

Optical Constants of Lead Sulfide in the Fundamental Absorption Edge Region

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Large discrepancies exist between the results of previous measurements of the optical constants of PbS at room temperature in the absorption edge region. For this reason the absorption coefficient α and the index of refraction n have been remeasured over the spectral range from 0.1 to 1.5 eV. These quantities were obtained from an analysis of the reflectance and transmittance of high-quality epitaxial PbS films. Our results for α are in approximate agreement with those of Scanlon from 0.4 to 1.0 eV and approach those of Avery at higher energies. Analysis of these data yields a value of 0.42 eV for the direct gap. Near the edge, the absorption coefficients obey the relation $\alpha = 4.29 \times 10^4 (E - 0.42)^{1/2} \text{cm}^{-1}$, where E is the photon energy in eV. Indices of refraction were determined from reflectance-transmittance data and also by using the more accurate interference fringe method described by Riedl and Schoolar. A sharp peak in n as a function of energy is observed near the absorption edge. A Kramers-Kronig analysis using experimental α 's yields values of n in excellent agreement with experiment. This agreement substantiates the absorption measurements.

I. INTRODUCTION

THE optical properties of lead sulfide in the spectral region of the fundamental absorption edge have been measured at room temperature several times.¹⁻⁵ Until recently, the absorption coefficients reported by Scanlon have been accepted as being valid to within his limits of error.⁶⁻⁸ However, recent determinations by Cardona and Greenaway differ by more than a factor of 2 from those of Scanlon. Smaller errors in Scanlon's results have been suggested also by the dispersion analysis reported by Stern.⁹ He used Scanlon's absorption coefficients and the Kramers-Kronig relations to calculate the index of refraction in the edge region. Good qualitative agreement was obtained with the experimental indices reported by Riedl and Schoolar,¹⁰ but the quantitative agreement was only approximate. The small differences between calculation and experiment which he reported would be largely removed if the absorption edge were somewhat steeper than Scanlon's data indicated.

The existence of these discrepancies served as motivation for the work reported here. An added inducement was the pertinence of these data to current fundamental and applied studies involving PbS.

We have remeasured the optical properties in the fundamental absorption edge region using epitaxial films of high crystalline and electrical quality. In addition, we relate our results to the discrepancies discussed above.

¹ A. F. Gibson, Proc. Phys. Soc. (London) **B63**, 756 (1950).

² A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

³ D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).

⁴ W. W. Scanlon, Phys. Rev. **109**, 47 (1958).

⁵ M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

⁶ N. B. Hannay, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), Chap. 13, p. 593.

⁷ T. S. Moss, *Optical Properties of Semiconductors* (Butterworths Scientific Publications, Ltd., London, 1959), Chap. 14, pp. 183, 185, 190, 193.

⁸ R. A. Smith, *Semiconductor* (Cambridge University Press, London, 1959), Chap. 11, p. 424.

⁹ F. Stern, Phys. Rev. **133**, A1653 (1964).

¹⁰ H. R. Riedl and R. B. Schoolar, Phys. Rev. **131**, 2082 (1963).

II. PREVIOUS WORK

Previous measurements of the absorption coefficient α of PbS in the edge region are presented in Fig. 1 and are discussed below.

*Gibson, 1950.*¹ The early results of Gibson are based upon transmission measurements through chemically deposited polycrystalline films over the spectral region from 0.2 to 6.0 eV. His results do not show the sharp fundamental absorption edge now known to be characteristic of single-crystal material.

*Gibson, 1952.*² Later, Gibson made transmission measurements on cleaved single-crystal material. Only relatively thick samples could be prepared by cleaving. Consequently, his measurements were limited to values of α less than 100 cm^{-1} .

*Avery, 1954.*³ Avery's results are based upon reflectivity measurements from cleaved crystal surfaces. He used polarized light at non-normal incidence and analyzed the results to obtain optical constants over the range from 0.4 to 3.0 eV. His method gives reliable results only in the region of high-absorption coefficients. Consequently, the measurements yield information about the edge only for absorption coefficients above $1 \times 10^4 \text{ cm}^{-1}$.

*Scanlon, 1958.*⁴ Scanlon was interested in studying the shape of the absorption edge throughout the region from low to high absorptions. He measured transmissions through single-crystal bulk samples ranging in thickness from 0.7 to 350μ . The thinnest samples were prepared by a delicate polishing procedure. His absorption coefficients are in reasonable agreement with those of Gibson (1952) and Avery. In addition, his data span the region between these earlier results.

*Cardona and Greenaway, 1964.*⁵ Cardona and Greenaway have measured the reflectivity at near-normal incidence of PbS from 0.5 to 25 eV. Cleaved single-crystal samples were used for measurements below 6 eV and thick evaporated epitaxial layers at higher energies. They have carried out a Kramers-Kronig analysis of these data to obtain optical constants from 0.5 to

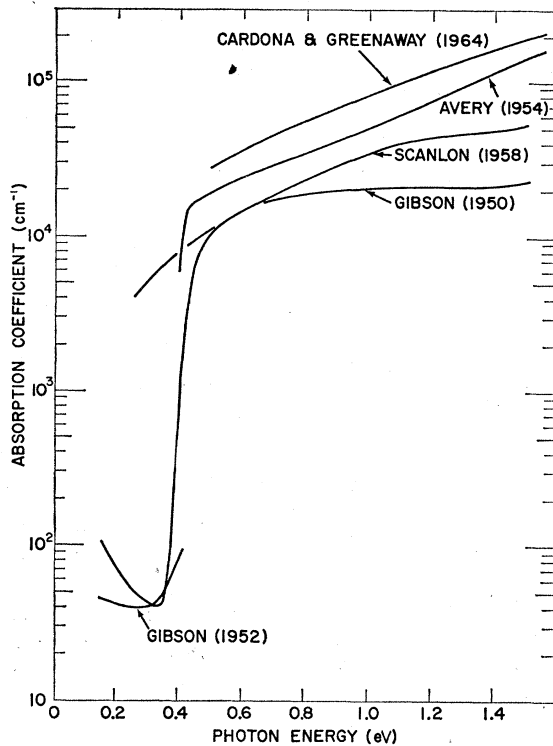


FIG. 1. Previous measurements of the absorption coefficient of PbS in the region of the fundamental absorption edge at room temperature.

15 eV. Their values of α in the neighborhood of the absorption edge are presented in Fig. 1. The magnitudes of these values are sensitive to the extrapolation of reflectivities beyond 25 eV which the authors employed in the Kramers-Kronig analysis. Because of the uncertainty inherent in their extrapolation, the resulting values of α should be considered only approximate.¹¹

III. EXPERIMENTAL

Materials

A major difficulty associated with transmission measurements in the edge region of PbS is in fabricating suitable samples. It is difficult to make the required thin bulk samples of this brittle material with areas large enough for conventional measurements. Therefore, we have adopted the technique of growing single-crystal films of PbS on heated rocksalt substrates. The good crystalline quality of such films has been well established.¹² These films are ideal for optical measurements, being of uniform thickness over large areas and having surfaces which are flat and mirror-like. Sample thicknesses are easily controlled and for these measurements were chosen to be in the range from 0.37 to 2.36 μ . The

¹¹ M. Cardona and D. L. Greenaway (private communication).
¹² R. B. Schoolar and J. N. Zemel, *J. Appl. Phys.* **35**, 1848 (1964).

material was *n*-type with carrier concentrations of approximately $3 \times 10^{18} \text{ cm}^{-3}$. The room-temperature Hall mobilities were comparable to those found in bulk PbS.

Apparatus

The optical system employed for transmittance and reflectance measurements was basically a Perkin-Elmer model-112 spectrometer with additional exit optics. A schematic of the exit optics is shown in Fig. 2. The spherical mirrors M_s were adjusted to produce images of the exit slit with a magnification of one throughout the system. The sample was placed at an image point of the exit slit and at one of the foci of the ellipsoidal detector mirror M_e . This arrangement greatly reduced the sensitivity of the measurements to small sample misalignments. A tungsten or globar source was used along with a lithium fluoride or rocksalt prism and a thermocouple detector. In the reflectance mode the maximum angle of incidence upon the sample was less than 15 deg. A "sample-in, sample-out" procedure was used involving either an open aperture or freshly deposited silver mirror as reference. The experimental error in the reflectance and transmittance measurements is estimated to be less than $\pm 4\%$. The slits were adjusted to give resolutions less than 0.01 eV in the vicinity of the edge.

IV. RESULTS AND DISCUSSION

Reflectance and Transmittance

Typical data on reflectance R and transmittance T are shown in Fig. 3. The analysis of these data to obtain n and α is complicated by the constructive and destructive interference phenomena producing the fringes. An additional complication is the influence of the film backing. Equations for R and T which take both of these factors into account have been derived previously.^{13,14} They are given in a convenient form for our purpose by Hall and Ferguson.¹⁵ These equations along with experimental values of R and T can be used to uniquely determine n and α , provided the film thickness and

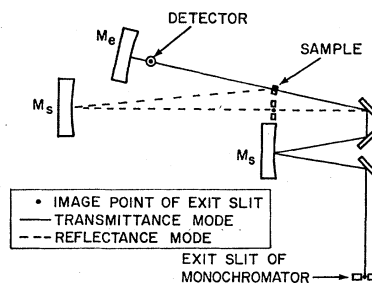


FIG. 2. Optical system for reflectance and transmittance measurements.

¹³ J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), 1st ed., pp. 496, 513.

¹⁴ R. L. Mooney, *J. Opt. Soc. Am.* **35**, 574 (1945).

¹⁵ J. F. Hall and W. F. C. Ferguson, *J. Opt. Soc. Am.* **45**, 714 (1955).

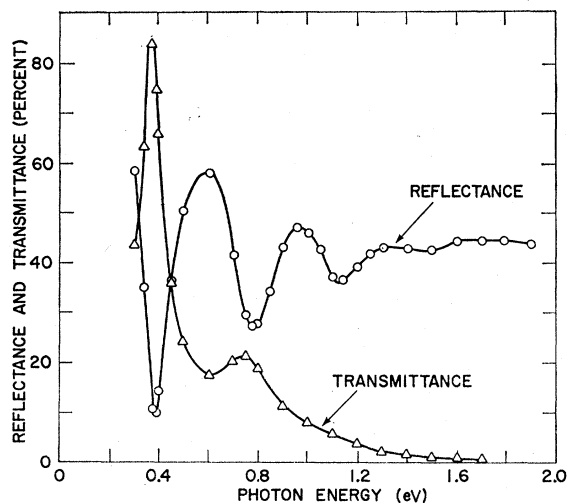


FIG. 3. Reflectance and transmittance data of a 0.37- μ -thick PbS film on a NaCl substrate at room temperature.

refractive index of the backing are known. We have determined film thickness using the positions of fringe extrema in the transparent region beyond the edge and the corresponding values of n reported by Riedl and Schoolar.¹⁰ Refractive indices for the sodium chloride backing were taken from the literature.¹⁶ Since n and α

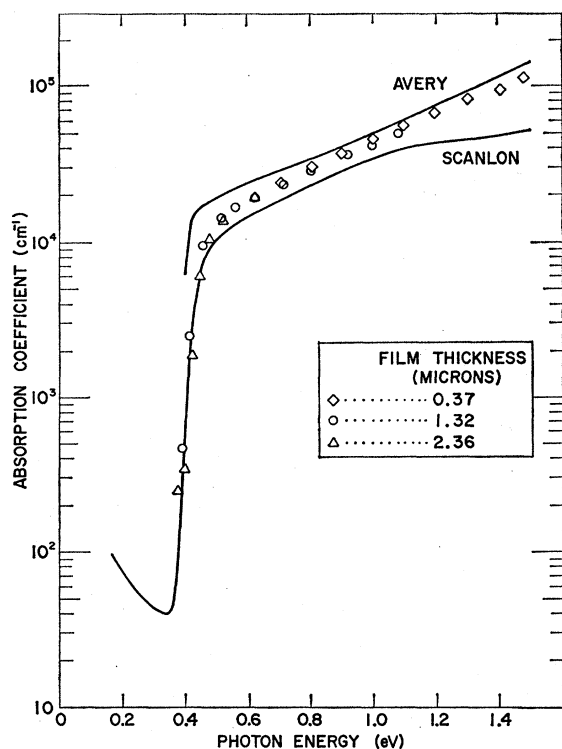


FIG. 4. The absorption coefficient of single-crystal PbS films compared with the results of Avery and Scanlon at room temperature.

¹⁶ W. W. Coblentz, J. Opt. Soc. Am. 4, 443 (1920).

cannot be expressed explicitly in terms of R and T , their values were determined by an iterative procedure carried out on an IBM-7090 computer.

Absorption Coefficients

Our main objective was to determine absorption coefficients as accurately as possible. For this reason we have chosen sample thicknesses and spectral ranges for each film so as to maximize the sensitivity of our measurements to α . Our results are shown in Fig. 4 and are uncertain to $\pm 7\%$. Scanlon's and Avery's results are replotted in the figure for comparison. Our data agree with those of Scanlon in the steep portion of the edge but differ from his by amounts up to 30% out to 1.0 eV. In the higher energy region our data approach

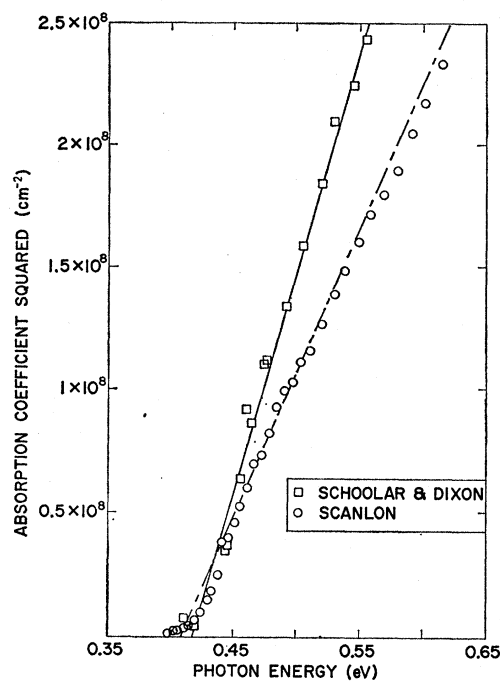


FIG. 5. The absorption coefficient squared versus photon energy of single-crystal PbS films compared with the results of Scanlon.

those of Avery. The large difference between our results and those of Cardona and Greenaway is attributed to the extrapolation of reflectivities which they used in their Kramers-Kronig analysis, as discussed in Sec. II.

Scanlon analyzed his data to determine indirect and direct transition energies. The indirect gap was obtained from an intercept on an $\alpha^{1/2}$ versus E plot. The absorption data involved are from the steep region of the edge where our results agree with those of Scanlon. Thus, the two sets of data yield the same indirect gap of 0.37 eV. The direct gap was determined by an intercept on an α^2 versus E plot. For this case the critical absorption coefficients are in the knee region

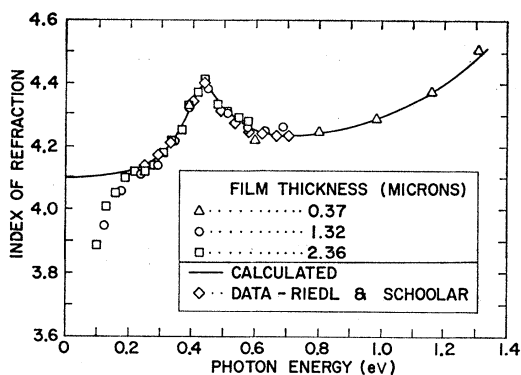


FIG. 6. The refractive index of single-crystal PbS films determined using interference fringes. The solid curve was calculated using the Kramers-Kronig dispersion relation as described in the text.

where the two sets of data are somewhat different. The significance of this difference to the analysis is indicated in Fig. 5. The slopes of the resulting straight line relations are considerably different, but their intercepts are nearly the same. Scanlon's data yield the relation $\alpha = 3.44 \times 10^4 (E - 0.41)^{1/2} \text{ cm}^{-1}$ while our data give $\alpha = 4.29 \times 10^4 (E - 0.42)^{1/2} \text{ cm}^{-1}$, where E is the photon energy in eV.

Indices of Refraction

The values of n which we have determined using the reflectance-transmittance method described above are uncertain to about 10%. A more accurate method, employed by Riedl and Schoolar,¹⁰ is based upon the positions of fringe extrema. For this reason, we used the latter method to determine n for our films. Our measurements duplicate and extend those of Riedl and Schoolar. Both sets of data are shown in Fig. 6 and are in good agreement. The sharp peak in n results from the rapid change in α at the absorption edge and has been discussed previously.^{9,10}

The calculated curve in Fig. 6 is based upon a Kramers-Kronig-type dispersion analysis using the relation⁹

$$n(E) - 1 = (\hbar c / \pi) \int_0^{\infty} \alpha(E') [E'^2 - E^2]^{-1} dE'. \quad (1)$$

We have used our values of α to evaluate the integral from 0 to 1.5 eV and those of Cardona and Greenaway in the region from 1.5 to 15 eV. These results of Cardona and Greenaway have been used because we have no reason to doubt them in this range, as we do at lower energies. Errors in their results associated with the reflectivity extrapolation discussed previously are expected to be much less significant in this region of high absorption coefficients. A numerical integration was carried out over these ranges using the trapezoidal rule and a computer. For $E' > 15$ eV the integrand is essentially independent of E for $E < 1.5$ eV. Consequently, the corresponding contribution of the integral to $n(E)$ in this region can be approximated by a constant Δn . We have chosen a Δn of 0.5 so that Eq. (1) yields an optical index of refraction, $n(E=0)$, of 4.1 in agreement with the experimental value reported by Riedl and Schoolar. The experimental and calculated curves are in excellent agreement throughout the region of the peak and at higher energies. The discrepancy at low energies is attributed to free-carrier and lattice dispersion. The calculated curve is particularly sensitive to the values of α near the edge. Therefore, we feel that the agreement between experiment and calculation serves to substantiate our absorption measurements.

Stern's dispersion analysis, described in the introduction, was similar to ours except that he used Scanlon's absorption data in the edge region and a delta-function approximation in the visible and ultraviolet. He obtained only approximate quantitative agreement with the indices of refraction reported by Riedl and Schoolar. We believe that the discrepancies are accounted for by the small differences between Scanlon's absorption coefficients and ours.

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