Observation of the Onset of Strong Scattering on High Frequency Acoustic Phonons in Densified Silica Glass

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The linewidth of longitudinal acoustic waves in densified silica glass is obtained by inelastic x-ray scattering. It increases with a high power α of the frequency up to a crossover where the waves experience strong scattering. We find that α is at least 4, and probably larger. Resonance and hybridization of acoustic waves with the boson-peak modes seems to be a more likely explanation for these findings than Rayleigh scattering from disorder.

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A controversy regarding the fate of very high frequency acousticlike excitations in glasses arose in recent years [1,2]. Acoustic waves propagate in glasses up to rather high frequencies, for example, up to at least $\Omega/2\pi \simeq 0.4$ THz in vitreous silica, v-SiO_2 [3,4]. However, silica shows a pronounced "plateau" in the temperature (T) dependence of its thermal conductivity $\kappa(T)$ [5]. This feature was explained by postulating the existence of a rapid *crossover* of acoustic waves into a regime where they experience *strong scattering* [6]. In v-SiO_2, this crossover is expected at a frequency $\Omega_{co}/2\pi \simeq 1$ THz [7]. For the observed horizontal plateau to occur, besides strong scattering of thermal phonons, phonons of lower Ω must also experience a sufficiently strong T-independent scattering [8]. Several models predict that the inhomogeneous width of acoustic waves can increase with a high power of Ω, typically in Ω^4 [9,10], leading to this rapid crossover. However, the origin of the high power remained debated, whether Rayleigh scattering from structural defects [6], or resonance with local modes [10–12]. Rayleigh scattering seems generally too weak in materials as homogeneous as dense glasses to be able to account for the relatively low Ω_{co} suggested by the position of the plateau [6,8]. The local modes are seen in the "boson peak" (BP) and produce an excess over the Debye specific heat [13]. Successful models based on resonance or on soft potentials were developed to describe the observed properties, e.g., in [10,14,15].

It might seem, judging from some recent literature [2], that the above picture should have been revised after it became possible to observe in glasses the spectrum of longitudinal acoustic (LA) waves at THz frequencies with x-ray Brillouin scattering (BS) [16]. This new experimental tool is important here, as it potentially allows one to check some of the previous conjectures. It led to many publications claiming to prove that sound *propagates* at frequencies much above the earlier expectations for Ω_{co}, e.g., [17,18]. In this respect, it must be emphasized that inelastic x-ray scattering (IXS) still is a difficult spectroscopy with severe limitations on resolution and intensity. First, it is practically not possible with current instruments to investigate *scattering* vectors Q below ~ 1 nm^{-1}, a value which happens to coincide with the expected *wave* vector q at crossover, q_{co}, in v-SiO_2 [7] and in many other glasses. Second, the narrowest instrumental profile allowing for sufficient intensity [19] still has an energy width around 1.5 meV (or $\simeq 0.4$ THz) and extended Lorentzian-like wings. Owing to the relatively strong elastic scattering of glasses, this tends to mask the weaker Brillouin signal. For these reasons it is still not possible to investigate with IXS the LA waves of v-SiO_2 at frequencies where their linewidth might grow in Ω^4 [20,21]. Finally, the signal-to-noise ratio being also small, the subtle changes in BS line shapes that indicate strong scattering might easily go unnoticed [22]. To alleviate several of these difficulties, we investigated permanently densified silica glass, d-SiO_2, in which $\Omega_{co}/2\pi \simeq 2$ THz and $q_{co} \simeq 2$ nm^{-1} [23,24]. A clear demonstration of a rapid increase of the LA width as Ω approaches Ω_{co} from below is still missing. This is a *crucial* check for the onset of strong scattering. It is all the more important that many recent Letters advocated acoustic linewidths that vary as Q^2 up to *very high* Q values, denying the onset of strong scattering and the existence of the corresponding crossover, e.g., [17,18,25–29]. In this Letter, we use the window between the smallest accessible Q and the q_{co} of d-SiO_2 to study the approach of the crossover. We find a width in Ω^α with α at least equal to 4 and probably larger, corroborating the early intuition of a rapid crossover to strong scattering.

The experiments were performed on the high-resolution IXS spectrometer ID16 at the European Synchrotron Radiation Facility in Grenoble, France. The x-ray energy is 21.7 keV. The main components of the spectrometer are a T-scanned monochromator, the sample, a battery of five T-stabilized spherical analyzers, and the corresponding detectors. The instrumental line shape was determined for each analyzer behind its standard slit of 20×60 mm (width $\times$ height), using the signal from the first sharp diffraction peak of polymethyl methacrylate at 20 K. Very clean Voigt-like shapes were obtained with half widths at half maximum of $\simeq$ 0.75 meV. The analyzers permit data collection at five Q in increments of $\simeq 3\ \mathrm{nm}^{-1}$. As we are now interested in small Q, the first analyzer was placed to the left of the forward direction, and the second to the right. This allows simultaneous collection of two interesting data points with $Q \leq 2\ \mathrm{nm}^{-1}$. The data presented here were thus acquired with only three different positions of the first analyzer, $|Q| = 2$, 1.8, and $1.6\ \mathrm{nm}^{-1}$. Each spectrum was accumulated for nearly two full days. The sample of d-SiO_2, of density $2.62\ \mathrm{g/cm}^3$, is the same as in previous measurements [23,24]. It is heated at 565 K to increase the inelastic signal. At this T, the densified structure does not relax. This was subsequently checked with optical BS, the sound velocity providing a sensitive test for the density [23].

Figure 1 illustrates typical spectra and their fits. The indicated values of Q correspond to the center of the collection slit which gives a spread $\Delta Q \simeq \pm 0.18\ \mathrm{nm}^{-1}$. The spectra consist of a strong elastic peak plus a weaker Brillouin doublet. In Fig. 1(a), the full raw spectrum is shown for the smallest usable Q, namely, $Q = 1.17\ \mathrm{nm}^{-1}$ [30]. The dashed line follows the elastic peak, illustrating the relative weakness of the doublet. To extract information on the position Ω and half-width Γ, the spectra are first adjusted to a damped harmonic oscillator (DHO) profile plus an elastic central peak (CP), convoluted with the instrumental function. Account is taken of the broadening due to the collection angle by summing over contributions from surface elements of the slit, each at its own Q, using $d\Omega/dQ = v_g$. Here v_g is the group velocity which is determined iteratively. There are four free parameters in the fits: the integrated intensities of the elastic (I_{CP}) and inelastic (I_{DHO}) components, Ω and Γ. The small background shown by the baselines is fixed to the detector noise, measured independently. Figures 1(b) and 1(c) illustrate, for the two extreme values of Q measured below crossover, the inelastic part that remains after subtraction of the adjusted elastic contribution I_{CP}. The solid lines are the DHO fits. In Fig. 1(b) the width is mostly instrumental, while in 1(c) it is due in large part to a real broadening of the Brillouin signal.

The values obtained for Γ are shown in Fig. 2 against those for Ω which agree with [23]. Γ increases very rapidly with Ω. There should be a homogeneous broadening contribution to this width, Γ_{hom}. It is estimated from $\Gamma_{hom} \propto \Omega^2$ by extrapolation of an optical BS determination, $\Gamma_{hom}/2\pi = 26 \pm 5$ MHz for $\Omega/2\pi = 41.5$ GHz at 600 K [31]. Interestingly, in that BS experiment the linewidths of d-SiO_2 are very near those of crystal quartz over a broad range of T, whereas the linewidths of v-SiO_2 are typically 4 times larger. Thus, it seems reasonable to assume $\Gamma_{hom} \propto \Omega^2$, as, e.g., the Akhiezer mechanism might extend up to the THz region in d-SiO_2 at these elevated T values. This gives the Γ_{hom}

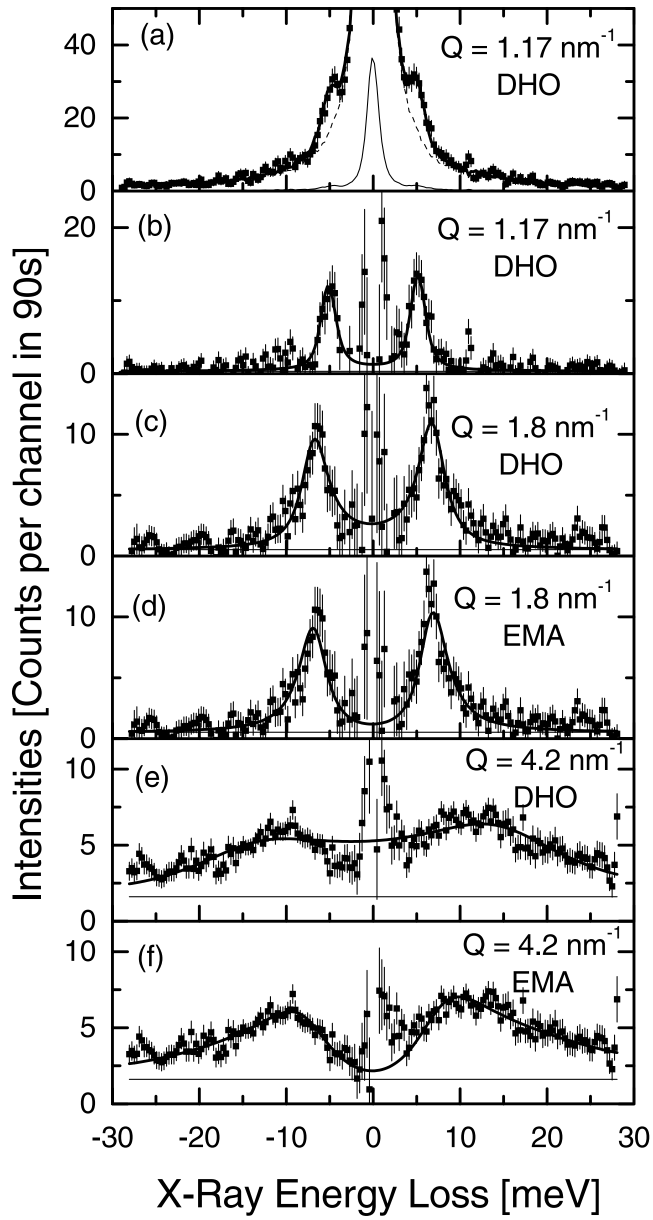

FIG. 1. IXS spectra of d-SiO_2 and their fits explained in the text: (a) a full spectrum and its central portion $\times 1/20$; (b),(c),(e) damped harmonic oscillator (DHO) fits of the inelastic part after subtraction of a central peak (CP) freely adjusted in the fits; (d),(f) effective-medium-approximation (EMA) fits of the inelastic part after subtraction of a CP also freely adjusted.

drawn in Fig. 2. The total rate is then approximated by Matthiesen's rule of adding rates due to independent processes, $\Gamma = \Gamma_{hom} + \Gamma_{inh}$ [21]. The inhomogeneous scattering width is adjusted to $\Gamma_{inh} \propto \Omega^{\alpha}$. A fit of the five measured points with this expression gives the solid line in Fig. 2 with $\alpha = 4.21 \pm 0.15$, and $\chi^2 = 0.76$. For comparison, if we force $\alpha = 2$, the best fit shown by the dotted line gives $\chi^2 = 5.4$.

The inelastic intensities, I_{DHO}, derived from these fits are shown in the inset of Fig. 2. With the very clean

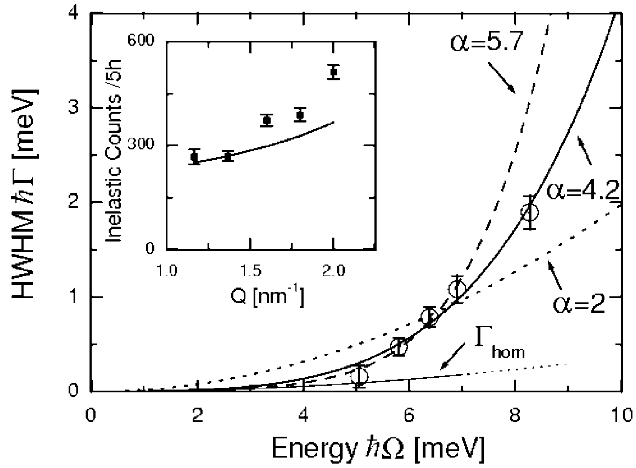

FIG. 2. The linewidths Γ extracted from DHO fits. Γ_{hom} extrapolated from optical Brillouin scattering is shown by a full line terminated by dots. A full line ($\alpha = 4.2$) shows the fit to $\Gamma_{hom} + \Gamma_{inh}$. The dashed line ($\alpha = 5.7$) is the same fit restricted to the four lowest data points. The dotted line illustrates the best fit with $\alpha = 2$, i.e., with Ω^2. The inset shows the total inelastic intensities (dots) normalized to 5 h accumulation on the best analyzer (#2) compared to a line $\propto v_{LA}^{-2}$.

instrumental profile and the long accumulation times, these are much more significant than previous ones [23]. They are compared to v_{LA}^{-2} (line), where $v_{LA} = \Omega/Q$ is the phase velocity determined in this experiment. The line is scaled to coincide with the most precise low Q point. One notes an excess in the observed I_{DHO} which grows as Q approaches q_{co}. One should ask whether this is due to the use of the DHO instead of the more appropriate effective-medium-approximation (EMA) line shape [23]. To investigate this we adjust all spectra to the EMA, including those obtained above q_{co} on the other detectors. We find that $\hbar\Omega_{co} = 8.5$ meV gives a good overall adjustment with the other parameters as in [23]. With these parameters fixed, there remain only the intensities I_{EMA} and I_{CP} to fit each individual spectrum. At small Q, for example, for $Q = 1.17$ nm^{-1}, the EMA and the DHO are equivalent. On the other hand, for $Q \gg q_{co}$, the EMA is superior as shown in Figs. 1(e) and 1(f). This particular spectrum is the average of three similar spectra acquired on the third analyzer at $Q = 4$, 4.2, and 4.4 nm^{-1}, for a total counting time of nearly one week. The three spectra were independently fitted and then added, reducing the size of the error bars. Figure 1(e) shows that the DHO demands a larger signal at small ω than the EMA in Fig. 1(f). The fit adjusts this by using a smaller I_{CP} for the DHO, but this is not able to represent properly the profile. Below q_{co}, a similar comparison is shown in Figs. 1(c) and 1(d). One notices the same trend. However, this is not the reason for the excess intensity. Indeed, we find that $I_{DHO} \simeq I_{EMA}$ well within the error bars for all five data points. The small dip in the center of the EMA fits is compensated by their more extended wings. The intensity excess seems thus real. For the present discussion, the main virtue of the EMA is to provide a fair estimate for Ω_{co}. There is, of course, no α to be extracted from this EMA which *postulates* $\alpha = 4$.

We now remark that the highest point in Fig. 2 is nearly at Ω_{co}. Owing to the Ioffe-Regel saturation of the damping, one cannot expect that $\Gamma_{inh} \propto \Omega^{\alpha}$ extends up to this point. The saturation of Γ_{inh} is an important aspect of the EMA [23]. Therefore, it is more reasonable to fit only the lowest four points to the power law. The result is shown by the dashed line in Fig. 2, which corresponds to $\alpha = 5.7 \pm 1.0$ with $\chi^2 = 0.28$. The extrapolation of this fit to the highest point gives a Γ_{inh} nearly equal to twice the observed one. This is precisely the saturation expected near crossover [23]. The value of α obtained in this manner does not change by allowing for the uncertainty in Γ_{hom}, only its uncertainty increases slightly. If α is really so large, the onset of strong scattering of sound cannot be due to Rayleigh scattering from structural inhomogeneities which give $\alpha = 4$ [9].

Resonance of sound with pointlike local modes, assuming a bilinear coupling, leads to $\Gamma_{inh}(\Omega) \propto \rho(\Omega)$, where $\rho(\Omega)$ is the mode density of states (DOS) [10,14]. Figure 3 shows the DOS of d-SiO_2 taken from [32] after subtraction of a Debye contribution of $1.44 \times 10^{-5} \times (\hbar\Omega)^2$, with $\hbar\Omega$ in meV. The BP, $\rho(\Omega)/\Omega^2$, with its maximum near Ω_{co} [24], is also shown. The values of Γ_{inh} and Γ are drawn on the same plot for comparison. They increase together with ρ but do not seem exactly proportional to ρ. There can be several reasons for this. One is that an exact determination of $\rho(\Omega)$ with neutron scattering is always a difficult task, especially for d-SiO_2 as a large sample can contain a few less densified fragments. Another possible reason is more profound. In silica the BP relates to rigid tetrahedra rotations [33]

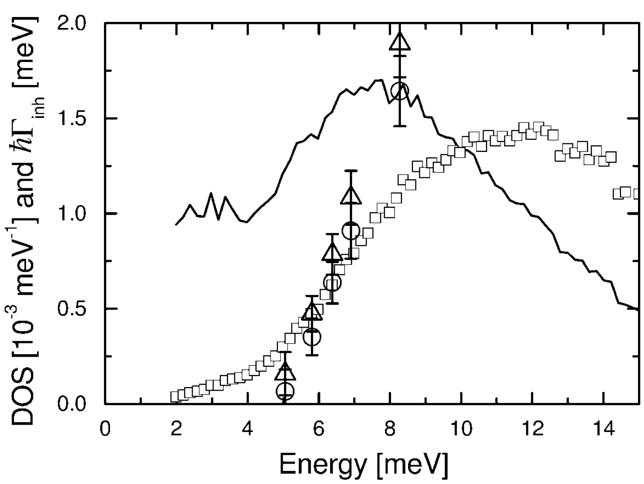

FIG. 3. The DOS of the local modes (squares) extracted from neutron scattering data [32] compared to Γ_{inh} (dots) and Γ (triangles). For illustration the boson peak calculated from this DOS is shown by the full line in 10^{-5} meV^{-3}.

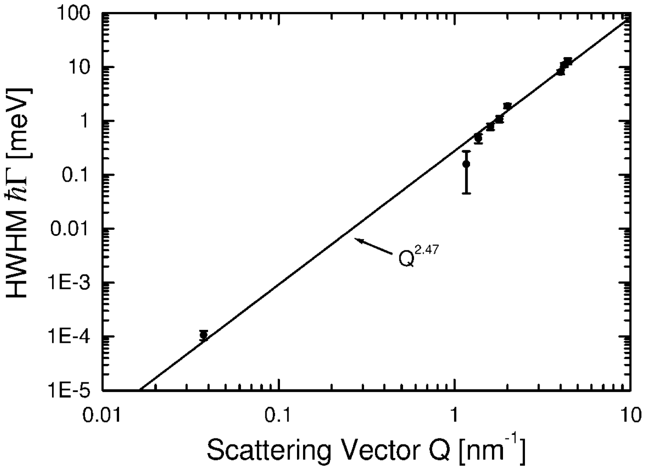

FIG. 4. Logarithmic presentation of $\Gamma(Q)$ for the optical Brillouin scattering point [31] and the IXS data obtained here. The straight line gives a power $\gamma = 2.47$ which averages over different regimes and which is of no further significance.

which cannot be pointlike in this connected network [34]. Thus, it produces a diffuse optic branch which hybridizes with the acoustic branch, an effect that depends both on the frequency and *size* of the excitations. Hence, there might be too few BP modes *of sufficient spatial extent* (a few nm) to appreciably hybridize with acoustic phonons at $q = 1.17$ nm^{-1}. The anomalous BS intensity increase near Ω_{co} can also result from this hybridization. Either the hybridization effectively softens the LA waves increasing their fluctuation amplitudes over what v_{LA} suggests, or the coupled local modes give themselves a coherent contribution to the BS amplitude. Further investigations are needed to clarify these points.

As final remark we stress that a logarithmic presentation of $\Gamma(Q)$ over a large range of Q can be misleading. This is illustrated in Fig. 4 for the data presented here. The line is a fit with $\Gamma \propto Q^{\gamma}$, which gives $\gamma = 2.47 \pm 0.08$. Such plots have often been taken as evidence for the absence of crossover phenomena, e.g., in [2,17,27]. The above discussion shows that this reasoning is unfounded. In Fig. 4, the lowest Q point is purely homogeneously broadened, the next four points are dominated by inhomogeneous broadening, the sixth point is near crossover, and the following three points are well above crossover. Hence, that presentation averages over three distinct regimes: one where $\Gamma = \Gamma_{hom}$, one which is dominated by Γ_{inh}, and finally one where Γ should not be extracted from DHO fits. The rapidly growing Γ_{inh} dominates Γ only over a narrow range in Ω (or Q). To be able to conclude about α as we do here, one needs (i) to know the position of Ω_{co} and (ii) to have a sufficient number of data points with significant values of Γ just below Ω_{co}. This was not the case in previous experiments, e.g., in [24] or in [35].

In this Letter, we reported the first spectroscopic observation of the onset of strong scattering of LA waves with $q < q_{co}$ in a network glass. In that region of q the inhomogeneous linewidth grows with a very high power of Ω, at least equal to 4, and probably higher. Also the intensity shows an anomalous increase with q. It seems that these results could be explained by the resonance and hybridization of the LA waves with the local BP modes. If so, these measurements might provide some information about the structure of glasses at extended length scales about which so little is known otherwise.

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