Evidence of High Frequency Propagating Modes in Vitreous Silica

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High energy resolution inelastic x-ray scattering measurements in the $1-6\ \mathrm{nm}^{-1}$ momentum transfer (Q) region in vitreous silica (v-SiO_2) at $T = 1050$ K show the existence of collective excitations propagating with a sound velocity of 5800 ± 200 m/s up to $Q = 3.5\ \mathrm{nm}^{-1}$. The linewidths of the excitations, which are found to obey a Q^2 law, are consistent with previous determinations made at low Q and low T. The picture of the atomic dynamics in v-SiO_2 emerging from this study indicates that these propagating modes must contribute to the *boson* peak. [S0031-9007(96)01466-4]

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The detailed understanding of the dynamical properties of topologically disordered systems, like glasses, is still an open question. At low momentum transfer (Q) values, the existence of propagating collective excitations is demonstrated by the sharp Brillouin lines observable in light-scattering experiments. This is straightforward from an intuitive point of view since at low Q's one samples particle-particle correlations on a long time and large space scales with respect to interatomic motions and distances.

In the mesoscopic time-space domain the situation is more complicated, and the existence of collective dynamics is doubted. The evidence of modes in glasses in the mesoscopic region comes from incoherent neutron scattering and light scattering studies [1], where a broad band is found around 2 to 10 meV, almost independently from the material. This band has been named *boson* peak because its intensity scales with temperature approximately according to the Bose-Einstein statistics. The relaxational or vibrational character of the excitations giving rise to the *boson* peak is highly debated [1], especially in view of the fact that the extrapolation of the dispersion relation found at small Q to the mesoscopic Q region would give excitation energies similar to those of the *boson* peak. In this region, the experimental determination of the dynamical structure factor $S(Q, E)$ became only recently possible, thanks to the development of inelastic x-rays scattering (IXS) with meV energy resolution. It was shown for some "intermediate" [2] and "fragile" [3] glasses that propagating excitations exist up to energies comparable to that of the *boson* peak. Similar determinations have not been attempted yet on "strong" network-forming glasses. Among them, *vitreous* silica, v-SiO_2, is probably the archetype [4].

In this Letter we present the measurement of the $S(Q, E)$ of v-SiO_2 at $T = 1050$ K, in the $1-6\ \mathrm{nm}^{-1}$ momentum transfer range. We report the existence of collective modes in the whole investigated Q range. These modes are found to propagate with a velocity of sound $v = 5800 \pm 200$ m/s up to $Q = 3.5\ \mathrm{nm}^{-1}$ and $E \approx 13$ meV. Hence, the energies spanned by these excitations cover the *boson* peak region [5], thus indicating that they must contribute to its origin. Moreover, the comparison of the present data with light-scattering data at $T = 300$ K shows that the linewidth of these excitations is temperature independent, suggesting that the peaks broadening is not associated with dynamical processes, but to the ill-definition of Q as a good quantum number.

The experiment was carried out at the new very high energy resolution inelastic x-ray scattering beam line (BL21-ID16) at the European Synchrotron Radiation Facility. This instrument is based on backscattering from high order reflections in perfect silicon crystals, and in this work we used the Si(999) reflection at $\approx$17.794 keV. The total instrumental resolution function was measured using a Plexiglas scatterer at the maximum of its static structure factor where the scattering is dominated by the elastic component; the energy resolution, full width at half maximum (FWHM), was 2.8 ± 0.2 meV. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$ (where k_0 and θ_s are the wave vector of the incident photon and the scattering angle, respectively), was selected between 1 and $6\ \mathrm{nm}^{-1}$. The Q resolution was set to $0.3\ \mathrm{nm}^{-1}$ by an aperture in front of the analyzer crystal. Energy scans were performed by varying the relative temperature between the monochromator and analyzer crystals. Each scan took about 120 min, and each Q point was obtained by typically averaging four scans. The data were normalized to the intensity of the incident beam. Further details on the beam line are reported elsewhere [2,6–9].

The SiO_2 suprasil sample, purchased from Goodfellow, was a 2 mm diameter rod. Its dimension was comparable to the x-ray photoabsorption length and gave negligible multiple scattering. A preliminary experiment performed at room temperature on v-SiO_2 showed very weak IXS intensity, strongly merged into the tails of the central peak, thus not allowing a determination of the spectral shape with the necessary accuracy [10]. To increase the expected inelastic scattering signal we performed the measurements at about 1000 K. This gave an enhancement of the excitations with $E \approx 10$ meV by a factor of $\approx$3.5. The v-SiO_2 rod was placed inside a graphite tube ($\approx$20 mm in length,

0.2 mm wall thickness, and 3 mm outer diameter), which was resistively heated in vacuum. A 1 mm diameter hole orthogonal to the graphite cylinder axis allowed the passage of the incoming and scattered beams without scattering from the graphite. The temperature of the sample, monitored with an optical pyrometer, was 1050 ± 50 K. The glassy structure of the sample was checked several times measuring *in situ* at $T = 1050$ K the static structure factor $S(Q)$, which was found to be in agreement with previous determinations [4].

A representative inelastic x-ray scattering spectrum of v-SiO_2 at $T = 1050$ K is reported in Fig. 1 together with the fit discussed in the following. The spectrum is dominated by an intense elastic peak, whose shape is determined by the instrumental resolution. At the sides of the central peak, well above the tails of the elastic scattering broadened by the resolution function, the inelastic signal is clearly visible. The inset of Fig. 1 shows a close-up of the region where the inelastic intensity is better visible, together with the residual of the fit reported in standard deviation units. This inelastic signal is due to collective density fluctuations, and it is observed at all investigated Q points. The inelastic x-ray scattering spectra taken in the $1 \leq Q \leq 4$ nm^{-1} region are shown in Fig. 2. In each spectrum, the dashed line representing the resolution function is shown aligned with the central peak. The energy position of the inelastic intensity is characterized by a clear Q dependence, indicating the propagating nature of the excitations. To determine their energy position and width, we have fitted the spectra to the convolution of the experimental resolution function with the model function $F(Q, E)$ given by

$$F(Q,E) = I_o(Q)\delta(E) + [n(E) + 1]I(Q) \times \frac{E\Gamma(Q)\Omega(Q)}{[\Omega(Q)^2 - E^2]^2 + \Gamma(Q)^2E^2}. \quad (1)$$

It consists of a δ function to account for the elastic scattering, and a damped harmonic oscillator (DHO) model [11]

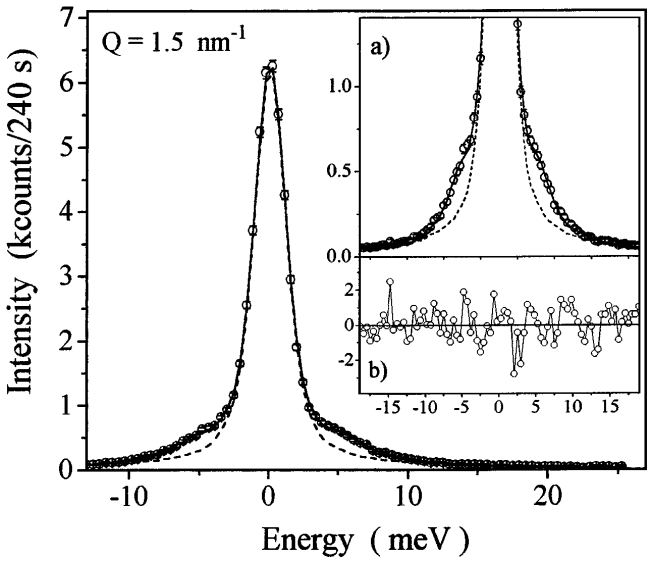

FIG. 1. Inelastic x-ray scattering spectrum of v-SiO_2 at $T = 1050$ K and $Q = 1.5$ nm^{-1} (open circles). The dashed line represents the instrumental resolution function, shown aligned with the central peak to emphasize the presence of inelastic scattering. The full line is the best fit to the data as discussed in the text. In the inset we report (a) the expansion of the region where the inelastic signal is better visible and (b) the residual of the fit in standard deviation units.

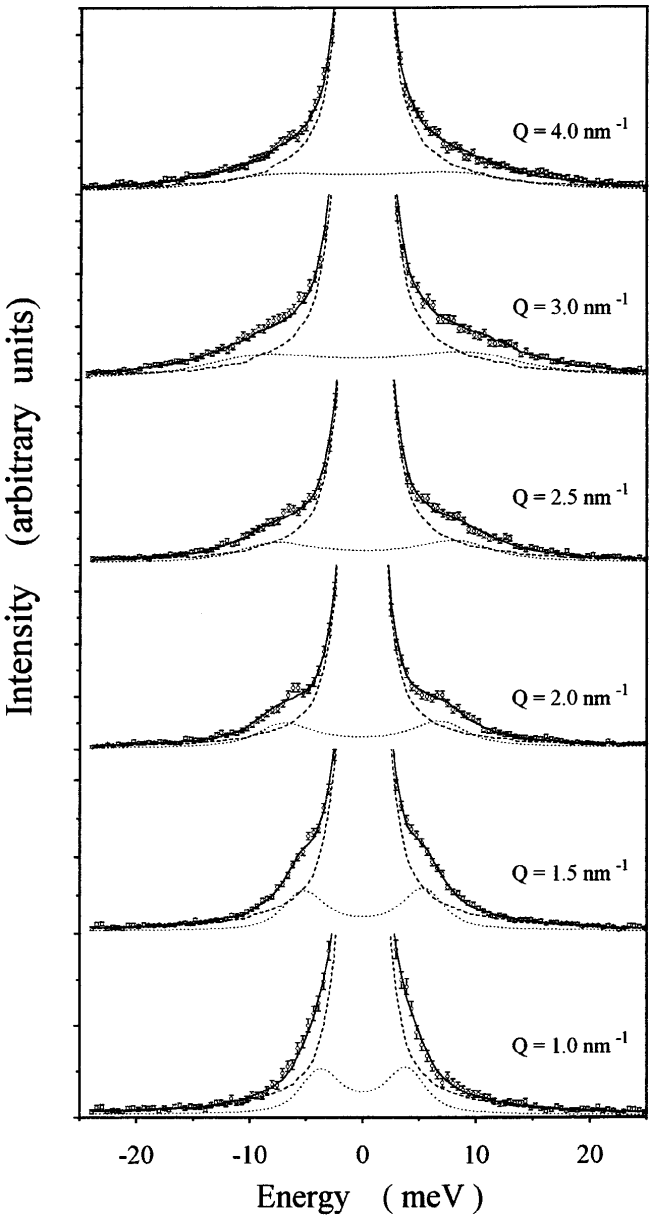

FIG. 2. X-ray spectra of v-SiO_2 at $T = 1050$ K taken at different Q values. The data are shown together with their best fits (full line) and the individual contributions to the fitting function: elastic peak (dashed line), and inelastic components (dotted line). To emphasize the presence of the inelastic contribution, the vertical scale has been chosen to show the tails of the central peak.

for the two side peaks. Here $I_o(Q)$ and $I(Q)$ are related to the intensities of the central peak and of the inelastic contributions, respectively, $\Omega(Q)$ and $\Gamma(Q)$ are the excitation energy and width, and $n(E)$ is the Bose factor. The DHO model function has already been successfully applied to describe the shape of the $S(Q, E)$ of disordered systems in previous inelastic neutron [12] and x-ray [2,6,9] scattering studies, and in a simulated model glass [13]. A standard χ^2 minimization procedure has been utilized to determine the relevant fitting parameters, namely, $\Omega(Q)$, $\Gamma(Q)$, and $R(Q)$, which is the ratio between inelastic and elastic integrated intensities.

The values of $\Omega(Q)$ obtained from the fit are reported in Fig. 3 for $Q \leq 3.5$ nm^{-1}. We observe a linear dispersion in Q with a sound velocity $v = 5800 \pm 200$ m/s (dotted line), a value consistent with the 6050 m/s one derived from elastic constant measurements at $T = 1050$ K [14] (dot-dashed line). At Q larger than 4 nm^{-1}, the fitting procedure was no longer stable probably due to the large broadening of the excitations. It was therefore not possible to determine a reliable value for $\Omega(Q)$. To estimate $\Gamma(Q)$ at $Q \geq 4$ nm^{-1}, we imposed to $\Omega(Q)$ in the $4 \leq Q \leq 6$ nm^{-1} region two extreme values, namely, $\Omega(Q) = vQ$ and $\Omega(Q) = \Omega(Q = 3.5 \text{ nm}^{-1}) \approx 13$ meV. The corresponding two values obtained for $\Gamma(Q)$ at each Q were equivalent within their error bars. The values of $\Gamma(Q)$ are reported in Fig. 4 in a log-log scale (open circles). The dotted line represents the best fit to the IXS data, and it has a slope of 1.95, thus indicating that $\Gamma(Q) \propto Q^2$ in the whole examined Q range. As observed in Fig. 4, this Q^2 behavior overlaps with the extrapolation in the IXS Q range of the linewidths obtained at low Q using the picosecond optical technique (POT) on v-SiO_2 at room temperature [15]. The excellent consistency between our data, taken at $T = 1050$ K and at $Q \geq 1$ nm^{-1}, with the data of Ref. [15], taken at $T = 300$ K and at Q values 1 order of magnitude smaller, provides a convincing indication that (i) the Q^2 dependence of Γ is genuine, and (ii) the temperature dependence of the excitations linewidths is negligible in the whole 300–1000 K temperature range.

We have measured the $S(Q, E)$ of v-SiO_2 also in the Brillouin light-scattering (BLS) region to further increase the explored Q range. The experiment was carried out using the 514.5 nm line of an Argon ion laser in backscattering geometry and a SOPRA DMDP2000 monochromator operating with 3.5 μeV total energy resolution [16]. The room temperature spectrum of the same v-SiO_2 sample utilized in the IXS measurement is reported in the inset of Fig. 5. In this figure, we also show the Stokes Brillouin line in detail, together with the instrumental resolution function. The FWHM of the Brillouin line measured at $Q = 0.036$ nm^{-1} is reported in Fig. 4 (open square): its value is also consistent with the $\Gamma(Q) \propto Q^2$ law. Another important consistency between the high-Q (IXS) and low-Q (BLS) measurements is found for the inelastic to elastic intensity ratio, $R(Q)$, as seen in Fig. 6, where values measured with IXS (full dots) and BLS (open dot) are reported.

In conclusion, we have shown for v-SiO_2 that: (i) Propagating modes exist in the 1–3.5 nm^{-1} Q region, and their sound velocity is 5800 ± 200 m/s at $T = 1050$ K; this value is consistent with low-Q measurements [14]. (ii) At $Q \geq 4$ nm^{-1}, i.e., for wavelengths $\lambda \leq 1.5$ nm, the width of the excitations becomes comparable to their energy. (iii) The width of the excitations follows a Q^2 law, matching the POT and BLS measurements at lower Q. (iv) The widths of the excitations do not change in the 300–1050 K temperature range. This last result confirms the T independence of the linewidths already observed in the 100–300 K region [15].

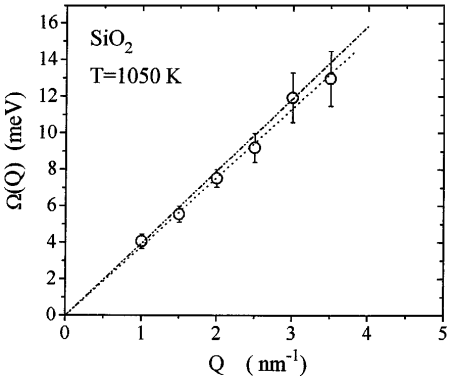

FIG. 3. Excitations energy, $\Omega(Q)$, from the DHO model for the data taken up to $Q \leq 3.5$ nm^{-1}; see text. The dotted line is the best fit to $\Omega(Q)$ and has a slope of 5800 m/s; the dot-dashed line has the slope of 6050 m/s; i.e., the sound velocity derived from the elastic constant at zero frequency measured at 1050 K [14].

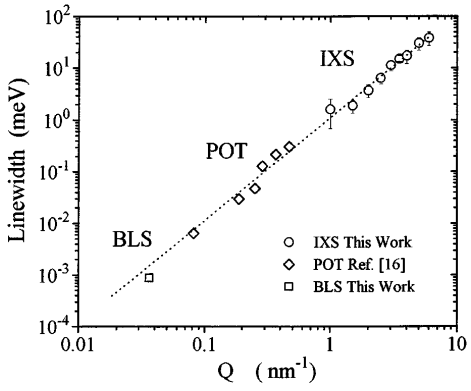

FIG. 4. Full width at half maximum of the excitations measured with different techniques. Open circles represent the parameter $\Gamma(Q)$ of the DHO model [Eq. (1)] obtained from the fit of the 1050 K IXS data. The error bars for the data at $Q = 4$, 5, and 6 nm^{-1} represent the range of variability obtained from the different choices of $\Omega(Q)$, as discussed in the text. The open diamonds refer to the 300 K POT data of Ref. [15], while the open square refers to the 300 K Brillouin light-scattering (BLS) data. The dashed line, with a slope of 1.95, is the best fit to the IXS data.

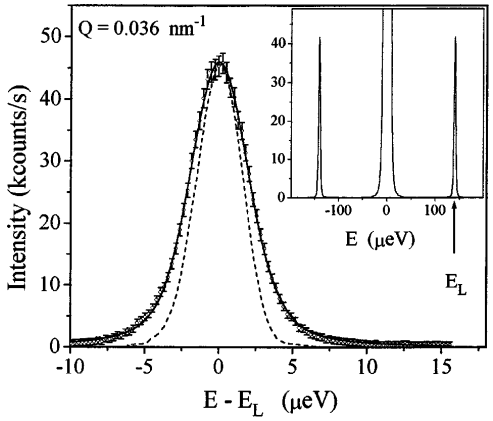

FIG. 5. Brillouin light-scattering measurement of the phonon broadening in v-SiO_2 at 300 K. The longitudinal Stokes Brillouin line is reported (open circles) together with the fit (full line) of the data to the convolution of the resolution function (dashed line) with a Lorentzian modeling the $S(Q, E)$. $E_L = 141$ μeV is the energy position of the Brillouin line, as indicated in the inset where the whole spectrum is also shown.

The scenario for the mesoscopic dynamics of v-SiO_2 emerging from this work can then be summarized as follows: (i) From long wavelengths down to $\lambda \approx 1.5$ nm there are density fluctuations described by phononlike, propagating, quasiharmonic modes with nonlocalized eigenvectors. This result complements earlier inelastic neutron work showing that the dynamics at energies above 2 meV and Q above 10 nm^{-1} have a dominant harmonic component [17]. (ii) The propagating dynamics extends to the same energy range as the *boson* peak, and therefore it must contribute to this debated spectral feature, and maybe it is at its origin. (iii) The temperature independence of the excitations linewidth is likely to be related to the structural disorder in v-SiO_2, also temperature independent in this region, rather than to dynamical processes.

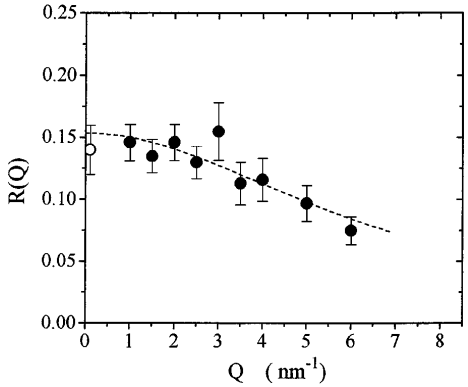

FIG. 6. The inelastic to elastic ratio $R(Q)$ is reported for the IXS data in v-SiO_2 at $T = 1050$ K (full circles) and for the BLS experiment at $Q \approx 0$ (open circle). The value $R(Q) = 0.04$, measured with BLS at room temperature, is multiplied for 1050/300 to account for the linear temperature dependence of the inelastic signal.

In this picture, at decreasing wavelengths, the disorder reduces the definition of Q as a good quantum number. It is interesting to point out that the Q^2 law of the linewidth found here does not have, to our knowledge, a theoretical explanation. (iv) For $Q \geq 4$ nm^{-1}, it is no longer possible to establish the propagating or nonpropagating nature of the excitations. It is worth mentioning, to this regard, that $Q = 4$ nm^{-1} corresponds to a wavelength value comparable to the structural correlations expected in SiO_2 at mesoscopic lengths: therefore, the disappearance of excitations with a definite E-Q relation could mark the onset of a new dynamical regime localized in strongly bonded nanovolumes of the material [4,5].

This scenario is very similar to that found in other more fragile glasses [2,3], and maybe one can start to speculate on the universality of the dynamics of topologically disordered systems.

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