# Dispersion of the Refractive Index near the Fundamental Absorption Edge in PbS

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A peak in the wavelength dependence of the index of refraction resulting from the increase in the extinction coefficient at the absorption edge has been observed in PbS. The results were obtained by analysis of the reflection spectra of $n$-type single crystal film and bulk samples. At 300°K the refractive index at the peak is approximately 7% larger than the square root of the optical dielectric constant. The peak moves with the absorption edge with decreasing temperature. The optical dielectric constant at room temperature was found to be 16.8.

## I. INTRODUCTION

A PEAK in the wavelength dependence of the index of refraction resulting from the increase of the extinction coefficient at the absorption edge has been observed in PbS. This peak in the index is suggested in the data of Avery.[1] In this paper we present a more detailed study of the index in the vicinity of the band edge. The results confirm the recent calculations of Stern[2] on the structure of the index near the edge of small-band-gap semiconductors. Similar measurements and calculations have been made by Moss, Smith, and Hawkins on InSb.[3] The variation of the index of refraction of semiconductors in this spectral region is of particular significance because it is an important parameter in determining the modes amplified by an injection laser.

## II. EXPERIMENTAL

The results were obtained by two procedures. These involved analysis of the interference pattern produced upon reflection from $n$-type single crystal films and analysis of the reflectivity from a cleaved surface of $n$-type bulk material.

The films were evaporated in vacuum from bulk PbS onto heated NaCl substrates as described previously.[4] X-ray analysis has shown the films to be single crystals with a lattice constant characteristic of the bulk to within the experimental error of 0.1%. The refractive index was determined from the maxima and minima in the reflectivity at near-normal incidence using the condition

$$2nd = m\lambda, \qquad m = \tfrac{1}{2}, 1, \tfrac{3}{2}, \cdots, \qquad (1)$$

where $n$ is the refractive index, $d$ is the film thickness, $m$ is an integer for minima and a half-integer for maxima, and $\lambda$ is the wavelength in free space. The thickness, $d$, was determined by dissolving away the NaCl substrate, measuring the area of the film and weighing. The calculation requires a knowledge of the density

which was determined from the x-ray analysis. The estimated error in $d$ obtained by this method is less than ±2%. The order, $m$, was assigned unambiguously by determining the wavelengths of the maxima or minima of at least two successive low-order fringes, by making a rough estimate of the magnitude and wavelength dependence of $n$, and by applying Eq. (1). For the films analyzed, assignment of $(m+1)$ and $(m-1)$ instead of the true value $m$ produced unreasonable values of the calculated $n$, such as values of $n$ indicating free-carrier dispersion of the wrong sign, and values of $n$ differing drastically even at short wavelengths from the values calculated from the bulk reflectivity measurements described below.

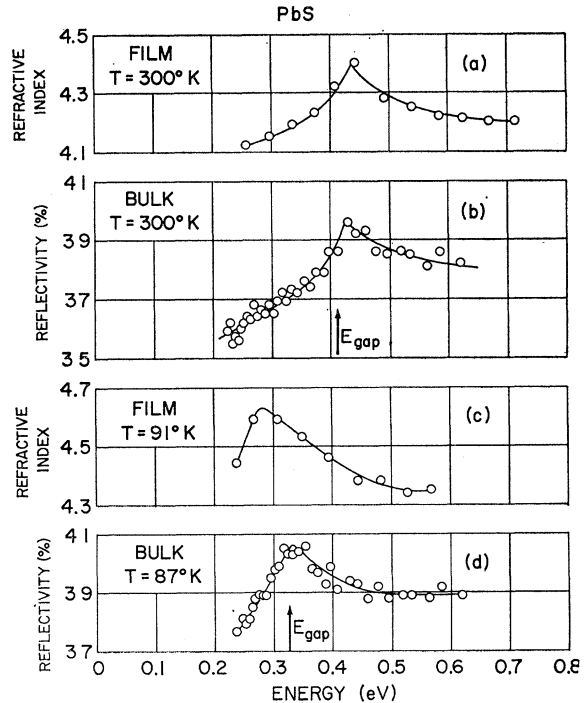Equation (1) takes into account the usual phase



Fig. 1. (a) The index of refraction obtained from interference fringes produced upon reflection from single crystal films at 300°K; (b) the reflectivity of the bulk material at 300°K; (c) the index of refraction obtained from interference fringes produced upon reflection from single crystal films at 91°K; (d) the reflectivity of the bulk material at 87°K.

[1] D. G. Avery, Proc. Phys. Soc. (London) **B66**, 134 (1953). Also see T. S. Moss, *Optical Properties of Semiconductors* (Butterworth's Scientific Publications, London, 1959), p. 188.

[2] F. Stern, Bull. Am. Phys. Soc. **8**, 201 (1963).

[3] T. S. Moss, S. D. Smith, and T. D. F. Hawkins, Proc. Phys. Soc. (London) **B70**, 776 (1957).

[4] R. B. Schoolar, J. D. Jensen, and J. N. Zemel, Bull. Am. Phys. Soc. **8**, 63 (1963).

change of $\pi$ between the light reflected from the front and back surfaces of the film. Variations from this phase difference associated with the nonzero values of the extinction coefficient and the optical properties of the substrate[5] were estimated and found to be negligible.

The index of refraction was determined from the reflectivity, $R$, at near-normal incidence of the bulk PbS using the expression

$$R = (n-1)^2/(n+1)^2. \quad (2)$$

The extinction coefficient terms, $k^2$, in the more exact expression for $R$ are negligible ($k^2 = 0.06$ at $\lambda = 2.0$ $\mu$ and $300°K$).[6]

### III. RESULTS

### A. Dispersion near the Absorption Edge

Figure 1 shows data obtained from the film and the bulk measurements. The dispersion is large enough in PbS that its effect is easily observed even in the more scattered data of the bulk reflectivity. At room temperature, the peak in the index of refraction of the film and the peak in the reflectivity of the bulk occur at approximately the same energy and at somewhat
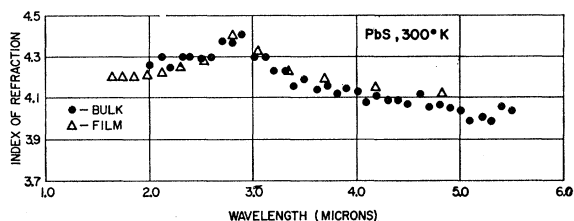
FIG. 2. The index of refraction at $300°K$ calculated from the re-reflectivity of the bulk material and from interference fringes produced upon reflection from single crystal films. Experimental error is estimated to be within $\pm 3\%$.

higher energy than the energy gap. At low temperature the peak in $n$ from the film data and the peak in $R$ from the bulk data move to smaller energy but differ in energy by a significant amount. From interband magneto-optical measurements, Mitchell et al. have obtained values of the energy gap, $E_g$, at liquid-nitrogen temperature both for bulk material and for one of the single crystal films.[7] Their results are $E_g = 0.305 \pm 0.002$ eV for the bulk and $E_g = 0.280 \pm 0.002$ eV for the film. They account for the discrepancy in $E_g$ in terms of large strains in the film arising from the differential contraction between film and substrate which occurs when the temperature is reduced. Their values of $E_g$ for bulk and film material are to be compared with the low temperature data in Fig. 1. This comparison illustrates the general feature that the short-wavelength dispersion follows the edge with changing strain and temperature. The energy gaps indicated on the curves were taken from

[5] J. F. Hall, Jr., and W. F. C. Farguson, J. Opt. Soc. Am. **45**, 714 (1955).

[6] W. W. Scanlon, J. Phys. Chem. Solids **8**, 423 (1959).

[7] D. L. Mitchell, E. D. Palik, J. D. Jensen, R. B. Schoolar, and J. N. Zemel, Phys. Letters **4**, 262 (1963).
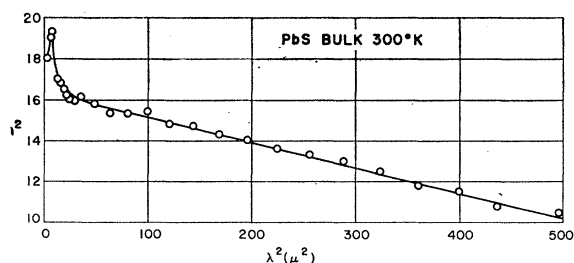
FIG. 3. The refractive index squared as a function of the wavelength squared for bulk PbS at room temperature. The peak at $\lambda^2 \approx 8$ $\mu^2$ is the result of the increase in the extinction coefficient at the absorption edge.

Scanlon's room temperature measurements[6] and from the change in the gap with temperature given by Gibson.[8]

Figure 2 shows the index of refraction at room temperature from both film and bulk measurements. Bulk reflectivity data have been reduced to values of $n$ using Eq. (2). Dispersion characteristic of free carriers and lattice vibrations in the bulk has been eliminated from the data by extrapolating long-wavelength dispersion data through the edge region and making the appropriate correction. The long-wavelength dispersion data for this sample are shown in Fig. 3. The linear portion of the curve was used as a basis for this extrapolation. These corrections led to increases in the index of refraction which were small, less than $1.3\%$ at all wavelengths. The corresponding corrections in the film data were even smaller and the data were not corrected.

Stern has applied his method of calculating the dispersion near the edge in semiconductors[2] to PbS at room temperature.[9] The calculated and experimental results are in qualitative agreement.

### B. Optical Dielectric Constant

A value of the optical dielectric constant was obtained using the dispersion at long wavelengths. As shown in Fig. 3 for the bulk sample at $300°K$, a straight line is obtained for $36$ $\mu^2 < \lambda^2 < 500$ $\mu^2$. This linear portion of the curve was extrapolated to zero wavelength yielding the optical dielectric constant, $n_0^2 = 16.3$. A relatively thick film sample in which the first-order interference fringe occurred at $\lambda^2 = 654$ $\mu^2$ yielded a value of $n_0^2 = 17.3$ at $300°K$ from the extrapolation procedure. The average value, $n_0^2 = 16.8$, is assumed to be the true value to within the experimental error.

### ACKNOWLEDGMENTS

[8] A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

[9] F. Stern (private communication).