

$L(0,T)$ for an uncompensated metal.¹⁵ These effects must also be present for a more general Fermi surface. For example in a compensated metal the variation in the relaxation time and effective mass will be reflected in the multiplying constant of (1). In the thermal case, the relaxation times will not be uniformly scaled from the values appropriate to the electrical case so the constant will in general be different. Thus the high-

¹⁵ In an earlier discussion (Ref. 8) results of the 2-band model were quoted but the particular assumption made, $(\omega\tau)_1 = (\omega\tau)_2$, was not stated.

field limits given cannot always be expected to be good approximations and it is possible that the decrease from $L(0,T)$ observed for indium,^{7,8} an uncompensated metal, may be due to this.

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Optical Band Gap and Birefringence of ZnS Polytypes*

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Birefringence and optical band-gap measurements were performed at 20°C on structurally uniform regions of ZnS crystals. The regions were of one of the following polytype structures: 4L, 6L, 10L, 14L, 24L, 26L, 28L, 40L, 120L; cubic (3L) and hexagonal (2L) regions were also investigated for reference. No stacking disorder was discovered in the regions studied. It was found that the absorption-edge positions (for polarization parallel and perpendicular to the optic axis) as well as the degree of birefringence Δn depend only on the value of a single structure parameter α . This parameter is defined as the percentage of (00.1) planes stacked in hexagonal order; its values were determined directly by x-ray structure analysis. The absorption edge positions were found to be linear functions of α . This linearity is explained on the basis of Birman's perturbation treatment for electron states with \mathbf{k} vectors parallel to the c axis. It implies that in a polytype the perturbation potential caused by partially hexagonal stacking is proportional to α . The degree of birefringence was found to be proportional to α ; an outline of a simple dispersion treatment is given for the explanation of this proportionality. The established linear relationships between absorption edges, birefringence, and α allow calculation of absorption-edge positions and α values from birefringence measurements. This may facilitate investigations of structure-sensitive properties (e.g., the anomalous photovoltaic effect) of ZnS samples which are composed of regions differing from each other in structure.

I. INTRODUCTION

IT has been known for more than a decade that, similarly to SiC, zinc sulphide also exhibits polytypism.^{1,2} All ZnS structures are built of alternating zinc and sulphur planes. The arrangement of each kind of atoms corresponds to that of close-packed spheres. The structures differ from each other in the stacking sequence of the planes. The most readily measured distinguishing feature of the lattices is the length c of the fundamental translation along the perpendicular to the close-packed planes. If d denotes the distance between two adjacent planes built of atoms of the same kind (e.g., sulphur), then $c = md$ for a m -layer polytype denoted by mL . For $m \geq 6$ different layer sequences are possible with the same m , thus the value of m does not define the structure completely. Though about ten

ZnS polytypes have been reported³ the layer sequences were determined only for two cases.⁴

Vapor-phase-grown ZnS crystals usually consist of a set of parallel strips separated from each other along (00.1) planes (the close-packed lattice planes in the hexagonal notation). These strips are in most cases very narrow, of the order of a few microns. Neighboring strips differ from each other in crystal structure. In other words the dimensions of a crystal region consisting of a single polytype are, in general, inconveniently small. In fact, very little is known about the physical properties of ZnS polytypes. Much more data have been published on SiC, as polytypes of this material are available with larger dimensions.

Under the polarizing microscope, most synthetic ZnS crystals appear as consisting of colored strips ("birefringence bands"), due to variations of the birefringence in the sample. It seems to be natural to

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¹ L. S. Ramsdell, *Am. Mineralogist* **32**, 64 (1947).

² C. Frondel and C. Palache, *Am. Mineralogist* **35**, 29 (1950).

³ M. Farkas-Jahnke, *Acta Cryst.* **18**, 571 (1965).

⁴ H. T. Evans and E. T. McKnight, *Am. Mineralogist* **44**, 1210 (1959).

attribute the birefringence variations to the changes in crystal structure.⁵ However, Singer⁶ did not find any correlation between structure and birefringence in his ZnS crystals. He emphasized that the same degree of birefringence occurred for different structures and that structurally indistinguishable regions differed in birefringence. The crystal regions investigated by Singer usually exhibited severe one-dimensional stacking disorder.

Until very recently⁷ almost all the data available on the optical band gap of ZnS referred to wurtzite ($2L$) or zincblende ($3L$).⁸⁻¹⁰ Only in one paper¹⁰ were results presented on crystals described as showing many colored birefringence bands, but no data are given in [10] on the crystal structure of each band. The change of the absorption coefficient μ with wavelength was much more gradual in such crystals than in wurtzite or in zinc blende¹⁰; apparently some sort of average μ value was determined for each λ .

Birman¹¹ performed calculations to determine the band structures of wurtzite and zinc blende. Though Birman did not deal explicitly with ZnS polytypes, it can be concluded from his work, that the band gap will vary smoothly with α , the percentage of hexagonality of the structure. α has to be defined as the percentage of close-packed planes which are in a hexagonal nearest-neighbor environment. For example, if the three possible positions of the close-packed planes are denoted by A , B and C , respectively,¹ then the $4L$ polytype is $ABACABAC\cdots$, the B 's and the C 's are in hexagonal environments and thus $\alpha=50$. Evidently $\alpha=100$ for wurtzite and $\alpha=0$ for zinc blende. For a polytype mL with $m\geq 6$, knowledge of the layer sequence is essential for the determination of α . It should be noted that in SiC the band gap seems to vary in an approximately linear manner with α .¹²

In the present work the absorption edge and birefringence of several ZnS polytype structures were determined and the results were correlated to the α -values found from x-ray structure analysis.

II. CRYSTALS AND EXPERIMENTAL METHOD

A. Birefringence Measurements

The degree of birefringence $\Delta n = n_e - n_o$, where n_e and n_o are the extreme values of the refractive index, was determined in each region investigated. Since

⁵ F. J. Baum and F. J. Darnell, J. Electrochem. Soc. **109**, 165 (1962).

⁶ J. Singer, J. Phys. Chem. Solids **24**, 1645 (1963).

⁷ O. Brafman and I. T. Steinberger, Appl. Phys. Letters **7**, 110 (1965).

⁸ W. W. Piper, Phys. Rev. **92**, 23 (1953).

⁹ W. W. Piper, P. D. Johnson, and D. T. F. Marple, J. Phys. Chem. Solids **8**, 457 (1959).

¹⁰ J. A. Beun and G. J. Goldsmith, Helv. Phys. Acta **33**, 508 (1960).

¹¹ J. L. Birman, Phys. Rev. **115**, 1493 (1959).

¹² W. J. Choyke, D. R. Hamilton, and L. Patrick, Phys. Rev. **133**, 1163 (1964).

$\Delta n = t/d$, the optical path difference t and the crystal thickness d were measured. t was determined at $\lambda = 5460 \text{ \AA}$ by means of a calibrated Ehringhaus-type rotary quartz compensator and d by focusing the microscope with a $\times 500$ magnification. The accuracy of Δn was limited mainly by the accuracy of the thickness measurements. The maximum error (systematic and statistical) of the Δn values presented in Table I is $\pm 4\%$.

B. Optical Band Gap Determinations

The absorption edge of the various polytypes was determined at 20°C by taking contact photographs of the crystals with a series of uv wavelengths in the absorption edge region. A full description of the method appeared elsewhere.⁷ It is based on the assumption that in the absorption edge region the μ versus λ curves (μ being the absorption coefficient) of all the polytypes are identical except for parallel translations along the λ axis. Several cross-checks were made which justified this assumption.⁷ It was convenient to define the absorption edge of a polytype for the purpose of this work as that wavelength λ_0 , for which $\mu(\lambda_0) = 60 \text{ mm}^{-1}$. Both λ_{011} and λ_{01} , referring, respectively, to polarizations parallel and perpendicular to the optical axis, were determined. The over-all reproducibility of the results for a given polytype was within $\pm 2 \text{ \AA}$.

C. Structure Determinations

X-ray oscillation photographs around the common c axis of the crystals were taken with a 3-cm camera mounted on a Hilger microfocus x-ray apparatus. The diameter of the x-ray beam emerging from the collimator was 0.1 mm. The band of uniform birefringence to be investigated was adjusted in the path of the x-ray beam by using crossed polarizing filters.

The length of the c axis of the unit cell of each polytype was measured directly from the (10.1) column on the photographs. The layer sequence determination of a polytype was based on comparison of visually determined diffraction spot intensities with the calculated intensity distribution.

D. Crystals

All the crystals used were vapor-phase grown in this laboratory, without intentionally added impurities. Growing conditions, shapes and impurity contents have been reported previously.¹³ Platelets of the thickness range 30 to 200 μ were used. All crystal samples consisted of several strip-shaped regions differing in structure. Single regions of uniform structure of adequate width (at least 0.1 mm, measured along the c axis) were selected in two steps:

- (1) Under the polarizing microscope, wide bands of

¹³ O. Brafman, E. Alexander, B. S. Fraenkel, Z. H. Kalman, and I. T. Steinberger, J. Appl. Phys. **35**, 1855 (1964).

TABLE I. Birefringence and absorption edge positions (for both polarizations) of ZnS polytypes. Layer sequences were determined from (10.l) column diffraction intensities. For the definition of the percentage of hexagonality see text.

Crystal notation	Polytype	$(n_e - n_o) \times 10^3$	Absorption edge, Å		Layer sequence ^a	Per cent hexagonality α
			λ_{011}	λ_{01}		
117 S11	2L	23.8	3315	3345	(11)	100
117 S22	2L	23.7	3315	3345	(11)	100
108 S1	2L	24.2	3315	3348	(11)	100
98 S8	3L	0	3410		(3)	0
117 S22	3L	0	3410	3410	(3)	0
134 S1	3L	0		3410	(3)	0
94 S1	3L	0	3410	3410	(3)	0
98 S6	4L	12.0	3361	3378	(22)	50
87 S6	6L	8.2	3375	3388	(33)	33.3
98 S7	6L	8.2	3375	3388	(33)	33.3
134 S1	10L	4.8	3390	3397	(82)	20
97 S8	14L	7.1	3385	3393	(5423) ^b	28.6 ^b
98 S8	24L	6.1	3387	3396	(35) ^c	25
90 S1	26L	3.6	3395	3400		15.4 ^e
94 S1	28L	3.6	3395	3400		14.3 ^e
	I ^d	4.8	3389	3396		20 ^e
	II	4.8	3390	3397		20 ^e
	III	3.7	3396	3400		15 ^e
104 S1	IV	2.4	3400	3404		10 ^e
	V	5.9	3385	3395		25 ^e
	VI	7.4	3379	3390		30 ^e
	VII	6.2	3385	3394		25 ^e
	VIII	4.9	3389	3397		20 ^e
	IX	6.1	3384	3393		25 ^e

^a Reference 14.^b Tentative.^c Inferred from the absorption edge and birefringence results.^d I, II, etc. refer to different bands of the crystal.

uniform birefringence were selected. In some crystals, very fine lines appear on otherwise uniform bands. In such cases care was taken not to include these lines in the region to be investigated.

(2) X-ray oscillation photographs were taken from the regions selected in step (1) and these were scrutinized for diffuse scattering (smearing out of diffraction spots) along columns with indices $h-k=3n\pm 1$. It turned out that uniformity of birefringence (step "1") ensured the absence of diffuse scattering. In other words, one-dimensional random stacking disorder⁶ was not detected in regions of uniform birefringence. However, if the borderlines between uniform birefringence bands were included in the x-ray beam, stacking disorder was often evident. A single well-defined crystal structure was found in each uniform birefringence band.

The intensity distribution of the x-ray oscillation photographs of the 6L, 10L and 24L polytypes was compared with the calculated distributions of all the geometrically possible layer sequences of the polytypes. The actual layer sequences were determined unambiguously from the comparison and the α -values found. The details of the procedure will appear elsewhere. A full calculation for all layer sequences of 14L has not yet been performed, but good correspondence was found between observed and calculated intensities for the layer sequence (5423).¹⁴ No attempt has

yet been made to determine the layer sequences of the 26L, 28L, 40L and 120L polytypes.

III. EXPERIMENTAL RESULTS

The degree of birefringence and the position of the absorption edges of the polytypes investigated are presented in Table I. All crystals mentioned in the table include at least one region of uniform structure with suitable width (>0.1 mm). Often several wide, uniform regions of the same structure were found in a single sample. In such cases the average of results obtained in the different regions are given. Whenever the structures of two regions were identical (the same cell dimensions and layer sequence) there were no differences in the absorption edges and in the birefringences either. An interesting case is that of the crystal 104S1. It included several regions having the same unit cell dimensions (40L or 120L) but differing in birefringences and absorption edges. The regions also differed in layer sequences as was revealed from comparison of x-ray spot intensities.

The results on birefringence and absorption edge for the various crystal structures can be correlated if α , the percentage of hexagonality, is used as a parameter. In Fig. 1a, the degree of birefringence Δn , is plotted as a function of α . In Fig. 1b the absorption edge positions for parallel and perpendicular polarizations (λ_{011} and λ_{01} , respectively) versus α are presented. It is seen that Δn , λ_{011} and λ_{01} are linear functions of α . This is the

¹⁴ For the notation see G. S. Zhdanov, Compt. Rend. Acad. Sci. U.S.S.R. 48, 43 (1945).

central result of the present paper. Equally linear dependencies are obtained if the absorption edge positions are expressed in terms of photon energy.

It follows from the three linear relations of Fig. 1, that if any one of the four quantities α , λ_{011} , λ_{01} or Δn is known, the other three can be determined by linear interpolation. Figure 2 demonstrates that the linear relationship between the λ_0 - s and Δn holds also for the 26L, 28L, 40L, and 120L polytypes, were the layer sequence was not determined by x-rays. The straight lines drawn in this figure were calculated (by elimination of α) from the lines presented in Fig. 1a and 1b. The new experimental points fit very well the calculated lines. This good fit justifies the estimation of the α values for the unknown structures from the birefringence and absorption edge data. These calculated α values appear in Table I for 26L, 28L, 40L, and 120L structures.

Since only certain α -values are possible for a given polytype mL (counting all possible layer sequences), it was also checked whether the estimated α - s are compatible with m ; full compatibility was found. In those cases where different α -values were calculated for regions with the same unit cell dimensions, the regions always differed in x-ray intensity distributions as well.

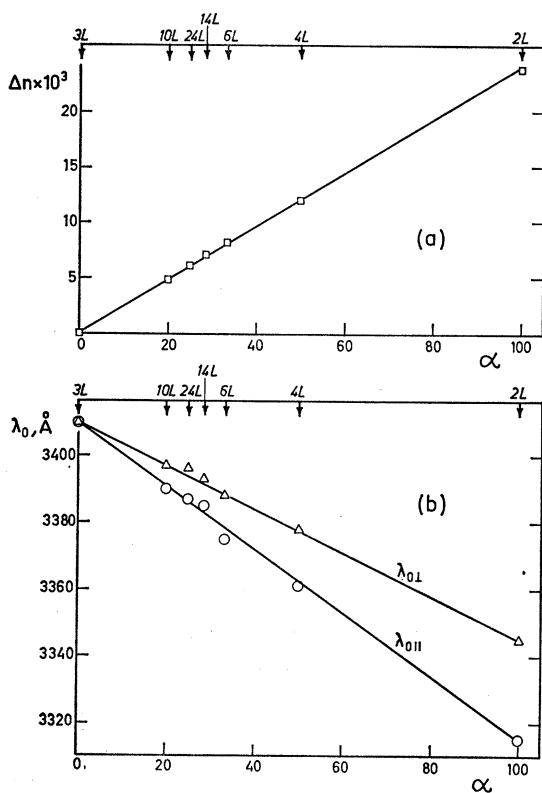


FIG. 1. Degree of birefringence (a) and absorption edge positions for polarization parallel and perpendicular to the c axis (b) as a function of the percentage of hexagonality α (see text).

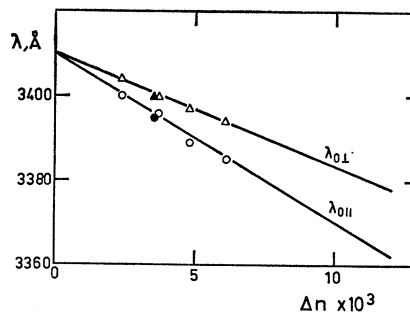


FIG. 2. Absorption edge positions of 40L and 120L polytypes (empty symbols) as well as of 26L and 28L (full symbols) as a function of the degree of birefringence. The drawn straight lines were determined from Fig. 1.

IV. DISCUSSION

Before discussing the implications of the experimental results, a brief comparison will be made with results obtained by other authors on the birefringence of ZnS crystals.

In the crystals investigated during the course of the present work, structure uniquely determined the degree of birefringence. This seems to be contradictory to Singer's results.⁶ Moreover, in the present case the maximum value of Δn was 0.024 (for 2L), while in other works^{5,6,15,16} markedly higher values of Δn were also obtained. The reason for these disagreements is not clear. In Singer's work the structural features of the crystals are described in detail. It seems at first sight from his work that the birefringence is determined mainly by faulting. However, Singer found anomalously high birefringence ($\Delta n=0.050$) even for some pure 2L regions as well, and thus the question remains unsettled.

It is probable that in heavily faulted crystals electrical inhomogeneities^{16,17} and mechanical stresses strongly influence the birefringence. In fact, in some *nonuniform* regions of our crystals, where the structure was twinned cubic (180° rotation twinning of 3L), Δn values up to 0.004 were measured, though a pure cubic ZnS yields, of course, $\Delta n=0$. Considerable faulting was also evident from the x-ray diffraction photographs and the regions consisted actually of a large number of narrow birefringence bands. Much higher Δn values (up to 0.028) were found in twinned cubic ZnS by other authors.¹⁵

For uniform birefringence bands, proportionality between Δn and the percentage of hexagonality α has been assumed.⁵ The results presented here are in full accord with this assumption. In principle, such proportionality will be obtained as a first approximation of

¹⁵ L. W. Strock, V. A. Brophy, and T. E. Peters, New York Meeting of the Electrochemical Soc. Electronics Division, Enlarged Abstracts, p. 61, 1958 (unpublished).

¹⁶ A. Lempicki, Ph.D. thesis, University of London, 1960 (unpublished).

¹⁷ O. Brafman, G. Shachar, and I. T. Steinberger, J. Appl. Phys. 36, 668 (1965).

any theory, where the contributions from planes in hexagonal and cubic environments to the total polarization P are additive. The proportionality is then a direct consequence of the differentiability of P , expressed as a function of the cubic and hexagonal refractive indices. This linear approximation is very good if the polarizability tensors of the hexagonal and cubic environments differ only slightly. Such seems to be the case in ZnS.

The linear relationships between the absorption edges and the percentage of hexagonality will be discussed in the framework of Birman's simplified linear-combination-of-atomic-orbitals (LCAO) calculations¹¹ on the energy states of zinc blende (3L) and wurtzite (2L). He pointed out that the crystal potentials of zinc blende $V(\text{ZB})$ and that of wurtzite $V(\text{W})$ differ from each other only by a small perturbation V' , provided the wurtzite structure is nearly ideal [$c/a = (8/3)^{1/2}$, $u = 3/8$]. A correspondence was found to exist at $k = (0,0,0)$ (point Γ) and along the c axis between zinc blende and wurtzite states. If the assumption of a small perturbation is correct and if the band extrema are at Γ then, for wave propagation along the c axis, the matrix elements contributed by the perturbation V' are the largest at the point Γ and they diminish as k approaches the zone edge. At this point the lowest conduction state of zinc blende (Γ_1) is shifted to somewhat higher energies in wurtzite. The uppermost valence state Γ_4 of zinc blende is split into Γ_1 and Γ_5 in wurtzite; from the higher energy valence band Γ_5 only transitions with polarization perpendicular to the c axis are allowed while both polarizations are allowed for transitions from Γ_1 . The relative positions of the experimentally determined absorption edges¹⁰ conform with the above model: $\lambda_{011}(\text{W}) < \lambda_{011}(\text{ZB}) < \lambda_0(\text{ZB})$.

It is proposed in the quoted work¹¹ that the perturbation calculation for states with k parallel to the c axis can be extended for a randomly faulted structure, i.e. where cubic stacking and hexagonal stacking alternate at random. The same approach is possible for a polytype where the two types of stacking alternate regularly. In this case the percentage of hexagonality α is chosen as a parameter characteristic for the structure. Then $V(\text{P.t.}) = V(\text{ZB}) - V'(\alpha)$ where $V(\text{P.t.})$ is the crystal potential (in Birman's sense) of the polytype which has α percent of its close-packed planes hexagonally stacked. For wurtzite $V(\text{P.t.}) = V(\text{W})$ and therefore $V'(100) = V(\text{ZB}) - V(\text{W})$. Also, $V'(0) = 0$.

The linear dependencies of the absorption edges (for both polarizations) on α as observed in this work, implies that the shifting and splitting of zinc-blende states at Γ are proportional to α . It follows that $V'(\alpha)$ is, to a good approximation, proportional to α . Further developments of Birman's perturbation calculation will

have to account explicitly for this fact. It would be of considerable interest to compare the observed degrees of splitting and shift with theory.

It will be noted that in the above considerations use is made of the assumption that the band extrema occur at Γ and that fundamental absorption is due to direct, allowed transitions at this point. The main justification for this assumption stems from a recent work,¹⁸ where specular reflectivities in a very wide spectral range are compared for several compounds (including ZnS) having wurtzite or zinc-blende structure. Still, the assumption of band extrema and transitions at Γ is not essential for the above discussion: the main point is the splitting of the valence band and the shift of the lowest conduction band. For example, if the maximum of the upper valence band is at Γ for all polytypes, but the deepest conduction band valleys are situated at points of lower symmetry, then the above model may still stay correct, provided the positions of the valleys change only slightly with crystal structure. Such seems to be the situation in SiC.¹⁹ A systematic study of reflectivity and edge emission spectra of ZnS polytypes would furnish detailed information on the band structure of ZnS polytypes. Such measurements should also yield a way for direct correlation and cross-checking of birefringence and absorption results.

Another aspect of the present work is related to the fact that several electrical and optical properties of ZnS crystals are structure-sensitive. One of the striking examples is the anomalous photo-voltaic effect²⁰ observed in crystal samples which include several birefringence bands. It was hitherto impossible to take explicitly into account the influence of each polytype, as practically nothing was known about their physical properties. With the help of the results obtained, however, the band gap of a polytype may be determined by means of birefringence measurement and thus a "map" of the crystal, indicating the band gap at each point, can be obtained. The main limitation of this "mapping" is in the unpredictable properties of faulted regions.

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¹⁸ M. Cardona and G. Harbeke, *Phys. Rev.* **137**, 1467 (1965).

¹⁹ L. Patrick, W. J. Choyke, and D. R. Hamilton, *Phys. Rev.* **137**, 1515 (1965).

²⁰ E.g., W. J. Merz, *Helv. Phys. Acta* **31**, 625 (1958).