

Anomalous photovoltaic effect and disorder in ZnS crystals

M T SEBASTIAN and P KRISHNA

Physics Department, Banaras Hindu University, Varanasi 221 005, India

Abstract. Some crystals of ZnS are known to produce an anomalously high photovoltage, up to several hundred volts per cm, when illuminated by UV light in the absorption edge region. This has been attributed to the presence of alternate regions of hexagonal and cubic packing with charged dislocations at the interfaces producing built-in electric fields. Differential absorption of the incident light in the hexagonal and cubic regions is believed to create the necessary asymmetry in the built-in fields, causing an addition of tiny photovoltages at a series of interfaces which finally results in the abnormally high photovoltages observed.

This paper investigates the possible mechanism by which disordered ZnS crystals containing alternating regions of cubic and hexagonal packing can result. X-ray diffraction studies show that such a disordered configuration results during the $2H$ to $3C$ phase transformation in ZnS. It is suggested that the transformation occurs by the non-random nucleation of deformation faults wherein the probability (α) of random nucleation of the faults is much less than the probability (β) for the faults to occur at two-layer separations.

Keywords. Zinc sulphide; stacking faults; photovoltaic effect; disorder; phase-transformation; polytypes

1. Introduction

The presence of imperfections in a crystal can drastically affect its physical properties. An example of this is presented by ZnS crystals, grown from the vapour phase at temperatures around 1100°C . They contain a variety of one-dimensionally disordered close-packed structures ranging from the cubic ($3C$) structure with a band gap of 3.7 eV (corresponding to 3400 \AA) to the HCP with a band gap of 3.8 eV (corresponding to 3250 \AA). Some ZnS crystals are known to display an anomalous photovoltaic effect of several hundred volts/cm (Ellis *et al* 1958; Merz 1958; Cheroff and Keller 1958; Cheroff *et al* 1959; Lempicki 1959) which is observed only in crystals containing faults. Since many materials used for preparing devices have a structure similar to that of ZnS, it is important to study the influence of defects in this material. This article reviews the anomalous photovoltaic effect (APE) in ZnS and the origin of the defect configurations responsible for it.

2. Anomalous photovoltaic effect in ZnS crystals

Certain types of ZnS crystals are found to develop an electromotive force of up to several hundred volts along the c -axis on illuminating with UV light in the absorption edge region (from $320\text{--}350\text{ nm}$). This high value of photovoltage compared to the bandgap in ZnS is anomalous since photovoltage in simple systems like p - n junctions in semiconductors must be smaller than the bandgap energy expressed in eV (Tauc 1962). In ZnS this sets an upper limit of 3.8 eV . It should be noted that the bandgap of the crystal depends on the perfection of the crystals (Brafman and Steinberger 1966). The

photovoltage is found to change sign at certain wavelengths near the absorption edge (Cheroff *et al* 1959; Lempicki 1959). As the wavelength is increased the first reversal of sign occurs around 3300 Å and the second around 3500 Å. This anomalous behaviour is found only in crystals which show stacking disorder. The anomalous photovoltaic effect does not occur in crystals having a uniform structure throughout.

To explain the observed effect Tauc (1959) proposed a model consisting of structural units composed of alternating 3C and 2H segments with opposing barriers or potential gradients. This model requires an asymmetry in the system to prevent the cancellation of voltages associated with these opposing barriers. It was suggested that this may be caused by variable impurities in the structural units. Neumark (1962) proposed that the spontaneous polarization of hexagonal ZnS causes opposing internal fields in ZnS crystals in the cubic and hexagonal regions. According to this model a small energy barrier ΔE exists at each cubic-hexagonal interface on account of the difference of 0.1 eV between the bandgaps of the hexagonal (2H) and cubic (3C) structures. Shachar and Brada (1970), however, pointed out that there was no experimental evidence for (a) spontaneous polarization (b) asymmetrical electroabsorption and (c) pyroelectric effect in perfect 2H ZnS crystals.

According to the theory of photovoltaic effects in semiconductors or insulators (Tauc 1962), photovoltages may appear only if a built-in electric field exists in the crystal in thermal equilibrium. At a *p-n* junction of a semiconductor, such built-in fields can exist due to carrier concentration gradients. If such a system is illuminated by light of a suitable wavelength free holes and electrons will be generated which move under the built-in field producing an electromotive force. A resultant photovoltage greater than the bandgap energy requires a mechanism of addition of photovoltages generated at a series of barriers. Evidence of built-in electric fields in ZnS crystals containing many structures was obtained by several workers (Pensak 1958; Baum and Darnell 1962; Brafman *et al* 1965; Shachar *et al* 1970; Jacobsen and van der Vorst 1973; Yacobi and Brada 1974, 1976). The direction of the field depends on the structure of the crystal. The field has the same sense in all 2H regions and an opposite sense in all 3C regions. The field direction in a polytype depends on the hexagonality of the structure and that of its neighbours. An etching study (Brafman *et al* 1964) showed that the sense of the [00.1] axis remains constant for a whole specimen and is independent of changes in the crystal structure and disorder. A large difference between the etching behaviour of the (00.1) face and (00. $\bar{1}$) face was found due to the absence of mirror symmetry perpendicular to the *c*-axis.

Internal fields responsible for the APE have been attributed to the occurrence of 60° dislocations at boundaries between uniform regions. Steinberger *et al* (1972) observed the presence of such dislocations at the boundaries between different structures by etching and Lang topography. It is believed that the internal fields are caused by layers of uncompensated charges associated with dislocations which occur at interfaces due to the mismatch of the lattice constants on either side. Holt (1962) described the 60° dislocations in zinc blende, so called because the angle between the dislocation lines and the Burgers vector is 60°. Slip occurs on (111) planes along $\langle 110 \rangle$ directions and there are positive β and negative α dislocations. A positive β dislocation consists of an extra plane (see figure 1) which terminates at the slip plane forming a row of B^{VI} atoms. Similarly a negative α dislocation has an extra plane terminating at a row of A^{II} atoms. Edge dislocations lying wholly within a basal plane in wurtzite, sphalerite or a polytype structure are charged electrically because of the partial polar character of the chemical

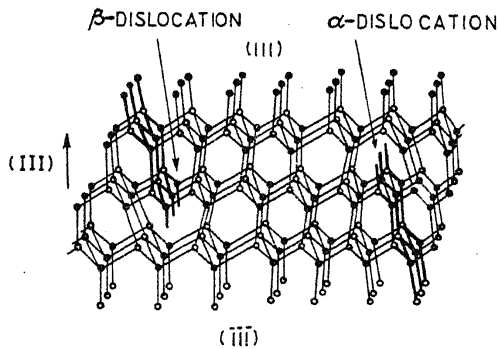


Figure 1. α and β dislocations in the zinc blende structure (after Roth 1967).

bonds (Steinberger *et al* 1972). The sign of the charge depends on whether the dislocation lies in a Zn-plane or a S-plane. Considering an edge dislocation as being the last row of an extra prismatic plane its sign will depend on the position of the edge of the extra plane with respect to the polarity of the c -axis, *i.e.* whether the edge borders the extra plane on its $(00\cdot1)$ side or its $(00\cdot\bar{1})$ side. As on the surface, the charge is positive if it is $(00\cdot1)$ and negative if it is $(00\cdot\bar{1})$. Thus any extra plane will have opposite electrical charges at its two edges and a set of extra planes will imply two sets of charged dislocation lines lying on different basal planes, especially at the boundaries between different structures. It is now believed that the 60° dislocations are responsible for these charged interfaces. Triangular etch pits on prismatic faces are identified with points of emergence of electrically charged dislocations. These are responsible for the internal fields in ZnS crystals. On exposing the crystal to light of a suitable wavelength, electron-hole pairs are produced, separated by the internal field due to the charged interfaces, giving rise to the observed photovoltage.

The following model has been proposed by Yacobi and Brada (1976) to explain the APE in ZnS crystals. It is known that the a -axis lattice constant of the hexagonal structure is smaller than the translation distance along the corresponding $\langle 110 \rangle$ direction in the cubic structure (Roth 1967). This results in the formation of extra charged planes at the interface between the hexagonal and cubic parts of the crystal. The model consists of a series of capacitors with constant total charge. Figure 2 shows schematically the model, consisting of alternating hexagonal and cubic ZnS "condensators" with charged layers at the interfaces of dielectrics. The energy band gap of the cubic structure is less than that of the hexagonal structure, so there is a narrow wavelength region where cubic material absorbs more than the hexagonal material. Due to this differential absorption of light between cubic and hexagonal regions the internal fields cause the asymmetry by changing the carrier concentration at energy gap

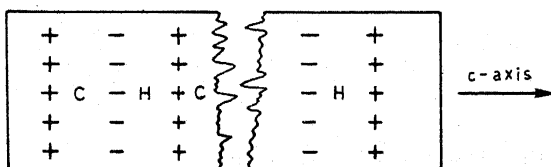


Figure 2. The electric model of the disordered ZnS crystal.

barriers between cubic and hexagonal materials. The addition of tiny photovoltages at a series of interfaces gives rise to the resultant anomalous photovoltaic effect. The observed changes in the sign of the photovoltage occur due to changes in the differential absorption of light between the cubic and hexagonal regions.

We shall now examine how such interfaces arise in ZnS crystals. What is the process of formation of alternating regions of $2H$ and $3C$ structures within the same "single crystal" specimen?

3. The crystal structure of ZnS

The structure of ZnS consists of two identical interpenetrating close packings, one of Zn and the other of S with the one displaced relative to the other along the stacking axis through one fourth of the layer spacing. All such structures can be conveniently described in terms of the ABC notation, where A , B and C represent the three possible positions for the close packed layers (Verma and Krishna 1966). Any sequence of the letters A , B and C , with the restriction that no two successive letters are alike, represents a possible close packed structure. The wurtzite $2H$ structure with the $ABAB\dots$ stacking and the sphalerite $3C$ structure with the $ABCABC\dots$ stacking are the two common modifications of ZnS. The letters H and C stand for the hexagonal and cubic lattice respectively and the numeral before H or C denotes the number of layers after which the ABC stacking sequence repeats itself. The $2H$ (α) modification and the $3C$ (β) modification of ZnS are related by a reversible phase transformation occurring around 1020°C , the $3C$ structure being the low temperature phase. In addition to these two modifications ZnS is known to exhibit a number of intermediate disordered structures containing both random and periodic faults. These structures have either a hexagonal (H) or a rhombohedran (R) lattice. The different polytypes and disordered structures have the same a and b dimensions of the hexagonal unit cell and differ only in the manner of stacking the layers along the c -axis. Figure 3 shows the arrangement of atoms in the $2H$, $3C$, $4H$, $6H$, $8H$, $10H$ and $15R$ polytypes. More than 150 ordered polytype structures have been reported in ZnS (Steinberger *et al* 1973).

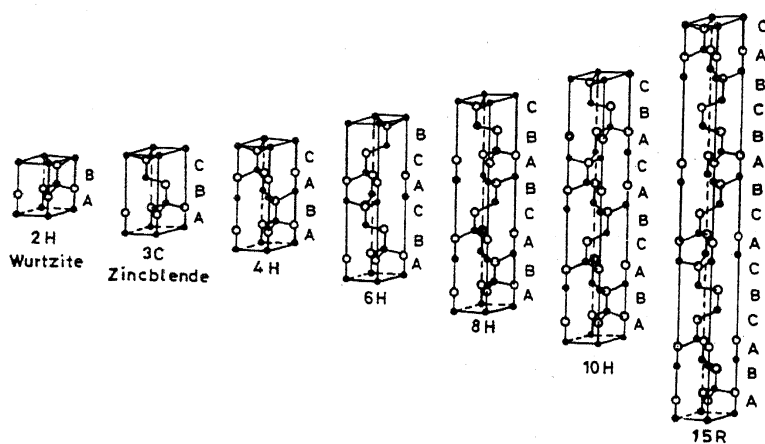


Figure 3. Polytypes of ZnS. The arrangement of Zn atoms (small filled circles) and sulfur atoms (large open circles) in the polytypic modifications of ZnS. The letters A , B and C locate the positions of Zn-S layers (after Roth 1967).

The reciprocal lattices of different polytype structures differ only in the value of c^* which is the reciprocal lattice vector perpendicular to a and b and has the same direction as c . When the c -spacing of the direct lattice of a polytype is large, the value of c^* becomes very small and the reciprocal lattice rows parallel to c^* are crowded with points lying close together. A structure with a completely disordered arrangement of layers corresponds to $c = \infty$, $c^* = 0$ and hence reciprocal lattice rows parallel to c^* become continuous lines (for $h-k \neq 3n$). Figures 4a–e show the $10\cdot L$ reciprocal lattice rows of different ZnS crystals as recorded on 15° c -axis oscillation photographs. The long-period polytype structures are believed to result from the expansion of basal-plane stacking faults around axial screw dislocations of large Burgers vectors (Steinberger *et al* 1973). The expansion of stacking faults occurs in the process of effecting a transformation from the metastable $2H$ structure to the stable $3C$ structure. When the crystal has not grown around an axial screw dislocation the $2H$ – $3C$ structural transformation occurs by the non-random nucleation of stacking faults giving rise to one-dimensionally disordered structures as explained below.

4. Structural transformations in ZnS

The $2H$ structure in ZnS is stable above 1020°C and tends to transform to the cubic $3C$ structure at temperatures below this. It is in the process of this transformation that stacking faults and polytype structures arise, the observed structures representing quenched intermediate states which are all metastable at room temperature. Several investigators have studied the $2H$ – $3C$ solid state transformation in ZnS crystals by thermal annealing (Müller 1952; Piper and Roth 1953; Roth 1960; Hartman 1966;

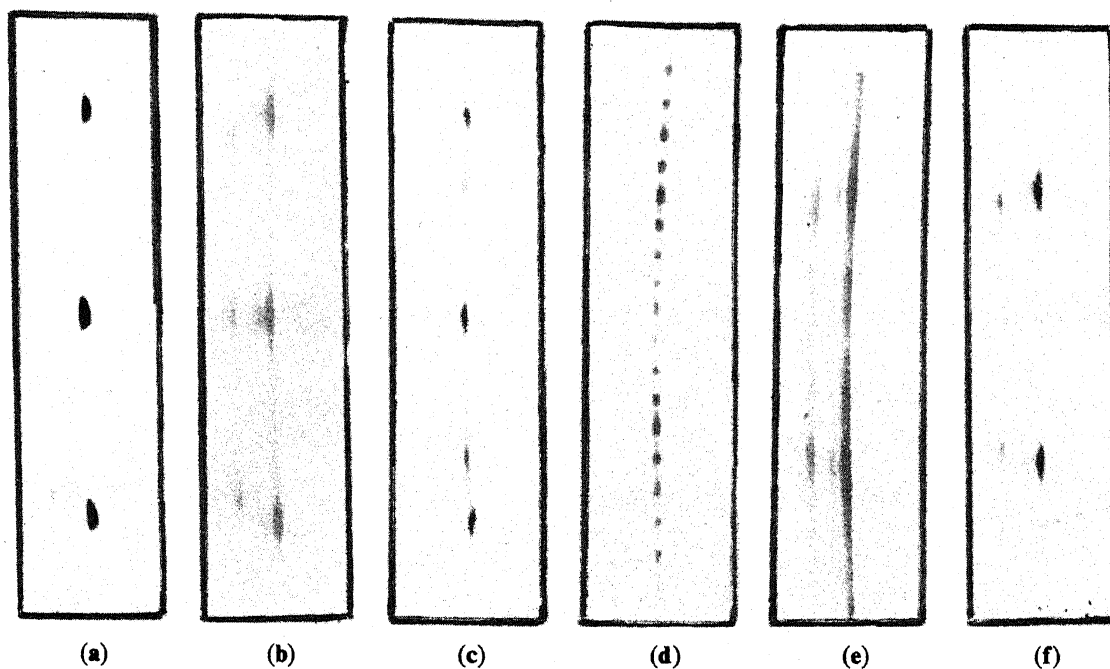


Figure 4. The $10\cdot L$ reciprocal lattice row of some typical observed ZnS crystals as recorded on 15° c -axis oscillation photographs (a) perfect $2H$ (b) disordered $2H$ (c) disordered $2H + 3C$ (d) long-period polytype (e) heavily disordered twinned $3C$ (f) twinned $3C$ with little disorder (camera radius 3 cm, CuK radiation).

Sebastian *et al* 1982). Important characteristics of the transformation are (i) the $2H$ crystals begin to disorder on heating at temperatures between 400 and 700°C depending on the initial perfection of the crystals (ii) they eventually transform to a disordered twinned $3C$ structure and (iii) the transformation is time- as well as temperature-dependent. Recently, Baars and Brandt (1973) confirmed from a high temperature x-ray diffraction study of ZnS crystals that the structural transformations in ZnS occur through a disordering process.

We have recently performed an extensive x-ray investigation of defect structure and the annealing behaviour of $2H$ crystals of ZnS grown from the vapour phase around 1100°C in the presence of H_2S gas. The crystals are found to contain $2H$, twinned $3C$, polytype and disordered structures. The concentration of stacking faults in the disordered structures varies from crystal to crystal and often along the length of the same crystal. The $2H$ crystals were annealed in vacuum in the temperature range 400°C to 1100°C for 1 hr each and quenched in cold water. The structure of the crystals was reexamined by x-ray diffraction after each annealing run to study the mechanism of the transformation. The structural transformations in different crystals commenced at different temperatures depending on the initial perfection of the crystals. Figure 5 shows the $10\cdot L$ reciprocal lattice row of a disordered $2H$ ZnS crystal as recorded on a 15° c -axis oscillation photograph after successive annealing runs. At 400°C the x-ray photograph shows a mixture of $2H$ and $3C$ structures and at 600°C the crystal has transformed to a disordered twinned $3C$ structure. The disordered $3C$ structure transformed back to a disordered $2H$ on further annealing at 1100°C. A study of the x-ray photographs shows that at an intermediate stage of the $2H$ - $3C$ transformation both hexagonal and cubic packings are present in the crystal.

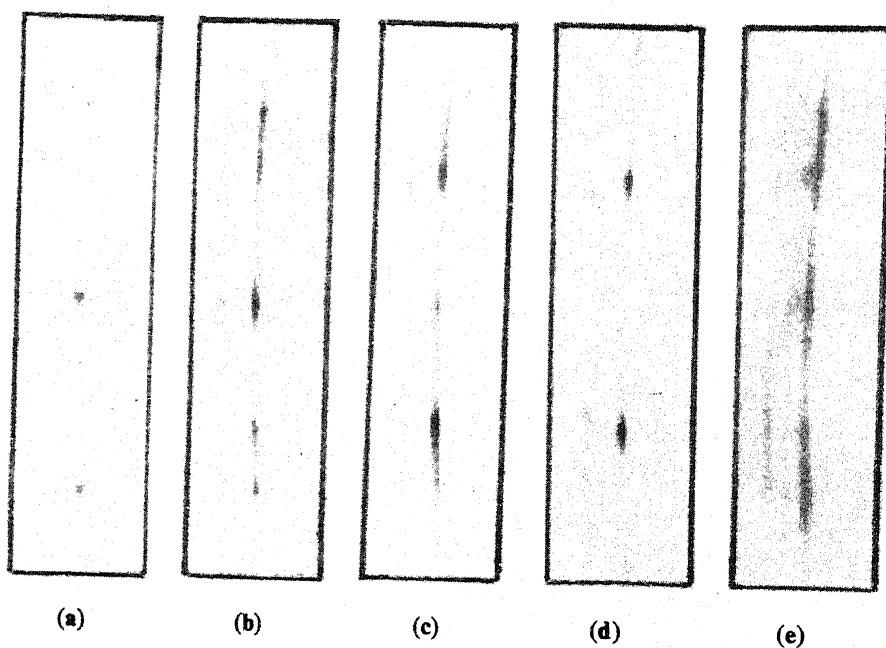


Figure 5. The $10\cdot L$ reciprocal lattice row of a disordered $2H$ ZnS crystal as recorded on 15° c -axis oscillation photographs taken after annealing for 1 hr each at successively higher temperatures (a) room temperature (b) 400°C (c) 500°C (d) 600°C (e) 1100°C. (camera radius 3 cm, CuK radiation).

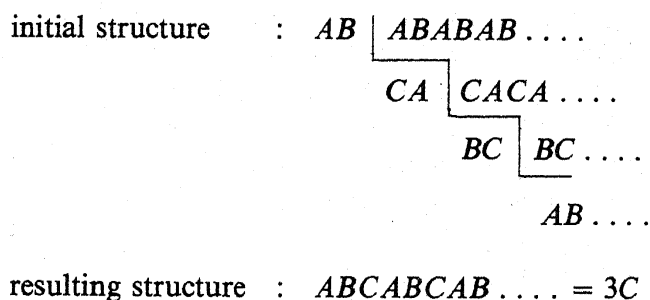
4.1 Mechanism of the structural transformation

It has been proposed that the structural transformation and the formation of polytype structures in ZnS result from a periodic slip mechanism (Daniels 1966; Alexander *et al* 1970). This mechanism is based on the rotation of Shockley partials bounding stacking faults around screw dislocations of multiple Burgers vectors along the c -axis of the $2H$ crystals. Going along the c -axis of a $2H$ crystal containing a screw dislocation with a $2n$ -layered Burgers vector, every $2n$ th basal plane is a part of the same spiral ramp. A stacking fault bounded by Shockley partials while expanding on the basal plane will not move out of the crystal but will climb up the spiral ramp causing the fault to occur periodically after every $2n$ layers. For $n = 1$, $3C$ structure results while for $n > 1$ polytypes will be formed. Mardix *et al* (1971) using x-ray topography obtained evidence of such screw dislocations with large Burgers vectors in long-period polytypes of ZnS. The crystals undergoing the $2H$ - $3C$ transformation by this mechanism produce easily measurable kinks in the external shape of the crystals. The kink angle for the $2H$ - $3C$ transformation is about 19° and has been observed by Daniels (1966) and Mardix and Steinberger (1970).

It is evident from the foregoing that a screw dislocation is necessary to operate the periodic slip mechanism in crystals. However, all crystals do not contain axial screw dislocations, but all of them undergo the $2H$ - $3C$ transformation. Therefore, it is also necessary to consider the mechanism of transformation in the absence of a screw dislocation. Even in crystals which do not contain a screw dislocation the faults can nucleate preferentially at two-layer separations to cause nucleation and growth of $3C$ nuclei during transformation (d'Aragona *et al* 1966; Sebastian *et al* 1982). The nature of stacking faults introduced during the $2H$ - $3C$ transformation can be determined by analysing the intensity distribution along $HK \cdot L$ reciprocal lattice rows parallel to c^* for which $H-K \neq 0 \pmod{3}$. Geometrically, the following four types of fault configurations can occur in the $2H$ structure.

- | | | |
|--|---|-----------------------|
| (i) Growth fault configuration | : | ABABAB CBCBCB |
| (ii) Deformation fault configuration | : | ABABAB CACACA |
| (iii) Layer displacement fault configuration | : | ABABABC <u>B</u> ABAB |
| (iv) Extrinsic fault configuration | : | ABABC <u>A</u> BABAB |

The fault planes are indicated. Our x-ray diffraction studies show that deformation faults are involved in the $2H$ - $3C$ solid state transformation in ZnS (Sebastian *et al* 1982). Deformation faults occurring on alternate layers in the $2H$ structure can result in a $3C$ structure as shown below:



According to this model the transformation commences with the random insertion of deformation faults. This produces continuous streak along the $10 \cdot L$ row seen in

figure 5b. Subsequent faults nucleate not at random but preferentially at two-layer separations, creating a large number of 3C nuclei in the 2H structure which grow with time. The final structure must invariably be a heavily twinned 3C, which fact is confirmed by figure 5d. In order to further confirm this model the diffuse intensity distribution was recorded along the 10·L row of partially transformed crystals at different stages of transformation. One such diffractometer record taken from a 2H ZnS crystal after annealing at 400°C for 1 hr is shown in figure 6. It shows that the 3C peaks develop at an early stage of the transformation and co-exist with the 2H peaks. As the transformation proceeds the 2H peaks decrease in intensity and the 3C peaks get accentuated, without too much broadening of the peaks. This implies that the probability (β) of faults to occur at two-layer separations is much larger than the probability (α) for the random occurrence of faults. It is therefore necessary to employ a two-parameter model of faulting to theoretically compute the diffraction effects from partially transformed crystals. Such a two-parameter model was recently applied by Lele and Pandey (1982) to explain the 3C to 2H martensitic transformation in cobalt.

The theories of x-ray diffraction from randomly faulted close-packed 2H and 3C structures are highly developed and have been well described by Warren (1969), but these do not apply to disordered crystals undergoing transformation since the disorder in this case is not random. However, the theories apply approximately in the very early stages of the transformation and again towards the end of the transformation because the fault-distribution is then nearly random. Our calculations confirm that the observed intensity distribution in the very early stages of transformation corresponds to that expected from a 2H crystal containing a random distribution of deformation faults (Sebastian *et al* 1982) and near the end of the 2H-3C transformation to that expected from a 3C structure containing a random distribution of twin faults.

In the intermediate stage the crystal displays an intensity distribution of the kind shown in figure 6, where both 2H and 3C peaks co-exist. The structure consists of a random distribution of 3C nuclei within the 2H phase. It is such a structure which contains alternating regions of 2H and 3C structures with a series of interfaces. It is therefore such partially transformed crystals which give rise to the anomalous photovoltaic effect.

5. Summary and conclusion

- (i) Disordered ZnS crystals containing alternating regions of 2H and 3C structure have built-in electric fields due to charged dislocations at the interfaces.
- (ii) These produce anomalous photovoltages due to differential absorption of light of suitable wavelength in the hexagonal and cubic regions.
- (iii) Such ZnS crystals containing alternating regions of 2H and 3C structure originate during phase-transformation from the high-temperature 2H phase to the low-temperature 3C phase.
- (iv) The 2H-3C transformation in ZnS crystals not containing an axial screw dislocation occurs by the non-random insertion of deformation faults. The probability (α) of random faulting is much less than the probability (β) of the deformation faults to nucleate at two-layer separations.

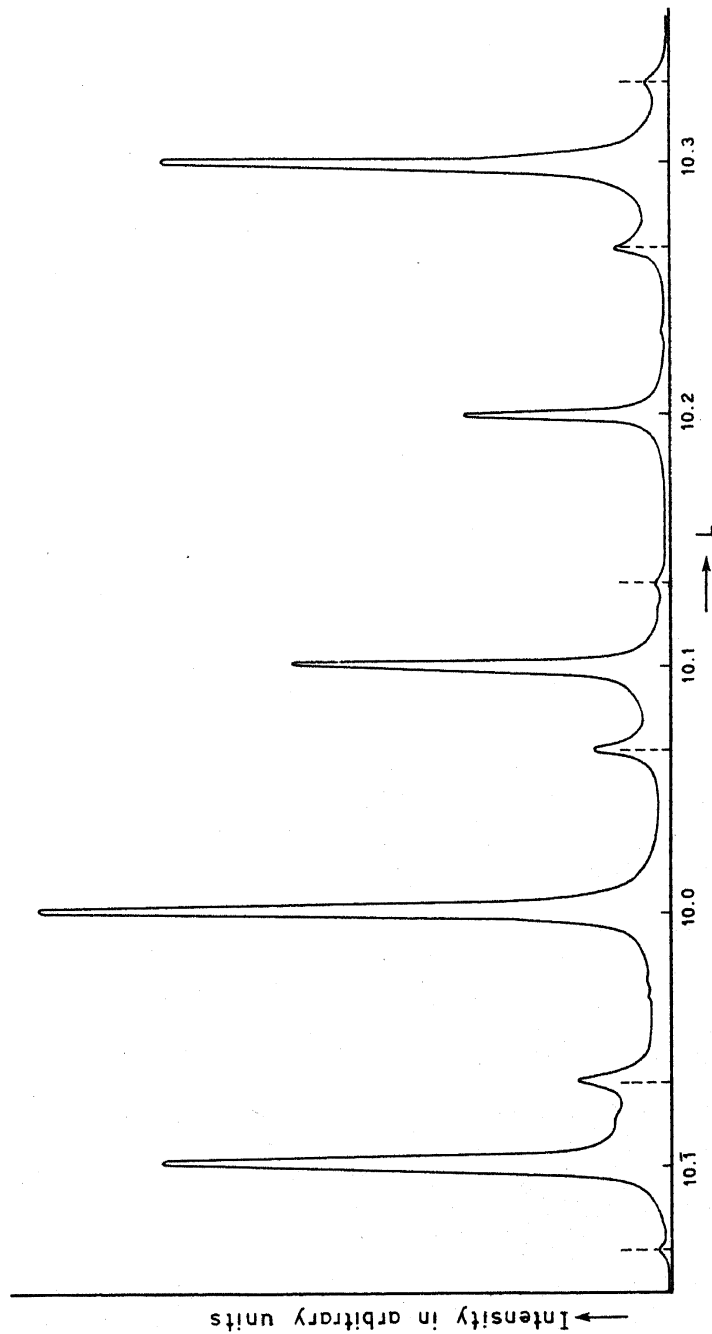


Figure 6. Single crystal diffractometer record of intensity vs L in reciprocal space along the $10-L$ row of a disordered $2H$ ZnS crystal obtained by annealing a nearly perfect $2H$ crystal at 400°C . Dashed vertical lines indicate the $3C$ positions.

Acknowledgements

The authors are grateful to the DST, New Delhi for providing financial assistance. One of them (PK) is thankful to Prof. H Schulz of the Max-Planck Institute (FKF), Stuttgart, for providing the single-crystal diffractometer facilities.

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