Relaxation Attenuation of Ultrasonic Waves in InAs†

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The attenuation of longitudinal and transverse ultrasonic waves with frequencies between 90 and 510 MHz and propagating in the [110] direction in InAs has been measured at room temperature. Measurements were also made at lower temperatures employing 210-MHz longitudinal waves. The attenuation at room temperature is observed to increase less strongly than f^2, where f is the frequency. However, when the residual attenuation observed at 4.2 K is subtracted from the room-temperature data, the difference approaches the f^2 dependence expected for the Akhieser phonon viscosity mechanism. It is found that the temperature dependence of the attenuation can also be accounted for within the framework of the Akhieser mechanism and is due mainly to the quantity $\sum_i \gamma_i^2 C_{V_i}$, where the γ_i's and C_{V_i}'s are the Grüneisen γ's and heat capacities of a small number of Debye continua and Einstein modes by which the actual phonon spectrum can be approximated.

I. INTRODUCTION

The attenuation of ultrasonic waves near room temperature in elemental and III-V compound semiconductors having diamond or zinc-blende lattices has been reported for Ge,[1-6] Si,[3,5,6] GaAs,[7,8] GaSb,[8] and InSb.[9] In this paper, we report measurements of the attenuation in InAs at room and lower temperatures at which the angular frequency of the ultrasonic wave ω is less than the rate $1/\tau$ at which the disturbance in the phonon spectrum is produced by the wave relaxes. The ultrasonic waves were propagated in the [110] direction of the crystal and ranged in frequency between 90 and 510 MHz Both transverse waves and longitudinal waves were employed. Measurements of the attenuation of these waves in the same sample of n-type InAs at low temperatures have been reported by us previously.[10] The experimental methods employed here are the same as those that were described for the low-temperature measurements. Analysis of our results indicate the primary importance of the Akhieser phonon viscosity mechanism.[11]

II. RESULTS

Figure 1 shows a plot of the log of the measured attenuation α versus the log of the frequency for longitudinal waves and two different shear waves propagating in the [110] direction of InAs. α represents the total apparent attenuation which contains not only the bulk attenuation of the InAs sample but also contributions from losses in the transducer and bond, and losses from reflections. Interference arising from different parts of the ultrasonic wave may also result in an apparent attenuation or a nonexponential decay pattern which can make it difficult to determine even what the apparent attenuation is. In view of these effects, the observed attenuation is most likely higher than that intrinsic to the sample itself. To estimate the magnitude of the extraneous attenuation we shall assume that it can be approximated by the temperature-independent residual attenuation α_0 measured at liquid-helium temperatures.[10] Figure 2 shows $\log \alpha_0$ versus $\log f$ taken from low-temperature measurements.[10] The values of α_0 determined from the curve of Fig. 2 are then subtracted from the measured attenuation values to obtain the results plotted in Fig. 3. From Fig. 3 we see that $\alpha - \alpha_0$ is proportional to f^2 at higher frequencies. An f^2 dependence for the attenuation would be expected from the Akhieser phonon viscosity mechanism (see Sec. III). The deviation of the low-frequency data from an f^2 dependence may be due to the fact that at such frequencies the apparent attenuation has an appreciable component due to diffraction effects. This is not taken care of properly by using α_0 because our measurements of the latter did not extend below 150 MHz, and we simply obtained values for α_0 at lower frequencies by extrapolation using the same frequency dependence ($f^{1.3}$) as was observed for α_0 at higher frequencies. Such extrapolation would be unsatisfactory if diffraction effects do occur since the attenuation due to diffraction[4] is expected to be proportional to $1/f$.

Figure 4 shows the temperature dependence of $\alpha - \alpha_0$ for 210 MHz longitudinal waves. The quantity actually plotted is $(\alpha - \alpha_0)/(\alpha - \alpha_0)_{273}$ K. Normalization to 273 K rather than to room temperature was used because it appears that α may decrease as the temperature increases above 273 K. This is not completely evident from our data, but other investigators[9] have found such an effect in another small-gap III-V compound semiconductor, namely, InSb.

III. DISCUSSION

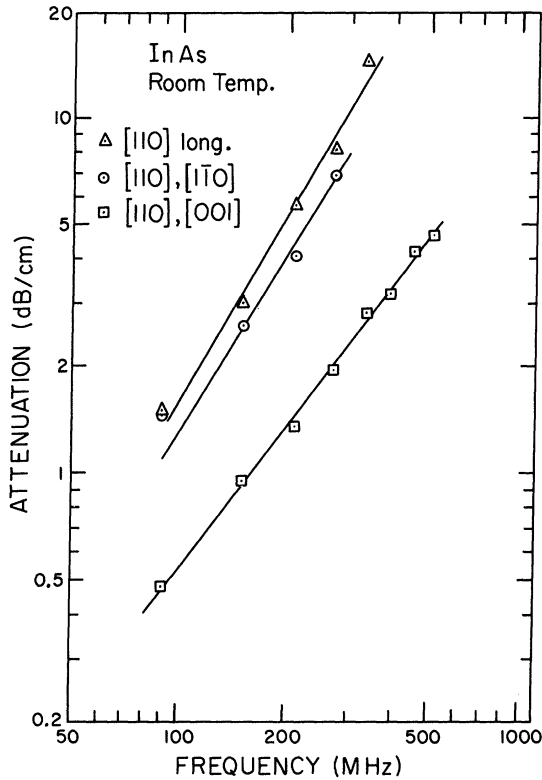Theory for the attenuation of ultrasound near

FIG. 1. Attenuation of ultrasonic waves propagating in the [110] direction in InAs at room temperature as a function of frequency. Long. stands for longitudinal, and the second set of indices give the polarization of the shear waves.

room temperature has been developed by a number of investigators.[5,11-13] It involves the dissipation of energy as quasithermal phonons relax after being modified in frequency and population by the ultrasonic waves. The relaxation is accomplished by interaction with other phonons. Unfortunately the most rigorous expression for the attenuation[12] is too complicated to allow direct comparison with experiment, unless a very large amount of specific information about the solid is available. The needed information included the dependence of phonon energy, relaxation time, and Grüneisen constant on phonon momentum q for each of the many phonon modes of the crystal.

For comparison with our data, we shall use a simplified form of the formula for the attenuation which we believe retains the essential physical parameters. It is

$$\alpha_{pp} = \frac{\omega^2 T}{\rho v^3} \sum \frac{C_{qi}\gamma_{qi}^2 \tau_{qi}}{1+\omega^2\tau_{qi}^2}, \tag{1}$$

where ω is the angular frequency, v is the velocity of the ultrasonic wave, T is the absolute tempera-

ture, ρ is the density of the solid, C_{qi} is the heat capacity, γ_{qi} the Grüneisen γ, and τ_{qi} the relaxation time of phonons of wave vector q of a particular type i. In order to arrive at this form, it was assumed that the difference between the distributions to which N processes and U processes cause relaxation[12] is negligible, and the effective temperature of the distribution is close to the thermal equilibrium one existing in the absence of the sound wave. The latter assumption need not be made to obtain a tractable formula[12] for α, provided that other simplifying assumptions are made. Among these is the Debye model of the solid.

Equation (1) is valid when $\omega\tau_{qi} < 1$, and it can be seen from Eq. (1) that when $\omega_{qi}\tau_{qi} \ll 1$ the attenuation is expected to be proportional to the square of the ultrasonic frequency. In order to estimate a value for $\omega\tau_{qi}$ we shall assume as is usually done that τ_{qi} can be replaced by an average τ_{th} deduced from the measured lattice thermal conductivity K_g by means of the relation $K_g = \frac{1}{3}C_V \bar{v}^2\tau_{th}$, where C_V is the heat capacity and $\bar{v}$ is the average Debye velocity.[5]

For our sample the measured thermal conductivity K is about 0.16 W cm^{-1} deg^{-1} at room temperature, and $K \approx K_g$ since the electronic thermal conductivity (as estimated from the Wiedemann-
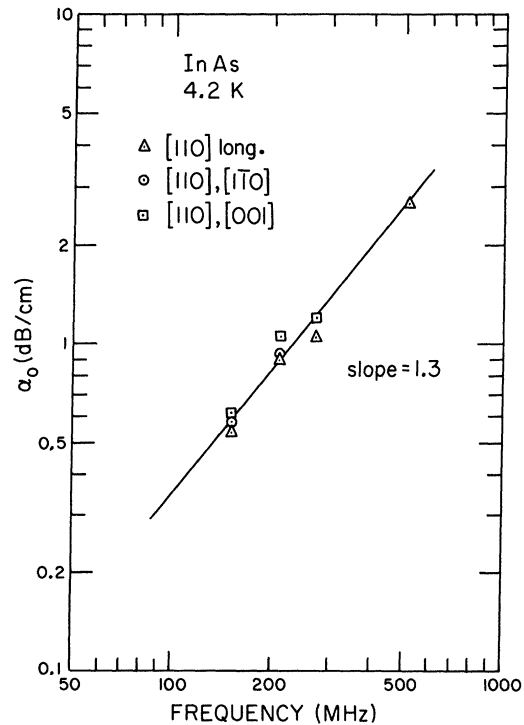

FIG. 2. Residual attenuation of longitudinal and shear waves in InAs at 4.2 K versus frequency. Data taken from Ref. 10.
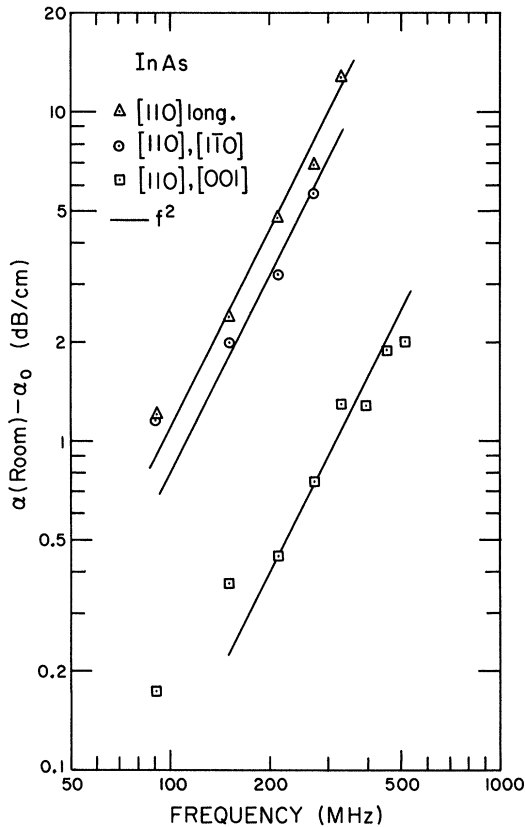
FIG. 3. Attenuation at room temperature minus residual attenuation at 4.2 K plotted versus frequency compared to frequency-squared lines.

time which is a function of q in fitting attenuation data.[19] Unfortunately, the theoretical attenuation formula which was employed in the latter investigation has recently been found to be incorrect.[13] Furthermore, the influence of other simplifying assumptions would have to be determined before the appropriateness of such a single q-dependent relaxation time could be assessed.

When we tried to fit the temperature dependence of our attenuation data by replacing all the τ_{qi} by τ_{th} ($\tau_{th} = 3K/C_V \bar{v}^2$ with K-versus-temperature data taken from the literature[20]) and $\sum_{qi} C_{V_i} \gamma_{qi}^2$ by $C_V \bar{\gamma}_{qi}^2$ as is usually done,[4,12] a very poor fit was obtained. In fact, the α_{pp} calculated under these conditions exhibited a maximum near the lower end of the temperature range of interest to us.

In view of this situation we decided to adopt a new point of view to try to account for our attenuation-versus-temperature data. It involves a more realistic treatment of the C_{V_i} and the γ_{qi} than is usually made in analyzing attenuation data. Specifically we utilized an approximation to the actual phonon spectrum like that employed by Daniels[17] to fit thermal expansion data on Ge. This spectrum is comprised of two Debye continua associated with the transverse and longitudinal acoustic modes with small wave number and three δ functions associated with the TA, LA+LO, and TO phonon peaks. The justification for doing this is the similarity between the phonon spectra of Ge, Si, and all III-V compounds measured so far.[21] Of course the characteristic temperatures Θ_i of the various components of the spectra are different for the different

Franz law) is negligible. Then using the experimental heat capacity at 300 K (5.75 cal/mole/deg),[14] $\rho = 5.70$ g/cm^3, and $\bar{v} = 5.62 \times 10^{10}$ cm^2 sec^{-1},[15] we find that $\omega\tau_{th} = 0.2$ at 510 MHz and of course proportionately smaller at lower frequencies. Therefore Eq. (1) predicts that $\alpha_{pp} \sim f^2$. Referring back to Fig. 3 we see that after the low-temperature residual attenuation has been subtracted from the attenuation measured at room temperature, the resulting quantity $\alpha - \alpha_0$ is about proportional to f^2 at least at frequencies above 200 MHz. Thus, agreement with Eq. (1) is obtained indicating that the Akhieser phonon viscosity mechanism is responsible for the nonextraneous attenuation.

In order to interpret the temperature dependence of the attenuation it is usually[4,5,16] assumed that γ_{qi} and τ_{qi} are independent of q and furthermore that all the τ_{qi} can be replaced by an average τ_{th} (as was done above to estimate the value of $\omega\tau_{qi}$). Attempts have been made to deduce the dependence of γ_{qi} on q in fitting thermal-expansion-versus-temperature data on Ge,[17,18] and to use a single relaxation
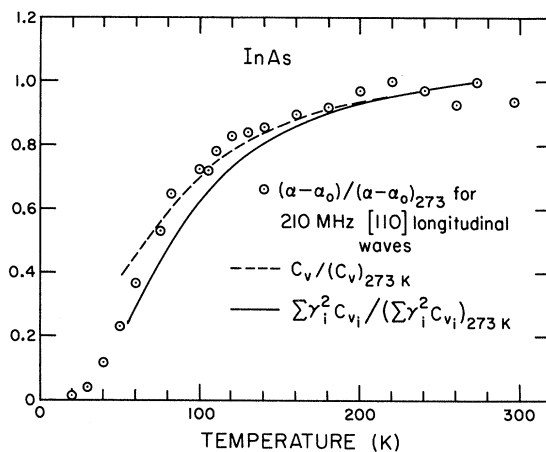

FIG. 4. Temperature dependences of the attenuation difference $\alpha - \alpha_0$, the experimental heat capacity (from Ref. 14), and the quantity calculated from Grüneisen γ's and heat capacities of a small number of Debye and Einstein modes by which the actual phonon spectrum can be approximated (see text).

TABLE I. Parameters for each mode used in calculating $\sum_i \gamma^2 C_{vi}$ as a function of temperature for InAs. Θ_D is the Debye temperature, Θ_E is the Einstein temperature, n is the fraction of $3N$ states in that mode, and γ is the corresponding thermal Grüneisen constant.

Mode	$\Theta_D(K)$	$\Theta_E(K)$	n	γ
Transverse continuum	54.5	$\cdots$	0.0065	0.398
Longitudinal continuum	218	$\cdots$	0.0495	1.28
TA	$\cdots$	91	0.327	-0.36
LA, LO	$\cdots$	248	0.284	1.21
TO	$\cdots$	300	0.333	1.21

materials. In order to determine the Θ_i for InAs we proceeded as follows. First, approximate values for the Θ_i were deduced simply by using a scaling factor derived from the ratio of the Debye Θ's for InAs and for Ge which are obtained from elastic constant data. Then the heat capacity was calculated as a function of temperature using the scaled Θ_i. Since the heat capacity so calculated was found to deviate from the experimental heat capacity, adjustments were made in the values of the Θ_i until the calculated heat capacity did agree well with the experimental one.

In order to have realistic values for the γ_{qi} we used the γ_i which allow thermal expansion data on Ge to be accounted for.[17] This again is a departure from the practice of fitting attenuation-versus-temperature data which employs γ's calculated from third-order elastic constants.[5,16] For the transverse-acoustic Einstein mode we used a value for γ_i of -36 rather than the other possible value of -0.04 because of theoretical calculations[21] and tunneling experiments.[22] In Table I is a summary of the parameters we used to calculate the quantity $\sum_i \gamma_i^2 C_{V_i}$ to which α_{pp} should be proportional according to Eq. (1). From Fig. 4 we see that the

quantity $\sum_i \gamma_i^2 C_{V_i}$ by *itself* has a temperature dependence which is only somewhat stronger than that of $\alpha - \alpha_0$. Before drawing any conclusions from this finding, one would of course like to determine whether or not $\sum_i \gamma_i^2 C_{V_i}$ fits the data better than does the heat capacity itself, for example. We have plotted the normalized experimental heat capacity in Fig. 4. (The calculated heat capacity $\sum_i C_{V_i}$ is of course almost equal to the experimental heat capacity in view of the procedure we used in choosing the Θ_i.) From Fig. 4 we see that the normalized heat capacity approximates the normalized $\alpha - \alpha_0$ well at the higher temperatures but lies too high at the lower temperatures. As mentioned before, contributions to the temperature dependence of α_{pp} due to T and the τ_{qi} in Eq. (1) would cause α_{pp} to lie higher than do C_V or $\sum \gamma_i^2 C_{V_i}$. This would *increase* the discrepancy between $\alpha - \alpha_0$ and the α_{pp} calculated using C_V but would *lessen* the discrepancy between $\alpha - \alpha_0$ and α_{pp} calculated using $\sum \gamma_i^2 C_{V_i}$. Thus the inclusion of the γ_i^2 is important.

In view of the above, we conclude that in order to obtain a physically meaningful interpretation of the temperature dependence of the phonon viscosity attenuation it is necessary to include the temperature dependence caused by the fact that different γ_i are associated with the various components of the phonon spectrum and the degree of excitation of the latter depends on temperature. Furthermore, we believe that incorporation of our point of view into a more realistic use of theory may serve to relieve some of the recent despair[13] about being able to account for the temperature dependence of phonon viscosity attenuation.

Additional tests of the validity and scope of applicability of our conclusions should be made. Ge and Si would seem to be prime experimental materials for such tests.

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Nonlinear Optical Susceptibilities of Covalent Crystals

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The two-band quantum-mechanical model of Phillips and Van Vechten is applied to the calculation of the second-order susceptibility. The theory contains no adjustable parameters and gives the correct sign and reasonable agreement with measured magnitudes of second-harmonic coefficients for nine zinc-blende crystals.

Recently Phillips and Van Vechten[1] (hereafter called PV) have applied the Phillips theory[2,3] of the dielectric constant (also called the "dielectric theory of electronegativity") to the second- and third-order susceptibilities of zinc-blende and wurtzite structure crystals. From their presentation it is clear that the theory is capable of giving order-of-magnitude agreement with the measured $|\chi^{(2)}|$. It can not account for the measured $|\chi^{(3)}|$ in Si, Ge, or GaAs, but this has been explained by Van Vechten and Aspnes[4] who have shown that a "Franz-Keldysh" mechanism is dominant for $\chi^{(3)}$ in semiconductors having a sufficiently small direct gap. In this paper the PV theory for $\chi^{(2)}$ will be reformulated to eliminate an objectionable approximation made by PV, and to bring out clearly just how the theory predicts the sign of $\chi_{123}^{(2)}$ (the only nonvanishing component) in zinc-blende crystals. Wurtzite crystals will not be discussed here.

At zero frequency the linear ($\chi^{(1)}$) and second-order ($\chi^{(2)}$) susceptibilities are defined by

$$P_i = \sum_j \chi_{ij}^{(1)} E_j + \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \cdots , \qquad (1)$$

where $\vec{E}$ is the macroscopic electric field and $\vec{P}$ is the macroscopic electric polarization. We consider only the electronic contribution to $\chi^{(1)}$ and $\chi^{(2)}$ and ignore the contribution of the infrared lattice vibration[5] which is negligible at optical frequencies. Adler[6] has shown that the electrons can be considered localized within cells which are small compared to optical wavelengths and large compared to atomic dimensions. The linear polarizability $\vec{\alpha}$ and second-order polarizability $\vec{\beta}$ of a single cell can be written[6,7]

$$\alpha_i = \sum_\nu{}' (2e^2/\hbar\omega_\nu) |\langle 0 | \hat{R}_i | \nu \rangle|^2 , \qquad (2)$$

$$\beta_{ijk} = \sum_{\nu\mu}{}'' \langle 0 | e\hat{R}_i | \nu \rangle \langle \nu | e\hat{R}_j | \mu \rangle \langle \mu | e\hat{R}_k | 0 \rangle \hbar^{-2} \omega_\nu^{-1} \omega_\mu^{-1}$$

$$+ (ijk \rightarrow ikj) + (ijk \rightarrow jik) , \qquad (3)$$

where the ground electronic state $|0\rangle$ is taken to be at zero energy, $\hbar\omega_\nu$ is the energy of state $|\nu\rangle$, the primed sum omits the ground state, and

$$e\hat{\vec{R}} \equiv e\sum \vec{r} - e\langle 0 | \sum \vec{r} | 0 \rangle \qquad (4)$$

is the total electric moment operator. The coordinates ijk refer to principal axes of α. Implicit in (2) and (3) is the assumption that $\vec{E}$ is constant over the cell (the electric dipole approximation). Although the macroscopic field can be assumed constant there is in general a microscopic *local-field correction*[8] having the periodicity of the crystal. If this local-field correction is neglected the susceptibilities are

$$\chi^{(1)} = N\alpha, \quad \chi^{(2)} = N\beta , \qquad (5)$$

where N^{-1} is the cell volume.

It is not necessary here to go into the question of the validity of neglecting local-field corrections, since (5) can be regarded as exact if (2) and (3) refer to a suitable macroscopic model for the electrons. We use the model introduced by PV based on Phillips dielectric theory[2,3] and, with no addition-