

(iii) *The system can be decomposed into two parts*, the condenser determining the function  $G$ , and the resistance determining  $\xi$ . This made it possible to stipulate that  $\xi$  is a function of  $V=q/C$  only [although *a priori*  $\xi$  refers to the system as a whole, and may therefore be an arbitrary function  $\xi(q,C)$  of two variables]. Subsequently it is possible to go the limit of large  $C$ , in order to compare  $\xi$  with  $R$ .

## APPENDIX II

Recently MacDonald<sup>10</sup> studied the same problem again. He now also gives the Fokker-Planck equation

<sup>10</sup> D. K. C. MacDonald, Phys. Rev. **108**, 540 (1957).

(1), but considers  $\xi(q)$  and  $\eta(q)$  as two mutually unrelated functions. Actually there is a relation (Sec. 2), which in MacDonald's notation takes the form

$$G(q) = F(q) - kTCF'(q)/q. \quad (18)$$

The equilibrium distribution (7) of MacDonald then reduces to the ordinary Gauss distribution. MacDonald proved on thermodynamic grounds that  $\langle q^2 \rangle_{\text{eq}}$  must be independent of the function  $R(V)$ , but in fact the whole distribution function of  $q$  turns out to be independent of the resistance. It seems to me that this fact can be generally postulated on statistical grounds. This postulate would then conversely lead to (18).

## Optical Properties of Hexagonal ZnS Single Crystals

W. W. PIPER, D. T. F. MARPLE, AND P. D. JOHNSON  
General Electric Research Laboratory, Schenectady, New York  
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The optical transmission of hexagonal zinc sulfide crystals has been measured in the spectral range from 0.32 to 15  $\mu$ . From the spacing of interference maxima, the dependence of index of refraction on wavelength has been determined. Measurements of the effects of temperature from 20°C to 120°C and of pressure up to 1700 atmos on the width of the forbidden energy band indicate an increase in band gap of  $9 \times 10^{-6}$  ev/atmos with pressure and a decrease of  $7 \times 10^{-4}$  ev/C<sup>3</sup> with temperature for both ordinary and extraordinary rays. Approximately one-fifth of the shift with temperature is the result of dilatation of the lattice. The origin of the larger portion of the shift is discussed.

### INTRODUCTION

**S**TUDIES of hexagonal ZnS single crystals have included the effect of temperature on the wavelength of the absorption edge<sup>1</sup> and determination of the energy of the band gap by optical absorption and electrical conductivity measurements.<sup>2</sup> In this paper we report further measurements of the optical properties of hexagonal ZnS crystals grown from the vapor phase. The effect of pressure up to 1700 atmospheres on the absorption edge is used to determine what fraction of the temperature shift of the absorption edge is due to lattice dilatation. These measurements were made for both the ordinary and the extraordinary rays in the crystal.

The well-defined interference fringes observed in the transmission measurements make possible the determination of the dependence of the index of refraction on wavelength in the spectral range 0.34 to 2.0  $\mu$ . A thick crystal was used to check the index of refraction in the range from 2 to 15  $\mu$ .

### EXPERIMENTAL

The optical system employed for the transmission measurements is shown in Fig. 1. A Beckman hydrogen

discharge or a tungsten incandescent source was focused on the sample by a spherical mirror which acts as the limiting aperture of the apparatus. This arrangement minimized loss of radiation by scattering or refraction through small angles. The light-collecting optics have been described in a previous publication.<sup>3</sup> The clear areas of the crystals used were not less than 2 mm square and the beam entering the monochromator

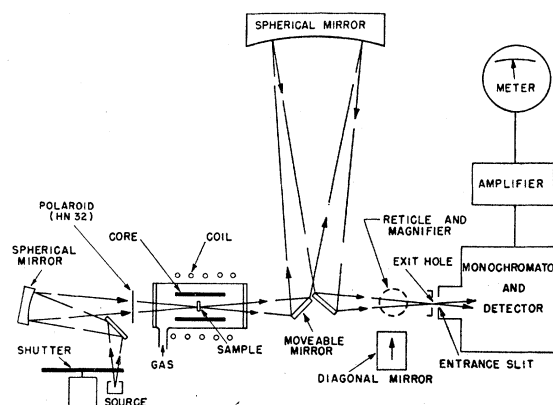


FIG. 1. Optical arrangement for transmission measurements.

<sup>1</sup> C. Z. Van Doorn, Physica **20**, 1155 (1954).

<sup>2</sup> W. W. Piper, Phys. Rev. **92**, 23 (1953).

<sup>3</sup> D. T. F. Marple, J. Opt. Soc. Am. **46**, 490 (1956).

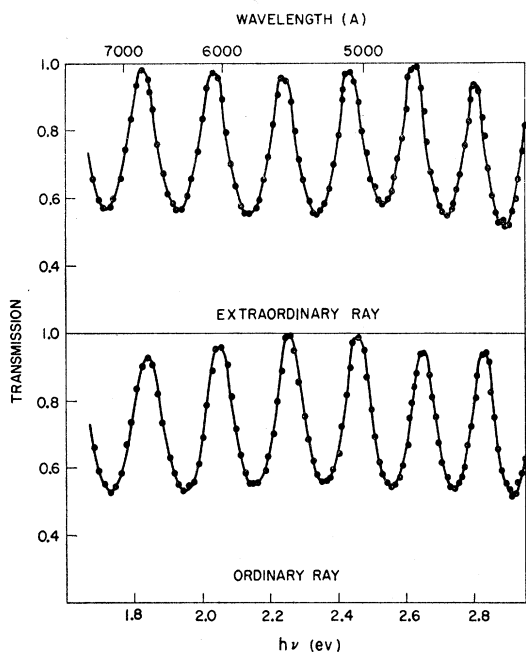


FIG. 2. Interference spectra for 1- $\mu$ -thick crystal.

included only radiation which passed through a circle approximately 1 mm in diameter in the center of the crystal. The polarizer could be accurately aligned with respect to the optic axis of the crystal by placing an analyzer in the optical path temporarily and adjusting the elements for total extinction. For the wavelength region 0.32 to 0.75  $\mu$  the detector was a 1P22 photomultiplier; for longer wavelengths a lead sulfide cell was used.

In Fig. 1 the sample holder is shown in the cell used for measurements at elevated temperatures. The sample holder was held rigidly in the center of the cylindrical nickel cell. Heating was accomplished by rf induction. Temperature was measured with a thermocouple in contact with the sample holder. The sample holder consisted of two nickel plates, separated by a nickel wire 0.001 inch in diameter which served as a spacer as well as a means of holding the crystal in place. With a small horizontal displacement of the holder, the unattenuated beam intensity could be measured. During the measurements argon flowed through the system. The high-pressure measurements were made with an American Instrument Company cell and Phillips "Spectro" grade iso-octane as the pressure transmitting fluid. The high-pressure cell was modified to accommodate the sample holder described above.

Transmission spectra of three crystals were observed at room temperature and pressure with polarized radiation in the spectral range from 0.32 to 2.2  $\mu$ . Two of these crystals, which were used for measurements of the wavelength variation of the refractive indices, had unusually flat and parallel faces as shown by their well-defined interference spectra. Figure 2 is a typical

example of these transmission spectra. These two crystals were one and two microns thick respectively, but the thickness could not be determined with enough accuracy for a useful absolute measurement of the refractive indices. All the measurements of temperature and pressure effects were made with a third crystal 4.6 microns thick. On a fourth crystal, transmission spectra were obtained in the spectral range from 2 to 15 microns with a Perkin-Elmer model 21 spectrophotometer. Interference maxima from order  $N=7$  to  $N=50$  were identified. The crystal thickness was  $23 \pm 0.5 \mu$ . These data were used to determine an average refractive index at long wavelengths. With the same apparatus, transmission measurements on the two-micron-thick crystal were also extended to 15  $\mu$  to check the assignment of the fringe order number made at shorter wavelengths.

All crystals were grown from the vapor phase in a manner similar to that of Reynolds and Czyzak.<sup>4</sup> The  $c$  axis of each crystal was positively identified with the polarizing microscope and in one case was checked by x-rays. In each case the  $c$  axis of the plate-like crystals was in the plane of the large crystal faces. Light polarized parallel to this axis traverses the crystal as the extraordinary ray.

#### INDEX OF REFRACTION

If one assumes zero phase shift upon internal reflection, interference maxima in transmitted radiation occur at wavelengths which satisfy the formula,

$$\lambda = 2nd/N, \quad (1)$$

where  $n$  is the index of refraction,  $d$  the thickness of the sample, and  $N$  can be any integer. If the order,  $N$ , can be established and the thickness is known,  $n$  can be calculated at the wavelength of each maximum.

The indices of refraction for the two rays were computed from the transmission data collected on the two

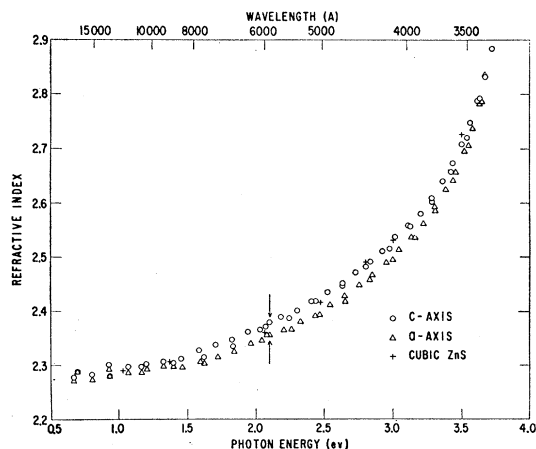


FIG. 3. Index of refraction of ZnS crystal vs wavelength.

<sup>4</sup> D. C. Reynolds and C. J. Czyzak, Phys. Rev. **79**, 543 (1950).

thin crystals and are shown in Fig. 3. The crystal thickness was assumed equal to the average of the thicknesses obtained when the published values of the index of refraction at 5893 Å were substituted in Eq. (1). The index of sphalerite at several wavelengths was calculated according to the formula deduced by DeVore<sup>5</sup> and by Czyzak *et al.*<sup>6</sup> and is also shown in Fig. 3. Within experimental error it may be concluded that this dispersion formula is still valid for both wurtzite and sphalerite at an absorption coefficient of  $10^4 \text{ cm}^{-1}$ . The indices of wurtzite appear to be converging in the neighborhood of the edge, but the magnitude of the dispersion in this region reduces the certainty of this observation.

By using Eq. (1), the index of refraction of the thickest crystal at  $\lambda=4 \mu$  was determined to be  $2.26 \pm 0.06$ . This result agrees with DeVore's value of 2.284 for sphalerite at  $1.54 \mu$ . Over the wavelength range  $\lambda=2 \mu$  to  $\lambda=15 \mu$  the index was constant within the error of determination of fringe positions ( $\pm 1\%$ ).

#### ABSORPTION EDGE

Figure 4 shows the effect of pressure on the transmission when the electric vector of the polarized radiation traverses the crystal parallel and perpendicular to the  $c$  axis of the crystal, respectively. Transmission was determined at 1, 680, and 1700 atmos. Since all effects are linear within experimental error in this pressure range, the data for 680 atmos are not

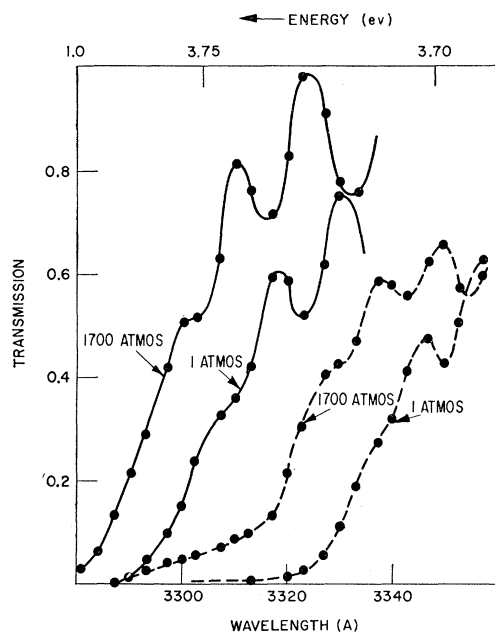


FIG. 4. Effect of pressure on optical transmission of hex-ZnS at the absorption edge: dashed lines—ordinary ray; solid lines—extraordinary ray.

<sup>5</sup> J. R. DeVore, *J. Opt. Soc. Am.* **41**, 416 (1951).

<sup>6</sup> Czyzak, Baker, Crane, and Howe, *J. Opt. Soc. Am.* **47**, 240 (1957).

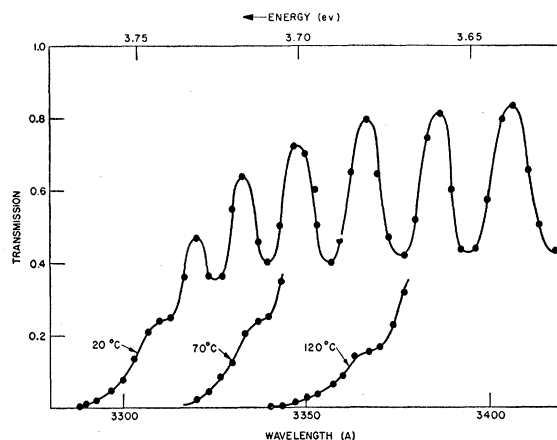


FIG. 5. Effect of temperature on optical transmission of the extraordinary ray in hex-ZnS.

shown in Fig. 4. A small amount of strain birefringence of the entrance window of the high-pressure cell may slightly depolarize the radiation incident on the sample, accounting for the short-wavelength tail in the transmission curve of the ordinary ray at 1700 atmos. For both orientations of polarized radiation the absorption edge moves to higher energies by  $9 \times 10^{-6} \text{ ev/atmos}$ . The position of the edge was also measured at 20°, 70°, and 120°C. From the data shown in Fig. 5 the temperature dependence of the edge is  $-7 \times 10^{-4} \text{ ev/C}^\circ$ , in good agreement with the data of Van Doorn,<sup>1</sup> which was taken at an absorption coefficient of  $50 \text{ cm}^{-1}$ . The shifts reported here were measured at 10% transmission which corresponds to an absorption coefficient of  $5000 \text{ cm}^{-1}$ . The magnitudes of these shifts are similar to those found in CdS.<sup>7,8</sup>

#### DISCUSSION

As in CdS some, but not all, of the temperature coefficient can be accounted for by the variation of lattice constant with temperature. The temperature coefficient corresponding to lattice dilatation,  $(\partial E_g / \partial T)_p$ , may be obtained from the pressure coefficient, provided the compressibility and the coefficient of thermal expansion are known, since

$$\left(\frac{\partial E_g}{\partial T}\right)_p = \left(\frac{\partial E_g}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p. \quad (2)$$

For ZnS this part of the temperature coefficient amounts to  $-1.3 \times 10^{-4} \text{ ev/C}^\circ$  if the assumptions are made that the compressibility of wurtzite is isotropic and that the cubical thermal expansion is equal to that of sphalerite.<sup>9</sup> This leaves a shift of  $-6 \times 10^{-4} \text{ ev/C}^\circ$  which is asso-

<sup>7</sup> R. Seiwert, *Ann. Physik* **6**, 241 (1949); *Chem. Zentr.* **1**, 2197 (1950).

<sup>8</sup> G. Hohler, *Ann. Physik* **6**, 371 (1949).

<sup>9</sup> Obtained from *International Critical Tables III* (McGraw-Hill Book Company, Inc., New York, 1929), p. 44.

ciated with an explicit temperature dependence of the energy gap.

Möglich, Riehl, and Rompe<sup>10</sup> attempted to explain this part of the coefficient for the temperature dependence of the band gap by suggesting that the lattice vibrations caused a temperature-dependent broadening of the energy levels and hence of the band gap. Their computation indicated too small an effect to explain the experimental results in CdS.<sup>8</sup> Later Radkowsky<sup>11</sup> derived a larger coefficient for polar crystals by including the broadening of energy levels due to the change in transition probability resulting from an electron interaction with the polar modes of vibration, an interaction neglected by Möglich, Riehl, and Rompe. More recently Radkowsky's expression for polar crystals was reproduced by Fan,<sup>12</sup> who considered the shift in energy levels associated with the coupling of phonons and electrons.

For polar crystals the formula, deduced by Radkowsky and by Fan, which describes the change in the band gap from its value at absolute zero, is

$$\Delta E_g = -\frac{2\pi(e^*e)^2}{\Omega M} \left(\frac{2}{\hbar\omega_l^3}\right)^{\frac{1}{2}} \frac{(m_c^{*\frac{1}{2}} + m_v^{*\frac{1}{2}})}{\exp(\hbar\omega_l/kT) - 1}, \quad (3)$$

where  $\Omega$  is the volume of a unit cell,  $M$  is the reduced atomic mass and  $m_c^*$  and  $m_v^*$  are the effective masses in the conduction and valence bands, respectively. The longitudinal fundamental optical frequency,  $\omega_l$  can be deduced from the experimentally observed reststrahl frequency,  $\omega_t$ , by the relationship

$$\omega_t = (\epsilon_0/\epsilon_\infty)^{\frac{1}{2}}\omega_l, \quad (4)$$

where  $\epsilon_0$  is the static dielectric constant and  $\epsilon_\infty$  is the optical dielectric constant. The appropriate effective ionic charge,  $e^*$ , has been defined by Callen<sup>13</sup> by the expression

$$4\pi e^{*2} = M\Omega\omega_l^2(\epsilon_\infty^{-1} - \epsilon_0^{-1}). \quad (5)$$

For ZnS,  $\epsilon_0 = 8.3$ ,  $\epsilon_\infty = 5.2$ , and  $\lambda_t = 33.5$  microns. When these quantities are substituted into Eq. (3), one obtains an average rate of change of the band gap between 300°K and 400°K of

$$\Delta E_g = -8.6 \times 10^{-5} [(m_c^*/m)^{\frac{1}{2}} + (m_v^*/m)^{\frac{1}{2}}] \text{ ev/degree.} \quad (6)$$

<sup>10</sup> Möglich, Riehl, and Rompe, *Z. tech. Phys.* **21**, 6, 128 (1940).

<sup>11</sup> A. Radkowsky, *Phys. Rev.* **73**, 749 (1948).

<sup>12</sup> H. Y. Fan, *Phys. Rev.* **82**, 900 (1951).

<sup>13</sup> H. B. Callen, *Phys. Rev.* **76**, 1394 (1949).

The agreement reported by Radkowsky for ZnS is incorrect as a result of using an ionic charge of  $e$ , whereas the appropriate effective charge,  $e^*$ , given by Eq. (5) is  $0.42e$ .

From Eq. (6) it is evident that the temperature coefficient not associated with lattice dilatation cannot be explained unless a rather large value of at least one of the effective masses is assumed. The validity of appealing to a large effective mass to be used in Eq. (3) is doubtful since this formula was derived using perturbation theory and therefore should be applicable only to systems in which the electron-phonon coupling is weak. The coupling constant,  $\alpha$ , is

$$\alpha = \Delta E_{g0}/\hbar\omega_l, \quad (7)$$

where  $\Delta E_{g0}$  is the shift in the band edge due to this interaction at absolute zero. For ZnS the coupling constant is  $1.2 (m^*/m)^{\frac{1}{2}}$ . Therefore, with a large effective mass, an intermediate coupling treatment of the temperature dependence of the band edge is more appropriate. Also it must be remembered that Fan's work relates to the thermal band gap and that the thermal and optical band gaps agree only to first order in the interaction energy between electrons and phonons.<sup>14,15</sup> If the coupling constant is not small the second-order term cannot necessarily be neglected. Finally, Fan's expression relates to a very simple band structure and may not be completely appropriate if the structure in ZnS is complex. Until these considerations have been evaluated, it does not seem possible to determine whether that part of the temperature coefficient which is not associated with a dilatation of the lattice can be explained satisfactorily by electron-phonon coupling or whether another effect not yet considered contributes to this coefficient.

#### ACKNOWLEDGMENTS

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<sup>14</sup> H. M. James, *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 204.

<sup>15</sup> H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p.123.