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TICAL PROPERTIES OF p-TYPE Bi_2Te_3–Sb_2Te_3 ALLOYS BETWEEN 2–15 MICRONS

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—Transmittance and reflectance measurements have been made on a number of p-type Te_3 alloys. With the electric vector in the cleavage plane, the index of refraction, energy verage effective mass have been calculated. The absorption edge indicates indirect transi- he analysis based on phonons of a single energy is inconsistent. The reduction of the nstant due to the free carrier susceptibility is observed in the alloys. In contrast to ther- gaps the optical energy gaps increase with increasing Sb content, a result attributed in ncreasing degeneracy of the charge carriers. Temperature dependencies of the optical re also reported.

TRODUCTION

operties of Bi_2Te_3 and its alloys een investigated in considerable rs.* In part, these studies have of immediate interest for the materials in thermoelectric ar room temperature. The perties of Bi_2Te_3 have been [1, 2] and the optical energy pounds have been reported t it appears that no work on has been published.

e and reflectance measure- t to determine the compo- f the energy gap, the index verage effective mass of the ree carrier absorption and In principle the experi- ovide some information on the analysis of the absorp- provide a consistent inter- cy of the charge carriers ible for this.

PARATION

ystals used in this work ing in a soft mold (see previous paper). Samples for optical measurements were taken from the central portions of the ingots.† For reflectance measurements the specimens were cleaved to yield, over the measured area, a mirrorlike surface with no visible stepping. Samples for transmission measurements were taken from the cleavage face of the reflectivity specimens. The sample thickness was found from mass and area measurements and the known density of the alloy compositions.[4] In the absence of visible stepping the uniformity of the thickness determined by interference fringes and sectioned sample density measurements was found adequate.

MEASUREMENTS

Room temperature reflectance and transmittance measurements were made on a Perkin Elmer Model 21 double beam spectrometer. For low temperature transmittance measurements the single beam Model 12B with the light chopped at the source was used to avoid the wavelength dependent zero shift due to temperature differences between the sample and detector. Sample thicknesses between 4 and 12 microns were used to obtain appreciable transmission losses from absorption ($Kd \geqslant 1$,

* partial list of references.

† The optical samples came from the same ingots as did the samples on which the transport properties, reported in the preceding paper, were measured.

with K, the absorption coefficient and d the sample thickness) while retaining a transmitted intensity of measurable magnitude.

Reflectance measurements were made at an angle slightly off normal incidence on the cleavage face of a thick specimen so that internally reflected radiation did not contribute to the observed intensity. From Fresnel's equations the slightly off normal angle of incidence generally was found to contribute a negligible error in the use of the reflectivity equation for normal incidence. The reflectance of the samples was measured relative to an aluminum reference mirror whose absolute reflectance has been reported elsewhere.[5]

If the interference fringes are not resolved the extinction coefficient, k, and the index of refraction, n, are obtained from the transmittance, T, the reflectance, R, and the sample thickness, d, by[6]

$$T = (1-R)^2 e^{-Kd}/(1-R^2 e^{-2Kd}) \qquad (1)$$

and

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \text{(normal incidence)}, \qquad (2)$$

with the absorption coefficient $K = 4\pi k/\lambda$. At low temperatures the reflectances were not measured and the absorption coefficient was obtained from transmission measurements on two samples of different thicknesses. In this case, to a fair approximation, K can be obtained by neglecting the second term in the denominator of equation (1).

RESULTS

The reflectances, R_B for Bi_2Te_3 and R_S for Sb_2Te_3 are given in Fig. 1. Both initially decline with increasing wavelength due to the decrease in the refractive index, but for Sb_2Te_3 the reflectance reaches a minimum around 9 microns and rises steeply thereafter to metallic values. This is the consequence of increasing free carrier absorption. Upon substitution of Bi for Sb in Sb_2Te_3 this minimum shifts to longer wavelengths.

The index of refraction for various alloy compositions (indicated by the mol per cent Sb_2Te_3) is given as a function of wavelength in Fig. 1 In the long wavelength region, n was obtained from equation (2) while at the shorter wavelengths more accurate values were obtained from the interference fringes by the relat

$$2nd = N\lambda$$

where N is the order of interfe
mate value for N was first obta
(3) using the value for n obtained

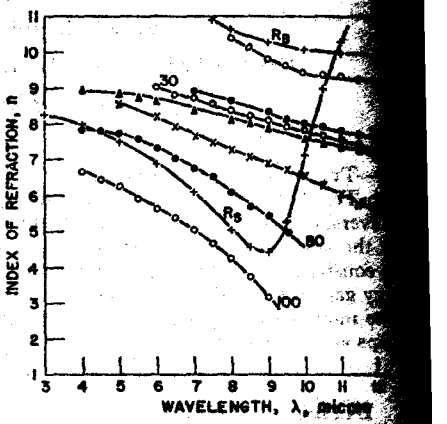


FIG. 1. Reflectance (R_B for Bi_2Te_3 and index of refraction, n, for various

With the nearest integer taken as t
for N, equation (3) was applied
fringe maxima to obtain the di
accurately. These results generall
within five per cent with the values
from reflectance and transmittance

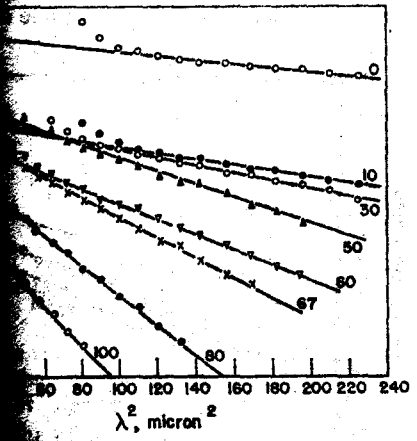
The refractive index at a given w
creases with increasing Sb content.
of n for Bi_2Te_3 has been repor
AUSTIN.[1]

SPITZER and FAN[7] have shown th
bution from the free carrier electron
to the real dielectric constant ϵ, can

$$\epsilon = \epsilon_l - \frac{Ne^2 \cdot \lambda^2}{4\pi^2 c^2 \epsilon_0 m_\chi^*} = n^2 -$$

where ϵ_0 and ϵ_l are the dielectric con
space and for the material in the absen
respectively, N is the carrier concen
m_χ^* is the electric susceptibility effect
Fig. 2 the real dielectric constant ϵ i
λ^2. Equation (4) is well followed a
wavelengths (assuming ϵ_l to be wavel
pendent) while at the shorter wave

results deviate from the λ^2 behavior proaching absorption edge. The di- ants of the intrinsic alloys appear to large for all compositions although the value for Bi_2Te_3. The electric from the large carrier concentrations in the as-grown state leads to a wavelength dependent, dielectric con- ear infrared. No simple correlation



ielectric constant $\epsilon = n^2 - k^2$ vs. λ^2 for ous alloy compositions.

duction of the dielectric constant itional dependence of the Hall dicated.

e of ϵ vs. λ^2, in Fig. 2, m^* may be the many valley model proposed tructure of Bi_2Te_3[8, 9] m_χ^* is inertial effective mass in the nd is given as α_1^{-1} in AUSTIN's ever, the carrier concentrations and N was replaced by the efficient, R_H, using

$$\left(\frac{\alpha_3'}{\alpha_1^2}\right)\cdot\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2}\cdot\frac{1}{Ne} \qquad (5)$$

α_1^2) is the Hall coefficient aniso- relaxation time averages were the scattering law and Fermi from the transport properties r). With equations (4) and (5) arameter (α_1/α_3') can be calcu- carrier electric susceptibility.

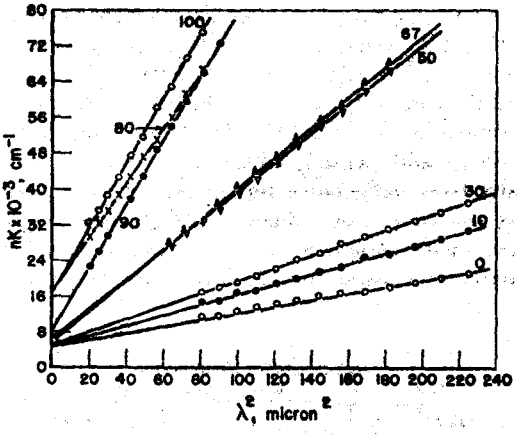


FIG. 3. Product of index of refraction and absorption coefficient, nK vs. λ^2 for various alloy compositions.

The compositional dependence of $(\alpha_1/\alpha_3')_\chi$ at 300°K is given in Fig. 4.

The same effective mass parameter evolves from the absorption coefficient measurements. With the electric vector in the cleavage planes the free carrier absorption coefficient, K is given by[10]

$$K = \frac{e^2\lambda^2}{4\pi^2 n\epsilon_0 m^2 c^3 \mu_H R_H \left(\frac{\alpha_1}{\alpha_3'}\right)_A^2}\cdot\left(\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2}\right)^2 \times\langle\tau\rangle\cdot\langle\tau^{-1}\rangle, \qquad (6)$$

where μ_H is the Hall mobility. The plot of nK for eight compositions, given in Fig. 3, shows that the desired λ^2 dependence of the free carrier absorption

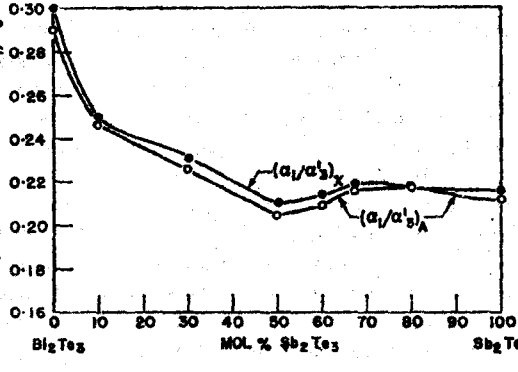


FIG. 4. The effective mass parameter α_1/α_3' determined from free carrier susceptibility, $(\alpha_1/\alpha_3')_\chi$ and from free carrier absorption, $(\alpha_1/\alpha_3')_A$ vs. composition.

is superimposed on a broad band absorption component of undetermined origin. The effective mass parameter $(\alpha_1/\alpha_3')_A$ obtained from equation (6) and the slopes in Fig. 3 are plotted as a function of composition in Fig. 3. The agreement between $(\alpha_1/\alpha_3)_A$ and $(\alpha_1/\alpha_3')_X$ which was obtained principally from reflectance measurements is to within five per cent. The values for Bi_2Te_3 are in agreement with Austin's results obtained from free carrier absorption and Faraday rotation measurements.

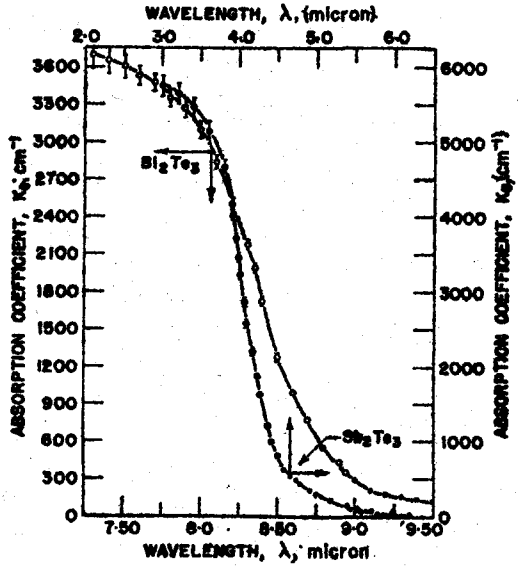


FIG. 5. Absorption coefficient, K_e, due to band to band transitions vs. λ for Bi_2Te_3 and Sb_2Te_3.

With the free carrier and broad band absorption components subtracted the remaining absorption coefficient K_e was analyzed to obtain the optical energy gap and characterize the transition as direct or indirect. In Fig. 5 K_e is plotted as a function of wavelength for the two extreme compositions of the alloy system. In determining the energy gap E_g we have followed Moss' criterion[11] which establishes E_g from the value of λ at which the slope of the absorption coefficient is a maximum. Fig. 6 gives the energy gap as a function of composition for three different temperatures. From Bi_2Te_3 to 80 per cent Sb_2Te_3/20 per cent Bi_2Te_3 the energy gap increases linearly with Sb_2Te_3 content. The temperature coefficient of E_g is approximately $1{\cdot}5\times10^{-4}$ eV/°K in this range although from the increased de lower temperatures a somewhat would be expected for intrin For the very Sb rich alloys E_g rises 0·28 eV for Sb_2Te_3 at room tempe compositions the Fermi level is ab ent of the temperature and a sma coefficient of E_g will be expected. and n-type specimens of the Sb ric ally cannot be obtained an accurate

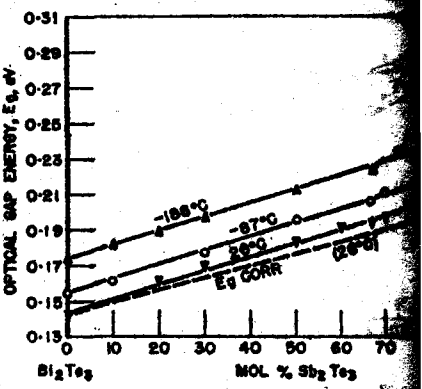


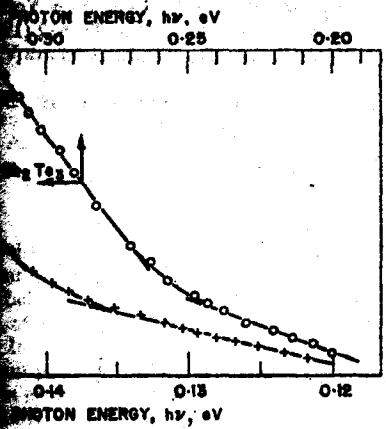
FIG. 6. Optical energy gap, E_g, vs. $E_{g\,corr} = E_g$ (observed) − Fer

of the effects of degeneracy was not least in part the increase in E_g w Sb_2Te_3 content results from the incr grown state of degeneracy and is situation found in InSb.[12] An es was provided by calculating the Fe from the observed Seebeck coefficien have been plotted in Fig. 6 as $E_{g\,corr}$ the transitions were direct an additi in E_g would be associated with the density of states effective masses for electrons. The bulk of the experimen however, indicates indirect transitio

The absorption edges of several analyzed to determine whether the tra direct or indirect. Generally, K_e where $h\nu$ is the incident photon energ or $\frac{2}{3}$ for direct transitions and $n = 2$ direct transitions. Our data are con $n = 2$ as shown in Fig. 7 for Bi_2Te_3 In both cases the plot of $K_e^{1/2}$ vs. $h\nu$

as predicted for indirect transi- expression of MACFARLANE and

$$\frac{(h\nu - E_g - k\theta)^2}{\exp(-\theta/T)} + \frac{(h\nu - E_g + k\theta)^2}{\exp(\theta/T) - 1} \quad (7)$$



ot of absorption coefficient, $K_\nu^{1/2}$, vs. energy for Bi_2Te_3 and Sb_2Te_3.

phonon energy necessary to con- . The first term corresponds to and the second to phonon absorp- s equation to our results at room obtain from the intercepts $k\theta$ d 400°K and E_g equal to 0·13 eV Bi_2Te_3 and Sb_2Te_3 respectively. g values of $k\theta$ from the slopes, ut three and four times larger, ilar discrepancy for Bi_2Te_3 has AUSTIN.[1] Although equation (7) for degeneracy this should be $_2Te_3$. Ignoring the modification y degeneracy the optical energy r indirect transitions from the are smaller than those obtained (Fig. 6). This result, together of degeneracy, will account at apparent discrepancy between l energy gaps. Values for the ps from high temperature re- nts have been obtained in this esults show an energy gap of which decreases on alloying to per cent Sb_2Te_3/30 per cent Bi_2Te_3. With increasing degeneracy our optical and thermal measurements would tend, respectively, to overestimate and underestimate the energy gap. For the very Sb rich compositions (including Sb_2Te_3) the strong degeneracy led to resistivity maxima at temperatures too close to the melting points to permit a determination of E_g. Attempts at compensation were unsuccessful.

CONCLUSIONS

The infrared studies have shown that most of the alloy system is characterized by a large dielectric constant although the effects of the free carrier susceptibility are quite marked for the more degenerate alloys. For the larger part the optical behavior was in agreement with the predictions of the Drude–Zener theory. An effective mass average obtained from electric susceptibility and free carrier absorption measurements is reported but more work is needed to establish the band structure parameters completely.

Evidence obtained from measurements of the transport properties indicate the effective mass to be insensitive to variations in carrier concentration or degeneracy, at least over changes in these two variables as occur in the as-grown materials. Although exact carrier concentrations cannot be obtained from Hall measurements without further knowledge of the band structure, it is estimated that a hole concentration in excess of 10^{19} cm^{-3} occurred in most of the alloys. A possible reason for independence of the effective mass on hole concentration at such levels seems to be the very large dielectric constant screening of the crystalline field. In a calculation for heavily doped Germanium CONWELL and SCHLOSSER[14] arrive at a similar conclusion.

In the analysis of the absorption edge the transitions appear as indirect but no satisfactory account was made of the effects of degeneracy. At least in the compositional range Bi_2Te_3 to 70 per cent Sb_2Te_3/30 per cent Bi_2Te_3 the energy gap should fall somewhere between the optical and thermal values and, therefore, does not vary to a great extent with composition.

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REFERENCES

1. AUSTIN I. G., *Proc. phys. Soc. Lond.* **72**, 545 (1958).
2. AUSTIN I. G., *Proc. phys. Soc. Lond.* **76**, 169 (1960).
3. BLACK J., CONWELL E. M., SEIGLE L. and SPENCER C. W., *J. Phys. Chem. Solids* **2**, 240 (1957).
4. TESTARDI L. R. and WIESE J. R., *Trans. Amer. Inst. min. (metall.) Engrs.* **221**, 646 (1961).
5. HASS G., *J. opt. Soc. Amer.* **45**, 945 (1955).
6. BECKER M. and FAN H. Y., *Phys. Rev.* **76**, 1530 (1949).
7. SPITZER W. G. and FAN H. Y., *Phys. Rev.* **106**, 882 (1957).
8. DRABBLE J. R. and WOLFE R., *Proc.* B69, 1101 (1956).
9. DRABBLE J. R., *Proc. phys. Soc.* (1958).
10. AUSTIN I. G., *J. Electron. Cont.*
11. MOSS T. S., *Optical Properties* p. 40. Academic Press, New Y
12. BURSTEIN E., *Phys. Rev.* **93**, 632 (1
13. MACFARLANE G. G. and ROBERTS 1714 (1955).
14. CONWELL E. M., SCHLOSSER H., *Soc.* **7**, 214 (1962).