

Optical Properties of Indium Oxide

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In an investigation of the fundamental optical absorption edge of indium oxide at room temperature, transitions identified as direct-allowed have been observed with an energy gap (probably at $k=0$) of 3.75 eV. Indirect-forbidden transitions have also been observed with an energy gap of 2.619 eV and an assisting phonon of 0.069 eV. It is proposed that the minimum of the conduction band is at $k=0$ and the maximum of the valence band is at $k \neq 0$.

I. INTRODUCTION

IN previous work¹ magnetoresistance was used in an attempt to locate, in k -space, the minimum in the conduction band of indium oxide. Although the data were inconclusive, the most likely model of surfaces of constant energy appears to be the "warped-spherical" at $k=0$. Similar transport measurements have not been made for the valence band because of the difficulty in obtaining p -type indium oxide. For this reason, we have attempted to identify fundamental band-to-band transitions optically in order to locate the maximum of the valence band in k -space.

In this paper we present a summary of recent measurements of the fundamental absorption of indium oxide (In_2O_3). Results are quantitatively interpreted in relation to the energy band structure of indium oxide, in which both direct and indirect transitions occur.

II. SAMPLE PREPARATION AND EXPERIMENTAL APPARATUS

Single-crystal plates of indium oxide with areas of approximately 5 mm² were grown from the vapor phase as previously described.² The plates were from 30–100 μ thick and pale yellow in color. Transmission measurements were made on a Perkin-Elmer recording spectrophotometer (model 350) modified with additional focusing optics to accommodate the tiny crystal plates. The resolution of the instrument varied with wavelength but the energy increment was maintained at 0.001 eV or less at all wavelengths. The fundamental reflectivity near normal incidence was measured on the crystal plates by comparison with an aluminum front-surface mirror. The absolute reflectivity of the mirror was, in turn, measured by the common multiple reflection technique.³

Thin films of indium oxide were used for transmission measurements at the shorter wavelengths where the crystal plates were essentially opaque. The thin films were prepared on fused quartz substrates by cathode sputtering of an indium electrode in an oxygen atmos-

phere. The films were highly transparent in the visible portion of the spectrum; they exhibited interference colors and very little light scattering. The thicknesses of the films varied from a few tenths to nearly one micron.

The transmission of the thin films was measured in the visible by the method described above and in the uv by a ratio-recording method. The ratio-recording technique consisted of measuring directly the ratio of transmissions of films of different thicknesses. This was accomplished by placing a thin sample in the reference beam and a thicker sample in the sample beam of the recording spectrophotometer. The net result is equivalent to measuring the transmission of a hypothetical thin film without reflectance losses of a thickness equal to the difference in thicknesses of those actually used.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Direct Transitions: Thin Films

It has been shown that for direct (vertical) band-to-band transitions the energy dependence of the absorption coefficient α is of the form⁴

$$\alpha = \alpha_0(h\nu - \Delta E)^x, \quad (1)$$

where $h\nu$ is the photon energy and ΔE is the energy band gap. The value of x is $\frac{1}{2}$ for allowed transitions and $\frac{3}{2}$ for forbidden transitions.

We have used a method of analyzing thin-film transmission data, for direct transitions, which requires no information of the reflection coefficients at the various interfaces or the thicknesses of the films.

An expression for the transmission of a thin film on a substrate has been given by Moss.⁵ For the case of low transmission this expression is closely approximated by

$$T = (1 - R_1)(1 - R_2)(1 - R_3)(1 + k^2/n^2)e^{-\alpha d}, \quad (2)$$

where R_1 , R_2 , R_3 are the reflection coefficients at the air-thin film, thin-film-substrate, and substrate-air interfaces, respectively. The parameters k , n , and d are the extinction coefficient ($k = \frac{1}{4}\alpha\lambda/\pi$), refractive index, and thickness of the thin film, respectively. For $T < 0.10$,

¹ R. L. Weiher and B. G. Dick, *J. Appl. Phys.* **35**, 3511 (1964).

² R. L. Weiher, *J. Appl. Phys.* **33**, 2834 (1962).

³ This technique is described with the reflectance accessory for the Perkin-Elmer model 350 recording spectrophotometer.

⁴ J. Bardeen, F. J. Blatt, and L. J. Hall, *Photoconductivity Conference, 1954* (John Wiley & Sons, Inc., New York, 1956), p. 146.

⁵ T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications, London, 1959).

the error introduced in calculating α using Eq. (2) is less than 0.1%. The ratio of transmissions of two films of different thicknesses, which is obtained directly from the ratio-recording technique described in Sec. II, is then given by

$$T_{1-2} = e^{-\alpha \Delta d}, \quad (3)$$

where T_{1-2} is the ratio of transmissions and Δd is the thickness difference of the two films. One can then accurately calculate $\alpha \Delta d$. Without determining Δd , Eq. (1) can be written to the form

$$\alpha \Delta d = \alpha_0' (h\nu - \Delta E)^x, \quad (4)$$

where α_0' is equal to $\alpha_0 \Delta d$. One can then proceed to determine x by plotting $(\alpha \Delta d)^{1/x}$ vs $h\nu$ to obtain a straight line with a slope of α_0' , the abscissa intercept giving the energy band gap ΔE .

A satisfactory fit to Eq. (4) is obtained with indium oxide for $x = \frac{1}{2}$ corresponding to allowed transitions. This is shown in Fig. 1 for two combinations of three films of different thicknesses. It is seen that two straight lines are obtained with different slopes corresponding to the different Δd 's but having a common intercept at 3.75 eV. The absorption coefficient α , shown in Fig. 2, was calculated using approximate values of Δd from interference fringes in the visible. The absorption coefficient reaches values exceeding 10^6 cm^{-1} at the higher photon energies, which is expected for direct-allowed transitions.

The energy gap of approximately 3.75 eV deduced from thin films is further suggested by a maximum in

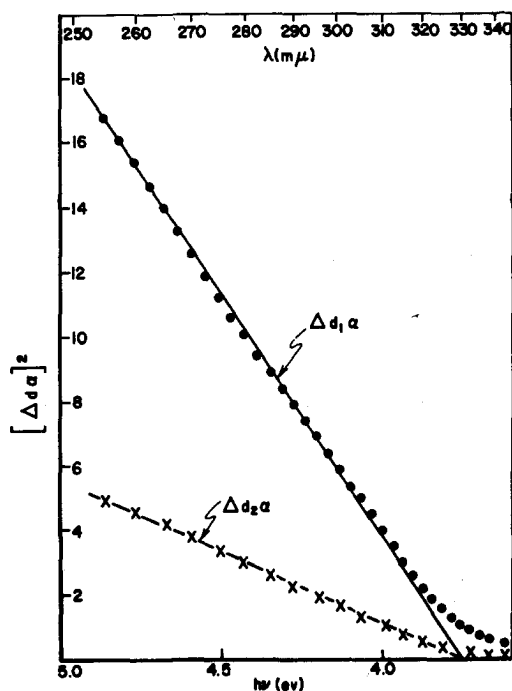


FIG. 1. Square of the absorption coefficient of indium oxide thin films as a function of photon energy.

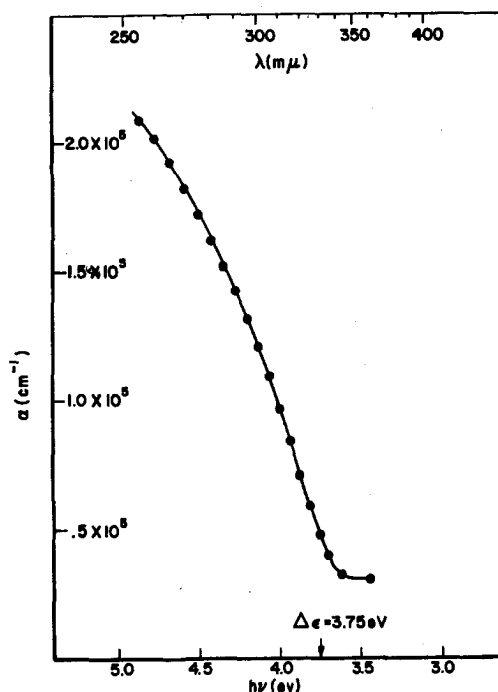


FIG. 2. Absorption coefficient of indium oxide thin films as a function of photon energy.

the fundamental reflectivity of the crystal plates as shown in Fig. 3. The maximum in the reflectivity at approximately 3.75 eV must be due solely to a maximum in the refractive index because the extinction coefficient at that photon energy is quite small. In turn, the interrelations of the optical constants predict a maximum in the refractive index where $d\alpha/d\nu$ has a maximum.⁵ This maximum should, of course, occur near $h\nu = \Delta E$ if the absorption is described by Eq. (1). We conclude that direct-allowed transitions are observed in indium oxide at room temperature with an energy gap of 3.75 eV.

It is also seen in Fig. 3, by the observed decrease in the contribution of the back surface of the crystals to the reflectivity, that the onset of absorption is at about 2.75 eV and increases slowly with photon energy. This broad tail on the absorption edge is indicative of an additional absorption mechanism which we next discuss in terms of an indirect (nonvertical) process.

B. Indirect Transitions: Crystal Plates

The absorption coefficient α for the crystal plates was calculated from transmission measurements using the expression

$$T = (1 - R)^2 e^{-\alpha d} / 1 - R^2 e^{-2\alpha d}, \quad (5)$$

where R is the reflection coefficient at the air-indium oxide interfaces. The reflection coefficient was calculated for normal incidence from the refractive index, which was determined from interference maxima and minima of the thin films. The refractive index was

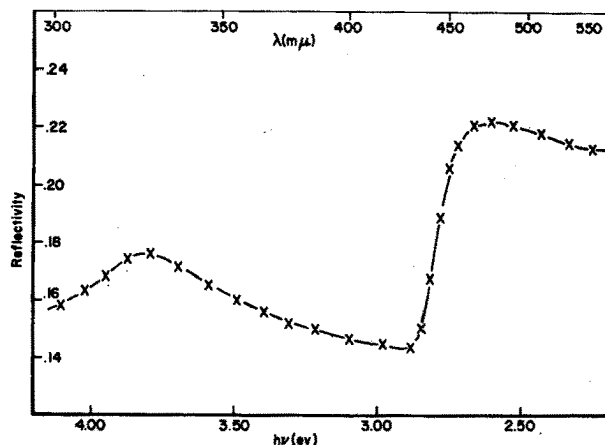


FIG. 3. Reflectivity of indium oxide single crystal as a function of photon energy.

normalized to 2.08 at 5893 Å,⁶ because only the product nd could be determined from the interference maxima and minima.

All of the crystal plates measured exhibited an apparent residual or wavelength-independent absorption which was evident at the longer wavelengths. The magnitude of the residual absorption varied from crystal to crystal reaching values as high as $\alpha = 50 \text{ cm}^{-1}$. Crystal C-1 was chosen for detailed analysis because it exhibited a nearly negligible residual absorption. The reflection coefficient calculated from transmission measurements at the longer wavelengths (assuming no absorption) differed from that discussed above by less than 3%.

The energy dependence of the absorption coefficient for crystal C-1 is shown in Fig. 4. Indirect vertical transitions at $k=0$, such as those discussed by Dumke⁷ or Thomas, Hopfield, and Power,⁸ seem unlikely because of the large energy difference ($\approx 1 \text{ eV}$) between the

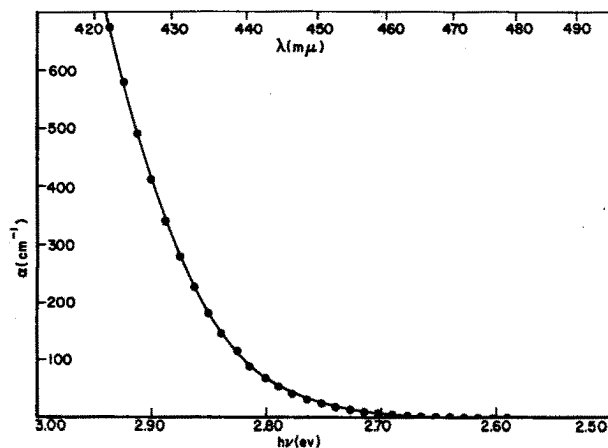


FIG. 4. Absorption coefficient of indium oxide single crystal as a function of photon energy.

⁶ E. Staritzky, *Anal. Chem.* **28**, 553 (1956).

⁷ W. P. Dumke, *Phys. Rev.* **108**, 1419 (1957).

⁸ D. G. Thomas, J. J. Hopfield, and M. Power, *Phys. Rev.* **119**, 570 (1960).

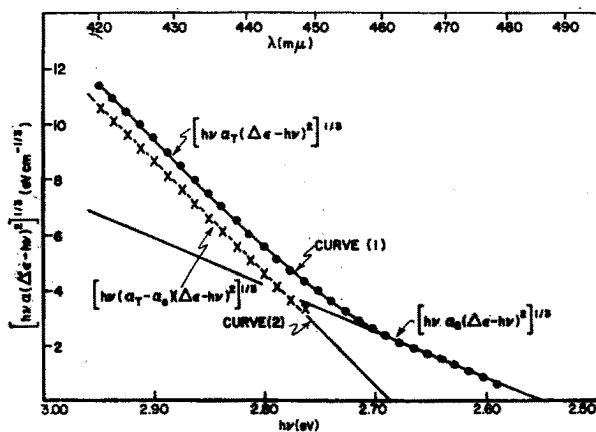


FIG. 5. Graphical analysis of absorption data (shown in Fig. 4) denoting forbidden-indirect transitions.

onset of absorption and the direct energy gap. This energy difference for the references cited is the energy of the appropriate phonon or the sum of the phonon energy and the energy difference between the bottom of the conduction band and the lowest lying exciton state. This would require a prohibitively high-energy phonon ($> 0.5 \text{ eV}$) for indium oxide. Our data are, however, consistent with indirect nonvertical transitions involving both the absorption and emission of phonons as for germanium and silicon.

The theory of indirect nonvertical transitions has been given by Bardeen, Blatt, and Hall⁴ and Fan.⁹ For a single phonon process, the absorption coefficient (α_a) due to the simultaneous absorption of a photon and phonon is given by¹⁰

$$\alpha_a = \frac{A(h\nu + E_p - E_g)^x}{h\nu(\Delta E - h\nu)^2(e^{E_p/kT} - 1)}, \quad h\nu > E_g - E_p, \quad (6)$$

$$\alpha_a = 0, \quad h\nu < E_g - E_p,$$

where A is a constant nearly independent of the photon energy $h\nu$, E_p is the phonon energy, E_g is the minimum energy gap, and ΔE is the energy gap of the virtual or intermediate state near $k=0$. The corresponding form for the emission of phonons is given by

$$\alpha_e = \frac{Ae^{E_p/kT}(h\nu - E_p - E_g)^x}{h\nu(\Delta E - h\nu)^2(e^{E_p/kT} - 1)}, \quad h\nu > E_g + E_p, \quad (7)$$

$$\alpha_e = 0, \quad h\nu < E_g + E_p.$$

The value of x is 2 for allowed transitions and 3 for forbidden. In the photon energy range $h\nu > E_g + E_p$, the total absorption coefficient (α_T) is given by

$$\alpha_T = \alpha_a + \alpha_e. \quad (8)$$

Additional terms corresponding to transitions through

⁹ H. Y. Fan, *Rept. Progr. Phys.* **19**, 107 (1956).

¹⁰ See also R. A. Smith, *Wave Mechanics of Crystalline Solids* (Chapman & Hall, London, 1961).

an intermediate state ΔE_1 , not at $k=0$, as well as other phonon energy terms, have been neglected for simplicity.

The data shown in Fig. 4 are satisfactorily described by Eq. (8) for forbidden transitions ($x=3$) and $\Delta E=3.75$ eV, as determined in Sec. IIIA for the direct energy gap. Shown by curve (1) in Fig. 5 is the quantity $[h\nu\alpha_T(\Delta E-h\nu)^2]^{\frac{1}{2}}$ plotted against the photon energy $h\nu$. The straight line obtained at the lower photon energies corresponds to the phonon absorption term (Eq. 6) having a slope of $[A/(e^{E_p/kT}-1)]^{\frac{1}{2}}$ and photon energy intercept at E_g-E_p . Thus the contribution of α_a can be subtracted from α_T . Shown also in Fig. 5 by curve (2) is a plot thus computed of $[h\nu(\alpha_T-\alpha_a)(\Delta E-h\nu)^2]^{\frac{1}{2}}$ corresponding to the phonon emission term [Eq. (7)] having a slope of $(Ae^{E_p/kT}/e^{E_p/kT}-1)^{\frac{1}{2}}$ and photon energy intercept at E_g+E_p . From the intercepts it is then found that $E_g=2.619$ eV and $E_p=0.069$ eV, and from the slopes it is found that $A=6.21\times 10^4$ cm⁻¹. The analysis is consistent in the sense that the ratio of slopes is indeed equal to $(e^{E_p/kT})^{\frac{1}{2}}$, where E_p is determined from the intercepts.

IV. CONCLUSIONS

The general behavior of the magnetoresistance of indium oxide was previously found to be consistent with constant energy surfaces in the conduction band corresponding to the "warped-spherical" model at $k=0$. If this is the case, the indirect transitions discussed in Sec. IIIB must then imply that the maximum in the valence band is *not* at $k=0$ and that the minimum energy gap at room temperature is 2.619 eV. The direct transitions discussed in Sec. IIIA are then probably vertical transitions at $k=0$ with an energy gap at room temperature of 3.75 eV. Preliminary measurements of the temperature dependence of the absorption edge indicate that $dE_g/dT \approx 1.0\times 10^{-3}$ eV·deg⁻¹.

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Hall Coefficient Behavior and the Second Valence Band in Lead Telluride

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Measurements of the temperature dependence of the Hall coefficient are presented for samples of *p*-type PbTe having carrier concentrations between 3×10^{17} and 1×10^{20} cm⁻³. As the temperature increases, the Hall coefficient for any given carrier concentration at first remains at the constant value R_L and then increases steadily at higher temperatures. As the carrier concentration increases from the lowest to the highest values studied, the Hall ratio R_{295°/R_L increases smoothly from about 1.1 to 2.5. The data are analyzed in terms of a simple two-valence-band model. The results indicate that the energy separation between the two band edges is about 0.14 eV at 0°K, and that carriers in the second band have a heavy mass and low mobility relative to those in the first. The data also suggest that there are no carriers in the second band in the liquid-helium temperature range, even at the highest carrier concentration. This requires that the first valence band be strongly nonparabolic.

INTRODUCTION

THE Hall coefficient measurements on *p*-type PbTe reported in this paper are an extension of an earlier study¹ to lower and higher carrier concentrations. The results are interpreted in terms of a simple two-valence-band model. We determine the parameters of the model from the Hall data at the lowest carrier concentration, using a formula derived by Aukerman and Willardson² (hereafter referred to as AW). We analyze the higher carrier concentration results with the aid of a generalization of the AW treatment,³

valid when the statistics in one or both bands are no longer classical.

The parameters deduced from the low-carrier-concentration Hall measurements do not bring the experimental data at all carrier concentrations into precise agreement with the simple model. We examine the effects of several modifications to the simple model which make it more realistic. We compare the Hall data and analysis with the results of other measurements and, finally, we consider briefly the possibility that a more sophisticated, single-band model might explain the Hall coefficient behavior.

REVIEW OF EARLIER DATA

Many features of the three lead salt semiconductors PbS, PbSe, and PbTe are qualitatively the same. For example, the extrinsic Hall coefficients are essentially

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¹ R. S. Allgaier, J. Appl. Phys. **32**, 2185 (1961).

² L. W. Aukerman and R. K. Willardson, J. Appl. Phys. **31**, 939 (1960); a similar analysis was presented by P. V. Gray and H. Ehrenreich, Bull. Am. Phys. Soc. **3**, 225 (1958).

³ R. S. Allgaier (to be published).