were derived from the Hartree equations. Since, however, we are interested in including exchange to first order, we substitute (5b) into (3b) and find the solutions

$$\alpha(\mathbf{k}_i)=e^2\left\{(A+B)C_{\mathbf{k}}\left(1-\frac{2me^2}{\hbar^2}\sum_i\left[\frac{C_{\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j}-C_{\mathbf{k}_i-\mathbf{k}_j}}{2(\mathbf{k}\cdot\mathbf{k}_j)}\right]\right)\right\}\Big/\{(\hbar^2/2m)(\mathbf{k}_i+\mathbf{k})^2-E_i-e^2\sum_j C_{\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j}\},\quad(7\text{b})$$

$$\beta(\mathbf{k}_i)=e^2(A+B)C_{\mathbf{k}}\left\{1+\frac{2me^2}{\hbar}\sum_i\left[\frac{C_{-\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j}-C_{\mathbf{k}_i-\mathbf{k}_j}}{2\mathbf{k}\cdot\mathbf{k}_j}\right]\right\}\Big/\{(\hbar^2/2m)(\mathbf{k}_i-\mathbf{k})^2-E_i-e^2\sum_j C_{-\mathbf{k}+\mathbf{k}_i-\mathbf{k}_j}\}.\quad(8\text{b})$$

In obtaining these formulas we have dropped exchange corrections to E in (5b) when substituting these into (3b). Also, we have neglected k^2 compared to $\mathbf{k}\cdot\mathbf{k}_j$ in several places.

To complete the calculation we apply the consistency conditions,

$$\sum_i\alpha(\mathbf{k}_i)=A \quad\text{and}\quad \sum_i\beta(\mathbf{k}_i)=B,$$

and proceed exactly as we did with Eqs. (6b). After doing a certain amount of algebra, we arrive at the dispersion relation,

$$\omega^2=\frac{4\pi e^2n_0}{m}\left\{1-\frac{4\pi e^4m^2}{\hbar^4}\times\sum_{i,j}\left[\frac{6\mathbf{k}\cdot(\mathbf{k}_i-\mathbf{k}_j)}{(\mathbf{k}\cdot\mathbf{k}_i)^2(\mathbf{k}\cdot\mathbf{k}_j)(\mathbf{k}_i-\mathbf{k}_j)^4}\right]\right\}+\bar{v}^2k^2.\quad(9\text{b})$$

In this expression, the $\mathbf{k}_i$, $\mathbf{k}_j$ in the sum are wave numbers in the coordinate system in which the plasma wave is at rest. Transforming to the laboratory system $(\mathbf{k}_i\rightarrow(\mathbf{k}\omega/k^2)(m/\hbar)+\boldsymbol{\lambda}_i)$, we immediately verify that the exchange correction in (9b) is proportional to k^2, which confirms the statement in Sec. IV.

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Some Electrical and Optical Properties of Synthetic Single Crystals of Zinc Sulfide

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The fundamental optical absorption edge and the temperature dependence of electrical conductivity of synthetic single crystals of hexagonal zinc sulfide have been measured, as well as the photoconductivity near the absorption edge. The fundamental absorption coefficient is 1 mm^{-1} at a photon energy of (3.58±0.02) ev and increases exponentially by a factor of ten every 0.07 ev up to 10^3 mm^{-1}. The logarithm of the electric resistivity varies linearly as a function of the inverse absolute temperature with a slope of (3.77±0.1) ev/$2k$. A peak in the spectral variation of photoconductivity has been observed at the optical absorption edge.

I. INTRODUCTION

INFORMATION pertinent to the energy gap between the valence band and the conduction band of an insulator or a semiconductor can be deduced from experimental data by two general techniques. First, the energy gap can be calculated from the temperature variation of intrinsic conductivity (or conduction electron density). Alternatively, one can study the long-wavelength edge of the fundamental optical absorption band by making measurements of the spectral variation of the absorption coefficient or the photoconductivity.

Gudden and Pohl[1,2] report a sharp rise of photoconductivity at approximately 3350A in natural crystals of zinc blende and in zinc sulfide phosphors. Gisolf[3] reports the ultraviolet limit of transmission of powdered samples of pure zinc sulfide (wurtzite) to be 3350A. This measurement was confirmed by Reynolds and Czyzak[4] on single crystals of synthetic wurtzite.

It is the purpose of this paper to report experiments relating to the band gap of the hexagonal form (wurtzite) of zinc sulfide. Measurements of photoconductivity and optical absorption have been made more exactly than in previously published work. In addition, temperature dependence of electrical conductivity has been measured.

This work was done with synthetic single crystals of zinc sulfide. These crystals were grown in an evacuated quartz container as described by the author elsewhere[5] and in a long quartz tube in an atmosphere of hydrogen by a technique similar to that reported by Reynolds

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[1] B. Gudden and R. Pohl, Z. Physik. **5**, 176 (1921).

[2] B. Gudden and R. Pohl, Physik Z. **23**, 417 (1922).

[3] J. H. Gisolf, Physica **6**, 84 (1939).

[4] D. C. Reynolds and S. J. Czyzak, Phys. Rev. **79**, 543 (1950).

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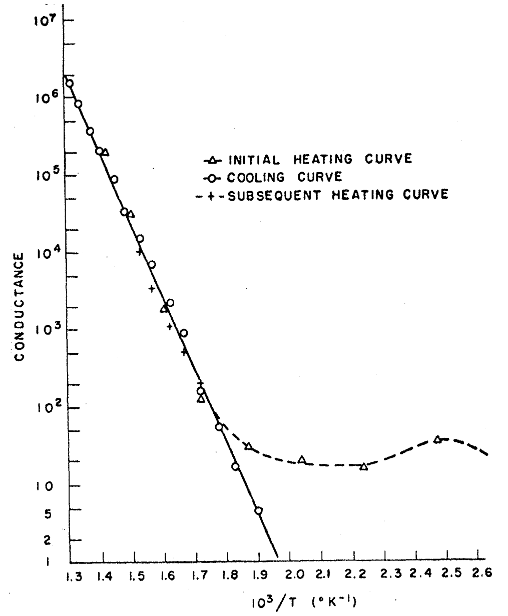

FIG. 1. Temperature dependence of electrical conductivity of ZnS.

and Czyzak.[4] In both cases a luminescence grade of zinc sulfide powder was used as a charge. The crystals grown by the former method were hexagonal columns as large as five millimeters long and two millimeters thick. The crystals were single except for a stacking disorder of the (00.1) planes.[6] The unique crystallographic axis (*c* axis) was parallel to the geometric axis of the cylinder. Hereafter, these crystals will be referred to as the columnar crystals. The crystals grown by the latter technique included flat plates 10–50 microns thick and several millimeters on an edge. The crystals were also hexagonal with the same sort of stacking disorder. The large plate faces were (11.0) planes and the *c* axis paralleled one edge of the large plate face. Hereafter these crystals will be designated as the laminar crystals. All the crystals used in these experiments were colorless in room light and showed no visible evidence of luminescent impurities under ultraviolet.

II. INTRINSIC CONDUCTIVITY

Measurements of the temperature dependence of electrical conductivity were made in a light-tight, evacuated chamber. The pressure did not at any time rise above 10^{-5} mm of mercury. The crystal was clamped under spring tension between two platinum electrodes each of which was in good thermal and electrical contact with a copper block about $2\times3\times4$ cm. These electrode blocks were clamped to and enclosed in a larger copper block. Thin sheets of mica provided adequate electrical insulation and thermal conduction. A dc potential was supplied to the electrodes by batteries, and the current passing through the crystal was measured with an electrometer. A chromel-alumel thermocouple was embedded in the large copper block near the surface to which the electrode blocks were clamped. The large copper block was suspended in the vacuum chamber by a stainless steel tube (1 inch o.d., 4 inches long, $\frac{1}{32}$-inch wall thickness). A nichrome ribbon heating element slipped through the tube into a recess in the large copper block.

With a crystal in place between the electrodes the copper block was heated at a rate of 5°K/min and was allowed to cool not faster than 5°K/min (at the lower temperatures the cooling rate was considerably slower than this). In Fig. 1 the logarithm of the current passed by a typical columnar crystal pinched between platinum electrodes maintained at a constant potential difference is plotted as a function of reciprocal absolute temperature. Upon subsequent heating and cooling cycles the points on the straight line were reproducible. The dotted curve to the right was the current passed on initial heating after exposure to room light. The straight line can be represented by a function

$$I = A\exp(-E/2kT).$$

The value of E as determined from the slope is 3.77 ± 0.1 ev.

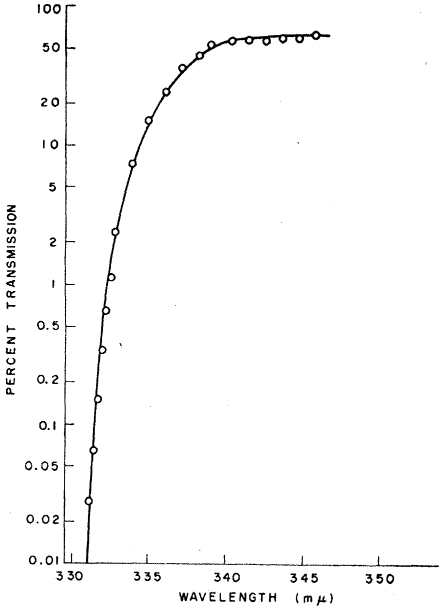

FIG. 2. Percent transmission through a flat plate of ZnS 15 microns thick as a function of wavelength.

III. OPTICAL ABSORPTION

Laminar crystals have been grown which appear optically clear over an area of 1 mm² when examined

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[6] Dr. W. L. Roth has made a careful crystallographic study of many single crystals of zinc sulfide grown by the author. The most probable interpretation of the streaking observed in x-ray reflection patterns is that one plane in fourteen has violated the stacking sequence of the (00.1) planes for a hexagonal crystal.

with a 50× microscope. These crystals were mounted on brass disks $\frac{1}{32}$ inch thick which had a 1-mm hole at the center. These disks could be mounted so that the hole was directly in front of, and bisected by, a 0.005-inch slit which was the exit slit of a spectroradiometer.[7] Light passing through the exit slit was measured with a 1*P*21 photocell. The recorded width of half-maximum intensity of monochromatic light was 6A. The peak intensity of a particular wavelength on the exit slit could be set with an error of less than two angstroms. The entrance slit of the spectroradiometer was illuminated by a low-voltage hydrogen lamp which was operated from a bank of storage batteries and supplied an extremely stable near ultraviolet spectrum. A similar lamp is described by Johnson.[8]

Percent transmission of a crystal was obtained by measuring and comparing the amount of light reaching the photomultiplier with and without the crystal mounted on the brass disk in front of the exit slit. Figure 2 shows a typical transmission curve as a function of wavelength for a crystal about 15 microns thick. This data can be used to compute the optical absorption coefficient of a crystal as a function of wavelength if the thickness of the crystal is known, and if corrections are made for reflection at the optical interfaces.

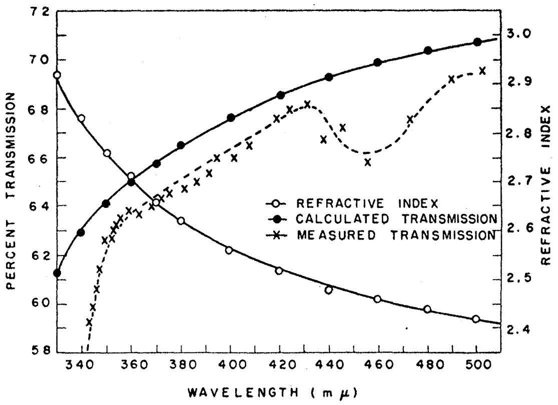

FIG. 3. Refractive index, theoretical transmission through a laminar plate of this index with no absorption and measured transmission through a flat plate of ZnS 15 microns thick.

The thickness *d* of these crystals can be determined by measuring the interference fringes at longer wavelengths if the index of refraction *n* is known. Well defined fringes were observed at $\lambda > 5000$A. The index of refraction for natural sphalerite (cubic form of zinc sulfide) has been reported by Brum[9] and DeVore.[10] This index should differ from the indices of wurtzite by less than 1 percent over the visible and near ultraviolet spectrum. By measuring the wavelengths of successive transmission maxima (which occur for integral values of $2\lambda/nd$), the thickness was determined with a probable error of less than four percent.

Barnes and Czerny[11] have derived an expression for the fraction of light transmitted through a laminar sheet of known optical index which includes the effects of absorption and interference. In the visible and near ultraviolet the measured crystal transmission in each case was a few percent less than the value calculated from this formula assuming no absorption (see Fig. 3). Assuming the difference to be due to scattering at surface imperfections the calculated transmission without absorption was adjusted by a constant factor. The absorption coefficient was then calculated from the difference between the measured transmission and the adjusted calculated transmission without absorption.

Figure 4 is the calculated absorption coefficient for the crystal whose transmission is shown in Fig. 2. Among four crystal plates the wavelength for an absorption coefficient of $\alpha = 1$ mm^{-1} varied from 3450A($h\nu = 3.60$ ev) to 3480A($h\nu = 3.56$ ev) and the slope, $d(\log \alpha)/d(h\nu)$ varied from 12 ev^{-1} to 16 ev^{-1}.

IV. PHOTOCONDUCTIVITY

A columnar crystal about 1 mm² in cross section and 2 mm long was mounted between silver paste electrodes so that the electric field paralleled the unique crystallographic axis. The crystal was then mounted in front of the exit slit of the ultraviolet monochrometer described by Johnson.[8] The axis of the crystal was parallel to the exit slit edges. The entire crystal was illuminated by radiation from the exit slit. The width at half-maximum intensity was 8A. The absolute intensity

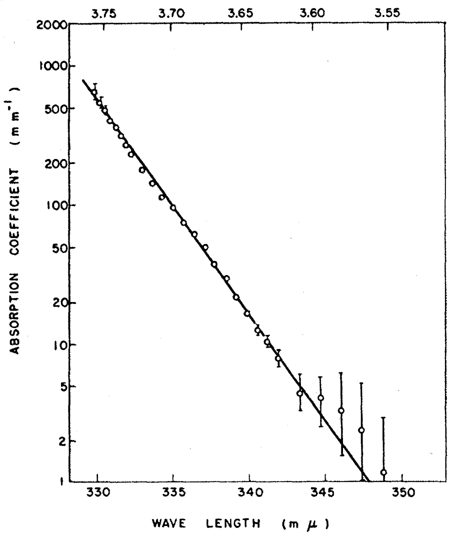

FIG. 4. Spectral variation of the optical absorption coefficient of hexagonal ZnS at the fundamental absorption edge.

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[7] This instrument was designed by Dr. F. J. Studer. It employs a one-meter replica diffraction grating (15 000 lines/inch) in a Wadsworth mounting.

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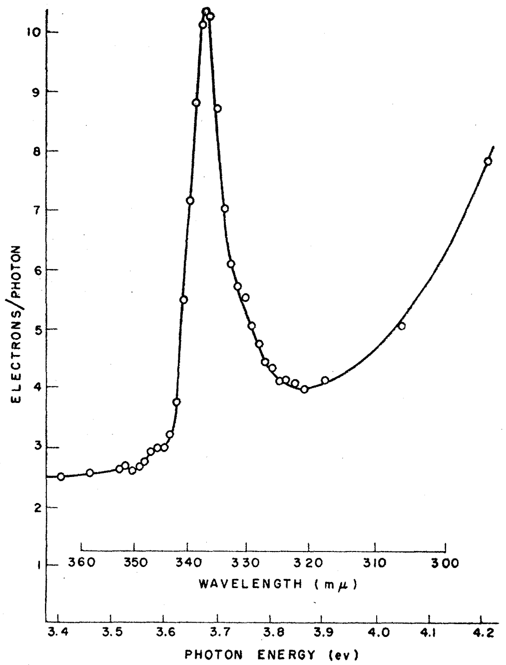

FIG. 5. Photoconductivity of a single crystal of ZnS as a function of the photon energy.

of the radiation was measured with a Cs-Sb photocell which had been calibrated to yield values correct within twenty percent. Fifty volts was applied between the crystal electrodes and the photocurrent was measured with an electrometer utilizing a split *FP*-54 electrometer tube.[12]

Figure 5 shows the photocurrent produced in units of electrons/incident photon as a function of photon energy. The width of the peak at half-maximum current is about 60A. The number of photons incident may be in error by a factor of two due mostly to geometric uncertainties in relative positioning of the exit slit and the sample. No correction is made for reflection at the front surface. The current behaved ohmically up to 500 volts. Doubling the radiation intensity doubled the photocurrent within five percent for all points on the curve. All points represent steady-state values as closely as possible. Two to ten minutes between wavelength settings was required to allow the current to reach a steady value. After a steady-state current had been reached with 3650A radiation from the monochromater the radiation was turned off and the photocurrent was allowed to decay to less than five percent of the initial value. The decay was exponential with a time constant of 1000 sec. Assuming a reasonable frequency factor, this value is in agreement with other experimental evidence for an electron trap about 1 ev below the conduction band.[13,14]

V. DISCUSSION

The density of electrons in the conduction band for the intrinsic case is[15]

$$n = AT^{\frac{3}{2}} \exp(-E_G/2kT), \qquad (1)$$

where E_G is the energy difference between the bottom of the conduction band and the top of the valence band, k is the Boltzmann constant, and T is the absolute temperature. A is a constant containing the effective masses of electrons and holes and certain fundamental constants. The conductivity is

$$\sigma = ne\mu, \qquad (2)$$

where e is the electronic charge and μ the mobility. Thus

$$\sigma = Ae\mu T^{\frac{3}{2}} \exp(-E_G/2kT). \qquad (3)$$

Fröhlich and Mott[16] have examined theoretically the temperature dependence of mobility of conduction electrons in polar crystals. They determined that

$$\mu = B \exp(\theta/T - 1), \qquad (4)$$

where B depends only on constants of the crystal lattice and θ is the temperature associated with the frequency of longitudinal polarization waves of the lattice. The formula is valid only for $T \ll \theta$. For metallic salts they estimate that θ varies from 300° to 800°K. They were not able to calculate μ for $\theta \leq T$.

TABLE I. Coefficient β of the linear term in the photon energy $E_e(T)$ for various materials.

Material	β(ev/°K)	Reference
ZnS	$5\text{–}10 \times 10^{-4}$	17
CdS	$5\text{–}7 \times 10^{-4}$	18, 19, 20
ZnO	10×10^{-4}	21
Ge	4×10^{-4}	22
Si	3×10^{-4}	23

The experimental data on the thermal variation of electrical conductivity is not precise enough to differentiate between the linearity of $\log\sigma$ *vs* $1/T$ and $\log(\sigma/T^m)$ *vs* $1/T$ for $m<3$. If one assumes

$$\sigma = A_m T^m \exp(-E_G/2kT) \qquad (5)$$

and determines E_G as a function of m from the conductivity data, one obtains

$$E_G = (3.77 - 0.07m) \text{ ev}. \qquad (6)$$

Hence, if the mobility is constant in the temperature range investigated, the band gap energy would be about 3.67 ev. If the mobility is increasing in this range, the correct band gap energy would be even lower. If $\theta = 800$°K and (4) is assumed to be correct in the temperature range from 400° to 600°K, $T^{\frac{3}{2}} \exp(\theta/T - 1)$

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is essentially constant, and the band gap would be 3.77 ev. Since θ is more likely lower than 500°K, a constant or only slowly varying mobility at this temperature is most probable.

The fundamental optical absorption edge has been observed to shift with temperature for several crystalline solids. The photon energy E_e at a constant value of the absorption coefficient decreases approximately linearly with temperature so that

$$E_e(T)=E_e(0)-\beta T. \tag{7}$$

A partial list of materials is given in Table I.[17–23] This shift has been attributed to a temperature dependence of band gap energy, i.e.,

$$E_G(T)=E_G(0)-\beta T. \tag{8}$$

Shockley and Bardeen[24] have demonstrated theoretically that a change in band gap energy is to be expected due to the change in lattice constant associated with thermal expansion. This was also suggested earlier by Moglich and Rompe.[25] An additional shift of E_G due to the change in the excitation of lattice vibrations with temperature has been calculated by Fan.[26]

When (8) is substituted in (1) or (5), it is evident that E_G as determined from the temperature dependence of electrical conductivity is the band gap energy at absolute zero. The optical absorption data, on the other hand, relates to the band gap at the crystal temperature.

Ideally the value of the absorption coefficient corresponding to a transition from the upper edge of the valence band to the lower edge of the conduction band would be very small. Actually, absorption may be present at this and lower energies for a variety of reasons. Cheeseman[27] has shown that it is theoretically possible for appreciable absorption to occur for photon energies less than the band gap energy.

Optical transitions to exciton levels might also alter the shape of the absorption edge. Assuming a Coulomb field in a continuous dielectric medium as an approximation, the two lowest exciton levels for an optical index of refraction of 2.7 are 0.12 and 0.03 ev below the bottom of the conduction band. With the resolution of the equipment used one would expect structure to be observed if exciton absorption were appreciable.

Assuming that neither of these effects alter the absorption edge appreciably and that the absorption coefficient at the band gap energy lies between 10 mm^{-1} and 0.1 mm^{-1}, the optical absorption data yield a value of the band gap energy at room temperature of $E_G(300°\text{K})=(3.58\pm0.1)$ ev. Assuming the mobility not to be changing significantly between 500°K and 700°K, the conductivity data yield an energy at absolute zero of $E_G(0°\text{K})=(3.67\pm0.1)$ ev. The temperature coefficient of band gap energy β as calculated from the two band gap values just suggested is 3×10^{-4} ev/°K, which is not in disagreement with the value reported in the literature (Table I).

If the shape of conduction and valence band energies are considered as a function of the electron wave vector $\mathbf{k}$, it is obvious that the value of the band gap determined from the temperature dependence of conductivity should be less than the optically measured gap (neglecting any temperature dependence of the gap) if the maximum of the valence band and the minimum of the conduction band do not occur at the same value of $\mathbf{k}$. It appears unlikely that the E_G determined electrically should be lowered appreciably for this reason and that the E_G determined optically should also be lowered by the same amount for one of the reasons discussed above, so that a reasonable value of β should be maintained.

The sharp rise of photoconductivity as the wavelength is decreased corresponds closely to the absorption of a significant fraction of the incident radiation by a crystal 1 mm thick. The sharp drop 60A further indicates some sort of dead layer approximately one micron thick. Recombination due to a high hole-electron concentration, the presence of special surface traps, and the possibility of minute surface cracks have been suggested as possible reasons for such a dead layer. Similar spectral response curves have been observed for other photoconducting materials (e.g., CdS[20,28]).

ACKNOWLEDGMENTS

I am indebted to Drs. F. J. Studer and P. D. Johnson for aid in making the optical measurements. I also wish to acknowledge the encouragement of Dr. F. E. Williams and Dr. M. H. Hebb's helpful criticism. Mr. P. Zeldes aided in growing the laminar crystals.

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