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LETTER TO THE EDITOR

Has the boson peak a contribution from propagating modes?

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Abstract. An upper bound for the correlation length l of the boson peak vibrations in glassy SiO₂ is estimated using precise measurements of the dependence of Raman scattering spectra on the scattering angle. No such dependence in the region of the boson peak down to 20 cm⁻¹ was found, with accuracy 0.3%. This provides an upper limit for l that is less than the acoustic phonon wavelength λ . The same result is obtained also for polycarbonate glass using light scattering data obtained by Surovtsev *et al* (Surovtsev N V, Wiedersich J, Novikov V N, Rössler E and Sokolov A P 1998 submitted). These results lead to the conclusion that the vibrations which contribute to the low-frequency light scattering spectra (the boson peak) in silica and polycarbonate are localized in the sense of the Ioffe–Regel criterion formulated as $\ell \leq \lambda$.

The terahertz dynamics of glasses has some peculiarities compared with that for crystals, arising due to the lack of long-range order in glasses. These peculiarities manifest themselves as a plateau in the low-temperature thermal conductivity and as the so-called boson peak in the specific heat (Zeller and Pohl 1971), inelastic neutron and light scattering spectra (Buchenau *et al* 1986, Jäckle 1981), and far-infrared absorption (Storm and Taylor 1977).

One of the basic peculiarities of the THz vibrational states of glasses is the strong deviation of the density of vibrational states from the Debye one. This deviation appears at much lower frequencies than in crystals (Zeller and Pohl 1971). Another fundamental peculiarity of the THz vibrational states of glasses is that they cannot be described by plane waves (or, at least, by plane waves alone). For example, the estimation of the phonon mean free path from low-temperature thermal conductivity data gives a value of the order of the phonon wavelength (Graebner *et al* 1986). It is clear that in such a case even a representation of THz vibrations as perturbed phonons in the framework of a perturbation theory cannot be valid, because the ratio of the phonon wavelength and the phonon mean free path is not small. Another argument against the description of THz vibrational states in glasses with plane waves is the existence of the continuous and broad low-frequency Raman scattering spectra in the frequency range <100 cm⁻¹ (that of the boson peak); in crystals the light scattering by acoustic waves can give only Brillouin lines.

There are different points of view concerning the THz vibrational states in glasses. According to one of them, these vibrational excitations are quasilocalized vibrations: localization is caused by structural nano-inhomogeneities (Malinovsky *et al* 1987, Malinovsky and Novikov 1994, Duval *et al* 1990) or homogeneous structure correlations on the medium-range scale (Elliott 1992). Some authors argue that in this frequency range

acoustic plane waves coexist with some type of additional vibrational excitation (Buchenau *et al* 1992, 1996) or have an uncorrelated random component (Mazzacurati *et al* 1996).

Recent experimental data, obtained by inelastic x-ray scattering from silica glass (Benassi *et al* 1996, Masciovecchio *et al* 1997), were interpreted as evidence of the existence of propagating modes up to frequencies higher than the position of the boson peak (2 THz). According to this interpretation, acoustic plane waves, strongly attenuated in the THz range, give a contribution to the low-frequency Raman scattering spectra of glasses. However, Foret *et al* (1996) interpreted their experimental data from inelastic neutron and x-ray scattering investigations of silica as indicating an acoustic localization edge at 1 THz. This controversy (Foret *et al* 1997, Benassi *et al* 1997) shows that the problem of the propagating character of the vibrational modes in the terahertz spectral range is not yet resolved. Our estimations show that, if the correlation length of vibrational excitations is approximately a few phonon wavelengths or more, it should be possible to observe an angular dependence (i.e. a q -dependence) of the low-frequency Raman scattering spectra, with changes of the intensity by several per cent.

This communication is devoted to an estimation of this angular effect and to the experimental testing of this prediction. The low-frequency Raman scattering of glassy SiO₂ is measured with a spectral shape accuracy about 0.3% for the frequency range of the boson peak (20–70 cm⁻¹). No angular dependence of the scattering intensity was found. We show that our experimental result makes evident the localization of the vibrational excitations in the sense of the Ioffe–Regel criterion (Ioffe and Regel 1960).

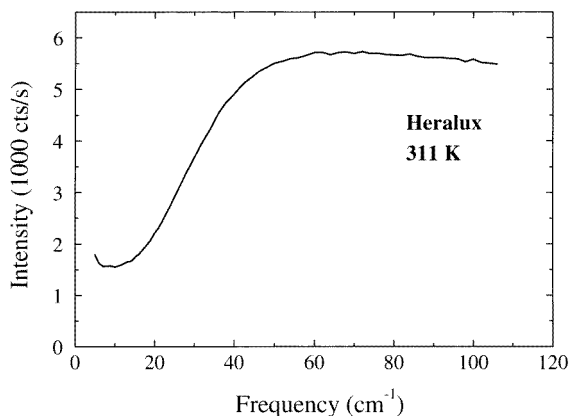


Figure 1. The low-frequency polarized Raman spectrum of glassy SiO₂.

Raman scattering experiments on a sample of glassy SiO₂ (Heralux) were performed using an argon-ion laser with a wavelength of 514.5 nm and a power of 900 mW, and a five-grating monochromator Z40. Polarized and depolarized Raman spectra were measured over the frequency range 4–100 cm⁻¹ at room temperature (the spectral slits were 2 cm⁻¹). The scattering angles were 20° and 160°; the respective wave vectors are $q_1 = 0.62 \times 10^{-2} \text{ nm}^{-1}$, $q_2 = 3.5 \times 10^{-2} \text{ nm}^{-1}$ with the refractive index $n = 1.46$ of the sample. An aperture limiter was placed on the lens in order to collect the scattering light within an interval of $\pm 14^\circ$. The temperature in the illuminated volume of the sample obtained from the Stokes–anti-Stokes ratio was $311 \pm 1.7 \text{ K}$. It is easy to show that such a temperature uncertainty leads to a spectral shape uncertainty of about 10^{-3} over the spectral range 0–40 cm⁻¹. It is known that at room temperature the vibrational contribution to the Raman scattering spectra of glassy

SiO₂ dominates in the low-frequency range down to 20 cm⁻¹ (Winterling 1975). To obtain the light scattering spectrum in the frequency range 20–74 cm⁻¹ with a high accuracy, 120 polarized spectra were accumulated for each scattering angle (the recording time for one spectrum was about five minutes). Analogous spectra for depolarized light scattering were also accumulated, but with a smaller number of accumulations.

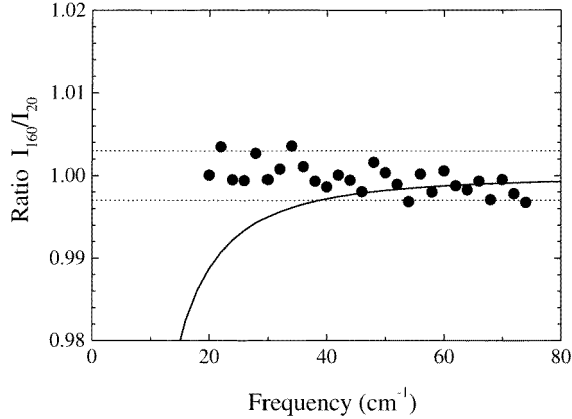


Figure 2. The ratios of the low-frequency Raman spectra of SiO₂ measured at two different angles: 160° and 20° (symbols). Dotted lines show ±0.3% deviations from an average value. The solid line indicates the ratio calculated from equation (6) and $b = 1/10$ on the assumption that l_ω is equal to the longitudinal phonon wavelength.

Figure 1 shows a polarized light scattering spectrum of SiO₂. The peak with its maximum near 60 cm⁻¹ is usually referred to as the boson peak. Figure 2 presents the ratio $R(\omega)$ of the low-frequency spectra recorded for 20° and 160° scattered light geometries over the frequency range 20–74 cm⁻¹, where the vibrational spectrum (the boson peak) dominates while quasielastic scattering is negligible. No frequency dependence of $R(\omega)$ is found with an accuracy of about 0.3%. The same result was also obtained for the ratio $R(\omega)$ of the depolarized light scattering spectra, but with a lower accuracy of 1%. Let us note that our previous experiments on glassy SiO₂ with a different experimental set-up (a double monochromator DFS-24 (Surovtsev *et al* 1997)) showed a lack of wave-vector dependence for the frequency range 10–700 cm⁻¹ (covering the optical modes spectrum) with a lower accuracy of about 2%.

The q -dependence of the inelastic light scattering intensity is determined by the Fourier transform of the correlation function of the dielectric susceptibility fluctuation $\delta\chi(\mathbf{r}, t)$:

$$I(q, \omega) \propto \int dt \, d\mathbf{r}_1 \, d\mathbf{r}_2 \, e^{i\omega t - iq \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \langle \delta\chi(\mathbf{r}_1, t) \delta\chi^*(\mathbf{r}_2, 0) \rangle \quad (1)$$

(tensor indices are omitted for simplicity since we are not interested here in the polarization dependence of the scattering). The brackets indicate the spatial and statistical averaging. The variation of the dielectric susceptibility due to acoustic phonons is proportional to the strain tensor, $\delta\chi_{\alpha\beta} \propto \partial u_\alpha / \partial r_\beta + \partial u_\beta / \partial r_\alpha$, where the $u_\alpha(\mathbf{r}, t)$ are the atomic displacements. Since the boson peak vibrations lie in the acoustic region and have a typical wavelength > 1 nm, one can assume for them the same type of coupling with light. In this case the following expression for the Raman intensity holds (see, e.g., Novikov *et al* 1995):

$$I(q, \omega) \propto \int d\mathbf{r} \, e^{iq \cdot \mathbf{r}} \langle \nabla u_\omega(\mathbf{r}) \nabla u_\omega^*(0) \rangle g(\omega). \quad (2)$$

In equation (2), $g(\omega)$ is the vibrational density of states and $u_\omega(\mathbf{r})$ is the amplitude of a vibration with frequency ω . It is convenient to use the normalized correlation function $F_\omega(r)$ defined by the equation

$$\langle \nabla u_\omega(\mathbf{r}) \nabla u_\omega(0) \rangle = F_\omega(r) \langle |\nabla u_\omega(0)|^2 \rangle. \quad (3)$$

$F_\omega(r)$ satisfies the normalization condition $F_\omega(r) \simeq 1$ for $r \ll l_\omega$ where l_ω is the vibration correlation length. The Fourier transform of the correlation function $F_\omega(q)$ determines the q -dependence of the Raman scattering intensity:

$$I(q, \omega) \propto F_\omega(q) \langle |\nabla u_\omega(0)|^2 \rangle g(\omega). \quad (4)$$

The exact form of $F_\omega(r)$ or $F_\omega(q)$ is unknown; however, since in our case $ql_\omega \ll 1$ we can expect that in the first approximation

$$F_\omega(q) \propto 1 - b(ql_\omega)^2 + O((ql_\omega)^4)$$

where the coefficient b depends on a particular form of the correlation function. Here we consider a few examples of the correlation function in order to make an estimate of the correlation length. For exponential functions of the type

$$F_\omega(r) \propto r^{-\alpha} \exp(-r/l_\omega)$$

one obtains $b = \Gamma(5 - \alpha)/6\Gamma(3 - \alpha) = 2, 1$ and $1/3$ for $\alpha = 0, 1$ and 2 , respectively. For a Gaussian correlation function $\exp(-r^2/l_\omega^2)$, $b = 1/4$ and $b = 1/6$ for

$$F(r) \propto r^{-2} \exp(-r^2/l_\omega^2).$$

The tendency is clear: the more quickly the correlation function decreases at a given l_ω , the smaller b is. For a limiting case, a step function:

$$F_\omega(r) = \begin{cases} \text{constant} & r < l_\omega \\ 0 & r > l_\omega \end{cases} \quad (5)$$

one obtains $b = 1/10$. This is the smallest value of b that can be expected. To obtain the q -dependence of the scattering function, we used the ratio of $I(q, \omega)$ measured at the largest wave vector, q_2 (close to backscattering), to that for a small scattering angle corresponding to the wavenumber q_1 :

$$R(q_1, q_2, \omega) \equiv \frac{I(q_2, \omega)}{I(q_1, \omega)} = \frac{F_\omega(q_2)}{F_\omega(q_1)} \cong 1 - b(q_2^2 - q_1^2)l_\omega^2. \quad (6)$$

So, at fixed wave vectors q_1 and q_2 , the dependence of the parameter R on ω (figure 2) is determined by the frequency dependence of the squared correlation length l_ω^2 . Even in the case of localization of vibrations (in terms of the Ioffe–Regel criterion of localization this means that l_ω is of the order of the phonon wavelength, so $l_\omega \sim 2\pi v/\omega$, v being the sound velocity), $R(\omega)$ has to show a hyperbolic deviation from a constant as a function of frequency. For example, figure 2 shows the $R(\omega)$ dependence given by equation (6) in the case in which l_ω is equal to the longitudinal phonon wavelength and $b = 1/10$.

However, we found experimentally that there is no frequency dependence of $R(\omega)$ (figure 2), with an accuracy of about 0.3%, for the frequency range down to 20 cm^{-1} . This means (from equation (6)) that $l_\omega < (0.003/(q_2^2 - q_1^2)b)^{1/2} \approx 1.6/b^{1/2} \text{ nm}$. For any of the values of b which are listed above, $l_\omega < 5 \text{ nm}$, and it does not exceed 3–4 nm for realistic exponential or Gaussian correlation functions. Let us compare this value with the phonon wavelength at $\omega = 20 \text{ cm}^{-1}$: $\lambda \approx 9.8 \text{ nm}$ for longitudinal phonons (the longitudinal sound velocity is 5.9 km s^{-1}) and $\lambda \approx 6.9 \text{ nm}$ for transverse phonons (the transverse sound velocity is 3.8 km s^{-1}). We see that the estimated correlation is smaller than the phonon

wavelengths. This means that there is localization of the vibrations down to $\omega \sim 20 \text{ cm}^{-1}$ in the sense of the Ioffe–Regel criterion (Ioffe and Regel 1960).

In the work of Surovtsev *et al* (1998), the low-frequency light scattering in polycarbonate was measured using a Sandercock six-pass interferometer also at two angles: 10° and 170° . It was found that the spectral shapes measured at different angles were the same with the accuracy 0.5% for $T = 100 \text{ K}$ down to 40 GHz. As was shown earlier (Surovtsev 1996), at $T = 100 \text{ K}$ the vibrational contribution in polycarbonate dominates the light scattering spectra down to 6 cm^{-1} . An analogous estimation using equation (6) with $b = 1/10$ gives a correlation length which does not exceed 7.8 nm while the corresponding phonon wavelength for 6 cm^{-1} is 6.1 nm (taking the transverse sound velocity 1.1 km s^{-1}). So, from the results of Surovtsev *et al* (1998) we can also conclude that the localization of vibrations contributes to the low-frequency Raman spectra of polycarbonate.

In conclusion, light scattering spectra of glassy SiO_2 were measured at two different angles. The lack of wave-vector dependence of the scattered light allows us to estimate an upper limit for the vibration correlation length l_ω . Comparison of this value of the correlation length with the wavelength of the vibrations λ at $\omega = 20 \text{ cm}^{-1}$ shows that the vibrations observed as the boson peak in Raman scattering spectra are localized in the sense of the Ioffe–Regel criterion of localization, $\lambda \geq l_\omega$. The same conclusion for polycarbonate was obtained from the analysis of the results of Surovtsev *et al* (1998). This conclusion is consistent with an interpretation of the low-frequency Raman scattering spectra as a manifestation of the vibrational states localized due to the inhomogeneous structure of glasses (Malinovsky *et al* 1987, Malinovsky and Novikov 1994, Duval *et al* 1990). On the other hand, the result of the experiment does not exclude the possibility that the phonon plane waves coexist with the localized vibrational states which do not give a contribution to the light scattering spectra, as was suggested by Engberg *et al* (1998).

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