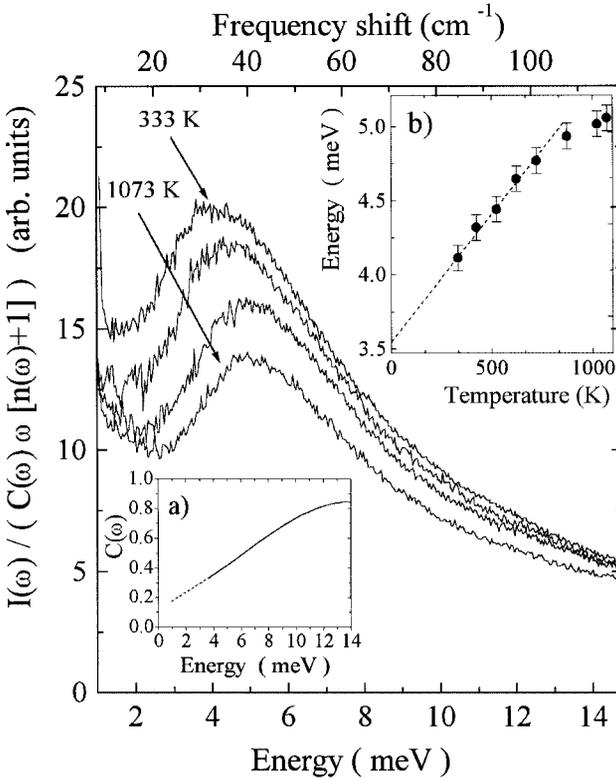


Figure 4. Examples of RS spectra taken, from top to bottom, at 333, 523, 823 and 1073 K. The reported data correspond to the reduced Raman intensities divided by the $C(\omega)$ (Fontana *et al.* 1999) and shown in inset (a). These spectra correspond to $g(\omega)/\omega^2$. In inset (b), the energy position of the maximum intensity at each temperature (\bullet) is reported together with its linear fit in the low-temperature region (---).

is reported in the inset (a) of figure 4, and it was used to scale all the RS spectra at different temperatures[†]. The energy of the maximum of the spectra of figure 4, derived by a local quadratic fit, is reported in inset (b) and the scaling factors $a_{RS}(T)$ are reported in figure 3. The two data sets (INS and RS) are equivalent within the error bar.

In the presence of deformation of the dispersion relation, it is striking to observe the identical temperature behaviours for two spectroscopic features that in principle may share only a similar energy: the BP maximum and the acoustic excitations at $Q^* = 1.6 \text{ nm}^{-1}$. This demonstrates their common origin. Consequently, the high-frequency acoustic excitations, in spite of their propagating nature, must have a density of states exceeding the Debye prediction.

A model that is consistent with a picture of linearly dispersing propagating excitations with an excess of states must take into account the effect of the topological disorder on the eigenvectors of the vibrational modes. It has been shown by molecular dynamics simulation that, in a glass up to the BP energy region, the

[†] It has been recently shown that the coupling function is not dependent on temperature in the energy region spanned by the BP (Fontana *et al.* 1999).

eigenvector of a given mode j can be thought as the sum of two very different components: firstly a plane-wave like part, with an average momentum Q_j , related to the eigenvalue by the linear dispersion $\omega_j \approx vQ_j$ (the Q distribution around Q_j becomes broader with increasing mode energy); secondly a random uncorrelated component whose spatial Fourier transform extends from Q_j up to Q values much higher than the first sharp diffraction peak position with a flat spectral distribution (Mazzacurati *et al.* 1996). The first component accounts for the peaks in the dynamic structure factor and for the existence of a dispersion relation. The finite width of the inelastic peaks in $S(Q, \omega)$, such as that in figure 1, is due to the finite projection of eigenmodes of different energies at the considered Q . The presence of the second component allows one to satisfy the orthogonality conditions of the eigenvectors without the constraint on mode counting holding for plane waves, that is without imposing the Q^2 dependence of the modes density at a given frequency. Specifically, with respect to the Debye behaviour, this can give rise to an accumulation of states at low energies.

In conclusion, a study on the temperature dependence of the dynamics in $v\text{-SiO}_2$ has allowed us to identify equivalent temperature behaviours for the maximum of the BP and for the high-frequency continuation of the sound branch at the same energy. This provides arguments in favour of the acoustic-like origin for the excess in the density of states in $v\text{-SiO}_2$. Recalling that the BP is observed basically in any disordered material, and that IXS has shown the presence of a propagating collective dynamics in all the glasses and liquids studied so far, it is natural to speculate on the generality of the conclusion reached here on the nature of the BP.

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