Nature of the Short Wavelength Excitations in Vitreous Silica: An X-Ray Brillouin Scattering Study

O. Pilla,[1] A. Cunsolo,[2] A. Fontana,[1] C. Masciovecchio,[3] G. Monaco,[4] M. Montagna,[1] G. Ruocco,[5]
T. Scopigno,[1] and F. Sette[4]
[1]*Dipartimento di Fisica and INFM, Università di Trento, I-38050 Povo, Trento, Italy*
[2]*Dipartimento di Fisica and INFM, Università di Roma III, I-00146 Roma, Italy*
[3]*Sincrotrone Trieste, Area Science Park, I-34012, Trieste, Italy*
[4]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France*
[5]*Dipartimento di Fisica and INFM, Università dell'Aquila, I-67100, L'Aquila, Italy*
(Received 11 April 2000)

The dynamical structure factor $[S(Q,E)]$ of vitreous silica has been measured by inelastic x-ray scattering varying the exchanged wave vector (Q) at fixed exchanged energy (E)—an experimental procedure that, contrary to the usual one at constant Q, provides spectra with much better identified inelastic features. This allows us to obtain the first direct evidence of Brillouin peaks in the $S(Q,E)$ of SiO_2 at energies above the boson peak (BP) energy, a finding that excludes the possibility that the BP marks the transition from propagating to localized dynamics in glasses.

PACS numbers: 63.50.+x, 61.10.Eq, 61.43.Fs, 78.35.+c

The nature of the high frequency collective vibrations in glasses is highly debated in the physics of disordered materials [1]. At long wavelengths, these vibrations are thought to be well approximated by propagating plane waves (sound waves) with a linear relationship between energy, E, and wave vector, Q. Increasing Q, and in particular when Q becomes comparable to the inverse of the interparticle separation a, the simple linear relation between E and Q no longer holds, and the dispersion relation shows a bend down, a maximum at $Q \approx \pi/a$, and a broad minimum at $Q \approx 2\pi/a$: this behavior closely resembles that of the phonon dispersion relation in crystals. At variance with this apparent crystal-like behavior, several evidences indicate that, even in the low Q limit, the nature of the excitations in glasses is by far more complicated than in crystals. Among these evidences there are the universal low temperature anomalies observed in the heat capacity and heat conductivity [2–4], and the presence of the so called boson peak in Raman [5,6] and inelastic neutron scattering (INS) [7] spectra. Despite the experimental and theoretical efforts that in the last years have been devoted to the characterization of the excitations in disordered systems, the central question about this issue, namely the propagating or localized character of the collective excitations, is not completely settled [8–12].

Two main interpretations of the existing experimental data have been proposed so far: they lead to a contrasting view of the nature of the collective excitations in the mesoscopic Q-E region ($Q = 1$–10 nm^{-1}) [1]. One view assumes that the static disorder in the glass produces strong elastic scattering of sound waves and, as a consequence, the vibrational modes become localized above a crossover energy (E_{CO}). In particular, it is assumed that the boson peak energy corresponds to this crossover energy marking the onset of localization. The second point of view is based on experimental evidences indicating that the vibrations in glasses maintain a collective propagating nature even at energies well above the boson peak energy. In this respect, the high energy dynamic structure factor $[S(Q,E)]$ of different glasses and glass-forming liquids, ranging from fragile systems to strong ones, have been recently investigated by the new inelastic x-ray scattering (IXS) technique [13]. These studies have shown the existence of inelastic features whose energy Ω_Q has an almost linear dispersion with Q. This extends up to Q values a few tenths of Q_o [the position of the first maximum in the static structure factor $S(Q)$] and up to energies in the boson peak energy region. These findings demonstrate that propagating collective excitations persist in the mesoscopic Q region, and, in particular, that the boson peak energy (E_{BP}) cannot be straightforwardly related to the crossover energy marking the transition between propagating and localized vibrations.

The IXS data reported so far for vitreous silica (v-SiO_2), despite the generality of the IXS data on the other studied glasses which support the second point of view, are utilized to support either the localized [10], or the propagating [8,9] picture. This conflicting situation is particularly unsatisfactory considering that v-SiO_2 is the prototype of strong glasses. This can be partly ascribed to the low intensity of the inelastic signal compared to the tail of the resolution broadened elastic one. Indeed, even at the highest investigated temperature, the inelastic contribution in the IXS spectra of v-SiO_2 is observed as a weak shoulder of the elastic line as can be seen in Fig. 2 of Ref. [9]. As a consequence, in order to deduce from the IXS data the existence of Brillouin peaks and compare their line shapes to theoretical predictions, the data must be fitted to a theoretical model and deconvoluted from the instrumental response function. As a matter of fact, these experimental data do not give a clear-cut indication on the choice among contrasting theoretical models. Even in a recent work on

0031-9007/00/85(10)/2136(4)$15.00

densified SiO_2 glass [14], where the inelastic peak was slightly better resolved than in v-SiO_2, the Brillouin intensity was so weak that a considerable effort of subjective data processing was needed to compare the experimental result to theories.

In this paper we present a *direct experimental evidence* on the existence of well-defined Brillouin peaks in the IXS spectra of amorphous silica. At variance with the previous IXS experiments on v-SiO_2 [8–10,14], where the spectra were measured at constant Q and as a function of E, here we present constant E cuts of $S(Q,E)$ taken as a function of Q. To appreciate the advantage of this approach, we remind one that in the constant Q spectra, as a consequence of the finite energy resolution, the elastic component gives rise to a $\sim E^{-2}$ tail whose intensity in the Brillouin peak region is often stronger than that of the peak itself. Therefore, the extraction of the spectroscopic parameters of the Brillouin peak necessarily requires a fitting procedure and the assumption of a model function for the $S(Q,E)$. On the contrary, in the constant E measurements—the procedure utilized in the present experiment—the elastic contribution, convoluted to the instrumental response function, gives rise to an almost Q-independent background which should not affect significantly the position and line shape of the inelastic signal. This approach allows us to demonstrate the presence of a Brillouin peak at an energy larger than the E_{BP}. Therefore, without any specific model for the $S(Q,E)$, we demonstrate that the boson peak does not mark the transition between propagating and nonpropagating dynamics in vitreous silica.

The experiment has been carried out at the very high energy resolution IXS beam line (ID16) at the European Synchrotron Radiation Facility. The instrument consists of a backscattering monochromator and five independent analyzer systems, held one next to each other with a constant angular offset on a 7-m-long analyzer arm. We utilized the Si(11 11 11) configuration, giving a total instrumental energy resolution of 1.5 meV full-width-half-maximum (fwhm) [15], and an offset of 3 nm^{-1} between two neighbor analyzers. The momentum transfer, $Q = 2k_0 \sin(\theta_s/2)$, with k_0 the wave vector of the incident photons and θ_s the scattering angle, is selected by rotating the analyzer arm. Few spectra at constant Q and as a function of E ($Q = 20$, 23, 26, 29, and 32 nm^{-1}) were measured with a Q resolution of 0.4 nm^{-1} fwhm for normalization purposes. The spectra at constant E and as a function of Q ($E^* = 0$, 5.3, and 8.5 meV) were made in two steps. In a first measurement, the spectra were taken in the $-2 \div 32$ nm^{-1}) range by using the five analyzers. In a further measurements the $-2 \div 6$ nm^{-1} region was studied in more detail and with a better accuracy using the analyzer number two with a Q resolution of 0.4 nm^{-1} fwhm. The obtained individual spectra have been then pasted together. The E scans at constant Q were performed by varying the monochromator temperature with respect to that of the analyzer crystals. The Q scans at constant E were performed by setting a constant temperature offset between the monochromator and the analyzer crystals and by rotating the analyzer arm to vary the scattering angle. Each spectrum, either at constant Q or E, took about $150'$, and each fixed-Q or fixed-E point was obtained by a typical average of five scans. The data were normalized to the intensity of the incident beam. The sample, a Spectrosil-grade SiO_2, was placed in a variable temperature oven stabilized at 1200 K within ± 10 K. This high temperature was used to enhance the inelastic signal.

The spectra taken at constant energy $E^* = 0$, 5.3, and 8.5 meV are reported in Figs. 1(a) and 1(b). For clarity the error bars are not reported, these are of the order of the scattering of the data with respect to a smooth behavior. Obviously, increasing energy, the scattering intensity decreases and the spectra become more noisy. The two energy transfers were chosen to be such to correspond to E_{BP} ($E^* = 5.3$ meV) and on the high frequency side of the boson peak ($E^* = 8.5$ meV). The $E^* = 0$ spectrum has been collected in order to establish the elastic contribution to the spectra at finite energy transfer. This latter spectrum shows, in the measured Q range, the intense feature usually referred to as the first sharp diffraction peak (FSDP) centered at about 15 nm^{-1} and, more importantly, it is almost flat in the 2–6 nm^{-1} Q-region, where one should expect Brillouin peaks.

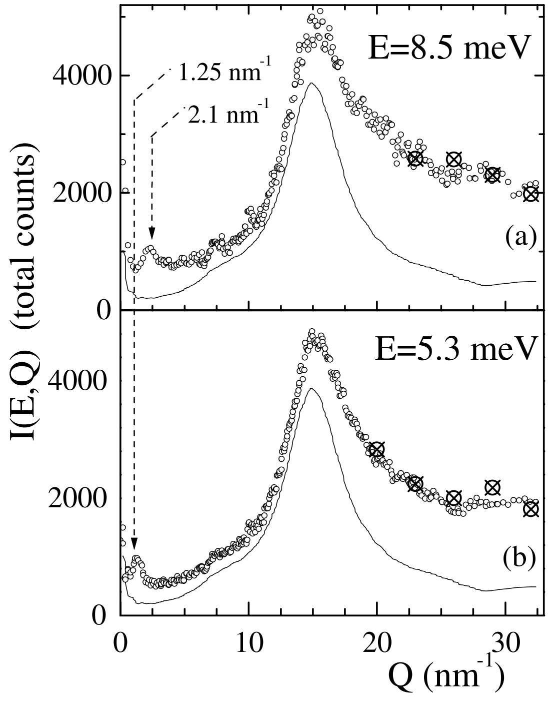

FIG. 1. IXS spectra of amorphous silica at $T = 1200$ K taken as function of Q at constant E: (a) $E^* = 8.5$ meV (circles) and $E^* = 0$ meV (full line); (b) $E^* = 5.3$ meV (circles) and $E^* = 0$ meV (full line). The arrows indicate the Q positions of the Brillouin peaks. The crossed circles are the total scattered intensity derived from the constant Q cuts at energies of $E^* =$ 8.5 and 5.3 meV.

Directly in the raw data of Fig. 1 one can see at low Q the existence of well-defined structures peaking at 1.25 nm^{-1} in the $E^* = 5.3$ meV cut and 2.1 nm^{-1} in the $E^* = 8.5$ meV cut. These two Q positions change almost proportionally to E^*. The peaks are superimposed to the featureless elastic contribution. The presence of these peaks in the constant energy spectra is the fingerprint for the existence of vibrational excitations bearing a strict relationship between energy and wave vector. This, in turn, can be seen as a demonstration of the spatially nonlocalized nature of these excitations, and, in particular, of their propagating character.

The spectra in Fig. 1 contain an elastic contribution as a consequence of the finite energy resolution. In order to subtract the elastic part a series of spectra at constant Q have been collected. Two examples of these spectra are reported in Figs. 2a and 2b for the constant Q cuts of $Q = 23$ and 32 nm^{-1} (circles). The resolution function (full line), aligned with the elastic peaks, is also reported to emphasize the presence of a clear inelastic contribution even at these high Q values. These data have been used to normalize the relative intensity between the inelastic and elastic spectra shown in Fig. 1 according to the following procedure. After aligning and scaling the experimentally determined resolution function to the elastic peaks in the spectra of Fig. 2, we estimate the relative intensity between the elastic and inelastic signals at the energy transfers, E^*, utilized in the constant-E cuts spectra (arrows in Fig. 2a). This elastic to inelastic intensity ratio has been obtained at $Q = 20, 23, 26, 29$, and 32 nm^{-1}. These ratios allow one, then, to put in the correct relative scale the spectra taken at $E^* \neq 0$ and at $E^* = 0$. The consistency of this procedure can be appreciated in Fig. 1 considering that the elastic contribution is shown on a scale determined by the ratio measured at $Q = 23$ nm^{-1} in the spectra in Fig. 2a, and that the crossed circles in Fig. 1b are the calculated values of total (elastic plus inelastic) scattering derived from the other constant Q scans.

This normalization procedure is used to derive the inelastic part of the $S(Q, E)$ by the subtraction of the normalized elastic contribution from the total scattering intensity. The difference spectra are reported in Fig. 3 (circles) together with the error bars as derived from the counting statistics. In these spectra the existence of well-defined Brillouin peaks is highly emphasized. Let us now compare the inelastic spectra reported in Fig. 3 with the predictions of the two models proposed in the literature as a "good" representation of the dynamics structure factor of vitreous silica. In the first one, the $S(Q, E)$ is derived within the framework of the generalized Langevin equation for the considered Q component of the density fluctuation correlator [16], with a choice of the memory function, $m_Q(t) = 2\Gamma_Q \delta(t) + \Delta_Q^2$ [17]. This choice is appropriate

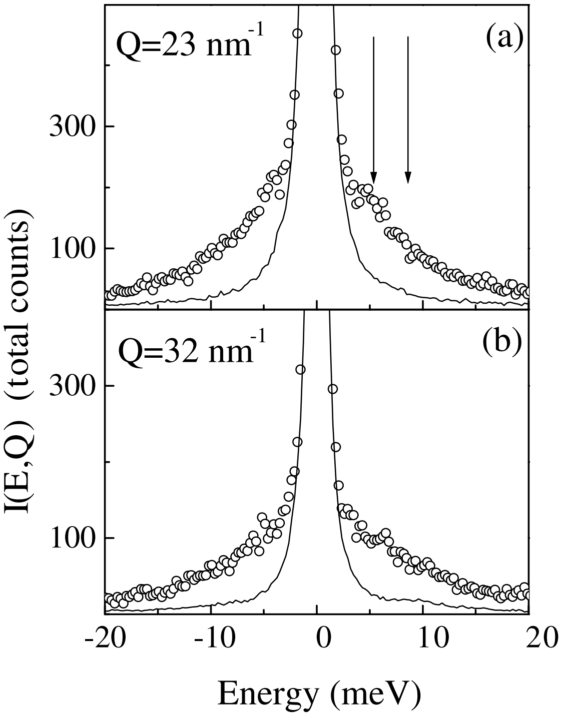

FIG. 2. IXS spectra of v-SiO$_2$ at $T = 1200$ K taken at constant Q (circles): (a) $Q = 23$ nm^{-1} and (b) $Q = 32$ nm^{-1}. The full lines are the resolution function aligned with the elastic peaks. The arrows indicate the energies values of 5.3 and 8.5 meV where the constant-E cuts were measured.

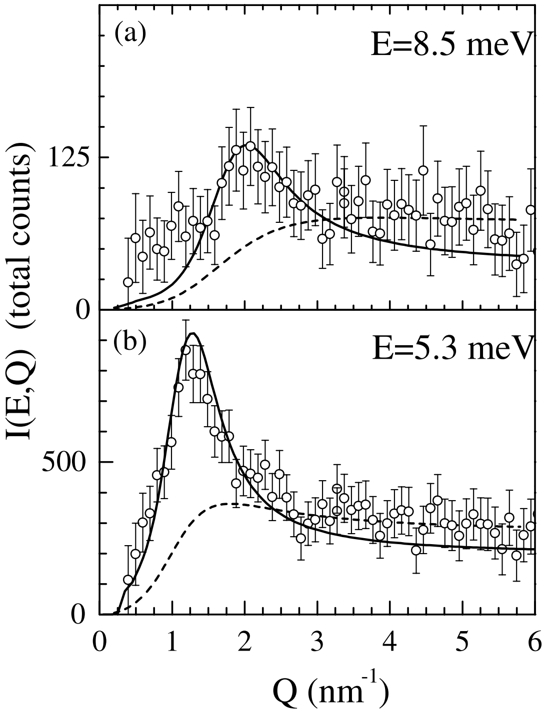

FIG. 3. The inelastic contribution to the spectra reported in Fig. 1 (circles) are reported together with their error bars in an expanded Q scale: (a) $E^* = 8.5$ meV; and (b) $E^* = 5.3$ meV. The full (dashed) lines are the parameter-free line shapes calculated via Eq. (1) (Eq. (2)). The two theoretical predictions have been multiplied by arbitrary scale factors.

for glassy systems. The time independent term Δ_Q, whose value determines the change of the sound velocity, c, between the fully relaxed (c_o) and unrelaxed (c_∞) limiting values, reflects the presence of the frozen structural α relaxation. The parameter Γ_Q determines the width of the side peaks, i.e., the sound wave attenuation coefficient, and summarizes the effects of very fast (or "instantaneous") sound absorption mechanisms. In Refs. [18,19] these mechanisms have been ultimately associated with the presence of structural disorder in the glass. Using the previous expression for $m_Q(t)$, the $S(Q,E)$ turns out to be

$$\frac{S(Q,E)}{S(Q)} = f_Q \delta(E) + \frac{1-f_Q}{\pi} \frac{\Omega_Q^2 \Gamma_Q}{(E^2 - \Omega_Q^2)^2 + E^2 \Gamma_Q^2}, \tag{1}$$

i.e., the sum of an elastic line of intensity f_Q [f_Q is the nonergodicity parameter, $f_Q = 1 - (c_o/c_\infty)^2$], and of an inelastic contribution, whose shape is known as damped harmonic oscillator (DHO). In previous IXS studies on v-SiO$_2$, Eq. (1) was used to fit the constant-Q measurements leaving Γ_Q and Ω_Q as free parameters. In these studies it turned out that, in the small Q limit, $\Omega_Q = vQ$ ($v = 6800$ m/s) [9] and $\Gamma_Q = DQ^2$ ($D = 1.3$ meV/nm^{-2}) [8].

Differently from the Langevin equation approach, the authors of Ref. [10] proposed a model (the so-called EMA model) for the $S(Q,E)$ where its inelastic part is assumed to be

$$S(Q,E) \propto \frac{c_E^2 Q^4}{E} \frac{\Gamma_E}{[(E^2 + \Gamma_E^2 - c_E^2 Q^2)^2 + 4\Gamma_E^2 c_E^2 Q^2]}, \tag{2}$$

where Γ_E and c_E are given by

$$\Gamma_E = E^4/E_{\mathrm{CO}}^3[1 + (E/E_{\mathrm{CO}})^m]^{-3/m} \tag{3}$$

$$c_E = c_0[1 + (E/E_{\mathrm{CO}})^m]^{z/m}. \tag{4}$$

Fitting the IXS data of Ref. [8], the authors of Ref. [10] found for the free parameters entering in Eqs. (2)–(4) the values: $m = 2$, $E_{\mathrm{CO}} = 3.9$ meV, $c_0 = 5900$ m/s, and $z = 0.37$.

In Fig. 3 we report as solid and dashed lines the inelastic part of the $S(Q,E)$ obtained by Eqs. (1) and (2) respectively convoluted with the experimental resolution function. In calculating the theoretical expressions for the $S(Q,E)$ we have used the values of the parameters listed before. The only adjustable parameter is an intensity factor, that has been arbitrarily chosen in order to best fit the experimental data. As can be seen, the DHO model is in a good agreement with both of the constant-E spectra in explaining the presence of the Brillouin peak and the high Q plateau, although the relative intensity of these two main features is not completely accounted for. On the contrary, the EMA model fails to reproduce the existence of the observed Brillouin peak. This is not surprising as the EMA models are based on the assumption that at ≈5 meV (the BP energy) the vibrational modes in vitreous silica became localized. This assumption can be now definitively discarded by the direct inspection of the raw data.

The data $E^* = 5.3$ meV clearly discriminate between DHO and EMA models, showing a striking agreement with the DHO. Also the data at $E^* = 8.5$ favor the DHO model predictions, although the higher noise level precludes a conclusion as firm as in the $E^* = 5.3$ meV case.

In conclusion, this study, independently of any specific model of the $S(Q,E)$, has experimentally demonstrated that in v-SiO$_2$ there are collective propagating excitations at energies above the boson peak energy. Moreover, it has shown that the model of the $S(Q,E)$ based on the generalized Langevin equation approach is successful in reproducing the main features observed in the experimental data.

[1] For a review, see *Special Issue on the Seventh International Workshop on Disordered Systems, Andalo, 1999,* edited by A. Fontana and G. Viliani [Philos. Mag. B **79** (1999)].

[2] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[3] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

[4] For a review, see *Amorphous Solids: Low-Temperature Properties,* edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

[5] A. Brodin, A. Fontana, L. Borjesson, G. Carini, and L. M. Torell, Phys. Rev. Lett. **73**, 2067 (1994).

[6] A. P. Sokolov, A. Kisliuk, D. Quitmann, and E. Duval, Phys. Rev. B **48**, 7692 (1993).

[7] U. Buchenau *et al.,* Phys. Rev. Lett. **60**, 1318 (1988).

[8] (a) P. Benassi *et al.,* Phys. Rev. Lett. **77**, 3835 (1996); (b) **78**, 4670 (1997); (c) C. Masciovecchio *et al.,* Phys. Rev. B **55**, 8049 (1997). We point out that, as a typographical error on the vertical label, the values reported in Fig. 3 of (c) correspond to Γ and not to 2Γ.

[9] C. Masciovecchio *et al.,* Philos. Mag. B **79**, 2013 (1999).

[10] M. Foret *et al.,* Phys. Rev. Lett. **77**, 3831 (1996); **78**, 4669 (1997).

[11] N. V. Surovtsev, J. Wiedersich, V. N. Novikov, E. Rössler, and E. Duval, Phys. Rev. Lett. **82**, 4466 (1999).

[12] S. Alexander and R. Orbach, J. Phys. (Paris) Lett. **33**, L625 (1982).

[13] C. Masciovecchio *et al.,* Phys. Rev. Lett. **76**, 3356 (1996); **80**, 544 (1998); F. Sette *et al.,* Science **280**, 1550 (1998); D. Fioretto *et al.,* Phys. Rev. E **59**, 4470 (1999); A. Sokolov *et al.,* Phys. Rev. E **60**, R2464 (1999).

[14] E. Rat, M. Foret, E. Courtens, R. Vacher, and M. Arai, Phys. Rev. Lett. **83**, 1355 (1999).

[15] C. Masciovecchio *et al.,* Nucl. Instrum. Methods **B111**, 181 (1996); **B117**, 339 (1996).

[16] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).

[17] G. Monaco, A. Cunsolo, G. Ruocco, and F. Sette, Phys. Rev. E **60**, 5505 (1999).

[18] G. Ruocco *et al.,* Phys. Rev. Lett. **83**, 5583 (1999).

[19] G. Ruocco *et al.,* Phys. Rev. Lett. **84**, 5788 (2000).