TABLE II. Capture cross sections for electrons and holes in n-type and p-type, gold-doped, silicon.

	n-type		p-type	
	σ_{n0}(cm²)	σ_{p0}(cm²)	σ_{n0}(cm²)	σ_{p0}(cm²)
300°K values	5×10^{-16}	1×10^{-15}	3.5×10^{-15}	$\geq10^{-16}$
Temperature dependence	Independent	T^{-4}	$T^{-2.5}$	
Capture at	Au^0	Au^-	Au^+	Au^0

(1) The capture of excess carriers by oppositely charged gold atoms shows a pronounced temperature dependence, while capture at neutral atoms does not.

(2) In n-type silicon at temperatures below 300°K the hole capture cross section due to negatively charged gold exceeds considerably the electron capture cross section at neutral gold atoms.

These two facts are consistent with the notion that the existence of either of the gold levels depends on the position of the Fermi level. They are also in accordance with Lax's[12] prediction that a charged center ought to exhibit a temperature dependence of the capture cross section in the form of T^{-n}, where n can be between 1 and 4, and that a neutral center should have a weaker temperature dependence.

The values of the capture cross sections when extrapolated to 77°K agree quite well with those observed by Davis,[13] particularly in the case of charged centers.

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[12] M. Lax, Second Symposium of Semiconductors, Washington, D. C., October, 1956 (unpublished).

[13] W. D. Davis (private communication): at 77°K, in n-type, $\sigma_{n0}\equiv4\times10^{-15}$ cm², $\sigma_{p0}\equiv3\times10^{-13}$ cm²; in p-type, $\sigma_{n0}=10^{-13}$ cm², $\sigma_{p0}=4\times10^{-15}$ cm².

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Optical Properties of n-Type InP

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Measurements of the intrinsic absorption edge of n-type InP at 77°K and 300°K are reported. Differences are found in the spectra of samples of differing origin. The effects are believed due to impurities. Reflection and absorption spectra in the vicinity of the reststrahlen peak are shown. The reststrahlen wavelength is 30.5 μ, the static and high-frequency dielectric constants are $\epsilon_0=15$ and $\epsilon_\infty=10.6$. Free-carrier absorption and reflection spectra are shown. A brief discussion of the implications of the various optical and electrical measurements as regards the conduction band structure is given.

INTRODUCTION

THIS note reports some of the optical properties of n-type InP. The material used came from two sources: a polycrystalline ingot prepared at the Battelle Memorial Institute (BMI) containing a free-carrier concentration at room temperature of $n=5\times10^{15}$/cm³, and polycrystalline ingots prepared at this laboratory having room-temperature carrier densities between 2×10^{16} and 5×10^{18}/cm³. None of the ingots were intentionally doped; the carriers presumably resulted from the presence of uncontrolled and unidentified impurities. The state of compensation of the impurities is also unknown.

A. Intrinsic Electronic Absorption

Figure 1 shows the intrinsic electronic absorption spectra of InP at 300° and at 77°K.[1] This is the absorption process which is due to the excitation of an electron from the valence to the conduction band. The data were taken using a Perkin-Elmer monochromator incorporating a diffraction grating for high dispersion. The spectral resolution was between 2×10^{-4} and 1×10^{-3} ev for the data shown.

Consider first the spectra for the BMI material. At both 77°K and 300°K the curves show a break at an absorption coefficient of about 10 cm⁻¹. Above the break point the slope of the curve is steeper than below. The slopes above the break are of the same magnitude as the slopes at comparable absorption coefficients and temperatures for such materials as InSb.[2] For the latter, calculations have indicated that the transitions are direct.[3,4] The absorption above the break point in the BMI InP, in all probability, may be regarded similarly as due to direct processes. How-

[1] F. Oswald, Z. Naturforsch. **9a**, 181 (1954).

[2] V. Roberts and J. E. Quarrington, J. Elec. **1**, 152 (1955); G. W. Gobeli and H. Y. Fan, Bull. Am. Phys. Soc. Ser. II, **2**, 121 (1957).

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

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

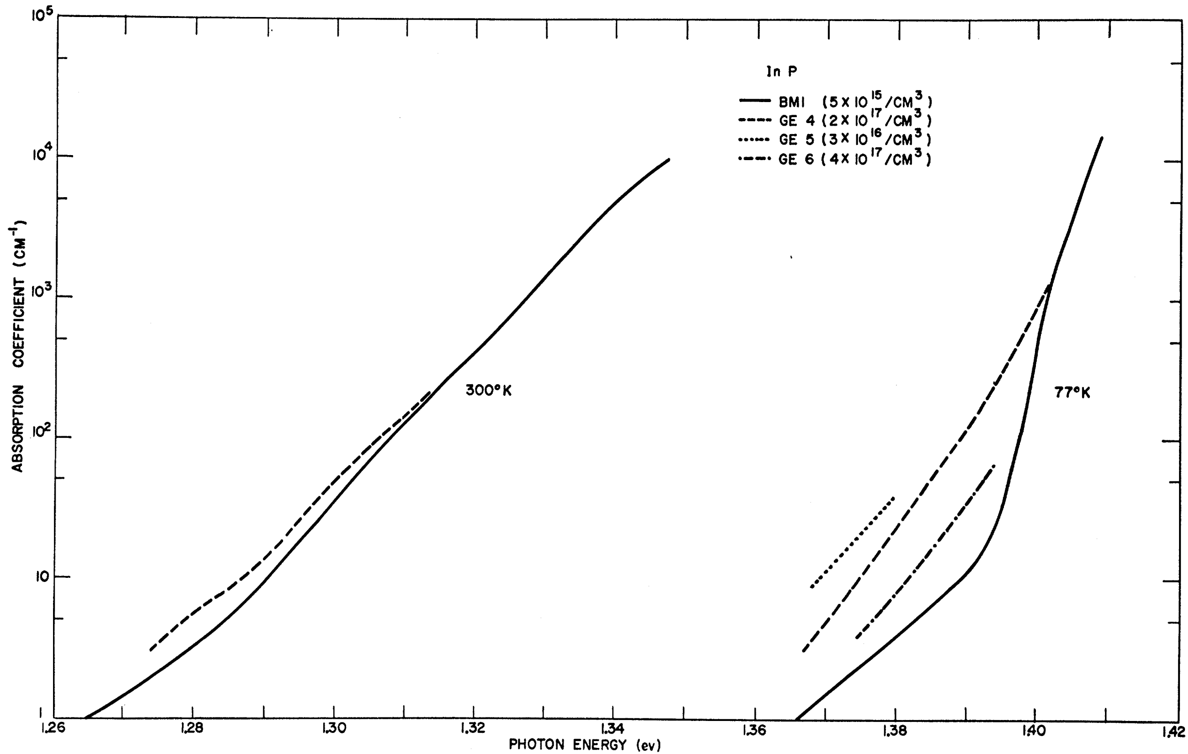

FIG. 1. Intrinsic absorption edge of InP at 77°K and 300°K. The different curves refer to different ingots as discussed in the text.

ever, until additional experimental evidence at higher absorption coefficient is obtained, or until one has greater theoretical understanding of the functional form (e.g., temperature dependence) of the absorption near the threshold, the question should not be regarded as settled.

A problem which remains is to understand the origin of the absorption below the break point for the BMI material and its relationship, if any, to the spectra of the General Electric (GE) material. We will consider only the low-temperature spectra where the differences between different materials are most pronounced. For comparison with the spectrum of the BMI material, we have shown a spectrum of one ingot of GE material over roughly the same total range of absorption coefficient and portions of the spectra of several other GE ingots of differing carrier density. The viewpoint that shall be adopted is that the spectra of the various ingots may be considered to result from a superposition of the absorption which we have characterized as due to direct processes and an absorption arising from a process of as yet undetermined origin. The magnitude of this latter process we suppose to be an extrinsic property. It is smallest in the BMI material and larger in the GE ingots.

Samples taken from the various ingots failed to show significant differences when inspected visually either with visible light in an ordinary microscope or in a polarizing microscope equipped with an infrared image converter to permit examination of the interiors of the samples. The densities of crystal boundaries and microscopic inclusions and the magnitude of the strain birefringence were comparable in all cases. No effects on the spectra were found with either annealing or thermal quenching. It is therefore not felt that the mechanical state of the samples would account for the observed differences in the spectra.

In a like manner it is not felt that the differing concentrations of free carriers could account for the observed effects. It would be expected that a free-carrier effect would be a monotonically increasing function of carrier concentration. This did not appear to be the case.

In a further attempt to characterize the material, mobilities were measured in the various samples as a function of temperature (300°K to 20°K). The BMI material had the highest mobility (3400 cm^2/volt sec at room temperature) and its temperature dependence showed a clear-cut separation into regions in which, respectively, lattice and impurity effects were dominant. The GE materials had much lower mobilities (1800 to 2400 cm^2/volt sec at room temperature) with no evidence for lattice scattering in the temperature range covered. In other measurements,[5,6] with samples having

[5] F. J. Reid and R. K. Willardson (to be published).

[6] M. Glicksman, data presented at Chicago American Physical Society Meeting, March, 1958 [Bull. Am. Phys. Soc. Ser. II, **3**, 120 (1958)].

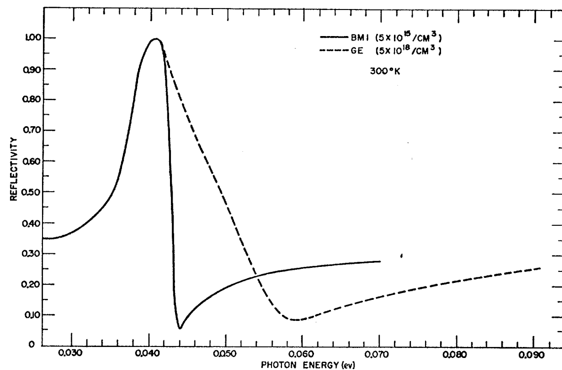

FIG. 2. Reflectance spectra (300°K) of InP for two samples having different free electron densities as noted.

free-carrier densities comparable with the highest (2 to 4 $\times 10^{17}/\mathrm{cm}^3$) used in this work, room temperature mobilities of about 4000 cm^2/volt sec have been obtained. All this indicates that the GE material contained much higher total concentrations of impurities than did the BMI material. It is therefore suggested that the differences in the absorption spectra might be understood in terms of an impurity effect. Specifically, if the impurity content were high enough, the impurity "tails" at the edges of the bands[7] could give rise to the enhanced absorption at lower energies. It is of interest that somewhat similar effects have been observed in highly compensated GaSb.[8]

B. Lattice Vibrations

Figure 2 shows the reflectance spectrum of the BMI material in the vicinity of the reststrahlen peak. It also shows the reflectance spectrum of a GE sample containing 5×10^{18} carriers/cm^3. The latter will be discussed below. From an analysis of the first curve (BMI) one can obtain the $k=0$ optical mode frequencies, $\hbar\omega_l \cong 0.043$ ev and $\hbar\omega_t \cong 0.036$ ev, the static dielectric constant, $\epsilon_0=15$, and the high-frequency dielectric constant, $\epsilon_\infty=10.6$. Similar data on InP have been obtained previously.[9] Complimentary to the reflectance data of Fig. 2, Fig. 3 shows a portion of the spectrum of a BMI sample in the lattice absorption range. The presence of the relatively weak subsidiary peaks in addition to the main lattice band is of interest. These subsidiary bands are presumably combination frequencies (e.g., optical and acoustical).

Using the reststrahlen frequency and the values of the static and high-frequency dielectric constants, it has been shown that polar scattering is the important lattice scattering contribution for the electron mobility.[10] To calculate the mobility, a simple conduction band with a minimum at $k=0$ and an effective mass of 0.07 was assumed. These assumptions are based on the belief that the InP band structure is similar to that of InSb and InAs. The results of the calculation give a temperature dependence for the mobility in good agreement with published data. The room-temperature mobility determined by lattice scattering alone is 6900 cm^2/volt sec. An independent calculation[5] which includes the effects of impurity scattering yields a mobility value in agreement with the observed mobility for uncompensated material.

The agreement between experimental and calculated mobilities lends strong support to the aforementioned band structure model. However, it should be pointed out that the sensitivity of the polar scattering contribution to the quantity $(\epsilon_0-\epsilon_\infty)$, with its relatively large experimental uncertainty, sets a limit on the reliability of the theoretical calculations and hence on the inferences concerning the reliability of the assumed effective mass value.

C. Free-Carrier Effects

Figure 4 shows the room-temperature free-carrier absorption in n-type InP. The curves show an absorption coefficient which varies as $\lambda^{2.5}$ and is proportional

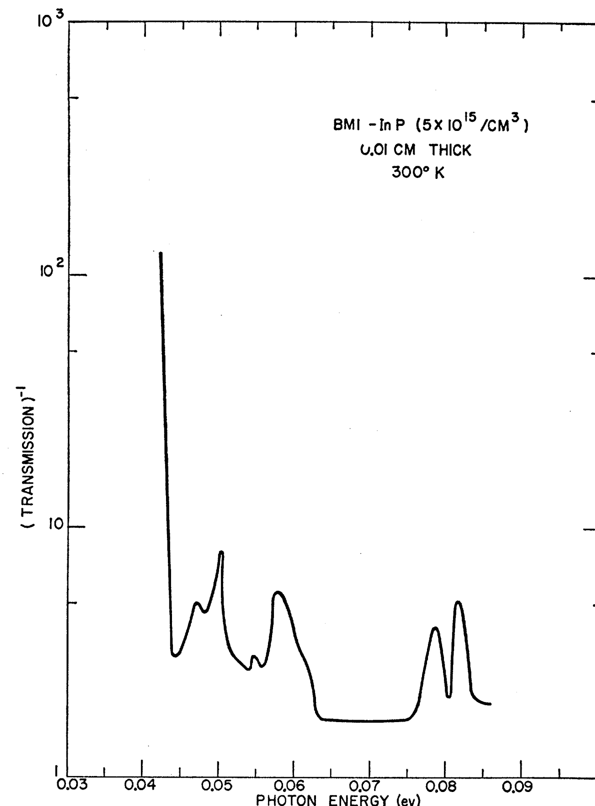

FIG. 3. Absorption spectrum (300°K) of an InP sample in the reststrahlen region.

[7] R. H. Parmenter, Phys. Rev. **97**, 587 (1955).
[8] A. K. Ramdas and H. Y. Fan, Bull. Am. Phys. Soc. Ser. II, **3**, 121 (1958).
[9] Picus, Burstein, and Henvis, Bull. Am. Phys. Soc. Ser. II, **2**, 66 (1957).
[10] H. Ehrenreich (to be published).

to free-carrier concentration. The effects of temperature in the 300°K to 77°K range were small.

The reflectivity spectrum of Fig. 2 for the sample with 5×10^{18} carriers/cm^3 (dashed curve) shows a minimum in the reflectivity at about 0.06 ev. (The reflectance spectra of the other samples available for measurement were indistinguishable from that of BMI.) It is believed that this minimum in the reflectance results from the contribution of the free carriers to the electric susceptibility in a manner described recently for Ge and InSb.[11] It can be shown that to a good approximation the frequency of this minimum is equal to $(1/2\pi)(4\pi ne^2/m^*\epsilon)^{\frac{1}{2}}$, where the symbols have their usual significance. Using this formula one calculates an effective electron mass of 0.2 electron mass unit for this case.

D. Further Discussion

It is not immediately obvious that the data that have been presented furnish a consistent picture of the conduction band structure of InP. The observation of an intrinsic absorption edge which appears to be due to direct transitions lends some support to the previously cited theoretical estimates that have been made for the conduction band parameters. It will be recalled that these estimates suggest that the band minimum occurs at the origin of the zone and that it is characterized by a small effective mass (0.07). Consistent with this is the observation, from magnetoresistance, of an isotropic mobility (or mass) for fairly pure InP.[6] On the other hand, the present reflectivity measurements have indicated a relatively large effective mass of 0.2 at the 5×10^{18} carriers/cm^3 level. Also magnetoresistance measurements on less pure samples have indicated an anisotropy in the effective mass with band minima located at points removed from the zone origin.[6] In summary, these various pieces of evidence suggest a picture in which the effective mass is a rather strong function of carrier concentration (or Fermi level), being characterized by an isotropic, small effective mass at low carrier densities and an anisotropic, larger effective mass at higher carrier densities. To determine if this interpretation was sustained by an entirely different type of measurement, the thermoelectric power was

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

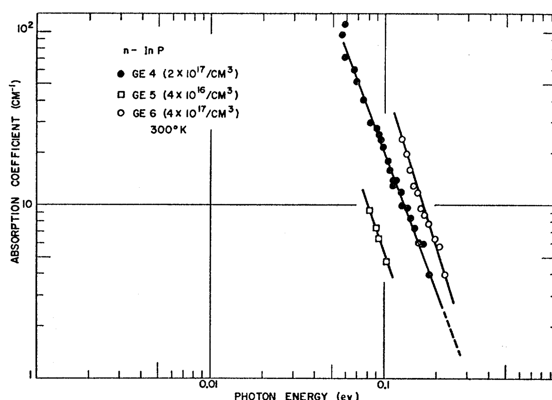

FIG. 4. Free-carrier absorption (300°K) in various InP samples.

measured at room temperature in a series of samples of differing carrier density. As examples of the results, at the low-concentration limit ($n=5\times10^{15}$/cm^3, $Q\cong-400$ μv/°C) the data, when analyzed according to the method of Howarth and Sondheimer,[12] indicate an effective mass of 0.03. For the most highly concentrated sample ($n=5\times10^{18}$/cm^3, $Q\cong-100$ μv/°C) the effective mass was calculated to be 0.2. The uncertainties in the analysis weaken the conclusions which can be drawn. However, they seem, at least, consistent with a small effective mass value at low concentrations, and the possibility of a strong concentration dependence of this value. If this picture is, indeed, correct, then at the present time the various evidence points toward the existence of a complex conduction band structure in InP with a minimum at the zone origin and other relative minima at other points in the zone at closely the same energy.

ACKNOWLEDGMENTS

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[12] H. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).