

## High-Order ZnS Polytypes and Their Identification

BY I. KIFLAWI, Z. H. KALMAN, S. MARDIX\* AND I. T. STEINBERGER

*The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel*

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A list of ZnS polytypes having thirty or more layers in their elementary stacking sequences is presented, including seven new polytypes:  $90R$  (18 2 7 3)<sub>3</sub>;  $90R$  (8 3 5 5 3 6)<sub>3</sub>;  $96R$  (17 4 6 5)<sub>3</sub>;  $102R$  (31 3)<sub>3</sub>;  $34L$  (7 5 3 5 5 2 2)<sub>2</sub>;  $120R$  (29 3 2 2 2 2)<sub>3</sub> and  $120R$  (13 3 3 5 11 5)<sub>3</sub>. Polytype identification procedures are discussed from the point of view of reliability. It is demonstrated that even for such polytypes unambiguous identification is possible without exact intensity measurements. For these polytypes, the Burgers vector of the generating [00.1] screw dislocation has a length of 90 Å or more.

### Introduction

ZnS polytypes having thirty or more layers in their elementary stacking sequence have unit cells with a  $c$  dimension of 90 Å or more. Such structures will be referred to as high-order polytypes.

Polytype formation in ZnS crystals was shown (Alexander, Kalman, Mardix & Steinberger, 1970) to be a two-step process: (a) growth of  $2H$  crystals around a large screw dislocation and (b) transformation, during the cooling period (Mardix & Steinberger, 1970) into polytypes. Step (b) is actually a periodic slip process, involving expansion of stacking faults, governed by the large screw. The Burgers vector of the large screw has the length  $mc_0$ , where  $m$  is the number of layers in the elementary stacking sequence and  $c_0$  is the distance between neighbouring (00.1) layers. This fact, together with the finding that apart from the generating screw the polytype regions are practically perfect crystals (Steinberger, Alexander, Brada, Kalman, Kiflawi & Mardix, 1971), makes ZnS crystals containing high order polytypes the object of rather unusual investigations. They are of much interest for basic dislocation theory and they also serve as a convenient system for studying single large dislocations by X-ray topography (Mardix, Lang & Blech, 1971). These subjects are beyond the scope of normal crystallographic investigations of polytypism.

In the present paper, all fully identified high-order ZnS polytypes will be listed. It will be shown that the elimination method (Mardix, Kalman & Steinberger, 1970) used for identification furnishes unambiguous results. The applicability of the two-step model of polytype formation (Alexander *et al.*, 1970) for these high-order polytypes will be also stressed.

### Method of identification

The polytypes listed in this paper (Table 1) were identified using the elimination method (Mardix, Kalman, & Stein-

berger, 1970). In this method, the  $c$  translation is determined from X-ray oscillation photographs by well known procedures (Verma & Krishna, 1966). At this stage, it is also determined whether the polytype is rhombohedral. Subsequently, a representative set of reflexion spots, with well-defined hierarchy of intensities, are selected and indexed; the information on this hierarchy is fed into the computer. The computer program† is designed in such a way that the intensities of only those polytypes which have the same hierarchy of intensities as the experimental set appear in the output. The final determination of structure takes place by comparison of all reflexions with  $-m/2 < l \leq m/2$ ; this comparison eliminates those polytypes which have the same hierarchy within the selected set, but do not fit the total distribution. However, the hierarchy of the selected set limits the possibilities to such an extent that in most cases only one structure is found by the computer.

For high-order polytypes, this procedure would have required very long computer times, if no auxiliary information had been fed into the computer. In fact, the number of symbols in the Zhdanov sequence was always known beforehand from birefringence measurements (Brafman & Steinberger, 1966) and this was used to reduce the number of possible structures. Also, in the case of rhombohedral polytypes, inspection of the photograph often‡ showed whether  $I-J=1 \pmod{3}$  or  $I-J=2 \pmod{3}$  (Mardix, Kalman & Steinberger, 1970).  $I$  and  $J$  are respectively the number of cyclic and anticyclic displacements between neighbouring layers within the elementary stacking sequence. In the first run, only polytypes which have no 1's in their Zhdanov symbol were considered. By the procedure outlined above, a fitting polytype (without 1's)

† In all calculations, the Hebrew University's C.D.C. 6400 computer was used. Maximum storage space used was 13000 computer words.

‡ This is very simple *e.g.* if one of the Zhdanov symbols is much larger than the others, especially in polytypes of low hexagonality. *E.g.* in Table 1, the information could be and was, indeed, used for  $120R$  (29 3 2 2 2)<sub>3</sub>, but was not used for  $120R$  (13 5 11 5 3 3)<sub>3</sub>.

\* Present address: University of Rhode Island, Kingston, Rhode Island 02881, U.S.A.

was found, and its cyclicity determined from the Zhdanov symbol. All polytypes having '1' in their Zhdanov symbol and being of this cyclicity were subsequently checked; this check gave negative results in accord with past experience with most ZnS polytypes. The justification of this procedure lies in the following facts: (a) that the final fit between the calculated and observed intensity distributions is very good; (b) that the value of  $I-J$  is not too sensitive to intensity changes, as it can vary only in steps of 6.

Finally, all polytypes with all possible cyclicity values and having 1's in their Zhdanov symbol were checked, provided they had the correct number of figures in their Zhdanov symbol. Table 1 also includes some relevant computer times; these should be useful for assessing the capabilities of the method for other materials, where it is more difficult to obtain auxiliary information. In such cases and for even higher polytypes the cyclicity and/or the number of 1's in the Zhdanov symbol should be determined at the outset from the experimental intensity distribution (Mardix, Steinberger & Kalman, 1970; Dornberger-Schiff & Farkas-Jahnke, 1971).

Table 1. List of high-order polytypes found in vapour-phase grown ZnS crystals

Polytype		Computer time for identification (sec)*		
		(a)	(b)	(c)†
90R (18 3 7 2) <sub>3</sub>	new	<5	~5	8
90R (8 6 3 5 5 3) <sub>3</sub>	new	~10	20	70
96R (17 5 6 4) <sub>3</sub>	new	<5	~5	8
102R (31 3) <sub>3</sub>	new			2.5
34L (7 5 3 5 5 2 2)	new	240	675	1800
114R (29 9) <sub>3</sub>	†			2.5
114R (35 3) <sub>3</sub>	†			2.5
114R (21 9 6 2) <sub>3</sub>	†			8
114R (13 5 2 2 6 2 6 2)	†	220	600	1900
120R (29 3 2 2 2 2) <sub>3</sub>	new	<12	26	245
120R (13 5 11 5 3 3) <sub>3</sub>	new		70	495
44L (37 7)	†			2.5
44L (17 6 17 4)	†			9

\* The authors are indebted to the referee for suggesting the inclusion of the computer times. The list is incomplete since these numbers have not been systematically stored.

† (a) Considering only polytypes without 1's in the Zhdanov symbols. (b) First considering polytypes without 1's and then checking polytypes with 1's and only one cyclicity. (c) Considering all polytypes having the appropriate periodicity and hexagonality.

‡ Already reported: Kiflawi, Mardix & Steinberger (1969).

### New high-order polytypes

Seven new high-order polytypes were found in four vapour-phase grown ZnS crystals. The new polytypes are listed in Table 1, together with all known high-order polytypes. The crystals were grown at about 1250°C. X-ray oscillation photographs about the  $c$  axis of the crystals were taken using Cu  $K\alpha$  radiation. (10. $l$ ) or (20. $l$ ) row lines of these photographs are shown in Fig. 1. The observed and calculated intensi-

ties of the X-ray reflexion spots of the new polytypes are compared in Table 2.

Table 2. Comparison of observed and calculated intensities of the new polytypes listed in Table 1

	Observed	Calculated
90R (18 3 7 2) <sub>3</sub>		
1	<i>vw</i>	0.39
4	<i>w</i>	1.10
7	<i>w</i>	1.03
10	<i>a</i>	0.09
13	<i>m</i>	2.89
16	<i>m</i>	2.87
19	<i>a</i>	0.09
22	<i>m</i>	3.82
25	<i>m</i>	4.59
28	<i>vw</i>	0.33
31	<i>m</i>	3.28
34	<i>m</i>	4.96
37	<i>vw</i>	0.57
40	<i>w</i>	1.95
43	<i>m</i>	4.09
-2	<i>vw</i>	0.44
-5	<i>a</i>	0.02
-8	<i>w</i>	0.81
-11	<i>w</i>	0.96
-14	<i>w</i>	0.87
-17	<i>w</i>	1.26
-20	<i>w</i>	0.90
-23	<i>m</i>	5.66
-26	<i>s</i>	8.04
-29	<i>vvs</i>	100.00
-32	<i>vs</i>	28.67
-35	<i>s</i>	6.53
-38	<i>s</i>	9.11
-41	<i>w</i>	1.62
-44	<i>w</i>	0.84
90R (8 6 3 5 5 3) <sub>3</sub>		
1	<i>w</i>	1.48
4	<i>vw</i>	0.65
7	<i>w</i>	1.33
10	<i>m</i>	6.60
13	<i>vw</i>	0.54
16	<i>m</i>	6.17
19	<i>s</i>	17.90
22	<i>m</i>	10.34
25	<i>w</i>	1.89
28	<i>vvs</i>	73.04
31	<i>vs</i>	28.51
34	<i>s</i>	22.28
37	<i>s</i>	18.47
40	<i>s</i>	13.55
43	<i>w</i>	3.95
-2	<i>vw</i>	0.21
-5	<i>w</i>	2.95
-8	<i>vw</i>	0.30
-11	<i>m</i>	6.46
-14	<i>w</i>	0.86
-17	<i>s</i>	13.41
-20	<i>m</i>	7.83
-23	<i>s</i>	20.77
-26	<i>w</i>	3.14
-29	<i>vvs</i>	100.00
-32	<i>vs</i>	39.81
-35	<i>w</i>	1.19
-38	<i>vs</i>	35.19
-41	<i>vw</i>	0.46
-44	<i>m</i>	6.32

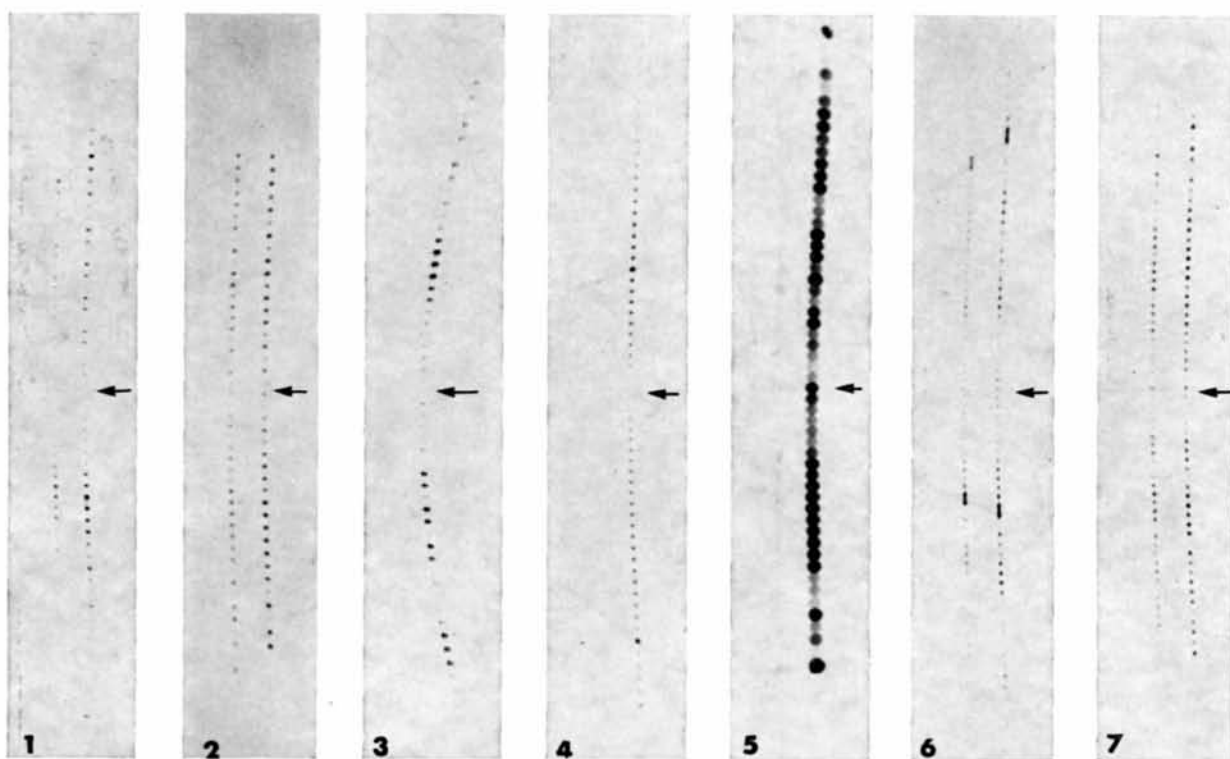


Fig. 1. (10.*l*) or (20.*l*) row lines of oscillation photographs about the *c* axis of the new polytypes. Cu *K* radiation, 60 mm diameter camera. Magnification  $\times 3$ . The zero line is indicated by an arrow. (1)  $90R(18\ 3\ 7\ 2)_3$ ; (2)  $90R(8\ 6\ 3\ 5\ 5\ 3)_3$ ; (3)  $96R(17\ 5\ 6\ 4)_3$  [(20.*l*) row line]; (4)  $102R(31\ 3)_3$ ; (5)  $34L(7\ 5\ 3\ 5\ 5\ 2\ 2)$ ; (6)  $120R(29\ 3\ 2\ 2\ 2\ 2)_3$ ; (7)  $120R(13\ 5\ 11\ 5\ 3\ 3)_3$ .

Table 2 (cont.)

<i>l</i>	Observed	Calculated
96R (17 5 6 4) <sub>3</sub>		
1	<i>vw</i>	0.42
4	<i>w</i>	2.60
7	<i>vw</i>	0.86
10	<i>vw</i>	0.67
13	<i>vw</i>	0.71
16	<i>w</i>	2.23
19	<i>vw</i>	0.68
22	<i>s</i> (22 > 25)	17.13
25	<i>s</i>	14.90
28	<i>vw</i>	1.58
31	<i>vs</i>	32.22
34	<i>s</i> (34 > 25)	21.07
37	<i>vw</i>	0.89
40	<i>s</i> (40 > 25)	19.34
43	<i>m</i>	9.48
46	<i>a</i>	0.19
-2	<i>vw</i> (-2 > -14)	1.32
-5	<i>w</i>	1.81
-8	<i>w</i>	1.53
-11	<i>w</i>	1.68
-14	<i>vw</i>	0.91
-17	<i>w</i>	2.04
-20	<i>w</i>	2.04
-23	<i>m</i>	8.50
-26	<i>m</i> (-26 > -23)	12.54
-29	<i>vs</i>	83.81
-32	<i>vs</i>	100.00
-35	<i>vs</i>	89.73
-38	<i>s</i>	13.23
-41	<i>w</i>	2.75
-44	<i>vw</i>	0.72
-47	<i>w</i>	2.65
102R (31 3) <sub>3</sub>		
1	<i>vw</i>	0.002
4	<i>vw</i> (4 > 1)	0.04
7	<i>vw</i>	0.11
10	<i>vw</i> (10 > 7)	0.21
13	<i>vw</i> (13 > 10)	0.34
16	<i>w</i>	0.47
19	<i>w</i> (19 > 16)	0.61
22	<i>w</i> (22 > 19)	0.73
25	<i>w</i>	0.83
28	<i>w</i>	0.90
31	<i>w</i>	0.94
34	<i>vs</i>	100.00
37	<i>w</i>	0.91
40	<i>w</i>	0.85
43	<i>w</i>	0.77
46	<i>w</i>	0.68
49	<i>w</i>	0.58
-2	<i>vw</i>	0.01
-5	<i>vw</i> (-5 > -2)	0.06
-8	<i>vw</i>	0.14
-11	<i>vw</i>	0.25
-14	<i>vw</i> (-14 > -11)	0.38
-17	<i>w</i>	0.52
-20	<i>w</i>	0.65
-23	<i>w</i> (-23 > -20)	0.77
-26	<i>w</i> (-26 > -23)	0.86
-29	<i>w</i>	0.91
-32	<i>w</i>	0.94
-35	<i>w</i>	0.93
-38	<i>w</i>	0.89
-41	<i>w</i>	0.82
-44	<i>w</i>	0.74
-47	<i>w</i>	0.65
-50	<i>w</i>	0.55

Table 2 (cont.)

<i>l</i>	Observed	Calculated
34L (7 5 3 5 5 2 2)		
0	<i>m</i> (0 > 1)	5.59
1	<i>m</i>	4.19
2	<i>vw</i> (2 ~ 4)	1.91
3	<i>vw</i> (3 > 5)	1.52
4	<i>vw</i> (4 > 3)	1.97
5	<i>vw</i>	1.27
6	<i>w</i>	2.78
7	<i>s</i>	18.11
8	<i>m</i>	4.93
9	<i>s</i> (9 > 7)	20.65
10	<i>s</i> (10 > 9)	39.66
11	<i>s</i> (11 > 10)	46.21
12	<i>s</i> (12 > 13)	20.94
13	<i>s</i>	15.35
14	<i>s</i> (14 > 15)	19.09
15	<i>s</i>	13.44
16	<i>s</i>	16.36
17	<i>vw</i>	1.52
-1	<i>vw</i>	1.23
-2	<i>vw</i>	0.73
-3	<i>vw</i> (-3 > -1)	1.39
-4	<i>w</i>	2.85
-5	<i>vw</i> (-5 > -3)	1.80
-6	<i>s</i>	13.55
-7	<i>m</i>	5.83
-8	<i>vw</i> (-8 ~ -3)	1.48
-9	<i>w</i> (-9 > -11)	3.38
-10	<i>vs</i>	100.00
-11	<i>w</i>	2.77
-12	<i>s</i>	18.20
-13	<i>m</i> (-13 > -7)	7.23
-14	<i>vs</i>	53.95
-15	<i>vw</i> (-15 > -16)	2.20
-16	<i>vw</i> (-16 > -17)	1.95
-17	<i>vw</i>	1.52
120R(29 3 2 2 2 2) <sub>3</sub>		
1	<i>w</i>	1.35
4	<i>w</i>	1.70
7	<i>w</i>	1.20
10	<i>vw</i> (10 > 13)	0.23
13	<i>vw</i>	0.11
16	<i>vw</i>	0.63
19	<i>vw</i> (19 > -11)	0.42
22	<i>a</i>	0.03
25	<i>w</i>	1.81
28	<i>m</i>	5.52
31	<i>m</i>	7.33
34	<i>m</i>	4.99
37	<i>w</i>	1.33
40	<i>vw</i>	0.16
43	<i>vw</i>	1.07
46	<i>vw</i>	1.15
49	<i>vw</i>	0.23
52	<i>vw</i>	0.87
55	<i>w</i>	3.66
58	<i>m</i>	5.71
-2	<i>vw</i> (-2 > -8)	1.06
-5	<i>vw</i> (-5 > -8)	1.05
-8	<i>vw</i> (-8 > 16)	0.76
-11	<i>vw</i> (-11 > 10)	0.32
-14	<i>vw</i> (-14 > -11)	0.38
-17	<i>vw</i>	0.67
-20	<i>vw</i> (-20 > -17)	0.77
-23	<i>vw</i> (-23 > -20)	1.37
-26	<i>w</i> (-26 > -32)	2.76
-29	<i>w</i> (-29 > -26)	3.16
-32	<i>w</i>	2.18
-35	<i>m</i> (-35 > -59)	7.32

Table 2 (*cont.*)

<i>l</i>	Observed	Calculated
-38	<i>vs</i>	65.26
-41	<i>vvs</i>	100.00
-44	<i>vw</i>	0.25
-47	<i>w</i>	2.50
-50	<i>vw</i>	1.16
-53	<i>vw</i>	0.65
-56	<i>w</i>	2.98
-59	<i>m</i>	5.22
120R (13 5 11 5 3 3) <sub>3</sub>		
1	<i>vw</i> (1 > 13)	1.26
4	<i>vw</i>	0.09
7	<i>vw</i> (7 < 1)	0.83
10	<i>vw</i>	0.98
13	<i>vw</i>	0.71
16	<i>vw</i>	0.61
19	<i>vw</i>	0.68
22	<i>m</i> (22 < 28)	5.33
25	<i>w</i>	1.73
28	<i>m</i> (28 > 46)	7.11
31	<i>w</i> (31 > 25)	3.94
34	<i>vw</i>	0.82
37	<i>s</i> (37 > 43)	20.21
40	<i>m</i> (40 > 28)	8.49
43	<i>s</i>	15.28
46	<i>m</i>	6.03
49	<i>vw</i>	1.26
52	<i>w</i> (52 > 55)	5.41
55	<i>w</i> (55 > 58)	4.28
58	<i>w</i>	3.40
-2	<i>vw</i> (-2 > -8)	0.30
-5	<i>a</i>	0.005
-8	<i>vw</i>	0.17
-11	<i>vw</i> (-11 > -8)	0.30
-14	<i>vw</i> (-14 > -8)	0.29
-17	<i>w</i>	3.40
-20	<i>w</i>	2.59
-23	<i>w</i> (-23 > -17)	5.69
-26	<i>vw</i>	0.90
-29	<i>vw</i>	0.09
-32	<i>vw</i> (-32 > -26)	1.47
-35	<i>w</i> (-35 > -20)	3.88
-38	<i>vvs</i>	100.00
-41	<i>w</i>	3.57
-44	<i>vs</i>	45.03
-47	<i>m</i>	7.60
-50	<i>vw</i>	0.35
-53	<i>w</i>	4.08
-56	<i>vw</i>	1.04
-59	<i>vw</i>	1.02

## Discussion

### A. The reliability of the identification method used

While the paper by Mardix, Kalman & Steinberger (1970) on the identification procedure used in the present paper and in previous ones was in press, a paper by Dornberger-Schiff and Farkas-Jahnke (1970) appeared, describing an elegant direct method for the identification of polytypes. The essentials of the method were published previously (Farkas-Jahnke, 1966); it was applied for identifying a SiC polytype by Gomes de Mesquita (1968) and for a ZnS polytype by Farkas-Jahnke and Dornberger-Schiff (1970). A similar method was also proposed by Tokonami Hosoya (1965), but not successfully applied (Tokonami, 1966).

In their paper, Dornberger-Schiff and Farkas-Jahnke express their doubt as to whether it is possible to determine reliably, by any method, the structure of a high-order polytype without making very exact intensity measurements. Since for the method used in the present paper no such measurements are necessary, its reliability will now be discussed.

A reliable identification method has to take into account all polytypes compatible with the experimental information available, and has to involve strict final comparison of calculated and observed intensities for all reflexions with  $-m/2 < l \leq m/2$ . If only the period  $m$  of the polytype is known, the first stage would involve in our case consideration of *all* polytypes of the given periodicity. Of course, this would require very long computer times for high-order polytypes. Preliminary information such as (a) percentage of hexagonality, (b) cyclicity, (c) number of 1's in the Zhdanov symbol (Dornberger-Schiff, Schmittler & Farkas-Jahnke, 1971) and (d) the assumption that only certain sequences and figures appear in the Zhdanov symbol can reduce drastically, at the outset, the number of structures to be considered. However, only preliminary information having a sound physical basis should be taken into account. For example, it has been commonly assumed that the Zhdanov symbols of SiC polytypes contain only the figures 2, 3 and 4. However, the polytype 24R (5 3)<sub>3</sub>, having the figure 5 in its Zhdanov symbol was identified in SiC (Gomes de Mesquita, 1965). For the polytypes presented here only information (a), obtained directly from birefringence measurements, was used. It seems to be likely, however, that for even higher polytypes (b) and (c) will have to be also supplied at the outset. These would involve rather exact intensity measurements.

At the final stage the intensity distribution of all reflexion spots is compared with the calculated intensities. This kind of comparison, where the hierarchy is emphasized, in contrast to refinement by means of  $R$  values cannot give a wrong answer, though in principle it may lead to more than one polytype (*e.g.* homometric polytypes). In this respect, it is instructive to consider the case of two polytypes: 66R (8 7 4 3)<sub>3</sub> and 66R (7 7 5 3)<sub>3</sub>. The polytype identified by Farkas-Jahnke and Dornberger-Schiff by their method was 66R (7 7 5 3)<sub>3</sub>. At the stage before the last they obtained, for their crystal, both structures and eliminated 66R (8 7 4 3)<sub>3</sub> essentially by comparison of the intensity distributions. This procedure is certainly correct, but we contest the conclusion that 'intensities measured quantitatively and with sufficient accuracy are needed for a reliable determination of the polytype'. As an illustration, in Table 3, the observed and calculated intensity distributions of the same structures, 66R (8 7 4 3)<sub>3</sub> and 66R (7 7 5 3)<sub>3</sub>, are given, taken from a previous publication (Kiflawi & Mardix, 1969). It is seen that although the intensities were determined visually, both identifications are unambiguous: consider *e.g.* the reflexions with  $l=7, 10, 16, 28$  and  $-8$ .

Both the elimination method and the direct method of Dornberger-Schiff and Farkas-Jahnke are in full accord with the criteria of reliability as discussed above. The elimination method needs, however, much less exacting experimental work (usually no quantitative determination of intensities) and is much faster. Going to higher-order polytypes only increases, in this case, the computer time, without causing any additional difficulty. Moreover, it should be pointed out again (see also Mardix *et al.*, 1970) that the probability for ambiguity actually decreases with increasing polytype order  $m$ : the number of possible polytypes increases roughly as  $2^{m-1}/m$ , while the number of possible intensity hierarchies increases approximately as  $m!$ .

Dornberger-Schiff & Farkas-Jahnke (1970) drew attention to the possibility of occurrence of homometric polytypes.

We would like to note that homometric polytypes can be classified into two categories. The first category consists of those mentioned by Dornberger-Schiff and Farkas-Jahnke, which may be called antipolar homometric pairs. It should be noted that none of the notations for polytype structures used at present does provide for a convention to distinguish between the two members of such pairs. The second category contains homometric polytypes having intrinsically different Zhdanov symbols,\* for example the hypothetical structures  $48L$  (15 9 3 12 3 6),  $48L$  (15 12 3 6 9 3) and  $48L$  (18 6 6 12 3 3). In such a case all structures must be mentioned. Both the direct method and the elimination method automatically reveal all homometric structures.

\* No such cases have been encountered so far.

### B. Formation of the polytypes

Though the main subject of this paper is the structure and identification of high-order polytypes, it should be emphasized that the model of polytype formation proposed by Alexander *et al.* (1970) is in full accord with the features of the high-order ZnS polytypes as well. In short, the crystals containing these polytypes grow with the  $2H$  wurtzite structure around a giant screw dislocation (Mardix, Lang & Blech, 1971) and transform during the growth process (Mardix & Steinberger, 1970) into polytypes by virtue of the expansion of stacking faults which have negative energy (Blank, Delavignette & Amelinckx, 1962). All the experimental evidence for this mechanism, brought forward by Alexander *et al.* (1970), pertains to the high-order polytypes as well: the polytypes in a given crystal belong to the same family; facets of polytypic regions and linear markings are tilted in accord with the periodic slip process (Kiflawi, unpublished results); the giant screw dislocations are observable by X-ray topography; there are no polytypes of odd periodicity. On the other hand, no indications were found with these polytypes which would favour a recent hypothesis (Rai, 1971) for polytype formation in ZnS. This author suggested that periodic occurrence of f.c.c. microtwins in  $2H$  and the presence of growth faults make possible direct growth of ZnS polytypes around a screw dislocation in a somewhat similar fashion as had been proposed for SiC (Frank, 1951; Mitchell, 1957; Verma & Krishna, 1966). The evidence that the tilt (and the accompanying structure change) occurs while the crystals are cooling down (Mardix & Steinberger, 1970) and the absence of temperature changes during growth (which would make possible the appearance of microtwins as well as the absence of odd-order

Table 3. Comparison of the observed and calculated intensities of the polytypes  $66R$  (7 7 5 3)<sub>3</sub> and  $66R$  (8 7 4 3)<sub>3</sub>

$l$	Observed intensities		Calculated intensities	
	$66R$ (7 7 5 3) <sub>3</sub>	$66R$ (8 7 4 3) <sub>3</sub>	$66R$ (7 7 5 3) <sub>3</sub>	$66R$ (8 7 4 3) <sub>3</sub>
1	$vw$	$vw$	1.26	1.14
4	$vw$	$vw$	1.49	0.72
7	$vvw$	$m$	0.37	7.95
10	$m$ (10 > 13)	$vvw$ (10 > 28)	11.55	0.31
13	$m$ (13 > 31)	$w$	7.16	4.02
16	$w$	$s$	2.11	25.98
19	$vs$ (19 > 25)	$s$ (19 > 22)	61.38	37.15
22	$vs$	$s$ (22 > 16)	32.00	31.70
25	$vs$ (25 > 22)	$vs$	44.16	76.18
28	$s$	$vvw$ (28 > -5)	16.21	0.18
31	$m$	$m$	4.73	6.36
-2	$w$	$w$	2.85	3.41
-5	$vw$	$vvw$	1.47	0.15
-8	$m$ (-8 ≈ 31)	$vw$	4.20	0.76
-11	$m$ (-11 ≈ -8)	$m$ (-11 > -14)	4.31	12.81
-14	$s$	$m$	13.16	8.30
-17	$s$ (-17 ≈ 28)	$m$ (-17 > -11)	18.13	15.18
-20	$vs$	$vs$	50.04	52.46
-23	$vvs$	$vvs$	100.00	100.00
-26	$w$	$w$ (-26 ≈ -2)	2.13	3.59
-29	$s$ (-29 > -17)	$m$ (-29 ≈ -17)	24.31	16.69
-32	$w$ (-32 > -26)	$m$ (-32 < -29)	3.28	9.70

polytypes in vapour-phase grown ZnS) are both in disaccord with Rai's proposal. It should also be noted that Rai does not mention the fact that stacking faults have negative energies in  $2H$  in a wide temperature range. This fact is closely related to the rarity of occurrence of figure 1 from the Zhdanov symbol. Though Rai's hypothesis also deals adequately with the 'absence of the 1's', it contradicts a wide range of experimental facts mentioned above.

### Conclusions

The highest polytype identified in ZnS has 44 layers in its elementary stacking sequence (Table 1). Thus, the length of the Burgers vector of the generating screw dislocation of the crystal containing polytypes of this family is about 140 Å.

Both the 'direct method' and the 'elimination method' are reliable for polytype identification, the second being simpler and faster. Both are superior to the trial and error procedures used for polytype identification, as the latter do not seem to fulfil the criteria of reliability.

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## Structure du Pentafluorodibéryllate $\text{CsBe}_2\text{F}_5$

PAR Y. LE FUR ET S. ALÉONARD

Rayons X, C.N.R.S., Cedex 166, 38 Grenoble Gare, France

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The structure of  $\text{CsBe}_2\text{F}_5$  has been studied by X-ray and neutron diffraction. This pentafluorodiberyllate is cubic, space group  $P4_32$ . The unit cell, with  $a=7.936$  Å, contains four molecules of  $\text{CsBe}_2\text{F}_5$ . The structure is characterized by the complex succession of linked ten-membered rings of  $\text{BeF}_4$  tetrahedra lying parallel to the [110] and [111] directions. The other pentafluorodiberyllates of potassium, ammonium, rubidium, thallium and the high temperature form of  $\text{CsBe}_2\text{F}_5$  have a sheet structure.

### Introduction

Dans une précédente note (Le Fur, 1972), nous montrons que  $\text{TlBe}_2\text{F}_5$  de même que  $\text{RbBe}_2\text{F}_5$  (et probablement  $\text{NH}_4\text{Be}_2\text{F}_5$  et  $\text{KBe}_2\text{F}_5$ ) présentent une structure 'en couche', caractérisée par la présence de feuillets  $\text{Be}_4\text{F}_{10}$  perpendiculaires à un axe pseudo-hexagonal.

Les données cristallographiques indiquées par Breusov & Simanov (1959) en ce qui concerne la forme  $\beta$ - $\text{CsBe}_2\text{F}_5$ , stable à température ordinaire, semblent indiquer un type de structure différent. Aussi avons-nous repris l'étude de ce composé et nous montrerons qu'effectivement il ne possède pas une structure 'en couche'.