Mechanism of phase transformations in ZnS

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Abstract. X-ray diffraction of the 2H–3C transformation in ZnS crystals has been studied to determine the mechanism of the phase transformation. Single crystals of 2H ZnS were annealed in vacuum at different temperatures to induce the phase transformation and then quenched to arrest it at different intermediate stages. The transformation is found to occur by the non-random nucleation of stacking faults in the 2H structure which produce characteristic diffuse steaks along reciprocal lattice rows parallel to c^* for which $H-K \neq 0$ (mod 3). All the crystals finally transform to a disordered twinned 3C structure. A study of the broadening of the x-ray diffraction maxima reveals that the stacking faults involved in the transformation are basal plane deformation faults. Initially these nucleate at random producing a random distribution of cubic nuclei within the 2H structure. As the transformation proceeds these 3C nuclei grow into thick 3C regions by a preferential nucleation of the faults at 2-layer separations. Since the 3C nuclei can have twin orientations the resulting 3C structure invariably contains a random distribution of twin faults. This is confirmed by comparing the experimentally observed intensity profile of the 10.L reflections as recorded on a single crystal diffractometer, with those calculated theoretically for a randomly twinned cubic structure.

Keywords. Phase transformation; ZnS; stacking faults; polytypism.

1. Introduction

It is well known that ZnS occurs in two polymorphic forms: the wurtzite modification with the hexagonal packing $ABAB$ . . . and the sphalerite modification with the cubic packing $ABCABC$ . . . where each letter A, B or C represents a double layer of Zn and S atoms. The two forms are related by a reversible phase transformation that occurs around 1020°C, the 3C being the low temperature modification. Several authors (Müller 1952; Piper and Roth 1953; Addamiano and Aven 1960; Roth 1960; Hartman 1966) have studied the transformation of 2H ZnS crystals to 3C on annealing at elevated temperatures. The transformation is found to be dependent on time and temperature of annealing as well as the initial perfection of the crystals. Baars and Brandt (1973) reported that the 3C-2H transformation in ZnS starts above 1000°C and is completed near 1150°C. On slow cooling the reverse transformation (2H–3C) commences at about 730°C. From this they concluded that the transition between the 3C and 2H phases is irreversible in the strict thermodynamic sense. In copper-doped crystals 3C, 4H, 6H and other long-period polytypes were observed during the slow cooling of the heated material. All these transformations occur through a disordering process. Several workers (Bridgman 1939; Frey 1948; Kellarud 1953; Strock 1955) have studied the effect of crushing on the 2H–3C transformation in ZnS and reported that the hexagonal structure transforms to 3C when crushed. However, Smith and Hill (1956) observed that crushing merely randomizes the structure. They obtained a similar product on crushing both 3C and 2H starting materials. Shachar et al (1968) observed that it is very easy to introduce stacking faults in 2H ZnS crystals at room temperature

by applying external stresses by a knife edge or a needle. More recently Farkas Jahnke and Gaĉs (1979) found that single crystals of 4H ZnS transform to a disordered twinned 3C structure on pressing the crystals in a line perpendicular to their c-axis and the [11·0] direction. These structural transformations caused by applying external stresses also occurred through the insertion of stacking faults in a manner similar to that observed during thermal annealing.

Structural transformations in ZnS have been explained (Daniels 1966; Mardix and Steinberger 1966) in terms of a periodic slip mechanism involving the expansion of stacking faults around an axial screw dislocation. Such a mechanism can only operate in those crystals which grow around an axial screw dislocation. A majority of the crystals do not grow around such a screw dislocation, but they all undergo the 2H–3C transformation. The present work investigates the mechanism of the transformation in the absence of a screw dislocation.

2. The mechanism of the 2H–3C transformation in the absence of a screw dislocation

In the absence of a screw dislocation the transformation can occur by the nucleation of stacking faults preferentially at two-layer separations in the 2H crystals in order to lower the energy of the structure. It was observed by Secco d'Aragona et al (1966) under the electron microscope that the 2H–3C transformation in thin films of ZnS occurs by the successive passage of partial dislocations across the basal plane at two layer separations. In order to determine the nature of the faults involved and confirm the mechanism of the transformation we have annealed 2H ZnS single crystals in vacuum at different temperatures in the range 300 to 1100°C for 1 hr and then quenched them in cold water to arrest the transformation in an intermediate state. The structure of the crystals was examined by x-ray diffraction after each annealing run. The crystals were also examined under an optical microscope to detect the development of any kinks in their external shape which are expected when the screw dislocation mechanism operates (Daniels 1966; Mardix and Steinberger 1966). No kinks were observed in any of the crystals studied by us. Figure 1 shows the 10.L reciprocal lattice row of a disordered 2H ZnS crystal as recorded on 15° c-axis oscillation photographs taken after successive annealing runs in the temperature range 300 to 1100°C. It is evident from the x-ray photographs that the transformation commences with a statistical insertion of stacking faults producing a diffuse streak along the 10.L reciprocal lattice row. Reflections corresponding to a twinned 3C structure then appear on this diffuse streak and the 2H reflections become progressively weaker (except where they coincide with 3C reflections). Finally the crystal transforms to a disordered twinned 3C structure and the 2H reflections disappear completely. On heating beyond 1050°C the reverse transformation takes place and the structure reverts to a disordered 2H. It was found that some of the 2H ZnS crystals transformed to the 3C structure through an intermediate 6H phase. The 2H–6H transformation was more prominent in crystals doped with small amounts of CdS or MnS (Sebastian and Krishna 1983, 1984).

Pandey et al (1980) studied the 2H–6H transformation in SiC and reported that a non-random insertion of layer displacement faults is involved in this transformation. Recently Lele and Pandey (1982) employed a two-parameter model to study the 3C–2H transformation in cobalt. In keeping with the experimental results cited above the following model is proposed for the 2H to 3C transformation in ZnS. The
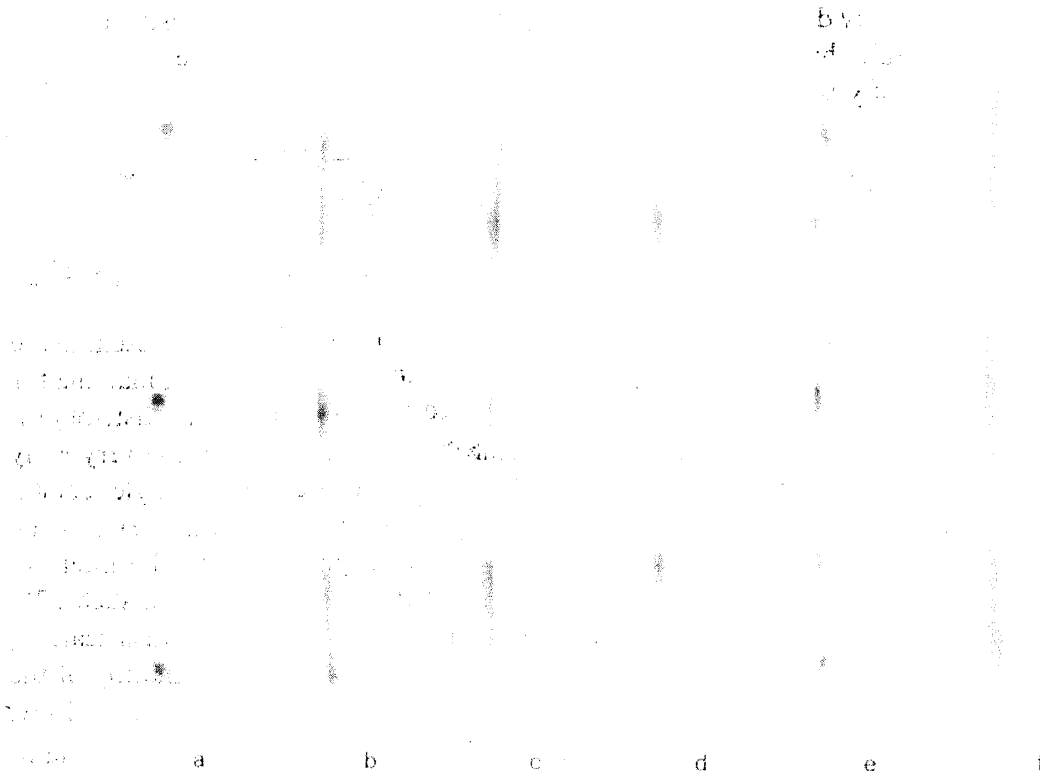
Figure 1. The $10.L$ reciprocal lattice row of a disordered 2H ZnS crystal as recorded on $15°$ c-axis oscillation photographs taken after annealing for 1 hr each at successively higher temperatures (**a**) room temperature (**b**) 400°C (**c**) 500°C (**d**) 600°C (**e**) 1050°C (**f**) 1100 (camera radius 3 cm, CuK radiation Mag. X4).

transformation occurs by the non-random nucleation of deformation faults on alternate layers as depicted below.

initial structure (2H): $A\ B\lfloor A\ B\ A\ B\ A\ B\ \ldots$

$C\ A\lfloor C\ A\ C\ A\ \ldots$

$B\ C\lfloor B\ C\ \ldots$

$A\ B\ \ldots$

resulting structure (3C): $A\ B\ C\ A\ B\ C\ A\ B\ \ldots$

Initially the deformation faults nucleate at different regions in the 2H structure in a random manner. Therefore in the initial stages of the transformation the 2H crystal would contain a random distribution of deformation faults. These act as nuclei for the cubic phase which grow during subsequent transformation into thick cubic regions by the preferential insertion of deformation faults at two-layer separations. The resulting 3C structure finally contains a random distribution of twin faults since the 3C nuclei have equal probability of being in any one of the two twin orientations namely $A\ B\ C\ A\ B\ C\ \ldots$ or $A\ C\ B\ A\ C\ B\ \ldots$

2.1 *Verification of the proposed model of the transformation*

According to the above model of the transformation the 2H crystal should contain a random distribution of deformation faults in the initial stages of the transformation.

The theory of x-ray diffraction from 2H crystals containing a random distribution of deformation faults has been developed by Christian (1954). The expression for the diffracted intensity is (Christian 1954; Pandey and Krishna 1977).

$$I_{(h_3)} = f^2 C \frac{(2\rho - 1)(1 - \rho^2)}{4\rho(1 - 2\rho \cos \pi h_3 + \rho^2)} + \frac{(2\rho + 1)(1 - \rho^2)}{4\rho[1 - 2\rho \cos \pi(h_3 + 1) + \rho^2]}, \quad (1)$$

where $\rho = (1 - 3\alpha + 3\alpha^2)^{\frac{1}{2}}$, $\alpha = $ deformation fault probability, $f^2 = f_{Zn}^2 + f_s^2 + 2f_{Zn}f_s \cos 2\pi LP$, $P = \frac{3}{8}$ and C is a scale factor.

We have determined (Sebastian *et al* 1982) the nature of stacking faults present in the disordered 2H crystals by studying the broadening of the x-ray diffraction maxima for reflections with $H-K \neq 3n$. To do this, we recorded the point intensity distribution along the $10.L$ reciprocal lattice row of 2H ZnS crystals quenched in the very early stages of transformation using a computer-controlled four-circle single crystal diffractometer. The intensity along the row was recorded in steps of $\Delta L = 0.01$ by the method described earlier (Pandey and Krishna 1977). Figure 2 shows the intensity distribution as obtained by plotting the total number of counts against L for such a 2H crystal. The ratio of the halfwidths of $10.L$ reflections with L even and L odd is nearly 1, confirming that the stacking faults present in these crystals are predominantly of the deformation type. In the case of growth faults (Pandey and Krishna 1977; Warren 1969) this ratio should be 3 for fault probabilities $\alpha \leqslant 4 - 2\sqrt{3}$. The deformation fault probability was calculated from the observed halfwidths using the following theoretical expression obtained from equation (1),

$$\text{halfwidth} = \frac{2}{\pi} \cos^{-1}\left[\frac{4\rho - \rho^2 - 1}{2\rho}\right]. \quad (2)$$

The deformation fault probability in this crystal is found to be 0.04 indicating that one in every 25 layers is faulted. Using this value, the intensity profile for the different $10.L$ reflections was theoretically computed in the interval $L - 0.1$ to $L + 0.1$. The calculated profiles are compared with the observed intensity distribution in figure 2 and show a good agreement. The slight discrepancy observed near the positions of cubic (3C) reflections is to be expected and indicates the commencement of non-random faulting at 2-layer separations. Similar analysis of the experimental data obtained from as-grown disordered 2H ZnS crystals showed that they also contain a random distribution of deformation faults. This confirms that the disorder in them also results from the initiation of the transformation during the cooling down period of the growth-furnace. It is not possible to perform a similar analysis of the crystals in a more advanced state of transformation since the fault distribution is no longer random and the theories of x-ray diffraction from randomly disordered close-packed structures become inapplicable. The intensity distribution must be calculated by developing a model of non-random faulting as was done by Lele and Pandey (1982) for the 3C–2H transformation in cobalt. However, as discussed above the resulting structure after the transformation is expected to be a randomly twinned cubic structure and the theories of random faulting can be applied again to analyse the faults in such a structure. The resultant structure expected after the transformation may be depicted as follows.

$A\,B\,C\,A\,B\,C\,A\,B\,C\,\underline{A}\,C\,B\,A\,C\,B\,\underline{A}\,B\,C\,A\,B\,\underline{C}\,B\,A\,C\,B\,A\,C\,B\,A\,C$ .... The underlined layers represent twin planes. Going along the $[00.1]$ direction in such a crystal there would be an equal probability of finding a cubic nucleus with layer arrangements in the
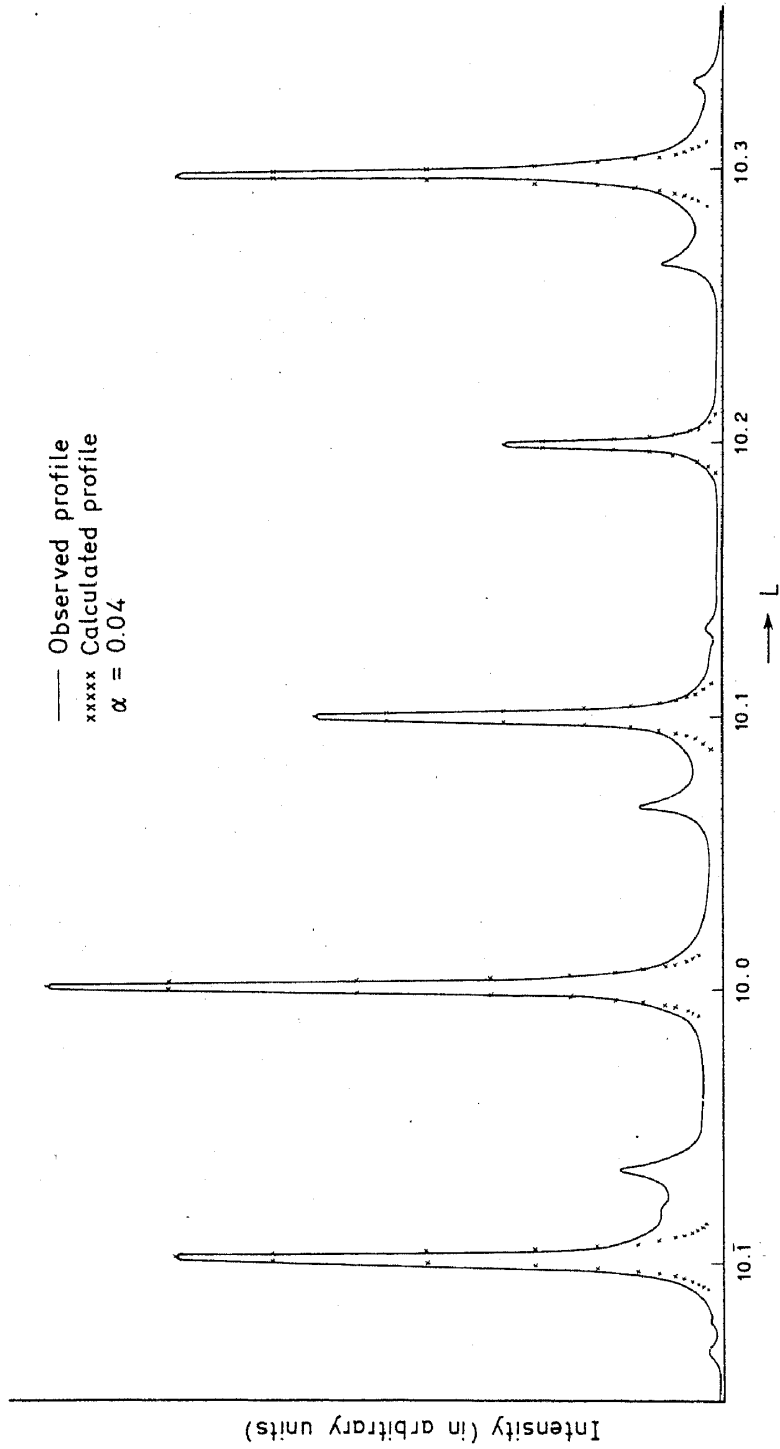
Figure 2. Plot of intensity versus *L* in reciprocal space for 10.*L* row of a disordered 2H ZnS crystal obtained by annealing a perfect 2H ZnS crystal at 400°C, 1 hr.

sequence *A B C A B C.* . . . as of finding a cubic nucleus with layer arrangements in the sequence *A C B A C B.* . . . Thus the resulting structure should produce diffracted intensities that are expected from a close-packed cubic structure containing a random distribution of twin faults along one set of $\{111\}$ planes. It is possible to verify this prediction experimentally by comparing the experimentally observed intensity distribution with that calculated theoretically for a cubic closepacked structure containing a random distribution of twin faults.

The theory of x-ray diffraction for cubic crystals containing random twin faults has been developed by Paterson (1952) and Warren (1969). The expression for the diffracted intensity from a fcc crystal containing random distribution of twin faults in terms of hexagonal axes is given by

$$I_{(h_3)} = \frac{\psi^2}{2} \frac{1 - Z^2 + 2\frac{\beta Z}{s} \sin\left(\frac{2\pi h_3}{3} + \theta + \pi\right)}{1 + Z^2 - 2Z\cos\left(\frac{2\pi h_3}{3} + \theta + \pi\right)}$$

$$+ \frac{\psi^2}{2} \frac{1 - Z^2 - 2\frac{\beta Z}{s} \sin\left(\frac{2\pi h_3}{3} - \theta - \pi\right)}{1 + Z^2 - 2Z\cos\left(\frac{2\pi h_3}{3} - \theta - \pi\right)}, \tag{3}$$

where $\beta \leqslant 2\sqrt{3} - 3$ (Paterson 1952), $Z = (1 - 2\beta)^{\frac{1}{2}}$, $s = (3 - 6\beta - \beta^2)^{\frac{1}{2}}$, $\theta = \text{arc}$ $\tan\frac{s}{1-\beta}$ and $\beta = $ twin fault probability.

Figure 3 shows the point intensity distribution along the 10.*L* reciprocal lattice row of a disordered 3C ZnS crystal obtained by solid state transformation from a 2H crystal by annealing. The observed intensity as recorded in steps of $\Delta L = 0.01$ using a single crystal diffractometer is plotted as a function of *L*. The presence of asymmetrically broadened reflections and the absence of peak shifts suggests that twin faults are present in these crystals. The twin fault probability β as calculated from the observed halfwidths using the following equation deduced from (3) is 0.12

$$\text{halfwidth} = \frac{3}{\pi}\cos^{-1}\left[\frac{4Z - Z^2 - 1}{2Z}\right].$$

The intensity profiles of different 10.*L* reflections were calculated in the interval $L - 0.15$ to $L + 0.15$ using (3). The calculated and the observed intensity profiles are compared in figure 3 and show fairly good agreement.

3. Discussion of results and conclusion

The structural transformations in ZnS can occur by the periodic slip mechanism only in those crystals which contain a suitable screw dislocation. The crystals undergoing transformation by the screw dislocation mechanism show easily measurable kinks in the external shape of the crystals. Such kinks are not expected to form when the
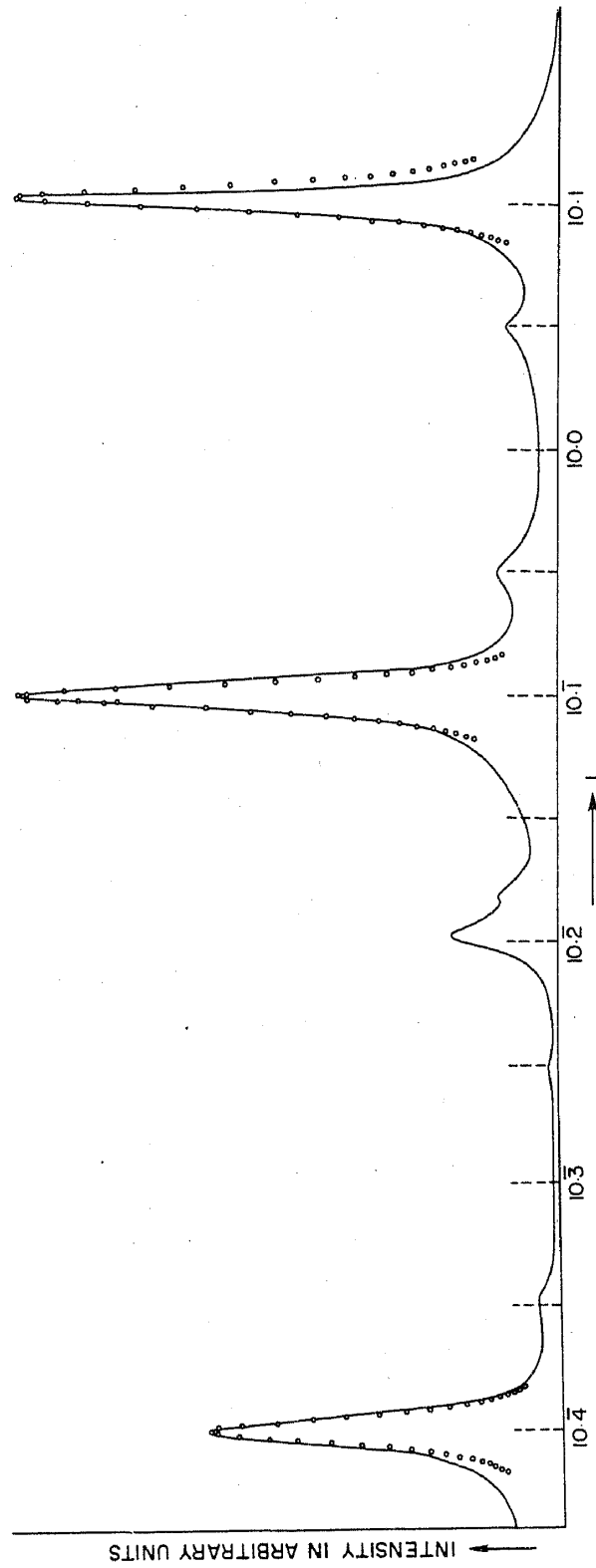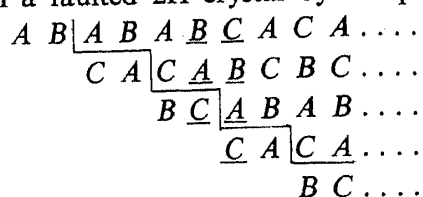
Figure 3. Plot intensity versus *L* in reciprocal space of a disordered 3C ZnS crystal obtained by annealing a 2H ZnS crystal at 500°C for 1 hour ooo calculated profile, —observed profile, $\beta = 0.12$. The dashed vertical lines indicate the 6H positions.

transformation occurs by the non-random nucleation of faults as there are three symmetry related directions possible for the Burgers vector of the partial dislocation bounding a stacking fault. Since each fault nucleates independently, all the three directions would occur with equal probability producing no macroscopic kinks. In the case of transformation by the screw dislocation mechanism, the spots corresponding to the 3C structure would appear at the very beginning of the transformation and the intensities of the twin reflections for the 3C structure would not be equal. There should be almost no diffuse streak along the 10.L row. Moreover, the periodic slip mechanism can operate unhampered only in perfect 2H regions. The presence of stacking faults in the initial structure would arrest the rotation of the partial dislocation around the screw (Alexander *et al* 1970) as it would violate the law of close-packing. This is illustrated below for the 2H–3C transformation in a faulted 2H crystal by the periodic slip mechanism. Initial faulted crystal (2H):. A B|A B A $\underline{B}$ $\underline{C}$ A C A . . . .

$$C\ A|C\ \underline{A}\ \underline{B}\ C\ B\ C\ \ldots$$
$$B\ \underline{C}|\underline{A}\ B\ A\ B\ \ldots$$
$$\underline{C}\ A|\underline{C}\ A\ \ldots$$
$$B\ C\ \ldots$$

resulting structure: A B C A B $\underline{C}$ $\underline{C}$ A B C . . . .
The layers which violate the law of close-packing are underlined.

The several disordered structures formed in ZnS crystals grown from the vapour phase represent intermediate states in the 2H–3C transformation which occurs when the growth furnace cools to temperatures below 1020°C. The observed disordered structures represent metastable states frozen during different stages of the transformation. This is confirmed by the fact that the nature of the stacking faults found when 2H crystals are annealed at temperatures below 1020°C and then quenched is identical to that found in as-grown crystals removed from the growth furnace.

The 2H–3C transformation in ZnS takes place by the statistical insertion of deformation faults which nucleate preferentially at two-layer spacings in order to lower the energy of the structure. The stacking faults expand rapidly over the entire layer as they have negative energy. The probability of faults nucleating at two-layer separations is much higher than that of random faulting.

A considerable amount of work has been done in the past using powder·diffraction methods to study the nature of faults and the fault concentration by measuring line widths and peak shifts. The information so obtained gives values that are averaged over all the grains in the powder sample. Such a method is unsuitable for the study of polytypic materials like ZnS where different grains may possess different crystal structures. Single-crystal studies provide more reliable information about the disorder in individual crystals, but very few such studies have been reported in literature. The present study shows that the single crystal diffractometer can be effectively used not only to study crystal structure but also to study the mechanism of phase-transformation in solids by arresting the transformation in an intermediate state and recording the diffuse intensity produced by the disorder. The diffuse intensity can be calculated from a model of the disorder, based on the mechanism of the transformation. This model can then be confirmed by comparing the calculated intensity profiles with those recorded experimentally on a single crystal diffractometer.

Acknowledgements

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