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Velocities of First and Zero Sound in Quartz*

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The temperature dependence of the velocity of sound in *X*-cut and *BC*-cut natural quartz crystals has been measured in the range 4 to 75 °K. Measurements were made at frequencies of 35, 100, and 1000 MHz. By assuming that at these frequencies the velocity is frequency independent at 4 °K, these results can be used to obtain the frequency dependence of the velocity at higher temperatures. At temperatures below 20 °K, or above about 65 °K, there is no velocity dispersion in the frequency range studied, to within the experimental uncertainty. In the temperature range between 20 and about 65 °K, the velocity is greater at 1000 MHz than at the lower frequencies, both for the *X*-cut and the *BC*-cut crystals. These results are compared with theories of velocity dispersion due to interaction with thermal phonons, and qualitative agreement is obtained.

I. INTRODUCTION

The classical theory of thermoelasticity predicts that low-frequency sound waves propagate adiabatically through a crystal.[1] The phase velocity s is a solution of the equation

$$\det|\overleftrightarrow{\Gamma} - \overleftrightarrow{I}\rho_T s^2| = 0 \ , \tag{1}$$

where $\overleftrightarrow{I}$ is the unit 3×3 matrix, ρ_T is the density at the temperature T, and $\overleftrightarrow{\Gamma}$ is a 3×3 matrix with components

$$\Gamma_{\alpha\gamma} = K_\beta K_\delta C^a_{\alpha\beta\gamma\delta}/\vec{K}^2 \ , \tag{2}$$

where $\vec{K}$ is the wave vector of the sound wave, $C^a_{\alpha\beta\gamma\delta}$ are the adiabatic elastic constants, and summation over repeated subscripts is assumed. Low-frequency waves propagate adiabatically because the time τ_c, taken for heat conduction to equalize the temperatures of the compressed and rarefied regions of the wave, is long compared to τ_0, the period of the wave.[2] It is straightforward to show that

$$\tau_c \sim \lambda^2 C/\kappa \ , \tag{3}$$

where λ is the sound wavelength, C the specific heat per unit volume, and κ the thermal conductivity. Since τ_c varies as Ω^{-2} (Ω = angular frequency), and τ_0 goes as Ω^{-1}, at low frequencies $\tau_c > \tau_0$ and the propagation is adiabatic. At sufficiently high frequencies, on the other hand, $\tau_c < \tau_0$ and so there is enough time for temperature differences to be equalized and the motion is isothermal. , The velocity is then determined by the isothermal elastic constants, i.e., s is still given by Eq. (1) but with $C^i_{\alpha\beta\gamma\delta}$ replacing $C^a_{\alpha\beta\gamma\delta}$ in $\overleftrightarrow{\Gamma}$.

It has recently been pointed out[3,4] that the prediction of thermoelasticity theory that waves of high frequency should have an isothermal velocity is incorrect. Thermoelasticity assumes that local thermodynamic equilibrium always exists throughout the crystal in which the wave propagates. For a dielectric crystal, this assumption is valid only if the stress due to the sound wave varies slowly in the time it takes the thermal phonon system to come to equilibrium after it is disturbed. Hence, for local thermodynamic equilibrium to exist it is necessary that the condition $\tau_0 \gg \tau_{th}$ be satisfied, where τ_{th} is an average thermal phonon lifetime. If one uses the approximate relationship for the thermal conductivity

$$\kappa = \tfrac{1}{3} C \langle s \rangle^2 \tau_{th} \ , \tag{4}$$

where $\langle s \rangle$ is an average velocity of the thermal phonons, it can be shown from Eq. (3) that it is not possible to have isothermal propagation ($\tau_0 > \tau_c$) while at the same time maintaining local thermodynamic equilibrium ($\tau_0 \gg \tau_{th}$). Hence, the thermoelasticity approach breaks down before high enough frequencies are reached for the propagation to be isothermal.

The results of the microscopic theory are that low-frequency waves, for which $\Omega\tau_{th} \ll 1$, have the adiabatic velocity and that waves of high frequency satisfying the condition $\Omega\tau_{th} \gg 1$ have a velocity different from the isothermal velocity. This new velocity is called the zero-sound velocity s_0, whereas the adiabatic velocity is referred to as the first-sound velocity s_1. The result of a previous theoretical calculation[4] of the difference of these velocities is given in Sec. III.

There is little experimental evidence with which to compare the microscopic theory. Svensson and Buyers[5] have observed a difference in the temperature dependence of sound velocities in potassium bromide, as measured by neutron scattering and by ultrasonic techniques. The neutron experiments involve sound waves (phonons) of

frequency ~10^{12} Hz and should satisfy the condition for having the zero-sound velocity. The ultrasonic experiments were performed[6] at a frequency of 9 MHz and should therefore measure the first-sound velocity. Svensson and Buyers were able to show that the temperature dependences of these two velocities were not the same, at least for some of the modes they studied. Their results were in reasonable agreement with theory.[3]

Another test of the theory is provided by Abraham *et al.*[7,8] who measured the velocity of sound in liquid helium 4 at frequencies between 12 and 84 MHz in the temperature range 0.1–0.5 °K. The velocity was found to *decrease* with increasing frequency, which indicates that the zero-sound velocity is less than the velocity of first sound.[9] For helium, theoretical expressions for the difference in velocity between first and zero sound have been derived by Khalatnikov,[10] Pethick and ter Haar,[11] Kwok *et al.*,[12] and Disatnik.[13] However, all these theories predict that zero sound should have a *greater* velocity than first sound, in direct disagreement with the experiments of Abraham *et al.*

Because of the rather limited experimental results and the discrepancy between experiment and theory in the case of liquid helium, measurements on other materials seem desirable. We have therefore investigated the velocity of first and zero sound in quartz for longitudinal and for shear waves. We describe these measurements in Sec. II, and in Sec. III compare these with theory.

II. EXPERIMENTAL MEASUREMENTS

In solids at room temperature, a typical thermal phonon lifetime τ_{th} is of the order of 10^{-11} sec. To make measurements in the zero-sound region at this temperature would therefore require frequencies of the order of 10^{11} Hz, but the attenuation at these frequencies would prohibit velocity measurements by the conventional pulse-echo technique. However, if lower frequencies are used to reduce the attenuation, the condition $\Omega\tau_{th} > 1$ for zero sound cannot be satisfied unless τ_{th} is increased by lowering the temperature. This has the disadvantage that the expected velocity difference between first and zero sound decreases rapidly with decreasing temperature. As a compromise, it was decided to make measurements at 1000 MHz to obtain the zero-sound velocity and at 35 and 100 MHz for the first-sound velocity. Measurements were made on single-crystal quartz because of the ease of generation of sound in this material, and also because the attenuation has already been studied in detail.[14,15] The general principle of the measurement technique was to determine the temperature dependence of the velocity from 4 °K to about 75 °K at a frequency of 1000 MHz and at a lower frequency ($\leq$ 100 MHz). At 4 °K, the thermal phonon lifetime is of the order of 10^{-6} sec and so both the 1000 MHz and the lower-frequency waves should propagate with the zero-sound velocity. When the temperature is increased, τ_{th} decreases and near some temperature T_1 the sound wave of lower frequency makes a transition to the first-sound velocity. The wave of higher frequency makes the corresponding transition at a temperature $T_2 > T_1$. At temperatures less than T_1, or greater than T_2, the velocity of both waves should be the same, but between T_1 and T_2 the difference in velocities of the two waves is equal to the difference in velocity of first and zero sound.

Low-Frequency Measurements

For measurements at 35 and 100 MHz, an echo-overlap method similar to that developed by Papadakis was used.[16] A block diagram of the electronics is shown in Fig. 1. The output of the frequency synthesizer triggers the oscilloscope directly. The output frequency divided by 1000 is used to trigger both the rf pulse generator and a delaying circuit which provides two pulses, each about 5 μsec wide, which strobe the oscilloscope. The rf pulse generator produces pulses of carrier frequency 35 or 100 MHz and duration ~1 μsec, which are used to drive the quartz crystal. The echoes from the sample are amplified and are displayed, unrectified, on the oscilloscope. If the frequency of the synthesizer is set to the reciprocal of the transit time of the sound wave in the crystal, all the echoes will appear superimposed

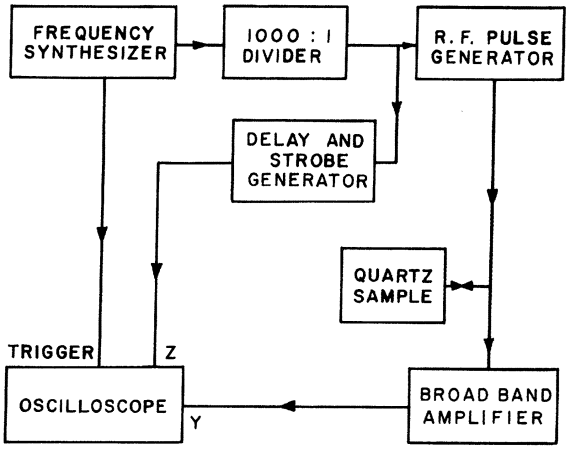

FIG. 1. Block diagram of system used for measuring velocity changes at low frequencies by the echo-overlap method. The operation of the system is described in the text.

on the oscilloscope. By reducing the intensity of the oscilloscope beam and suitably adjusting the delay of the strobe pulses, it is possible to make only two selected echoes visible. The frequency of the synthesizer is then adjusted to bring two cycles (one from each echo) into exact alignment. Let $\nu(0)$ be the frequency of the synthesizer when the crystal is at 4.2 °K. At a higher temperature T, the transit time in the sample will change from $\tau(0)$, its value at 4.2 °K, to some new value $\tau(T)$, and to bring the two cycles back into coincidence it is necessary to change the frequency of the synthesizer to $\nu(T)$. Then we have

$$\tau(T) = 1/\nu(T), \quad \tau(0) = 1/\nu(0) \ .$$

Since the fractional change in frequency is small, we have to a good approximation

$$\tau(T) - \tau(0) = [\nu(0) - \nu(T)]/\nu^2(0) \ . \tag{5}$$

If the lengths of the crystal at 4.2 and at T °K are $l(0)$ and $l(T)$, respectively, and if $s(0)$ and $s(T)$ are the velocities at these temperatures, we have

$$\tau(T) - \tau(0) = 2[l(T)/s(T) - l(0)/s(0)] \ . \tag{6}$$

Since the fractional changes in length and velocity are very small, we can combine Eqs. (5) and (6) to give

$$\frac{s(T) - s(0)}{s(0)} = \frac{l(T) - l(0)}{l(0)} + \frac{\nu(T) - \nu(0)}{\nu(0)} \ . \tag{7}$$

The temperature dependence of the velocity of 100-MHz longitudinal waves was measured in an X-cut quartz sample 1 cm diam and 2 cm long. As a check, measurements were also made at 35 MHz, using another electronic system developed in this laboratory by Chick. This system works by "brute force" in the sense that it starts an accurate clock when the rf generator is turned on, and the clock runs until it is turned off by a selected cycle from a returning echo. The reproducibility of the data obtained by each method was about ±2 ppm, and within this error the velocity changes obtained by both methods agreed throughout the temperature range studied. Figure 2 shows the results obtained for longitudinal waves by combining the data taken on two helium runs by Papadakis's method and four runs using Chick's apparatus.[17] The error bars represent the standard deviation of the mean. The change in length of the crystal due to thermal expansion has not been taken into account in calculating the results shown in Fig. 2, because the length change is probably not known as accurately as the change in transit time.[18]

The velocity of 35-MHz shear waves was measured in a BC-cut quartz cylinder 0.8 cm diam and 2 cm long using Papadakis's method only. In Fig. 3, the data from three runs on BC-cut quartz are shown. The change in length of the crystal has not been included in calculating these results. The standard deviation of the mean in this case is generally about 2 parts in 10^6 and is too small to be shown on the graph. In these experiments, the sample temperature was measured with a germanium resistance thermometer. The accuracy of the sample temperature is estimated to be ±0.2 °K.

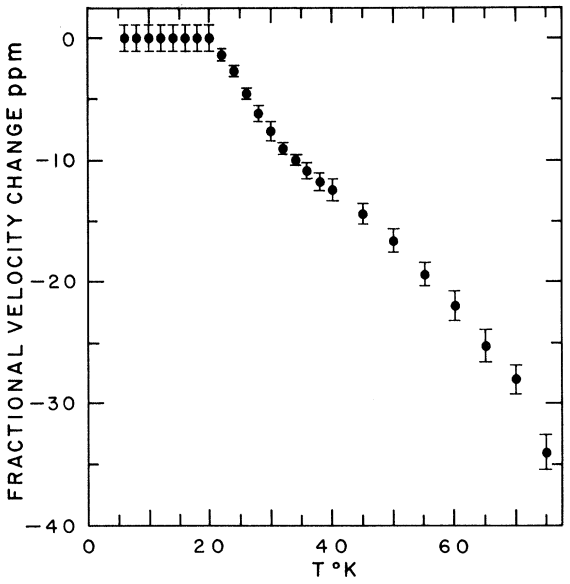

FIG. 2. Fractional velocity change $[s(T) - s(0)]/s(0)$ as a function of temperature for longitudinal waves in X-cut quartz. The error bars represent the standard deviation of the mean for the combined values of data taken on two different samples at 35 and 100 MHz.

Measurements at 1 GHz

A block diagram of the apparatus is shown in Fig. 4. The transmitter produces 1-GHz pulses approximately 1 μsec long and of peak power about 200 W. The repetition rate is 200 sec^{-1}. These are fed to a resistive divider and half the energy then goes via a variable attenuator E to a reentrant cavity C_1 in the cryostat. This cavity is used to excite ultrasonic waves in a quartz crystal Q_1 by a method similar to that used by Bömmel and Dransfeld.[14] The remaining energy from the transmitter is fed via a "trombone" variable-delay line D to a second reentrant cavity C_2 at room temperature, the temperature of this cavity being held constant to ±0.05 °K. This cavity is used to excite waves in a quartz crystal Q_2 of the same orientation and dimensions as the crystal Q_1 in the low-temperature cavity. The electrical signals

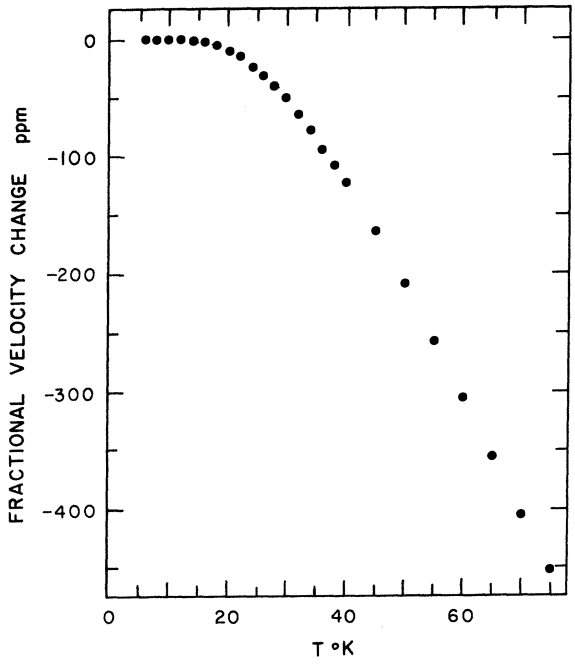

FIG. 3. Fractional velocity change $[s(T)-s(0)]/s(0)$ as a function of temperature for 35-MHz shear waves in *BC*-cut quartz.

produced by the returning acoustic echoes from the samples in both cavities are then recombined, and displayed on an oscilloscope after amplification and detection in the usual way.

The experimental procedure was as follows. Liquid helium was transferred into the low-temperature cryostat and as soon as the temperature of cavity C_1 stabilized at 4.2 °K the transmitter frequency was adjusted to match the frequency of the cavity. The tuning stubs S_1 were then adjusted so that the impedance looking towards the cavity from point A was 50 Ω. Cavity C_2 was then tuned so that its frequency also matched that of the transmitter, and the tuning stubs S_2 were adjusted so that the impedance was 50 Ω towards the cavity at point B. The trombone D was now adjusted to maximize the amplitude of the first combined echo. The temperature of the cavity C_1 and crystal Q_1 was then raised slowly and the trombone settings $L_1(T)$ and $L_2(T)$ that maximized the first and second combined echoes were recorded at each temperature. If the corresponding lengths of the trombone at 4.2 °K are denoted by $L_1(0)$ and $L_2(0)$, the extra time delay introduced by the trombone for the first combined echo at temperature T is

$$\Delta t_{D,1} = 2[L_1(T) - L_1(0)]/c \quad , \tag{8}$$

where c is the speed of light. The factor of 2 occurs because the signal passes through the trombone twice. On raising the temperature from 4.2 to T °K, the time taken for the sound wave to travel through the crystal and back increases by an amount

$$\Delta t_{C,1} = 2[l(T)/s(T) - l(0)/s(0)] \quad , \tag{9}$$

where $s(T)$ and $s(0)$ are the phase velocities at temperature T and at 4.2 °K, respectively, and $l(T)$ and $l(0)$ are the lengths of the crystal at these temperatures. The time taken for an echo to return may also include some other time delay Δt_0 which will change with temperature but which is independent of whether the first or second echo is considered. We discuss contributions to Δt_0 below. Since $L_1(T)$ is always such that the first echoes returning from both samples are in phase,

$$\Delta t_{D,1} = \Delta t_{C,1} + \Delta t_0 \quad . \tag{10}$$

For the second combined echo we have the corresponding result

$$\Delta t_{D,2} = \Delta t_{C,2} + \Delta t_0 \quad , \tag{11}$$

where $\Delta t_{D,2}$ is defined analogously to $\Delta t_{D,1}$, and $\Delta t_{C,2}$ is equal to twice $\Delta t_{C,1}$ since the second echo travels twice as far through the crystal. If we eliminate Δt_0 from Eqs. (10) and (11) and assume that the fractional velocity change is very small, it follows that

$$[s(T) - s(0)]/s(0) = [l(T) - l(0)]/l(0) + [s(0)/cl(0)][L_1(T) - L_1(0) - L_2(T) + L_2(0)] \quad .$$

Measurements were made on the first and second echoes as described above, and also on the second and third echoes. The ultrasonic attenuation of

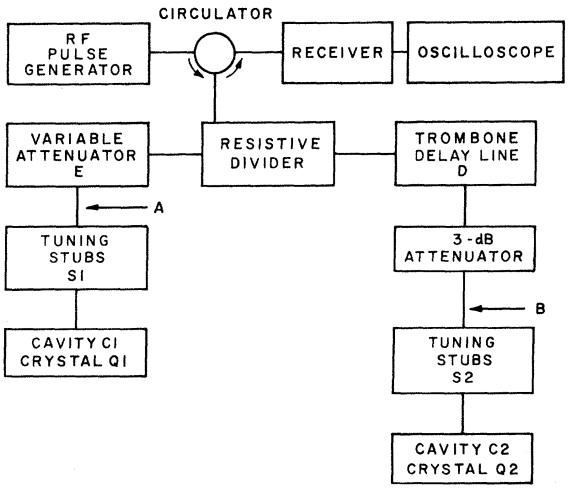

FIG. 4. Block diagram of system used for measuring velocity changes at 1 GHz. The operation of the system is described in the text.

the room-temperature sample was such that the fourth and higher echoes were too low in amplitude to be useful for reliable measurements.

In the first few runs, helium gas at a pressure of approximately 1 atm was maintained in the low-temperature cavity. This was to prevent ionization occurring in the cavity during the operation of the transmitter and also to give good thermal contact between the crystal and cavity. However, it was found that since the density, and hence the dielectric constant, of the helium varied considerably with temperature, particularly below 10 °K, the resonant frequency of the cavity became temperature dependent. This detuning of the cavity led to a large Δt_0 corresponding to several cm of delay on the trombone. Although the method described above eliminates the effect of Δt_0, we took the precaution in later runs of reducing the helium pressure to approximately 50-mm Hg. This was still high enough to prevent arcing but Δt_0 was reduced to a few-millimeter movement of the trombone at most.

The variable attenuator E was adjusted during the run so that the amplitudes of the echoes from the room-temperature and low-temperature cavities were of roughly the same magnitude. Any phase shift occurring in this attenuator will contribute to Δt_0 but will not affect the measurement of the velocity change. The main source of error in the experiment was the determination of the position of the trombone for maximum echo amplitude. Two methods were used. One was simply to view the echo on an oscilloscope and to determine by eye when the maximum amplitude was reached. The other was to use an electronic pulse-height measuring device.[19] Both methods led to comparable uncertainties in determining the trombone position for maximum amplitude. These uncertainties were usually about ± 2 mm and led to an error of approximately ± 4 parts in 10^6 in the determination of the temperature dependence of the velocity of sound. Sample temperature was measured with the same thermometer as in the low-frequency measurements.

Velocity measurements were made for longitudinal waves in an X-cut quartz sample which was 0.795 cm diam and 0.952 cm long. Shear wave measurements were performed in the same BC sample that was used at low frequencies. The error in these high-frequency measurements, expressed as standard deviation of the mean, was between 2 and 5 parts in 10^6. The fractional velocity difference defined by

$$\Delta s(T)/s_{1f}(0) \equiv [s_{1000}(T) - s_{1f}(T)]/s_{1f}(0) \ ,$$

where $s_{1000}(T)$ and $s_{1f}(T)$ are, respectively, the velocities at 1000 MHz and at low frequencies, was then calculated. This is shown in Fig. 5 for longitudinal and shear waves.

III. COMPARISON WITH THEORY

In Ref. 4, the following result was derived[20]:

$$s_0 - s_1 = \frac{2\pi^2 s_h(\vec{K}J)\beta\hbar^2}{\Omega\rho V} \times \sum_{\vec{k}j} [e_\alpha(\vec{K}J)K_\beta \Omega_{\alpha\beta}(\vec{k}j)]^2 \frac{n(\vec{k}j)[n(\vec{k}j)+1]}{[\Omega - 2\pi\vec{K}\cdot\vec{v}(\vec{k}j)]_\rho} - \frac{2\pi^2 T s_h(\vec{K}J)}{\Omega^2\rho C}[e_\alpha(\vec{K}J)K_\beta C^h_{\alpha\beta\gamma\delta}\alpha_{\gamma\delta}]^2 \ . \quad (12)$$

In this equation, $s_h(\vec{K}J)$ is the phase velocity in the harmonic approximation of a sound wave with wave vector $\vec{K}$, frequency Ω, polarization J, and polarization vector $\vec{e}(\vec{K}J)$. $\Omega_{\alpha\beta}(\vec{k}j)$ is the derivative with respect to Lagrangian strain $\eta_{\alpha\beta}$ of the frequency $\omega(\vec{k}j)$ of a thermal phonon with wave vector $\vec{k}$ and polarization j. $n(\vec{k}j)$ and $\vec{v}(\vec{k}j)$ are the

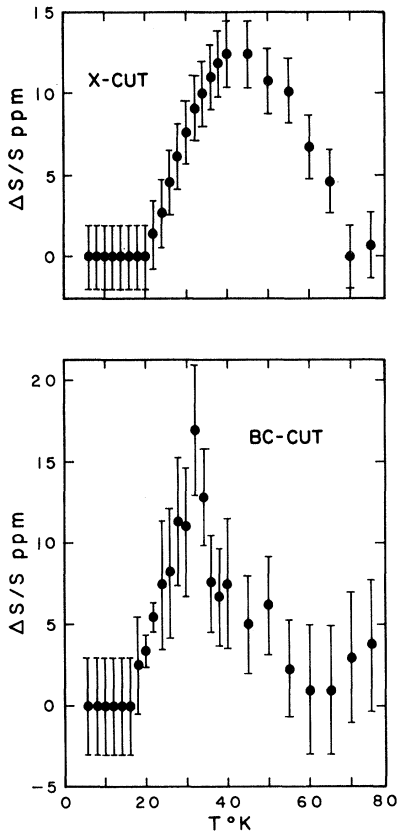

FIG. 5. Fractional velocity difference $[s_{1000}(T) - s_{1f}(T)]/s(0)$ as a function of temperature for longitudinal waves in X-cut quartz and for shear waves in BC-cut quartz. $s(0)$, the velocity at 4 °K, is assumed independent of frequency.

Bose-Einstein distribution function and the group velocity for this phonon. $C^h_{\alpha\beta\gamma\delta}$ and $\alpha_{\gamma\delta}$ are components of the elastic constants in the harmonic approximation and components of the thermal expansion tensor. β is $1/k_BT$, C is the specific heat, ρ is the density, and V is the volume of the crystal. In order to make a comparison between experiment and theory, Eq. (12) can be put into more convenient form as follows. We introduce the Grüneisen tensor with components

$$\gamma_{\alpha\beta}(\vec{k}j) = -\Omega_{\alpha\beta}(\vec{k}j)/\omega(\vec{k}j) \quad . \tag{13}$$

We then define an effective Grüneisen constant $\gamma_s(\vec{k}j)$ describing the coupling between the phonon $\vec{k}j$ and the strain due to the sound wave:

$$\gamma_s(\vec{k}j) = e_\alpha(\vec{K}J)\hat{K}_\beta\gamma_{\alpha\beta}(\vec{k}j) \quad . \tag{14}$$

$\hat{K}$ is a unit vector in the direction of $\vec{K}$. The first term on the right-hand side of Eq. (12) can now be written as

$$\frac{\beta\hbar^2}{2\rho s_h(\vec{K}J)V}\sum_{\vec{k}j}\gamma_s^2(\vec{k}j)\omega^2(\vec{k}j)n(\vec{k}j)\frac{n(\vec{k}j)+1}{[1-\hat{K}\cdot\vec{v}(\vec{k}j)/s_h(\vec{K}J)]_p}$$

$$=\frac{CT}{2\rho s_h(\vec{K}J)}\left\langle\!\!\left\langle\frac{\gamma_s^2(\vec{k}j)}{[1-\hat{K}\cdot\vec{v}(\vec{k}j)/s_h(\vec{K}J)]_p}\right\rangle\!\!\right\rangle \quad , \tag{15}$$

where we have introduced the notation that the average of some function of $\vec{k}j$ is defined by

$$\langle\langle f(\vec{k}j)\rangle\rangle = \sum_{\vec{k}j} f(\vec{k}j)\omega^2(\vec{k}j)n(\vec{k}j)[n(\vec{k}j)+1]/\sum_{\vec{k}j}\omega^2(\vec{k}j)n(\vec{k}j)[n(\vec{k}j)+1], \tag{16}$$

and we have used the result

$$C = (\beta\hbar^2/VT)\sum_{\vec{k}j}\omega^2(\vec{k}j)n(\vec{k}j)[n(\vec{k}j)+1] \quad . \tag{17}$$

The second term on the right-hand side of Eq. (12) can be rewritten using

$$C^h_{\alpha\beta\gamma\delta}\,\alpha_{\gamma\delta} = (\beta\hbar^2/VT)\sum_{\vec{k}j}\gamma_{\alpha\beta}(\vec{k}j)\omega^2(\vec{k}j)n(\vec{k}j)[n(\vec{k}j)+1], \tag{18}$$

which follows from Eq. (27) of Ref. 4. Then we find

$$e_\alpha(\vec{K}J)\hat{K}_\beta C^h_{\alpha\beta\gamma\delta}\alpha_{\gamma\delta} = C\langle\langle\gamma_s(\vec{k}j)\rangle\rangle \quad , \tag{19}$$

and so the second term in Eq. (12) becomes

$$-[CT/2\rho s_h(\vec{K}J)]\langle\langle\gamma_s(\vec{k}j)\rangle\rangle^2 \quad . \tag{20}$$

If we combine this with Eq. (15), we obtain

$$s_0 - s_1 = [CT/2\rho s_h(\vec{K}J)]\gamma^2_{\text{eff}} \quad , \tag{21}$$

where

$$\gamma^2_{\text{eff}} = \left\langle\!\!\left\langle\left(\frac{\gamma_s^2(\vec{k}j)\hat{K}\cdot\vec{v}(\vec{k}j)/s_h(\vec{K}J)}{1-\hat{K}\cdot\vec{v}(\vec{k}j)/s_h(\vec{K}J)}\right)_p\right\rangle\!\!\right\rangle$$

$$+\langle\langle\gamma_s^2(\vec{k}j)\rangle\rangle - \langle\langle\gamma_s(\vec{k}j)\rangle\rangle^2 \quad . \tag{22}$$

It is always true that

$$\langle\langle\gamma_s^2(\vec{k}j)\rangle\rangle \geq \langle\langle\gamma_s(\vec{k}j)\rangle\rangle^2 \quad . \tag{23}$$

Moreover, for a longitudinal sound wave one normally expects that for all thermal phonons

$$\hat{K}\cdot\vec{v}(\vec{k}j) \leq s_h(\vec{K}J) \quad .$$

It follows from Eq. (22) that for longitudinal waves zero sound must have a greater velocity than first sound. We now compare the theory with the experimental results in quartz.

Temperature Dependence of $\Delta s(T)$

The maximum difference in velocity $\Delta s(T)$ between high- and low-frequency waves is expected to occur in the temperature range where $\Omega\tau_{\text{th}} > 1$ for the 1000-MHz wave and $\Omega\tau_{\text{th}} < 1$ for the low-frequency wave. In this temperature range, we expect $\Delta s(T) = s_0 - s_1$. To find where this range should be, we have computed the average thermal phonon lifetime τ_{th} as defined by Eq. (4). For κ, we used the conductivity in the X direction as measured in this laboratory by McCurdy, and for C used the data of Westrum.[21] For the average phonon velocity in Eq. (4), we took $\langle s\rangle = 4.5\times10^5$ cm sec^{-1}. $\Omega\tau_{\text{th}}$ was calculated as a function of temperature for the sound-wave frequencies used in the experiments and the result is shown in Fig. 6. For waves with frequency 35, 100, and 1000

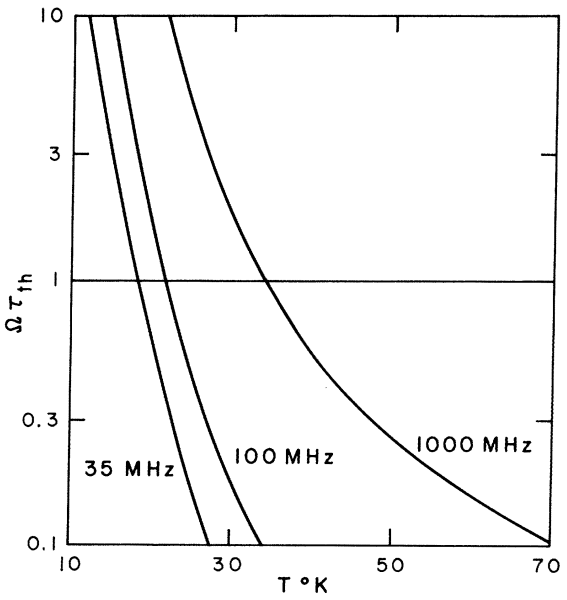

FIG. 6. The quantity $\Omega\tau_{\text{th}}$ as a function of temperature for the sound-wave frequencies used in the experiments. τ_{th} is calculated from the kinetic formula $\kappa = \frac{1}{3}Cs^2\tau_{\text{th}}$.

MHz, we find $\Omega\tau_{th}=1$ at temperatures of 18.3, 21.8, and 34.2 °K, respectively. One therefore expects that $\Delta s(T)$ will be a maximum between 25 and 30 °K. Experimentally, however, for longitudinal waves the maximum is at 40 °K, and is at 32 °K for shear waves. The result for longitudinal waves is at first sight particularly surprising since at 40 °K, $\Omega\tau_{th}=0.52$ for the 1000-MHz wave, and so both high- and low-frequency waves should have the first-sound velocity. However, this apparent discrepancy between theory and experiment is probably not too serious because our estimate of τ_{th} using Eq. (4) is very rough. For example, for κ we have used the conductivity parallel to the X axis, whereas if we had used the conductivity parallel to Z, all the $\Omega\tau_{th}$ values would have come out roughly a factor of 2 higher and would have agreed better with experiment. Also, one expects τ_{th} to vary considerably for thermal phonons of differing polarization and frequency, and so it is possible that those phonons that make the major contribution to s_0-s_1 may have longer lifetimes than the average. We note that even at 65 °K the longitudinal velocity at 1000 MHz is significantly higher than the low-frequency velocity, indicating that there are still *some* thermal phonons at this temperature for which $\Omega\tau_{th}\approx 1$. This also is understandable if there is a broad distribution of thermal phonon lifetimes.

Magnitude of $\Delta s(T)$

The most important result is that for longitudinal waves the velocity increases with increasing frequency, in agreement with theory. The maximum value of $\Delta s(T)/s$ for longitudinal waves is $(12.4\pm 2.0)\times 10^{-6}$ at 40 °K. At this temperature, the specific heat[21] is 17.5×10^5 erg cm^{-3} °K^{-1}. From Eq. (21), the value of γ_{eff} which makes s_0-s_1 agree with the experimental $\Delta s(T)$ at 40 °K is found to be 0.56. Unfortunately, there is insufficient information available regarding the Grüneisen tensor and the frequency spectrum of quartz to enable us to make a theoretical calculation of γ_{eff} using Eq. (22). Some information may be obtained using the measured third-order elastic constants of quartz. From the form of Eq. (22), it is clear that a large contribution to γ_{eff} will come from longitudinal thermal phonons traveling parallel to the sound wave, because the denominator of the first term on the right-hand side of Eq. (22) is small for these phonons. For a longitudinal sound wave propagating along the X axis, we have, from Eq. (14),

$$\gamma_s(\vec{k}j)=\gamma_{11}(\vec{k}j) \ .$$

For longitudinal thermal phonons traveling in the X direction, the following relation holds (from the results of Brugger[22]) if the thermal phonon wavelength is much greater than the lattice parameter:

$$\gamma_{11}(\vec{k}j)=-(c_{111}+3c_{11})/2c_{11} \ ,$$

where c_{11} and c_{111} are, respectively, second- and third-order elastic constants in the Voigt notation. Using measured values[23] of these elastic constants gives $\gamma_s(\vec{k}j)=-0.29$.

Further information on Grüneisen constants may be obtained from thermal expansion. For a longitudinal sound wave propagating in the X direction, it follows from Eq. (19) that

$$\langle\langle\gamma_s(\vec{k}j)\rangle\rangle=[(c_{11}+c_{12})\alpha_\perp+c_{13}\alpha_\parallel]/C \ ,$$

where $\alpha_\perp$ and $\alpha_\parallel$ are thermal expansion coefficients perpendicular and parallel to the optic axis. Using the results of White[18] for $\alpha_\perp$ and $\alpha_\parallel$ give

$$\langle\langle\gamma_s(\vec{k}j)\rangle\rangle=1.74, \quad \text{at } 30\ ^\circ\text{K}$$
$$=1.21, \quad \text{at } 75\ ^\circ\text{K} \ .$$

This implies the existence of some large positive $\gamma_s(\vec{k}j)$, probably as large as 2. Because of the large spread in γ values, our result that $\gamma_{eff}=0.56$ is certainly reasonable.

For the transverse wave measurements, the maximum value of $\Delta s(T)/s$ is $(16.9\pm 4.2)\times 10^{-6}$ and occurs near 32 °K. The specific heat at this temperature is 11.0×10^{-5} erg cm^{-3} °K^{-1}. A calculation similar to that performed for longitudinal waves gives a result of 0.82 for γ_{eff}.

It was noted above that the temperature dependence of $\Delta s(T)$ suggests that there is a broad distribution of thermal phonon relaxation times. This means that our experimental determination of the magnitude of s_0-s_1 at 40 °K is probably an underestimate, since at this temperature there will be *some* phonons for which $\Omega\tau_{th}>1$ at 35 MHz and some others for which $\Omega\tau_{th}<1$ even at 1000 MHz. It is difficult to estimate the magnitude of this effect. The problem would be reduced if measurements could be made with a greater difference between the low and high frequencies used.

IV. CONCLUSIONS

The velocity of sound has been measured as a function of frequency and temperature in quartz for longitudinal and for transverse waves. It is found that the high-frequency (zero-sound) velocity is greater than the low-frequency (first-sound) velocity, in agreement with theory. The magnitude of the difference in velocities is also in reasonable agreement with theoretical predictions. The results suggest that there is a broad distribution of thermal phonon relaxation times in quartz.

It is noted that the theory which has been used

here to explain the results does not agree at all with measurements which have been made of the velocity of sound in liquid helium. To investigate this discrepancy, we plan to make further measurements of the velocity over a wide frequency range, both in dielectric solids and in liquid helium.

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