

Hypersonic Absorption in Quartz at Temperatures Below 30°K*

R. NAVA,† R. AZRT, I. CICCARELLO,‡ AND K. DRANSFELD
Physics Department, University of California, Berkeley, California
 (Received 15 November 1963)

We have extended earlier absorption measurements between 500 and 10 000 Mc/sec to temperatures below 30°K where the mean free path of thermal phonons is likely to be larger than the ultrasonic wavelength. The absorption of transverse waves follows in magnitude, as well as in the dependence on temperature and frequency, as expected for a three-phonon process. However, the measured absorption per cm for longitudinal waves depends only slightly on frequency in contrast to the expectations for a four-phonon process; instead it supports a different absorption mechanism discussed here in detail. Finally, experiments with imperfect and neutron-irradiated quartz are reported in which strong additional absorption appears, which may be related to the absorption in fused quartz.

1. INTRODUCTION

ULTRASONIC waves of frequencies above 10^9 sec⁻¹ in perfect dielectric crystals are strongly absorbed by their interaction with thermal lattice vibrations. This conclusion can be drawn at least above 20°K from absorption measurements^{1,2} on quartz extending up to a frequency of 2.4×10^{10} sec⁻¹. The temperature and frequency dependence of the absorption agrees well in this high-temperature range with theoretical expectations^{3,4} which were based on an absorption process first proposed by Akhiezer.⁵ According to Akhiezer, an ultrasonic wave is absorbed in perfect crystals at finite temperatures because it perturbs the distribution of thermal phonons from equilibrium which is only re-established after a relaxation time θ determined by phonon-phonon collisions. This delayed re-establishment of equilibrium increases the entropy, and thereby acoustic energy is dissipated.

At sufficiently high temperatures where the theories just mentioned are valid, the mean free path of thermal phonons is much smaller than the acoustic wavelength so that they are exposed to the sound wave for only a fraction of one acoustic cycle ($\omega\theta \ll 1$). This makes it possible to neglect all effects arising from the direction which thermal phonons pursue with respect to the sound wave. Such a procedure is no longer justified at low temperatures, when $\omega\theta \gg 1$, as pointed out by Woodruff and Ehrenreich.⁴ Now thermal phonons continue to interact with an acoustic wave for many acoustic cycles, and—as we will see in detail—this interaction is quite different for thermal phonons “running with the wave” and those running at arbitrary odd angles with respect to it. Those fast thermal phonons

which are able to “run with the wave,” or more precisely, to keep up with the ultrasonic wave fronts, can interact with the sound wave in three-phonon processes, as first described by Landau and Rumer.⁶ Consequently, very fast acoustic waves, usually of longitudinal polarization, should not be absorbed by these three-phonon processes because few thermal phonons can keep up with them. The manner in which these fast ultrasonic waves are absorbed has seemed to be uncertain and processes of higher order, for example, involving four phonons, have been invoked to explain the absorption.

In view of the sparse experimental evidence concerning the ultrasonic absorption in dielectric crystals at low temperatures, it is the purpose of this paper to describe more extensive absorption measurements on quartz at kilomegacycle frequencies and at temperatures below 20°K. The experimental part is followed by a theoretical description of the absorption processes for slow and fast ultrasonic waves in pure crystals and, finally, some results on imperfect quartz are discussed.

2. EXPERIMENTAL PART

For the absorption measurements the ultrasonic waves were mostly generated and detected by use of the surface excitation technique described earlier^{7,8}: A pulsed microwave signal of 1 μ sec duration was fed into one of two cavities. One surface of the quartz specimen to be measured was exposed to the rf electric field of the cavity for the excitation of traveling acoustic waves which could then be detected in the second cavity. The resulting echo pattern of pulses received again after each round trip was displayed on the oscilloscope and photographed. For the measurements on the Z-cut quartz, which is not piezoelectrically active, thin X-cut quartz disks were bonded to the end faces, or magnetic Permalloy films were evaporated on in order to excite sound by the magnetic-film technique.⁹

* This work was supported by the U. S. Atomic Energy Commission.

† On leave of absence from Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela.

‡ NATO Fellow; on leave of absence from Physics Department, University of Palermo, Palermo, Italy.

¹ E. H. Jacobsen, *Phys. Rev. Letters* **2**, 249 (1959).

² H. Bömmel and K. Dransfeld, *Phys. Rev. Letters* **2**, 298 (1959).

³ H. Bömmel and K. Dransfeld, *Phys. Rev.* **117**, 1245 (1960).

⁴ T. O. Woodruff and H. Ehrenreich, *Phys. Rev.* **123**, 1553 (1961).

⁵ A. Akhiezer, *J. Phys. (USSR)* **1**, 277 (1939).

⁶ L. Landau and G. Rumer, *Physik. Z. Sowjetunion* **11**, 18 (1937).

⁷ H. Bömmel and K. Dransfeld, *Phys. Rev. Letters* **1**, 234 (1958).

⁸ E. H. Jacobsen, *J. Acoust. Soc. Am.* **32**, 949 (1960).

⁹ H. Bömmel and K. Dransfeld, *Phys. Rev. Letters* **3**, 83 (1959).

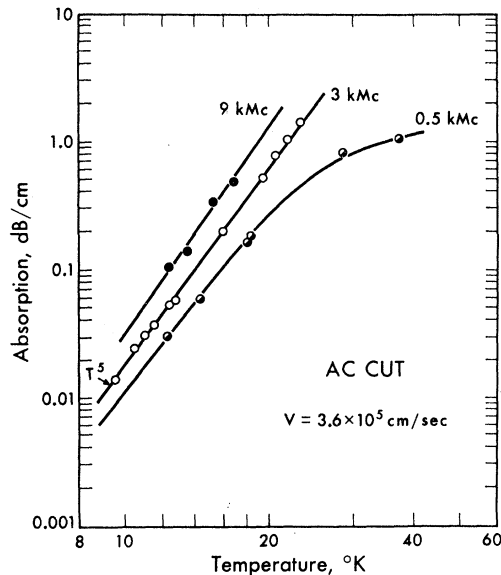


FIG. 1. The intrinsic absorption in an AC-cut crystal.

The acoustic absorption could then be determined from the heights of the echo pulses. For various reasons,¹⁰ such as misalignment of the two end faces, bulk inhomogeneity of the crystal, and diffraction effects, all of which do not vary with temperature, the echo pattern usually shows a sample-dependent non-exponential decay—even at the lowest temperatures. As the sample is heated, an additional relative decrease of the later echo pulses occurs from which the temperature-dependent absorption reported here was deter-

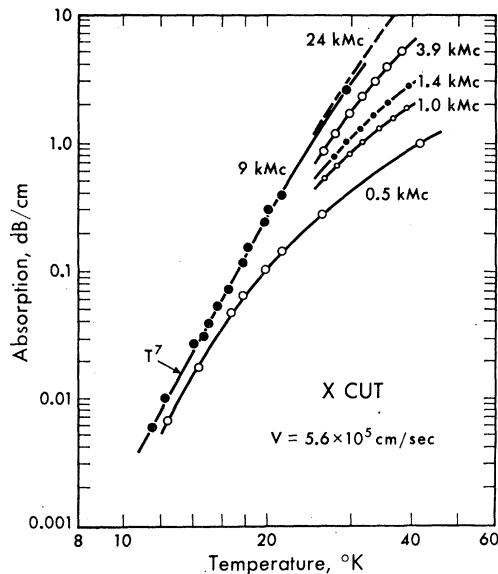


FIG. 2. The intrinsic absorption in an X-cut crystal.

¹⁰ E. H. Jacobsen, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 468.

mined. For the measurement of very small absorptions at the lower temperatures pulses were used which had completed 20–40 round trips in rods of 4 cm length.

The cavities with the quartz sample could be cooled to 1.6°K, and the temperature was measured by carbon resistors and thermocouples both carefully calibrated against a gas thermometer.

The microwave pulses of a few hundred watts peak power and a repetition rate of 100–200 per second were supplied by triode oscillators and magnetrons. The measured absorption did not depend significantly on the peak power or repetition rate.

The quartz rods varied in length between 25 and 40 mm, and in diameter between 3 and 9 mm. No dependence of the absorption per cm on these dimensions was found. Their end faces, normal to the rod axis, were polished optically flat and parallel, the other surfaces

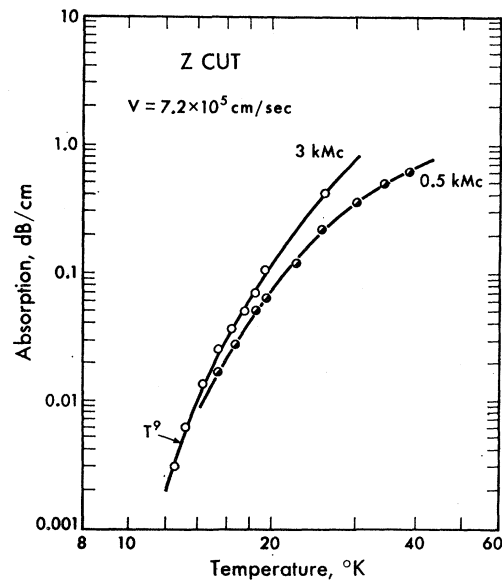


FIG. 3. The intrinsic absorption in a Z-cut crystal.

remaining unpolished. All samples were natural quartzes and surrounded during the experiment by helium gas.

The measured absorption of ultrasonic waves propagating in the different crystalline directions of quartz is plotted in Figs. 1, 2, and 3 as a function of temperature for frequencies between 500 and 10 000 Mc/sec. Figure 2 also included measurements by Jacobsen¹⁰ at 24 000 Mc/sec. The notation of the crystal cuts follows standard convention.¹¹ Here it is interesting to note only that the waves excited in an AC cut are slow transverse waves ($v_{AC} = 3.6 \times 10^5$ cm/sec) and that waves propagating along the X and Z axes have longitudinal polarization and are increasingly faster ($v_X = 5.6 \times 10^5$ cm/sec and $v_Z = 7.2 \times 10^5$ cm/sec).

¹¹ W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand, Inc., New York, 1958).

By comparing the temperature dependence of the absorption for the different waves, it is evident from Figs. 1, 2, and 3 that the absorption varies more rapidly with temperature for the fast longitudinal than for the slow transverse waves. The variation of the absorption with frequency is summarized for the different waves in Table I, fast waves (*X* cut, *Z* cut) show a considerably smaller frequency dependence than slow waves (*AC* cut).

Figures 1, 2, and 3 represent reproducible results for a number of different specimens. However, for one *X*-cut crystal the absorption was found to be considerably higher than usually observed with *X* cuts and is shown in Fig. 4. This extra absorption could be completely removed by an annealing treatment, and it is concluded, therefore, that it was caused by crystal imperfections, while the usually observed lower absorption (Fig. 2) is the intrinsic absorption of "pure" quartz. Similarly, a higher absorption than usual (Fig. 5) was also observed by us with one *AC*-cut quartz, and apparently also by Jacobsen.¹⁰ This additional "extrinsic" absorption always exhibits characteristic steps in its temperature dependence which are visible in Fig. 4 at

TABLE I. The frequency dependence of the intrinsic absorption.^a

Cut <i>V</i> (cm/sec)	<i>AC</i> 3.6×10^5	<i>X</i> 5.6×10^5	<i>Z</i> 7.2×10^5
$(\alpha_{10} - \alpha_{0.5}) / \alpha_{0.5}$	2.37	0.53	...
$(\alpha_8 - \beta_{0.5}) / \alpha_{0.5}$	0.69	...	0.25

^a α taken at 14°K.

the lowest temperatures. That the extra absorption in this specimen arises from imperfections is further supported by comparing its absorption to that measured in neutron-irradiated quartz also shown in Fig. 4. In both cases there is the same additional absorption varying with temperature in almost the same way. Finally, it is interesting that, in this specimen and some others, the pulse pattern at helium temperatures can be improved drastically by annealing. As is shown in Fig. 6, before the annealing only a few pulses were visible, while several hundred could be seen after the heat treatment. This strong scattering of sound on the imperfections even at the lowest temperatures may indicate that the size of these imperfect regions before annealing can be comparable to an acoustic wavelength¹

3. THEORY OF INTRINSIC ULTRASONIC ABSORPTION

Here the two processes which are mainly responsible for the absorption of ultrasonic waves in ideal crystals at low temperatures will be outlined. The first, described in Sec. 3A, is the well-known three-phonon

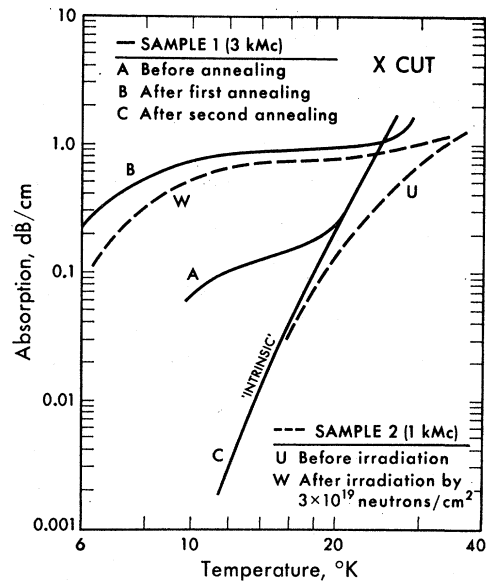


FIG. 4. The absorption in an imperfect *X*-cut crystal showing the effect of heat treatments and, for a second crystal, the result of neutron irradiation. Curve B resulted after annealing at 400°C for 24 h in vacuum, and curve C after similar annealing for another 48 h.

process^{6,12} which leads to the absorption of slow and, to a lesser degree, fast ultrasonic waves. That it is usually not affected by the dispersion of phonons in crystals is shown in Sec. 3B. The second process, which in certain circumstances may dominate the three-phonon process as in our experiments on *X* cuts, is described in Sec. 3C.

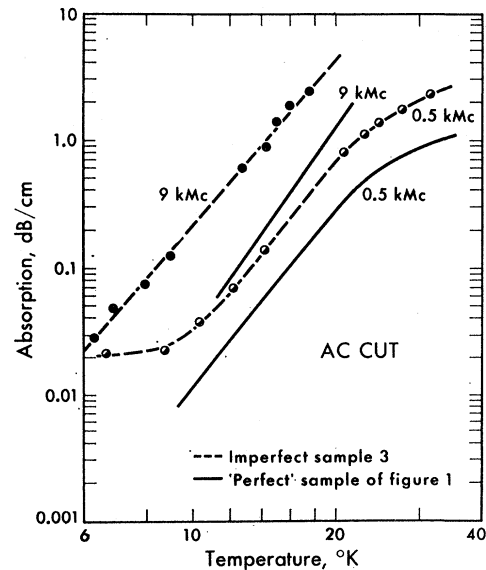


FIG. 5. Excessive absorption of an imperfect *AC*-cut crystal. The full lines indicate the behavior of perfect crystals.

¹² J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

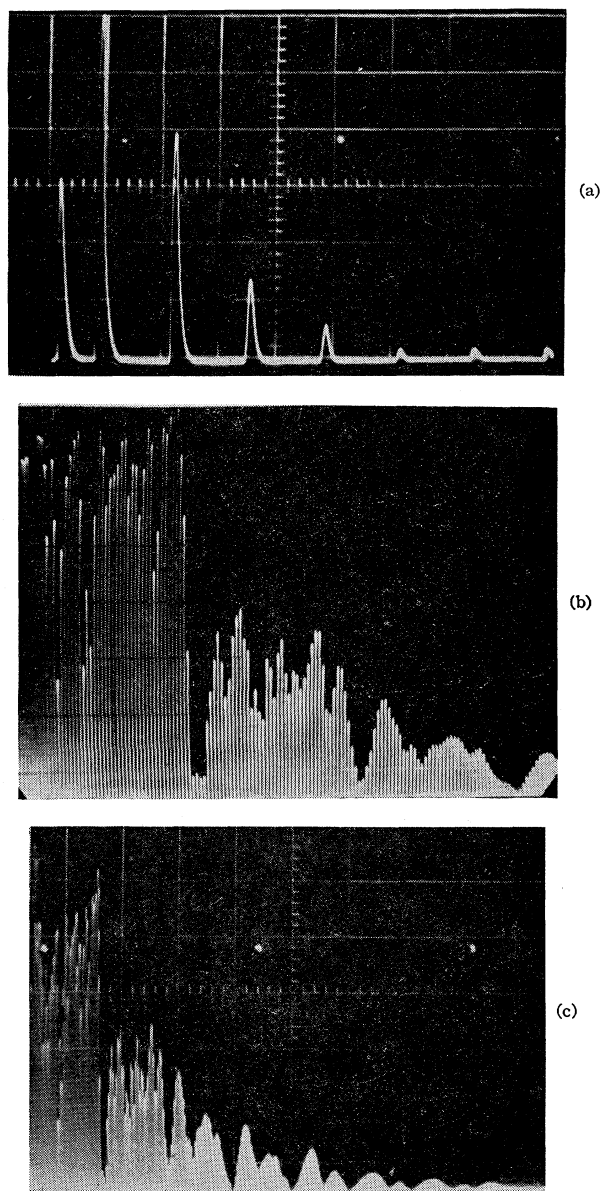


FIG. 6. Pulse pattern in an imperfect *X*-cut crystal before treatment (a), and after annealing it at 400°C for 24 h in vacuum (b) and (c). The time scale is compressed from 7 μ sec/cm in (a) by a factor 23 in (b) and 70 in (c).

The theoretical expectations for these two processes will then be compared with our experimental results in Sec. 3D.

As is well known,¹² interaction among lattice vibrations is only possible if the medium is elastically nonlinear, i.e., if Hooke's law is not valid. The degree of nonlinearity is customarily expressed, if the elastic energy is developed in powers of the strain, in the terms of the third or higher order of the strain. For the discussion of our results only the third-order elastic constants need to be considered, which is equivalent to

neglecting all processes in which more than three phonons¹² are involved.

A basic consequence of the third-order elastic constant is the variation of the velocity of sound with an applied elastic strain δS which can be expressed as

$$\frac{\delta v}{v} = \gamma \delta S, \quad (1)$$

where γ , which is related to the Grüneisen-constant,¹³ varies with polarization and direction of the sound wave as well as the nature of the strain, and seems to be of the order of unity as far as it is known for quartz.¹⁴

In our experiments we are dealing with ultrasonic waves of frequencies up to 10^{10} sec⁻¹ interacting with thermal phonons whose frequency kT/h above 10°K is still considerably higher than the ultrasonic frequencies. Consequently, our acoustic wavelengths are much larger than the wavelengths of most thermal phonons with which they interact. The extent of a wavepacket representing a thermal phonon of long lifetime ($\omega\theta \gg 1$) is much longer than the acoustic wavelength and we will consider it as infinite here. The phonon velocities we will also consider to be independent of the energy and direction of a phonon, thereby neglecting dispersion and anisotropy.

Let us now, at first, concentrate on those thermal phonons which propagate with such velocities v_{ph} and under such angles α with respect to the sound wave that they are able to stay within the same acoustic wavefront for a long time. As shown in Fig. 7, the condition for this "synchronism" is

$$v_{ph} \cos \alpha = v_0, \quad (2)$$

where v_0 is the ultrasonic velocity. All thermal phonons fulfilling this condition we will call *synchronous* phonons here.

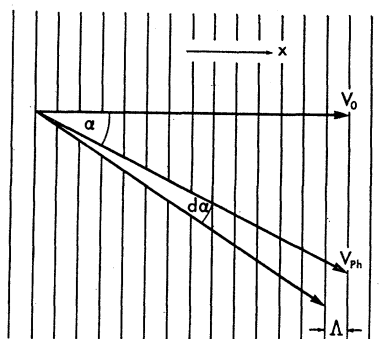


FIG. 7. A thermal phonon traveling under an angle α with respect to the direction of an ultrasonic wave. λ is the acoustic wavelength.

¹³ See, for example, J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939).

¹⁴ C. Susse, *J. Phys. Radium* 16, 348 (1955).

The velocity of a thermal phonon propagating in a given direction with a given polarization depends according to (1) also on the strain S of the simultaneously present ultrasonic wave. Let us indicate this dependence in Fig. 8 representing an ultrasonic wave traveling to the right with velocity v_0 . The part of a synchronous thermal wave traveling in region B would always have a higher speed than the portion in D. This leads to a compression of the wave or, more precisely, to a reduction of the thermal wavelength in region C. Since the velocity for thermal waves in region C remains always the same, the decreased wavelength represents an increase of frequency in "C." The reverse is true in region A. Thus the ultrasonic wave causes a frequency modulation of a synchronous thermal wave. We will make use of this phenomenon later on. In addition the energy and amplitude of a synchronous thermal wave in regions C and A are affected by the ultrasonic wave as will be shown next.

The average energy density of a thermal wave, for example in region C, is

$$\epsilon = Ks^2, \quad (3)$$

where s is the amplitude of the strain of the thermal wave, and K the elastic constant relevant to the thermal velocity v_{Ph}

$$K = \rho v_{Ph}^2.$$

For a fixed observer this elastic stiffness $K(x)$ at a point x is now time-dependent, because the ultrasonic wave in region C changes $K(x)$ at a rate

$$\left(\frac{\partial K}{\partial t}\right)_x = -\frac{K}{\rho} \left(\frac{\partial \rho}{\partial t}\right)_x + \frac{2K}{v_{Ph}} \left(\frac{\partial v_{Ph}}{\partial t}\right)_x.$$

If we disregard the density change, since its inclusion would not change the final result in any important way, and express $(\partial v_{Ph}/\partial t)$ in the second term by $-v_0 |\text{grad} v_{Ph}|$ we find

$$\left(\frac{\partial K}{\partial t}\right)_x \cong -2K \left(\frac{\partial v_{Ph}(x)}{\partial x}\right)_t, \quad (v_{Ph} \cong v_0). \quad (4)$$

This time dependence of $K(x)$ makes the medium non-conservative and the energy density ϵ at the point x changes according to (3) at a rate

$$\left(\frac{\partial \epsilon}{\partial t}\right)_x = s^2 \left(\frac{\partial K}{\partial t}\right)_{x,s} + 2Ks \left(\frac{\partial s}{\partial t}\right)_{x,K}.$$

The second term disappears, because in a conservative case ($K = \text{const}$) the average amplitude of a thermal wave at a point x does not grow or decay in time. We are thus only left with the first term, which by using (3) and (4) becomes

$$\left(\frac{\partial \epsilon}{\partial t}\right)_x = s^2 \left(\frac{\partial K}{\partial t}\right)_x = -2\epsilon \left(\frac{\partial v_{Ph}}{\partial x}\right)_t,$$

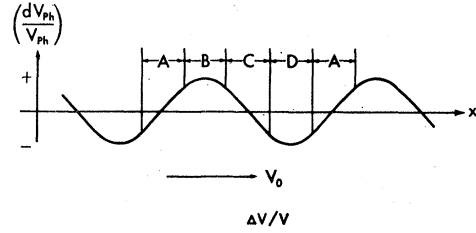


FIG. 8. An ultrasonic wave traveling to the right creates regions B and D in which the velocity of thermal phonons is altered.

describing the rate at which the energy density of a thermal wave increases at the point x , while region C of the ultrasonic wave which is characterized by $(\partial v_{Ph}/\partial x)_t$, passes over it.

For an observer, who moves with the ultrasonic velocity v_0 in region C, the energy density of the synchronously traveling thermal wave grows as

$$\frac{d\epsilon}{dt} = \left(\frac{\partial \epsilon}{\partial t}\right)_x - \epsilon \text{grad} v_{Ph} = -3\epsilon \left(\frac{\partial v_{Ph}}{\partial x}\right)_t. \quad (5)$$

At this rate the energy density of a thermal wave increases as long as it stays in region C of the ultrasonic wave where $(\partial v_{Ph}/\partial x)_t$ is negative. Vice versa in region A with $(\partial v_{Ph}/\partial x)_t > 0$, the energy density decreases at the same time. Because of the relationship (3) between ϵ and s , similar statements could be made for the amplitude of a thermal wave.

When the thermal wave travels a *finite* time t with the ultrasonic wave in region C, its total energy increment is, from integrating (5)

$$\frac{\Delta \epsilon}{\epsilon} = \exp \left[-3 \left(\frac{\partial v_{Ph}}{\partial x}\right)_t t \right] - 1,$$

or for small ultrasonic amplitudes, when $(\partial v_{Ph}/\partial x)_t t \ll 1$,

$$\frac{\Delta \epsilon}{\epsilon} = -3 \left(\frac{\partial v_{Ph}}{\partial x}\right)_t t + \frac{1}{2} \left[3 \left(\frac{\partial v_{Ph}}{\partial x}\right)_t t \right]^2 \dots \quad (6)$$

It is obvious that energy is exchanged most efficiently with "synchronous" thermal waves, for which t can become long. We will therefore, in the following, first describe the interaction of synchronous thermal phonons with the ultrasonic wave, and deal with the nonsynchronous case later.

A. Acoustic Absorption by Synchronous Thermal Phonons

It is evident from condition (2) that the large synchronous energy exchange with the ultrasonic wave is only possible for phonons with a velocity higher than or equal to the ultrasonic velocity, i.e.,

$$v_{Ph} \geq v_0.$$

We will therefore now consider a slow (for example,

transverse) ultrasonic wave to interact in a synchronous way with faster thermal phonons. These thermal phonons have, at low temperatures, a long but not infinite mean free path, the free time between collisions being θ . These phonons, which can keep up with the wave for a time θ , not lagging behind the wave by more than one acoustic wavelength Λ , are those which are contained within $d\alpha$ of Fig. 7, for which one finds by geometrical arguments:

$$d\alpha = \frac{\Lambda}{\theta v_{\text{Ph}}} \frac{1}{\sin \alpha}.$$

The relative number of phonons between the angles α and $\alpha+d\alpha$ is equal to the ratio of the solid angle $d\alpha$ to 4π ,

$$\frac{\Delta N}{N} = \frac{2\pi \sin \alpha d\alpha}{4\pi} = \frac{1}{\omega \theta} \pi \cos \alpha,$$

with $\omega/2\pi$ being the ultrasonic frequency. We note that $\cos \alpha = v_0/v_{\text{Ph}}$ varies for phonons of different polarization only between $\frac{1}{2}$ and 1. Thus, we omit the factor $\pi \cos \alpha$ as being of the order of unity, resulting in

$$\Delta N/N = 1/\omega \theta. \quad (7)$$

This is the fraction of all phonons or thermal waves with $v_{\text{Ph}} \geq v_0$ which are capable of synchronous interaction for the time θ . Before the interaction the energy of these fast thermal waves will be distributed equally over all 4 regions (A,B,C,D), and thus the initial energy of all synchronous thermal waves in regions A is per unit volume, $\epsilon = (\Delta N/4)kT$. In the time θ , this energy is changed according to (6) by an amount

$$\frac{\Delta N}{4} kT \left[-3 \left(\frac{\partial v}{\partial x} \right)_A \theta + \frac{9}{2} \left(\frac{\partial v}{\partial x} \right)_A^2 \theta^2 \right]$$

and in regions C by

$$\frac{\Delta N}{4} kT \left[-3 \left(\frac{\partial v}{\partial x} \right)_C \theta + \frac{9}{2} \left(\frac{\partial v}{\partial x} \right)_C^2 \theta^2 \right].$$

The net energy gained from the ultrasonic wave is the sum of both terms. If we remember from Fig. 8 that $(\partial v/\partial x)_A = -(\partial v/\partial x)_C$, we find

$$dW = (9/4) \Delta N kT \left(\frac{\partial v}{\partial x} \right)_C^2 \theta^2,$$

or expressing $(\partial v/\partial x)_C$ by the strain amplitude S , following (1):

$$\left| \left(\frac{\partial v}{\partial x} \right)_C \right| = \gamma v \left| \frac{\partial S}{\partial x} \right| = \gamma \omega S. \quad (8)$$

Dividing by θ we find the energy lost by the ultrasonic wave per second per cm^3 :

$$(dW/dt) = (9/4) \Delta N kT \gamma^2 \omega^2 S^2 \theta.$$

Replacing ΔN according to (7) by $N/\omega \theta$, we find

$$(dW/dt) = (9/4) N kT \gamma^2 \omega S^2,$$

which is now independent of the collision time θ . The ultrasonic absorption coefficient, which is defined (with $W = \text{acoustic energy flux} = \rho v_0^3 S^2$) as

$$\alpha = \frac{(dW/dt)}{W}, \quad (9)$$

becomes

$$\alpha \cong 2N kT \gamma^2 \omega / \rho v_0^3. \quad (10)$$

Here N is according to the definition (7) not the number of all thermal phonons but only of those which are at least as fast as the ultrasonic wave and therefore capable of synchronous interaction. At low enough temperatures, as in our case, N is expected to vary with temperature as T^3 .

It is interesting to note that the result just arrived at is essentially the same as calculated for absorption by three-phonon processes,^{6,12} in which acoustic phonons are absorbed in collisions with thermal phonons. Such a collision process requires conservation of momentum, such that the momenta of the thermal and acoustic phonon before the collision must be equal to the momentum of the thermal phonon after collision. It is easy to show that this requirement of conservation of momentum is identical with our condition (2) for synchronism.

The identity with a three-phonon process becomes even more apparent if we recall that both the frequency and the amplitude of a thermal wave is modulated with the ultrasonic frequency resulting in a lower and upper sideband. The lower sideband corresponds to the emission and the upper band to the absorption of an acoustic phonon. For a simultaneous frequency-and-amplitude modulation the two sidebands are not equally strong, resulting in a net absorption of ultrasonic energy.

We will not pursue the description of the three-phonon process along these lines, but refer to an excellent review of previous work by Orbach.¹⁵

B. Effects of Dispersion on Synchronous Absorption

Condition (2) allows synchronous interaction not only for thermal phonons which are faster than the ultrasonic wave but also for those of equal speed, resulting in $\alpha=0$. These "collinear processes" in which acoustic wave and thermal phonons travel in the same direction are particularly important for the synchronous absorption of fast ultrasonic waves, because there may only be a few thermal phonons of still higher speed available.

Pomeranchuk¹⁶ first mentioned that the phonon dis-

¹⁵ R. L. Orbach, thesis, University of California, Berkeley, 1960 (unpublished).

¹⁶ I. J. Pomeranchuk, J. Phys. (USSR) 4, 259, 529 (1941); 6, 237 (1942); Phys. Rev. 60, 820 (1941).

persion in crystals seems to exclude such collinear processes. His argument was that—due to the dispersion—the group velocity of thermal phonons is always lower than the acoustic velocity in the same branch, and that therefore collinear thermal phonons cannot keep up with the ultrasonic wave. In many cases, however, this argument is not valid as will become clear in the following.

By using a standard dispersion relation, with a cutoff frequency defined by the Debye temperature T_D , it is easy to derive the group velocity v_{Ph} of a thermal phonon of energy kT and to show that it is smaller than the acoustic velocity v_0 of the same branch by

$$v_0 - v_{Ph} = (v_0/3)(T/T_D)^2.$$

The synchronism between an ultrasonic wave of velocity v_0 and collinear thermal phonons of velocity v_{Ph} is only affected if the thermal phonons lag behind the wave by more than half an acoustic wavelength

$$\Lambda = v_0/(\omega/2\pi),$$

during the time θ which they spend in the collinear direction. This condition is

$$(v_0 - v_{Ph})\theta > \Lambda/2,$$

or

$$\omega\theta > 3\pi(T_D/T)^2, \quad (11)$$

and is not, in general, fulfilled. In all of these cases, as in our experiments, when θ is too small to fulfill condition (11) the dispersion can be neglected and collinear thermal phonons contribute fully to the ultrasonic absorption.

C. Absorption by Nonsynchronous Thermal Phonons

The next question is: How are *very fast* ultrasonic waves absorbed? In this case the number N of thermal phonons with a sufficiently high velocity to achieve synchronism is quite minute and, consequently, the absorption by synchronous phonons according to (10) is very small, and cannot account for the observed considerable absorption of fast ultrasonic waves (see Sec. 2).

On the other hand, we have so far considered only the small minority of synchronous phonons and have neglected any interaction with the large majority of the other thermal phonons, which are generally not synchronous with the ultrasonic wave, according to definition (2). In the following it is shown how fast ultrasonic waves can be absorbed by these nonsynchronous thermal phonons.

Nonsynchronous phonons are, by definition, not able to stay within the same region of the wave for long times. Rather they may lag behind, or lead a fast ultrasonic wave and traverse the ultrasonic wave fronts at a frequency Ω which depends on the relative velocities of the phonon and the ultrasonic wave and which for

most thermal phonons is of the order of the ultrasonic frequency ω .

Let us consider a short element of a nonsynchronous thermal wave maybe only a few thermal wavelengths long. As this small wavepacket is traversing the regions A and C of the ultrasonic wave, its energy ϵ is according to (5) undergoing a change

$$\frac{1}{\epsilon} \frac{d\epsilon}{dt} = -3 \left(\frac{\partial v_{Ph}}{\partial x} \right), \quad (12)$$

where now $(\partial v_{Ph}/\partial x)$, taken at the thermal wavepacket, is no longer constant but changes periodically

$$\left(\frac{\partial v_{Ph}}{\partial x} \right) = \left(\frac{\partial v}{\partial x} \right)_C \cos(\Omega t + \varphi). \quad (13)$$

$(\partial v/\partial x)_C$ and Ω refer to thermal waves of particular direction and polarization. A thermal wave or phonon moves in this direction only for the time θ between two collisions. Let us define ϵ_0 as the energy of our wavepacket immediately after the first collision ($t=0$) and ϵ_θ its energy just before the second collision ($t=\theta$). The net change of energy in the time θ becomes according to (8), (12), and (13):

$$\int_{\epsilon_0}^{\epsilon_\theta} \frac{d\epsilon}{\epsilon} = - \int_{t=0}^{\theta} 3\gamma\omega S \cos(\Omega t + \varphi) dt,$$

or for small amplitudes when $A = 3\gamma(\omega/\Omega)$, $S \ll 1$

$$\frac{\epsilon_\theta - \epsilon_0}{\epsilon_0} = -A \sin(\Omega\theta + \varphi) + \frac{A^2}{2} \sin^2(\Omega\theta + \varphi).$$

Since an average thermal wavepacket can spend its time θ in any phase φ between 0 and 2π with equal probability we find the mean energy change $\langle \Delta\epsilon/\epsilon_0 \rangle$ by averaging over all φ

$$\left\langle \frac{\Delta\epsilon}{\epsilon_0} \right\rangle = \frac{1}{2\pi} \int_0^{2\pi} \frac{\epsilon_\theta - \epsilon_0}{\epsilon_0} d\varphi = \frac{1}{4} A^2 = \frac{3}{4} \gamma^2 S^2 \frac{\omega^2}{\Omega^2} \cong \gamma^2 S^2$$

for $\frac{3}{4}(\omega/\Omega)^2 \approx 1$. This indicates the average energy gain of a thermal wavepacket of energy ϵ_0 from the ultrasonic wave in the time θ between collisions. The total energy lost per second by the acoustic wave is

$$\frac{dW}{dt} = N_0 kT \left\langle \frac{\Delta\epsilon}{\epsilon_0} \right\rangle / \theta = N_0 kT \langle \gamma^2 \rangle_{av} S^2 / \theta,$$

where N_0 is now the *total* number of thermal phonons and $\langle \gamma^2 \rangle_{av}$ a suitable average over directions, presumably of the order of unity. The absorption coefficient, as defined by (9) becomes now

$$\alpha = \frac{N_0 kT \langle \gamma^2 \rangle_{av}}{\rho v_0^3 \theta} [\text{cm}^{-1}], \quad (14)$$

with v_0 being the ultrasonic velocity.

The lifetime θ of a thermal phonon, used here, may be limited by collisions with other thermal phonons, or by impurity and boundary scattering. In the former case θ may be limited by normal (N)—or umklapp (U)—collisions¹² with other thermal phonons, the respective collision times being θ_N or θ_U . θ_U corresponds to momentum-changing collisions, and it describes well the acoustic absorption at high temperatures, where it is determined largely by the heat conductivity.^{4,15} However, for the nonsynchronous ultrasonic absorption at low temperatures *all* collisions which change the direction or propagation of a phonon are important, which includes the normal collisions as well. In fact, at low temperatures normal collisions are far more frequent than U processes, because they do not require thermal phonons near the zone boundary and therefore, do not freeze out as rapidly on cooling as do U collisions. Thus at low temperatures the nonsynchronous absorption is probably mainly determined by normal momentum-conserving collisions in the thermal phonon gas ($\theta = \theta_N$).

A further enhancement of the absorption may result when θ is effectively reduced, because ultrasonic pulses of very short duration or cross section are used. In this case the thermal phonons only spend a short time in the ultrasonic wave, however long their mean free path in the crystal may be. This situation is not realized in our experiments.

Finally, it may be pointed out that the absorption process for fast ultrasonic waves described here only arises from the third-order elastic constants, and is therefore basically different from so-called 4-phonon processes discussed elsewhere.¹⁶

D. Comparison with Experiments

Since both the synchronous and nonsynchronous thermal phonons contribute independently to the decay of ultrasonic waves, the total ultrasonic absorption coefficient is made up of both contributions (10) and (14):

$$\alpha = \frac{2NkT\gamma^2\omega}{\rho v_0^3} + \frac{N_0kT\langle\gamma^2\rangle_{av}}{\rho v_0^3\theta}, \quad \omega\theta > 1. \quad (15)$$

The ratio between the synchronous and nonsynchronous contributions to the absorption is from (15)

$$\frac{\alpha_s}{\alpha_{Ns}} = \frac{2\gamma^2}{\langle\gamma^2\rangle_{av}} \frac{N}{N_0} (\omega\theta). \quad (16)$$

Since both γ^2 and $\langle\gamma^2\rangle_{av}$ are two averages of similar γ values, we will for the following discussion simply assume that the whole factor $2\gamma^2/\langle\gamma^2\rangle_{av}$ is of the order of unity.

N represents the number of those thermal phonons which are not slower than the ultrasonic wave. For an estimate of the ratio (N/N_0) we note that the number

of phonons in each mode is proportional to the inverse cube of the phonon velocity. Therefore, phonons of a low velocity are much more abundant than fast thermal phonons.

Only for very *slow* ultrasonic waves the ratio (N/N_0) in (16) attains a value close to unity. In this case the absorption is, at low temperatures ($\omega\theta > 1$), dominated by the first term in (15), representing the synchronous interaction, or the 3-phonon process. Our experiments with very slow ultrasonic waves in AC -cut quartzes, as shown in Fig. 1 are in fair agreement with this. The absorption increases about linearly with frequency and with the fifth power of the temperature, not too far from the expected T^4 dependence.

For *faster* ultrasonic waves the ratio (N/N_0) becomes very small, and consequently, the nonsynchronous contribution to the absorption in (17) may predominate if θ is not too large. For example, in the case of a longitudinal ultrasonic wave in an X cut ($v_0 = 5.6 \times 10^5$ cm/sec) a rough estimate leads to (N/N_0) = 0.1. With this ratio the nonsynchronous absorption should, according to (16), prevail as long as $\omega\theta \leq 10$. For the still faster waves in the Z cut, naturally (N/N_0) is even smaller.

The experimentally observed absorption in pure X cuts, as shown in Fig. 2 and Table I is basically in agreement with the expectations for nonsynchronous processes. In contrast to the behavior of slow ultrasonic waves, the absorption of these fast waves in X and Z cuts is almost independent of frequency and increases with temperature noticeably steeper than T^4 .

As just mentioned the predominance of the nonsynchronous contribution in (17) for an X cut implies $\omega\theta < 10$. For an ultrasonic frequency of 10^{10} sec⁻¹ it means that the lifetime of thermal phonons θ is shorter than 2×10^{-10} sec. At 20°K this is almost 2 orders of magnitude shorter than the collision time between umklapp processes as known⁴ from heat-conductivity data. It seems likely that this short lifetime is limited by momentum-conserving normal processes which are expected to be, at low temperatures, much more frequent than U collisions, and for which little other experimental evidence is known at present. The role of these normal processes for the existence of second sound in solids has recently been discussed.¹⁷

Summing up, we have shown that the intrinsic absorption of slow ultrasonic waves at low temperatures ($\omega\theta > 1$) can be adequately described by synchronous- or three-phonon processes, the absorption varying as ωT^4 . Also faster ultrasonic waves are absorbed by these processes if $\omega\theta > (N_0/N)$. If, however, ($\omega\theta$) is in the range $1 < (\omega\theta) < (N_0/N)$, nonsynchronous absorption is predominant. It is frequency-independent and varies with temperature as T^4/θ .

¹⁷ F. W. Prohofskey, thesis, Cornell University, 1963 (unpublished).

4. ABSORPTION IN IMPERFECT CRYSTALS

Imperfections in quartz can either modify the intrinsic processes discussed above or create a new absorption of their own.

The reduction of the lifetime θ of thermal phonons in imperfect crystals does not influence the synchronous absorption, which is independent of θ as long as $\omega\theta > 1$. But the nonsynchronous absorption (14) will be enhanced if θ is reduced, for example, by impurity scattering. If the scattering rate $1/\theta$ is now independent of temperature or, as in the case of Rayleigh scattering increasing with temperature, the temperature dependence T^4/θ should be at least as steep as T^4 .

The experimental observations on the imperfect and the neutron-irradiated X cuts of Fig. 4 do not confirm this picture. The extra absorption varies only little with temperature above 10°K, but rapidly disappears below 7°K. A similar step-like behavior of the absorption was

also reported by Jacobsen¹⁰ for an AC cut. This extra absorption may arise within the imperfect regions of the crystal: Jones¹⁸ *et al.* found recently at 930 Mc/sec in fused quartz an enormous ultrasonic absorption which could only be frozen out at a few degrees Kelvin. This suggests that the imperfections in our X cut, as well as in the neutron-irradiated sample, are small regions of vitrification with a characteristic high absorption. The size of these imperfect regions has been discussed in Sec. 2.

Note added in proof. In a recent experiment on aluminum [Appl. Phys. Letters 3, 195 (1963)], Hikita *et al.* have demonstrated that the anharmonicity of a crystal—as expressed by Grüneisen's constant in our Eqs. (10) and (14)—can be strongly increased by the presence of imperfections as, for example, dislocations.

¹⁸ C. K. Jones, P. G. Klemens, and J. A. Rayne, Phys. Letters 8, 31 (1964).

Electron-Spin Resonances in Gamma-Ray-Irradiated Aluminum Oxide*

F. T. GAMBLE,† R. H. BARTRAM, C. G. YOUNG,‡ AND O. R. GILLIAM

University of Connecticut, Storrs, Connecticut

AND

P. W. LEVY

Brookhaven National Laboratory, Upton, New York

(Received 18 November 1963)

Single crystals of α -aluminum oxide were subjected to gamma-ray irradiation at 77°K. A single, asymmetric, paramagnetic-resonance absorption was produced with $g_{11}=2.012\pm 0.002$ and $g_{\perp}=2.008\pm 0.002$, where \parallel and \perp are with respect to the c axis. The line width is about 50 G at 300 and 77°K. The absorption line has been analyzed as a superposition of three Gaussian lines with the isotropic g values: $g_1=2.020\pm 0.003$, $g_2=2.006\pm 0.003$, $g_3=2.006\pm 0.003$. The component lines are tentatively attributed to two types of centers: a trapped hole localized on an anion adjacent to a cation site which is deficient in positive charge, and an electron trapped at an anion vacancy. The cation site may be vacant, or may contain a monovalent or divalent substitutional impurity.

I. INTRODUCTION

IRRADIATION of single crystals of α -aluminum oxide by ultraviolet, gamma-ray, reactor and high-energy-electron radiation, or by combinations of these, produces or ionizes lattice defects. These defects are manifested in a variety of ways including electron-spin resonance (ESR). The modified properties of irradiated Al_2O_3 not only are of intrinsic interest, but also provide information about the radiation-damage mechanism; consequently, they have been studied extensively by

measurement of optical absorption spectra,¹⁻⁵ long-wavelength neutron scattering cross sections,⁶ thermal conductivity,⁷ lattice expansion,⁸ and thermoluminescence.⁹ However, none of these measurements has provided conclusive identification of the underlying cen-

¹ R. A. Hunt and R. H. Schuler, Phys. Rev. 89, 664 (1953).

² P. W. Levy and G. J. Dienes, *Report of the Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 256.

³ P. W. Levy, Phys. Rev. 123, 1226 (1961).

⁴ E. W. J. Mitchell, J. D. Rigden, and P. W. Townsend, Phil. Mag. 5, 1013 (1960).

⁵ G. W. Arnold and W. D. Compton, Phys. Rev. Letters 4, 66 (1960).

⁶ J. Antal and A. Goland, Phys. Rev. 112, 103 (1958).

⁷ R. Berman, E. L. Foster, B. Schneidmeyer, and S. M. A. Tirmizi, J. Appl. Phys. 31, 2156 (1960).

⁸ D. G. Martin, Phys. Chem. Solids 10, 64 (1955).

⁹ A. F. Gabrysh, H. Eyring, V. LeFebvre, and M. D. Evans, J. Appl. Phys. 33, 3389 (1962).

* This research was supported by the U. S. Atomic Energy Commission.

† Present address: Department of Physics and Astronomy, Denison University, Granville, Ohio.

‡ Present address: American Optical Company, Southbridge, Massachusetts.

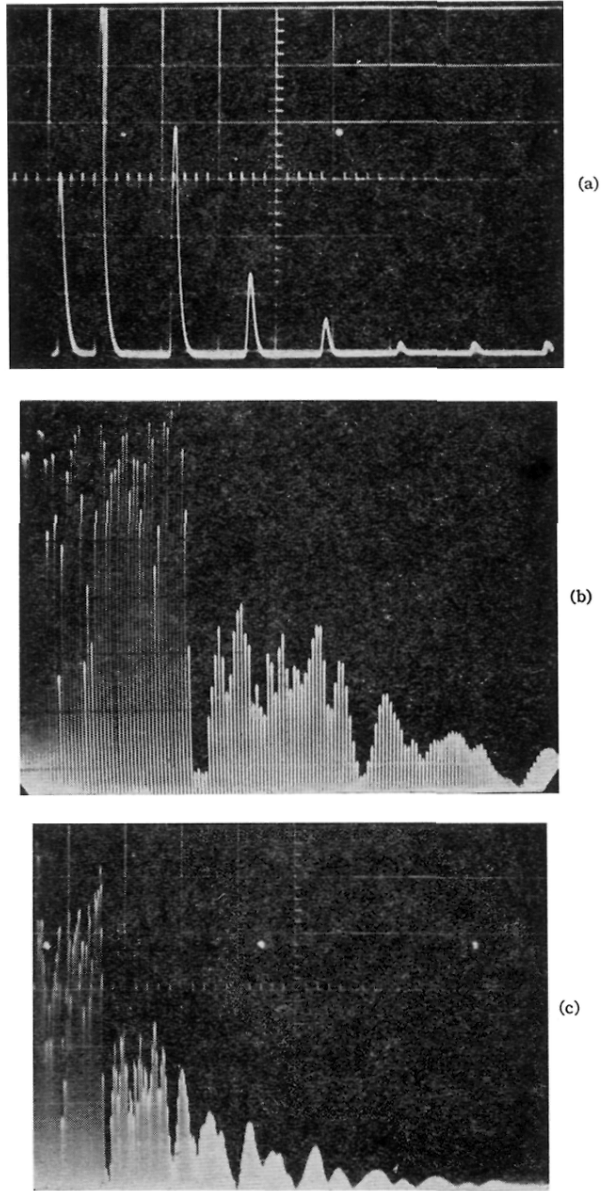


FIG. 6. Pulse pattern in an imperfect *X*-cut crystal before treatment (a), and after annealing it at 400°C for 24 h in vacuum (b) and (c). The time scale is compressed from 7 μ sec/cm in (a) by a factor 23 in (b) and 70 in (c).