obtained here. If the defect is placed in a position where

$$\epsilon(q_1\cdots q_i\cdots q_r)=\epsilon(q_1\cdots-q_i,\cdots q_r)$$

for each q_i, then $\partial\epsilon/\partial q_i=0$, which satisfies one of the conditions for a minimum or maximum. It is sometimes possible to define parameters such that this type of symmetry is the case, for example, by defining the parameter to be the distance from a symmetry position. If in addition the parameters p_i are chosen so that

$$E(\cdots p_i\cdots,\cdots q_j\cdots)=E(\cdots p_i\cdots,\cdots-q_j\cdots),$$

then

$$\partial^2 E/\partial p_i\partial q_j=0 \qquad (A22)$$

and the conditions for a minimum (with respect to this choice for the parameters) become that

$$|N| \text{ and its principal minors}>0, \qquad (A23)$$

which reduces to

$$\partial^2 E/\partial q^2>0 \qquad (A24)$$

for a single defect parameter. This situation would arise again by choosing parameters symmetrically about a particular position of symmetry for the defect and then relaxing the symmetry to evaluate the required derivatives. Substituting Eq. (A22) in Eq. (A15) leads to $\partial p_k/\partial q_j=0$ which implies that changing the q_j slightly from the values used to calculate the p_i's, does not change the values of the p_i's. Without Eq. (A22) this would not necessarily be the case showing that to ascertain the nature of a certain position the p_i's and the q_i's have to be varied. It should be pointed out that the choice implied by Eq. (A22) may force stability on the problem in the sense that a different (more realistic) choice of parameters could lead to a different type of stability.

Optical Absorption in HgTe and HgCdTe

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Absorption and reflectivity near the fundamental absorption edge have been measured in the HgTe-CdTe alloy series for CdTe concentrations of up to 28%. In the HgTe rich region, the edge shifts to longer wavelengths with decreasing temperature. For HgTe, the absorption rises to 2×10^4 cm^{-1} at $\hbar\omega=0.6$ eV. Absorption did not decrease below 1.4×10^3 cm^{-1} at room temperature. The theory of optical absorption in zincblende compounds is reviewed. Absorption in this alloy series agrees with theory for direct transitions with an energy-independent matrix element evaluated by Kane for InSb. Analysis of reflectivity in HgTe indicates an electron effective mass of $0.02m$ at 100°C.

I. INTRODUCTION

WITH the zincblende structure HgTe and CdTe are intermetallic semiconductors. The lattice parameter varies by 0.3% between HgTe and CdTe,[1] and the compounds form solid solutions at all compositions.[2]

Measurements of the electrical properties of HgTe have been reported by several workers.[3-5] The results have usually been interpreted as indicating an energy gap near 0.02 eV, although band overlap has been suggested as an explanation for the high carrier concentrations.[6-7]

The electrical and optical properties of CdTe have also been studied.[8-10] The conduction-band minimum appears to be at the zone center,[11] and 1.6 eV (at 20°K) above the valence band as determined from the position of the exciton lines.[12] This result is in accord with observed regularities in the zincblende compounds.

Measurements of optical transmission in HgTe — CdTe alloys were reported by Lawson et al.[2] Their results indicated that the absorption edge shifted to longer wavelengths with increasing additions of HgTe in CdTe. Magnetoreflection measurements[13] are consistent with this view.

Measurements of the reflectivity of crystalline HgTe and CdTe and the transmission of thin films of CdTe

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[2] W. D. Lawson, S. Nielsen, E. H. Putley, and A. S. Young, Phys. Chem. Solids 9, 325 (1959).

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[4] T. C. Harman, M. J. Logan, and H. L. Goering, Phys. Chem. Solids 7, 228 (1958).

[5] R. O. Carlson, Phys. Rev. 111, 476 (1958).

[6] H. Rodot, M. Rodot, and R. Triboulet, Compt. Rend. 256, 5535 (1963).

[7] A. J. Strauss, T. C. Harman, J. G. Mavroides, D. H. Dickey, and M. S. Dresselhaus, *Proceedings of the International Conference on Semiconductor Physics, Exeter, 1960* (Institute of Physics and the Physical Society, London, 1962), p. 703.

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[10] S. Yamada, J. Phys. Soc. Japan 17, 645 (1962).

[11] B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. 129, 2471 (1963); Phys. Chem. Solids 22, 109 (1961).

[12] D. G. Thomas, J. Appl. Phys. 32, 2298 (1961).

[13] T. C. Harman, A. J. Strauss, D. H. Dickey, M. S. Dresselhaus, G. B. Wright, and J. G. Marroides, Phys. Rev. Letters 7, 403 (1961).

and HgTe have been reported by Cardona,[14] and Cardona and Harbeke.[15] These measurements reveal details of the band structure corresponding to energies greater than the fundamental absorption edge and assist in establishing HgTe and CdTe in their proper places in the zincblende family of intermetallic compounds.

Herman[16] has indicated the close relationship between the band structure of the group 4 elements and the 3−5 and 2−6 compounds. The energy gap in horizontal sequence such as Ge−GaAs−ZnSe varies as λ^2 where λ equals 0 for the group 4 elements, and takes the values 1 and 2 for the 3−5 and 2−6 compounds, respectively. Using the perturbation approach, Callaway[17] calculated the energy bands of GaAs from the band structure of Ge. Callaway's results indicated a lowering of the valence-band states while the conduction-band states remained stationary. The sensitivity of the various band edges to a perturbation of the core potential was examined by several authors.[18]

These papers furnish a basis for interpretation and analysis of experimental data concerning band structure for materials with the diamond and zincblende structures.[18,19] The sequence Sn−InSb−CdTe should show the same relationship between members as the parallel sequence beginning with Ge. We may thus expect that the conduction band of CdTe has a minimum at the Γ point (zone center), and that the gap is much larger than in InSb. In addition, the gap at Γ should be smaller than the gap at the L point ([111] direction) or the X point ([100] direction) in CdTe. Other reasons for believing the conduction-band minimum in CdTe lies at Γ have been summarized by Segal et al.[11]

The optical spectra of HgTe [14,15] indicate that this compound should also obey the observed relationships for zincblende compounds. From the systematic variation of band edges, we may anticipate a band structure for this compound similar to that of CdTe, but with the gap at Γ suffering a greater reduction than the gaps at X or L.

The optical-absorption measurements reported in this paper were motivated by the interesting electrical properties of the HgTe−CdTe alloys, and unanswered questions regarding details of their band structure in the HgTe rich region. The results indicate a shift of the absorption edge to longer wavelengths with decreasing CdTe content, with the edge finally being masked by free-carrier absorption. The value of the absorption coefficient agrees with values calculated, assuming

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[15] M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).

[16] F. Herman, J. Electronics 1, 103 (1955).

[17] J. Callaway, J. Electronics 2, 330 (1957).

[18] F. Herman and S. Skillman, Proceedings of the International Conference on Semiconductor Physics, Exeter, 1960 (Institute of Physics and the Physical Society, London, 1962), p. 20; F. Bassani and M. Yoshimine, Phys. Rev. 130, 20 (1963).

[19] M. Cardona and D. L. Greenaway, Phys. Rev. 125, 1291 (1962).

transitions at Γ, and shows effects of nonparabolic contributions to the density of states.

II. OPTICAL ABSORPTION THEORY

In recent years, the theory of optical absorption in semiconductors has developed rapidly. In particular, the theory for the tetrahedrally bonded elements and compounds (diamond and zincblende structures) is in good quantitative agreement with the experimental measurements. From the position and detailed shape of the absorption edge, it is possible to obtain information about the electronic states at the band edges. Additional information concerning higher and lower lying bands may in principle be obtained by measuring absorption at energies beyond the edge, although this technique is limited by rapidly increasing opacity in this region.

In this section, the theory of direct and indirect transitions will be briefly reviewed. The results will then be extended to include modifications appropriate to the subject matter of this paper, the region of very small energy gaps.

Direct Transitions

The standard formula for the transition rate for transitions between bands has the form

$$\omega_{cv}(\hbar\omega) = (2\pi/\hbar) |M_{cv}|^2 \rho_{cv}(k), \qquad (1)$$

where $|M_{cv}|$ is the matrix element between bands c and v for the interaction between the incoming radiation of energy $\hbar\omega$ and electrons, and $\rho_{cv}(k)$ is the density-of-states function for the electron transitions of wave vector k assumed to be unchanged in the transition. If only a pair of standard parabolic valence and conduction bands characterized by effective masses m_v and m_c contribute to absorption, the absorption coefficient for direct allowed transitions takes the form

$$K(\hbar\omega) = \left(\frac{n}{cN}\right)\left(\frac{2\pi}{\hbar}\right) |M_{cv}|^2 (2\pi)^{-1}$$
$$\times (2m^*/\hbar^2)^{3/2}(\hbar\omega - E_g)^{1/2}, \quad (2)$$

where $m^* = m_c m_v/(m_c + m_v)$, and E_g is the energy gap. The absorption coefficient is thus given by the number of transitions per unit time per unit volume divided by the flux density of quanta cN/n (N is taken to be the density of quanta of energy $\hbar\omega$) in the material of refractive index n.

Implicit in the derivation of Eq. (2) is the assumption that the excited electron is free to move throughout the crystal unaffected by the other electrons. It has been found necessary to take account of the mutual attraction of the electron-hole pair formed in the absorption process in order to satisfactorily explain features of the experimental measurements. These revisions modify the expected form of the absorption coefficient near the edge. In this region, the absorption does not rise from

zero as indicated by Eq. (2) but from a finite value $K(E_g)$. For this value, Elliott[20,21] obtains

$$K(E_g) = \left(\frac{n}{cN}\right)\left(\frac{2\pi}{\hbar}\right)|M_{cv}|^2 (2m^*/\hbar^2)^{3/2} E_{ex}^{1/2}(0), \quad (3)$$

where $E_{ex}(0)$ is the binding energy of the ground state of an exciton of zero-wave vector. For photon energies greater than E_g by more than $100\,E_{ex}(0)$, the absorption coefficient approaches that given by Eq. (2).

For quantitative comparisons with experiment, it is necessary to take into account the actual band structure and evaluate the optical-interband matrix element. Kane has evaluated this matrix element for InSb,[22] and the result may be adapted to other compounds of related band structure.[11,23] The joint density of states mass m^* of Eqs. (2) and (3) must be summed over the heavy- and light-hole bands which contribute to the absorption at the edge. Assuming that m_s now represents this sum, and taking a value for the optical matrix element characteristic of the 3—5 compounds,[23,24] Eq. (3) becomes

$$K(E_g) = 32.5 \times 10^6 (m_s/m)^{3/2} E_{ex}^{1/2}(0)/nE_g, \quad (4)$$

in cm^{-1} with energies measured in eV. In this way, good agreement has been obtained with the experimental values for the absorption at the edge in[25] GaAs and for the direct absorption edge in Ge.[21]

Indirect Transitions

In considering transitions between levels at differing values of the wave vector k, it is apparent that fairly strong absorption can begin at energies corresponding to the indirect energy gap in violation of the selection rule appropriate to a perfect lattice. The deviations from the perfect lattice (phonons, impurity atoms, dislocations, carrier-carrier interactions, etc.) are regarded as perturbations. There are no matrix elements directly connecting the initial and final states for such a transition, but absorption may take place *via* intermediate states. Such transitions are treated in second-order perturbation theory.

The matrix element appropriate to Eq. (1) becomes

$$\sum_i (H_f)(p_\nu)/(W_i - W_0), \quad (5)$$

where the sum is over all intermediate states. H_f is the matrix element for the electron interaction with the lattice flaw, and p_ν is the interaction with the radiation. $(W_i - W_0)$ is the energy difference between the initial and intermediate states.

In highly purified materials, the most important

indirect transitions are those associated with the lattice vibrations of the crystal. The absorption coefficient resulting from this mechanism has been discussed by McLean.[20] As in the case of direct transitions, the final form of the equations must include appropriate modifications resulting from consideration of the Coulomb attraction of the electron-hole pairs. It is not proposed to discuss further the final form of these equations, but to conclude with an indication of how the theory may be made quantitative.

From measurements on the absorption spectrum of Ge it is found that absorption involving LA phonons (which contribute substantially at low temperatures) takes place virtually exclusively through the conduction-band states at $k=0$. A matrix element for this direct transition p_ν may be calculated as outlined above. The matrix element H_f may, in the case of phonon scattering, be related to the appropriate deformation constant of the intermediate state. The energy difference $(W_i - W_0)$ is now the direct gap (neglecting the phonon energy). In this way, the matrix element of Eq. (5) may be evaluated leading to an estimate of the absorption coefficient. Indirect absorption coefficients are found to be several orders of magnitude lower than the direct absorption given by Eqs. (2) and (3).

Absorption in Small Gap Zincblende Compounds

In the theory of optical absorption outlined in the previous section, it was assumed that the bands were of standard parabolic form and that the transitions were from filled bands to empty ones. As the energy gap is allowed to approach zero, we do not expect these assumptions to be well satisfied. In particular, the absorption spectrum should be modified by the appreciable deviation from the standard density-of-states function anticipated at photon energies moderately greater than the energy of the absorption edge.

The absorption spectrum of InSb has been calculated by Kane[22] using a nonparabolic conduction band derived from the $\mathbf{k} \cdot \mathbf{p}$ approach. In the approximation of large spin-orbit splitting, the expression for the conduction band becomes

$$E_c = \hbar^2 k^2/2m + \tfrac{1}{2}(\eta - E_g), \quad (6)$$

where

$$\eta^2 = E_g^2 + 8P^2 k^2/3,$$

where E_c is the energy above the bottom of the conduction band, and P is a band parameter. The density-of-states function for a band of this form was obtained by Ehrenreich.[26] Further simplification of the result is possible[27] in the small gap region where

(a) $m_c \ll m, m_v$,

(b) $(m_c/m_v)E_c \ll E_g$.

[20] T. P. McLean, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 53.

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[22] E. O. Kane, Phys. Chem. Solids **1**, 249 (1957).

[23] H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).

[24] T. S. Moss and A. K. Walton, Physica **25**, 1142 (1959).

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[26] H. Ehrenreich, Phys. Chem. Solids **2**, 131 (1957).

[27] J. Blair, Sci. Rept. No. 2, Energy Conversion Group, Massachusetts Institute of Technology, 1960 (unpublished).

With these assumptions, tractable expressions for effective mass m_c, wave vector k, and density of states dN/dE_c may be derived. The results are

$$m_c(E_c) = m_c(0)(1+2E_c/E_g), \qquad (7)$$

$$m_c(0) = 3\hbar^2 E_g/4P^2, \qquad (8)$$

$$k(E_c) = [2m_c(0)/\hbar^2]^{1/2}(E_c/E_g)^{1/2}(E_g+E_c)^{1/2}, \qquad (9)$$

$$dN/dE_c = (2\pi^2)^{-1}[2m_c(0)/\hbar^2]^{3/2}$$
$$\times E_c^{1/2}(1+E_c/E_g)^{1/2}(1+2E_c/E_g). \quad (10)$$

With these approximations, the k·p band has $(1+E/E_g)^{3/2}$ more states up to an energy E than a parabolic band with the same curvature at $k=0$.

These results may be used to rederive Eq. (2) using a conduction band given by Eq. (6) and a heavy-hole band approximated by an isotropic effective mass m_v as before. The expression for absorption resulting from transitions between the nonparabolic conduction band and the heavy-hole band becomes

$$K_H(\hbar\omega) = 38\times10^4(m_v'/m)(m_c/m)^{-1/2}$$
$$\times (E_g/\hbar\omega)^{1/2}A(\hbar\omega-E_g)^{1/2}\alpha^2(k_H)/n, \quad (11)$$

in cm^{-1}, where $A = (2\hbar\omega-E_g)(2\hbar\omega+m_v'E_g/m_c)^{-1}$.

In the above expressions, $m_v' = m_v m/(m_v+m)$, and m_c refers to the conduction-band mass at $k=0$. Energies are measured in eV. The quantity $\alpha(k_H)$ gives the ratio of the value of the optical matrix element at the point k_H in the zone to the value of the matrix element at the bottom of the band at $k=0$. k_H is the value of the wave vector of the electron making the transition of energy $\hbar\omega$. Consistent with the approximations thus far, $\alpha^2(k_H) = \frac{1}{2}(1+E_g/\eta)$.

An expression for the absorption resulting from transitions between the conduction and the light-hole band may be derived in a similar manner. The expression for the light-hole band given by Kane is

$$E_l = \hbar^2 k^2/2m + \frac{1}{2}[(E_g-\eta)^{1/2}]. \qquad (12)$$

Again Eq. (2) must be modified to include an altered density-of-states function for the bands given by Eqs. (6) and (9). The resulting expression for the absorption due to transitions from the light-hole band, K_L may be reduced to

$$K_L(\hbar\omega) = 5.0\times10^4[(\hbar\omega)^2-E_g^2]^{1/2}\beta^2(k_L)/n \quad (13)$$

in cm^{-1} where $\beta^2(k_L) = \frac{1}{3}+\frac{2}{3}(E_g/\eta)^2$.

In Fig. 1, the E versus k curves are drawn according to (6) and (12) with a heavy-hole mass of $0.4m$. The curves for energy gaps of 0.02 and 0.03 eV are similar. Values of k for the transitions $K_H(0.2)$ and $K_L(0.2)$ are indicated.

If the valence bands are full, and the conduction band empty, the total absorption coefficient K_T is given by the sum of the heavy- and light-hole contributions:

$$K_T(\hbar\omega) = K_H(\hbar\omega)+K_L(\hbar\omega). \qquad (14)$$
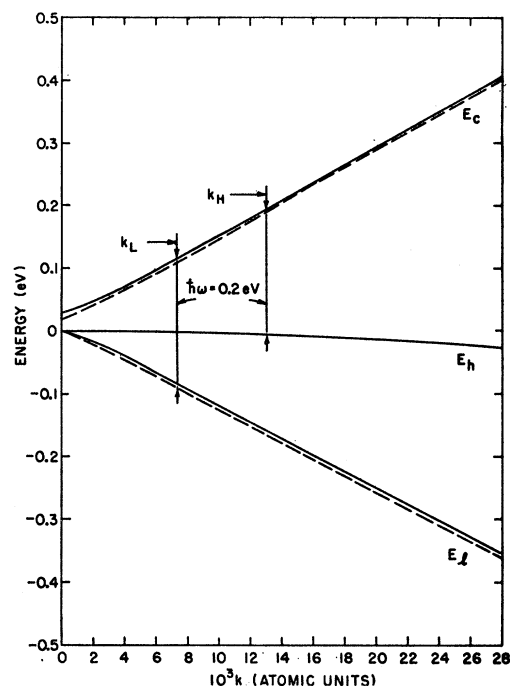

FIG. 1. Energies of conduction and valence bands versus k for an average direction in a very small gap zincblende compound. The heavy-hole mass has been taken arbitrarily as $0.4m$, and the spin-orbit splitting assumed infinite. Solid and dashed lines refer to energy gaps of 0.03 and 0.02 eV, respectively.

As the Fermi level E_F approaches the base of the conduction band, a fraction of the conduction-band states are no longer empty and are not available for absorption. For this case, the absorption becomes[28]

$$K_T(\hbar\omega) = f(E_H)K_H(\hbar\omega)+f(E_L)K_L(\hbar\omega), \quad (15)$$

where $f(E) = [1+\exp(E_F-E)kT]^{-1}$ is the probability that the conduction-band level at E is unoccupied. Energies E_H and E_L refer to energies of levels in the conduction band corresponding to the heavy- and light-hole transitions at photon energy $\hbar\omega$.

At the center of the zone, the bands become parabolic, and the expression given by Eq. (4) for $K(E_g)$ (derived for parabolic bands) agrees with experiment for E_g of the order of one eV. The value of $K(E_g)$ decreases monotonically with decreasing energy gap. For GaAs,[25] with $E_g=1.5$ eV, $K(E_g)=9000$ cm^{-1}. For an energy gap of 0.03 eV, $K(E_g)$ would be only a few hundred cm^{-1}. With such small relative values for the absorption coefficient, the shape of the edge would be expected to show considerable modifications from the form observed with larger gaps. Transitions aided by lattice disorder and phonon-assisted transitions should cover the absorption edge obscuring the details of exciton absorption.

The theory described above neglects spin splitting

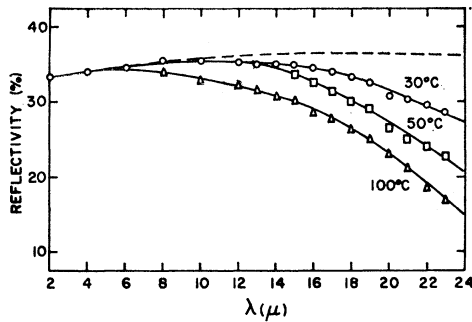[28] J. R. Dixon and J. M. Ellis, Phys. Rev. 123, 1560 (1961).

FIG. 2. Reflectivity of HgTe as a function of wavelength for three temperatures. The dashed line indicates assumed reflectivity in the absence of a free-carrier contribution.

and exchange effects.[22,29] The theory assumes a static lattice and does not consider the details of the vibrational spectrum of the solid.[30] The effect of the lattice vibrations should be most pronounced in the small gap region where the energy absorbed in an interband transition corresponds to the energy of a lattice phonon.

III. EXPERIMENTAL DETAILS

Ingots of HgTe, or HgTe—CdTe of the desired nominal composition were prepared from the purified elements. The weighed constituents were sealed in a cleaned and baked quartz tube and heated to above the calculated melting point for a period of over 30 h. The tube was then slowly cooled, placed in a vertical Bridgman furnace, and reheated to a temperature above the melting point. A slow dropping rate of 2 mm/h through the furnace gradient yielded ingots containing large single-crystal regions. Because segregation causes the CdTe content to vary along the ingot length, chemical analyses are made of the Hg, Te, and Cd content at several points along the ingot.

Samples were prepared for optical transmittance and reflectance measurements from sections of known composition cut normal to the axis of the ingot. It was found possible to prepare freely suspended samples thinner than 6μ by careful lapping and polishing. Typical specimens were more like 20μ in thickness. Reflectance measurements were made on polished sections cut adjacent to the transmission samples to eliminate possible errors from the variation in composition due to the segregation of Cd along the ingot length.

Transmittance measurements were made with the sample mounted in a Dewar at the exit aperture of a Perkin-Elmer Model 112 infrared spectrometer. A radiation thermocouple was used as the detector. Both NaCl and KBr optics were used to cover the range from 1 to 25μ. Measurements were made over the temperature range from 90 to 373°K.

Almost all samples were found to be highly absorbing

[29] E. O. Kane, Phys. Chem. Solids **6**, 237 (1958).
[30] E. D. Palik, G. S. Picus, S. Teitler, and R. F. Wallis, Phys. Rev. **122**, 475 (1961).

at long wavelengths which prevented determination of the sample thickness by the interference fringe technique. As a result, thicknesses of all samples were determined using an electronic thickness gauge. Accuracy was limited by the variation in thickness of the samples across the region illuminated by the image of the spectrometer slits. Standard deviations were 2 to 3% of the total thickness.

For a sample of thickness d and absorption coefficient K, the transmittance (defined as the ratio of the intensities transmitted with the sample in and out of the beam) is given by

$$\frac{I_t}{I_0} = \frac{(1-R)^2 \exp(-Kd)}{1-R^2 \exp(-2Kd)} . \tag{16}$$

The expression takes into account multiple reflections within the sample, but excludes interference effects. For the measurements reported here, the denominator of the expression is always close to unity.

IV. ELECTRON EFFECTIVE MASS IN HgTe

The effect of the free carriers on the optical constants of semiconductors has been discussed by Spitzer and Fan.[31] An effective mass m^* for a band may be defined independently of the relaxation time τ of the carriers if $(\omega\tau)^2 \gg 1$ where ω is the frequency of the radiation. The result may be written

$$\epsilon_0(\lambda) - \epsilon(\lambda) = \lambda^2 Ne^2/\pi c^2 m^* , \tag{17}$$

where N is the carrier concentration, and λ is the wavelength of the radiation. The dielectric constants of the low- and high-carrier concentration material $\epsilon_0(\lambda)$ and $\epsilon(\lambda)$ are obtained from the reflectivity and absorption by the expressions

$$R = [(n-1)^2 + k^2]/[(n+1)^2 + k^2] , \tag{18}$$

$$k = K_T \lambda/4\pi , \tag{19}$$

and

$$\epsilon(\lambda) = n^2 - k^2 . \tag{20}$$

The mass m^* for a spherical nonparabolic band may be expressed as[31]

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\left(\frac{1}{k}\frac{dE}{dk}\right)\Bigg|_{E_F} . \tag{21}$$

For the nonparabolic band discussed in II, the definition of (21) leads to (7).

Figure 2 shows the experimentally measured reflectivity of a HgTe surface at three temperatures. The increasing carrier concentration as the temperature increases causes a decrease in the reflectivity at long wavelengths. For this compound, a carrier concentration low enough to eliminate a contribution to the reflectivity could not be attained. An estimate of the

[31] W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).

TABLE I. Effective mass in HgTe at 100°C.

Sample	Electron concentration in cm^{-3}	Effective mass m^*/m
1	4.8×10^{17}	0.020
2	5.6×10^{17}	0.022
3	6.0×10^{17}	0.028

effective mass may be made using an $\epsilon_0(\lambda)$ curve obtained by extrapolating the reflectivity curve from short wavelengths in a manner consistent with the variation of reflectivity in HgTe—CdTe alloys with lower carrier concentrations. The assumed reflectivity curve for very low concentration HgTe is shown in Fig. 2.

In Fig. 3 the value of $\epsilon_0(\lambda) - \epsilon(\lambda)$ is plotted against λ^2. At long wavelengths, the value of k^2, obtained from the absorption coefficient K_T, becomes approximately 0.1. The relatively high absorption causes a maximum reduction of about 5% from $\epsilon(\lambda)$ calculated assuming k to be negligible.

The slope of the line drawn through the data points of Fig. 3 is proportional to N/m^*. N was determined from the Hall constant R_H with the expression

$$N = -r/R_H e.$$

The value of the Hall scattering constant r was taken to be unity for these samples where the electron concentration appears to be partially degenerate. From the Hall effect and reflectivity data, an effective mass of $0.02m$ at a carrier concentration of 4.8×10^{17} electrons cm^{-3} was obtained at 100°C. Results for this sample and two other samples of different carrier concentrations are summarized in Table I. The measured values of
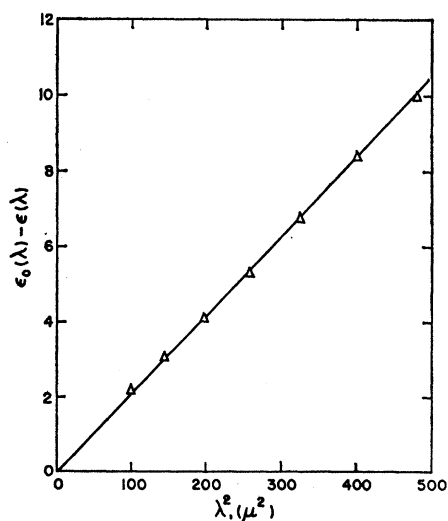

FIG. 3. Free electron contribution to the dielectric constant of HgTe at 100°C determined from the data of Fig. 2.
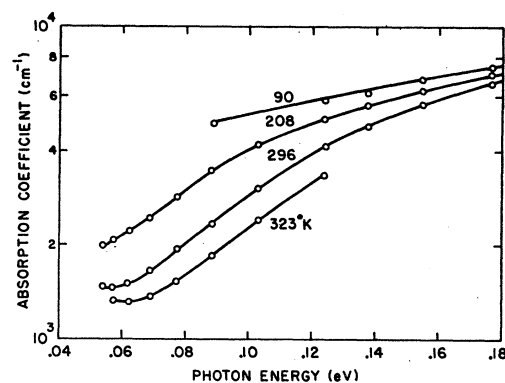

FIG. 4. Absorption coefficient of HgTe measured at several temperatures. This plot represents a composite of three samples of varying thickness.

m^* show the expected tendency to increase with an increase in carrier concentration.

A value of $0.02m$ for the conduction-band effective mass is in reasonable agreement with an energy gap near 0.03 eV using the conduction-band model described by Eqs. (6)–(10). The required mass is obtained at an energy of $E_c = 4E_g$, where E_g is taken as 0.03 eV. With the Fermi level 0.12 eV above the base of the conduction band at 100°C, a carrier concentration of 3.4×10^{17} cm^{-3} is obtained by integration of (10). The result is in reasonable agreement with the experimentally determined value of 4.8×10^{17} cm^{-3}.

V. ABSORPTION RESULTS

Absorption in HgTe

HgTe and HgTe—CdTe alloys are very susceptible to plastic damage during lapping and optical polishing. Damage, introduced for example by light pressure on the surface of a HgTe crystal, is visible after etching away several hundred microns from the surface. Such behavior is similar to[32] Te in which damage could be greatly reduced by low-temperature cleavage. Our samples, prepared by lapping and polishing, necessarily contain bulk damage extending through the samples which contributes to the apparent optical absorption. Absorption measurements on samples of decreasing thickness gave increasing absolute values similar to the results of Sturge on GaAs.[25] For example, absorption coefficients for a 7.5 μ thick sample were 30% greater than a 30 μ thick sample. A series of absorption measurements on samples of varying thickness leading to an extrapolation to infinite thickness, as reported by Loh and Newman,[33] would be desirable, although the strong absorption and difficulty of sample preparation constitute severe experimental limitations to the utility of this technique.

[32] J. S. Blakemore, J. W. Schultz, and K. C. Nomura, J. Appl. Phys. 31, 2226 (1960).
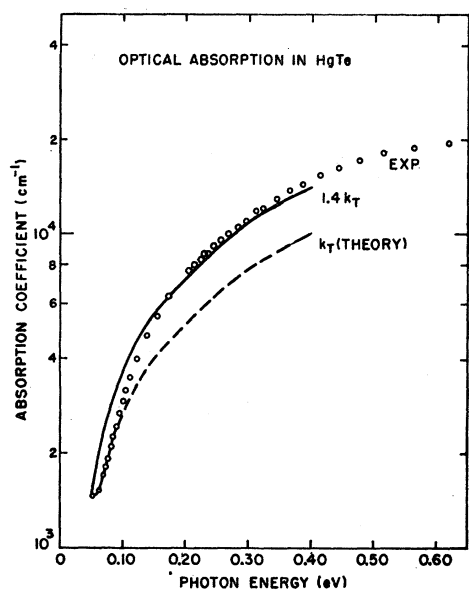[33] E. Loh and R. Newman, Phys. Chem. Solids 21, 324 (1961).

FIG. 5. Absorption coefficient of HgTe at room temperature compared with theory. The theoretical curve K_T is calculated using expressions derived in II. The curve of $1.4K_T$ is in better agreement with experimental values.

Absorption data for several HgTe samples are shown in Fig. 4. These data are normalized to the absorption of a $30\,\mu$ sample. The absorption is quite intense and does not decrease below 1400 cm^{-1} at room temperature. The indicated increase at low photon energies is due to free-carrier absorption which masks the shape of the actual absorption edge.

The temperature dependence of the absorption is also quite interesting. With increasing temperature, the absorption shifts to higher photon energies. This shift has a value of 2×10^{-4} eV/°K for absorption coefficients of 2×10^3 to 5×10^3 cm^{-1}. HgTe appears to be the only zincblende semiconductor exhibiting a positive shift of absorption edge with temperature. Further comments on the temperature dependence of the edge will be discussed with the data on the HgTe—CdTe alloys.

In Fig. 5 the absorption coefficient of HgTe is compared to the absorption coefficient K_T calculated using the expressions derived in II, and using an index of refraction $n=4$. The absorption was calculated assuming an energy gap of 0.03 eV. A calculation assuming a gap of 0.02 or 0.04 eV yields essentially the same results at higher photon energies because the density of states contributions are similar (see Fig. 1). The experimental absorption curve has the expected shape but lies about 40% higher than the calculated curve. The curve of 1.4 K_T fits the experimental curve quite well and lies above the experimental curve at the lowest photon energies where partially filled conduction-band states reduce the absorption.

The 40% difference between the calculated and observed absorption appears to arise primarily from

two sources; absorption and scattering due to structural damage introduced during sample preparation, and additional sources of intrinsic absorption not considered in II.[34]

An estimate of the absorption resulting from indirect transitions from the valence-band to a conduction-band minimum in the [111] direction was calculated using the method outlined in II and evaluating the transverse conduction-band mass in the $\mathbf{k}\cdot\mathbf{p}$ approximation. We would expect absorption from this transition to reach about 100 cm^{-1} at ten phonon energies above threshold. Such an absorption edge is found in InP and GaP.[35]

In HgTe an absorption level of 3×10^3 cm^{-1} is obtained in less than 0.10 eV or in approximately three phonon energies. We conclude that the assumed band structure and direct absorption mechanism for HgTe constitute a satisfactory explanation for the observed absorption.

Absorption in HgTe-CdTe

In Fig. 6 the absorption of HgTe and several HgTe —CdTe alloys are shown as functions of photon energy measured at room temperature. The alloys are numbered according to the CdTe concentration in atomic percent. The CdTe concentrations in the alloys were determined by chemical analysis and are believed accurate to better than 1%. Theoretical absorption curves, cal-culated according to II, are also shown for several assumed positions of the absorption edge. Figure 7 shows the measured reflectivity for HgTe and some HgTe—CdTe alloys.
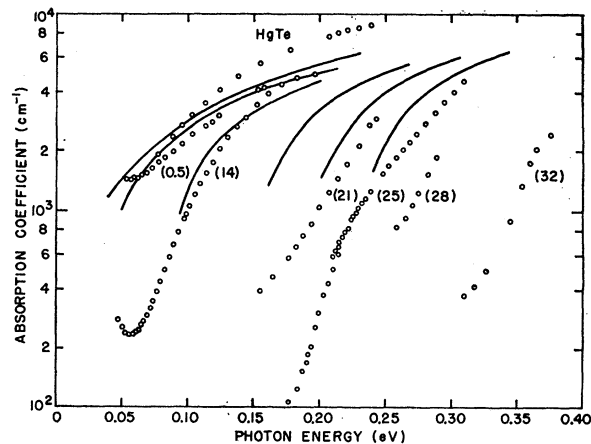
While the general agreement between the calculated

FIG. 6. Absorption coefficients of HgTe and several HgTe —CdTe alloys. Mole percent CdTe is indicated for each experimental curve. Solid curves are drawn for energy gaps of 0, 0.03, 0.09, 0.16, 0.20, and 0.24 eV as discussed in the text.

[34] For a similar result in InAs, see F. Stern, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovak Academy of Sciences, Prague, 1961), p. 366.

[35] C. Hilsum and A. C. Rose-Innes, *Semiconducting III–V Compounds* (Pergamon Press, Inc., New York, 1961), p. 169.

absorption curves and experiment is good, the expected steep rise to the absorption edge followed by a break in slope does not occur prominently in these alloys. The measured shapes are the result of slight variations in composition in the sample region illuminated by the image of the spectrometer slits. Because the segregation coefficient of CdTe in HgTe is high (we find a value of approximately 4) small temperature gradients during growth lead to small variations in composition in a direction transverse to the ingot axis. The effect of segregation may be minimized by using thin samples and narrow slitwidths. For example, sample 25 (Fig. 6) was 18 μ thick. Measurements were made with a resolution of 4×10^{-4} eV. The absorption edge rises with a steepness of $(1.5/kT)$ at room temperature and the shape of the edge shows very little change with temperature. The steepness of the edge and high absolute value of absorption lead to the conclusion that the absorption edge in the alloy series is caused by vertical transitions. In addition, the agreement between calculated absorption and experiment permits the assertion that the transition probability for this alloy series is close to the value calculated for 3–5 compounds of identical structure.

The temperature dependence of absorption of several samples is shown in Fig. 8. In this figure the photon energy at which the absorption coefficient reaches 1000 cm^{-1} is plotted for several temperatures (for HgTe a value of 2000 cm^{-1} was used).

The temperature coefficients are positive and near 10^{-3} eV/°K. In one polycrystalline sample, containing 53% CdTe, the temperature coefficient was negative and about half the value reported for CdTe.[36]

The shift of the absorption edge with temperature is usually considered to result from changes in the

FIG. 8. Temperature dependence of absorption in HgTe—CdTe alloys. The photon energy at which absorption attains 10^3 cm^{-1} is shown (for HgTe a value of 2×10^3 cm^{-1} is used). For each sample, the slope and the CdTe content is indicated.

volume of the crystal and the excitation of atomic vibrations. The effect of contributions from phonon excitation has been derived by Fan.[37] These terms contribute only toward a negative shift. We calculate -3×10^{-4} eV/°K and -10^{-5} eV/°K for the contributions from the acoustical and optical modes, respectively. The lattice dilatation term may be positive or negative and also appears to be in the 10^{-4} eV/°K range. The dilatation term is commonly negative and contributes about one-third of the observed shift in 3–5 compounds.

The positive shift found here may be the result of a positive dilatation term overcoming the negative phonon contribution. Alternatively, the problem of explaining a positive shift may be fundamental. The usual practice of treating phonon interaction as a perturbation of a larger electron excitation energy may be invalid for the very small gaps, of the order of the vibrational energies, found in HgTe.

VI. DISCUSSION

Measurements of the optical absorption of HgTe indicate a direct gap of a few hundredths eV. For several reasons it is difficult to establish the value more precisely. The theoretical shape is a slowly varying function of the gap in this region. At photon energies near the edge, the free-carrier absorption and partial filling of conduction-band states alter the shape of the edge and make exact comparisons difficult. Moreover, at higher photon energies, the contribution of neglected
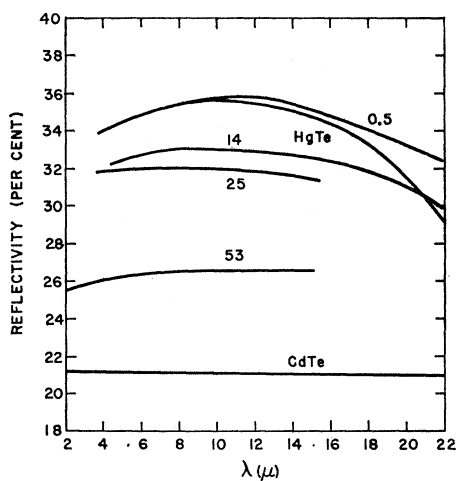

FIG. 7. Reflectivity of HgTe, several HgTe—CdTe alloys, and CdTe from D. T. F. Marple, Phys. Rev. **129**, 2466 (1963). The numbers with the curves refer to the mole percent CdTe content.

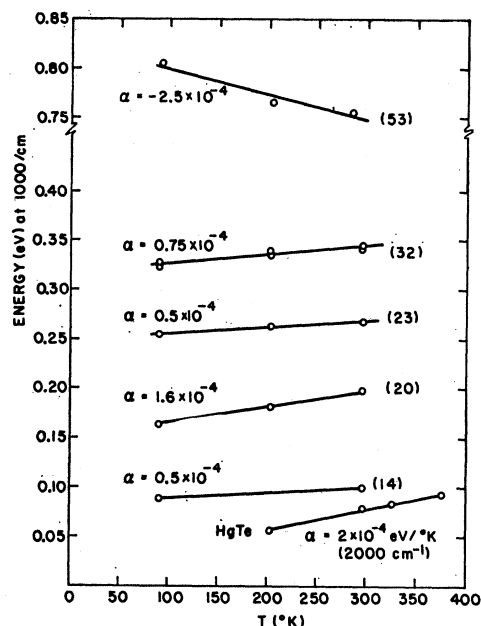[36] P. W. Davis and T. S. Shilliday, Phys. Rev. **118**, 1020 (1960).

[37] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

TABLE II. Energy gap for HgTe—CdTe alloys from absorption measurements.

Composition % CdTe	$E_g \pm \Delta E_g$ eV
0	0.03 ±0.02
0.5	0.04 ±0.02
14	0.12 ±0.04
22	0.22 ±0.02
25	0.25 ±0.02
28	0.28 ±0.02
32	0.365±0.01

FIG. 9. Variation of optical energy gap with composition for the HgTe—CdTe system. The trend of a linear variation is also shown for comparison.

sources of absorption plus the experimental problems resulting from a large absorption coefficient complicate the picture.

The experimentally measured absorption shows the curvature expected from $\mathbf{k \cdot p}$ theory, and the absolute values expected by analogy to similar 3–5 compounds. As this band structure gives satisfactory agreement for the shape of the [000] minimum in[23] GaP (a gap of 2.5 eV), the results reported here indicate that the $\mathbf{k \cdot p}$ approach to the band structure of zincblende compounds is also valid for energy gap values another two orders of magnitude smaller.

The observed increase in the absorption edge energy with increasing temperature can be of the order of the gap itself, and is of possible assistance in interpreting the electrical properties of HgTe. This may be seen from the following considerations. The curvature of the conduction band is not given directly by the value for E_g related to the position of the absorption edge, as the position of the edge at a given temperature is a result of dilational and lattice vibrational effects. As noted by Palik et al.,[30] the band structure derived by Kane for a rigid lattice does not include lattice vibrational effects. If, at low temperatures where the energy gap approaches zero, the band is characterized by a curvature corresponding to a larger gap of a few hundredths eV, unusually large intrinsic carrier concentrations are permitted. For example, assume at 50°K the energy gap has decreased to zero but the band has a shape corresponding to a gap of 0.03 eV. The intrinsic carrier concentration will be 5×10^{15} cm^{-3} for a hole mass of $0.4m$.

Therefore, carrier concentrations in the 10^{15} cm^{-3} range are possible with the small gap band structure assumed in this paper. A temperature-dependent energy gap has not been previously employed in the interpreta-
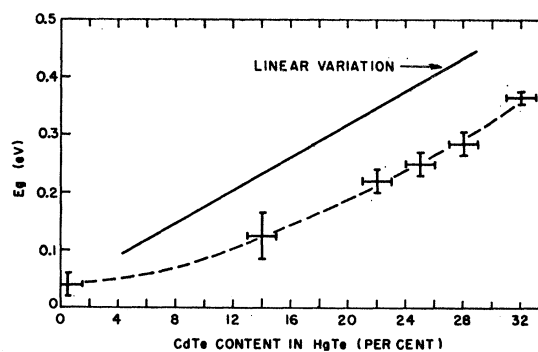
tion of the electrical properties of HgTe. The results of the absorption measurements suggest that the effect of this temperature dependence on the electrical properties could be substantial.

The absorption curves of Fig. 6 permit an estimation of E_g for the samples by comparing the experimental curves to the theoretical curves at absorption values above 10^3 cm^{-1}. Because of the many experimental difficulties previously discussed, this approach should be more reliable than choosing the photon energy at which the absorption curve breaks from an initial steep rise or choosing some arbitrarily high value. In addition, for the samples of lowest CdTe concentration, no other approach seems feasible. The results for the seven samples shown in Fig. 6 are tabulated in Table II. Figure 9 shows the trend of optical energy gap versus composition obtained in this manner. The trend of a linear variation is also shown for comparison. Accuracy of E_g is estimated from the fit to theoretical absorption curves. Accuracy of chemical analysis is assumed to be one percent. A variation of energy gap of the form observed may be anticipated from the variation of lattice parameter with composition[1] which has the same form.

ACKNOWLEDGMENTS