Behavior of thermal phonons in amorphous media from 4 to 300 K

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The intensity, frequency shift, and linewidth of the longitudinal Brillouin lines have been measured from 4 to 300 K in crystal quartz, fused quartz, and borosilicate glass. Differences in intensity between Stokes and anti-Stokes components have been found, extending to low temperatures the observation of long-lived vibrational states with occupation numbers equal to $(e^{h\nu/kT}-1)^{-1}$. Some anomalies in the frequency dependence of the elastic properties of fused quartz are eliminated. The measurements of the attenuation, which modify previous results between 77 and 300 K, are in good agreement with stimulated Brillouin scattering measurements below 10 K.

I. INTRODUCTION

In the last five years, a very extensive study of the thermal and elastic properties of glasses has been developed,[1-3] in order to explain the anomalies observed in the thermal conductivity and specific heat of amorphous media at very low temperatures.[4] These anomalies have been described in a theoretical model, by assuming the existence of a tunneling process in a distribution of two-level systems.[5] From this model, the absorption of sound waves has also been calculated.[6,7]

The study of the Brillouin scattering spectrum allows the direct observation of the thermal phonons and the measurement of their velocity and lifetime. In 1973, Love[8] demonstrated the existence of thermal phonons at low temperatures in fused silica and borosilicate glass by the observation of thermal Brillouin scattering (TBS). The results given by this author were concerned with temperatures above 20 K. The only measurement given at very low temperature was not completely unquestionable. The anomalous intensity observed was attributed by the author to a possible sample heating by the laser. The parasitic effects due to the I_2-vapor filter hindered the comparison of the relative intensities of the Stokes and anti-Stokes components, as the longitudinal Stokes component was strongly absorbed by this filter. The measurement of the attenuation of the elastic wave responsible for the scattering was not possible, as the resolving power of the interferometer was lower than 3×10^5. Last, the variation with temperature of the velocity of hypersounds was not given in this work. The only measurements, between 4.2 and 300 K, of the velocity of hypersounds for frequencies of about 25 GHz, were obtained by means of stimulated Brillouin scattering[9] (SBS). The measurements of attenuation were also given between 1.1 and 10 K.[9,10]

On the other hand, the elastic properties of fused quartz and silicate glasses have been extensively studied by ultrasonic techniques in the range from 1 MHz to 1 GHz.[11-13] By comparing these measurements to SBS results below 10 K and to TBS measurements[14] between 77 and 300 K, Krause[15] pointed out an anomalous frequency dependence of the acoustic properties of fused quartz.

We present here the results of a study of TBS in fused quartz, borosilicate glass, as well as in crystal quartz used as a test material, from 4.2 to 300 K. The ratio of the intensities of the Stokes (I_S) and anti-Stokes (I_{AS}) components is given and compared to theoretical calculations. The values of the velocity and attenuation of longitudinal hypersounds are also given. These results allow us to extend to high frequencies the studies of the minimum in the velocity and of the secondary relaxation peak in attenuation observed previously by means of ultrasonic techniques.

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Experimental method

The frequency shift ν_B of the Brillouin lines in an isotropic medium is given by

$$\nu_B/\nu_0 = 2n(v/c)\sin\tfrac{1}{2}\theta, \tag{1}$$

where ν_0 is the frequency of the monochromatic incident light, n the refractive index, v the phase velocity of the elastic wave responsible for the scattering, c the light velocity, θ the scattering angle (the angle between the incident and scattered beams). The propagation velocity of the hypersonic wave at the frequency ν_B may be deduced from the measurement of ν_B when n and θ are known.[16]

The Brillouin line shape is related to the time decay of the acoustic waves in the medium. As far as this decay is proportional to $e^{-t/s}$ the profile is Lorentzian. The measurement of the halfwidth at halfmaximum Γ gives s and the spatial attenuation coefficient α according to the expression

$$\Gamma = (2\pi s)^{-1} = \alpha v/2\pi . \tag{2}$$

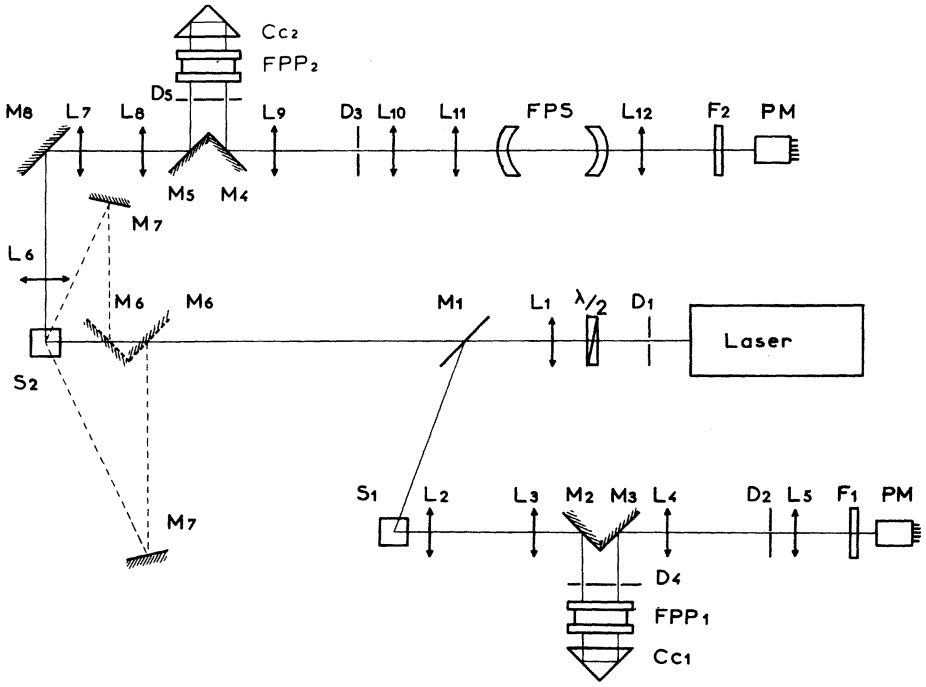

FIG. 1. Schematic representation of the optical device. *D*: apertures; *L*: lenses; *M*: mirrors; *F*: interferential filters; PM: photomultipliers; *S*: samples; FPP and FPS: plane and spherical Fabry-Pérot interferometers; *Cc*: corner cubes (retroreflectors); λ/2: half-wave plate.

An interferential spectrometer of high resolving power ($R > 10^7$) is necessary for studying the Brillouin spectrum with sufficient accuracy. The Rayleigh component of the scattered spectrum is generally strong. The contrast of the spectrometer has therefore to be high to avoid overlapping.

A sketch of the device is given in Fig. 1 (see Ref. 17 for a detailed description). The incident light was provided by an argon-ion laser with an output power of 800 mW for $\lambda_1 = 4880$ Å or $\lambda_2 = 5145$ Å (Spectra Physics model 165). The apparatus was composed of two spectrometers.

The resolving unit of the first (lower part of the figure) was a double-passed plane Fabry-Pérot interferometer. The thickness was varied from 2 to 20 mm, corresponding to a resolving power of 2×10^5 and 2×10^6, respectively. This device gave the values of the intensity and the preliminary frequency-shift measurements which were necessary to adjust the second spectrometer and to interpret the final results.

In the second device (upper part of the figure) used for the measurement of the frequency shift and linewidth of the Brillouin component, a double-passed plane FP, whose free-spectral range and finesse were equal to 83 GHz and 40, respectively, was used as a monochromator. Using our preliminary measurements of frequency shift, the frequency corresponding to the maximum transmission of this filter was matched with the frequency of the Brillouin line by air-pressure adjustment. For measurements at temperatures higher than 20 K, the resolving unit was a spherical FP interferometer, with a free spectral range of 1.48 GHz, and a finesse of 50. To increase the resolving power for lower temperatures, we used a spherical FP interferometer with a free spectral range of 0.7464 GHz and a finesse of 50. The maximum resolving power was equal to 5×10^7 and the total contrast was higher than 10^7. The relative accuracy obtained with this instrument was about 0.1% for velocity and 5%, for both attenuation and intensity measurements.

In these experiments, the scattering angle was about 170°. The broadening due to the aperture of the scattered beam was corrected by the method described in Ref. 18. In such a geometrical configuration, the elastic component added to the Rayleigh component due to frozen-in density fluctuations was small. The Landau-Placzek ratio $I_R/2I_B$, where I_R and I_B are the intensities of the Rayleigh and Brillouin components, respectively, is equal to about 25 for fused quartz and 200 for borosilicate at room temperature. The contrast obtained with a double-passed Fabry-Pérot (FP) interferometer was high enough to allow the Brillouin spectrum to be analyzed with a good accuracy. Since excessive parasitic light was avoided, it was thus unnecessary to use a I_2 filter in this study.

The samples were Puropsil fused quartz manufactured by Electro-Quartz (France), with an OH content lower than 10 ppm and potassium borosilicate glass (Sovirel A 248, composition SiO_2: 40; B_2O_3: 50; K_2O: 10, in mole percent).

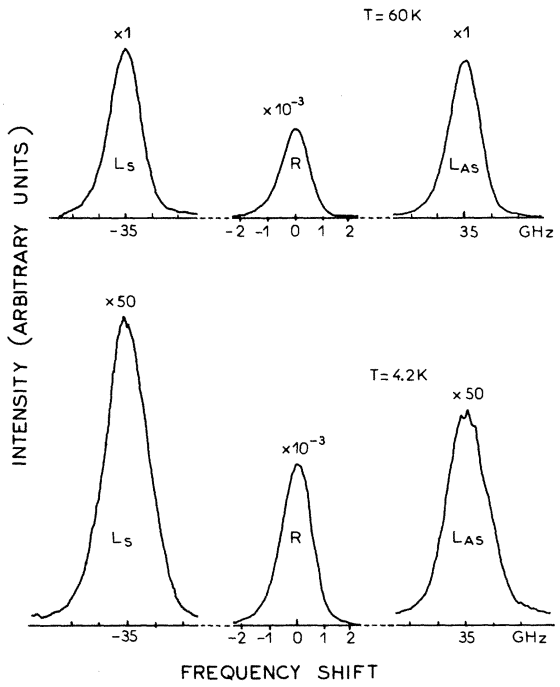

FIG. 2. Typical traces of spectra obtained with a double-passed plane Fabry-Pérot interferometer in fused quartz. The linewidth of the incident light was equal to 4880 Å. L_S, L_{AS}, and R are the longitudinal Brillouin Stokes, longitudinal Brillouin anti-Stokes and Rayleigh components, respectively.

B. Intensity of Brillouin lines

The intensity was measured by using the first spectrometer with the lower resolving power. A modification of the height of the recorded Brillouin line may be due to coupling between the two successive FP. This effect has been eliminated by fast repetitive piezoelectric displacement of the corner-cube retroreflector used to achieve double passing of light through the FP. Typical traces of spectra obtained for $T = 60$ and $T = 4.2$ K are given in Fig. 2.

From the dynamical theory of crystal lattices and the quantum theory of Brillouin scattering, it is known that, in crystals, the Brillouin Stokes and anti-Stokes intensities are proportional to $\langle n \rangle + 1$ and $\langle n \rangle$, respectively, where $\langle n \rangle$ is an occupation number given by

$$\langle n \rangle = (e^{h\nu/kT} - 1)^{-1}, \tag{3}$$

ν is the phonon frequency, h the Planck's constant, k the Boltzmann's constant, and T the absolute temperature. It may be assumed that this expression is valid for the long-lived vibrational states responsible for the scattering in amorphous media.

It follows that

$$I_{AS}/I_S = e^{-h\nu/kT}. \tag{4}$$

The measurements of this ratio are given in Fig. 3 for both crystal and fused quartz. The theoretical values from Eq. (4), which are also given, are in good agreement with the experimental results for crystal as well as for amorphous SiO_2. A similar observation has been made in borosilicate glass.

As the signal-to-noise ratio at very low temperatures was high enough to allow us to reduce the incident power, experiments were performed with laser powers of 150, 300, 600 mW in order to analyze the influence of sample heating by the laser. Even for $T = 4.2$ K, there was no noticeable difference between the values obtained with these different powers. This result shows that sample heating can be neglected in these experiments.

C. Velocity of hypersonic waves

Some examples of the high-resolution spectra used for the measurement of the frequency shift and of the linewidth in fused quartz are shown in Fig. 4. The values of the refractive index, needed for the calculation of the velocity, were taken from Refs. 19 and 20 for crystal and fused quartz, and from our measurements in borosilicate glass, for temperatures above 70 K. The curves were extrapolated to lower temperatures. The velocity of longitudinal waves in the range from 4.2 to 300 K is plotted in Figs. 5–7 for crystal quartz, fused quartz, and borosilicate glass, respectively.

In crystal quartz, the velocity increases slightly as the temperature is lowered. In fused quartz, a minimum in the velocity is observed near 70 K. This value is not in agreement with the result obtained by Heinicke *et al.*[21] from SBS experiments for frequencies of about 25 GHz. If we assume,

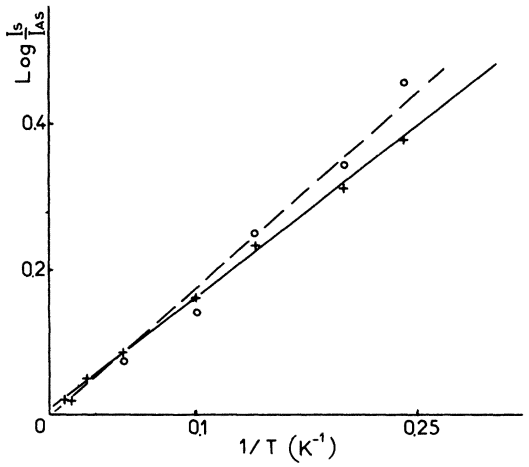

FIG. 3. Variation with temperature of the ratio of the anti-Stokes and Stokes intensities in crystal (O) and fused (+) quartz. The dashed and solid lines show the theoretical calculation.

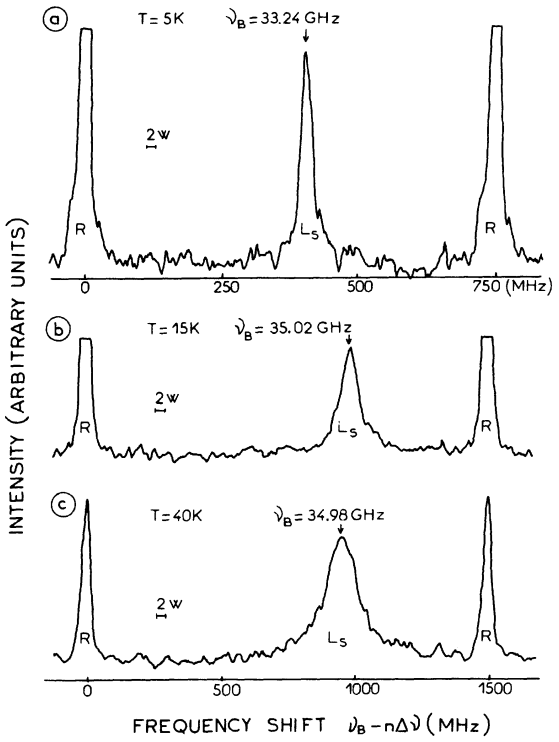

FIG. 4. Typical traces of spectra obtained with a spherical Fabry-Pérot interferometer. The incident linewidth was equal to 5145 Å for Fig. 4(a) and 4880 Å for Figs. 4(b) and 4(c).

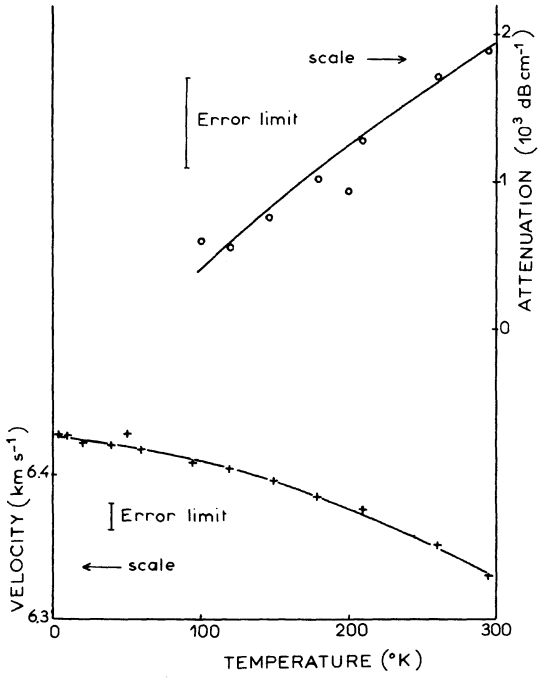

FIG. 5. Velocity (+) and attenuation (o) of 40-GHz hypersounds in crystal quartz.

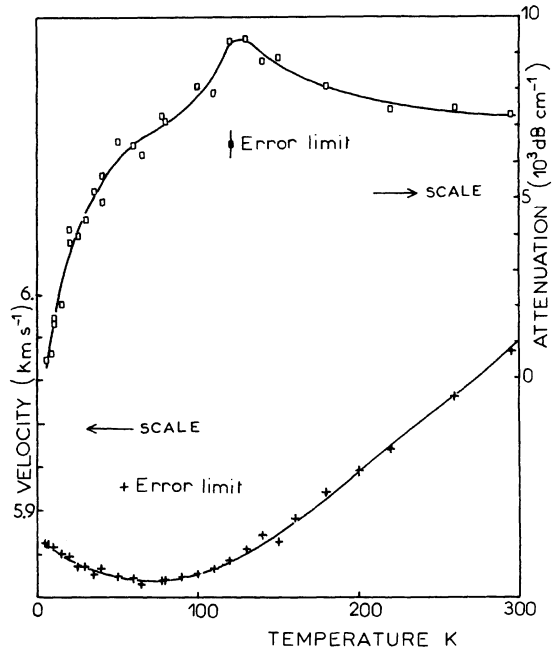

FIG. 6. Velocity (+) and attenuation (□) of 35-GHz hypersounds in fused quartz.

as demonstrated previously for transverse waves,[13] that the position of this minimum is independent of the type of silica, the anomalous frequency dependence of the position of this minimum noted by Krause is then eliminated and we obtain the surprising result that this position seems to be independent of frequency. On the other hand, our results are not accurate enough to allow the study of the maximum in velocity indicated by Piché *et al.*[3] near 1.5 K in the 100-MHz frequency range. We plan to perform new low-temperature experiments in order to study this maximum for hypersonic frequencies.

In borosilicate glass, a minimum in the velocity is noted near 120 K, which is the temperature of the absorption peak in this glass. We will return to this point in Sec. III.

D. Attenuation of hypersonic waves

The measurements of the sound attenuation are given in Figs. 5–7. In crystal quartz, the attenuation decreases strongly as the temperature is lowered, and cannot be measured below 80 K within the accuracy of our experiments.

The curves for the two glasses are very similar,[22] and we will restrict our discussion to fused quartz. For this material, numerous other studies of its acoustic properties are available, and the comparison of these results to our measurements is possible.

At temperatures higher than 80 K, the hypersonic attenuation is governed by a broad peak due to a

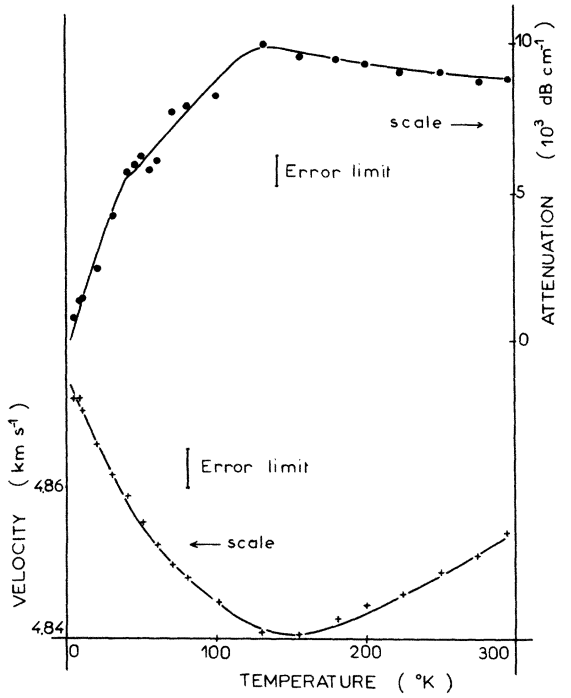

FIG. 7. Velocity (+) and attenuation (●) of 33-GHz hypersounds in borosilicate glass.

thermally activated structural relaxation process. This confirms the necessity, suggested by the low-frequency data, to use a complex distribution of relaxation times for fitting the experimental results.[11]

Our results connect the previous TBS[23] measurements above 80 K to those obtained by SBS below 10 K. The large secondary maximum in attenuation near 20 K predicted by Krause from Pine's results was not observed. A plateau was noted in the vicinity of 30 K, which had to be compared to the slight secondary maximum near 5 K for ultrasonic frequencies.[12] Krause[24] has shown that this maximum can be attributed to a relaxational process following an Arrhenius law with an activation energy of 60 cal mol^{-1}. The position of the plateau in our experiments agrees with an extrapolation of Krause's results. Therefore, the same relaxational process can account for our observation.

At temperatures lower than 10 K, the linewidth to be measured varies from 1 to 10 MHz. The instrumental linewidth is about 10 MHz. The parasitic broadening due to the aperture of the beams is approximately equal to 2 MHz. The effect of the finite dimensions of the scattering volume can cause a broadening of about 1 MHz. It is therefore difficult to measure the actual linewidth with a sufficient accuracy. After eliminating the above parasitic broadenings, the attenuation was found nearly proportional to T^2 between 4.2 and 15 K and the mean free path equal to 4×10^{-2} cm for $T=4.2$ K. These results, which are different from the measurements given by Heinicke,[9] are in good agreement with the SBS values given by Arnold *et al.*[10]

In the tunneling model theory given by Jäckle[25] the sound attenuation is found proportional to ω^2/T for the resonant absorption process at temperatures below 1 K. For the relaxational mechanism occurring at higher temperatures, the attenuation is proportional to T^3 and independent of the frequency when $\omega\tau_m \gg 1$, and to ω and independent of the temperature when $\omega\tau_m \ll 1$. τ_m is the minimum value in the distribution of relaxation times of the two level systems. In our experiments, the relation $\omega\tau_m > 1$ is verified at 4 K, while $\omega\tau_m \simeq 1$ at higher temperature. The T^2 dependence indicated above can be interpreted tentatively as the transition between the two limiting regimes or, alternatively, as the superposition of the T^3 dependence corresponding to the relaxational process, and of a constant part due, for instance, to geometrical "Rayleigh-like" scattering of elastic waves,[26] which could be of the order of 2 MHz and obviously independent of the temperature.

III. CONCLUSION

The above results show, for the first time to our knowledge, differences in intensity between Brillouin Stokes and anti-Stokes lines. In crystal quartz, this is only a verification of a result of the quantum theory of Brillouin scattering. On the other hand, in fused quartz, this result extends to low temperatures the observation of long-lived vibrational states with occupation numbers similar to those observed in crystals. Our measurements of velocity and attenuation of acoustic waves eliminate some of the anomalies pointed out previously in the frequency dependence of the elastic properties of fused quartz. For borosilicate glass, the minimum in the velocity occurs at the temperature corresponding to the maximum of the absorption. By comparing this result to ultrasonic measurement, the classical shift to higher temperatures with increasing frequency of the structural relaxational process is observed. On the other hand, in fused quartz, the minimum in velocity occurs at a temperature intermediate between the ones corresponding to the two relaxational processes. In order to obtain more information on this behavior, we intend to carry out on the same sample a study of the frequency dependence of this minimum, and also to extend to low temperatures the measurement of the linewidth of the transverse Brillouin lines.

The agreement between the SBS measurements[10] and our results below 10 K shows that the attenuation is independent of the acoustic intensity above 4 K, and that the same behavior is observed for thermal and coherent phonons.

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