

Temperature Dependence of Attenuation of 3- and 9-GHz Ultrasound in Rutile (TiO_2)[†]

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The attenuation of 3- and 9-GHz ultrasound in pure TiO_2 (rutile) was measured as a function of temperature from 4 °K to the highest temperature at which echoes were observed. Measurements were made of transverse waves and some longitudinal waves propagating in the [001], [110], and [100] directions. In general, it is observed that the attenuation increases rapidly with temperature beginning at a fairly low temperature (≈ 20 °K), but that for some modes this rapid increase is cut off before the attenuation is very large. For these modes, the subsequent increase is small so that the echoes are readily observed at room temperature. This behavior is discussed in terms of theories of ultrasonic attenuation. The high-temperature behavior may be related to the existence of low-lying optical modes to which acoustic thermal phonons may scatter. The attenuation in TiO_2 is contrasted with that in Si where such optical modes are not present.

I. INTRODUCTION

The attenuation of microwave frequency ultrasound in rutile (TiO_2) has been measured by several authors,¹⁻⁵ following the observation by Shaw *et al.*⁶ that at 3 GHz a shear mode had low attenuation at room temperature. In the present work we made comprehensive measurements at 3 and 9 GHz, from 4 °K to room temperature, and for the pure mode axes [100], [110], and [001]. A prime motivation was to try to understand the low attenuation. A more general objective is to study the nature of the ultrasonic interaction with thermal phonons in a crystal which is complex enough so that a variety of interactions may appear, and about which much additional information is available. We find, in fact, that at low temperatures there is evidence for several different interaction processes. Moreover, several modes have the potentially useful property of having relatively low attenuation at room temperature.¹ We shall make some suggestions, based on the lattice dynamics of TiO_2 , about the causes of the low attenuation of these ultrasonic modes. We shall be concerned only with pure stoichiometric rutile; Lange⁷ has reported some effects of reducing rutile, thereby removing some oxygen, on the attenuation at 1 GHz.

II. EXPERIMENTAL METHODS AND PROBLEMS

The basic procedure we used for measuring the temperature dependence of attenuation has been described earlier.^{8,9} The data reported are the changes in attenuation above 4 °K from their values at 4 °K. We are concerned with the effects of thermal phonons, so that it seems reasonable to subtract the apparent attenuation at 4 °K which may be due to impurities, defects, imperfect sample orientation and polishing, and transducer losses.

The sample orientation was nominally to $\pm 0.5^\circ$ of the specified crystal axis. X-ray and polarized light examination by J. Angilello revealed that the single crystals contained regions slightly misaligned from the faces. These low-angle misorientations of about $\pm 3^\circ$ probably resulted from the Verneuil (or flame fusion) method by which TiO_2 is normally grown.¹⁰ The presence of misaligned regions may explain the reported variation of attenuation with different samples.² We have also observed large variations in the apparent attenuation at 4 °K of some modes which may be caused by the misaligned regions. In particular, the slow transverse mode propagating in the [110] direction (called t_2 hereafter), showed large sample-dependent attenuation. In some samples t_2 was weaker than the fast transverse mode (t_1) by as much as -30 dB/cm at 9 GHz; in others it differed by as little as -5 dB/cm. The explanation may be found in a calculation by Waterman¹¹ who derived the changes in velocity and direction of energy propagation of ultrasonic waves propagating in slightly misaligned crystals. The symmetry of rutile is tetragonal (D_{4h}^{14} , $P4_2/mnm$). For the case of propagation nearly along the [110] direction of a tetragonal crystal, substituting the elastic constants of rutile into Waterman's formulas, we find $\Delta v(t_1)/v(t_1) = 0.43\theta^2 \cos^2\phi$ for the relative change of velocity of the fast transverse wave (t_1) and $\Delta v(t_2)/v(t_2) = \theta^2(0.85 \cos^2\theta + 8.6 \sin^2\phi)$ for the slow shear wave t_2 . θ and ϕ are the polar and azimuthal angles of misorientation. θ is presumably small, but ϕ can have any value, according to Waterman's definitions. It can, therefore, happen that $\Delta v(t_2)/v(t_2)$ can be dominated by the term in $\sin^2\phi$ and be an order of magnitude larger than $\Delta v(t_1)/v(t_1)$. In traveling through an irregularly shaped misoriented crystallite, the phase fronts of the t_2 wave can be

much distorted, thereby reducing the observed echo amplitude.

In addition to making t_2 virtually unobservable in some [110] crystals, the presence of misaligned crystallites impedes accurate measurements at high temperatures even in the cases where t_2 is strong. The difficulty at high temperatures is that the thermal expansion of rutile is anisotropic so that the shapes of the misaligned regions change with temperature. Thus the shapes of the phase fronts, and the observed echo amplitudes, change due to this spurious effect of thermal expansion. Different echoes can be affected differently. Since we deduce the attenuation by comparing the amplitudes of the echoes, accuracy is considerably reduced. This effect is mitigated by the fact that the most rapid increases in attenuation occur below about 50 °K. The thermal expansion is relatively small, being proportional to the specific heat, in this temperature region. When we observe unusual behavior of the echoes it is usually at temperatures greater than 60 °K. Thus, we believe that at temperatures below about 50 °K our results are not grossly affected by the crystallite structure.

In the temperature region above 50 °K we have tried to approach the true values of attenuation by making measurements on a variety of samples. The results presented are the averages of these measurements. For the 9-GHz measurements in the [110] direction, measurements were made on at least six different crystals. In no case were measurements made on fewer than three crystals at 9 GHz, where the crystallite problem is expected to be more severe than at 3 GHz. At 3 GHz we sometimes measured the attenuation in only one sample if the echo behavior was reasonable, but in the [110] direction we made measurements on at least six different crystals to check the reproducibility. Furthermore, we took some care to try to mitigate the phasing effects on some echoes by averaging techniques applied to the data.

Despite these efforts, we feel we do not have satisfactory data for the transverse mode propagating in the [001] direction. The problem is acute here because along this axis the two transversely polarized waves are degenerate. Slight x-ray misalignment or crystallite misalignment splits the degeneracy and causes one polarization to travel at a slightly different velocity from the other. The signal produced by the transducer results from the sum or interference of these waves; when the thermal expansion is large the relative phase of the two waves varies with temperature, producing a modulation of the echo amplitudes. In Fig. 2, we have indicated by a dotted curve an average of the data we obtained at 9 GHz, but it can only be considered accurate to perhaps a factor of 2.

Previously reported measurements^{1,2,6} of the

attenuation of this wave at high temperatures do not refer to this problem. This may be because those measurements were made at only one temperature. The problem could be avoided by the use of a linearly polarized transducer oriented along a [100] axis. In Refs. 1 and 6 magnetic transducers were used, as in our experiments. They produce both transverse polarizations. In Ref. 2 CdS film transducers were employed, but the orientation was not specified.

The use of magnetic film transducers¹² is a convenience in most cases because it usually allows all modes of polarization to be measured with the same transducer. We used the same samples and transducers at both 9 and 3 GHz. At 3 GHz, however, we were able to observe the longitudinal (l) mode only for a [001] oriented sample. We have observed in materials other than rutile that l modes are not always generated at 3 GHz, whereas they are always observed at 9 GHz. The reason for this is not clear, but in order to generate l modes the d. c. magnetic field H_0 must be inclined to the film normal. The field H_0 is fairly low (≈ 6 kG) at 3 GHz, and it may be that the demagnetizing fields due to the planar geometry cause much of the magnetization to lie in the plane of the film. In this configuration the l mode is not generated.¹²

The temperatures of the samples were measured by lightly pressing a thermocouple on a surface. In all the data reported here except in the [100] direction at 9 GHz, an Au 2.1 at. % Co thermocouple was used. The thermocouple was checked against a Ge thermometer. In the range $15 < T < 40$ °K the two thermometers agreed to within 2 °K. The relative temperature is probably more accurate. We also made a number of measurements using a Cu constantan thermocouple, and the relative temperature change was usually close to that measured with the Au-Co thermocouple.

III. LOW-TEMPERATURE RESULTS: EXPERIMENT AND THEORY

As an aid in interpreting the experimental observations, we summarize the results of the theory of ultrasonic attenuation due to interaction with thermal phonons at low temperatures. For our purposes, low- and high-temperature regions will be differentiated by the value of the parameter $\omega\tau$. ω is the circular frequency of the ultrasound and τ is a thermal phonon relaxation time, presumably of thermal phonons of energy of order kT that are the dominant source of ultrasonic attenuation. The low-temperature region is characterized by $\omega\tau \geq 1$; in this region a description in terms of individual thermal phonons is appropriate. In the high-temperature region $\omega\tau < 1$; the ultrasound behaves as a quasistatic modulation of the short-lived thermal phonons. The theory¹³ of ultrasonic attenuation by

thermal phonons can be summarized in three cases.

(a) Ultrasound of polarization i interacting with phonons¹⁴ of higher branch, h :

$$\alpha_i = \frac{\pi^3 \hbar \omega}{240 \rho v_i v_h^5} \left(\frac{kT}{\hbar} \right)^4 \gamma_{ih}^2 \text{ (Np/cm) for } \omega \tau > 1. \quad (1)$$

This is the well-known Landau-Rumer case; the result is independent of phonon relaxation time, and is insensitive to lattice dispersion and anisotropy. ω is the ultrasonic frequency, ρ is the density, v_i and v_h are the ultrasonic and phonon phase velocities, respectively, γ^2 is a constant containing second- and third-order elastic constants. By "branch" we mean the entire phonon dispersion curve of given polarization.

(b) Ultrasound of polarization i interacting with phonons of same branch, i :

$$\alpha_i = \frac{\pi^2 \hbar}{38.4 \rho v_i^4} \left(\frac{kT}{\hbar} \right)^2 \gamma_{ii}^2 \frac{1}{\tau_i a^2} \text{ for } \pi \omega \tau_i (T/\Theta_i) \gg 1 \quad (2a)$$

and

$$\alpha_i = \frac{\pi^3 \hbar}{240 \rho v_i^5} \left(\frac{kT}{\hbar} \right)^4 \gamma_{ii}^2 \text{ for } \pi \omega \tau_i (T/\Theta_i) \ll 1 \ll \omega \tau_i. \quad (2b)$$

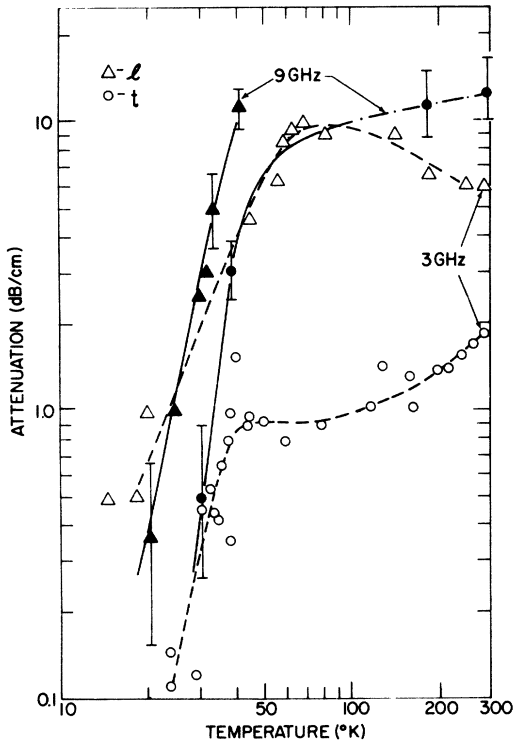


FIG. 1. Temperature dependence of ultrasonic attenuation along the [001] or c axis of TiO_2 . The 9-GHz curve is the average of data of several samples and runs; the error bars indicate the scatter among these data. The 3-GHz curves are the results of a typical run, to indicate the scatter of data obtained in a single run at this frequency. All polarizations indicated in Figs. 1–8 refer to the ultrasound, not the phonons.

In Eq. (2a), lattice dispersion has been included in the energy uncertainty by approximating the lattice by a linear chain of spacing a . Θ_i is the characteristic temperature of the i th branch in the Debye approximation: $\Theta_i = \pi \hbar v_i / ka$. Special consideration must be given to $t_i + T_i - T_i$ since for collinear interactions along axes of evenfold symmetry $\gamma_{ii} = 0$ in this case. The t waves must then interact via the anisotropy of the γ_{ii} . The solution by Shiren¹⁵ is of the form

$$\alpha_i = \frac{\pi^2 \hbar}{15 \rho v_i^6} \left(\frac{kT}{\hbar} \right)^4 \frac{\gamma_{\text{eff}}^2}{\tau_i}, \quad (2c)$$

where γ_{eff} is an average Grüneisen parameter which may be a decreasing function of temperature. Since τ_i^{-1} varies strongly with temperature, perhaps^{16,17} as T^5 , Eqs. (2a)–(2c) allow for temperature dependences from T^9 through T^4 .

(c) Ultrasound of polarization i interacting with phonons of lower branch, u :

$$\alpha_i = \frac{\pi^2 \hbar}{480 \rho v_i^3 v_u^3} \left(\frac{kT}{\hbar} \right)^4 \frac{\gamma_{iu}^2}{\tau_u}. \quad (3)$$

The derivation of the above formulas generally neglects the anisotropy of the ultrasonic velocity. Recent detailed calculations¹⁸ indicate that this anisotropy can result in weakened temperature dependences, particularly for transverse waves in cubic crystals, and perhaps in rutile¹⁹ also.

We will now compare the observed frequency and temperature dependences with the various possibilities given in Eqs. (1)–(3).

A. [001] Direction

1. t Wave

Both Lange⁴ and Nava *et al.*,⁵ report approximate $\alpha \propto \omega T^4$, although Lange's data are shifted to lower temperature than those of Nava *et al.* At 3 GHz our data also give T^4 dependence, and Lange's data are shifted to lower temperature than ours. At 9 GHz our accuracy is lower since we have fewer echoes. Our most accurate runs indicate a higher temperature dependence than at 3 GHz; it appears that $\alpha \propto T^{6 \pm 1}$. This behavior is rather difficult to explain since one would expect that any process having a temperature dependence higher than T^4 would have frequency dependence lower than ω^1 . One would not expect such a process to catch up to a process that has an ω^1 dependence. However, the difficulty in obtaining accurate data at 9 GHz makes too much speculation unwarranted. (See Fig. 1.)

2. l Wave

The earlier data of de Klerk³ indicate a T^9 behavior at the lowest temperatures, Lange⁴ finds T^7 , and Nava *et al.*⁵ show a T^8 dependence. At 9 GHz, our data give $T^{7 \pm 2}$. At 3 GHz we find a T^4

dependence. This exemplifies another experimental difficulty. The attenuation rises rapidly in a certain temperature region and then bends over at high temperatures. The temperature dependence is largest at very low temperature and decreases at high temperature. Thus in measuring a particular temperature dependence one is not sure that by going to a lower temperature he could not find a higher temperature dependence. The lowest temperature at which attenuation can be observed is related to the number of echoes one can measure. This varies with frequency and with the polarization. Evidently for the l attenuation at 3 GHz there is a more rapid temperature dependence in a temperature range where we do not have sufficiently accurate data.

We cannot add much to the interpretation of Nava *et al.*⁵ that the t -wave attenuation is due to a process given by Eq. (1), which is $t+L \rightarrow L$. Our data at 9 GHz suggest a higher temperature dependence, which could be produced by a $t+T \rightarrow T$ interaction. The data are not accurate enough to be definitive. The l attenuation was explained by Nava *et al.* as $l+L \rightarrow L$. At the lowest temperature, the theory predicts a weaker temperature dependence than is observed.^{3,5}

One general comment about the low-temperature attenuation is that it begins at exceptionally low temperatures. In an earlier paper,⁹ it was observed that in many materials (Ge, Si, MgO, Al₂O₃, etc.) an attenuation of 3 dB/cm at 9 GHz occurred at about $T/\Theta \approx 0.1$, where Θ is the Debye temperature. Although this "rule" is only an empirical observation, it is interesting to see if it applies to TiO₂. The reported²⁰ Debye temperature of TiO₂ is $\Theta_D = 778$ °K, which suggests that attenuation should start at about 80 °K. Instead we find considerable attenuation at 40 °K. However, we should examine how the Debye temperature is to be obtained for complex lattices. The most common procedure, and the one followed²⁰ in the case of TiO₂, is the strict Debye approximation: the number of acoustic modes is set equal to $3N$, where N is the total number of atoms in the crystal. For a mole, $N = nN_0$, where n is number of atoms per molecule and N_0 is Avogadro's number. In this approximation the measured molar specific heat is fitted by a formula

$$C_v = \frac{12}{5} \pi^4 k(nN_0)(T/\Theta_D)^3 \text{ (J/mole } ^\circ\text{K)}, \quad (4)$$

which thus determines Θ_D . The total number of acoustic modes accounted for in Eq. (4) is $3(nN_0)$. More refined treatments²¹ of the specific heat, originating with the Born-von Karman model, separate the lattice motion into acoustic and optical branches. According to such an interpretation the number of acoustic modes is three times the number of unit cells in the crystal. For crystal struc-

tures in which there are r molecules per unit cell, there are thus $3N_0/r$ acoustic modes per mole. The appropriate Debye formula for these acoustic modes is

$$C_v = \frac{12}{5} \pi^4 k(N_0/r)(T/\Theta)^3 \quad (5)$$

for the molar heat capacity at very low temperatures. For monatomic lattices not containing a basis, Eqs. (4) and (5) are identical since $n=1$ and $r=1$. For TiO₂, however, the number of atoms in a molecule is $n=3$ and the number of molecules per unit cell²² is $r=2$. The Debye temperatures deduced from Eqs. (4) and (5) are in the ratio $\Theta/\Theta_D = (nr)^{-1/3}$. Thus we find that a more correct interpretation of the specific-heat data gives $\Theta = 428$ °K at 0 °K, instead of 778 °K, for rutile. This brings rutile more into line with the rule that $\alpha \approx 3$ dB/cm at $T/\Theta \approx 0.1$.

One may ask whether the rule would be obeyed for other crystals if Θ were consistently determined in the above manner. We have not checked how the Debye temperatures of all the materials surveyed in Ref. 9 were obtained. We have checked the data²³ for Si, however, and find that Eq. (4), with $n=1$, was used to derive $\Theta = 645$ ° for Si at 0 °K. We believe the appropriate formula is Eq. (5) with $r=2$, since there are two Si "molecules" (they are single Si atoms in this case) per unit cell. Use of Eq. (5) would give a Debye temperature of 516 °K for Si at 0 °K. This would make the agreement of the attenuation in Si with the rule poorer; more likely the rule would have to be modified if values of Θ obtained from Eq. (5) were used. Materials that have low attenuation tend to have complex crystal structures.²⁴ Thus, the definition of the Debye temperature, and its significance, should be carefully treated in these cases. At high temperatures it is more correct to use Θ_D because all modes are excited.

B. [110] Direction

1. Fast Transverse (t_1) Wave (Polarized || [001])

At 3 GHz, the temperature dependence was $T^{7.2}$, and at 9 GHz we found $\alpha \propto T^{6.2}$, in a somewhat higher temperature range. The number and accuracy of these measurements was greater than for the [001] direction, so we are more confident that the temperature dependence of this wave is greater than T^4 . This implies that the attenuation process is not the Landau-Rumer $t+L \rightarrow L$, but is more likely governed by Eq. (2a), which is a $t+T \rightarrow T$ process. The frequency dependence is weak, but it is difficult to distinguish an ω^0 from an ω^1 dependence, within the experimental error. Our result differs greatly from that of Lange⁴ who finds a T^3 dependence shifted to a lower temperature. (See Figs. 2 and 3.)

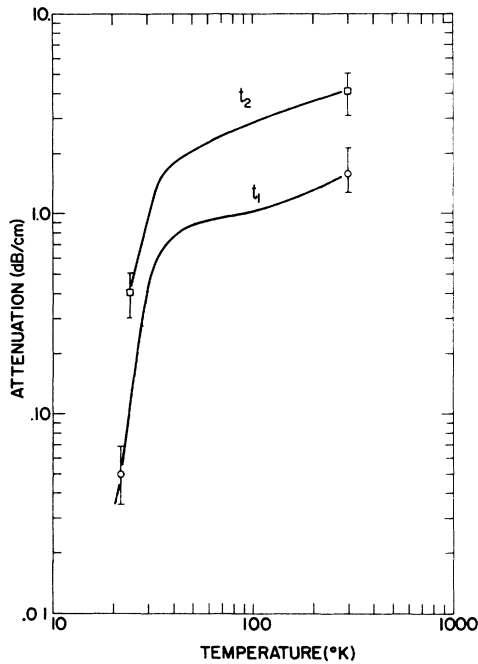


FIG. 2. Temperature dependence of attenuation of 3-GHz ultrasound propagating along a [110] axis of TiO_2 . t_1 is the fast transverse wave, polarized parallel to [001] and t_2 is the slow transverse wave polarized parallel to [110]. The curves are averages of several samples and runs, and the error bars indicate the scatter among these.

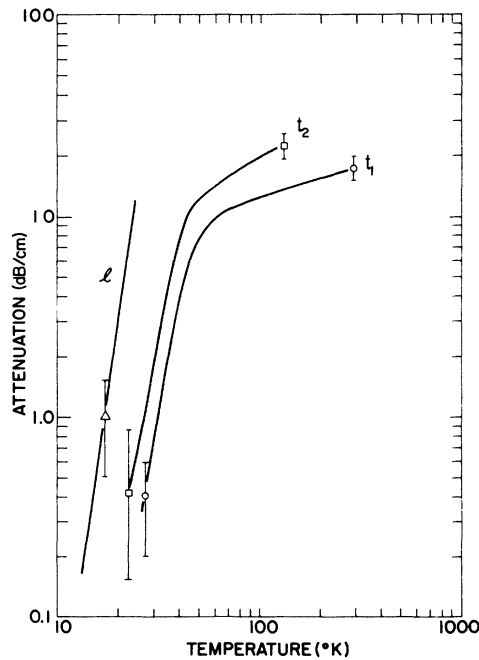


FIG. 3. Temperature dependence of attenuation of 9-GHz ultrasound propagating along a [110] axis of TiO_2 . Cf. caption of Fig. 2 for details.

2. Slow Transverse (t_2) Wave (Polarized $\parallel [1\bar{1}0]$)

The minimum attenuation that we could observe for t_2 was less than for t_1 at 3 GHz because there were fewer t_2 echoes. The strongest temperature dependence was $\alpha \propto T^{4.1}$ at the lowest temperatures of observation. At 9 GHz we find $\alpha \propto T^{5.2}$. The frequency dependence between 3 and 9 GHz is weak, but it is difficult to distinguish between ω^0 and ω^1 dependences within experimental uncertainty. Our dependences differ from Lange's⁴ measurement which yielded $\alpha \propto \omega^{0.6} T^2$.

3. Longitudinal (l) Wave

The l wave was measured only at 9 GHz, and was found to have $\alpha \propto T^{7.1}$. On one occasion, we saw an l echo in the temperature range 60–100 °K, which suggests that the l attenuation decreases from about 30 to 60 °K. This decrease was observed by Lange⁴ at 3 GHz, who also measured a T^9 dependence at the lowest temperature. Lange's result suggests a process governed by Eq. (3) ($l + T - T$); our result is compatible with that, since our measurement may be at a higher temperature.

C. [100] Direction

1. Fast Transverse (t_3) Wave (Polarized $\parallel [010]$)

This wave has one of the strongest temperature dependences ever reported for a transverse wave.

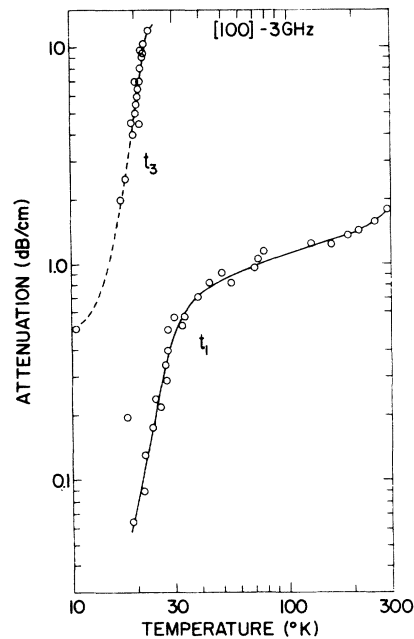


FIG. 4. Temperature dependence of attenuation of 3-GHz ultrasound propagating along a [100] axis of TiO_2 . t_3 is the fast transverse wave, polarized parallel to [010]. t_1 is the slower transverse wave polarized parallel to [001].

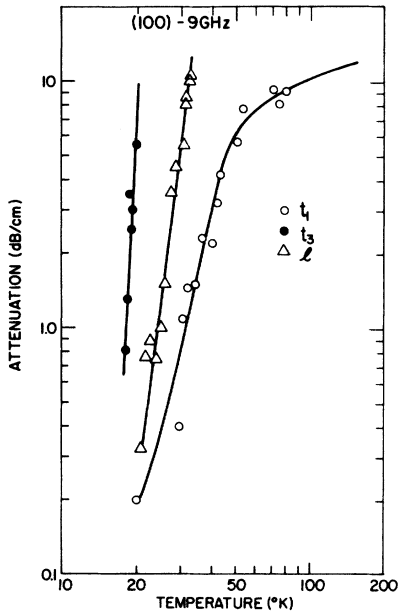


FIG. 5. Temperature dependence of attenuation of 9-GHz ultrasound propagating along a [100] axis of TiO_2 . l is the longitudinal wave. t_1 and t_3 are defined in the caption of Fig. 4.

At 3 GHz we find $\alpha \propto T^{10 \pm 3}$. It is difficult to estimate the possible experimental error since the attenuation varies so rapidly. At 9 GHz, we only have measurements using a Cu-Cn thermocouple as the thermometer, so our accuracy is somewhat reduced. At 9 GHz we find $\alpha \propto T^{15 \pm 5}$, a very rapid temperature dependence indeed. (See Figs. 4 and 5.)

In order to explain this strong temperature dependence one must go beyond the usual approximations used in calculating the ultrasonic attenuation. According to Eq. (3) the highest temperature dependence one might expect is $\alpha_i \propto T^4/\tau_u \propto T^9$. This result depends on assuming that v_u is constant. Because of dispersion v_u depends on the phonon frequency. As the temperature increases, higher phonon frequencies become important so that effectively v_u decreases. This produces an increased temperature dependence of α_i . The effect of this correction, suggested by Shiren, is calculated in detail in a recent paper²⁵ in which it is shown that at temperatures around $0.1\Theta_D$ the temperature dependence can be increased to about $T^{10.4}$.

2. Slow Transverse (t_1) Wave (Polarized \parallel [001])

The temperature dependence is $\alpha \propto T^{5 \pm 1}$. This wave is interesting because in this propagation direction t_1 has two phonon branches higher than itself; it can have allowed (Landau-Rumer) interaction with both of these, Eq. (1). Nevertheless, this

t_1 is similar to t_1 propagating in the [001] and [110] directions. This suggests that there is very little $t_1 + T_3 \rightarrow T_3$ interaction.

3. Longitudinal Mode

At 9 GHz we find a $T^{7 \pm 2}$ temperature dependence. At the lowest temperature Lange⁴ reported a T^7 temperature dependence for the mode, but his curve is shifted to lower temperature than ours.

IV. HIGH-TEMPERATURE RESULTS: EXPERIMENT AND THEORY

The theory of ultrasonic attenuation discussed in Sec. III predicts that in the limit of $\omega\tau \ll 1$ the attenuation is of the form

$$\alpha \propto \gamma^2 \omega^2 \kappa T \quad (\omega\tau \ll 1), \quad (6)$$

where γ is an anharmonic (Grüneisen) constant which in general has different values from the ones discussed in Sec. III, and κ is the thermal conductivity. This predicts that at high temperatures, where the thermal conductivity is a decreasing function of temperature, the temperature dependence of α will be T^m where $m < 1$. This weak temperature dependence is observed experimentally in many materials at high temperatures. The rather unusual feature of our results on rutile is the relatively low temperature at which the modes enter the $\omega\tau < 1$ regime. This has the advantageous effect of cutting off the rapid increase in attenuation of some modes before the attenuation is too high. As the temperature increases in this high-temperature region the increase in attenuation is small or negative. This results in the shear wave t_1 having relatively low attenuation at room temperature, as others^{1,2,6} have noted.

To illustrate this point, let us contrast the behavior of TiO_2 with another crystal that resembles it in many respects, but does not have as low ultrasonic attenuation. Such a crystal is Si. As shown in Fig. 6, the measured Debye temperatures [in the

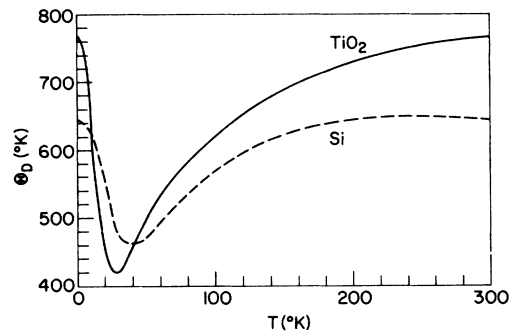


FIG. 6. The Debye temperatures Θ_D , TiO_2 and Si as functions of temperature, T . [After Traylor *et al.* (Ref. 22) and Flubacher *et al.* (Ref. 23).]

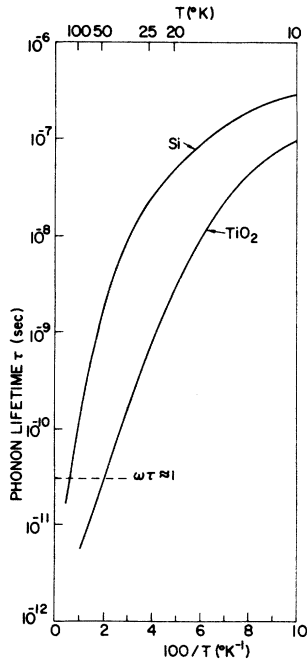


FIG. 7. Phonon lifetimes of TiO_2 and Si as functions of temperature T . The values are derived from measurements of thermal conductivity, specific heat, and sound velocities.

sense of Eq. (4), cf. discussion there] of TiO_2 ²² and Si²³ are similar in both magnitude and temperature dependence. This is a gross indication of lattice dynamical similarity. In Fig. 7 we compare the thermal phonon lifetimes τ , as derived from the measured thermal conductivities of Si²⁶ and TiO_2 ²⁷ according to $\tau = 3\kappa/Cv^2$, where C are the measured heat capacities.^{20,23} At a given temperature the phonon lifetimes are shorter in rutile. In agreement with the observed bending over of the attenuation curves, the temperature at which $\omega\tau \approx 1$ ($\tau \approx 3 \times 10^{-11}$ sec) is found to be $T \approx 50^\circ\text{K}$ in TiO_2 . In Si one would expect from Fig. 7 that $\omega\tau \approx 1$ at $T \approx 160^\circ\text{K}$. To check the temperature at which the transition between low-temperature and high-temperature attenuation occurs in Si, we have measured the temperature dependence of 3-GHz transverse waves in the [110] direction in Si. The results, shown in Fig. 8, are that for the fast transverse (t_1) wave the attenuation deviates from the low-temperature T^4 dependence at about 130°K . This is substantially in agreement with $\omega\tau \approx 1$ for Si. The slow transverse mode similarly shows departures from the low-temperature T^3 dependence at $T \approx 130^\circ\text{K}$.

The remaining fundamental question is why two materials having some similarity of thermal and lattice properties (Debye temperature, sound velocities) differ so greatly in the thermal phonon

lifetimes. A possible answer may be surmised from a comparison of the phonon dispersion curves of TiO_2 ²² and Si,²⁸ some of which are reproduced in Fig. 9. Of the 15 optical branches of TiO_2 , the figure shows only the lower ones. It is evident that in addition to the acoustic branches in rutile there are low-lying optic branches that may participate in the scattering of acoustic branch thermal phonons. This is the greatest difference from the lattice modes in Si. The acoustic branches of both materials are roughly similar which explains the similarity of their Debye temperatures. One would also expect the umklapp scattering of the transverse phonons to be similar in these lattices because it depends on the acoustic branches.

The presence of many low-lying optical branches in TiO_2 could affect the thermal phonon lifetimes of the longitudinal acoustic (LA) phonons by allowing processes of the type $\text{LA} + \text{LA} \rightarrow \text{optic}$, or $\text{LA} + \text{TA} \rightarrow \text{optic}$, where the process can either be normal or umklapp. Umklapp scattering of LA phonons is impossible in the absence of optical phonons. Additional scattering of the TA phonons of the type $\text{TA} + \text{TA} \rightarrow \text{optic}$ is also possible. It is difficult to calculate the rate of acoustical phonon scattering to optical phonons. We note that the phase space for acoustic + acoustic \rightarrow optic is similar to that of acoustic scattering to other acoustic branches,

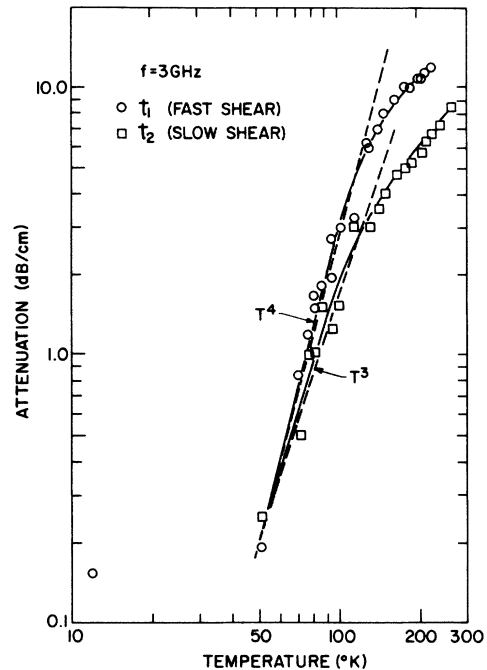


FIG. 8. Temperature dependence of attenuation of 3-GHz ultrasound propagating along a [110] axis of silicon. t_1 is the fast transverse wave, polarized parallel to [001]. t_2 is the slow transverse wave, polarized parallel to [110].

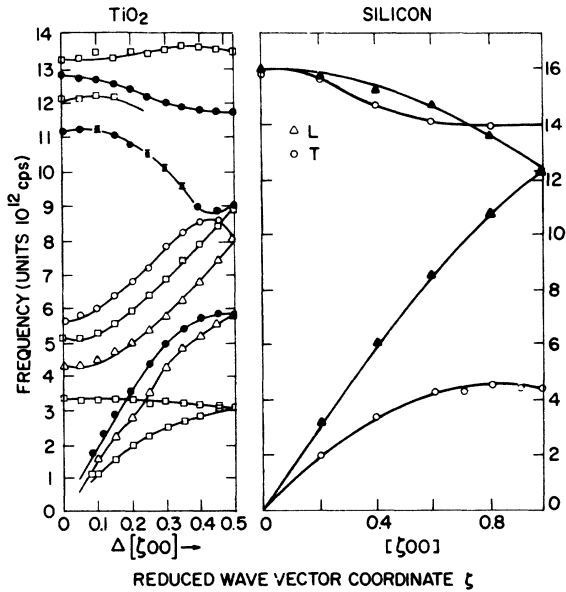


FIG. 9. Phonon dispersion curves of TiO_2 and Si as measured by neutron diffraction [after Traylor *et al.* (TiO_2) (Ref. 22) and Dolling (Si) (Ref. 28)].

which would tend to make their magnitudes similar. Optic mode scattering has been invoked²⁹ to explain thermal conductivity results in Ge, Si, and III-V compounds at temperatures near or above their Debye temperatures. In rutile there are optic modes with energies as low as 140 °K, so that they may have an influence at temperatures around 40 °K, despite a nominal Debye temperature of 778 °K at 0 °K.

It has been pointed out by Oliver and Slack²⁴ that "complex" crystals tend to have low thermal conductivity and low ultrasonic attenuation. In our explanation, the idea of "complexity" must be refined, not only are optic modes present but some of them have low energies. This may explain why crystals like SiO_2 (α quartz) and Al_2O_3 , which seem fairly complex, nevertheless have normally high attenuation. In quartz there are 24 optic modes, even more than in rutile, but according to the reported neutron scattering measurements,³⁰ there are no low-energy optical modes comparable to rutile. One would expect further that the same crystal structure could have quite different ultrasonic attenuation depending on whether the optical modes have energies well above or below the acoustic branches.

Detailed neutron scattering measurements are usually not available, particularly for complex crystals, so that it will not often be possible to predict which crystals will have low attenuation from dispersion curves. An indication of possible low ultrasonic attenuation might be a high dielec-

tric constant. The dielectric constant is related to the optical mode frequency by the Lyddane-Sachs-Teller relation, which in its simplest form is $\epsilon_0/\epsilon_\infty = \omega_L^2/\omega_T^2$, where ϵ_0 (ϵ_∞) are the low (optical) frequency dielectric constants, and ω_L (ω_T) are the longitudinal (transverse) optical mode frequencies. Thus a high value of ϵ_0 may be associated with a low value of ω_T , which would favor low ultrasonic attenuation. In the case of rutile the Γ_1^- optical mode is responsible for the high dielectric constants,²² which are $\epsilon_0 = 170$ ($\parallel c$) and $\epsilon_0 = 90$ ($\perp c$). By comparison, for Si, $\epsilon_0 = 12$; for Al_2O_3 , $\epsilon_0 = 10$; and for α quartz, $\epsilon_0 = 5$, which gives no indication of unusually low polar modes. In these materials, the ultrasonic attenuation is higher than for TiO_2 at room temperature. Of course, a normal dielectric constant ($\epsilon_0 \approx 10$), does not necessarily mean attenuation will be high; it means only that the polar modes have similar frequencies. There could also be *nonpolar* modes with low frequencies which could participate in acoustic phonon scattering. This may be the case in the garnets. Nor does a high dielectric constant necessarily prove that attenuation will be low, since it is the ratio ω_L/ω_T that enters; both ω_T and ω_L could be much higher than the acoustic branches. However, if ϵ_0 is high it may be because ω_T is low. ϵ_0 may thus be an indicator of low attenuation, but the correlation need not be perfect. In the extreme case of ferroelectric materials, the soft optical mode may be of such low frequency that it can couple directly to the ultrasound. Despite the increased acoustic-optic phonon scattering, the net effect in ferroelectrics may be an increase in ultrasonic attenuation.³¹

V. SUMMARY AND CONCLUSIONS

We have surveyed the low- and high-temperature ultrasonic attenuation of waves traveling in the [001], [110], and [100] axes of TiO_2 . Complete understanding of the attenuation processes depends on the knowledge of the coupling constants between the ultrasound and the phonons, and on the lifetimes of the phonons. The Grüneisen constants are presently unknown but are independently measurable.

The short lifetimes of the phonons which seems to be responsible for the low attenuation of some ultrasonic modes may be caused by either the strong acoustic phonon-phonon interaction or by the presence of low-lying optic modes. If the latter is a general effect then it may be possible to use the dielectric constant of a material as an indicator of potentially low ultrasonic attenuation.

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¹R. A. Wilson, H. J. Shaw, and D. K. Winslow, *J. Appl. Phys.* **36**, 3269 (1965) (shear mode, propagating in *c* direction, 1.4–8 GHz, room temperature).

²T. A. Medford and S. Wanuga, *J. Appl. Phys.* **36**, 3362 (1965) (*c*-axis propagation, longitudinal mode 0.3–0.9 GHz; transverse mode, 0.15–0.33 GHz, room temperature).

³J. deKlerk, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1970), Vol. IV A (longitudinal mode propagating in *c* direction, 1 GHz, 1.5–100 °K).

⁴J. N. Lange, *Phys. Rev.* **176**, 1030 (1968). (Longitudinal and most of the transverse modes propagating in *c*, [110] and [100] directions. 1 and 3 GHz, all at low temperature, some up to room temperature.)

⁵R. Nava, R. Callarotti, H. Ceva, and A. Martinet, *Phys. Rev.* **185**, 1177 (1969) (*c*-axis propagation, longitudinal mode, 0.5–3 GHz, transverse mode 0.5 and 1 GHz, 4–40 °K).

⁶H. J. Shaw, D. K. Winslow, A. Karp, and R. A. Wilson, *Appl. Phys. Lett.* **4**, 28 (1964) (shear mode propagating in *c* direction, 2.9 GHz, room temperature).

⁷J. N. Lange, *Phys. Rev.* **179**, 860 (1969).

⁸M. Pomerantz, *IEEE Trans. Sonics Ultrason.* **SU-11**, 68 (1964).

⁹M. Pomerantz, *Phys. Rev.* **139**, A501 (1965).

¹⁰Most of the samples were cut from boules purchased from National Lead Co. They had a slight yellowish color and we did not heat treat them prior to the experiments reported here. We also measured two (110) samples grown by Nakazumi Crystal Co., Japan, which gave results similar to the National Lead Co. material. We thank Prof. O. Johnson and Dr. J. Shaner for providing the latter materials.

¹¹P. C. Waterman, *Phys. Rev.* **113**, 1240 (1959).

¹²M. H. Seavey, Jr., *Proc. IEEE* **53**, 1387 (1965).

¹³A recent authoritative review is by H. J. Maris, in Ref. 3, Vol. VIII, p. 279.

¹⁴For brevity, we refer to the impressed sound wave as “ultrasound”; the term “phonon” will refer only to thermal phonons. We use lower case *l/t* to indicate the ultrasonic polarizations, longitudinal/transverse. Similarly, upper case *L/T* indicate phonon polarizations. When *T* is used in a formula, it represents absolute temperature. “Attenuation” refers only to the ultrasound, whereas “scattering” or

“lifetime” refers only to phonons.

¹⁵N. S. Shiren, *Phys. Lett.* **20**, 10 (1966); R. C. Purdom and E. W. Prohofsky, *Phys. Rev. B* **5**, 617 (1972).

¹⁶H. Ziman, *Electrons and Phonons* (Oxford U. P., Oxford, England, 1960).

¹⁷R. J. von Gutfeld and A. H. Nethercot, Jr., *Phys. Rev. Lett.* **23**, 299 (1966).

¹⁸Temperature dependences lower than T^4 for transverse waves in cubic crystals can arise from the elastic anisotropy according to P. J. King [*J. Phys. C* **4**, 1306 (1971)]. This is observed for the slow transverse waves in the [110] direction of Si and Ge (cf. Ref. 9 and Fig. 8 of the present paper), and seems rather exceptional.

¹⁹R. C. Purdom, in *Conference on Phonon Scattering in Solids*, Paris, 1972 (unpublished).

²⁰T. R. Sandin and P. H. Keesom, *Phys. Rev.* **177**, 1370 (1969).

²¹A recent survey is in A. K. Ghatak and L. S. Kothari, *An Introduction to Lattice Dynamics* (Addison-Wesley, Reading, Mass., 1972). A formula particularly pertinent to our discussion is Equation 7.50. Confer W. G. Lyon and E. F. Westrum [*J. Chem. Phys.* **49**, 3374 (1968)] for an example of separation of the specific heat into acoustic and optic mode contributions (CaWO_4).

²²J. G. Traylor, H. G. Smith, R. M. Nicklow, and M. K. Wilkinson, *Phys. Rev. B* **3**, 3457 (1971).

²³P. Flubacher, A. J. Leadbetter, and J. A. Morrison, *Philos. Mag.* **4**, 273 (1959).

²⁴D. W. Oliver and G. A. Slack, *J. Appl. Phys.* **37**, 1542 (1966); G. A. Slack, D. W. Oliver, and F. H. Horn, *Phys. Rev. B* **4**, 1714 (1971).

²⁵M. Pomerantz and N. S. Shiren, *Phys. Lett. A* **45**, 209 (1973).

²⁶M. G. Holland and L. J. Neuringer, in *Proceedings of the International Conference on the Physics of Semiconductors*, Exeter (The Institute of Physics and the Physical Society, London, 1962), p. 475.

²⁷W. R. Thurber and A. J. H. Mante, *Phys. Rev.* **139**, A1655 (1965).

²⁸G. Dolling, in *Inelastic Scattering of Neutrons in Solids and Liquids* (IAEA, Vienna, 1963), Vol. 2, p. 37.

²⁹E. F. Steigmeier and I. Kudam, *Phys. Rev.* **141**, 767 (1966).

³⁰M. M. Elcombe, *Proc. Phys. Soc. Lond.* **91**, 947 (1967).

³¹H. H. Barrett, in Ref. 3, Vol. VI, p. 65.