

Electrical and Optical Properties of Intermetallic Compounds.

I. Indium Antimonide*

R. G. BRECKENRIDGE, R. F. BLUNT, W. R. HOSLER, H. P. R. FREDERIKSE, J. H. BECKER, AND W. OSHINSKY†
National Bureau of Standards, Washington, D. C.

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The conductivity and Hall coefficient of InSb have been measured over the temperature range 78°K to 750°K. At low temperatures an electron mobility of 30 000 cm²/volt-sec and a mobility ratio of 29 are observed. The effective mass of electrons is 0.04*m* and the width of the forbidden energy gap is 0.23 ev at *T*=0°K.

Optical absorption studies have been made at temperatures between 13°K and 300°K. The position of the absorption edge of degenerate *n*-type samples depends on the impurity content and is in good agreement with Burstein's predictions.

INTRODUCTION

INDIUM antimonide is one of a series of semiconducting compounds formed between elements of the B-subgroups of the third and fifth columns of the periodic table. In 1952 Welker¹ focused attention on this family of materials (antimonides, arsenides, and phosphides) and reported briefly on their properties. These compounds possess the zincblende structure; the nearest neighbor distance in InSb is 2.80 Å, equal to that of grey tin. The melting point of the compound is 523°C. An earlier publication² indicated some of the interesting features of this compound, namely, the small forbidden energy gap and the high electron mobility. Measurements of resistivity and Hall effect have now been made on a number of samples; the optical absorption of the compound has also been studied in detail.

EXPERIMENTAL PROCEDURES AND RESULTS

Samples

The compound is prepared by melting the components together in stoichiometric proportions. The starting materials used were antimony obtained from the Bradley Mining Company and indium from the Anaconda Copper Mining Company. The antimony has a purity of 99.95 percent and contains small amounts of Pb, As, Cu, and Fe. The purity of the indium is 99.954 percent, the major impurities being Zn, Sn, Ni, Cd, Fe, Cu, and a trace of Pb. The melting process is done in an induction furnace with helium or argon as a protecting atmosphere. The melt is contained in a grade A carbon crucible. Further purification of the compound was achieved by repeated zone melting. Ingots were drawn from the melt by the Kyropoulos technique starting with a small seed. In some cases the compound was prepared by melting together antimony and indium in an evacuated vycor tube. The antimony

used was chemically purified, following the method of Groschuff.³ All ingots showed *p*-type conductivity and were slightly polycrystalline. The samples cut from ingot SC-5 are, however, single crystals. The *n*-type specimens were prepared by adding tellurium to the melt.

X-ray analysis confirmed the zincblende structure with a lattice constant⁴ of 6.4782 Å at 25°C in reasonable agreement with the values reported by Goldschmidt.⁵

Electrical Properties

The measurements of resistivity and Hall effect were made with the conventional dc method.⁶ For the low-temperature experiments the probes were soldered to the sample with indium metal; pressure contacts were used at high temperatures. Measurements were made in the range 78°K to 700°K with results given in Figs. 1 and 2. These results are in good agreement with data of other investigators.^{1,7,8}

The striking feature of these results is that the Hall coefficient of the *p*-type samples reaches much higher values in the intrinsic range than in the extrinsic region. The Hall and resistivity curves are practically flat in the extrinsic range, indicating very small activation energies for imperfections.

Optical Properties

The optical absorption of several *n*- and *p*-type samples has been investigated. These samples were cut from the same ingots as those used for the electrical measurements, except *P4* which is an impure *n*-type specimen. The samples were ground and polished, and ranged in thickness from 3 to 5 mil.

³ E. Groschuff, *Z. anorg. u. allgem. Chem.* **103**, 164 (1918).

⁴ These measurements were made by the Microstructure Section of the National Bureau of Standards.

⁵ V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad., Oslo. I. Mat.-Natur. Kl. No. 2* (1926).

⁶ R. G. Breckenridge and W. R. Hosler, *Phys. Rev.* **91**, 793 (1952).

⁷ H. Weiss, *Z. Naturforsch.* **8a**, 463 (1953).

⁸ M. Tanenbaum and J. P. Maita, *Phys. Rev.* **91**, 1009 (1953).

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† Now at Army Engineering Laboratories, Fort Belvoir, Virginia.

¹ H. Welker, *Z. Naturforsch.* **7a**, 744 (1952); **8a**, 248 (1953).

² R. G. Breckenridge, *Phys. Rev.* **90**, 488 (1953).

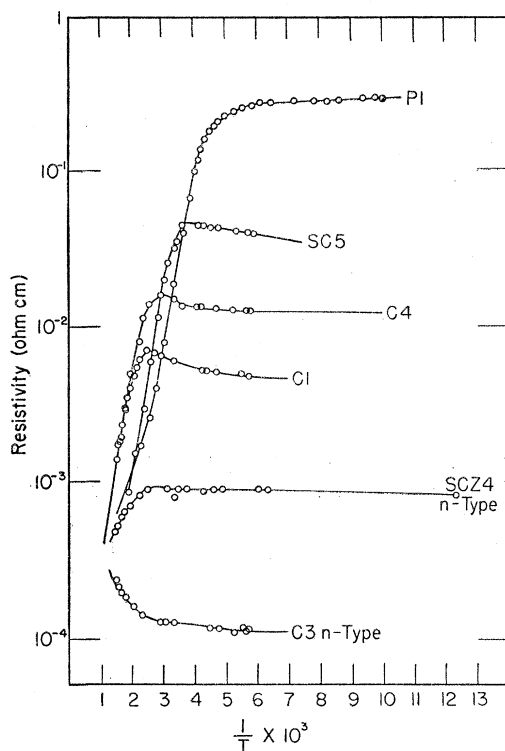


FIG. 1. Resistivity of various InSb samples.

The determination of the optical transmission follows closely the conventional method. The radiation from a source is focused on the sample by means of mirrors. An incandescent lamp is used as a source up to 2μ and a globar for wavelengths between 1 and 15μ . The transmitted radiation is refocused on the entrance slit of a Perkin-Elmer model 83 monochromator (NaCl prism) which is used to analyze the transmitted radiation. The light beam is chopped at 10 cps near the source and the analyzed radiation measured with a Perkin-Elmer vacuum thermocouple and a tuned amplifier. The effect of stray radiation on the apparent transmissivity is reduced and checked by means of appropriate transmission filters. Measurements are made at wavelength intervals of 0.5μ over most of the range and 0.1μ at the absorption edge.

For measurements at liquid nitrogen temperature, the samples are mounted in a small metal Dewar while data near liquid helium temperature are obtained with a cryostat similar to the one designed by Duehrig and Mador.⁹ However, the absorbed radiation heats the samples to a temperature somewhat higher than that of the refrigerant. An Ag-Au thermocouple¹⁰ indicated that the actual temperatures of the sample obtained for liquid nitrogen and helium cooling were about 85°K and about 15°K , respectively.

Several runs were made using a slightly different

experimental procedure. In this case monochromatic light from the spectrometer was focused onto the sample and then collected by the detector. The results are essentially the same as those obtained with the previous method.

One very thin *p*-type sample (1 mil) showed regular maxima and minima of the absorption coefficient in the long wavelength tail (7 – 15μ). This interference pattern is caused by multiple reflections inside the sample. The refractive index κ can now be calculated from the well-known interference relation and yields an average value for κ of 3.5 over the range 7 to 15μ . This value is in good agreement with the one reported by Briggs *et al.*¹¹ This enables us to correct the transmission for reflection losses and plot the spectra in terms of the absorption coefficient.¹² Absorption spectra for several samples at room temperature are given in Fig. 3. One notices that the location of the absorption edge changes from sample to sample between 3 and 7μ . This anomaly has been reported also by Tanenbaum and Briggs.¹³ Figure 4 shows the temperature variation of the absorption coefficient for a pure *p*-type sample (SC-5) and for an impure *n*-type specimen (P4). The shift of the absorption edge with temperature (expressed in ev/deg) appears to be much larger for the *n*-type sample than for the *p*-type specimen.

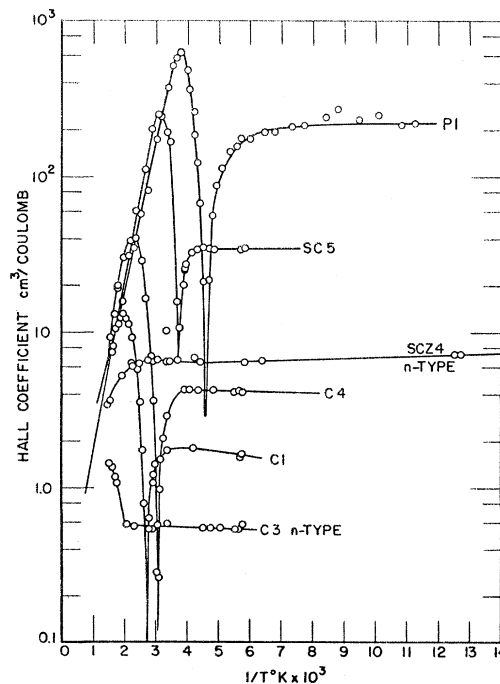


FIG. 2. Hall coefficient of various InSb samples.

¹¹ Briggs, Cummings, Hrostowski, and Tanenbaum, *Phys. Rev.* **93**, 912 (1954).

¹² H. Y. Fan and M. Becker, *Semiconducting Materials* (Butterworths Publications, London, 1951).

¹³ M. Tanenbaum and H. B. Briggs, *Phys. Rev.* **91**, 1561 (1953).

⁹ W. H. Duehrig and I. L. Mador, *Rev. Sci. Instr.* **23**, 421 (1952).

¹⁰ Sigmund Cohen, New York, New York.

DISCUSSION

In order to calculate the different parameters, such as charge carrier concentration, carrier mobility, and forbidden band width, we use a procedure slightly different from that of Pearson and Bardeen.¹⁴ We will apply this analysis to the results for sample SC-5 (*p* type).

The Hall coefficient (in cm³/coulomb) is given by

$$R = -\frac{3\pi}{8e} \frac{n\mu_n^2 - p\mu_p^2}{(n\mu_n + p\mu_p)^2} = -\frac{3\pi}{8e} \frac{nb^2 - p}{(nb + p)^2}, \quad (1)$$

where n =concentration of electrons in the conduction band, p =concentration of holes in the valence band, μ_n =electron mobility, μ_p =hole mobility, $b=\mu_n/\mu_p$, and e =electronic charge in coulombs. Furthermore,

$$p = n + N, \quad (2)$$

in which N =number of acceptor impurities per cm³, which are all ionized over the temperature range studied. We want to determine the value of R at its maximum, R_{\max} . Now in the case of a *p*-type semiconductor, n is a function only of T and further a monotonic increasing function of T such that R_{\max} can be determined from the condition

$$\delta R / \delta n = 0. \quad (3)$$

The value for n for which R reaches its maximum is

$$n_{\max} = N / (b - 1) \quad (4)$$

and

$$R_{\max} = \frac{-3\pi}{8eN} \frac{(b-1)^2}{4b}. \quad (5)$$

N is related to the Hall coefficient in the exhaustion

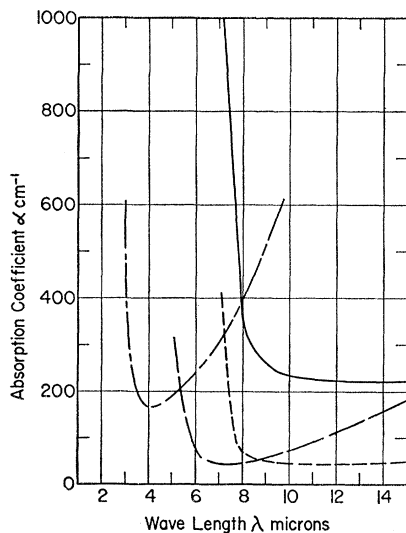


FIG. 3. Absorption spectra of several *n*- and *p*-type samples of InSb at 305°K. — SC-5, --- Z4, ---- P4-A, - - - - P4.

¹⁴ G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).

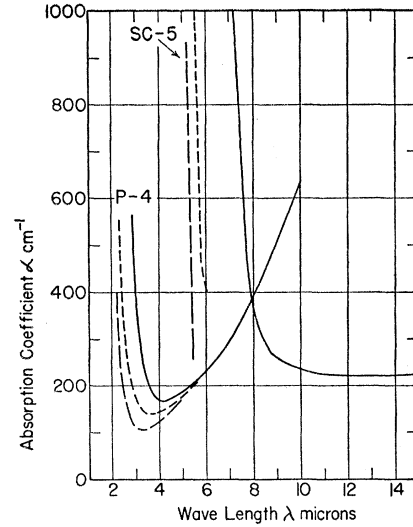


FIG. 4. Temperature dependence of the absorption edge of two InSb samples.

SC-5 (<i>p</i> type)	P-4 (<i>n</i> type)
— 307°K	— 303°K
--- 86°K	--- 83°K
- - - 15°K	- - - 13°K

range,

$$R_{\text{ex}} = 3\pi / 8eN. \quad (6)$$

Hence,

$$R_{\max} / R_{\text{ex}} = (b-1)^2 / 4b. \quad (7)$$

Substituting the numerical values from Fig. 2, we find a mobility ratio $b=29$ for sample SC5.¹⁵

The number of electrons n in the intrinsic range can then be calculated from the Hall coefficient

$$n = -\frac{3\pi}{8Re} \frac{b-1}{b+1}, \quad (8)$$

and the number of holes p follows from Eq. (2). These numbers have been plotted in Fig. 5. One can now compute the product np , which is given by the expression¹⁶:

$$np = 4(2\pi mkT/h^2)^3 (m_n m_p / m^2)^{3/2} e^{-E/kT}, \quad (9)$$

where m_n =effective mass of electrons, m_p =effective mass of holes, and E =width of the forbidden energy gap. This last quantity depends, however, on temperature; assuming a linear temperature dependence as found in other semiconductors,¹² we can replace E by

¹⁵ This ratio depends not only on the total impurity concentration, but also on the number of grain boundaries, and varies widely from sample to sample. Tanenbaum and Maita (see reference 8), report a mobility ratio of 85.

¹⁶ This relation is accurate for completely nondegenerate samples but gives a value of the product np which is too large by about 5 percent for $n=0.4N_c$ and four times too large for $n=20N_c$. The degeneracy temperature of sample SC5 is 99°K. N_c =effective density of states in the conduction band $=2(2\pi mkT/h^2)^{3/2}$ [see W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand and Company, Inc., New York, 1950), p. 240].

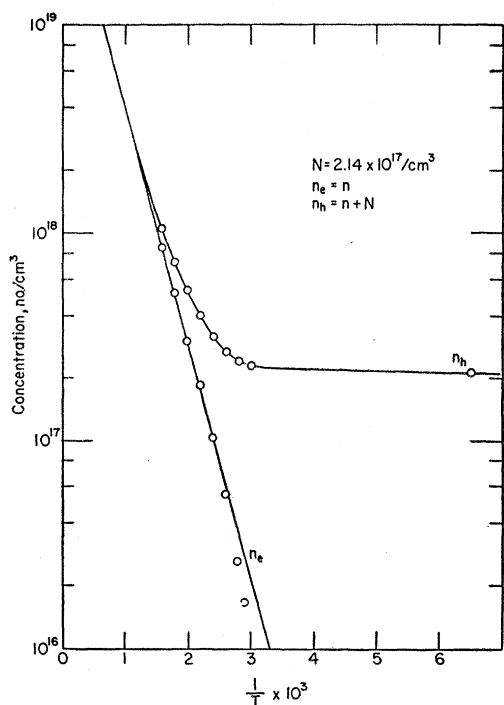


FIG. 5. Charge carrier concentrations of InSb single crystal.

$E_0 + \beta T$. Equation (9) can then be written

$$np = 4 \left(\frac{2\pi mkT}{h^2} \right)^3 \cdot \left(\frac{m_n m_p}{m^2} \right)^{3/2} \cdot e^{-\beta/k} \cdot e^{-E_0/kT}. \quad (9a)$$

The slope of the plot of $\ln[np/T^3]$ vs $1/T$ will therefore give the quantity E_0 (see Fig. 6). This value appears to be 0.23 ev. The intercept in this plot determines the coefficient before the exponential $e^{-E_0/kT}$ in Eq. (9a). This coefficient contains two unknown parameters: β and $(m_n m_p/m^2)$. The quantity β can be calculated from optical absorption measurements (see Table I). Substituting this value we find for the intercept 2.9×10^{29} and, subsequently,

$$(m_p m_n/m^2)^{3/2} = 0.077, \quad (10)$$

in good agreement with the value given by Tannenbaum and Maita.⁸ The effective masses are also related to the mobilities¹⁷:

$$b = \mu_n/\mu_p = (m_p/m_n)^{5/2}. \quad (11)$$

A combination of Eqs. (10) and (11) yields the following values for the effective masses of electrons and holes:

$$m_n = 0.04m \quad \text{and} \quad m_p = 0.15m.$$

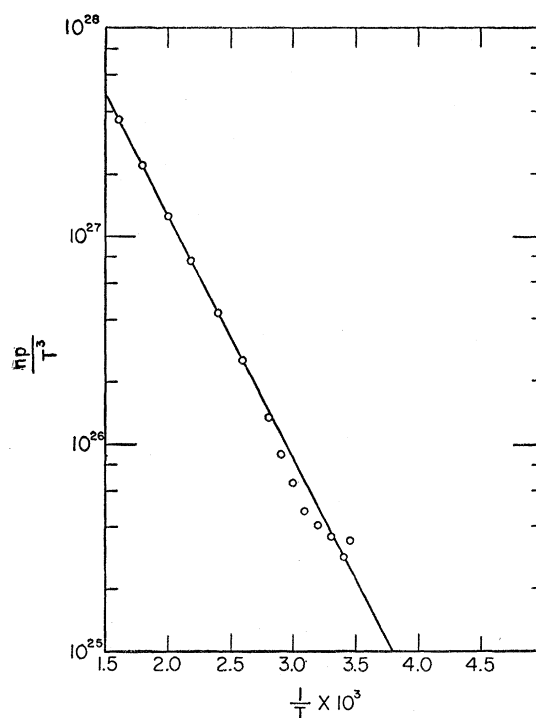
At high temperatures in the intrinsic range the effect of electrons is predominant and R_σ should give a value which is approximately equal to the mobility of electrons. In the low-temperature region where the con-

ductivity is mainly by holes, this product should give the hole mobility. Assuming a constant mobility ratio $b=29$, one finds mobility curves for electrons (top) and holes (bottom) as presented in Fig. 7.

Similar calculations have been made for the other samples. Electron and hole concentrations are listed in Table I.

The forbidden band width is also related to the steep rise observed in the absorption spectrum. The exact location of this edge is rather arbitrary. We have chosen the value where the straight line portion of the edge intersects with the extrapolated long-wavelength tail. These values are given in the column marked E_{obs} in Table I and appear to be in good agreement with results reported by other investigators.^{13,18}

Burstein¹⁹ has recently offered an explanation for the anomalous behavior of *n*-type InSb based on the very small effective mass m_n observed for conduction electrons. The consequences of this small value of m_n will be a very small density of states in the lower part of the conduction band and also a relatively small degeneracy concentration (10^{17} per cm^3 at room temperature). The Fermi level of degenerate samples will therefore be located at a considerable distance from the bottom of the conduction band, depending on the impurity content. Hence, the energy necessary to excite electrons optically from the valence band into the con-

FIG. 6. Plot of np/T^3 vs $1/T$ for InSb single crystal.

¹⁸ W. Kaiser and H. Y. Fan, Phys. Rev. **95**, 1431 (1954).

¹⁷ W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand and Company, Inc., New York, 1950), p. 287.

¹⁹ E. Burstein, Phys. Rev. **93**, 632 (1954). See also: Beer, Willardson, and Middleton, Phys. Rev. **93**, 912 (1954).

duction band will be larger than the width of the forbidden energy gap.

Assuming spherical energy surfaces, Burstein calculates the following expression for the optical activation energy in degenerate n -type samples ($n > 6.5N_c$):

$$E_{\text{calc}}^n = E + (1 + m_n/m_p)(E_F - E_c - 4kT), \quad (12)$$

where

$$E_F - E_c = \frac{\hbar^2}{2m_n} \left(\frac{3n}{8\pi} \right)^{1/3}, \quad (13)$$

E_F = Fermi level, and E_c = bottom of conduction band.

It has been assumed in the derivation of this expression that the lowest unfilled level lies approximately $4kT$ below the Fermi level. In order to calculate E_{calc}^n we have used the following parameters. The energy gap E is taken from the values obtained on the non-degenerate p -type samples. For the effective masses we have used $m_n = 0.04$ and $m_p = 0.15$ (see above). The results of this calculation are given in column 7 of Table I.

A comparison of the observed and calculated values of the activation energy shows a fair agreement; our measurements seem to substantiate Burstein's explanation of degenerate behavior in InSb.

It is clear that the temperature variation of the forbidden energy gap E can only be derived from the data on the p -type samples. The values of $\beta (= dE/dT)$ are listed in Table I.

It has been shown²⁰ that transitions of free carriers

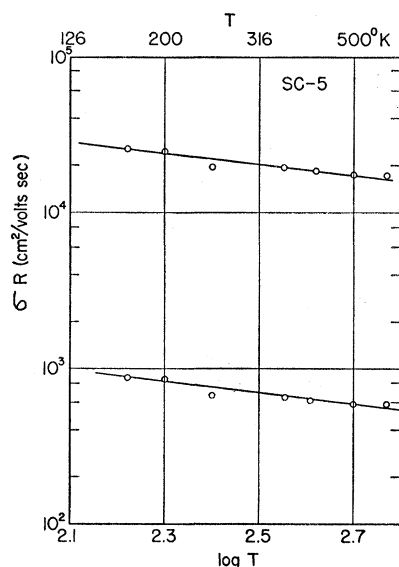


Fig. 7. Temperature dependence of σR for a single crystal of InSb. (Top: electrons. Bottom: holes.)

²⁰ See reference 12, p. 139.

TABLE I. Carrier concentrations, effective densities of states, and activation energies of InSb samples.

Sample	T (°K)	n (cm^{-3})	p (cm^{-3})	N_c (cm^{-3})	E_{obs} (ev)	E_{calc}^n (ev)	β (ev/deg)
Z-4	307	1.35×10^{18a}		2.0×10^{17}	0.22	0.17	
n type	85	1.35×10^{18a}		2.8×10^{16}	0.30	0.32	
P-4	307	5.1×10^{18a}		2.0×10^{17}	0.36	0.38	
n type	85	5.1×10^{18a}		2.8×10^{16}	0.46	0.54	
	13	5.1×10^{18a}		1.7×10^{16}	0.51	0.59	
SC-5	307		2.1×10^{17}	1.2×10^{18}	0.16		-2.5×10^{-4}
p type	85		2.1×10^{17}	1.7×10^{17}	0.21		
	15		2.1×10^{17}	1.4×10^{16}	0.23		
P4-A	307		1×10^{17}	1.2×10^{18}	0.16		-2.3×10^{-4}
p type	85		1×10^{17}	1.7×10^{17}	0.21		
P-1	307		3.4×10^{16}	1.2×10^{18}	0.16		-1.6×10^{-4}
p type	85		3.4×10^{16}	1.7×10^{17}	0.20		

^a These values are calculated from electrical measurements on the samples used in the optical investigations.

TABLE II. Absorption coefficient of InSb samples at room temperature (cm^{-1}).

Sample		$\lambda = 4\mu$	$\lambda = 6\mu$	$\lambda = 8\mu$	$\lambda = 12\mu$
p -type	SC-5	calc 4.5	10	18	39
		obs ...	220	220	220
	P4-A	calc 2.5	5.7	10	22
		obs ...	50	50	50
p -type	P-1	calc 2.4	5.4	10.0	21
		obs ...	180	180	180
n -type	Z-4	calc 39	87	150	340
		obs ...	25	40	110
	P-4	calc 720	1600	2900	6500
		obs 150	230	360	...

within the allowed energy bands will also contribute to the absorption. The absorption coefficient α due to this mechanism is given by

$$\alpha = 5.06 \times 10^{-17} \lambda^2 N / \kappa \mu (m^*/m)^2, \quad (14)$$

where N = carrier concentration and m^* = effective mass of carrier. We have evaluated the absorption coefficient at a number of wavelengths using the measured values of the parameters N , κ , μ , and m^* . The results of this calculation together with the observed values of α are listed in Table II. It is apparent from the data on the n -type samples that α is indeed proportional to λ^2 . The absolute magnitude, however, is not too well predicted by the theory. (Even larger discrepancies have been found in the cases of germanium and silicon.) The absorption of the p -type samples is, within experimental error, independent of wavelength; the observed discrepancies can presumably be attributed to unaccounted reflection losses.

Equation (14) shows that α is very sensitively dependent on the effective mass m^* and the mobility μ . The values of μ taken from the electrical measurements are very low, presumably due to the polycrystalline nature of the samples. It seems reasonable to assume that the mobility within the grains is considerably higher. This in turn would decrease the calculated values of α .