

## Effective Electron Mass in CdTe†

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Measurements of the infrared Faraday effect and infrared reflectance of CdTe crystals are reported. Comparison of data on pure and on  $n$ -type doped crystals gave the free-carrier contributions to the Faraday rotation and to the dielectric constant, which, in turn, yielded the electron effective mass and carrier concentration in the doped crystals. The electron effective-mass ratio was found to be  $m^*/m=0.11\pm 0.01$ , independent of the carrier concentration up to  $N=1.7\times 10^{18}$  cm $^{-3}$ . Comparison of the optically measured carrier concentrations with Hall effect data on the same samples determined the Hall scattering constant,  $r$ , which changed from 1.5 to 1.2 in the transition from nearly classical to nearly degenerate electron statistics.

### INTRODUCTION AND METHOD OF MEASUREMENT

THE effective electron mass ratio,  $m^*/m$ , has been determined in CdTe by several methods. Free carrier optical absorption spectra<sup>1</sup> and temperature variation of carrier concentration<sup>2</sup> in  $n$ -type doped crystals have given  $m^*/m=0.24$  and 0.14, respectively, but in both studies the analysis of the data required theoretical results which had uncertain validity for the samples and experimental conditions employed. This problem has been discussed<sup>1</sup> in detail for the free carrier absorption experiment; in this case the result for  $m^*$  is sensitive to unproved assumptions regarding the relative importance of different scattering mechanisms and the correct statistics of the electrons, as well as approximations in the absorption theory.

In a companion paper<sup>3</sup> on electrical transport properties of pure and  $n$ -type doped CdTe, Hall mobility has been studied over a wide range of temperature and impurity concentration. In the analysis, all the scattering processes of possible importance have been included, and the data are fitted best with  $m^*/m=0.11$ .

In the study reported here,  $m^*$  and the free electron concentration,  $N$ , have been determined in  $n$ -type-doped CdTe crystals by an optical method which is insensitive to the scattering mechanisms and statistics. The free carrier contributions to the Faraday rotation and to the dielectric constant have been measured to find  $N/m^{*2}$  and  $N/m^*$ , respectively, and from these both  $N$  and  $m^*$ . The theory for these effects has already been extensively developed and the essential results are summarized below.

Spitzer and Fan<sup>4</sup> have evaluated the free carrier contribution to the high-frequency electric susceptibility in semiconductors. Their results lead<sup>5</sup> to the expression

$$\frac{N}{m^*} = \frac{\pi c^2}{e^2} \left[ \frac{\epsilon_0(\lambda) - \epsilon(\lambda)}{\lambda^2} \right], \quad (1)$$

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<sup>1</sup> K. J. Planker and E. Kauer, *Z. Physik* **12**, 425 (1960).

<sup>2</sup> D. de Nobel, *Phillips Res. Rept.* **14**, 442 (1959).

<sup>3</sup> B. Segall, M. R. Lorenz, and R. E. Halsted, following paper [*Phys. Rev.* **130**, 2471 (1963)].

<sup>4</sup> W. G. Spitzer and H. Y. Fan, *Phys. Rev.* **106**, 882 (1957).

<sup>5</sup> W. W. Piper and D. T. F. Marple, *Suppl. J. Appl. Phys.* **32**, 2237 (1961).

where  $\epsilon_0(\lambda)$  and  $\epsilon(\lambda)$  are the real part of the dielectric constant of the pure and doped semiconductor, respectively. In the derivation it is assumed that  $\omega\tau \gg 1$ , where  $\tau$  is a mean free time.  $\tau$  was estimated from the Hall mobility in the doped CdTe samples (400 cm $^2$  V $^{-1}$  sec $^{-1}$  or higher) together with our effective mass result and this assumption was found to be well satisfied for all wavelengths studied. The optical effective mass appearing in Eq. (1) is numerically equal to the usual effective mass (related to the curvature  $d^2E/dk^2$  of the  $E$  vs  $k$  curve) and Eq. (1) is independent of the specific scattering processes or the statistics of the free carriers provided the free carriers are in a single parabolic minimum with spherical surfaces of constant energy. The validity of this assumption will be discussed later.

The dielectric constants were determined from the reflectance,  $R$ , measured at near-normal incidence. Provided the extinction coefficient,  $k$ , is small enough that  $k^2 \ll (n-1)^2$ , where  $n$  is the refractive index,

$$[\epsilon(\lambda)]^{1/2} = (1 + \sqrt{R}) / (1 - \sqrt{R}). \quad (2)$$

This approximation was useful at relatively short wavelengths where free carrier absorption could be neglected. Its validity in the present experiments will be discussed later.

The carrier concentration in the two doped CdTe samples studied was in the transition range between degenerate and nondegenerate statistics. In this range it is not possible to accurately calculate the carrier concentration from the Hall constant without precise information about the electron scattering mechanisms. To avoid this difficulty,  $N/m^{*2}$  was determined from the free carrier contribution to the Faraday rotation.

The observed Faraday rotation,  $\theta_r$ , is the sum of the free carrier rotation,  $\theta_e$ , and the intrinsic rotation due to the pure crystal,  $\theta_i$ . Stephen and Lidiard<sup>6</sup> and Moss<sup>7</sup> have shown that

$$N/m^{*2} = (2\pi c^4 / e^2 \lambda^2) (n\theta_e / lH), \quad (3)$$

where  $l$  is the sample thickness and  $H$  is the magnetic field strength in the direction parallel to the direction of

<sup>6</sup> M. J. Stephen and A. B. Lidiard, *J. Phys. Chem. Solids* **9**, 43 (1959).

<sup>7</sup> T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications, Ltd., London, 1959) pp. 84-5.

propagation of the radiation. This expression is valid within the same restrictions mentioned above for the dielectric constant, provided  $\omega$  is much greater than the cyclotron resonance frequency. The free carrier contribution to  $n$  should be included.

The intrinsic component of the rotation has been discussed both in classical terms<sup>7</sup> and in terms of band theory.<sup>8,9</sup> The band theory predicts that the intrinsic rotation is independent of crystal doping so long as the band gaps are unaffected. This result is supported by our data obtained at the shortest wavelengths, where the free carrier effect is negligible, and we shall assume that this component is unchanged in all the crystals at all wavelengths.

In Eqs. (1) and (3) it is assumed that the conduction band minimum at the center of the Brillouin zone is an absolute minimum, as is the case in ZnO<sup>10</sup> and CdS.<sup>11</sup> This assumption is in conflict with the analysis of optical absorption near the band edge made by Davis and Shilliday.<sup>12</sup> They concluded that in CdTe there is an "indirect" band gap about 0.1 eV lower in energy than the direct gap, and hence either the lowest conduction band minimum or the highest conduction band maximum is not at  $k=0$ . Magnetoresistance data led Yamada<sup>13</sup> to suggest that the lowest conduction band minima are not at  $k=0$ . Considering the possible effects of impurities and that the possibility of phonon assisted "direct" exciton absorption<sup>9</sup> was not included in the analysis, it is questionable if the absorption spectra conclusively prove that the band gap is indirect. Preliminary magnetoresistance studies<sup>3</sup> have given results similar to Yamada's, with certain electrodes, but have also shown that electrode effects may be of the same order of magnitude or even greater than the actual magnetoresistance itself. Exciton absorption spectra,<sup>14</sup> emission spectra,<sup>15</sup> and detailed analysis of the electrical transport properties<sup>3</sup> in CdTe all tend to support the "direct transition" hypothesis, but are not entirely conclusive. Should a "multivalley" model for the lowest conduction band prove correct our data should be re-analyzed with the appropriate theory, which has already been developed by Lax and Zwerdling<sup>16</sup> and Spitzer and Fan.<sup>4</sup>

### SAMPLE PREPARATION

Faraday rotation and reflectance measurements were made on one "pure" and two  $n$ -type doped samples. All the crystals were grown in this Laboratory by M. R. Lorenz. The pure sample was taken from a multiple zone-refined crystal<sup>3</sup> of high resistivity. The indium-doped crystal was grown from the melt.<sup>17</sup> Indium was added to the starting material and incorporated during growth. The indium concentration in the crystal was found to be  $1 \times 10^{18}$  In/cc by spectroscopic analysis. The iodine-doped crystal was grown from the melt in a pyrolytic graphite-coated quartz ampoule heated by an rf-heated graphite sleeve,<sup>15</sup> annealed for 48 h at 845°C, and then quenched by oil immersion. The iodine concentration in the crystal was not determined. The initial charge of the ampoule contained  $5.4 \times 10^{19}$  I/cc.

The doped samples were cut in the form of bars with two parallel polished faces 1 cm  $\times$  0.4 cm separated by about 0.4 cm. A similar bar of pure material was used for the Faraday rotation measurements. For the reflectance measurements on the pure crystal, the sample was cut into a wedge so that radiation reflected from the back face was not included in the measured beam. Due to the free carrier absorption, multiple reflection was not a problem with the doped material. After mechanical polishing, the samples were all chemically polished for about two minutes in Ichimiya's<sup>18</sup> etch, washed in distilled water, and stored in vacuum or dry nitrogen.

### REFLECTANCE AND FARADAY ROTATION APPARATUS

Figure 1 is a schematic diagram of the apparatus used for the reflectance measurements in the 4 to 22 $\mu$  wavelength range. A Perkin-Elmer model 99 monochromator was used with KBr prism and thermocouple detector. An image of the globar and sample was formed at the monochromator entrance slit by a mirror train adjusted

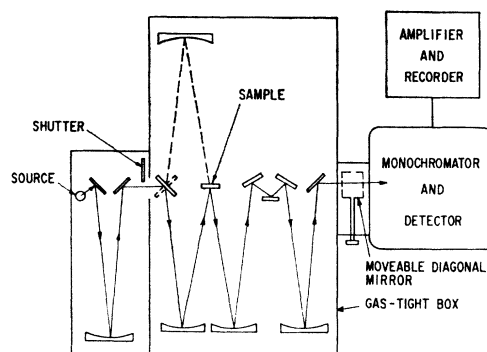


FIG. 1. Schematic diagram of the optical system used for reflectance measurements.

<sup>8</sup> B. Lax and Y. Nishina, *Phys. Rev. Letters* **6**, 464 (1961).

<sup>9</sup> I. Boswarva, R. Howard, and A. Lidiard, *Proc. Roy. Soc. (London)* **A269**, 125 (1962).

<sup>10</sup> R. E. Dietz, J. J. Hopfield, and D. G. Thomas, *Suppl. J. Appl. Phys.* **32**, 2282 (1961).

<sup>11</sup> D. G. Thomas, J. J. Hopfield, and M. Power, *Phys. Rev.* **119**, 570 (1960) and other references cited there.

<sup>12</sup> P. W. Davis and T. S. Shilliday, *Phys. Rev.* **118**, 1020 (1960).

<sup>13</sup> S. Yamada, *J. Phys. Soc. Japan* **17**, 645 (1962).

<sup>14</sup> D. G. Thomas, *Suppl. J. Appl. Phys.* **32**, 2298 (1961).

<sup>15</sup> R. E. Halsted, M. R. Lorenz, and B. Segall, *J. Phys. Chem. Solids* **22**, 109 (1961).

<sup>16</sup> B. Lax and S. Zwerdling, in *Progress in Semiconductors*, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1960), vol. 5, p. 221.

<sup>17</sup> M. R. Lorenz, *J. Appl. Phys.* **33**, 3304 (1962).

<sup>18</sup> 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), Vol. 2, p. 845.

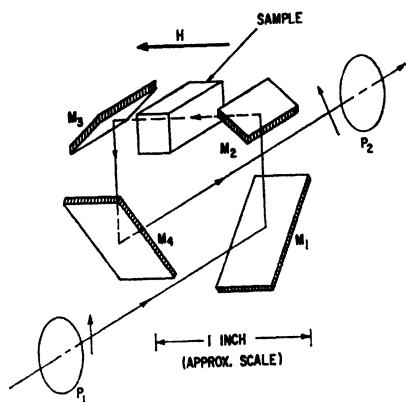


FIG. 2. Schematic diagram of the optical system used for Faraday rotation measurements. This system was fitted into the sample area of the unit shown in Fig. 1.

to minimize astigmatism and spherical aberration in the sample image. A diagonal mirror could be inserted just in front of the entrance slit to cast this image on a reticle and magnifier system so that the sample area reflecting radiation into the slit could be carefully examined. All the samples, as well as a freshly evaporated Al mirror which served as a standard,<sup>19</sup> were mounted with the reflecting faces accurately coplanar on a holder which permitted each to be brought into position, in turn, to reflect radiation into the monochromator. Data were collected "point-by-point" to minimize drift in the source intensity and amplifier gain. The entire procedure was repeated after a much more extensive chem-

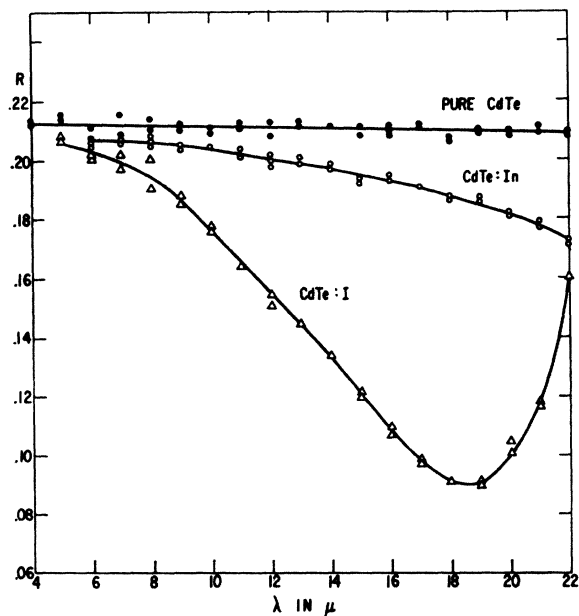


FIG. 3. Near-normal incidence reflectance,  $R$ , of pure and  $n$ -type-doped CdTe crystals as a function of wavelength.

<sup>19</sup> Reflectance given in *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 6-109.

ical polishing procedure and with a new Al standard. Within experimental error, the reflectance was unchanged.

The apparatus used for the Faraday rotation studies is shown schematically in Fig. 2. Radiation entered the first polarizer via the alternate path shown in Fig. 1 and was reflected through the sample by the evaporated Al mirrors  $M_1$  and  $M_2$ . The angle of incidence at both these mirrors was  $45^\circ$  and the planes of incidence were perpendicular. With this arrangement the elliptical polarization produced by  $M_1$  was cancelled by  $M_2$  so that the plane polarization was preserved. A small magnetron magnet with 5/8-in. gap and 13/16-in. diam pole faces provided a field of 4860 G, uniform within 3% when in position centered on the sample. The field could be reduced to 110 G by moving the magnet away from the sample on a slide. After traversing the sample where the plane of polarization was rotated by the field, the radiation was reflected through the analyzer  $P_2$  by  $M_3$  and  $M_4$  and on through the mirror train into the monochromator. A tungsten ribbon source was used instead of the globar, with a  $\text{CaF}_2$  prism, and PbS or photomultiplier detector. The angular aperture of the system was reduced to about  $f/10$ . Calcite polarizing prisms were used. With crossed polarizers and no sample in position the intensity was about  $2 \times 10^{-4}$  of that obtained with parallel polarizers. This residual intensity was caused by imperfect compensation of the elliptical polarization and by dust on the mirrors. Magnetic shielding of the photomultiplier detectors was necessary to eliminate spurious changes in detector sensitivity produced by movement of the magnet.

To measure the Faraday rotation,  $P_1$  was first set to an angle  $20^\circ$  "less than" the extinction angle. With the magnetic field reduced to 110 G the transmitted intensity was noted. Next the field was increased to 4860 G and the angular change in  $P_1$  required to re-obtain the initial intensity was noted. This procedure was repeated for an initial angle  $20^\circ$  "greater than"

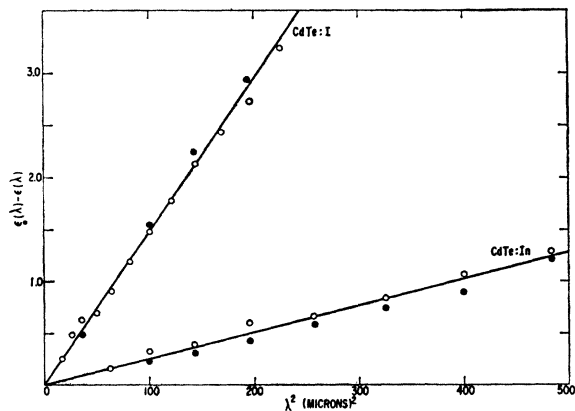


FIG. 4. Free carrier component of the dielectric constant in doped CdTe,  $\epsilon_0(\lambda) - \epsilon(\lambda)$ , as a function of the square of the wavelength. The dielectric constants are calculated from data in Fig. 3.

the extinction angle. The average of the two angular changes gives the Faraday rotation. The effect of the slight polarization of the radiation incident on  $P_1$  was approximately cancelled out by this procedure. For small rotation angles (less than  $3^\circ$ ) intensity changes produced by the field were measured for fixed polarizer settings and were converted to equivalent angular changes with an angle-vs-intensity calibration obtained with the sample in position but without the field.

### RESULTS AND DISCUSSION

Figure 3 shows the reflectance of pure and doped CdTe crystals in the 4 to  $22\mu$  range. The free carriers cause the progressive decrease in refractive index and reflectance with increasing wavelength in the doped materials. The reflectance of the doped samples was found to be the same on the two opposite faces. While not conclusive, this result suggests that there was little change in carrier concentration across the thickness of the sample. The increase in reflectance seen at the longest wavelengths in the most heavily doped material is due to the free carrier absorption which increases rapidly with wavelength; in this region Eq. (2) is grossly inaccurate. The limit of validity of Eq. (2) was estimated from free carrier absorption spectra observed in the

1 to  $4\mu$  range in a second sample cut from the most heavily doped crystal. When extrapolated, the data gave  $k \approx 0.2$  at  $15\mu$ , and Eq. (2) (where  $k$  is neglected) leads to a value for  $\epsilon_0(\lambda) - \epsilon(\lambda)$  about 6% too small. For this reason the analysis of the reflectance data for the CdTe:I sample has been restricted to wavelengths less than  $15\mu$ . A similar estimate for the CdTe:In sample shows that  $k$  is unimportant in the whole range of reflectance data.

The results for the pure crystal are in good agreement with the refractive index as measured by prism refraction at  $2.5\mu$ ,  $n = 2.70$ , and with the high-frequency dielectric constant reported by Fisher and Fan,<sup>20</sup> but are 5% to 10% lower than the reflectance reported by Planker and Kauer.<sup>1</sup> Figure 4 shows  $\epsilon_0(\lambda) - \epsilon(\lambda)$  as a function of  $\lambda^2$  for the two doped crystals as calculated with Eq. (2) from the results in Fig. 3. As expected from Eq. (1),  $\epsilon_0(\lambda) - \epsilon(\lambda)$  is directly proportional to  $\lambda^2$ , within experimental error, for both samples. The slope of the lines is proportional to  $N/m^*$ .

Figure 5 shows the product of specific Faraday rotation and refractive index as a function of wavelength for the same samples. The refractive index of pure CdTe was obtained from prism refraction measurements, and will be published elsewhere. In this wavelength range the difference in refractive index between pure and doped material is negligible, and the same values were used throughout. The free carriers cause the progressive increase in rotation with wavelength seen in Fig. 5 at the longest wavelengths in the doped materials. Figure

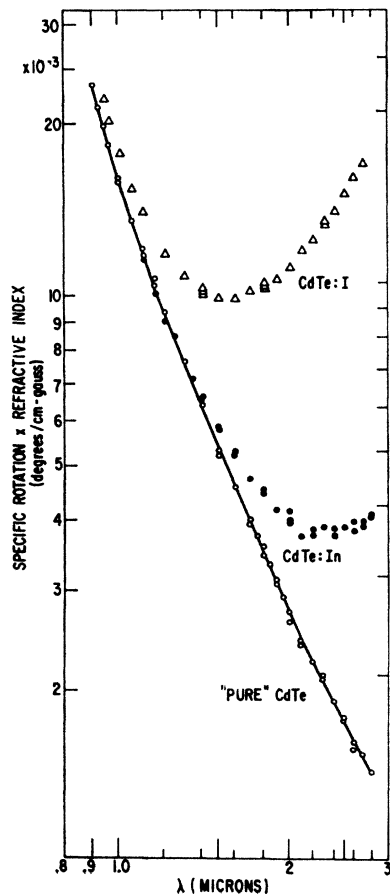


FIG. 5. Product of specific rotation and refractive index,  $n\theta_x/\lambda H$ , for pure and  $n$ -type-doped CdTe as a function of wavelength. The pure sample shows the intrinsic rotation.

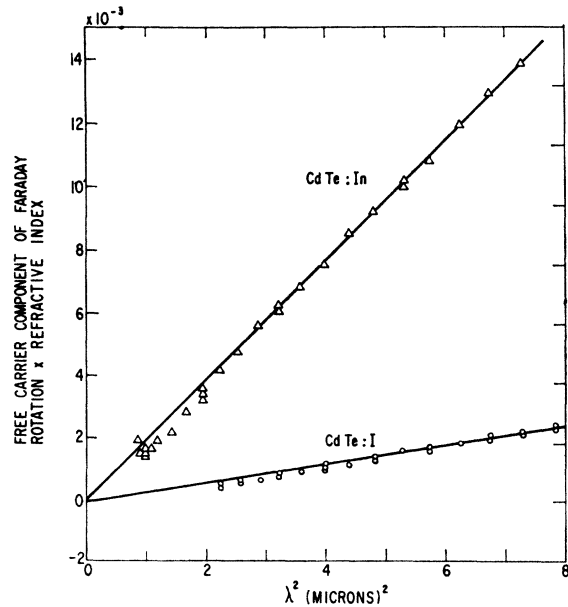


FIG. 6. Free carrier component of the product of specific rotation and refractive index for  $n$ -type-doped CdTe crystals as a function of the square of the wavelength, as calculated from data in Fig. 5.

<sup>20</sup> P. Fisher and H. Y. Fan, Bull. Am. Phys. Soc. 4, 409 (1959).

TABLE I. Results from Faraday rotation, reflectance, and Hall effect experiments on two *n*-type-doped CdTe crystals, together with effective masses, carrier concentrations, and Hall scattering constants obtained from these experiments.

Quantity	Sample	
	CdTe:I	CdTe:In
$N(m/m^*)^2$ (Faraday effect)	$14.7 \times 10^{19} \text{ cm}^{-3}$	$2.42 \times 10^{19} \text{ cm}^{-3}$
$N(m/m^*)$ (reflectance)	$16.1 \times 10^{18} \text{ cm}^{-3}$	$2.89 \times 10^{18} \text{ cm}^{-3}$
$m^*/m$	$0.110 \pm 0.01$	$0.119 \pm 0.02$
$N$	$1.76 \times 10^{18} \text{ cm}^{-3}$	$3.43 \times 10^{17} \text{ cm}^{-3}$
$r$	$1.19 \pm 0.15$	$1.49 \pm 0.25$

6 shows the difference between the product of specific rotation and refractive index for the pure sample, and the corresponding quantity for the doped samples, as a function of  $\lambda^2$ . As expected from Eq. (3), this is directly proportional to  $\lambda^2$  within the experimental error, for both samples. The slope of the lines is proportional to  $N/m^{*2}$ .

The values of  $N(m/m^*)$  and  $N(m/m^*)^2$  for the two doped samples are given in Table I together with  $N$  and  $m^*/m$  derived from them. The Hall constant,  $R_H$ , was measured<sup>3</sup> on the samples already used for the optical experiments. Results for the Hall scattering constant,  $r$ , given in Table I were calculated with the expression  $r = -NR_H e$  from  $R_H$  and the "optical" values for  $N$ .

A detailed calculation of  $r$  has not been given for charged impurity scattering in the transition range of impurity and electron concentration between classical and degenerate statistics. For nondegenerate statistics and impurity dominated scattering, Blatt<sup>21</sup> found that  $r$  ranged from 1.1 to 1.75 or more depending on several factors such as  $T$ ,  $m^*$ ,  $\epsilon$ , and  $N$ . Qualitatively, his results predict that at a given temperature  $r$  should decrease as  $N$  increases, as observed experimentally. The degeneracy concentration for CdTe at room temperature is  $N_{\text{deg}} = 1.2 \times 10^{18} \text{ cm}^{-3}$ . The carrier concentration in the CdTe:I is  $1\frac{1}{2}$  times this great, but the fact that  $r$  is still slightly greater than unity for this sample is

<sup>21</sup> F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), pp. 343-355.

consistent with Shockley's<sup>22</sup> remark that complete degeneracy is not expected unless  $N \gtrsim 3 N_{\text{deg}}$ . These results are all qualitatively consistent with somewhat similar observations on doped germanium carried out by Walton and Moss.<sup>23</sup>

The values of  $m^*/m$  are the same for both samples within the experimental error. As the carrier concentration in the highly doped sample is five times as great as in the lightly doped one, this result shows that no deviation of the conduction band from parabolic shape was detected. Such a deviation has been observed, for example, in InAs and GaAs<sup>24</sup> and InSb.<sup>25</sup> In CdTe, the "optical" effective mass at the highest carrier concentration studied is estimated<sup>24</sup> to be only about 3% greater than at the bottom of the band, a change which is too small to detect in the present experiments. The best average value for the effective mass is  $m^*/m = 0.11 \pm 0.01$ . This supports the analysis of Hall mobility data,<sup>3</sup> where  $m^*/m = 0.11$  gave the best agreement between the calculated and observed mobility.

Planker and Kauer<sup>1</sup> obtained  $m^* = 0.24$  from their study of free carrier absorption in an *n*-type CdTe crystal at 90°K. They assumed  $r = 1.93$  and pointed out that their data would give  $m^*/m = 0.14$  if  $r = 1.3$ . The carrier concentration in their sample,  $N = 6.5 \times 10^{16} \text{ cm}^{-3}$ , is approximately one-half the degeneracy concentration for 90°K. Our room-temperature results show that for  $N \approx \frac{1}{2} N_{\text{deg}}$ ,  $r$  should be between 1.5 and 1.2. Hence, their result is not inconsistent with ours.

#### ACKNOWLEDGMENTS

We are greatly indebted to Dr. M. R. Lorenz for the CdTe samples, and to Dr. B. Segall for several discussions of the theoretical problems. Miss G. P. Lloyd assisted ably in obtaining the data.

<sup>22</sup> W. Shockley, *Electronics and Holes in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 243.

<sup>23</sup> A. K. Walton and T. S. Moss, Proc. Phys. Soc. (London) **78**, 1393 (1961).

<sup>24</sup> M. Cardona, Phys. Rev. **121**, 752 (1961). The free carrier contributions to the Faraday effect and dielectric constant are discussed for nonparabolic bands. Methods for estimating the effect of the nonparabolicity on the "optical" effective mass are given, based on the work of Kane, J. Phys. Chem. Solids **1**, 249 (1957), and were used to estimate the change in mass for CdTe.

<sup>25</sup> S. D. Smith, T. S. Moss, and K. W. Taylor, J. Phys. Chem. Solids **11**, 131 (1959).