# Infrared Absorption of Indium Antimonide*

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Indium antimonide samples of a wide range of carrier concentrations were measured from $\sim 5°$K to $500°$K, over a wavelength region of 3 to 35 microns. Experimental results on the shift of the absorption edge in degenerate $n$-type samples are presented and discussed. Both $n$-type and $p$-type samples show the same absorption at long wavelengths, after becoming intrinsic at elevated temperatures. At lower temperatures, the absorption in $n$-type samples increases with wavelength, whereas in $p$-type samples it remains practically constant over a wide wavelength region. The absorption coefficient in different samples, $n$-type or $p$-type, does not increase proportionately with the carrier concentration. Possible mechanisms for the absorption are discussed.

OF the large group of intermetallic-compound semi-conductors, indium antimonide is of particular interest. The material exhibits a very high electron mobility, up to 60 000 cm²/volt-sec, and a small energy gap, 0.18 ev at 300°K in samples of high purity.[1-5] Its optical properties have been reported by several investigators with emphasis on the absorption edge.[5-12] We present in the present paper some results obtained from transmission measurements at different temperatures on samples of various carrier concentrations.[8] Measurements were made not only near the absorption edge but also at longer wavelengths, up to 35 microns. The results show some interesting behaviors of the absorption coefficient, for which tentative explanations are suggested. The samples used are not single crystals but consisted of several large crystallites.

## THE ABSORPTION EDGE

It has been found that absorption edges in $n$-type InSb samples of high carrier concentrations are at much shorter wavelengths than in purer specimens. Burstein[7] proposed that due to the small effective mass the conduction electrons become degenerate at high concentrations and the absorption edge should then shift with the Fermi level. The displacement of the absorption edge with increasing carrier concentration can be derived in the following way. The absorption coefficient $\alpha$ should be proportional to the probability of the excited state to be unoccupied

$$\alpha = \alpha_0 \left( 1 - \frac{1}{\exp[(E-\zeta)/kT]+1} \right), \quad (1)$$

where $\alpha_0$ is the absorption coefficient if the excited state is unoccupied, $E$ is the electron energy in the excited state, and $\zeta$ is the Fermi energy. Let $E_0$ be the energy of the electron in the valence band before the excitation and let all energies be measured from the bottom of the conduction band. Then

$$h\nu = E - E_0$$

$$= \frac{h^2}{2m_e}k^2 - \left( -E_G - \frac{h^2}{2m_h}k^2 \right) = E_G + E\left( 1 + \frac{m_e}{m_h} \right), \quad (2)$$
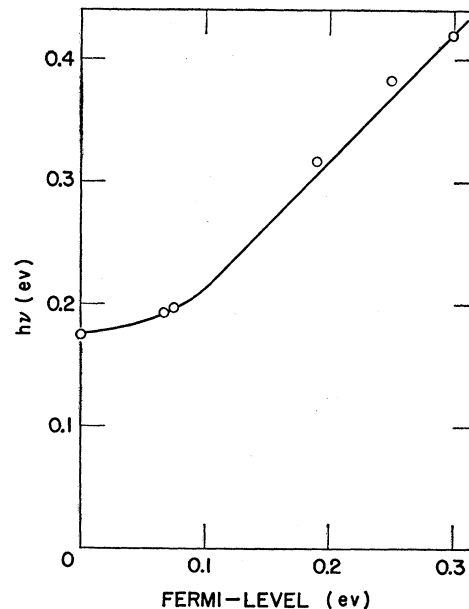


FIG. 1. The shift of the absorption edge. Photon-energy at an absorption coefficient of 300 cm⁻¹ *versus* Fermi-level for various $n$-type samples with carrier concentrations up to $5 \times 10^{18}$ cm⁻³. Points are experimental results. The solid curve is calculated from Eq. (1).

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[1] H. Welker, Z. Naturforsch. 7a, 744 (1952).
[2] M. Tannenbaum and J. P. Maita, Phys. Rev. 91, 1009 (1953).
[3] Cunnell, Saker, and Edmond, Proc. Phys. Soc. (London) A66, 1115 (1953).
[4] O. Madelung and H. Weiss, Z. Naturforsch. 9a, 527 (1954).
[5] Breckenridge, Blunt, Hosler, Frederikse, Becker, and Oshinsky, Phys. Rev. 96, 571 (1954).
[6] M. Tannenbaum and H. B. Briggs, Phys. Rev. 91, 1561 (1953).
[7] E. Burstein, Phys. Rev. 93, 632 (1954).
[8] W. Kaiser and H. Y. Fan, Phys. Rev. 94, 1431 (1954). This abstract gives a brief account of the work reported here.
[9] Koch, Miller, and Goering, The Electrochemical Society Spring Meeting 1954 (unpublished).
[10] F. Oswald and R. Schade, Z. Naturforsch. 9a, 611 (1954).
[11] Hrostowski, Wheatley, and Flood, Phys. Rev. 95, 1683 (1954).
[12] T. S. Moss, Conference on Photoconductivity, Atlantic City, 1954, will appear in the Conference Proceedings to be published.

where $E_G$ is the energy gap. The electron wave number $k$ remains the same before and after the excitation due to the selection rule. Combining (1) and (2) we get

$$h\nu(\alpha) = E_G + \left[\zeta - kT \ln\left(\frac{\alpha_0}{\alpha} - 1\right)\right]\left(1 + \frac{m_e}{m_h}\right). \quad (3)$$

The second term gives the displacement of $h\nu$ for a given $\alpha$ with varying carrier concentration which is related to $\zeta$. The solid curve in Fig. 1 is calculated according to (3), using the following values: $\alpha = 300$ cm$^{-1}$, $T = 295°$K, $m_e/m_h = 0.15$, and $E_G = 0.175$ ev. The value of $E_G$ is taken from the absorption edge (at $\alpha = 300$
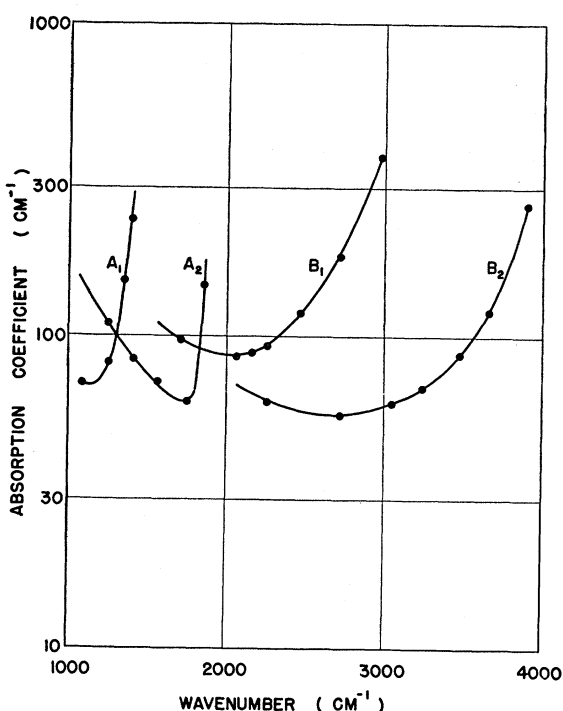


FIG. 2. The absorption edge of a nondegenerate InSb sample ($p$-type). Curve $A_1$ at 300°K, curve $A_2$ at $\sim$5°K. Curves $B_1$ and $B_2$ show the absorption edge of a highly degenerate $n$-type specimen at 300°K and $\sim$5°K, respectively.

cm$^{-1}$) of samples with small carrier concentrations. In our transmission measurements absorption coefficient was measured up to $10^3$ cm$^{-1}$ for samples of small carrier concentrations. From reflection measurements, Moss[12] has estimated higher absorption coefficients at shorter wavelengths. The values for $\alpha_0$ to be used in (3) were obtained from these data. The experimental results are given by the points in Fig. 1. Values of $h\nu$ corresponding to $\alpha = 300$ cm$^{-1}$ were taken from the absorption coefficient curves measured for $n$-type samples with different carrier concentrations as given by Hall effect and resistivity measurements. The value of $\zeta$ corresponding to each carrier concentration is calculated
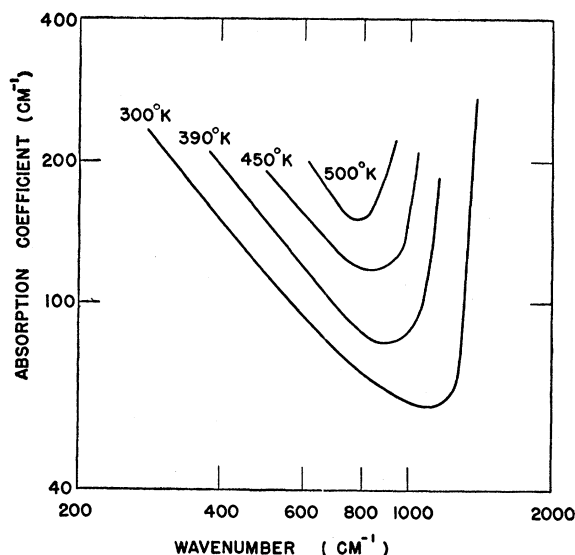


FIG. 3. Absorption of an $n$-type sample ($n = 10^{17}$ cm$^{-3}$) at high temperatures.

assuming $m_e = 0.03m$. The agreement between the points and the calculated curve seems to be quite satisfactory.

Measurements at different temperatures show that the absorption edge shifts to shorter wavelengths with decreasing temperature. For samples of small carrier concentrations, this shift indicates a change of the energy gap amounting to $-2.8 \times 10^{-4}$ ev/°K, in the temperature range 5°K to 520°K. Figure 2 shows two curves $A_1$ and $A_2$ taken on such a sample at 300°K and $\sim$5°K, respectively. The same figure shows also the curves $B_1$ and $B_2$ taken on a degenerate $n$-type sample at the same temperatures. These curves show a much larger shift, nearly all of which took place between 300°K and 77°K. According to (3), one might indeed expect that for a drop in temperature the increase in $h\nu$ will be larger than the increase in $E_G$ on account of the term involving $kT$. However, this term comes from (1) and expresses the fall-off of the distribution function at the Fermi energy; with decreasing temperature the fall-off becomes sharper. According to (1), $\alpha$ at a given temperature should rise exponentially with increasing $E$ or $h\nu$, so long as $\alpha \ll \alpha_0$, and $\ln\alpha$ plotted against $h\nu$ should have a slope $1/kT$, disregarding the variation of $\alpha_0$ in the small interval of $h\nu$. Curves $B_1$ and $B_2$ in Fig. 2 have much smaller slopes than $1/kT$, especially curve $B_2$ for the lower temperature. In fact $B_2$ has about the same shape as $B_1$ instead of being much steeper, and both curves are much flatter than the curves $A_1$ and $A_2$ for the nondegenerate sample. It is possible that there is some broadening of the absorption edge in the low range of $\alpha$ covered by these curves, but it is not yet clear what is the most likely mechanism for such broadening.
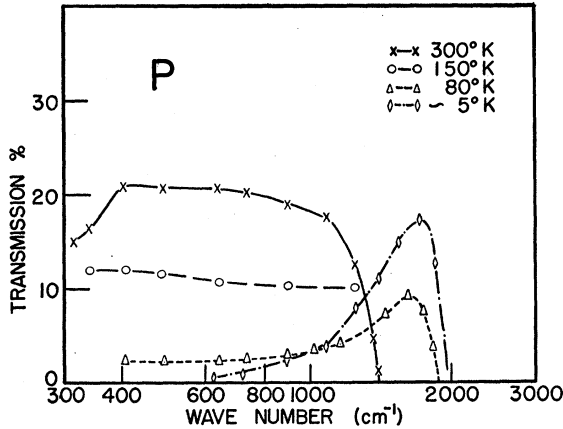
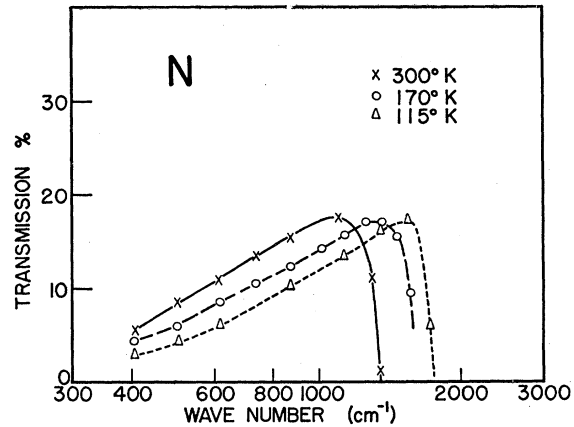FIG. 4. Transmission of a $p$-type sample ($p=9\times10^{16}$ cm$^{-3}$) at low temperatures.



FIG. 5. Transmission of an $n$-type sample ($n=10^{17}$ cm$^{-3}$) at low temperatures.

## LONG-WAVELENGTH ABSORPTION

Measurements were made up to 35 microns. Figure 3 shows a series of absorption curves at different elevated temperatures for an $n$-type sample. The absorption increases with wavelength and rises with increasing temperature. The sample is well in the intrinsic range at 500°K. The curves for the two higher temperatures agree with the results obtained on a $p$-type sample which becomes intrinsic above 400°K. Thus the long-wavelength absorption at high temperatures in the intrinsic range seem to be due to free carriers.

The situation is more involved at lower temperatures with samples in the extrinsic range. Typical transmission curves are given in Fig. 4 for a $p$-type sample and in Fig. 5 for an $n$-type sample. These curves show that the absorption in $n$-type samples increases with wavelength whereas it remains practically constant in $p$-type samples, begining to rise only beyond 25 microns (400 cm$^{-1}$) at room temperature. In contrast to germanium and silicon, the absorption coefficient for different samples is not proportional to the carrier concentration, e.g., at room temperature $n$-type samples with carrier concentrations ranging from $10^{17}$ cm$^{-3}$ to $4.6\times10^{18}$ cm$^{-3}$ gave absorption coefficients varying by a factor of 6 only, and in $p$-type samples with hole concentrations varying from $3.5\times10^{16}$ cm$^{-3}$ to $10^{18}$ cm$^{-3}$ the absorption coefficient varied only by a factor of 2.5. Furthermore, the variation of the absorption coefficient with temperature is interesting. For both $n$-type and $p$-type samples the absorption coefficient increases with decreasing temperature, very strongly in the $p$-type. On the other hand, Hall effect and resistivity measurements indicate that the carrier concentration in these samples remains practically constant between 77°K and 300°K and the mobility does not show much change. All these observations indicate

that it is difficult to attribute the absorption to the free carriers.[13]

It might be suggested that the absorption is caused by optical ionization of impurities or localized electronic states in general. As the temperature decreases, the Fermi level approaches to either one of the band edges. In $n$-type material impurity levels very close to the conduction band become more occupied by electrons which can be excited to the conduction band giving absorption. Analogous effect can be obtained in $p$-type samples with impurity level close to the valence band. The absorption is proportional to the electron or hole population of these impurities. To agree with the electrical data, we have to assume that the concentration of such impurity states is sufficiently small so that changes in their electron population do not affect appreciably the concentration of free carriers. However, calculations show that it is difficult to account for the experimental observations using this model which confines the variation of the absorption coefficient to much smaller temperature ranges.

A possible mechanism is the excitation rather than ionization of electrons or holes in localized states. The probability for the carrier to be in the excited state having energy $E$ above the ground state is given by the Boltzmann factor. For a constant number of electrons or holes, the absorption at a given wavelength will be proportional to $[1-\exp(-E/kT)]$. The experimentally observed temperature variations of $\alpha$ can be fitted by choosing a suitable value for $E$, e.g., for the $p$-type sample an approximate fit can be obtained with $E=0.006$ ev.

This work is a part of the investigations on intermetallic compounds initiated by Professor K. Lark-Horovitz and we wish to thank him for stimulating discussions.

[13] See H. Y. Fan and M. Becker, Semiconducting Materials (Butterworths Publications, London, 1951).