

The Relative Occurrence of Hexagonal and Rhombohedral Structures in ZnS Single Crystals

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Besides the three-layered cubic (3C) and two-layered hexagonal (2H) forms, ZnS crystallizes into a number of hexagonal and rhombohedral polytypes. The polytypes of zinc sulphide are considered to generate during the 2H-3C structural transformation around axial screw dislocations with various Burgers vector strengths. By consideration of energies involved in producing axial screw dislocations, it has been pointed out that the growth of rhombohedral polytypes alone is favoured at the limit of higher unit-cell height and the growth of both the hexagonal and rhombohedral polytypes at the limit of lower height. The possibility of the relative occurrence of the hexagonal and rhombohedral polytypes, with the same unit-cell heights but with different stacking modes of ZnS double layers, has also been discussed.

Introduction

Similarly to silicon carbide, cadmium iodide and other polytypic substances, ZnS has been investigated extensively with respect to its polytypism. The polytypes in this compound have been considered to be intermediate states which grow during the 3C-2H structural transformation. The 3C-2H transformation has been considered to be a phenomenon of diffuse first-order phase transformation (Smith, 1955; Hill, 1958). A direct observation of the phase transition from 3C-2H has been attempted by recrystallizing thin films of 3C type ZnS under an electron-microscope (Rai, Srivastava & Krishna, 1970), and it was found that this transformation proceeds through micro-twins and polytypes at intermediate steps and a structurally perfect 2H phase was never obtained. By considering the ZnS polytypes as a result of a high order phase transformation, Rai & Krishna (1968*a,b*) attempted to explain the polytypism in terms of Schneer's (1955) theory. Alexander, Mardix, Kalman & Steinberger (1970), however, expressed doubt about the applicability of Schneer's theory to the phenomenon of polytypism.

Other theories, based on thermodynamic principles (e.g. Jagodzinski, 1954), were successful in explaining the phenomenon of polytypism only at a qualitative stage, and it was felt that they cannot deal with the individual structures of polytypes. The screw dislocation theory (Frank, 1951; Mitchell, 1957; Krishna & Verma, 1965), on the other hand, appeared to be simpler and more promising. In subsequent years, Daniels (1966), Mardix, Kalman & Steinberger (1968) and Alexander, Mardix, Kalman & Steinberger (1970) discussed the polytypism in terms of the axial and basal dislocations in the 2H structure. Despite considerable experimental support for these explanations, their validity was also questioned (Rai, Agrawal & Krishna, 1968; Rai 1971*a,b*; Dubey, Pandey & Singh, 1971). The author, therefore, proposed a more adequate mechanism involving an ordering of f.c.c. type

microtwins, by which the complete growth and structural features of ZnS polytypes can be explained (Rai, 1971*a,b*). The formation of polytypes was attributed to the structural transformation (2H-3C) of a faulted 2H structure containing axial screw dislocations and it was shown that the cell height and the lattice type of polytypes are governed by the Burgers vector concerned. However, no consideration has been given by previous workers to the relative occurrence of hexagonal and rhombohedral polytypes, which involves an empirical relation, such that the observed number of rhombohedral polytypes is considerably greater than that of hexagonal ZnS polytypes.

The aim of the present paper is to discuss the relative abundance of hexagonal and rhombohedral polytypes in terms of the Burgers vector strength of the axial screw dislocation, on the basis of the results given in the previous study (Rai, 1971*a,b*).

Growth of hexagonal and rhombohedral polytypes and their relative abundance

When the 2H structure containing growth faults undergoes 2H-3C transformation, the transformed structure contains sets of microtwins of the f.c.c. type. The axial screw dislocation in this region exposes a growth step on the growth surface. The exposed ledge (step) consisting of f.c.c. type microtwins will motivate the endless growth of a polytype with the structure consisting of a repeated assembly of the micro-twins forming the growth step.

If the step height or the Burgers vector strength is N and the bottom and top layers of the exposed step are in the same orientation of stacking (i.e. A and A , B and B or C and C), then the rhombohedral polytypes $3NR$ will be formed; while if these layers are in different orientations (i.e. A and B , B and C or C and A), the hexagonal polytypes NH will be formed (Krishna & Verma, 1965). It is evident that the probability of the top and bottom layers of the exposed ledge, being in

different orientation from each other, should be nearly twice the probability of these layers being in the same orientation. Thus for low values of N , the probability of finding a rhombohedral polytype $3NR$ is expected to be nearly a half of the probability of finding a hexagonal polytype, NH .

The Burgers vector strength of an axial screw dislocation, however, should be subject to energy relations. For simplicity, one may assume that the value of the maximum possible strength of the Burgers vector is equal to N , and all other axial screw dislocations with Burgers vector strengths smaller than this are possible. According to the screw dislocation mechan-

ism, the unit-cell height of the hexagonal polytypes should always be equal to the Burgers vector strength of the axial screw dislocation. In the case of rhombohedral polytypes, however, the unit-cell height should always be three times the strength of axial screw dislocations. Thus, if N is the maximum possible limit of Burgers vector strength, the hexagonal polytypes will be formed with unit-cell heights only from 4 to N , while for the rhombohedral polytype unit-cell heights from 9 to $3N$ are possible. It is clear from the above argument that the polytypes beyond the unit-cell height equal to N , should be only of rhombohedral symmetry. Below this limit, both the hexagonal and

Table 1. ZnS Polytypes

Sample number	Hexagonal polytypes (NH)	Zhdanov symbol	Reference	Rhombohedral polytypes (3NR)	Zhdanov symbol	Reference
1	4H	(2 2)	(4)	9R	(2 1) ₃	(6)
2	6H	(3 3)	(4)	12R	(3 1) ₃	(6)
3	8H	(4 4)	(16)	15R	(3 2) ₃	(4)
4	10H	(5 5)	(3)	18R	(4 2) ₃	(12)
5	10H	(8 2)	(1)	21R	(2 1 1 3) ₃	(6)
6	10H	(3 3 2 2)	(9)	24R	(5 3) ₃	(1)
7	12H	(6 6)	(11)	24R	(6 2) ₃	(16)
8	12H	(9 3)	(11)	30R	(6 4) ₃	(9)
9	12H	(4 4 2 2)	(9)	30R	(7 3) ₃	(7)
10	14H	(7 7)	(12)	30R	(4 2 2 2) ₃	(9)
11	14H	(4 3 3 4)	(10)	36R	(8 4) ₃	(11)
12	14H	(5 4 2 3)	(1)	36R	(7 5) ₃	(17)
13	16H	(8 8)	(12)	36R	(10 2) ₃	(17)
14	16H	(14 2)	(15)	36R	(5 2 2 3) ₃	(17)
15	16H	(5 3 3 5)	(15)	36R	(3 4 3 2) ₃	(17)
16	16H	(3 3 2 2 3 3)	(15)	36R	(6 2 2 2) ₃	(15)
17	18H	(5 4 4 5)	(10)	42R	(9 5) ₃	(9)
18	18H	(6 5 3 4)	(10)	42R	(8 6) ₃	(10)
19	18H	(6 3 3 6)	(9)	42R	(11 3) ₃	(10)
20	18H	(7 5 2 4)	(10)	42R	(12 2) ₃	(11)
21	20H	(10 10)	(11)	42R	(5 4 3 2) ₃	(10)
22	20H	(13 7)	(7)	42R	(6 4 2 2) ₃	(10)
23	20H	(3 4 7 6)	(11)	42R	(5 3 3 3) ₃	(9)
24	20H	(5 3 3 4 2 3)	(13)	48R	(13 3) ₃	(15)
25	20H	(5 2 2 3 6 2)	(13)	48R	(12 4) ₃	(12)
26	20H	(2 3 8 7)	(11)	48R	(10 6) ₃	(15)
27	20H	(7 3 3 7)	(7)	48R	(9 7) ₃	(12)
28	20H	(5 3 2 2 3 5)	(7)	48R	(6 4 3 3) ₃	(9)
29	22H	(20 2)	(7)	48R	(8 4 2 2) ₃	(15)
30	22H	(17 5)	(7)	48R	(7 3 3 3) ₃	(9)
31	22H	(7 4 4 7)	(7)	48R	(7 4 2 3) ₃	(12)
32	24H	(21 3)	(8)	48R	(4 3 3 2 2) ₃	(12)
33	24H	(15 9)	(14)	54R	(10 8) ₃	(11)
34	24H	(7 5 5 7)	(12)	54R	(7 5 3 3) ₃	(11)
35	24H	(9 5 6 4)	(14)	54R	(7 3 6 2) ₃	(11)
36	24H	(8 9 4 3)	(14)	54R	(5 5 5 3) ₃	(7)
37	24H	(7 10 5 2)	(14)	60R	(18 2) ₃	(13)
38	24H	(16 4 2 2)	(14)	60R	(17 3) ₃	(11)
39	24H	(6 5 3 5 3 2)	(8)	60R	(12 8) ₃	(7)
40	24H	(3 3 2 4 2 2 5 3)	(14)	60R	(11 9) ₃	(7)
41	24H	(3 3 4 2 2 4 3 3)	(14)	60R	(11 4 3 2) ₃	(12)
42	24H	(2 2 6 2 2 6 2 2)	(7)	60R	(9 3 5 3) ₃	(9)
43	26H	(17 4 2 3)	(1)	60R	(9 4 5 2) ₃	(11)
44	26H	(7 3 3 3 3 7)	(7)	60R	(9 5 3 3) ₃	(9)
45	28H	(23 5)	(11)	60R	(9 6 2 3) ₃	(17)
46	28H	(9 5 5 9)	(1)	60R	(9 3 6 2) ₃	(11)
47	28H	(21 3 2 2)	(11)	60R	(3 4 7 6) ₃	(11)
48	44H	(37 7)	(11)	60R	(7 8 2 3) ₃	(17)
49	44H	(17 4 17 6)	(11)	60R	(6 3 3 3 3 2) ₃	(11)

Table 1 (cont.)

Sample number	Rhombohedral polytypes (3 NR)	Zhdanov symbol	Reference
50*	60R	(5 4 5 2 2 2) ₃	(11)
51*	60R	(8 4 2 2 2 2) ₃	(11)
52*	60R	(5 3 3 4 2 3) ₃	(12)
53*	60R	(5 2 2 3 6 2) ₃	(12)
54*	60R	(7 4 2 3 2 2) ₃	(7)
55*	60R	(5 2 2 3 5 3) ₃	(12)
56*	60R	(10 3 5 2) ₃	(11)
57*	66R	(15 7) ₃	(7)
58*	66R	(7 7 3 5) ₃	(5)
59*	66R	(7 7 5 3) ₃	(7)
60*	66R	(8 7 4 3) ₃	(7)
61*	66R	(5 5 4 2 3 3) ₃	(7)
62*	66R	(7 3 2 4 3 3) ₃	(2)
63*	72R	(9 5 4 6) ₃	(14)
64*	72R	(6 11 5 2) ₃	(14)
65*	72R	(6 5 3 3 5 2) ₃	(8)
66*	72R	(6 3 5 6 2 2) ₃	(8)
67*	72R	(10 7 3 4) ₃	(8)
68*	72R	(11 5 5 3) ₃	(8)
69*	72R	(7 3 5 2 5 2) ₃	(8)
70*	72R	(9 3 5 3 2 2) ₃	(8)
71*	72R	(14 5 2 3) ₃	(8)
72*	72R	(14 5 3 2) ₃	(8)
73*	78R	(13 5 5 3) ₃	(7)
74*	78R	(17 3 4 2) ₃	(7)
75*	78R	(7 7 3 3 4 2) ₃	(7)
76*	78R	(9 3 3 3 5 3) ₃	(7)
77*	84R	(25 3) ₃	(11)
78*	84R	(11 8 4 5) ₃	(11)
79*	114R	(35 3) ₃	(11)
80*	114R	(29 9) ₃	(11)
81*	114R	(21 9 6 2) ₃	(11)
82*	114R	(13 5 2 2 6 2 6 2) ₃	(11)

* For these samples the hexagonal polytypes have not yet been observed.

- (1) Brafman, Alexander & Steinberger (1967).
- (2) Daniels (1966).
- (3) Evans & McKnight (1959).
- (4) Frondel & Palache (1950).
- (5) Farkas-Jahnke & Dornberger-Schiff (1970).
- (6) Haussühl & Müller (1963).
- (7) Kiflawi & Mardix (1969a).
- (8) Kiflawi & Mardix (1969b).
- (9) Kiflawi & Mardix (1970).
- (10) Kiflawi, Mardix & Kalman (1969).
- (11) Kiflawi, Mardix & Steinberger (1969).
- (12) Mardix, Alexander, Brafman & Steinberger (1967).
- (13) Mardix & Brafman (1967).
- (14) Mardix & Brafman (1968).
- (15) Mardix, Brafman & Steinberger (1967).
- (16) Mardix & Kiflawi (1970).
- (17) Mardix, Kiflawi & Kalman (1969).

rhombohedral polytypes are possible, and the frequency of finding a hexagonal polytype will be nearly twice the frequency of finding a rhombohedral polytype. On average, therefore, the number of rhombohedral polytypes should be greater than the number of the hexagonal polytypes.

On the basis of the above considerations, the rhombohedral and hexagonal polytypes should exhibit the following trend of occurrence:

1. For smaller unit-cell heights, both the rhombohedral and hexagonal polytypes will be observed.
2. In this region of unit-cell heights, the hexagonal polytypes should occur with a frequency approximately twice that of the occurrence of rhombohedral polytypes.
3. Beyond a certain limit of unit-cell height only rhombohedral polytypes should be observed.
4. On average, the number of rhombohedral polytypes may exceed the number of hexagonal polytypes because of condition (3).

However, as the above considerations are based on the statistical distribution of the Burgers vector strengths of axial screw dislocations, the results obtained should be tested only for a large number of observed polytypes. Fortunately, more than one hundred kinds of ZnS polytypes have so far been reported with completely known atomic structures. These with their Ramsdell and Zhdanov symbols are listed in Table 1. It may thus be possible to test the above mentioned results and explain the relative abundance of hexagonal and rhombohedral ZnS polytypes in the light of the present arguments.

The total number of these polytypes is 131. The maximum unit-cell height amongst all the hexagonal polytypes of ZnS so far discovered is equal to 44 layers of ZnS (44H). The total number of hexagonal polytypes from 4H to 44H is 49, where 2H is not counted as it is taken as the parent phase. The number of rhombohedral polytypes within the same range of the unit-cell heights (*i.e.* from 9R to 42R) is 23 only. This is nearly a half of the number of hexagonal polytypes (*i.e.* a half of 49). The polytypes with the unit-cell heights beyond 44 layers of ZnS are all rhombohedral (non-hexagonal) and they are 59 in number. The total number of hexagonal polytypes (49) is thus considerably smaller than the total number 82 of rhombohedral polytypes. The relative occurrence of hexagonal and rhombohedral polytypes therefore, can be explained by a dislocation-controlled ordered twinning model (Rai, 1971a,b).

It may also be interesting to consider the features of the relative abundance of the hexagonal and rhombohedral polytypes with the same unit-cell heights. Although only a few experimental data are available at present, it is expected that hexagonal polytypes will be encountered with a greater frequency than rhombohedral polytypes with the same unit-cell heights. The reason may be a greater number of possible rearrangements of the stacking sequence of ZnS layers in the case of hexagonal polytypes compared with the rhombohedral case. There are two main possible conditions to be taken into account in this connexion. The first is concerned with the minimum value of a number that can appear in the Zhdanov symbols for the ZnS polytypes. It can not be smaller than 2 in normal cases (Table 1). (There is no limit in the maximum value of these numbers.) The second is concerned with the

number of layers which define a rhombohedral or hexagonal polytype. For example, the structure of a $3NH$ (hexagonal) polytype will be completely determined by the detailed stacking sequence of $3N$ close-packed layers of ZnS, while the structure of a rhombohedral polytype with the same unit-cell height (*i.e.* $3N$ layers of ZnS) will be precisely governed by the stacking sequence of only N layers. Under these two structural conditions (for the same unit-cell height), the possible number of rhombohedral polytypes turns out to be less than that of the hexagonal polytypes. In support of these arguments, it may be seen in Table 1 that there are three $12H$ polytypes and only one $12R$; four $18H$ polytypes and only one $18R$; eleven $24H$ polytypes and only two $24R$ polytypes.

Discussion

The problem of the relative occurrence of the rhombohedral and hexagonal polytypes has been discussed above in the light of the stability of the Burgers vector strengths of the screw dislocation, by taking account of their accidental occurrence in a specific manner which, in one case, produces hexagonal polytypes and, in the other case, rhombohedral polytypes. It has also been pointed out that the probability of arranging close-packed layers into various possible modes, subject to the structural characteristics of ZnS polytypes, increases with the number of layers involved in a $3NH$ ($3N$ layers) or in a $3NR$ (only N layers) polytype. Although the Burgers vector strength N is duly controlled by energy relations, the various possible modes of layer stacking occur statistically. Combining all these factors, the present model may be considered of semi-statistical nature.

In Table 1, it can be seen that the maximum unit-cell height of ZnS polytypes ($44H$, $114R$) corresponds to a Burgers vector strength of less than 44 layers of ZnS. Although this list is not final, and it is felt that more ZnS polytypes with relatively larger unit-cell heights may be observed in future, it is worth asking why this limit to the unit-cell height occurs. This situation can be understood in the light of the energy required to produce an axial screw dislocation. If N is the strength of the Burgers vector of an axial screw dislocation, the corresponding self energy is equal to $(KN^2/4\pi) \ln R/r$, where N is to be understood now as the length of the Burgers vector instead of the corresponding number of unit layers, K is the elastic modulus, R is the radius of a crystal and r is the core radius of the screw dislocation. From this relation it is evident that the self energy of the screw dislocation increases proportional to N^2 . Thus the formation of screw dislocations will become increasingly difficult if the value of N is too large. As a result, there should be a limit to the value of N , beyond which axial screw dislocations with higher Burgers vector strength will not be stable. Therefore, as the unit-cell height of polytypes is directly related to the Burgers vector strength

N of axial screw dislocations, the polytypes corresponding to values of N higher than the limit will become unstable. It is probably for this reason that the polytypes with N larger than 44 have not yet been reported. However, the possibility of finding new polytypes corresponding to $N > 44$ in future cannot be excluded. At present there is no any physical theory to predict accurately the upper limit of N . On the other hand, it is likely that the polytypes with smaller unit-cell heights will occur more frequently than those having larger unit-cell heights. For instance, the frequent occurrence of $6H$ and $4H$ polytypes may be attributed to the small energies required in their formation by the screw dislocation mechanism. In fact, Alexander *et al.* (1970) have explained the relative abundance of $4H$ and $6H$ on the same assumption. As the zinc sulphide polytypes have behaviour (Rai & Krishna, 1968*a,b*) in common with the polytypes of silicon carbide, it is expected that some of the results for ZnS may also be valid for SiC polytypes.

The results in this paper have been derived on the assumption that the polytypes are formed as a result of axial screw dislocations operating in $2H$ type crystals. Although very little information is available regarding the role of axial screw dislocations in the growth of polytypes, there is still a growing belief that screw dislocations are solely responsible for the formation of ZnS polytypes (Mardix, 1969; Alexander *et al.*, 1970). Mardix (1969) has also noticed the existence of large screw dislocations in polytypic crystals of ZnS. Hanaoka and his co-workers (Hanaoka & Vand, 1968; Hanaoka, Raymond & Greer, 1969) have also reached similar conclusions from their studies of lead iodide polytypes. The growth of ZnS single crystals is, however, known to occur around a single screw dislocation (Lendvay & Kovacs 1965, 1970; Mardix & Kiflawi, 1970).

One may finally point out some disagreements between theory and experimental observations. Although it has been pointed out that the number of hexagonal polytypes should be larger than the number of rhombohedral polytypes for the same unit-cell height, Table 1 indicates that, while there are three $30R$, six $36R$ and seven $42R$ polytypes, there are none of the hexagonal polytypes. However, the number of ZnS polytypes listed in the Table 1 is not final. At the present stage, it seems to be only the result of chance that various $30H$ and $42H$ polytypes have not been discovered while corresponding rhombohedral polytypes have been observed.

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The Influence of Thermal Diffuse Scattering, Secondary Extinction and Crystallite Size Distribution on X-ray Line Profiles

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A method is given for correcting the integral intensities of X-ray reflexions from platelets of single crystals or powders for secondary extinction and thermal diffuse scattering (TDS). The line profiles are calculated as folding integrals from theoretical functions considering the crystallite size distribution, the total absorption, and TDS. By means of variation of the unknown parameters (fraction of TDS to the overall intensity, mean crystallite size and their polydispersity, and absorption coefficient, secondary extinction included) the calculated function has to fit the measured line profile. A detailed description of this method according to Bradaczek and Hosemann is given after introducing some modifications such as collimation errors of the primary beam and anisotropy of the lattice vibrations. The method is applied to measured line profiles of NaCl and LiF single crystals.

Introduction

From absolute X-ray intensities the structural amplitudes cannot be obtained with accuracies better than 1% until the present (Jennings, 1969). The reasons for this are systematic errors such as insufficient corrections of absorption (primary and secondary extinction) and of thermal diffuse scattering. The influence of these corrections on the measured integral intensities can be considerable. It is therefore necessary to measure these corrections. By the method of Bradaczek & Hosemann (1968) one obtains directly the true absorp-

tion coefficient, the influence of thermal diffuse scattering, and the crystallite size distribution function by means of a line-profile analysis. Contrary to the known methods (Bragg, James & Bosanquet, 1921), where the angular distribution of the mosaic blocks influences the profile of the rocking curve, here the reflexions will be measured by means of a film in a fixed position. In the present paper this method is refined and applied to the line-profile analysis of NaCl and LiF single crystals. By careful development and analysis of several films of the same reflexion much more information is available than by counter meas-