

## X-ray Diffraction Effects from Randomly Twinned f.c.c. Crystals Undergoing Transformation to the h.c.p. Phase

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### Abstract

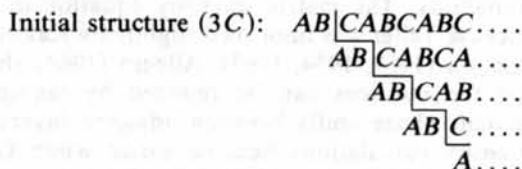
F.c.c. crystals of ZnS often contain a random distribution of twin faults. The f.c.c. to h.c.p. transformation in this material occurs by a nonrandom insertion of deformation faults at two layer separations. The kinematical theory of diffraction from f.c.c. crystals containing randomly distributed twin faults and undergoing solid-state transformation to the h.c.p. phase is developed.

### Introduction

Zinc sulfide exists in two polymorphic forms, the sphalerite (3C) with the ABCABC... packing of atomic layers and the wurtzite (2H) with ABAB... packing. The two forms are related by a reversible phase transformation that occurs at 1293 K, the wurtzite being the high-temperature modification. Recently, Sebastian, Pandey & Krishna (1982) made a systematic study of the 2H-3C transformation in ZnS. The 2H crystals begin to disorder [Sebastian *et al.*, 1982; Roth, 1960] on annealing at temperatures around 570 K and at around 870 K they transformed to a disordered twinned 3C structure. On further annealing (Sebastian & Krishna, 1984a) it transformed to a disordered 2H structure at about 1320 K. Fig. 1 shows the 10.L reciprocal-lattice row of a heavily disordered twinned ZnS-3C crystal recorded after annealing and quenching at different temperatures. On annealing at 970 K, the intensity of the diffuse streak decreased. The 2H reflections appeared on annealing at 1320 K and the crystal transformed to a disordered 2H at 1370 K. An analysis of the diffraction profiles showed (Sebastian *et al.*, 1982; Roth, 1960; Sebastian & Krishna, 1984b) that the as-grown and annealed disordered 2H crystals contain a random distribution of deformation faults whereas the as-grown and 3C crystals obtained by annealing 2H always contain (Sebastian & Krishna,

1984a,b) a random distribution of twin (growth) faults.

The insertion of deformation faults at two-layer separations can effect the 3C-2H transformation as depicted below:



Resulting structure (2H): ABABABABA...

The f.c.c. to h.c.p. transformation can be accomplished (Christian, 1951; Kotval & Honeycomb, 1968; Fujita & Ueda, 1972) by the movement of  $(a/6)\langle 112 \rangle$  Shockley partials on alternate (111) planes. Recently,

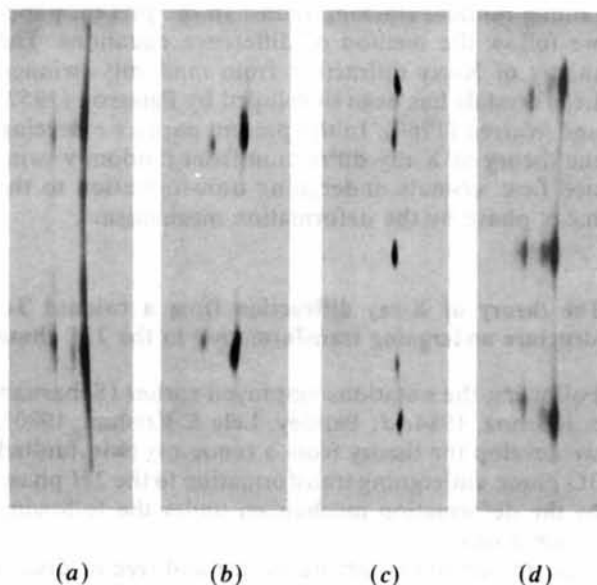


Fig. 1. The 10.L reciprocal-lattice row of a disordered twinned ZnS-3C crystal recorded after annealing at successively higher temperatures for 1 h. (a) Room temperature, (b) 973 K, (c) 1323 K, (d) 1373 K (camera radius 3 cm, Cu  $K\alpha$  radiation, mag.  $\times 3$ ).

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Lele & Pandey (1985) developed a theoretical model to explain the f.c.c.-h.c.p. transformation in cobalt. Their model considers an initial untwinned 3C crystal in which deformation faults occur at two-layer separations to effect the transformation. This model is not applicable to the cubic ZnS crystals grown from the vapour phase at temperatures above 1290 K or to those obtained from the wurtzite form by solid-state transformation since they invariably contain (Sebastian & Krishna, 1984*a,b*; Qin, Li & Kuo, 1986) a random distribution of twin (growth) faults. The intensity of the scattered X-rays from close-packed structures containing stacking faults can be calculated either by the use of difference equations developed by Wilson (1942) or by means of a matrix intensity equation introduced by Hendricks & Teller (1942). Wilson's difference equation is constructed for the probability of finding a kind of layer and later Prasad & Lele (1971) constructed difference equations taking into account phase shifts of layers in addition to the probability. The matrix intensity equation of Hendricks & Teller was improved slightly by Kakinoki & Komura (1952, 1954, 1967). Allegra (1964) showed that the matrices can be reduced by taking into account phase shifts between adjacent layers. The intensity calculations became easier when Gevers (1954) and Holloway (1969) showed that the intensity could be calculated with the coefficients of the characteristic equation of the difference equation without solving the characteristic equation. Recently, Berliner & Werner (1986) introduced a computer modelling method for the calculation of the diffracted intensity from one-dimensionally disordered structures containing random stacking faults. In the present paper we follow the method of difference equations. The theory of X-ray diffraction from randomly twinned f.c.c. crystals has been developed by Paterson (1952) and Warren (1969). In the present paper we develop the theory of X-ray diffraction from randomly twinned f.c.c. crystals undergoing transformation to the h.c.p. phase by the deformation mechanism.

### The theory of X-ray diffraction from a twinned 3C structure undergoing transformation to the 2H phase

Following the notations employed earlier (Sebastian & Krishna, 1984*c,d*; Pandey, Lele & Krishna, 1980), we develop the theory from a randomly twin-faulted 3C phase undergoing transformation to the 2H phase by the deformation mechanism under the following assumptions:

- (i) the crystal is infinite in size and free of distortions;
- (ii) the scattering power for all the layers is the same;
- (iii) there is no change in the layer spacings at the faults;

(iv) the faults extend right across the crystal boundaries;

(v) the probability ( $\beta$ ) of occurrence of deformation faults at two-layer separations is larger than the probability ( $\alpha$ ) of their occurrence at larger separations;

(vi) once a deformation fault occurs on a particular layer, the probability of another fault occurring on the next layer is negligible;

(vii) the initial 3C structure may contain a small probability  $\gamma$  of occurrence of random twin faults.

Since the (111) close-packed planes of the cubic structure become the (0001) planes of the hexagonal structure after transformation, we shall use hexagonal axes and a three-layered hexagonal unit cell to describe the f.c.c. structure. There are two types of layers in the perfect f.c.c. and h.c.p. structures denoted by 0 and 1 according to whether the stacking offset vector is  $+S_i$  or  $-S_i$ , where  $S_i$  denotes

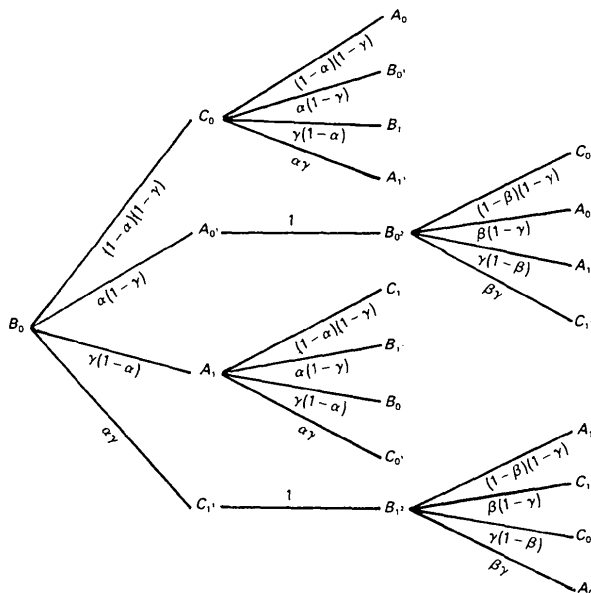
$$S_1 = \frac{a}{3}[1\bar{1}00], \quad S_2 = \frac{a}{3}[01\bar{1}0] \quad \text{and} \quad S_3 = \frac{a}{3}[\bar{1}010].$$

The perfect 2H and 3C structures can be written as

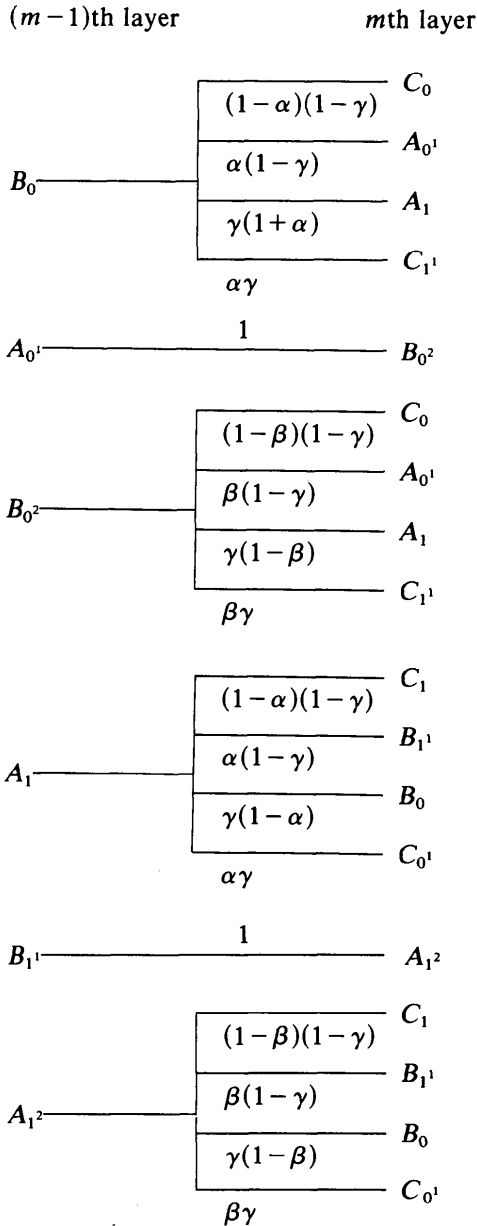
$$A_0B_1A_0B_1A_0B_1 \dots$$

$$A_0B_0C_0A_0B_0C_0 \dots$$

respectively. There are four more types of layers for crystals undergoing transformation to the h.c.p. structure. Let the subscripts  $0^1$  and  $1^1$  denote the first layer of the slipped stack following a 0-type or 1-type layer respectively. It is assumed that the next layer after a  $0^1$ - or  $1^1$ -type layer is unfaulted. One can obtain a 2H structure only under this assumption. The next layer after  $0^1$  or  $1^1$  type is denoted by  $0^2$  or  $1^2$  since there is a probability  $\beta$  of a fault occurring at these layers. We use the following probability trees which



consider the transitions from the  $(m-1)$ th to the  $m$ th layer with each type of layer at the origin and follow Sebastian & Krishna (1984c).



We get

$$J_{(m,0)} = (1-\alpha)(1-\gamma)J_{(m-1,0)}\omega_1 + (1-\beta)(1-\gamma)J_{(m-1,0^2)}\omega_1 + \gamma(1-\beta)J_{(m-1,1^2)}\omega_1 + \gamma(1-\alpha)J_{(m-1,1)}\omega_1 \quad (1)$$

$$J_{(m,1)} = (1-\alpha)(1-\gamma)J_{(m-1,1)}\omega_2 + (1-\beta)(1-\gamma)J_{(m-1,1^2)}\omega_2 + \gamma(1-\beta)J_{(m-1,0^2)}\omega_2 + \gamma(1-\alpha)J_{(m-1,0)}\omega_2 \quad (2)$$

$$J_{(m,0^1)} = \alpha(1-\gamma)J_{(m-1,0)}\omega_2 + \beta(1-\gamma)J_{(m-1,0^2)}\omega_2 + \alpha\gamma J_{(m-1,1)}\omega_2 + \beta\gamma J_{(m-1,1^2)}\omega_2 \quad (3)$$

$$J_{(m,1^1)} = \alpha(1-\gamma)J_{(m-1,1)}\omega_1 + \beta(1-\gamma)J_{(m-1,1^2)}\omega_1 + \alpha\gamma J_{(m-1,0)}\omega_1 + \beta\gamma J_{(m-1,0^2)}\omega_1 \quad (4)$$

$$J_{(m,0^2)} = J_{(m-1,0^1)}\omega_1 \quad (5)$$

$$J_{(m,1^2)} = J_{(m-1,1^1)}\omega_2 \quad (6)$$

where  $\omega_1 = \exp(i2\pi/3)$  and  $\omega_2 = \exp(-i2\pi/3)$ .

Let the solution of the system of difference equations (1) to (6) be of the form

$$J_{(m,j)} = c_j^m; \quad m \geq 0, \quad (7)$$

where  $c_j$  and  $\rho$  are functions of the fault probabilities. Since the crystals contain a small amount of twin faults higher-order terms in  $\gamma$  are neglected. Substituting (7) in (1) to (6) and eliminating the various  $c$ 's, we finally get the so-called characteristic equation

$$\rho^6 + (1-\alpha)(1-\gamma)\rho^5 + [(1-\alpha)^2(1-2\gamma) - 2\beta(1-\gamma)]\rho^4 + [(1-2\gamma)(\alpha + \alpha\beta - 2\beta)]\rho^3 + [2(1-\alpha)(1-3\gamma)(\alpha - \beta) + \beta^2(1-2\gamma)]\rho^2 + (1-3\gamma)(\beta^2 - \alpha\beta)\rho + (\alpha - \beta)^2(1-4\gamma) = 0. \quad (8)$$

Holloway (1969) obtained an analytical solution for the diffracted intensity in terms of the coefficients and boundary conditions of the characteristic equation. His intensity expression is

$$I = f^2 c \left( \left\{ \frac{1}{2} + \left[ \sum_{j=1}^{n-1} \sum_{k=0}^{j-1} A_{h-k} T_{j-k} \exp(n-j)i\pi L - A_0 \right] \times \left[ \sum_{j=0}^n A_j \exp(i\pi L) \right]^{-1} \right\} + \text{c.c.} \right), \quad (9)$$

where the  $A$ 's are the coefficients of the characteristic equation, the  $T$ 's are the boundary conditions,  $f^2$  is the scattering power for a single layer of the structure and  $c$  is a scale factor.

In the present case,

$$\begin{aligned} n &= 6 \\ A_6 &= 1 \\ A_5 &= (1-\alpha)(1-\gamma) \\ A_4 &= (1-\alpha)^2(1-2\gamma) - 2\beta(1-\gamma) \\ A_3 &= (1-2\gamma)[\alpha - 2\beta + \alpha\beta] \\ A_2 &= 2(1-\alpha)(1-3\gamma)(\alpha - \beta) + \beta^2(1-2\gamma) \\ A_1 &= (1-3\gamma)(\beta^2 - \alpha\beta) \\ A_0 &= (\alpha - \beta)^2(1-4\gamma). \end{aligned}$$

Let  $W_j$  be the probability of finding a layer with subscript  $j$  on passing through an arbitrary region of

the crystal. From the probability tree we get

$$W_0 = (1 - \alpha)(1 - \gamma)W_0 + (1 - \beta)(1 - \gamma)W_{0^2} \\ + \gamma(1 - \beta)W_{1^2} + \gamma(1 - \alpha)W_1$$

$$W_1 = (1 - \alpha)(1 - \gamma)W_1 + (1 - \beta)(1 - \gamma)W_{1^2} \\ + \gamma(1 - \beta)W_{0^2} + \gamma(1 - \alpha)W_0$$

$$W_{0^1} = \alpha(1 - \gamma)W_0 + \beta(1 - \gamma)W_{0^2} \\ + \beta\gamma W_{1^2} + \alpha\gamma W_1 = W_{0^2}$$

$$W_{1^1} = \alpha(1 - \gamma)W_1 + \beta(1 - \gamma)W_{1^2} \\ + \beta\gamma W_{0^2} + \alpha\gamma W_0 = W_{1^2}$$

$$W_0 + W_1 + W_{0^1} + W_{1^1} + W_{0^2} + W_{1^2} = 1.$$

Solving the above equations we get

$$W_0 = W_1 = (1 - \beta)/(2 - 2\beta + 4\alpha)$$

$$W_{0^1} = W_{1^1} = W_{0^2} = W_{1^2} = \alpha/(2 - 2\beta + 4\alpha).$$

The boundary conditions can now be obtained by considering all possible sequences starting with layers of each type 0, 1, 0<sup>1</sup>, 1<sup>1</sup>, 0<sup>2</sup> and 1<sup>2</sup> at the origin and writing  $T$  in each case

$$T_m = \sum_j W_j \exp(i\varphi_m)_j.$$

Thus,

$$T_1 = -\frac{1}{2}$$

$$T_2 = (-1 + 4\alpha + \beta - 3\alpha\gamma - 3\beta\gamma + 3\gamma)/(2 - 2\beta + 4\alpha)$$

$$T_3 = (2 - 5\alpha - 2\beta + 3\alpha\beta - 6\gamma + 6\beta\gamma - 9\alpha\beta\gamma \\ + 9\alpha\gamma)/(2 - 2\beta + 4\alpha)$$

$$T_4 = (-1 + \beta - 2\alpha + 3\alpha^2 + 6\alpha\beta - 3\alpha^2\beta + 3\gamma - 6\alpha^2\gamma \\ + 9\alpha\gamma - 3\beta\gamma + 6\alpha^2\beta\gamma - 15\alpha\beta\gamma)/(2 - 2\beta + 4\alpha)$$

$$T_5 = (-1 + \beta + 13\alpha - 18\alpha^2 - 18\alpha\beta + 3\alpha\beta^2 + 18\alpha^2\beta \\ + 6\alpha^3 - 6\alpha^3\beta - 57\alpha\gamma - 24\alpha^3\gamma \\ + 24\alpha^3\beta\gamma - 69\alpha^2\beta\gamma + 69\alpha^2\gamma + 72\alpha\beta\gamma \\ - 15\alpha\beta^2\gamma - 6\beta\gamma + 6\gamma)/(2 - 2\beta + 4\alpha).$$

Substituting the coefficients ( $A$ 's) and the five boundary conditions ( $T$ 's) in (9) and carrying out the summations we get the intensity expression

$$I = f^2 c \{ [\frac{1}{2} + T_1 \exp(5i\pi L) + (T_2 + A_5 T_1) \exp(4i\pi L) \\ + (T_3 + A_5 T_2 + A_4 T_1) \exp(3i\pi L) \\ + (T_4 + A_5 T_3 + A_4 T_2 + A_3 T_1) \exp(2i\pi L) \\ + (T_5 + A_5 T_4 + A_4 T_3 + A_3 T_2 \\ + A_2 T_1) \exp(i\pi L) - A_0] \\ \times [A_0 + A_1 \exp(i\pi L) + A_2 \exp(2i\pi L) \\ + A_3 \exp(3i\pi L) + A_4 \exp(4i\pi L) \\ + A_5 \exp(5i\pi L) + \exp(6i\pi L)]^{-1} \\ + \text{complex conjugate} \}. \quad (10)$$

### Prediction of diffraction effects

The variation of the diffracted intensity along the 10. $L$  reciprocal-lattice row for different values of  $\alpha$ ,  $\beta$  and  $\gamma$  calculated from (10) in steps of  $\Delta L = 0.01$  is depicted in Fig. 2. The reflections along reciprocal-lattice rows with  $H-K = 0 \pmod{3}$  are unaffected by the transformation and remain sharp throughout. For reflections with  $H-K \neq 0 \pmod{3}$ , the different diffraction effects are clearly visible in the figures and can be described as follows:

(i) For small values of  $\alpha$  and  $\gamma$  ( $< 0.08$ ): The 3C reflections remain almost unbroadened and new reflections start appearing at the 2H positions as  $\beta$  increases to 0.6. The 2H peaks are initially broad and become sharper as  $\beta$  increases to 0.9. The resultant structure shows the co-existence of 3C and 2H peaks (see Fig. 2a).

(ii) For  $\gamma = 0.05$  and  $\alpha = 0.1$  to 0.2: The 3C reflections are initially broadened and are shifted towards the neighbouring 2H positions. New reflections corresponding to the 2H structure start appearing as  $\beta$  increases to 0.6. As the transformation proceeds ( $\beta$  increases), the shift of the 3C peaks decreases and the peaks approach their normal positions  $L = \pm\frac{2}{3}, \pm\frac{4}{3}$  (see Fig. 2b).

(iii) For  $\gamma = 0.1$  and  $\alpha \geq 0.1$ : The 3C reflections are greatly broadened and shifted towards the neighbouring 2H peaks. As the values of  $\gamma$  and  $\alpha$  increase, the shift of the 3C peaks and their broadening increases. The resultant 2H structure contains a very small fraction of the 3C fragments.

(iv) For  $\gamma = 0.05$  and  $\alpha = \beta$ : For this case the 3C reflections are initially greatly broadened and considerably shifted towards the nearby 2H positions. As  $\alpha (= \beta)$  increases, the  $L = \pm\frac{2}{3}$  and  $L = \pm\frac{4}{3}$  of the 3C structure approach each other and become a single peak at  $L = 1$  for  $\beta = 0.9$ . In this particular case there is no co-existence of the 2H and the 3C peaks (see Fig. 2c).

(v) For  $\gamma = 0$ : This corresponds to the case where the initial 3C structure is unfaulted (see Fig. 2d).

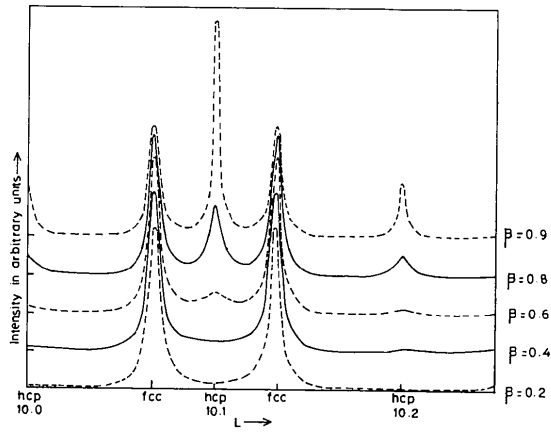
The intensity distribution shown in Fig. 1 is computed without considering  $f^2$  which is the scattering power for a single layer of structure and can as such be used to compare the phase transformation in cobalt. In order to compare the intensity distribution in partially transformed ZnS, one should take into account the scattering factor  $f^2$ . For ZnS,

$$f^2 = f_{Zn}^2 + f_S^2 + 2f_{Zn}f_S \cos 2\pi LP,$$

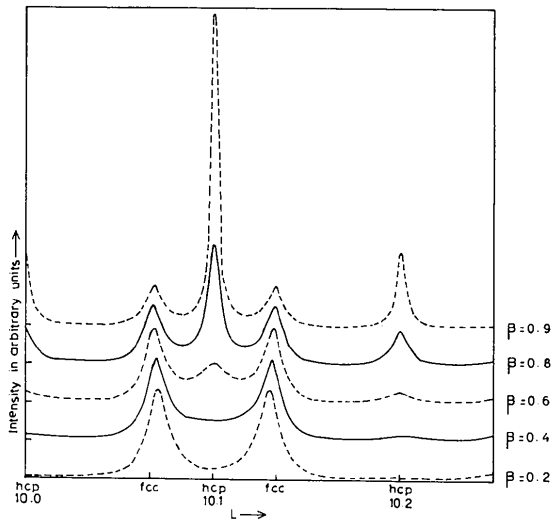
where  $P = 3/4n$  and  $n$  is the number of layers in the unit cell.

### Discussion

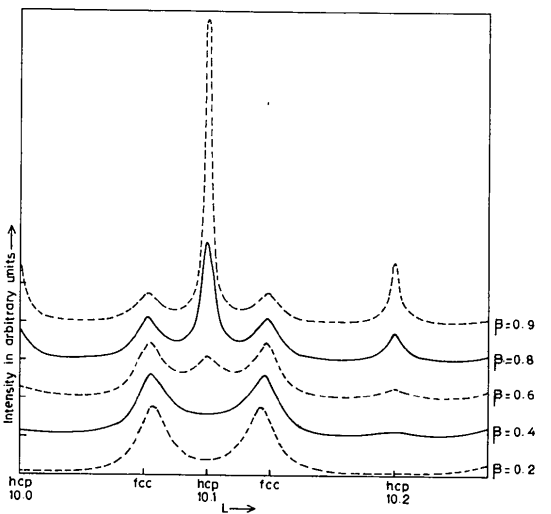
The solid-state transformations in ZnS have been explained (Daniels, 1966; Mardix & Steinberger,



(a)

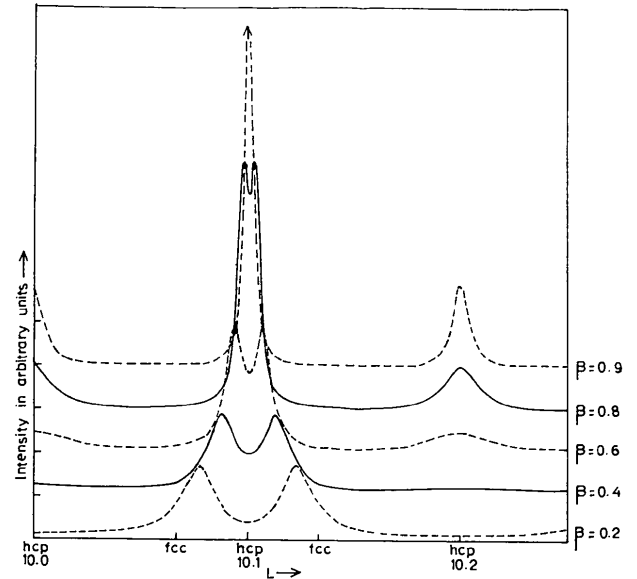


(b)

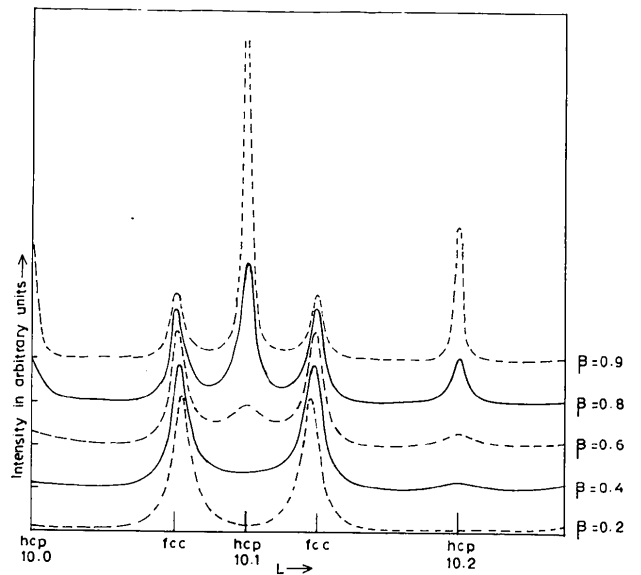


(c)

1965/66) in terms of a periodic slip mechanism which envisages the expansion of a stacking fault around a screw dislocation and is akin to the pole mechanism suggested (Seeger, 1953) for the transformations in cobalt. Such a mechanism cannot operate in a ran-



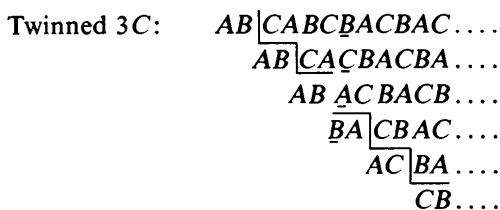
(d)



(e)

Fig. 2. Calculated variation of the diffracted intensity along the  $10.L$  reciprocal-lattice row for a twinned  $3C$  structure undergoing transformation to the  $2H$  structure with  $\beta = 0.2, 0.4, 0.6, 0.8$  and  $0.9$ . The calculated curves have been shifted vertically for different values of  $\beta$  for clarity. (a)  $\alpha = 0.04, \gamma = 0.05$ ; (b)  $\alpha = 0.1, \gamma = 0.05$ ; (c)  $\alpha = 0.1, \gamma = 0.1$ ; (d)  $\alpha = \beta, \gamma = 0.05$ ; (e)  $\alpha = 0.1, \gamma = 0.0$ .

domly twinned 3C structure as shown below:



Resulting structure:  $ABABAB\overline{BAACCB} \dots$

Thus the operation of the screw dislocation mechanism in a randomly twinned 3C structure violates the rules of close packing. In the absence of a screw dislocation the 3C-2H transformation can occur by the insertion of deformation faults at two layer separations. Fujita & Ueda (1972) made a transmission electron microscope study of the mechanism of formation of a  $\xi$ -phase crystal induced by deformation in 18/8-type stainless steels. The f.c.c. ( $\gamma$ ) to h.c.p. ( $\xi$ ) phase transformation occurs when stacking faults are regularly formed on every second layer of  $\{111\}$  slip planes in an f.c.c. lattice. This can occur by two different processes: (i) regular insertion of stacking faults; (ii) irregular insertion of stacking

faults at first and then a gradual change to the regular sequence. In stainless steel, the second process is found to occur since there is considerable diffuse intensity indicating a large number of stacking faults and the f.c.c. spots are broadened. The h.c.p. spots appear at a later stage on this. The screw dislocation mechanism corresponds to the first process.

The movement of  $(a/6)\langle 112 \rangle$  Shockley partials on alternate (111) planes can effect the 3C-2H transformation. In the stress-induced or in the periodic slip mechanism f.c.c.-h.c.p. transformation, only one  $(a/6)\langle 112 \rangle$  shear operates on a given set of  $\{111\}$  planes producing tilting or kinking of the crystals. In specimens in which transformation is induced by heating, all three shears  $(a/6)\langle 112 \rangle$  occur with equal probability producing no macroscopic kinks.

As predicted by the theory, Fig. 1 shows the co-existence of the 2H and 3C reflections at an intermediate stage. The values of  $\alpha$ ,  $\beta$  and  $\gamma$  change from crystal to crystal and also in the same crystal after different thermal treatment and quenching. The photometric curves recorded by Frey, Jagodzinski & Steger (1986) from a ZnS-3C crystal partially transformed to 2H are in agreement with the theoretical profiles (Fig. 3). A quantitative comparison of the calculated diffraction effects with those recorded experimentally from a partially transformed ZnS crystal using single-crystal diffractometry would enable a final and better confirmation of the proposed model.

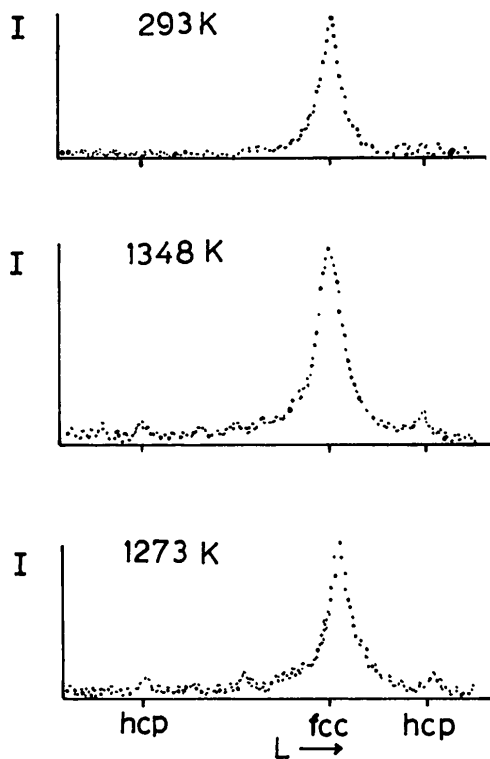


Fig. 3. Intensity profiles (10.L) of a ZnS crystal recorded at 293 K, after heating to 1373 K and cooling to 1348 K, and then at 1273 K (after Frey *et al.*, 1986).

#### References

- ALLEGRA, G. (1964). *Acta Cryst.* **17**, 579-586.  
 BERLINER, R. & WERNER, S. A. (1986). *Phys. Rev. B*, **35**, 3586-3603.  
 CHRISTIAN, J. W. (1951). *Proc. R. Soc. London Ser. A*, **206**, 51-64.  
 DANIELS, B. K. (1966). *Philos. Mag.* **14**, 487-500.  
 FREY, F., JAGODZINSKI, H. & STEGER, G. (1986). *Bull. Mineral.* **109**, 117-129.  
 FUJITA, H. & UEDA, S. (1972). *Acta Metall.* **20**, 759-767.  
 GEVERS, R. (1954). *Acta Cryst.* **7**, 337-343.  
 HENDRICKS, S. & TELLER, E. (1942). *J. Chem. Phys.* **10**, 147-167.  
 HOLLOWAY, H. (1969). *J. Appl. Phys.* **40**, 4313-4321.  
 KAKINOKI, J. & KOMURA, Y. (1952). *J. Phys. Soc. Jpn*, **7**, 30-35.  
 KAKINOKI, J. & KOMURA, Y. (1954). *J. Phys. Soc. Jpn*, **9**, 169-176, 177-183.  
 KAKINOKI, J. & KOMURA, Y. (1967). *Acta Cryst.* **23**, 875-885.  
 KOTVAL, P. S. & HONEYCOMB, R. W. K. (1968). *Acta Metall.* **16**, 597-607.  
 LELE, S. & PANDEY, D. (1985). *Mater. Sci. Forum*, **3**, 143-156.  
 MARDIX, S. & STEINBERGER, I. T. (1965/66). *Isr. J. Chem.* **3**, 243.  
 PANDEY, D., LELE, S. & KRISHNA, P. (1980). *Proc. R. Soc. London Ser. A*, **367**, 435-449.  
 PATERSON, M. S. (1952). *J. Appl. Phys.* **23**, 805-811.  
 PRASAD, B. & LELE, S. (1971). *Acta Cryst.* **27**, 54-64.  
 QIN, L. C., LI, D. X. & KUO, K. H. (1986). *Philos. Mag.* pp. 543-555.  
 ROTH, W. L. (1960). *Faulting in ZnS*. Report No. 60-R1-2563m. General Electric Research Laboratory, Schenectady, New York, USA.  
 SEBASTIAN, M. T. & KRISHNA, P. (1984a). *Pramana*, **23**, 395-403.  
 SEBASTIAN, M. T. & KRISHNA, P. (1984b). *Philos. Mag.* **49**, 809-821.  
 SEBASTIAN, M. T. & KRISHNA, P. (1984c). *Bull. Mater. Sci.* **6**, 369-393.

SEBASTIAN, M. T. & KRISHNA, P. (1984*d*). *Phys. Status Solidi*, **84**, 401–409.  
 SEBASTIAN, M. T., PANDEY, D. & KRISHNA, P. (1982). *Phys. Status Solidi A*, **72**, 633–640.

SEGER, A. (1953). *Z. Metallkd.* **44**, 247–253.  
 WARREN, B. E. (1969). *X-ray Diffraction*. New York: Addison-Wesley.  
 WILSON, A. J. C. (1942). *Proc. R. Soc. London Ser. A*, **180**, 277–285.

*Acta Cryst.* (1987). **B43**, 415–416

## On the Structure and Twinning of Monoclinic $\beta$ -V<sub>2</sub>H\*

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### Abstract

The structure of the monoclinic [ $a = 4.4566$  (5),  $b = 3.0022$  (2),  $c = 4.4760$  (5) Å,  $\beta = 95.609$  (8)°,  $Z = 2$ ] form of  $\beta$ -V<sub>2</sub>H, formerly described in space group  $Cm$  [Noda, Masumoto, Koike, Suzuki & Sato (1986). *Acta Cryst.* **B42**, 529–533] is properly described in  $C2/m$ . The crystal used for the original intensity measurements was surely twinned, across the  $ab$  plane, so that all reflections of the type  $5n, k, l$  were composite; the twin component was about 55% as large as the main crystal. When the intensities were corrected for this twinning, refinement in space group  $C2/m$  led to an  $R$  of 0.023 for 668 reflections, compared to 0.080 for the earlier investigation. Despite the improvement in refinement, the H atom could not be located from the X-ray data.

### Introduction

The structure of the monoclinic (unstressed) form of  $\beta$ -V<sub>2</sub>H was described (Noda, Masumoto, Koike, Suzuki & Sato, 1986; NMKSS) in space group  $Cm$  with two formula units per cell [ $a = 4.4566$  (5),  $b = 3.0022$  (2),  $c = 4.4760$  (5) Å,  $\beta = 95.609$  (8)°]. In this description, the V atoms were placed in two independent sites on a mirror plane and the H atoms were ignored. In terms of atom positions, such an arrangement can be equally well described in  $C2/m$  with a twofold axis midway between the V atoms. However, NMKSS reported that space groups  $C2/m$  and  $C2$  could be ruled out 'on the basis of Hamilton's test' and their reported structure showed very large differences in the  $U_{ij}$  terms of the two V atoms which

could, in principle, lower the symmetry to  $Cm$ . But such differences seemed very surprising, especially in view of the simplicity of the structure. Accordingly, I have reinvestigated the structure and shown that it is properly described in  $C2/m$ . During the process, it became clear that the crystal used for intensity measurements included a twin component that contributed in a systematic way to many reflections; when the intensities were corrected for this twinning, refinement led to an  $R$  of 0.023 compared to the 0.080 reported by NMKSS for the  $Cm$  description.

### Experimental

Values of  $F_o$  (corrected for extinction) and  $\sigma(F_o)$  for 672 reflections were recovered from Supplementary Publication No. SUP 42832, and the starting model in  $C2/m$  was quickly derived by averaging the coordinates and  $U_{ij}$  values reported in Table 3 of NMKSS. Preliminary least-squares refinement led to an  $R$  of 0.074 – already better than the 0.080 of NMKSS. However, reflections with  $h = 5n$  were clearly aberrant:  $R$  for these 145 reflections was 0.18, compared to 0.04 for the remaining reflections, and their values of  $F(\text{obs.})$  averaged about 22% larger than  $F(\text{cal.})$ . That this effect could be due to twinning was confirmed by the fact that the reciprocal lattice maps onto itself, with an 'index' of 5, if it is reflected across the  $ab$  plane (or, alternatively, rotated by 180° about the  $a$  axis): reflections of the type  $5n, k, l$  of one lattice fall very nearly on top of  $5n, k$  (or  $-k$ ),  $-l - n$  of the other.

In order to correct for this apparent twinning, I first refined the structure (including the scale factor) on the basis of the reflections with  $h \neq 5n$ ;  $R$  for these reflections became 0.0202 and the goodness-of-fit was 1.85. The intensities for those with  $h = 5n$  were then adjusted by dividing  $F^2(\text{obs.})$  by 1.55 for  $h = 0$  and,

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