

## Attenuation of Ultrasonic Waves in InAs at Low Temperatures\*

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The attenuation  $\alpha$  of ultrasonic waves propagating in the [110] direction of InAs has been measured by the pulse-echo technique between 1.5 and 100°K in the frequency range 150 to 510 MHz. Both transverse and longitudinal waves have been employed. At the lowest temperatures, the measured attenuation  $\alpha_0$  was found to be independent of temperature and the type of wave propagated, but dependent on frequency. At higher temperatures, the increased attenuation was found to be the result only of interactions with the lattice. (Electronic or impurity-related effects do not appear to cause any measurable attenuation.) The temperature and frequency dependence of  $\alpha - \alpha_0$  indicates that the interactions with the lattice which are responsible for absorption are the three-phonon collision processes between the low-energy phonons of the sound wave and the transverse thermal phonons of the lattice. This was found to be the case both for longitudinal and for slow transverse sound waves. The dependence on temperature for various modes and frequencies is compared with theoretical expressions derived by Maris for the attenuation of ultrasonic waves by the above processes.

### I. INTRODUCTION

PREVIOUS investigations of the attenuation of ultrasonic waves in elemental and III-V compound semiconductors having diamond or zinc-blende lattices have been conducted at low temperatures on Ge,<sup>1-7</sup> Si,<sup>1-3</sup> GaAs,<sup>1,7</sup> and InSb.<sup>8</sup> Those studies which were on the III-V compounds employed higher frequencies than those which we have used in this work to study another III-V compound semiconductor InAs. The previous measurements have shown that when electronic or impurity-related effects<sup>6</sup> are negligible, the ultrasonic attenuation at appropriately low temperatures is proportional to  $\omega^m T^n$  with  $m \approx 1$  and  $3 < n < 5$ . Here  $\omega$  is the angular frequency of the sound wave. For such temperatures, the time between thermal phonon collisions  $\tau_{th}$  becomes greater than the period of the sound wave, and thus the attenuation of the sound wave is attributed to discrete collisions between the low-energy phonons of the sound wave and the thermal phonons of the crystal.

In this paper we report the results of our measurements of the attenuation of ultrasonic waves traveling in the [110] direction of InAs between 1.5 and 100°K in the frequency range 150 to 510 MHz. Both transverse

waves and longitudinal waves were employed. For transverse waves the highest frequency of measurement was 270 MHz. The condition  $\omega\tau_{th} > 1$  was satisfied for temperatures below 58°K at the highest frequency (510 MHz) and for temperatures below 36°K for the lowest frequency (150 MHz). The value of  $\tau_{th}$  was deduced from thermal conductivity data as will be indicated later.

### II. EXPERIMENTAL METHOD

To measure the attenuation of ultrasonic waves in InAs, we used the well-known pulse-echo method. Pulses of rf were used which typically had a length of 1.6  $\mu$ sec and a repetition rate of 400 per sec. Figure 1 shows a schematic diagram of the experimental arrangement. An exponential generator and synchronizer superimposes an exponential signal on the decaying echo train. The time constant of this signal is variable so that one can observe if the echo train is exponential, and if so, measure its decay time. The attenuation recorder allows one to select any two echoes and then record the logarithm of the ratio of the two amplitudes. The recorder is calibrated directly in decibels. This feature is particularly useful for determining if equilibrium has been reached, and for measuring as a function of some time-dependent variable, such as temperature in our case. We obtain a given temperature by cooling to liquid-helium temperature and then allowing the system to warm up. This occurred at the rate of about

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<sup>1</sup> M. Pomeranz, *Phys. Rev.* **139**, A501 (1965).

<sup>2</sup> W. P. Mason and T. B. Bateman, *Phys. Rev.* **134**, A1387 (1964).

<sup>3</sup> W. P. Mason and T. B. Bateman, *J. Acoust. Soc. Am.* **36**, 644 (1964).

<sup>4</sup> B. I. Miller, *Phys. Rev.* **132**, 2477 (1963).

<sup>5</sup> E. R. Dobbs, B. B. Chick, and R. Truell, *Phys. Rev. Letters* **3**, 332 (1959).

<sup>6</sup> M. Pomeranz, *Proc. IEEE (Inst. Elec. Electron. Engrs.)* **53**, 1438 (1965).

<sup>7</sup> K. R. Keller and B. Abeles, *J. Appl. Phys.* **37**, 1937 (1966).

<sup>8</sup> K. W. Nill, Ph.D. thesis, Massachusetts Institute of Technology, 1966 (unpublished).

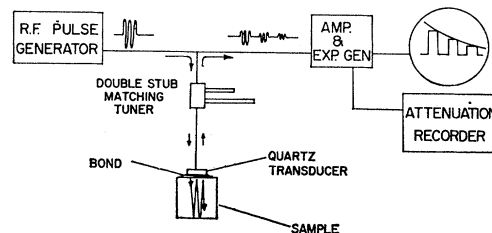


FIG. 1. Schematic diagram of the experimental arrangement.

0.2°K per min. Once the sample temperature was lowered to 4.2°K, the exact frequency for the measurements was chosen in the following manner. The frequency was first adjusted to resonance which gave a maximum height for the first echo, a large apparent loss, and a poor exponential decay pattern overall. Then as the frequency was lowered, the echo pattern became exponential and the apparent loss became much smaller. If the frequency was lowered further, the apparent loss remained the same, and the echo pattern remained exponential but decreased in amplitude. The frequency selected was that at which the pattern first became exponential and the apparent loss small. This occurred at a frequency somewhat below an odd multiple of the transducer frequency, e.g., 205 instead of 210 MHz. As the temperature of the sample increased it was not found necessary to change the frequency, since when the above procedure was tried at the higher temperatures, the same operating frequency resulted.

Tuning stubs were used to match the impedance of the transducer at a particular frequency to the 50- $\Omega$  coaxial line. It is important to keep the transmission line coaxial everywhere, even at the transducer, so as to avoid large signal losses by radiation.

In order to measure the attenuation at liquid-helium temperature, the coaxial transmission line must be brought into a liquid-helium Dewar system. In order to minimize heat losses, the 50- $\Omega$  coaxial line is stripped of its outer conductor and thin-wall stainless-steel tubing is put in its place. If the tubing fits snugly, the impedance of the line will be about the same as that of the original coax. The sample is mounted in a holder which is suspended by means of a long, thin-walled, stainless-steel tube. The holder consists of copper top and bottom pieces held together by threaded rods. The copper pieces touch the sample in annular rings whose inner diameters are larger than that of the transducer bonded to the top of the sample. Spring loading is used to provide secure holding without excessive pressure on the sample and to compensate for the difference in the thermal expansions of the holder and of the sample. The higher thermal conductivity of the copper helps to insure temperature uniformity across the sample. A copper-constantan thermocouple is used to measure the temperature above 4.2°K, and is attached to the copper piece just above the sample.

The transducers used in these measurements were X-cut and AC-cut quartz discs,  $\frac{1}{4}$  in. in diameter, with a nominal fundamental resonance frequency of 30 MHz. These crystals were optically polished for overtone operation and electrodes were vacuum evaporated on the quartz in a coaxial configuration and consisted of gold over chromium. The resulting diameter of the effective area of the transducer was  $\frac{1}{8}$  in. This is large enough to keep diffraction losses small, but small enough to minimize reflections from the side walls of the sample which would cause the echo train to be nonexponential.

For low temperatures Dow Corning 200 Fluid<sup>9</sup> was used to bond the transducer to the sample. This fluid comes in various viscosities, and we used successfully fluids having viscosities of 1000 and 12 500 centistokes. After a small drop of the bond is put on the sample, the transducer is put on top and is then pushed down hard with an optical flat so as to squeeze out excess fluid. In this way a thin and uniform bond is achieved.

The sample used in our measurements was a cube approximately  $\frac{1}{2}$  in. on a side cut from a large single crystal of *n*-type InAs grown in a  $\langle 111 \rangle$  direction. Two  $\{110\}$  planar surfaces of the cube were ground and polished flat and parallel to within 0.2  $\mu$ .

At room temperature the carrier concentration of the sample, deduced from the measured Hall coefficient  $R_H$  at 4 kG using the relation  $N = 1/R_H e$ , was  $2.4 \times 10^{17}$  cm<sup>-3</sup>. The electrical conductivity was  $6.7 \times 10^2 \Omega^{-1}$  cm<sup>-1</sup>, and the electron mobility was 17 000 cm<sup>2</sup>/V sec.

### III. RESULTS

We show the attenuation  $\alpha$  measured for longitudinal waves propagating in a  $\langle 110 \rangle$  direction in InAs in Fig. 2. Data for four frequencies are included. In Figures 2-7, the values quoted for the frequencies are simply odd multiples of the fundamental frequency of the transducer, whereas the actual working frequencies were about 4% lower. The nominal frequencies are indicated, since the computations were made employing them. At the lowest temperatures,  $\alpha$  becomes independent of temperature. It is customary to call this the residual attenuation  $\alpha_0$ . Such behavior has been observed in a wide variety of samples by various investigators. It is not limited to cases in which measurements are made with transducers bonded to samples, where one expects a relatively large bond loss, but it

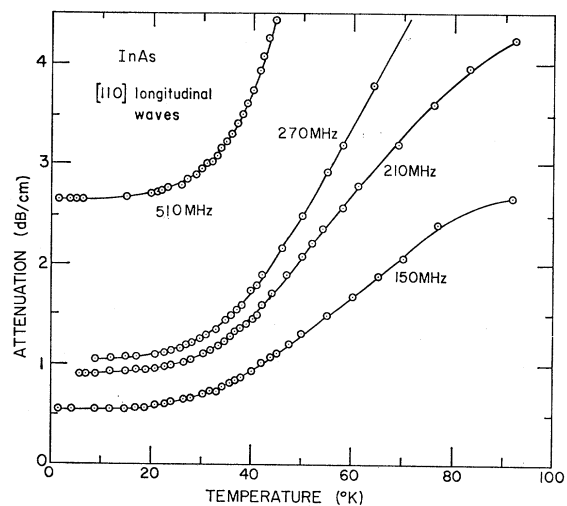


Fig. 2. Attenuation of  $[110]$  longitudinal ultrasonic waves in InAs as a function of temperature at four frequencies.

<sup>9</sup> H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

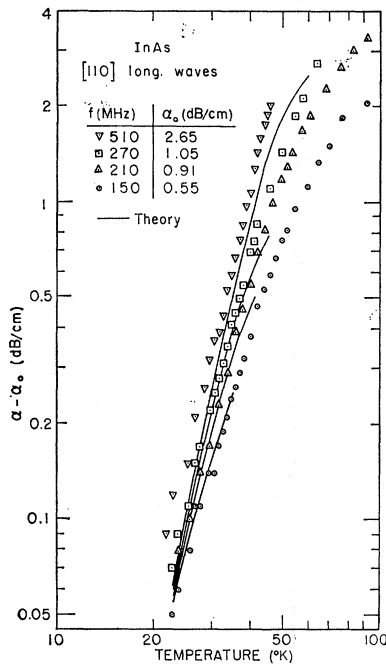


FIG. 3. Temperature-dependent part of the attenuation of [110] ultrasonic waves in InAs as a function of temperature at four frequencies. The theory curves are calculated for process 3. The calculated attenuation is set equal to the value of  $\alpha - \alpha_0$  obtained experimentally at 35°K and 270 MHz.

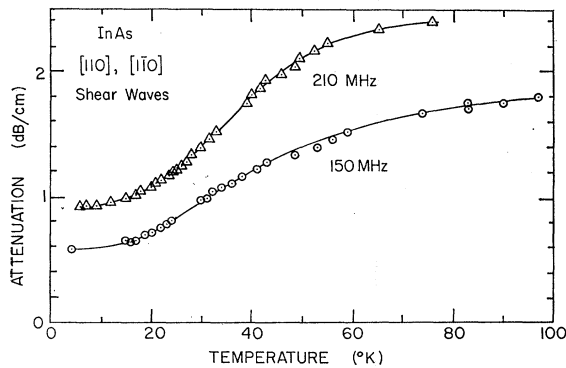


FIG. 4. Attenuation of [110], [110] transverse ultrasonic waves in InAs as a function of temperature at two frequencies.

is also observed where the transducers are thin films evaporated onto the sample, where no bond loss is expected.<sup>10</sup> In our case,  $\alpha_0$  is probably caused by absorption in the transducer and bond and reflection losses at the two sample surfaces. To obtain the temperature-dependent part of  $\alpha$  we subtract  $\alpha_0$  from  $\alpha$ .  $\text{Log}(\alpha - \alpha_0)$  is plotted in Fig. 3 as a function of  $\text{log}T$ .

Since there are two different types of pure transverse waves which will propagate in the  $\langle 110 \rangle$  direction of InAs, the fast shear wave with polarization in the  $\langle 001 \rangle$  direction, and the slow shear wave with polarization in

the  $\langle 1\bar{1}0 \rangle$  direction, results for both of these types of transverse waves are plotted in Figs. 4-7.

#### IV. DISCUSSION

The attenuation of an ultrasonic wave by direct interaction with conduction electrons is significant only in metals where large numbers of free electrons are available. Thus we do not expect attenuation from this source in InAs. However, since InAs is piezoelectric, we expect the sound wave to interact with free electrons through piezoelectric coupling. We have estimated the attenuation in InAs for the [110] [001] shear wave, which is piezoelectrically active, from expressions given by Hutson and White.<sup>11</sup> At 25°K and 270 MHz, we obtain  $\alpha \approx 10^{-4}$  dB/cm. This is too small a value to be detected in our measurements. It is also expected that

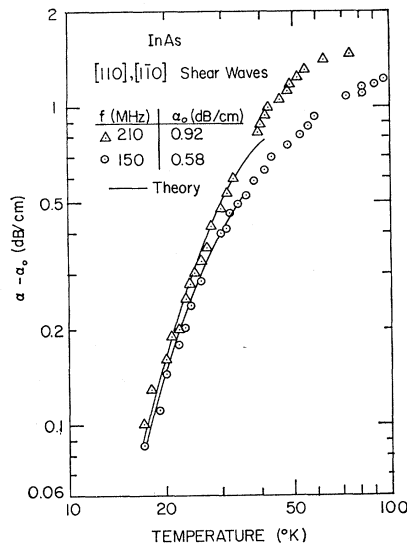


FIG. 5. Temperature-dependent part of the attenuation of [110], [110] transverse ultrasonic waves in InAs as a function of temperature at two frequencies. The theory curves are calculated for process 2. The calculated attenuation is set equal to the value of  $\alpha - \alpha_0$  determined experimentally at 25°K and 210 MHz.

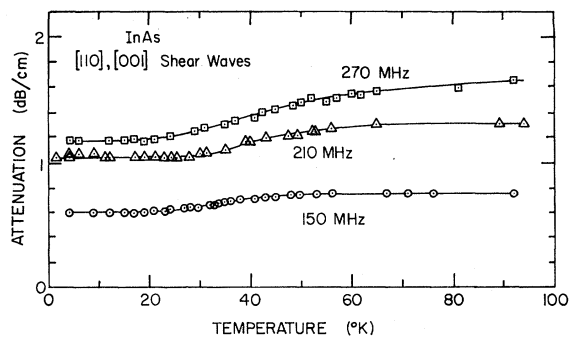


FIG. 6. Attenuation of [110], [001] transverse ultrasonic waves in InAs as a function of temperature for three frequencies.

<sup>10</sup> J. de Klerk, Phys. Rev. **139**, A1635 (1965).

<sup>11</sup> A. R. Hutson and D. L. White, J. Appl. Phys. **33**, 40 (1962).

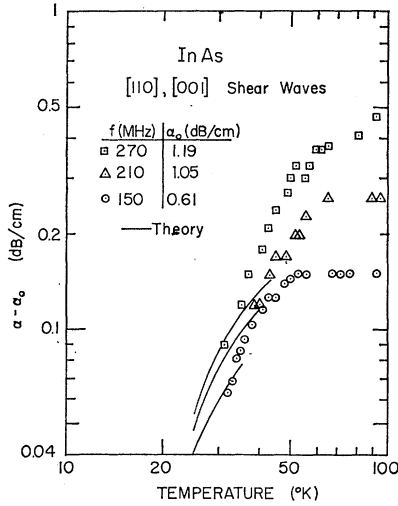


FIG. 7. Temperature-dependent part of the attenuation of [110], [001] shear ultrasonic waves in InAs as a function of temperature at three frequencies. The theory curves are calculated for process 2. The calculated attenuation is set equal to the value of  $\alpha - \alpha_0$  determined experimentally at 34°K and 150 MHz.

the sound wave will interact with free electrons through deformation potential coupling. We have estimated this contribution to the attenuation by employing a formula as given by Nill,<sup>8</sup> and it is found to be much smaller than the contribution from piezoelectric coupling at the frequencies employed in our measurements.

The attenuation of an ultrasonic wave in a dielectric solid at low temperatures is due to discrete interactions of the low-energy phonons of the sound wave and the thermal phonons in the solid. These discrete interactions are restricted because (1) the energy of the sound wave phonon is much less than the energy of the thermal phonons, (2) for a given wave number, the velocity of the longitudinal modes is greater than shear-wave velocities, (3) dispersion occurs at the larger wave numbers. When  $\tau_{th}$  is greater than the period of the sound wave, i.e.,  $\omega\tau_{th} > 1$ , discrete and localized collisions between the low-energy phonons of the sound wave and the thermal phonons result in other thermal phonons. In this manner energy is transferred from the sound wave to the thermal phonons of the solid. The attenuation in an isotropic dielectric solid due to this three-phonon collision process was first calculated by Landau and Rumer.<sup>12</sup> They found that the attenuation of transverse waves was proportional to  $\omega T^4$  and that the attenuation of longitudinal waves was zero. However, several authors<sup>13-17</sup> have since shown that

<sup>12</sup> L. Landau and G. Rumer, *Physik. Z. Sowjetunion* **11**, 18 (1937).

<sup>13</sup> K. Kawasaki, *Progr. Theoret. Phys. (Kyoto)* **26**, 795 (1961).

<sup>14</sup> S. Simons, *Proc. Phys. Soc. (London)* **82**, 401 (1963).

<sup>15</sup> H. J. Maris, Ph.D. thesis, University of London, 1963 (unpublished).

<sup>16</sup> H. J. Maris, *Phil. Mag.* **9**, 901 (1964).

<sup>17</sup> I. S. Ciccarello and K. Dransfeld, *Phys. Rev.* **134**, A1517 (1964).

longitudinal waves can also be absorbed by this process if one includes the condition that the thermal phonons have a finite lifetime and therefore an uncertainty in their energy which is large enough to allow the conservation of energy to within  $\hbar/\tau_{th}$  in the following three-phonon collision processes:

$$\text{Trans(sound)} + \text{Long(thermal)} \rightarrow \text{Long(thermal)}, \quad (\text{process 1})$$

$$\text{Trans(sound)} + \text{Trans(thermal)} \rightarrow \text{Trans(thermal)}, \quad (\text{process 2})$$

$$\text{Long(sound)} + \text{Trans(thermal)} \rightarrow \text{Trans(thermal)}, \quad (\text{process 3})$$

$$\text{Long(sound)} + \text{Long(thermal)} \rightarrow \text{Long(thermal)} \quad (\text{process 4}).$$

Expressions for the attenuation caused by the above four three-phonon processes have been given by Maris<sup>15,16</sup> and by Kalejs, Maris, and Truell.<sup>18</sup>

If the solid is assumed to be isotropic and  $\omega\tau_{th} > 1$ ,  $kT/\hbar \gg \omega$ , and  $\Theta_D \gg T$ , then Maris<sup>15</sup> shows that the attenuation of a transverse sound wave resulting from processes 1 and 2 is given in dB/unit length by

$$\alpha_{\text{shear}} = \frac{8.68\bar{F}_1^2\omega C_V T}{s_t 8\rho^3 s_t s_l^5} [\tan^{-1}(s_t + s_l)q\tau_{th} - \tan^{-1}(s_t - s_l)q\tau_{th}] + \frac{8.68\bar{F}_2^2\omega C_V T}{s_t 8\rho^3 s_t^5 s_l} \times \left[ \tan^{-1}(2\omega\tau_{th}) - \tan^{-1}\left(\frac{0.33\omega\tau_{th}k^2 L^2 T^2}{\hbar^2 s_t^2}\right) \right], \quad (1)$$

where  $C_V^l$  and  $C_V^t$  are the specific heats per unit volume associated with longitudinal and transverse modes, respectively;  $\bar{F}_1$  and  $\bar{F}_2$  involve averages of the third-order elastic constants,  $L$  is the lattice spacing,  $\rho$  is the density,  $s_t$  and  $s_l$  are the transverse and longitudinal sound wave velocities, respectively, and  $q = \omega/s$ .

The attenuation of a longitudinal sound wave resulting from process 3 and 4 is given in dB/unit length by

$$\alpha_{\text{long}} = \frac{8.68\bar{F}_3^2\omega C_V T}{s_l 8\rho^3 s_t^5 s_l} [\tan^{-1}(s_t + s_l)q\tau_{th} - \tan^{-1}(s_l - s_t)q\tau_{th}] + \frac{8.68\bar{F}_4^2\omega C_V T}{s_l 8\rho^3 s_t^5 s_l} \times \left[ \tan^{-1}(2\omega\tau_{th}) - \tan^{-1}\left(\frac{0.33\omega\tau_{th}k^2 L^2 T^2}{\hbar^2 s_l^2}\right) \right], \quad (2)$$

where  $\bar{F}_3$  and  $\bar{F}_4$  involve averages of the third-order elastic constants.

<sup>18</sup> J. Kalejs, H. Maris, and R. Truell, *Phys. Letters* **23**, 299 (1966).

If we try to fit these theoretical expressions for the attenuation to our data, we find that for both longitudinal waves and slow shear waves the transverse thermal phonon term (process 2 for shear waves and process 3 for longitudinal waves) agrees very well in temperature and frequency dependence with the data. This is shown in Fig. 5 for  $[110]$ ,  $[1\bar{1}0]$  shear waves and in Fig. 3 for the  $[110]$  longitudinal waves. Furthermore, the process-1 term in the theoretical expression for the attenuation has a much larger frequency dependence than that which we observed for slow shear waves and the process-4 term has a much smaller temperature dependence than that which we observed for longitudinal waves. Thus there seems to be no evidence that longitudinal thermal phonons make an important contribution to the attenuation. The fact that only transverse thermal phonons are important in attenuating longitudinal waves and slow shear waves in InAs is reasonable in view of interpretation of data on  $\text{Al}_2\text{O}_3$  obtained at higher values of  $\omega\tau_{\text{th}}$ . Namely, in  $\text{Al}_2\text{O}_3$  the attenuation of longitudinal ultrasonic waves is due to interaction with transverse thermal phonons.<sup>18</sup>

From the measured values of  $\alpha - \alpha_0$  we can evaluate the constants  $\bar{F}_2$  and  $\bar{F}_3$ . But before doing so, we note that Eqs. (1) and (2) are for an isotropic solid in which all transverse thermal waves would have the velocity  $s_t$ . Since this is not the case in InAs, we obtain an appropriate average value for  $C_V^t/s_t^5 \propto 1/s_t^8$  by taking into account the velocities and relative numbers of transverse waves propagating in the main crystallographic directions ( $[100]$ ,  $[110]$ , and  $[111]$ ) by means of the relation

$$\frac{26}{s_t^8} = \frac{6}{s_{t[100]}^8} + \frac{6}{s_{t[110][001]}^8} + \frac{6}{s_{t[110][1\bar{1}0]}^8} + \frac{8}{s_{t[111]}^8}. \quad (3)$$

Using the elastic constants of Gerlich<sup>19</sup> at 4.2°K, we found  $s_t = 2.14 \times 10^5$  cm/sec. In order to obtain  $C_V^t$  and  $C_V^l$  we assumed that the measured heat capacity,  $C_V$ ,<sup>20</sup> is given by

$$C_V = C_V^t + C_V^l \propto 1/s_t^3 + 2/s_t^3, \quad (4)$$

and that  $s_l = 2s_t$ . The density<sup>20</sup> of InAs was taken to be 5.70 gm/cm<sup>3</sup>, and the lattice spacing<sup>20</sup> to be  $6.04 \times 10^{-8}$  cm. A value for  $\tau_{\text{th}}$  was obtained from the measured values of the lattice thermal conductivity  $K_{\text{th}}$ <sup>21</sup> and  $C_V$  for InAs and the relation  $\tau_{\text{th}} = 3K_{\text{th}}/C_V\bar{v}^2$ , where  $\bar{v}$  is the Debye average velocity which is found to be  $2.5 \times 10^5$  cm/sec using  $\Theta_D = 247^\circ\text{K}$ .<sup>20</sup> Now we can obtain  $\bar{F}_2$  by using the  $[110]$ ,  $[1\bar{1}0]$  shear wave velocity ( $1.8 \times 10^5$  cm/sec) in the  $1/s_t^2$  factor in  $\alpha_{\text{shear}}$  at 25°K and 210 MHz. This gives  $\bar{F}_2 = 4.4 \times 10^{10}$  dyn/cm<sup>2</sup>.

<sup>19</sup> D. Gerlich, J. Appl. Phys. **35**, 3062 (1964).

<sup>20</sup> U. Piesbergen, Z. Naturforsch. **18A**, 141 (1963); and in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 2, p. 49.

<sup>21</sup> See M. G. Holland, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 2, p. 3.

Similarly, we can obtain  $\bar{F}_3$  by using the  $\langle 110 \rangle$  longitudinal wave velocity ( $4.3 \times 10^5$  cm/sec) in the  $1/s_t^2$  factor in  $\alpha_{\text{long}}$  at 25°K and 210 MHz. This gives  $\bar{F}_3 = 2.4 \times 10^{11}$  dyn/cm<sup>2</sup>.

Since the third-order elastic constants of InAs have not been measured yet, we cannot calculate values for  $\bar{F}_2$  and  $\bar{F}_3$  to compare with those determined above. However, by employing the elastic constants of InSb, we calculated the attenuation of longitudinal waves to be about twice the value of  $\alpha - \alpha_0$  which we obtained for InAs. In making the calculation, we employed a simple theoretical formula<sup>1</sup> for collinear processes which is appropriate when  $\omega\tau_{\text{th}} \gg 1$ . This formula was used by Pomerantz<sup>1</sup> to calculate the attenuation of 9-GHz longitudinal waves in some cubic and trigonal materials. He found reasonably good agreement with experimental values for cubic materials, including the semiconductors Ge and Si (but not for trigonal materials).

Our results for fast shear waves (see Fig. 7) do not extend to low enough temperatures to determine whether or not they can be accounted for by Maris's theory. However, in the range where we have determined it,  $\alpha - \alpha_0$  for fast shear waves seems to have a frequency dependence more like that of process 2 than of process 1. It is interesting to note that in  $X$ -cut and  $BC$ -cut quartz the attenuation of fast transverse waves<sup>22</sup> can be interpreted using an expression for the attenuation of the type to be expected for noncollinear processes due to anisotropy of the anharmonicity of the material.<sup>23</sup>

## V. CONCLUSIONS

For temperatures low enough that the condition  $\omega\tau_{\text{th}} > 1$  is satisfied, analysis of our measurements indicates that the attenuation of both longitudinal and slow transverse ultrasonic waves in InAs is caused by a three-phonon collision processes in which the thermal phonons involved are those with transverse polarization.

Previous studies of the attenuation of longitudinal waves in other materials have led to various conclusions. Maris<sup>15</sup> found that for longitudinal waves in  $X$ -cut quartz the predominant three-phonon interaction was with longitudinal thermal phonons. Measurements by de Klerk<sup>10</sup> show that at 1000 MHz the attenuation of longitudinal waves in  $\text{Al}_2\text{O}_3$  varies as  $T^9$  below 55°K, and Kalejs, Maris, and Truell<sup>18</sup> attribute this behavior to collisions with transverse thermal phonons when  $\omega\tau_{\text{th}} \gg 1$ . We believe that three phonon collisions involving longitudinal thermal phonons in InAs are not important for the attenuation of longitudinal waves, because the observed temperature dependence of  $\alpha - \alpha_0$  is much larger than that predicted by Maris's expression for the process involving longitudinal thermal phonons.

For transverse waves in  $AC$ -cut quartz Maris<sup>15</sup>

<sup>22</sup> M. F. Lewis and E. Patterson, Phys. Rev. **159**, 703 (1967).

<sup>23</sup> N. S. Shiren, Phys. Letters **20**, 10 (1966).

found that the attenuation of ultrasonic phonons was due partly to longitudinal thermal phonons and partly to transverse thermal phonons. Lewis and Patterson<sup>22</sup> measured the attenuation of fast transverse waves in *X*-cut and *BC*-cut quartz, and for  $\omega\tau_{th} > 10$ , they found that longitudinal thermal phonons made a negligible contribution to the attenuation. We have ruled out the longitudinal thermal phonon collision term in InAs because it gives a much larger frequency dependence of the attenuation than is observed experimentally.

#### ACKNOWLEDGMENTS

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### Exciton Excitation Spectra in CdS

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Optical excitation spectra of exciton emission lines in CdS are presented. It is shown that the center responsible for the  $I_1$  emission, an exciton bound to a neutral acceptor, is created by the formation of free excitons which are subsequently trapped or bound to the impurity, or by the direct formation of bound excitons on the impurity site. The centers responsible for an  $I_5$  emission line at 4869.5 Å and for an  $I_2$  emission line at 4868.3 Å are also created by the formation of free excitons which are subsequently bound to a localized site, but more importantly they are created by direct LO phonon assisted formation of excitons bound to neutral and ionized impurities. It is concluded that the impurity is a donor. Evidence of thermal dissociation of these complexes is also presented.

#### INTRODUCTION

THE optical properties of CdS have been under investigation for some time. It is now fairly well established that the observed narrow lines in the absorption and reflection spectra at wavelengths less than 4860 Å at helium temperatures are due to intrinsic excitons<sup>1,2</sup> and that many of the sharp lines in the absorption and fluorescence spectra at energies slightly lower than the intrinsic excitons are due to transitions involving bound excitons,<sup>3-5</sup> in which an exciton bound to a neutral or ionized donor or acceptor is created or destroyed.

Nearly all crystals of CdS show a line at 4888.5 Å which has been labeled  $I_1$  and which has been shown to be an exciton bound to a neutral acceptor.<sup>4</sup> In emission this line is replicated at lower energies with the spacing between lines equal to the LO phonon energy. At somewhat higher energies there appears a group of absorption and emission lines in the wavelength interval 4867-4870 Å. These lines have been labeled  $I_2$  by Thomas and Hopfield,<sup>4</sup> and have been identified by them as arising

from excitons bound to neutral donors. Reynolds and Litton<sup>5</sup> have seen an absorption and emission line at 4869.14 Å, labeled  $I_5$ , which was tentatively identified as an exciton bound to a neutral acceptor, but recent experiments by Reynolds<sup>6</sup> have established that  $I_5$  is also an exciton bound to a neutral donor.

The complexes responsible for the emission of lines such as  $I_1(I_2)$  involve an electron (hole) and two holes (electrons) bound to an acceptor (donor) impurity. No information is available in the literature regarding the formation of these complexes. It is the purpose of the present study to identify the various modes of formation of bound exciton complexes in CdS.

We shall demonstrate that this identification can be made by an examination of the variation of luminescence efficiency as a function of the wavelength of the exciting radiation, i.e., by the excitation spectra of the emission lines. Although this technique has been previously reported in the literature,<sup>7-12</sup> the present work

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