Sound-wave scattering in silica

A. Wischnewski and U. Buchenau
Institut für Festkörperforschung, Forschungszentrum Jülich, D–52425 Jülich, Federal Republic of Germany

A. J. Dianoux
Institut Laue-Langevin, Boîte Postale 156, F-38042 Grenoble Cedex 9, France

W. A. Kamitakahara
National Institute of Standards and Technology, Reactor Radiation Division, Gaithersburg, Maryland 20899

J. L. Zarestky
Ames Laboratory, Iowa State University, Ames, Iowa 50011

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The combination of x-ray Brillouin scattering data with coherent inelastic neutron scattering results in vitreous silica allows us to identify the scattering mechanisms for high-frequency sound waves in the glass. Below one THz, one has resonant scattering from low-frequency vibrations, above one THz Rayleigh scattering from the atomic disorder. [S0163-1829(98)01705-6]

One of the most controversial issues in the field of disordered solids is the scattering of sound waves at higher frequencies, above 100 GHz. The existence of a very strong scattering mechanism at these frequencies is evidenced by the universal plateau in the thermal conductivity of glasses around 5 K, where the thermal conductivity of the glass is often many orders of magnitude lower than that of the corresponding crystal.[1–3] The many different theoretical explanations for that plateau can be grouped into two fractions. The first assumes a strong scattering of the sound waves by some form of disorder (frozen-in free volume,[4] clusters,[3,5,6] fractals,[7] and disorder in the force constants,[8] to name only a few). The second group of explanations attributes the scattering to a resonant interaction of the sound waves with soft local vibrational modes, similar in eigenvector to the tunneling states and to low-barrier classical relaxations of the glass.[9–11]

In both cases, the explanations tend to link to the boson peak, another controversial feature of glasses, an excess of low-frequency modes over the Debye model expectation in the same frequency region. For those who believe in the scattering of the sound waves from some kind of disorder, it is a consequence of the strong localization of the sound waves. For the soft mode proposers, it demonstrates the existence of additional modes coexisting with the high-frequency sound waves.

The recent development of a high-resolution x-ray Brillouin technique[12] for the measurement of sound waves in the THz region has further stimulated the interest in the dispersion and damping of high-frequency sound waves in glasses. In the particular case of silica, there are two opposing interpretations for the x-ray Brillouin data, one of them in terms of damped sound waves[13] and the other one in terms of a crossover from sound waves to boson peak modes.[14]

The present paper combines the x-ray Brillouin data[13] with inelastic neutron scattering measurements of vitreous silica at higher temperatures. As earlier measurements at lower temperature,[15] the neutron data give convincing evidence for non-sound-wave modes at the boson peak. The number of additional modes can be determined to give a solid basis for an estimate of the scattering of the sound waves by the local modes. Together with the evidence from the x-ray Brillouin technique,[13] that estimate leads to a clear and simple picture for the phonon scattering in glasses.

The neutron scattering data for silica at higher temperatures were taken at two different spectrometers. The first was the time-of-flight spectrometer IN6 at the cold source of the high-flux reactor of the ILL at Grenoble. On the IN6 with 4.1 Å neutron wavelength and measuring in energy gain of the neutron, one has excellent resolution and intensity, but only a limited range in elastic momentum transfer Q up to about 2.6 $Å^{-1}$. Therefore, the measurements were complemented by a second experiment on a triple axis spectrometer with thermal neutrons of 2.3 Å wavelength at the Oak Ridge High Flux Reactor.[16] This measurement was taken with a constant final wave vector k_f in order to more easily relate the elastic to the inelastic intensities. On the IN6, data were taken up to 1673 K, 200 K above the glass transition temperature. The triple axis measurements extended up to 1273 K. Here we concentrate on the measurements near the temperature of 1050 K of the x-ray Brillouin measurement.[13] For the IN6, we took a measurement at 1104 K. On the Oak Ridge triple axis spectrometer, we summed two measurements at 841 and 1273 K to obtain data at the average temperature of 1057 K.

Figure 1 shows a comparison of these two sets of data. Figure 1(a) compares the elastic intensity in the intensity scale of the triple axis spectrometer. Figure 1(b) compares the inelastic intensities at an energy transfer corresponding to 1.3 THz, the position of the boson peak at that temperature. Both inelastic data sets have frequency windows of about 300 GHz width. The same scaling factor was used for both cases, showing a very satisfactory agreement between the two measurements. The data look like a mirror image of earlier low-temperature data,[15] but have a higher counting rate and better statistics.

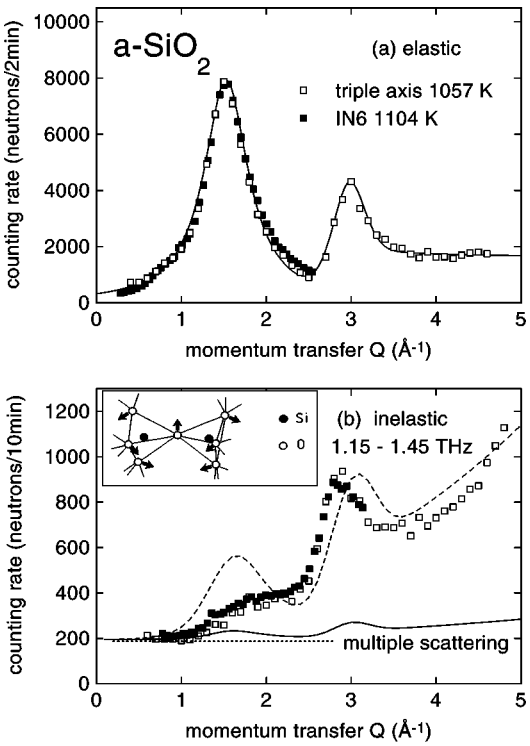

FIG. 1. Q dependence of the neutron scattering from vitreous silica at elevated temperature (a) elastic (the line is a guide to the eye) (b) at 1.3 THz (between 1.15 and 1.45 THz), together with calculated curves showing the failure of the sound wave picture. The inset of (b) shows the motional model proposed in Ref. 15.

In order to assess the meaning of the results in Fig. 1, imagine that one had only long wavelength sound waves in silica at 1.3 THz. The wavelength of the longitudinal modes (sound velocity 6370 m/s) at 1.3 THz is 49 Å, that of the transverse modes with 3950 m/s is 30 Å, corresponding to phonon wave vectors q of 0.13 and 0.21 $Å^{-1}$, respectively. These q values are still small compared to the momentum transfers at the first sharp diffraction peak at 1.6 $Å^{-1}$, so the atomic neighbors giving rise to that peak still essentially move in phase. If they did that for all modes in the frequency window, one should find the very marked first sharp diffraction peak of the elastic scattering reproduced in the inelastic scattering. Since there is only a weak trace of that peak in the inelastic data at the boson peak frequency, one is forced to conclude that one does not deal with pure sound waves.

The argument can be put on a quantitative basis using the formulas of Carpenter and Pelizzari[17] for the scattering from sound waves in glasses in the one-phonon approximation. In the long-wavelength limit, these formulas yield an inelastic dynamic structure factor proportional to $Q^2S(Q,0)$, where $S(Q,0)$ denotes the elastic intensity. For somewhat shorter wavelengths, one gets a broadening and a shift of the peaks of $S(Q,0)$. The continuous line in Fig. 1(b) shows the expectation using the Debye density of states on the basis of the light Brillouin scattering sound velocities.[18,19] As expected, the signal is much too small to explain the data.

But even if we assume that sound waves of higher wave vector q get down to the boson peak frequency, say, by some vibrational localization mechanism as envisaged by the first group of theoretical models for the boson peak,[3,5–8] one cannot explain the data. These models suggest vibrations of

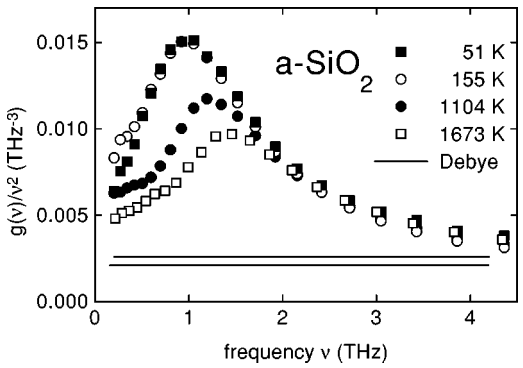

FIG. 2. Density of states of vitreous silica for four temperatures in the representation $g(\nu)/\nu^2$ vs frequency. The solid lines represent the Debye density of states for the lowest (upper line) and highest (lower line) temperature.

clusters of about 20 to 30 Å diameter, i.e., effective wavelengths of the same order. Assuming plane waves with the corresponding average wave vector of 0.3 $Å^{-1}$ and adapting the number of modes to give the best agreement, one finds the dashed curve in Fig. 1(b), which still gives a very bad fit.

The weakness of the first peak rather requires a mode eigenvector where second-nearest oxygen neighbors move out of phase. Earlier results at lower temperatures[15] show a reasonable description of the data by the model of coupled SiO_4-tetrahedra libration shown in the inset of Fig. 1(b). Since there is perfect agreement between these high-temperature data and the low-temperature measurement, one can take over this explanation, which has been also recently corroborated in numerical work on silica.[20] Using such a motional model, one can calculate the vibrational density of states from the neutron data on an absolute scale. The earlier work[15] determined a vibrational density of states from 51-K data that agreed within experimental error with specific heat data around 10 K. A similar evaluation was done for the high-temperature data reported here, with only a slight change. That change was to first subtract the calculated Debye signal (calculated on the basis of the sound velocities[18,19]) from the data, in order to obtain the density of states of the additional modes. The same kind of evaluation was repeated for the older low-temperature data. Figure 2 shows the resulting total vibrational density of states. Note the unusual temperature dependence of the boson peak in silica, a shift to higher frequency with increasing temperature.

With that density of states of additional modes, one then turns to the second possible explanation of the plateau in the thermal conductivity at low temperatures, assuming resonant scattering of the sound waves from these additional modes. The coupling parameter describing the bilinear coupling between the sound wave strain and the displacement of an additional mode can be taken from soft potential fits[21] of the low-temperature glass anomalies. One then gets[11]

$$\lambda l_{\mathrm{res,vib}}^{-1} = 6\pi^2 \nu_0^2 \frac{g_{\mathrm{add}}(\nu)}{\nu}, \quad (h\nu_0)^2 = \frac{W\Lambda^2}{Mv^2}, \tag{1}$$

where λ denotes the wavelength of the sound wave, v the sound velocity, and Λ the bilinear coupling coefficient between the strain of the sound wave and the displacement of

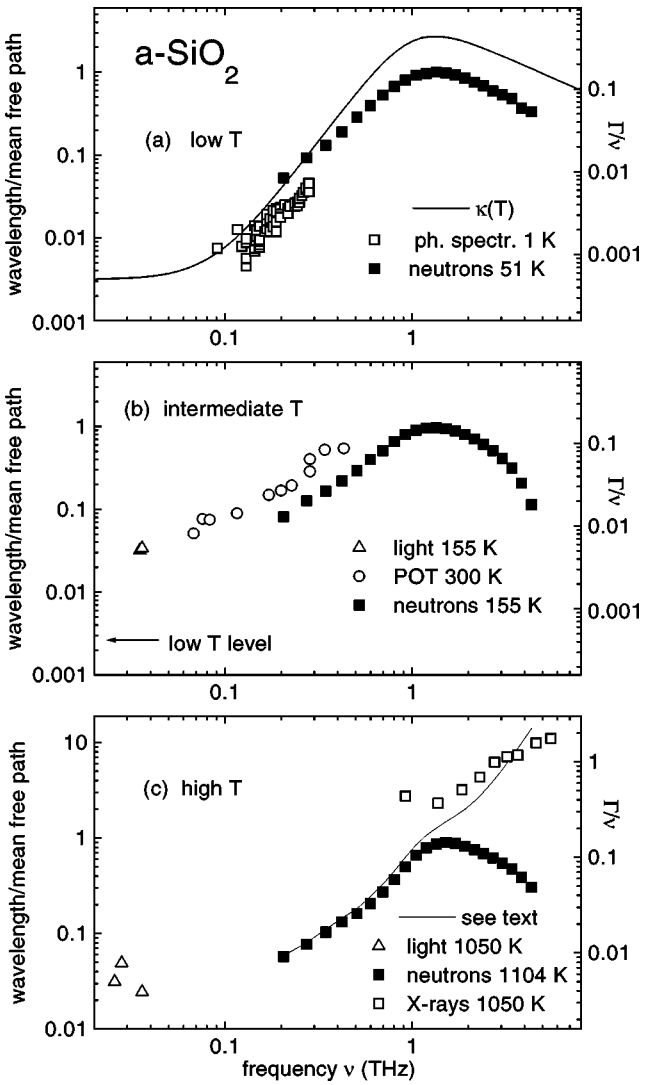

FIG. 3. Inverse mean free path times wavelength vs frequency at three different temperatures in silica. Comparison of values calculated from neutron data at (a) 51 K to fits of the thermal conductivity $\kappa(T)$ (Ref. 3) and to phonon spectroscopy data at 1 K (Ref. 23); (b) 155 K to light scattering Brillouin data at 155 K (Refs. 24,25), and to data obtained by POT between 100 and 300 K (Ref. 26); (c) 1104 K to light scattering Brillouin data at 1050 K (Refs. 13,18,19) and to the x-ray Brillouin results at 1050 K (Ref. 13).

the additional mode (these three quantities have to be taken separately for longitudinal and transverse sound waves; however, the coefficient Λ^2/v^2 is very nearly equal for the two kinds of modes). M is the average atomic mass of the glass, ν the frequency, $g_{\mathrm{add}}(\nu)$ the density of additional modes, and W the crossover energy between tunneling states and resonant vibrations of the soft potential model.

For silica, one finds from specific-heat and ultrasonic attenuation data[21,22] $W=0.34$ meV and $\Lambda=0.65$ eV for the longitudinal modes, yielding $\nu_0=1.09$ THz.

Figure 3 shows a comparison of the mean free path determined in that way from neutron data to other results in this heavily studied glass. Since the mean free path at lower frequencies is temperature dependent, the comparison is carried out at three different temperatures, 51 K for the low-temperature regime, 155 K for intermediate temperatures, and 1104 K to compare with the 1050 K x-ray Brillouin data.[13] The right scale of the data shows the ratio Γ/ν of the damping Γ (for small damping the full width at half-maximum of a Lorentzian) to the frequency ν. One has

$$\lambda l^{-1}=\frac{2\pi\Gamma}{\nu} \tag{2}$$

(the factor 2 in this equation was erroneously omitted in Ref. 16).

The low-temperature data at 51 K compare favorably with estimates from the thermal conductivity[3] and with phonon spectroscopy data at about 1 K.[23] That good agreement has been pointed out before[21] and serves to validate the whole procedure. The 155-K data extrapolate to light scattering Brillouin values,[24,25] and agree within a factor of 2 with those of a picosecond optical technique (POT).[26] The 1104-K data also extrapolate to the three light Brillouin values available[18,19,13] at the low-frequency end.

The comparison to the x-ray Brillouin data shows that the resonant scattering from low-frequency vibrations fails to describe the strong scattering above 2 THz. In view of this discrepancy, we return to old ideas on the scattering of sound waves from the static atomic disorder in the glass.[1,2,27] Zaitlin and Anderson[2] were the first to give a quantitative estimate for Zeller and Pohls[1] simple idea that each atom in a glass, not sitting at an ordered place, gives rise to Rayleigh scattering of the sound waves. They derived a mean free path

$$l_{\mathrm{static}}^{-1}=B\nu^4 \tag{3}$$

with a parameter B of the order of $2.6\ 10^{-3}\text{Å}^{-1}\text{THz}^{-4}$. If one adds that inverse mean free path to the one calculated from the resonant scattering via the neutron measurement, one finds the continuous line in Fig. 3(c), in reasonable agreement with the high-frequency x-ray Brillouin results.[13]

That interpretation is further supported by a recent analysis of low-frequency modes in a simple model glass,[28] which showed that about half of the damping of the sound waves at the boson peak comes from the interaction with the quasilocalized modes, while the other half had to be attributed to scattering from the atomic disorder.

We conclude that the combination of the x-ray Brillouin results with the interpretation of neutron data in terms of local vibrational modes reveals two scattering mechanisms for sound waves in silica. The first at low frequencies below 1 THz is the scattering from local modes coexisting with the sound waves. Earlier papers[11,22] have shown that this mechanism is not only able to explain the sound wave scattering at the plateau in the thermal conductivity, but also at lower frequencies, assuming tunneling states and classical relaxation over low barriers related to the additional vibrations. The second mechanism above 1 THz is the static Rayleigh scattering from the atomic disorder as proposed by Zeller and Pohl[1] and evaluated in the classical papers of Zaitlin and Anderson[2] and Jäckle.[27]

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