Exciton Absorption and Emission in InP

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Sharp peaks due to exciton formation have been observed in the intrinsic optical-absorption-coefficient data for undoped indium phosphide at 6, 20, and 77°K. At 298°K, the absorption data do not show a peak, because of thermal broadening. Low-temperature photoluminescence data obtained on the same InP used for absorption data exhibited an exciton emission peak at the same energy as the absorption peak and confirm the earlier identification of the emission line due to Turner and Pettit. At 6 and 77°K, the exciton peak energies are 1.416 and 1.409 eV, respectively. From the absorption data, the exciton binding energy at both temperatures is 0.0040 eV. The temperature dependence of the gap in the linear region above 100°K is -2.9×10^{-4} eV/°K, in sharp disagreement with the earlier value of Oswald.

INTRODUCTION

OVER the past 10 years, InP has received the attention of several workers, but the extensive materials research yielding pure crystals, as in the case of GaAs, has not been carried out. Consequently, fundamental optical data on relatively pure InP have not been available. Renewed activity in InP has been generated by Weiser and Levitt's[1] observation of laser action in InP diodes and Turner and Pettit's[2] observation of a sharp near edge photoinduced emission line in bulk InP, which they identified as an exciton recombination line. This latter interpretation rested on the similarity between InP and GaAs where Nathan and Burns[3] had earlier observed comparable photoluminescence spectra. Furthermore, Sturge[4] has published GaAs absorption data which supported their interpretation except for a small energy difference between Nathan and Burns' emission line and Sturge's "corrected" exciton absorption peak. There were no comparable absorption data for InP and there was a question as to whether the small energy difference between Nathan and Burns' data resulted from an error introduced by Sturge in correcting his absorption data or some fundamental difference in the exciton emission line and the absorption line. One possible example of the latter would be that Nathan and Burns observed an exciton bound to an impurity while Sturge observed the formation of the free exciton.

In this paper we shall present optical absorption data obtained on undoped samples of *n*-type indium phosphide in the region of the intrinsic edge at 6, 20, 77, and 298°K. These data show the formation of the exciton and provide the first InP absorption data from which the exciton energy, exciton binding energy, and intrinsic optical gap can be obtained. While Newman[5]

has reported data on relatively pure crystals up to $K = 10^4$ cm^{-1} at 77 and 298°K, he did not observe the exciton probably due to too large a Kx product or less perfect material. The earliest work of Oswald[6] was limited to absorption coefficients of less than 100 cm^{-1} and temperatures above 100°K.

In order to examine the energies of exciton absorption and emission lines, new photoluminescence data will be presented on the identical samples used for the absorption studies. These data show that within experimental error the emission and absorption exciton line in InP have the same energy. Thus the emission data are useful in providing a more complete curve of energy gap versus tempertaure.

EXPERIMENTAL

Single-crystal samples of InP with a net donor concentration of 5×10^{15} cm^{-3} were successively mechanically polished to eight thicknesses of from 0.17 cm to 6.9 μ for freely suspended samples. Two additional samples supported on glass were polished to 8.0 and
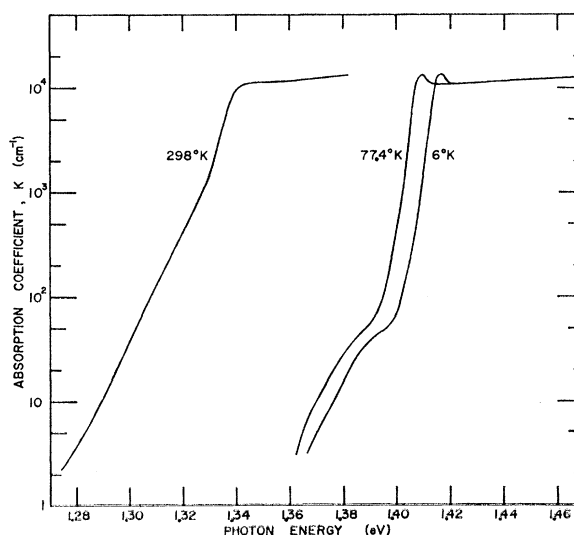

Fig. 1. Absorption coefficient of InP.

[1] K. Weiser and R. S. Levitt, Appl. Phys. Letters 2, 178 (1963).
[2] W. J. Turner and G. D. Pettit, Appl. Phys. Letters 3, 102 (1963).
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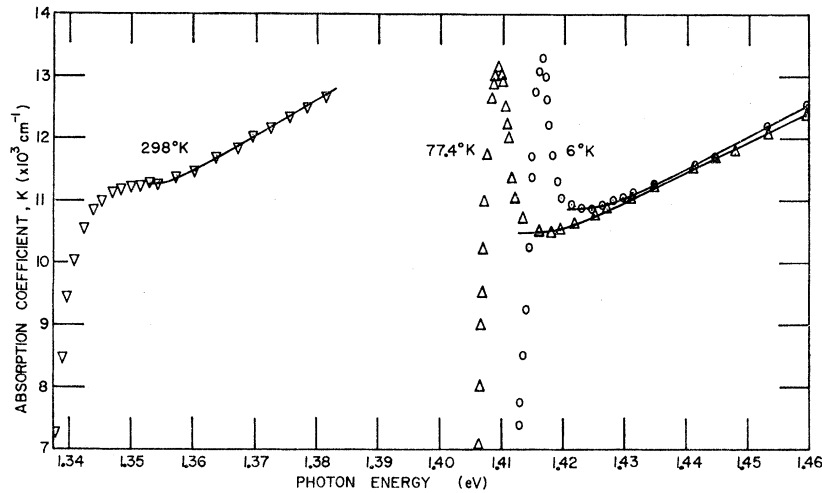[6] F. Oswald, Z. Naturforsch. 10a, 927 (1955); 9a, 181 (1954).

FIG. 2. Absorption of InP in the exciton region. The points are representative experimental values for a 4.4-μ-thick sample supported on glass. The low-temperature data have been corrected for strain as indicated in the text. The solid lines are a theoretical fit to Elliott's theory.

4.4 μ, respectively. In order to reduce mechanical damage the thinnest samples received a final chemical etch in a bromine-alcohol solution. The samples were placed in an exchange-gas cooling type of optical cryostat which made possible accurate determination of sample temperature. All absorption measurements were carried out in the monochromatic beam of a Cary 14R double-beam prism-grating monochrometer, which has a resolution <3Å and stray light of $<10^{-3}\%$ in the region of interest. Absorption coefficients were machine calculated from transmission data and a fixed value of reflectivity, R. Although R increases with photon energy, the effect on the value of the absorption is negligible when the product of absorption coefficient K and thickness x is kept between 0.6 and 6 as it was

in almost all our measurements. These limits of Kx product, coupled with a reduction of sample thickness by successive factors of two, insured excellent agreement of K from sample to sample. For the two glass supported samples, a strain correction was necessary at low temperature due to the difference in thermal-expansion coefficients for glass and InP.

The photoluminescence measurements were made on the identical material used for the absorption measurements. The samples were etched in bromine-alcohol solution and cooled to low temperature in an exchange-gas-type Dewar or for the lowest temperature (2°K), a liquid-helium immersion Dewar. Photoexcitation of hole and electron pairs was accomplished by light of photon energies greater than 2 eV from a filtered mercury arc. The emitted radiation was observed from that side of the sample which received the exciting radiation. A Perkin-Elmer 210 grating monochrometer and a cooled photomultiplier were used to measure the emission.

RESULTS AND DISCUSSION

A. Absorption

Figure 1 shows the absorption coefficient K in cm^{-1} versus photon energy in electron volts on a semilog plot for InP at 6, 77, and 298°K. The curves are composite curves made up of several experimental runs per thickness and 10 separate thicknesses with the previously mentioned limits on Kx product to provide accurate results. Data taken at 20°K are not shown in this figure because they essentially coincide with the 6°K data. For the three low temperatures, the absorption curves exhibit a sharp peak due to exciton formation. Figure 2 shows the region of high absorption coefficient on a linear plot of K versus photon energy. The points are typical experimental values measured on the 4.4-μ-thick sample of InP which was supported by a thin glass slide. The 77 and 6°K data have been
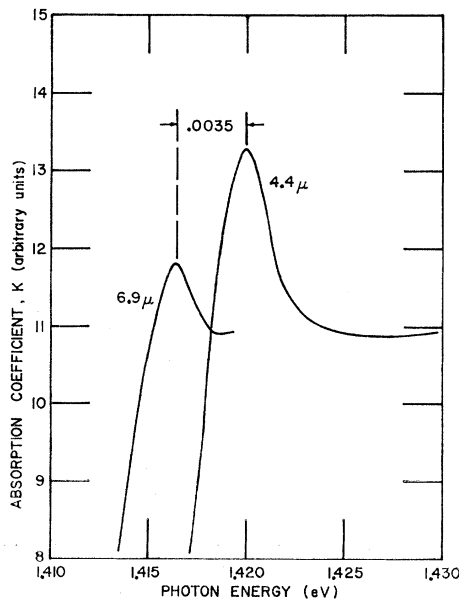

FIG. 3. Comparison of InP exciton absorption for 6.9-μ freely suspended sample and 4.4-μ glass-supported sample at 6°K.
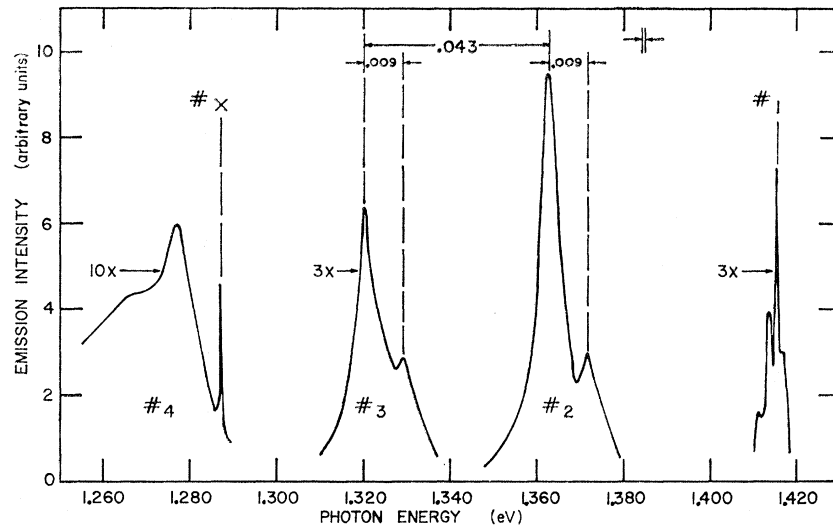
FIG. 4. InP photoluminescence data at 2.2°K. The experimental accuracy of this data is ±0.0005 eV.

energy-corrected for the strain shift which was introduced by the glass support. At 6°K this shift was 0.0035 eV and was obtained by comparison of the exciton peak energy observed for a 6.9-μ freely suspended sample and the observed energy for the 4.4-μ-thick glass-supported sample. Figure 3 shows the data at 6°K. While the 6.9-μ sample is too thick to give the correct peak height, the energy of the center of the peak is clearly 3.5 mV lower than the peak energy for the 4.4-μ glass-supported sample. Returning to Fig. 2, it can be seen that the 298°K data show the effect of thermal broadening of the exciton in contrast to the sharp exciton peak observed at low temperature. The solid curves are a result of a theoretical fit of the energy dependence of the absorption coefficient at energies greater than the energy gap. The expression was derived by Elliott for direct allowed optical transitions between nondegenerate parabolic energy bands including the contributions due to exciton formation.[7] However, Sturge[4] has recently applied Elliott's theory to GaAs which has nonsimple valence bands as does InP. The expression used is given in Eq. (1)

$$K = K'(\epsilon_g) \exp z / 2 \sinh z ,$$

$$z = \pi [\epsilon_x / (h\nu - \epsilon_g)]^{1/2} , \quad (1)$$

where $K'(\epsilon_g)$ is the value of the absorption coefficient at the energy gap, ϵ_x is the binding energy of the exciton,

and ϵ_g is the energy gap equal to the exciton peak energy, $\epsilon_p + \epsilon_x$. To obtain the fits seen in Fig. 2 the value of the absorption coefficient at the minimum on the high-energy side of the exciton was used as $K'(\epsilon_g)$ and the value of ϵ_x was varied to get the best fit. Thus ϵ_g was determined as $\epsilon_p + \epsilon_x$ at low temperature. At 298°K, where the exciton peak is unresolved, the value of ϵ_g was obtained by varying both ϵ_g and ϵ_x to obtain a fit. The results of the fit are given in Table I. The accuracy of the exciton peak energy, exciton binding energy, and energy gap are, respectively, ±0.0013, ±0.0002, and ±0.0015 eV at low temperature and twice these values at 298°K.

TABLE I. Energy of exciton peak, ϵ_p, exciton binding energy, ϵ_x, and energy gap, ϵ_g.

T °K	ϵ_p (eV)	ϵ_x (eV)	ϵ_g (eV)
6	1.4165	0.0040	1.4205
20	1.4165	0.0040	1.4205
77	1.4095	0.0040	1.4135
298	1.3475	0.0036	1.3511

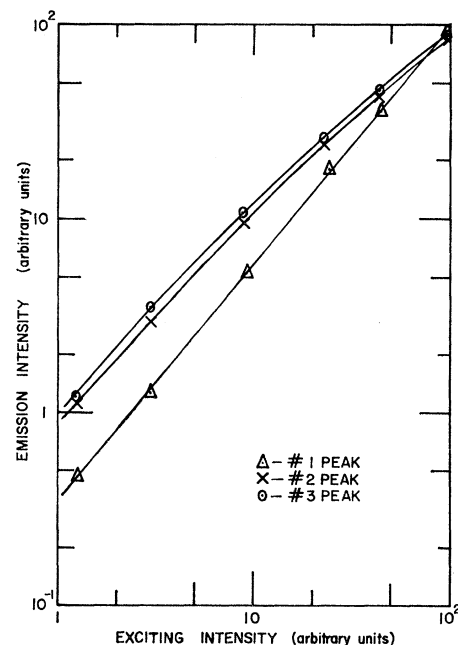[7] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

FIG. 5. Intensity dependence of emitted light as a function of intensity of excitation.
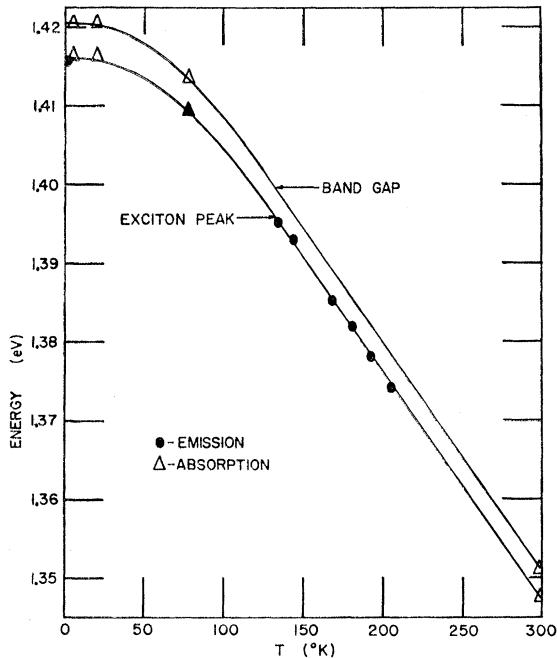
FIG. 6. Energy gap and exciton peak energies versus temperature from absorption data (Δ) and emission data (0).

It is of interest to compare the exciton binding energy deduced from the absorption data with the value one calculates from simple theory, which is conveniently given as $\epsilon_x = \mu^* 13.6 \text{ eV}/k^2$, where $\mu^* = \mu/m_0$, and μ is the reduced mass of the exciton; m_0 is the mass of a free electron; k is the static dielectric constant, taken here as 12.09.[8] The value of μ is 0.043 m_0 from $\mu^{-1} = m_e^{-1} + m_h^{-1}$ where $m_e = 0.077 m_0$ from infrared cyclotron-resonance data on InP[9] and $m_h = 0.1 m_0$ as in GaAs. This latter value has been assumed, since the band-structure contants for the degenerate valence bands of InP have not been published and it is reasonable to use Ehrenreich's GaAs values.[10] Based on the foregoing numbers, one calculates $\epsilon_x = 0.0040$ eV in excellent agreement with the values deduced from the fit of the absorption data.

B. Emission

Figure 4 shows the photoluminescence data obtained at 2.2°K on the identical material used for the absorp-

tion studies. Line 1 is seen to have the same energy, within experimental error of 0.001 eV, as the 6°K absorption exciton shown in Fig. 2. Lines 2, 3, and 4 are due to recombination through an impurity center with the emission of 0, 1, 2, or more longitudinal optical phonons as previously reported.[2] The structured or doublet nature of these lines was first seen at the lowest temperature in the material used for the present investigation. The ~ 0.009 eV separation of the lines of the doublets agrees reasonably well with recently determined energy of the transverse acoustic phonon.[8] Thus the impurity lines are recombinations through a shallow impurity with the emission of 0 or 1 TA phonon as well as the 0, 1, or 2 LO phonons. One line, X, of unknown origin, exists which is sharper than the other impurity lines and masks the 0 TA line of #4. The spacing of lines 1 and 2 is almost the same as the longitudinal optical phonon but as previously reported, the linewidth and temperature dependence are entirely different.[2] Furthermore, Fig. 5 shows that intensity dependence of the emitted light with exciting intensity is different for line #1 than for lines #2 or #3. This suggests that the origin of line #1 is different from that of the other lines. The absorption data of Fig. 1 and 2 taken with other facts from luminescence data support the original identification of line 1 as an exciton emission line.

SUMMARY

Figure 6 shows the energy gap and exciton peak energy versus temperature as determined from absorption data and emission data. As stated previously, the exciton absorption and emission peak energies are the same within experimental error. The temperature dependence of the energy gap in the linear region above 100°K from either curve is -2.9×10^{-4} eV/°K in contrast to the previously accepted value of -4.6×10^{-4} eV/°K given by Oswald.[6]

ACKNOWLEDGMENTS

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