Optical Properties of *n*-Type Indium Arsenide in the Fundamental **Absorption Edge Region**

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The optical properties of InAs in the fundamental absorption edge region have been studied experimentally as a function of impurity content over a temperature range extending from 18° to 300°K. The addition of donor impurities moves the absorption edge to higher energies and changes its shape in accordance with the theory of Burstein. For nondegenerate material the energy dependence of absorption coefficients larger than 10^3 cm⁻¹ is $\alpha^2 = 3.0 \times 10^8 \ (E - 0.35) \ \mathrm{cm}^{-2}$ at room temperature and is in good agreement with calculations by Stern based on a nonparabolic conduction band. Absorption coefficients below 10³ cm⁻¹ depend exponentially upon energy down to at least 3 cm⁻¹, a result which has not yet been explained. The addition of acceptor impurities to the purest material available moves the absorption edge to lower

I. INTRODUCTION

HE fundamental absorption edge region of indium arsenide, an intermetallic compound semiconductor, has been studied previously.¹⁻⁵ As a consequence, many of the general characteristics of the infrared absorption in this spectral region are well established. However, significant discrepancies do exist in the early results. For example, the values reported for the width of the forbidden energy gap at room temperature range from 0.31 to 0.36 ev,²⁻⁶ and values given for the temperature coefficient of the forbidden energy gap vary from -2.5×10^{-4} to -4.5 $\times 10^{-4}$ ev/°K.^{2,5,7,8} Recently, single-crystal material of higher purity than used by most of the previous workers has become available to us. Using this material we have repeated some of the early work. We have made no effort to resolve the existing discrepancies because this would have required detailed information about materials and experimental conditions which was not available to us. Our results do suggest, however, that the discrepancies in the early work are related to the fact that the position and shape of the absorption edge is sensitive to the impurity content. These impurity effects have been studied in detail. In addition, the experimental work has been extended into regions which are of particular interest because of recent theoretical studies of the band structure of InAs.9-11

energies by an amount which increases with the acceptor concentration. When 2.4×10^{17} cm⁻³ acceptor atoms are added, the absorption edge measured at 100 cm^{-1} is shifted by 0.013 ev. The temperature dependence of the forbidden energy gap was found to be linear from 300° to 80°K with a temperature coefficient of -2.8×10^{-4} ev/°K. Below 80°K the change of the energy gap with temperature becomes smaller and nonlinear. It is estimated that lattice dilation accounts for only one-fourth of the total variation of the energy gap with temperature. The radiative lifetime of added carriers in intrinsic material at room temperature was calculated from the optical constants by the method of van Roosbroeck and Shockley and was found to be 1.3×10^{-5} sec.

II. EXPERIMENTAL

Transmission measurements were made using a Perkin-Elmer model 12B spectrometer with a lithium fluoride prism. In some cases, when the optical samples were very small, an infrared microscope attachment¹² was used which served to produce an image of the exit slit reduced by a factor of 8.5 at the position of the sample. In this way transmission measurements were made on samples having areas as small as 0.1×0.1 mm². The slits were adjusted to give resolutions varying from 0.001 to 0.008 ev, depending upon the part of the spectrum being studied. In all cases it was established that the resolutions were small enough so that the measured spectral structure was independent of slit width. Low-temperature measurements were made using an optical cell similar to that described by Duerig and Mador.13

InAs was produced by reacting the components in an evacuated sealed Vycor container as described previously.¹⁴ The ingots prepared in this way consisted of large single-crystal sections from which samples were cut. Parallel flat surfaces of the samples were polished using a beeswax lap and aluminum oxide powder. Sample thicknesses varied from 3μ to 1 mm and were determined either by direct measurement or by using interference fringes. Unsupported samples having thicknesses less than 30 μ were difficult to prepare and handle without breaking. For this reason such samples were often attached to a sapphire backing with glycol phthalate, a thermoplastic resin. The absorption of the very thin layer of resin involved was found to be negligible in the spectral regions studied.

¹ H. J. Hrostowski and M. Tanenbaum, Physica 20, 1065 (1954).

 ² F. Oswald, Z. Naturforsch. 10a, 927 (1955); 14a, 374 (1954);
 ³ F. Stern and R. M. Talley, Phys. Rev. 100, 1638 (1955).
 ⁴ W. G. Spitzer and H. Y. Fan, Phys. Rev. 106, 882 (1957).
 ⁵ F. Matossi, Z. Naturforsch. 13a, 767 (1958).
 ⁶ S. Zwerdling, B. Lax, and L. M. Roth, Phys. Rev. 108, 1402 (1977). (1957)

⁷ R. M. Talley and D. P. Enright, Phys. Rev. 95, 1092 (1954).

 ⁸ O. G. Folberth, O. Madelung, and H. Weiss, Z. Naturforsch.
 9a, 954 (1954).
 ⁹ F. Stern, Bull. Am. Phys. Soc. 2, 347 (1957).

 ¹⁰ F. Stern and J. R. Dixon, J. Appl. Phys. 30, 268 (1959).
 ¹¹ F. Stern, Proceedings of the International Conference on Semiconductor Physics in Prague, 1960 (to be published).

¹² V. J. Coates, A. Offner, and E. H. Siegler, J. Opt. Soc. Am. **43**, 984 (1953). ¹³ W. W. Duerig and I. L. Mador, Rev. Sci. Instr. **23**, 421

^{(1952).} ¹⁴ D. P. Enright, Naval Ordnance Laboratory Report 6024

^{1958 (}unpublished).

Absorption coefficients α were calculated from the transmissions T using the relationship¹⁵

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

where *d* is the sample thickness, and *R* is the reflectivity. The reflectivity was measured directly and was found to have a constant value of 0.31 through the absorption edge region. For samples glued to a sapphire backing, an effective reflectivity of 0.22 was used. This was determined by comparing the results obtained from transmission measurements on a sample before and after it was mounted. The difference between the two reflectivities is due to the substitution of glue for air at the second reflecting surface of the sample. The effective reflectivity of mounted samples is a slowly varying function of αd . The value stated above applied to large values of αd for which the last term in the denominator of Eq. (1) is negligible. The data reported were taken from this range.

The carrier concentrations *n* stated in the paper were calculated from values of the Hall coefficient, R_H (cm³/coul), measured at room temperature using the relationship $n = 7.0 \times 10^{18} / R_H \text{ cm}^{-3}$.

III. RESULTS AND DISCUSSION

A. Position of the Edge as a Function of **Carrier Concentration**

The experimental curves A, B, and C of Fig. 1 give the energy dependence of the absorption coefficients for *n*-type materials of relatively low compensation prepared so as to have carrier concentrations ranging from 3.6×10^{16} to 3.8×10^{18} cm⁻³ as indicated on the figure. It can be seen that as the carrier concentration increases the curves shift to higher energies. This effect was first explained by Burnstein¹⁶ for InSb and was studied later by Stern and Talley³ for the case of InAs as well as InSb. The shift of the optical absorption edge is due to the fact that materials like InAs and InSb have low densities of states near the bottom of the conduction band and become degenerate at relatively small carrier concentrations. The Fermi level moves up into the band as the carrier concentration increases, making optical transitions to lower states less probable and, as a result, the absorption edge moves to higher energies. The data of Stern and Talley were limited to the low-absorption region. The data of Fig. 1 represent an extension of their work to high absorption coefficients.

B. Energy Dependence of the Absorption Coefficient

All the curves of Fig. 1 are identical at high absorption coefficients. This is to be expected since the high-energy

¹⁵ H. Y. Fan, *Reports on Progress in Physics* (The Physical Society, London, 1956), Vol. 19, p. 107. ¹⁶ E. Burstein, Phys. Rev. 93, 632 (1954).





FIG. 1. The fundamental absorption edge of n-type InAs at room temperature and its dependence upon carrier concentration.

optical transitions involved are to the upper portions of the conduction band and should not be affected by the carrier density. At low absorption coefficients the shapes of the curves differ. Curve A for the purest sample has a much steeper slope than those of curves B and C. This result is, also, to be expected. The Fermi level of sample A is near the bottom of the conduction band whereas samples B and C are degenerate and have Fermi levels which are considerably higher. For the former case the values of the absorption coefficients are characteristic of transitions to the states in the conduction band which are nearly all empty. Such absorption coefficients would be expected to increase rapidly with energy in the edge region. However, for a degenerate sample the absorption coefficients α are reduced by the fact that many of the states in the conduction band are occupied and, consequently, not available for optical transitions. The occupancy of these states is described by the Fermi distribution function. Thus, for a degenerate sample at room temperature the increase in the absorption coefficient with increasing energy would be less abrupt than for a nondegenerate sample.

For a given photon energy, $h\nu$, the total absorption coefficient α_T is given by

$$\alpha_T(h\nu) = \alpha_1(h\nu) f\left(\frac{E_F - E_1}{kT}\right) + \alpha_2(h\nu) f\left(\frac{E_F - E_2}{kT}\right), \quad (2)$$

where α_1 and α_2 are, respectively, the absorption coefficients which would be associated with transitions from the heavy and light hole bands to states at energies E_1 and E_2 in the conduction band, if all these states were empty. f is the probability that the states in the conduction band are unoccupied, and is given by $[1+e^{(E_F-E)/kT}]^{-1}$. E_F is the energy of the Fermi level. The energy E_2 is less than E_1 by an amount which is determined by the relative curvatures of the light and heavy hole bands, and the conduction band. If it is assumed that the conduction and valence bands are parabolic and that the contribution of α_2 to the total absorption is small, then Eq. (2) can be written in the form given by Kaiser and Fan¹⁷:

$$h\nu = E_G + \{E_F - kT \ln[(\alpha_1/\alpha_T) - 1]\} [1 + (m_e/m_h)]. \quad (3)$$

 E_G in this expression is the width of the forbidden energy gap, and m_e and m_h are the effective masses of the electrons and heavy holes. It follows from Eq. (3) that for $\alpha_T \ll \alpha_1$ the slope of a $\ln \alpha_T$ vs $h\nu$ plot for degenerate samples should be $\{kT[1+(m_e/m_h)]\}^{-1}$, assuming a constant α_1 . The ratio m_e/m_h is small for InAs and contributes little to the slope. We have used a value of 0.056 for this ratio. The theoretical slope is drawn in Fig. 1 and includes a small correction to take into account the variation of α_1 with energy as given by curve A in its plateau region. The theory is in good agreement with the experimental data for sample C. In addition, the slope of the experimental curve varies with temperature as predicted down to the lowest temperature studied, which was 78°K.

The positions of the Fermi level for samples B and C can be determined by fitting Eq. (3) to the corresponding absorption curves. In doing this, E_{G} was taken as 0.35 ev and it was assumed that α_1 is given by curve A. A good fit was obtained in both cases for values of α_T above 1000 cm⁻¹. At lower absorption coefficients, values deduced from Eq. (3) fall slightly below the experimental data. This is possibly due to the contribution of absorption mechanisms which have not been taken into account in the derivation of Eq. (3). In this connection, it should be pointed out that the near-coincidence of curves A and B for absorption coefficients less than 60 cm⁻¹ is not in agreement with simple model described above. According to this model curve B would be shifted to higher energies than curve A by approximately 0.02 ev for all values of α in this range. It is possible that the near-coincidence is due to a lowering of the bottom of the conduction band resulting from the addition of donor impurities. Such an effect has been predicted by Stern and Talley.³ Their calculations indicate that for sample B, the corresponding shift in the edge to lower energies would be 0.03 ev. In general, the mechanisms controlling optical absorption for small absorption coefficients are not well understood and are sensitive to impurity effects as discussed in Sec. III.C. Regardless of their origin, the shifts of the experimental curves from the ones to be expected on the basis of the simple model are



FIG. 2. Position of the Fermi level at absolute zero measured from the bottom of the conduction band as a function of carrier concentration in *n*-type InAs. The experimental points apply to samples B and C of Fig. 1. The calculated curve is based on the density of states masses given as a function of donor concentration by Stern. The vertical lines attached to the experimental points represent the maximum variations which would be expected by taking into account the nonparabolic nature of the conduction band and the contribution of transitions from the light hole band.

small and would be expected to have little effect upon the results reported here.

The position of the Fermi level determined from Eq. (3) has been plotted as a function of carrier concentration in Fig. 2. The ordinate represents the shift in the Fermi level with respect to the bottom of the conduction band. The usual relationship¹⁸ for the temperature dependence of the Fermi level has been used to shift these data so that they apply to a temperature of 0°K. This was done to permit direct comparison with the theoretical curve represented by the solid line which applied to InAs at absolute zero. The accuracy of the experimental points is dependent upon the validity of the assumptions on which Eq. (3) is based. The assumptions were that the bands are parabolic and that the absorption associated with the transitions from the light-hole band is negligible.¹⁹ Estimates of the errors involved have been made on the basis of previous band-structure calculations.9,20 The maximum variations which would be expected as a result of taking into account the nonparabolic nature of the conduction band and the contribution of transitions from the lighthole band would be reductions of point B by 8% and of point C by 10%. These percentages are represented in the figure by the vertical lines attached to the experimental points. The theoretical curve was calculated using the density-of-states masses given as a function

¹⁷ W. Kaiser and H. Y. Fan, Phys. Rev. 98, 966 (1955).

¹⁸ A. J. Dekker, *Solid State Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1957), p. 216. ¹⁹ A tacit assumption which has been made in deriving Eq. (3)

¹⁹ A tacit assumption which has been made in deriving Eq. (3) is that the bands do not shift relative to one another as a function of donor concentration. Stern and Talley (reference 10) have shown that the conduction band is lowered by the addition of donors. It is expected that donors will also lower the valence band. The latter effect has not yet been studied theoretically. For this reason, our data are not corrected for the relative band shifts.

 $^{^{20}}$ We are indebted to Dr. Frank Stern of our Laboratory for making unpublished results of absorption coefficient calculations available to us. The calculations were based on the parameters given in reference 9.

temperature.

of donor concentration by Stern.⁹ The band-structure calculations which led to the density-of-states masses were based upon a rather arbitrary choice of parameters. The fact that the experimental data deviate by a maximum of 12% from the theoretical curve indicates that the choice of parameters was not an unreasonable one. The density-of-states masses determined from the experimental Fermi levels taken to be at the midpoints of the deviation lines in the figure are 0.028m and 0.038m for points B and C, respectively, where m is the free electron mass. These are to be compared with the corresponding values of 0.028m and 0.035m calculated by Stern.

The absorption coefficients associated with the nondegenerate sample A at room temperature also vary exponentially with energy in the low-absorption range, but much more rapidly than the coefficients associated with the degenerate material. This is illustrated by the data of Fig. 3. These data can be described by the relationship

$$\alpha = A \exp(E/kT_{\rm eff}), \tag{4}$$

200000

0.37

LIMIT OF RESOLUTION

0.33 0.34 0.35 0.36

PHOTON ENERGY (EV)

where the effective temperature $T_{\rm eff}$ is 80°K, in approximate agreement with a result of Matossi.⁵ The effective temperature was found to be dependent upon crystal temperature, being approximately 15°K at a crystal temperature of 78°K. A similar exponential dependence has been reported for several other materials.21 However, in these cases the effective and crystal temperatures were the same. Kurnick and Powell²² have asserted that the lower portion of the absorption edge region of InSb can also be described by Eq. (4) with the effective temperature equal to the crystal temperature. An examination of their data indicates, however, that the effective temperatures are considerably lower than reported. For example, $T_{\rm eff}$ for the purest sample (b) at room temperature appears to be approximately 60°K rather than 300°K as implied

10

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COEFFICIENT

ABSORPTION

10

3

FIG. 3. The exponential energy dependence of the absorption coefficients below 103 cm⁻¹ applying to nondegenerate sample A of Fig. 1 at room temperature.

²¹ References and a discussion are found in T. S. Moss, Optical Properties of Semiconductors (Academic Press, Inc., New York, 1959), p. 39.
²² S. W. Kurnick and J. M. Powell, Phys. Rev. 116, 597 (1959).

0.32



by Kurnick and Powell. No mechanisms have been proposed which are consistent with any of the results described above. It is possible that phenomena of this type are related to a tailing-off of the density of states into the forbidden band. Such a tailing-off resulting from various crystal imperfections has been predicted theoretically.23,24

The energy dependence of the absorption coefficient which is to be expected in the region of large absorption coefficients has been studied theoretically. It has been shown²⁵ for materials which have parabolic conduction and valence bands that near the edge

$$\alpha \propto (h\nu - E_G)^{\frac{1}{2}}/h\nu, \qquad (5)$$

where E_G is the width of the forbidden energy gap and $h\nu$ is the photon energy. This expression is based on the assumption that the matrix element for optical transitions is constant and that the transition at k=0 is allowed. Thus, near the absorption edge α^2 would be linear in $h\nu$. The data of curve A replotted in Fig. 4 so as to test this relationship fall on a straight line over an extended energy range and are represented by α^2 $=3.0\times10^{8}$ (E-0.35) cm⁻². This result is not in complete agreement with Eq. (5), which is represented by curve 1 in the figure. The discrepancy is due to the fact that the parabolic band and constant transition matrix element approximations on which the theory was

²⁸ P. Aigrain, Physica **20**, 978 (1954); R. H. Paramenter, Phys. Rev. **97**, 587 (1955); H. L. Frisch and S. P. Lloyd, *ibid*. **120**, 1175 (1960).

²⁴ M. Lax and J. C. Phillips, Phys. Rev. 110, 41 (1958).

 ²⁵ J. Bardeen, F. J. Blatt, and L. H. Hall, *Photoconductivity Conference*, edited by Breckenridge *et al.* (John Wiley & Sons, Inc., New York, 1956), p. 149.

based are not applicable to InAs over the energy interval shown in Fig. 4. Calculations by Stern¹¹ based on Kane's band-structure model, which take variations of these quantities into account, yield an energy dependence of the absorption coefficient which is consistent with the experimental data over the energy interval from 0.35 to 0.50 ev. The two dashed lines 2 and 3 represent his results for effective masses of 0.020m and 0.025m at the bottom of the conduction band. From a comparison of the theoretical and experimental results Stern concludes that the effective mass at the bottom of the conduction band in InAs is $0.024m \pm 0.003m$. This value is in agreement with the value of $0.023m \pm 0.002m$ obtained by Palik and Wallis²⁶ from measurements of the infrared cyclotron resonance absorption.

The intercept of the experimental curve of Fig. 4 yields a value of 0.35 ev for the width of the forbidden energy gap at room temperature. This is to be compared with the values reported by other workers for non-degenerate InAs which range from 0.31 to 0.36 ev.²⁻⁶ It is likely that this variation is partly due to the different criteria used by the authors to define the position of the edge. However, a study of the data upon which these values were based indicates that the differences in the criteria cannot completely account for the variation.

C. Position of the Edge as a Function of Acceptor Concentration

A possible explanation for the discrepancies described above is that the position of the absorption edge depends upon the impurity content, a factor which was probably not well controlled in the early experiments. It has been reported that the absorption edges of indium antimonide,²² and gallium arsenide and cadmium telluride²⁷ move to smaller energies as the acceptor concentration is increased. We have found that a similar shift occurs in InAs as shown in Fig. 5. The data represented by the squares apply to the purest InAs available to us, the Hall coefficient and electron mobility at liquid nitrogen temperature being -381cm³/coul and 57 000 cm²/v-sec. The other two sets of data apply to materials prepared by adding zinc acceptor impurities to the pure material as indicated in the figure. These curves are shifted to lower energies by an amount which increases with acceptor concentration and which is strongly dependent upon the absorption coefficient. For an acceptor concentration of 2.4×10^{17} cm⁻³, the shift measured at an absorption coefficient of 100 cm⁻¹ is 0.013 ev. The slopes of the exponential portions of the curves decrease as the acceptor concentrations increase, a behavior which is similar to that reported for InSb.²² The curves applying to the doped materials were not extended to lower energies because



FIG. 5. The fundamental absorption edge of n-type InAs at room temperature and its dependence upon acceptor concentration. The two p-type samples were prepared by adding zinc to the relatively pure material.

transitions between the light- and heavy-hole bands contribute significantly to the absorption in this region.

Eagles has proposed²⁷ that shifts in the absorption edge associated with the addition of acceptor impurities are due to electronic transitions between shallow acceptor levels and the conduction band. He has derived a relationship for the absorption coefficient associated with transitions from a single acceptor level to the conduction band. By summing such single-level absorption coefficients over a distribution of acceptor states he obtained agreement between theory and experiment for the case of gallium arsenide. The distribution of states was taken from the work of Lax and Phillips²⁴ dealing with the impurity band arising from a random one-dimensional array of interacting impurities. It was assumed by Eagles that these results were applicable to the three-dimensional situation. We have applied Eagles' theory to the case of InAs and have found that it indicates that absorption coefficients at low energies such as 0.34 ev in the figure should be proportional to the acceptor concentration. This prediction is substantiated by our experimental results. On the other hand, the theoretical energy dependence of the absorption coefficient is considerably weaker than found experimentally. It is possible that the discrepancy is due to other absorption mechanisms such as phononassisted transitions which have not been taken into account. Another possibility is that the discrepancy is due to a failure of some of the simplifying assumptions on which the theory is based and which have been discussed by Eagles.

D. Temperature Dependence of the Forbidden Energy Gap

The temperature dependence of the forbidden energy gap of nondegenerate, *n*-type InAs is shown in Fig. 6. The positions of the fundamental absorption edge, which were equated to the corresponding forbidden energy gaps, were determined by extrapolations of α^2 vs *E* plots to zero absorption. This method is based

 ²⁶ E. D. Palik, and R. F. Wallis, Phys. Rev. 123,131 (1961).
 ²⁷ D. M. Eagles, J. Phys. Chem. Solids 16, 76 (1960).

upon the band-structure considerations described in Sec. III.B. The temperature dependence is linear from 300° to approximately 80°K with a temperature coefficient of $(-2.8\pm0.1)\times10^{-4}$ ev/°K. Previously reported values of the temperature coefficient range from -2.5×10^{-4} to -4.5×10^{-4} ev/°K.^{2,5,7,8} When the linear part of the curve is extrapolated to absolute zero, the corresponding gap is found to be 0.44 ± 0.01 ev. This is considerably smaller than the value of 0.47 ± 0.02 ev determined by Folberth et al.⁸ from linear extrapolations of electrical measurements taken at temperatures above 350°K. Below 80°K the change in the energy gap with temperature becomes smaller and nonlinear. This behavior is similar to that reported for Ge,28 and InSb and GaSb.29

Two mechanisms have been associated with the temperature dependence of the energy gap in semiconductors:

(1) A shift in the relative position of the conduction and valence bands due to the temperature-dependent dilation of the lattice.³⁰

(2) A shift in the relative position of the conduction and valence bands due to a temperature-dependent electron-lattice interaction.³¹

The relative significance of these two mechanisms can be estimated by evaluating the change in the energy gap due to lattice dilation as given by the relation³²

$$(\partial E_G/\partial T)_p = -(3\beta/K)(\partial E_G/\partial p)_T, \qquad (6)$$

where β and K are, respectively, the coefficient of linear expansion and the compressibility, and $(\partial E_G/\partial p)_T$ is the rate of change of the energy gap with pressure at constant temperature. Using this equation and the values $\beta = 5.3 \times 10^{-6}$ (°C)⁻¹,³³ $K = 1.25 \times 10^{-12}$ cm²/d,³⁴ and $(\partial E_G / \partial p)_p = 5.5 \times 10^{-6}$ ev/atm,³⁵ it is found that $(\partial E_G/\partial T)_p = -7 \times 10^{-5}$ ev/°K. Thus lattice dilation accounts for only one-fourth of the total variation of

- ²⁹ V. Roberts and J. E. Quarrington, J. Electronics 1, 152 (1955).
 ³⁰ J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).
 ³¹ H. Y. Fan, Phys. Rev. 82, 900 (1951).

³² H. Brooks, in Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955),

³³ H. Welker and H. Weiss, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3, p. 51.

³⁴ Measurements of the elastic constants of InAs have not been reported in the literature. The value of K stated here is an estimate based on the approximate constancy of the ratio V/kT_m when applied to various solids. [C. Zwikker, *Physical Properties* of Solid Materials (Interscience Publishers Inc., New York, 1954), p. 159.] V and T_m are the molar volume and melting point, respectively. Our estimate was made using InSb as a reference. The constancy of the ratio was tested for the cases of Ge, Si, InSb, and GaSb using the elastic constant given by Huntington. [H. B. Huntington, in Solid-State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, pp. 274 and 276.] The ratios applying to these materials varied by less than 25% from their average value. ³⁵ J. H. Taylor, Phys. Rev. 100, 1593 (1955).



FIG. 6. Temperature dependence of the energy gap of nondegenerate, *n*-type InAs. The energy gaps were determined by extrapolations of α^2 vs *E* plots to zero absorption.

the energy gap with temperature. This result is similar to that obtained by Ehrenreich³⁶ who found for the case of indium antimonide that the lattice dilation accounts for only one-third the total variation of the energy gap with temperature.

E. Radiative Lifetimes

Van Roosbroeck and Shockley³⁷ have shown that the lifetimes associated with the direct recombination of electrons and holes in a solid can be determined from optical properties of the material being considered. Their relationship for the radiative lifetime associated with small disturbances in the equilibrium carrier concentration is

$$\tau = np/(n+p)\mathfrak{R},\tag{7}$$

where n and p are the electron and hole concentrations and \mathfrak{R} is equal to the rate of radiative recombination per unit volume. R can be determined if the index of refraction and the absorption coefficients associated with transitions across the forbidden gap are known as a function of energy. Using the absorption coefficient-energy relationship of curve A in Fig. 1 and an index of refraction of 3.5, the value of R has been computed to be 5.8×10^{19} cm⁻³ sec⁻¹ at room temperature. Using this value and Eq. (7) the radiative lifetime of a small number of added electrons and holes in intrinsic material at room temperature is calculated to be 1.3×10^{-5} sec. In this calculation, the intrinsic carrier concentration at room temperature has been taken to be 1.5×10^{15} cm⁻³, a value based upon an extrapolation of the experimental electrical data of Folberth et al.⁸ The purest InAs available to us has an *n*-type carrier concentration of approximately 1×10^{16} cm⁻³. For material of this carrier concentration, Eq. (7) yields a radiative lifetime for minority carriers of 3.9×10^{-6} sec.

A meaningful comparison between calculated radiative lifetimes and experimental lifetimes cannot be made on the basis of the information which is now available, for two reasons. First, the significance of radiative lifetimes is not well established. It has been

²⁸ G. G. Macfarlane and V. Roberts, Phys. Rev. 97, 1714 (1955).

³⁶ H. Ehrenreich, J. Phys. Chem. Solids 2, 131 (1957).

³⁷ W. van Roosbroeck and W. Shockley, Phys. Rev. 94, 1558 (1954).

suggested that they represent upper limits to the observable lifetimes in materials of high purity and crystal perfection.^{37,38} Dumke³⁹ has pointed out, however, that because of successive reabsorptions of photons emitted in the direct recombination process, the maximum effective lifetimes of electrons and holes in perfect crystals may be considerably longer than the radiative lifetimes. This reabsorption mechanism is expected to be particularly important in materials like InAs which have large absorption coefficients near the absorption edge. Second, the experimental values of

³⁸ I. M. Mackintosh and J. W. Allen, Proc. Phys. Soc. (London) **B68**, 985 (1955). ³⁹ W. P. Dumke, Phys. Rev. 105, 139 (1957).

the carrier lifetimes in InAs which have been reported were determined using the photoelectromagnetic-photoconductive ratio method.⁴⁰ They have been both larger and smaller than corresponding values of the calculated radiative lifetimes. However, experimental lifetimes determined in this way are not always equal to the lifetimes of the carriers when carrier trapping is involved.41 Since the significance of trapping in InAs has not been studied, the carrier lifetimes which have been reported must be considered uncertain.

J. R. Dixon, Phys. Rev. 107, 374 (1957); J. R. Dixon and D. P. Enright, J. Appl. Phys. 30, 753 (1959).
 ⁴¹ R. N. Zitter, Phys. Rev. 112, 852 (1958).

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Critical Percolation Probabilities (Bond Problem)

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Monte Carlo estimates of the critical percolation probabilities for the "bond problem" are presented for a number of two- and three-dimensional lattices. The agreement between the Monte Carlo estimates and the estimates obtained by Domb and Sykes obtained from series expansion for the mean cluster size are quite satisfactory.

WO simple percolation problems¹ of physical interest arise when "particles" are distributed at random over an infinite regular space lattice in two or three dimensions: In the "site problem" a "particle" occupies a "vertex" of the space lattice (and in the "bond problem" a "bond" connecting two "vertices") independently of all others with fixed probability p. The site problem arises, e.g., in models of random binary alloys or a dilute ferromagnetic crystal²⁻⁵ while the bond problem arises, e.g., in a simple model of singlephase dispersive flow of a fluid (i.e., the percolation of a fluid into and through a "random maze"^{1,5}). When pis less than the critical probability p_c , then there is zero probability that a given site or bond is occupied by a "particle" which is a member of an infinite set of "particles" linked to one another through adjoining bonds and sites (cluster). (For the random ferromagnet p_c is simply related to the critical susceptibility at

0°K while for the percolation of a fluid through a "random maze" the expected fraction of "wetted" vertices is finite for $p > p_c$.)

Using a Monte Carlo method, adapted for an IBM 7090 computer to be described elsewhere,⁶ we have numerically estimated the critical probabilities for the bond problem for a number of two- and three-dimensional crystal lattices. In Table I, we present the mean critical probabilities in 100 runs in which finally 2000 vertices are "wetted" (average machine computation time per run is about seven seconds). The agreement between the Monte Carlo estimates of p_c and the estimates, $p_c^{\text{D.S.}}$, obtained from series expansions for the mean cluster size^{2,7} are quite satisfactory.

The value of p_c shown in Table I is the sample mean for those runs in which a higher p was required to "wet" 2000 vertices than to "wet" 100 vertices. This criterion is intended to reduce the systematic positive bias on p_c introduced by local irregularities at the beginning of the simulated flow. The remaining biases are believed

¹S. R. Broadbent and J. M. Hammersley, Proc. Cambridge Phil. Soc. 53, 629 (1957). ² C. Domb, Nature 184, 509 (1959).

³ R. J. Elliott, B. R. Heap, D. J. Morgan, and G. S. Rushbrooke, Phys. Rev. Letters 5, 366 (1960).
⁴ H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids 10, 19 (1959).
⁵ M. E. Fisher, J. Math. Phys. (to be published).

⁶ J. M. Hammersley, V. A. Vyssotsky, S. B. Gordon, and H. L. Frisch (to be published). ⁷ C. Domb and M. F. Sykes, Phys. Rev. **122**, 77 (1961) gives

results for both bond and site problems.