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Faulting in ZnS: Analysis by a Two-Parameter Model

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The two-parameter model of Jagodzinski has been employed to calculate the X-ray scattering from faulted ZnS. The agreement with the observed scattering from single crystals is sufficiently close to establish the need for the two independent parameters to define the one-dimensional disorder. Departure from perfect agreement is attributable to heterogeneity, or non-randomness, of the faulted structure, which is probably a result of the transformation mechanism. Direct evidence of independently diffracting domains has been obtained in a micro-diffraction study of the bands of uniform birefringence which accompany the disorder. Implications from the ZnS findings are made for other cases of one-dimensional disorder.

An Appendix provides intermediate equations required for calculating Jagodzinski's function for any combination of α and β.

1. Introduction

One-dimensional stacking fault disorder and its effect on X-ray scattering have been variously treated, usually with models defining a single disorder parameter (Wilson, 1942; Houska & Averbach, 1958; Houska, Averbach & Cohen, 1960; Barrett, 1950; Zachariasen, 1947). In such models, the fraction of planes, α, out of the one sequence (*e.g.*, hexagonal) is the same as the fraction in the other sequence (*e.g.*, cubic). However, in some cases of stacking fault disorder it has been indicated that at least two independent parameters are needed for adequately defining the disorder (Jagodzinski, 1949*a*, *b*; Muller, 1952).*

Jagodzinski provided a two-parameter model which was employed by Muller (1952) with faulted ZnS in attempts to fit the observed X-ray scattering with calculated distribution functions. However, the few good fits which he reported were for special cases; in particular, the fits obtained with the two parameters α and β equal to each other represent merely the reduction of Jagodzinski's function to that of the one-parameter model. Furthermore, Muller indicated that very few crystals produced good fits; no reason was advanced for this, yet it was implied that the two-parameter model did generally apply to faulted ZnS.

In the present work the applicability of this model has been re-examined. It is shown that Jagodzinski's function does apply where the faulting is random, and that the principal difficulty in obtaining good fits with typical ZnS crystals is that these are fundamentally non-random, or heterogeneous, in structure probably because of transformation faulting. Implications from these findings are made for other cases of stacking fault disorder; with some, the one-parameter model may have been incorrectly employed, while in others, heterogeneity may have gone unnoticed. The independent scattering by the X-ray resolved domains of a heterogeneous structure is additive and so cannot be represented by any single distribution function, whatever the model.

* *Note added in proof.* Sato (1962) hns shown the applicability of the Jagodzinski model to growth-faulted CdS.

2. Experimental

(A) *The* ZnS *crystals*

Thin needles of ZnS were grown from the vapor phase in the hexagonal region, >1100 °C, by Samelson (1961). One batch, for unknown reasons, contained many unfaulted ones; these appear to be the only perfect synthetic wurtzite reported, except for whiskers (Piper & Roth, 1953). When it was found that the usual faulted synthetic crystals produced X-ray scattering of a variety of types, the general matter of homogeneity was investigated in a separately reported work employing micro-beam diffraction and birefringence measurements (Singer, to be published). This established the prevalence of heterogeneity which could affect the quality of fit in testing the calculated distributions, since a random distribution of faults is the assumption underlying any such calculation. Therefore an attempt was made to favor homogeneity by heat treating perfect hexagonal crystals at moderate temperatures. The Jagodzinski model was then tested with these specially faulted crystals.

Observed and calculated X-ray scattering distribution functions are reported here for two heat treatments of the same crystal, consisting of ten minutes in an open capillary tube at 400 and 530 °C. In addition, a similar crystal was directly heated to 530 °C.

In the associated work reported elsewhere (Singer, to be published), measurements were made of the birefringences produced in these crystals by the heatings. Results from this work relevant to the present study will be given in context in what follows.

(B) *Observed X-ray scattering distributions*

The (10·*l*) REL row may be used to represent the fault-sensitive rows which are those with $H-K \neq 3n$ (Wilson, 1942). The (10·*l*) scattering distributions were obtained with filtered Cu $K\alpha$ radiation on film in 15° oscillation diagrams designed to bring in this row from the equatorial (10·0) hexagonal spot to beyond the (10·1). This range includes the position for scattering by coherent cubic domains which lies about $\frac{2}{3}$ the way towards the (10·1) hexagonal spot from the (10·0). This cubic position may be indexed $(10\cdot1)_3$, the subscript referring to the cubic 3 layer, or $3L$, sequence of close-packed planes. (The nomenclature associated with close-packing is given in many of the appended refences.) The row was scanned with a recording microdensitometer and the observed transmittance record converted to an intensity distribution by means of a calibration scale. Completely independent rendering of the same film produced no detectable difference in the final intensity distributions as plotted.

(C) *Calculated X-ray scattering distributions*

Making a slight change in a symbol used by Jagodzinski, his general expression for the intensity along the fault-sensitive REL rows may be condensed to

$$I \simeq |F|^2 \sum_{\nu=2}^{5} \frac{K_\nu(1-X_\nu^2)}{1-2X_\nu \cos A_3 + X_\nu^2}$$

where

F is the layer structure factor (Muller, 1952);
A_3 is the distance, in degrees, along the row, where adjacent hexagonal maxima are separated by π degrees;
K_ν, X_ν are sets of values, given by solution of difference equations which contain the two independent fault-sequence probabilities α and β.

This equation has the same form as Wilson's for the one-parameter model (Wilson, 1942) and reduces to the latter when $\alpha=\beta$. In calculating the distributions, use was made of Jagodzinski's and Muller's intermediate calculations and also of interpolated values obtained as shown in the Appendix.*

3. Results

Fig. 1 shows the observed X-ray scattering for the two heat treatments of an initially unfaulted hexagonal ZnS crystal. The crystal which was separately heated directly to 530 °C yielded a distribution practically identical with the one shown for that temperature. Fig. 2 compares the observed distribution for the 400° heating with that calculated by Jagodzinski's model for $\alpha=0\cdot15$, $\beta=0\cdot65$. Calculations were made at intervals of 0·05 in each of the two parameters; the fit worsened as they departed from the values indicated. The critical region for evaluating the fit—which would not necessarily apply to other ranges of α and β—appeared to lie in the vicinity of the $(10\cdot1)_3$ position. Intercomparisons among Figs. 1 and 2 and the other calculated distributions disclosed that the higher temperature had produced a distribution which departed significantly further from the general form of the Jagodzinski function;

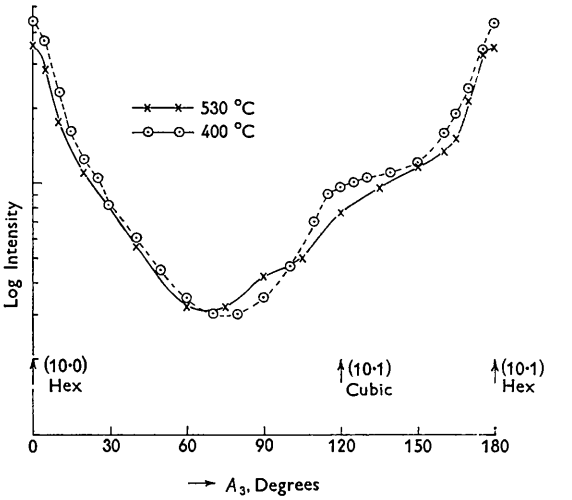

Fig. 1. Observed X-ray scattering for 400 and 530 °C heat treatments of crystal no. 1.

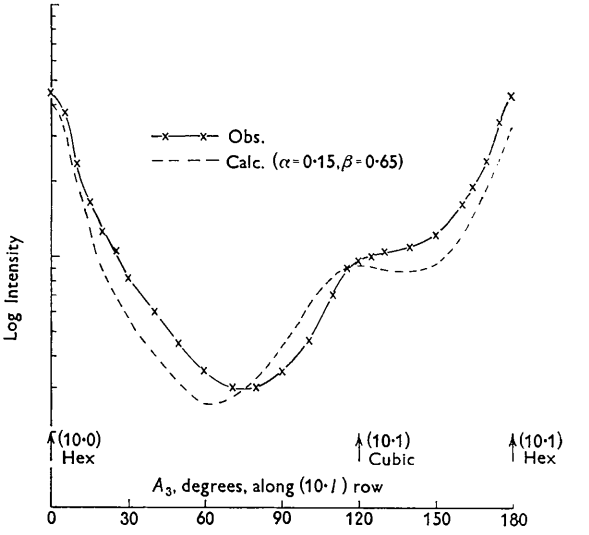

Fig. 2. Calculated and observed X-ray scattering for crystal no. 1 faulted at 400 °C.

* A few non-numerical typographical errors appear in the publications.

moreover, some of the 4-layer polytype had been formed, as shown by the slight accrual of scattering at $\pi=90$ deg. It may be useful to note here that this model can represent mixtures of 2, 3, and 4 layer sequences.

Some of the associated birefringence and microdiffraction work mentioned previously is relevant here. The 400° heating produced fine bands of uniform birefringence with Δn ranging from 0·015–0·020. The 530° treatment extended the range to 0·0085–0·020. The crystal separately heated directly to 530 °C developed a range of 0·011–0·020. Some bands were too thin to be measured, so that these extrema cannot be taken too literally. The birefringence of Wurtzite, 0·024, is germane to this information.

4. Discussion

The usual vapor phase grown hexagonal ZnS crystal is faulted and shows, between crossed polarizers, many fine bands of uniform birefringence of some range in Δn. It has been generally assumed that Δn is lower the more the faulting, although no precise work has been done on the correlation. The present author's work on this subject may be abstracted for the present discussion as follows: (*a*) it has been found that the basic difficulty in correlating a structural parameter with the specific value of Δn in a band is the existence of independently diffracting domains of small size; (*b*) the *range* of Δn may be taken as a rough indicator of the degree of this kind of heterogeneity, rather than of the more precise degree of disorder. It is herewith suggested that the two-parameter model basically describes the disorder in thermally faulted ZnS and that the departure from fit derives from the heterogeneity of this faulted structure.

This suggestion implies that homogeneous domains, many larger than 1,000 Å in the direction of c_0, exist in the faulted crystal, each requiring its own two-parameter distribution function. The independent scattering from these domains is additive and the resultant cannot be precisely fitted by a calculated distribution, whatever the model.

It is not unreasonable that transformation faulting be expected to produce a heterogeneous structure. Jagodzinski suggested that transformation might interfere with fitting by calculated functions. In cooling the synthesized ZnS from the hexagonal region, transformation occurs at a variety of nuclei, such as occurs in martensitic transformations. Without attempting to specify their nature, these nuclei may be different and may be activated at different temperatures; furthermore, their distribution along the crystal may be quite accidental. The observed superiority of fit for the lower temperature of faulting a perfect crystal is compatible with the foregoing. Muller's difficulties in obtaining good fits may be similarly explained. What constitutes Muller's best proof of the applicability of Jagodzinski's model to ZnS is the fit he showed for a case with $\alpha=0{\cdot}1$, $\beta=0{\cdot}9$. It is conceivable that the effect of heterogeneity on the observed scattering is comparatively obscured for cases, such as this, where the coherence in the two types of sequence is high. It is interesting that the 530° heating in the current work appears to have produced some $4L$ polytype, which would augment the heterogeneity.

One cannot adequately test for this type of heterogeneity by successive exposures along a crystal with a conventional X-ray beam. Visual inspection could indicate that the same diffraction pattern is obtained all along the crystal, yet heterogeneity could be widespread. Powder patterns also may obscure heterogeneity; some incompatibility between line broadening in the parent phase and the diffuse scattering would be difficult to observe (Singer, to be published). A solitary instance of a single-crystal pattern of faulted cobalt was depicted in the first work on this substance (Edmunds & Lipson, 1942). The pattern was made with a fragment in accidental orientation, yet the isolated REL row shows two phases and further suggests the possibility of heterogeneity; these observations were not made by the authors, nor has any attention been paid to this photograph in the subsequent extensive literature on faulting in cobalt. The question might be raised, then, whether the one-parameter model, which has always been employed with it, is correct for cobalt. Of related interest is the paper by Barrett (1950) wherein many randomly oriented crystallites are resolved, along with some of their REL rows, on Debye rings obtained with short range oscillation exposures; the substance was a faulted Cu–Si compound. Barrett suggested that 'fault-clustering' might explain some of the observations, a term analogous to heterogeneity in its diffraction effects. Notice was taken, however, of the possibility that a one-parameter model might be inadequate.

In the course of the present work, some attention was given to the elegant analysis of Gevers (1954). It was soon found that the further refinement offered by this method in terms of additional independent parameters, as well as separate ones for growth and transformation faults, could not be utilized owing to the irregularities in the observed distributions stemming from heterogeneity.

5. Summary

(A) Jagodzinski's two-parameter model, with interaction across 3 layers, basically fits the observed scattering from faulted hexagonal ZnS.

(B) Departures from fit are caused by the independence of scattering from domains large enough to be resolved by the X-rays. Each domain requires its own distribution function to describe its structure.

(C) The usual synthetic crystal has been faulted by

transformations occurring during the post-synthesis cooling. Thus, transformation faults are superimposed on any growth faulting.

(D) Homogeneity may be favored by faulting in a limited temperature range. In ZnS, the range of birefringence can be used as a rough indication of the range of heterogeneity, but not of the range of degree of disorder.

(E) Stacking fault disorder should be investigated by single-crystal methods at least to establish whether one- or two-parameter models are applicable and whether the structure is homogeneous.

APPENDIX

Calculation of Jagodzinski two-parameter functions for S=3

By G. Gashurov

It has been shown by Jagodzinski that the diffracted intensity for his two-parameter model of one-dimensional disorder is proportional to

$$I \propto \sum_{\nu=2}^{5} \frac{K_\nu(1-X_\nu^2)}{[1-2X_\nu \cos A_3 + X_\nu^2]} .$$

The terms appearing in this equation have been defined elsewhere (Jagodzinski, 1949*b*).

To facilitate the intensity calculation, Jagodzinski has tabulated X_ν and K_ν for various combinations of α and β parameters. For α, β pairs not included in the table, X_ν and K_ν are calculated by means of the following equations:*

$$X^4+\beta X^3+[(2\alpha-1)-(\alpha^2-\beta^2)]X^2 + (\alpha-\beta)(1-\alpha)X-(\alpha-\beta)^2=0 \qquad (1)$$

$$K_\nu = \tfrac{1}{3}\times \frac{(X_\nu+X_1)}{(X_1-1)\prod_{\nu'=2}^{5}(X_{\nu'}-X_\nu)} \times \left\{\prod_{\nu'=2}^{5}(1+X_{\nu'})-3\alpha+\frac{g(X_{\nu'})}{(1+X_1)}\right\} \qquad (2)$$

where

$$X_1=\beta-\alpha$$

$$\nu' \neq \nu$$

$$g(X_{\nu'})=[(1+X_\alpha X_\beta)(1+X_\gamma X_\delta)+(X_\alpha+X_\beta)(X_\gamma+X_\delta)]$$

$\alpha, \beta, \gamma, \delta$ are integers 1–5 $(\nu' \neq \nu)$.

Equation (1) (which, in general, will have two real and a pair of complex roots) may be solved as follows. The real roots of the equation may be found by the Newton–Raphson method. The complex roots, $\varrho \exp(i\varphi)$ and $\varrho \exp(-i\varphi)$, are then calculated by means of

$$(\beta-\alpha)^2=-X_2X_3X_4X_5 = -X_2X_3\varrho^2$$

and

$$\beta=-(X_2+X_3+X_4+X_5) = -(X_2+X_3+2\varrho\cos\varphi) .$$

It may be mentioned that for the case $\alpha=\beta$, equations (1) and (2) reduce to

$$X^2+\alpha X+(2\alpha-1)=0 \qquad (3)$$

and

$$K_\nu=(2+X_{\nu'}-3\alpha)/(3X_\nu(X_\nu-X_{\nu'})) = (1+2X_{\nu'})/3(X_{\nu'}-X_\nu) \qquad (4)$$

respectively, which are identical with equations VI–9 and VI–11 of Wilson's one-parameter model.

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* The corresponding equations derived by Jagodzinski, equations (10) and (21*b*), were found to contain several typographical errors. It may also be noted that equation (23) in Jagodzinski's paper (Jagodzinski, 1949*b*) has been rewritten correctly by Muller as his equation II (Muller, 1952), the error having been the omission of a parenthesis.

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