

## Optical Absorption Edge in CdTe: Experimental\*

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Optical absorption in CdTe single crystals is reported for photon energies just below the transmission limit at about 1.5 eV at several temperatures between 2 and 300°K. Chemical removal of damaged surface layers was required to obtain concordant results from mechanically polished samples of different thicknesses. At the lowest temperatures, impurity bands dominated the absorption in all crystals except those taken from the purest parts of zone-refined ingots. The intrinsic absorption edge observed in such crystals was considerably sharper than previously reported. In contrast with the earlier data, the energy and temperature dependence of this intrinsic absorption could not be explained as resulting from indirect interband or indirect exciton transitions.

### INTRODUCTION

PREVIOUS studies of the optical and electrical properties of CdTe have led to conflicting conclusions about the locations in  $k$  space of the absolute extrema of the valence and conduction bands. On the one hand, if it is assumed that there is an absolute minimum in the conduction band at the center of the Brillouin zone, then the electron effective mass deduced from the optical effects of free electrons<sup>1</sup> agrees with the isotropic mass found by cyclotron resonance.<sup>2</sup> This assumption and effective-mass result also lead to good quantitative agreement between calculated and observed transport properties.<sup>3</sup> On the other hand, some magnetoresistance data<sup>4</sup> have indicated that the lowest minimum is not at the center of the zone; however, because of the experimental difficulties, the significance of this result has been questioned.<sup>3</sup>

A second group of experiments suggests that the absolute extrema in the conduction and valence bands are at considerably different points in  $k$  space. Davis and Shilladay,<sup>5</sup> and Koňák,<sup>6</sup> measured optical transmission through crystalline samples to obtain the absorption coefficient near the fundamental absorption limit at about 1.6 eV. The photon energy and temperature dependence showed that part or all of this absorption could be due to indirect interband transitions, and in both studies the indirect gap was found to be about 0.1 eV smaller than the direct gap. An indirect transition model was also found to account best for the results obtained by Spitzer and Mead<sup>7</sup> on the photovoltaic effect in barrier-type photorectifiers. These models were also supported by an effective-mass calcu-

lation<sup>8</sup> which suggested that the absolute valence-band maximum was not at the center of the Brillouin zone; however, this calculation has recently been shown to be in error.<sup>9</sup>

Finally, at low temperatures, Thomas<sup>10</sup> has observed sharp reflection structure due to an intense, narrow absorption band at slightly higher energy than the optical transmission limit. The interpretation of this band as due to the creation of "direct" excitons is consistent with strain-induced splitting in the reflection spectra and with the linewidth for such excitons as seen, for example, in CdS.<sup>11</sup> The energy difference between the peak exciton absorption and the optical transmission limit sets a rough upper limit of 0.1 to 0.2 eV on the difference between the direct and indirect band gaps. It is not known if this limit is consistent with the apparent absence of lifetime broadening of the exciton absorption due to interaction with lower energy bands.

In view of the uncertainties and possible conflict in these conclusions about the nature of the band extrema and since zone-refined CdTe single crystals of high purity were available in this laboratory,<sup>3</sup> it appeared worthwhile to study the optical absorption edge again rather carefully. Transmission measurements were used since indirect transitions would be expected to be evident for absorption coefficients of less than 1000 cm<sup>-1</sup>. It was found, first, that mechanical polishing of CdTe crystals can produce a surface layer with absorption properties quite different from the bulk of the crystal. Suitable chemical polishing, applied after mechanical polishing, suffices to remove this layer, so that concordant results for the absorption are obtained on samples of different thickness without any corrections for surface damage. Second, crystalline defects such as vacancies or impurities were found to produce absorption bands in the region of the intrinsic absorption edge. Unless samples are carefully selected from among the purest presently available, these bands can mask the intrinsic absorption over a significant range

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<sup>1</sup> D. T. F. Marple, *Phys. Rev.* **129**, 2466 (1963).

<sup>2</sup> K. K. Kanazawa and F. C. Brown, *Phys. Rev.* **135**, A1757 (1964).

<sup>3</sup> B. Segall, M. R. Lorenz, and R. E. Halsted, *Phys. Rev.* **129**, 2471 (1963).

<sup>4</sup> S. Yamada, *J. Phys. Soc. Japan* **17**, 645 (1962).

<sup>5</sup> P. W. Davis and T. S. Shilladay, *Phys. Rev.* **118**, 1020 (1960).

<sup>6</sup> Č. Koňák, *Phys. Status Solidi* **3**, 1274 (1963).

<sup>7</sup> W. G. Spitzer and C. A. Mead, *J. Phys. Chem. Solids* **25**, 443 (1964).

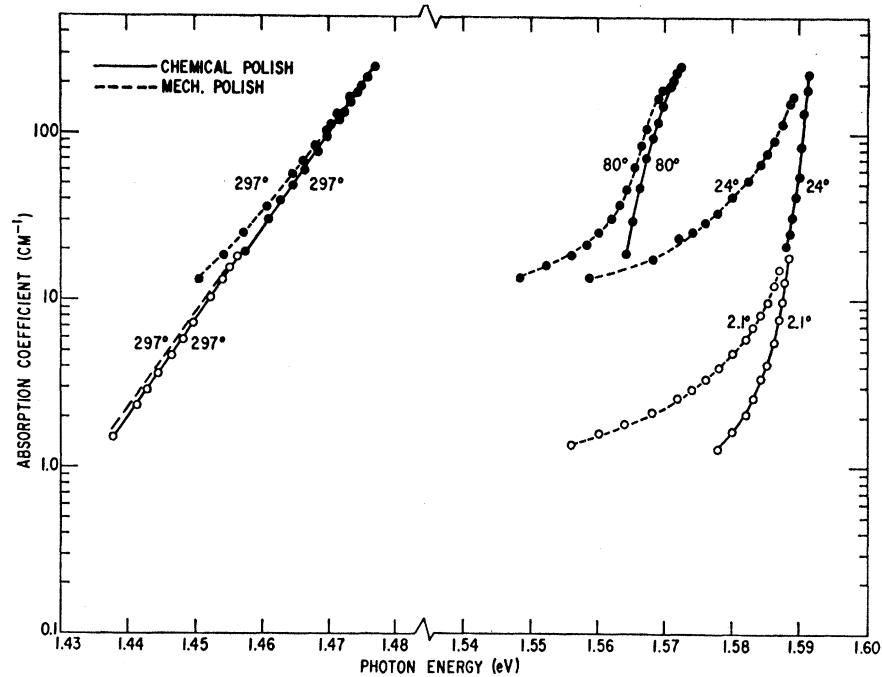
<sup>8</sup> M. Cardona, *J. Phys. Chem. Solids* **24**, 1543 (1963).

<sup>9</sup> M. Cardona, *J. Phys. Chem. Solids* **26**, 1351 (1965).

<sup>10</sup> D. G. Thomas, *J. Appl. Phys. Suppl.* **32**, 2298 (1961).

<sup>11</sup> D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **116**, 573 (1959).

FIG. 1. Absorption coefficient of CdTe as a function of photon energy and temperature. Dashed curves obtained with mechanically polished samples. Solid curves show results on the same samples, after chemical polishing. Open circles: about 2 mm thick. Closed circles: About 0.2 mm thick. The samples were obtained from the purest section of a zone-refined ingot.



of energies. Last, several attempts were made to fit the photon energy and temperature dependence of the intrinsic absorption with the theory for indirect interband and indirect exciton transitions that adequately accounts for the edge in Ge and Si. None of these attempts was successful. In the following paper, the phonon-assisted direct exciton absorption process is discussed and is shown to quantitatively account for the data throughout the entire photon energy and temperature range.

#### EXPERIMENTAL TECHNIQUES

All the transmission data were obtained with a Cary Model 14R spectrophotometer. To obtain adequate spectral resolution in the steepest part of the absorption edge, it was necessary to replace the PbS detector (supplied with the instrument) with a cooled RCA 7102 photomultiplier detector. This improved the spectral bandwidth in the 1.3 to 1.6 eV range from about  $1.8 \times 10^{-3}$  eV to about  $4 \times 10^{-4}$  eV for the same signal-to-noise ratio.

Transmission was measured at several temperatures ranging from 2.1 to 300°K. To obtain 2.1°K, the samples were immersed in liquid helium. All other low temperatures were obtained with samples cooled by thermal contact with a copper block fastened to the bottom of a liquid coolant reservoir. The crystals were clamped to this block with moderate pressure applied by springs. Indium-foil spacers were always used between sample and block to increase the area of contact between crystal and metal, and hence reduce strains and improve thermal contact. Sample temperatures were indicated

by a gold-cobalt thermocouple cemented to the copper block. To obtain 24 and 80°K, the cryostat reservoir was filled with liquid hydrogen or nitrogen. For the time required to obtain spectra, intermediate temperatures could be maintained within  $\pm 0.5^\circ\text{K}$  of a selected nominal value by gentle heating or cooling of the reservoir with nitrogen gas or liquid refrigerant as needed.

#### PREPARATION OF THE SAMPLES

Samples were sawed from single-crystal sections of zone-refined CdTe ingots.<sup>3</sup> They often contained twin boundaries. Crystallographic orientation of the samples was not determined or controlled. Two parallel rectangular faces, usually about  $4 \times 12$  mm, were ground with carborundum grit and mechanically polished with Linde "A" abrasive. Glass spacers were arranged to surround the sample during polishing to preserve flatness and parallelism of the faces. This technique was quite satisfactory in the range of sample thicknesses studied, about 3 mm to 100  $\mu$ .

Chemical polishing<sup>12</sup> was carried out at room temperature with continuous gentle agitation of the crystal for 4 min in 40 cc of a solution consisting of seven parts saturated aqueous solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  and three parts concentrated  $\text{H}_2\text{SO}_4$ . This treatment removed about 10  $\mu$  of material from each face per minute. Grain or twin boundaries were not preferentially attacked,

<sup>12</sup> This procedure for chemical polishing of CdTe has already been described by T. Ichimiya, T. Niimi, K. Mizuma, O. Mikami, Y. Kamia, and K. Ono, *Solid State Physics in Electronics and Telecommunications* (Academic Press Inc., New York, 1960), p. 845.

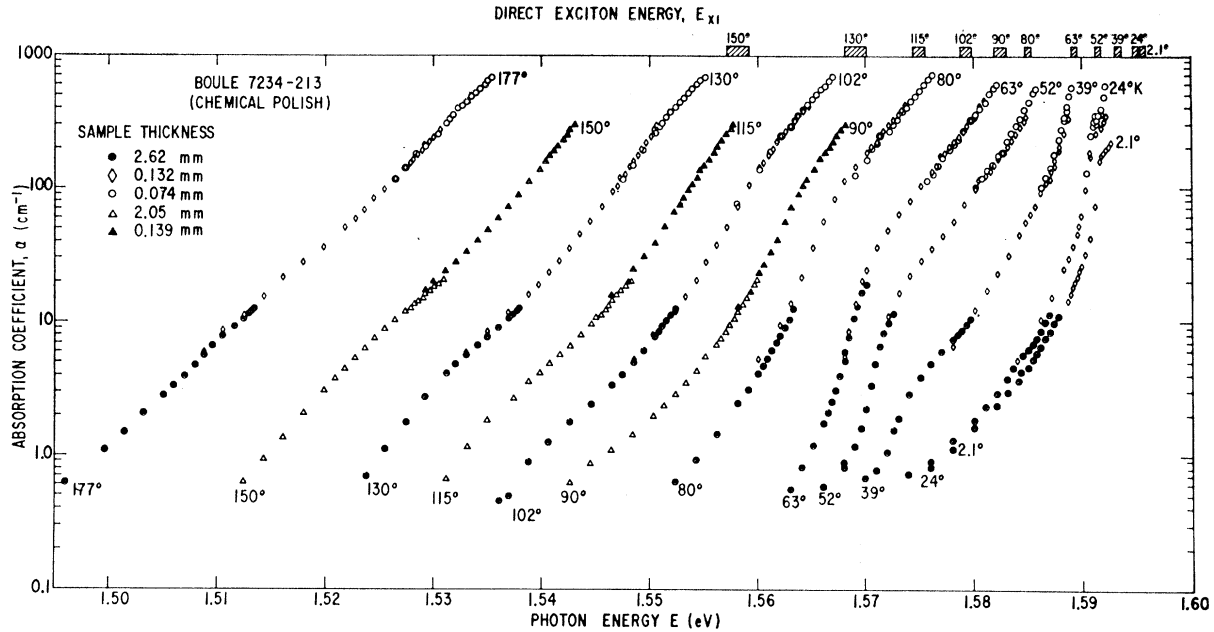


FIG. 2. Absorption coefficient for the purest section of a zone-refined CdTe ingot as a function of photon energy and temperature. Chemically polished samples.

and scratches or other flaws in surface preparation were smoothed by this procedure. The final minute of chemical polishing was always carried out in fresh solution to remove a reddish film which sometimes partially coated samples etched longer than 3 min in one operation.

#### REFLECTION-LOSS CORRECTIONS

Corrections for the reflection losses at air-sample interfaces were needed to calculate the absorption coefficient  $\alpha$  from the measured transmittance  $t$ . Two different methods were used. In the first, values for  $R$ , the interfacial reflectance, were calculated from refractive-index data.<sup>13</sup> For  $t > 0.1$ , the relation between  $\alpha$ ,  $t$ , and  $R$  was read from a graph and included the effects of multiple reflections between the interfaces<sup>14</sup>; for  $t < 0.1$ , sufficient accuracy was obtained from the formula  $\exp(-\alpha d) = t/(1-R)^2$ , which is obtained when multiple reflections are neglected. An alternative method was used to obtain  $\alpha$  for the lower temperatures where refractive-index and reflectance data were not available. A straight line was drawn through the portion of the spectrophotometer chart record that corresponded to negligible absorption and extrapolated through the absorbing region as a "base line" representing the reflection losses. Comparison of the two methods when applied to room-temperature data indicated that reliable results for  $\alpha$  could be obtained by the "base line" method when the optical density of the sample due to absorption was about 0.2 or larger. An upper limit

<sup>13</sup> D. T. F. Marple, *J. Appl. Phys.* **35**, 539 (1964).

<sup>14</sup> H. O. McMahon, *J. Opt. Soc. Am.* **40**, 376 (1950).

of about 2.5 was set by the light scattered in the monochromator and cryostat. Interference fringes observed in the 3- to 10- $\mu$  wavelength range gave the thickness of samples thinner than 150  $\mu$ ; a micrometer caliper was used for thicker samples.

## RESULTS AND DISCUSSION

### A. Surface Damage

Figure 1 shows absorption spectra obtained at several temperatures with mechanically polished crystals contrasted with those obtained after the same samples were chemically polished for 6 min. All the samples were taken from the purest section of a zone-refined ingot. Particularly at 80°K and below, it is apparent that in the chemically polished samples the absorption is smaller and increases more rapidly with energy than in the mechanically polished crystals.

Figure 2 shows the absorption coefficient as observed at 12 temperatures on several chemically polished samples of different thickness, all cut from adjacent parts of the purest section of a zone-refined ingot. It will be noted that among crystals of different thickness the absorption coefficients deduced for the same photon energy and temperature are entirely concordant. Note also that between 24 and 2.1°K the only change is a shift of the curve by about  $1 \times 10^{-3}$  eV. In contrast, Fig. 1 shows that for mechanically polished samples of different thickness there is a far larger change between these two temperatures.

The data in Figs. 1 and 2, taken together, show that the absorption coefficient in the skin removed by the

chemical polishing is much greater than in the bulk and is relatively independent of wavelength and temperature. Grazing-incidence electron diffraction photographs have shown that the surface of a mechanically polished crystal is amorphous. Similar photographs have not been made on samples chemically polished for 6 min; however, it has been found that while two minutes' treatment is not sufficient, 20 min suffices to remove this amorphous layer.

### B. Defect Absorption

Effects of crystalline defects on the absorption were most evident at the lowest temperatures. Some of these effects are illustrated in Fig. 3, which shows absorption at 2.1°K in the purest section of an as-grown zone-refined ingot, the same material used to obtain the results in Fig. 2. An analysis of electrical measurements on this sample showed that it was *n* type, with donor and acceptor concentrations of  $N_D = 1.05 \times 10^{15} \text{ cm}^{-3}$  and  $N_A = 6.7 \times 10^{14} \text{ cm}^{-3}$ . At 2°K the intense absorption due to the ground state of the direct excitons falls at about 1.596 eV, and as a result between 1.594 and 1.598 eV the transmission was too small to measure in even the thinnest crystals. The energies for the exciton peak,  $E_{x1}$ , (i.e., energies for maximum  $\epsilon_2$ , the imaginary part of the dielectric constant) were obtained by Kramers-Kronig inversions<sup>15</sup> of reflection spectra. These

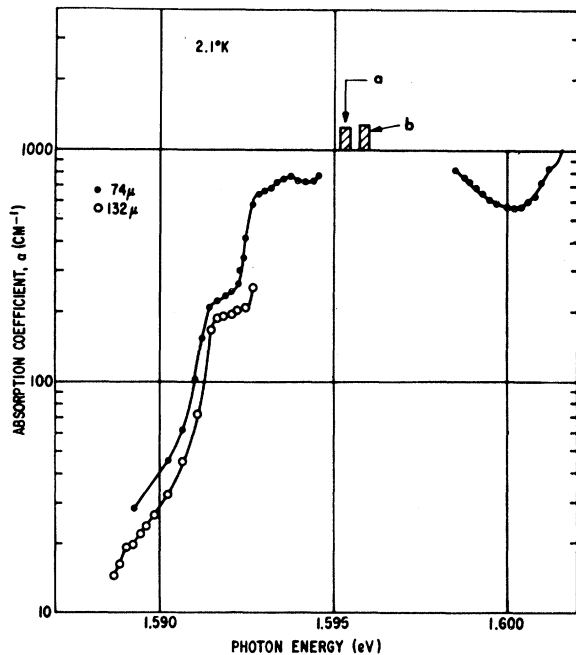


FIG. 3. Absorption coefficient of the purest section of a zone-refined CdTe ingot as a function of photon energy, at 2.1°K for two chemically polished samples. The photon energies for maximum direct exciton absorption are also shown for comparison. (a) Exciton peak (Ref. 10). (b) Exciton peak (Ref. 15).

<sup>15</sup> For example, see W. G. Spitzer and D. A. Kleinman, *Phys. Rev.* **121**, 1324 (1961).

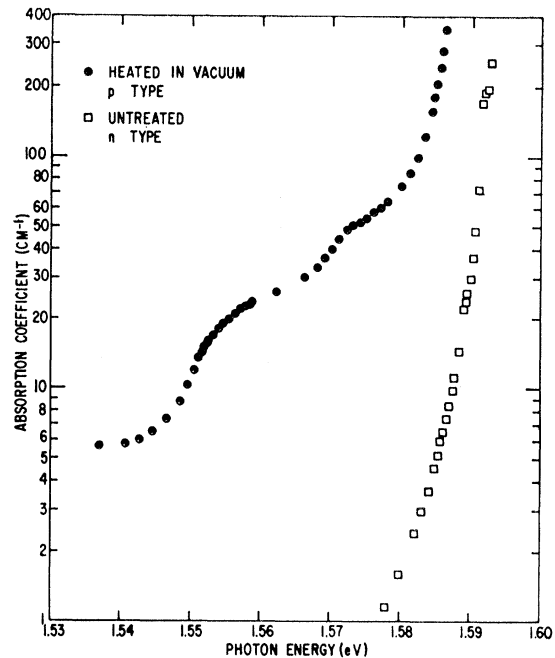


FIG. 4. Absorption coefficient as a function of photon energy at 2.1°K for the purest (*n*-type) zone-refined CdTe and for the same material after conversion to *p* type.

are indicated for several temperatures by the bars at the tops of Figs. 2 and 3. The reflection spectrum for 2°K and the corresponding results for the oscillator strength and dielectric constant have been published.<sup>10,16</sup>

A narrow transmission band is seen in Fig. 3 from about 3 to about  $5 \times 10^{-3}$  eV above  $E_{x1}$ . This is the region of (relatively) weak absorption expected between the direct-exciton ground state and its excited states. Starting about  $3 \times 10^{-3}$  eV below  $E_{x1}$  the absorption is seen to decrease rapidly through a series of peaks and shoulders. This structure may exceed the resolution limit of the spectrophotometer. It has been found to coincide in energy with fluorescence emission peaks in the same crystals.<sup>17</sup> By analogy with other II-VI compounds it is plausible to ascribe this absorption to the creation of excitons bound to lattice defects or chemical impurities,<sup>18</sup> but further study of this structure will be necessary to identify the specific centers involved. For the present discussion, however, the important point is that the intrinsic absorption in the purest samples at 2.1°K is certainly not greater than that shown in Fig. 3 and is probably significantly smaller.

Figure 4 illustrates some defect absorption effects found at 2.1°K in *p*-type crystals. Here, for comparison,

<sup>16</sup> B. Segall and D. T. F. Marple, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Company, Amsterdam, to be published), Fig. 2, Chap. 7.

<sup>17</sup> R. E. Halsted, M. R. Lorenz, and B. Segall, *J. Phys. Chem. Solids* **22**, 109 (1961).

<sup>18</sup> M. Lampert, *Phys. Rev. Letters* **1**, 450 (1958); R. E. Halsted and M. Aven, *Bull. Am. Phys. Soc.* **9**, 631 (1964).

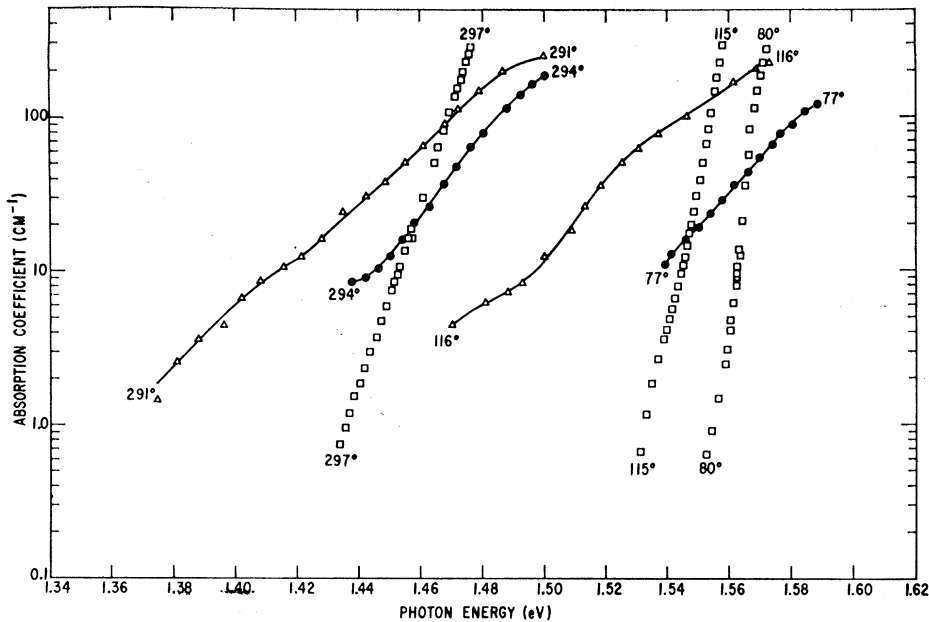


FIG. 5. Comparison of results from Fig. 2 with those obtained in earlier studies.  $\Delta$ —C. Koňák, *Phys. Status Solidi* **3**, 1274 (1963);  $\bullet$ —P. W. Davis and T. S. Shilladay, *Phys. Rev.* **118**, 1020 (1960);  $\square$ —Present study (chemically polished samples).

the open squares give the results taken from Figs. 2 and 3 for the purest, slightly *n*-type, material. The closed circles show the absorption after such an *n*-type crystal was converted to *p* type by 70 h heating at 905°C in vacuum. They illustrate the shoulders introduced at 1.55- and 1.57-eV energy. Similar spectral dependence was found in a less strongly *p*-type sample taken from an untreated but less pure section of an as-grown zone-refined ingot, and in a sample made still more strongly *p*-type by  $4\frac{1}{2}$  h heating at 800°C in Te vapor; in these samples the absolute absorption increased with the room-temperature hole concentration. Lorenz and Segall<sup>19</sup> have suggested that this structure is caused by transitions to the conduction band from a shallow acceptor state at  $(E_p + 0.05)eV$ . The shoulder in this absorption at 1.57 eV has not been previously observed. Its interpretation as the acceptor-to-conduction-band absorption accompanied by the emission of 1 longitudinal optical (LO) phonon is consistent with the phonon energy,  $E_p = 21 \times 10^{-3}$  eV.<sup>17</sup>

Effects of intentionally added donor impurities were not extensively studied. One example is the absorption measured at 2.1°K in a heavily iodine-doped crystal,<sup>17,1</sup> with room-temperature carrier concentration,  $N_e = 2 \times 10^{18}$  cm<sup>-3</sup>. As might be expected in this case, the absorption rose significantly less steeply and was shifted to lower energy by several hundredths of an eV as compared to the purest crystals.

### C. Comparison with Earlier Results

Figure 5 shows the absorption coefficient as a function of photon energy as reported by Davis and Shilladay at 294 and 77°K, and at two of five temperatures,

<sup>19</sup> M. R. Lorenz and B. Segall, *Phys. Letters* **7**, 18 (1963).

291 and 116°K, studied by Koňák, together with our data from Fig. 2 for similar temperatures. Compared with our results, the previous studies indicate a much less steep increase in  $\alpha$  with photon energy, with larger values for  $\alpha < 50$ , and smaller values for  $\alpha > 100$  cm<sup>-1</sup>. Some of this difference certainly arises because mechanically polished crystals were used in earlier studies. Other possible reasons are: First, since the earlier studies were made on material taken from less highly purified ingots, crystalline defects may have made significant contributions to the absorption observed near the band edge; second, although the spectral resolution was adequate for their samples, the scattered radiation in the monochromator used by Davis and Shilladay (a single-pass Littrow instrument with NaCl prism) might have been sufficient to make their results significantly too small at large  $\alpha$ . The resolution or scattered-light limit was not stated in Koňák's study. Last, Davis and Shilladay cemented their samples to glass plates which were in turn cooled by contact with a cold finger in their cryostat. This procedure must have strained the samples, possibly enough to cause significant splitting in the exciton-absorption line.<sup>10</sup> This, in turn, may have produced an apparent broadening in the absorption edge. The sample mounting technique was not given in Koňák's study.

### D. Indirect Interband and Exciton Absorption

In a companion paper,<sup>20</sup> Segall has extended the theory of phonon-assisted direct-exciton absorption<sup>21,22</sup>

<sup>20</sup> B. Segall, following paper, *Phys. Rev.* **150**, 734 (1966).

<sup>21</sup> D. G. Thomas, J. J. Hopfield, and M. Power, *Phys. Rev.* **119**, 570 (1960).

<sup>22</sup> R. E. Dietz, D. G. Thomas, and J. J. Hopfield, *J. Appl. Phys. Suppl.* **32**, 2282 (1961).

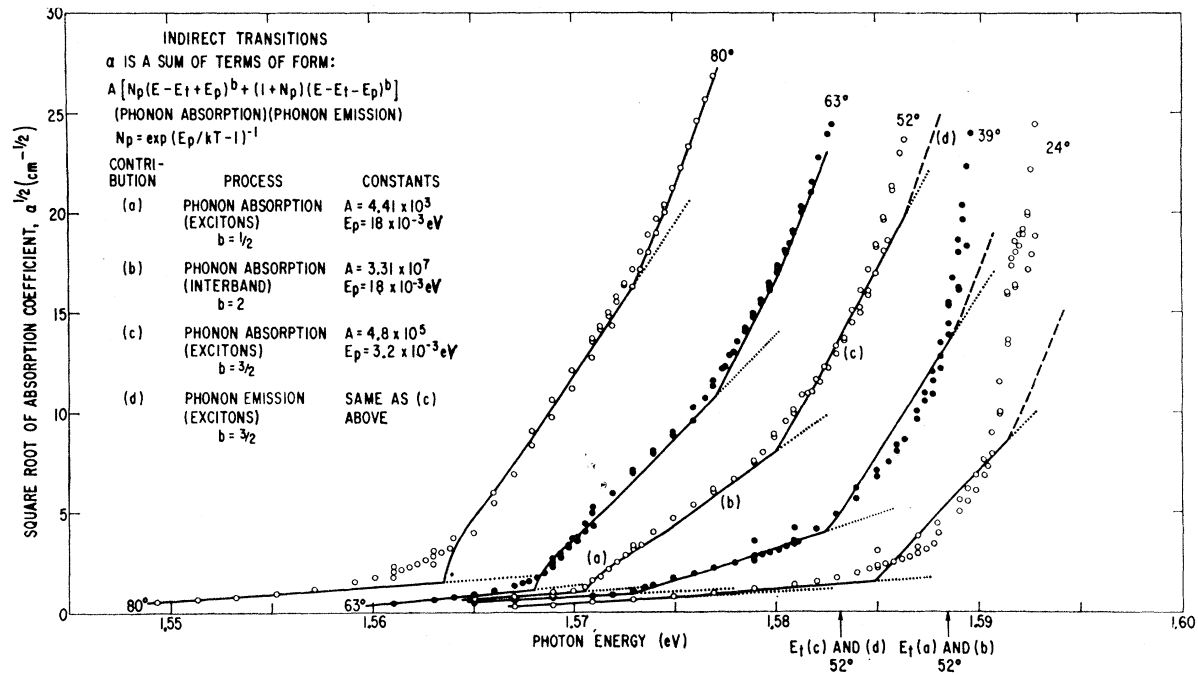


FIG. 6. An attempt to fit the data of Fig. 2 (circles) with the theory for indirect interband and indirect exciton absorption.

and shown that it accounts quantitatively for the data shown in Fig. 2 at all temperatures. In spite of this success, it seemed worthwhile to attempt to understand the results in terms of the theory of indirect interband and indirect exciton absorption developed by Elliott<sup>23</sup> and successfully applied to the data<sup>24</sup> for Ge and Si. According to this theory, the absorption coefficient is given by a sum of terms each of the form

$$A[N_p(E - E_t + E_p)^b + (1 + N_p)(E - E_t - E_p)^b], \quad (1)$$

where

$$N_p = \{\exp(E_p/kT) - 1\}^{-1}.$$

The first term describes processes involving phonon absorption, the second those involving phonon emission. The relative importance of the two terms as a function of temperature is controlled by the probabilities for absorbing or creating a phonon with energy  $E_p$ . Depending on the process involved, the threshold energy  $E_t$  is either the (indirect) band gap energy  $E_g$  or  $E_g - G$ , where  $G$  is an exciton binding energy. The analysis predicts that for indirect interband absorption  $b = 2$ , while for indirect exciton absorption with nondegenerate bands  $b = \frac{1}{2}$ , or, if the valence band is degenerate, perhaps  $b = \frac{3}{2}$ .

The earlier experiments<sup>5,6</sup> on CdTe were interpreted on the assumption that indirect exciton absorption was unimportant. Thus, in (1) above, one term was

used, with  $b = 2$ , and at the lowest temperatures where the phonon emission process dominates,  $\alpha^{1/2}$  is expected to rise linearly above the threshold energy. The circles in Fig. 6 are the data from Fig. 2, for 80°K and below, plotted on this scale to test this prediction. The absence of linear segments in the data at any of these temperatures shows that indirect interband transitions cannot alone account for the results.

The curves in Fig. 6 show the absorption calculated from the more complete form of the theory<sup>23</sup> which includes possible contributions to the absorption from indirect excitons. The phonon energies and other constants used in the calculation are included in Fig. 6. They were selected because they gave the best fit to the data in this temperature range, without regard to their physical plausibility. The segments in the curve for 52°K are labeled to show the contributions of the different processes. The "phonon emission" components expected to be associated with the "phonon absorption" processes labeled (a) and (b) lie beyond the highest energy shown in Fig. 6. As this component is smaller than the observed absorption, it is not considered to be in contradiction with it.

There are several reasons for questioning the physical significance of the agreement between these calculated curves and the data. First, although a reasonably good fit is obtained at 63°, it becomes poorer at lower temperatures. Although the possible onset of components (c) and (d) is discernible, perhaps, in the data for 63°, it is not at all evident at lower temperatures, where it should be most clearly evident. Such thresholds are clearly seen in the data for Ge and Si even at tempera-

<sup>23</sup> R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

<sup>24</sup> G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957); **111**, 1245 (1958).

tures as high as 300°K, and there is no obvious reason why these thresholds should not also be evident for CdTe if they are really present. Second, this analysis leaves unexplained the lowest segments of the absorption which are drawn in to fit the data below segment (a) in each case. These segments cannot be fitted into the theoretical framework already described. Last, the indirect band gaps and threshold energies used in the calculation are only 10 to  $15 \times 10^{-3}$  eV smaller than the energy for the peak absorption by the direct excitons. In this part of the spectrum, less than one LO phonon away from the exciton center, phonon-assisted absorption by direct excitons is expected and, as shown in the following paper, all of the observed intrinsic absorption can be accounted for by this process. Thus it is concluded that no major fraction of the intrinsic absorp-

tion observed in CdTe below the direct-exciton peak can be plausibly understood as indirect interband or indirect exciton absorption, and there is no definite evidence that any of the absorption arises from such processes.

#### ACKNOWLEDGMENTS

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### Optical Absorption Edge in CdTe: Theoretical\*

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Optical absorption in the "edge region" (i.e., for photon energies just below the first exciton peak) due to the creation of direct excitons with the simultaneous absorption of one and two longitudinal optical phonons is calculated by perturbation theory for Wannier excitons formed from the conduction and valence bands around  $\mathbf{k}=0$ . It is shown that the contributions from the  $n > 1$  exciton bands, neglected in earlier calculations, are quite important and are required for a quantitative study. The results quantitatively account for the magnitude and for the temperature and energy dependences of the absorption coefficient observed in CdTe using a (average) hole mass of  $0.4m$ , where  $m$  is the free-electron mass. These results strongly support the assignment to CdTe of a "direct" minimum band gap at  $\mathbf{k}=0$ , contrary to a number of recent contentions (also based on absorption measurements) that the material is "indirect." It is noted that the agreement between the calculated results (including a rough correction for level broadening) and the data extends up to the temperature range at which the absorption coefficient begins to exhibit Urbach's-rule behavior. It is argued from this fact that the mechanism employed in these calculations, as opposed to others recently considered, underlies Urbach's rule in, at least, the compound semiconductors.

#### I. INTRODUCTION

THE temperature and energy dependence of the optical absorption of CdTe has been repeatedly measured in the neighborhood of the lowest-energy absorption edge<sup>1</sup> and the analyses of these data have suggested that this semiconductor has an "indirect" minimum band gap. The results of an investigation of a related phenomenon, the photovoltaic effect,<sup>2</sup> have been interpreted as favoring this assignment. Furthermore, a calculation of the valence band structure has supported this picture.<sup>3,4</sup> However, the results of the

measurements of the intrinsic absorption edge in CdTe by Marple, which are presented in the previous paper<sup>5</sup> (hereafter referred to as I) differ in some significant respects from the earlier data. In addition, it was shown that the data in I could not be understood in terms of a reasonable indirect band gap model.

In this paper we start with the opposite assumption about the lowest band gap in CdTe, that is, that it is direct.<sup>6</sup> Furthermore, on the basis of the study of the

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<sup>1</sup> P. W. Davis and T. S. Shilliday, *Phys. Rev.* **118**, 1020 (1960); C. Konak, *Phys. Status Solidi* **3**, 1274 (1963); W. Giriat, *Acta Phys. Polon.* **24**, 191 (1963).

<sup>2</sup> W. G. Spitzer and C. A. Mead, *J. Phys. Chem. Solids* **25**, 443 (1964).

<sup>3</sup> M. Cardona, *J. Phys. Chem. Solids* **24**, 1543 (1963).

<sup>4</sup> Professor Cardona has kindly brought to our attention the dis-

covery of an algebraic error in Ref. 3 [see M. Cardona, *J. Phys. Chem. Solids* **26**, 1351 (1965)]. When the correction is remedied, the calculations yield a positive heavy hole mass.

<sup>5</sup> D. T. F. Marple, preceding paper, *Phys. Rev.* **150**, 728 (1966), hereafter referred to as I.

<sup>6</sup> The fact that this assignment is quite reasonable for CdTe, and indeed for all the II-VI semiconducting compounds, is discussed by B. Segall, in *Physics and Chemistry of II-VI Semiconducting Compounds*, edited by M. Aven and J. S. Prener (North-Holland Publishing Company, Amsterdam, to be published), Chap. 1.