Acta Cryst. (1969). A**25**, 35

A Direct Method for the Determination of Polytype Structures.
II. Determination of a 66*R* Structure

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(*Received* 7 *October* 1968 *and in revised form* 5 *June* 1969)

A periodic polytype 66*R* was found to constitute part of a ZnS crystal. Oscillation photographs were taken with Cu $K\alpha$ radiation. A test was applied to these data showing that the crystal was better approximated by the assumption of a perfect crystal ($I \sim |F|$), than by that of a mosaic crystal ($I \sim |F|^2$).

The method described by Dornberger-Schiff and Farkas-Jahnke in part I is applied to the experimental data and the result discussed. The homometric pair of polytypes with Zhdanov symbols $(7753)_3$ and $(7735)_3$ gives a much better fit to the experimental data (traditional R value equal to 0·147) than any other polytype.

Introduction

In the first part of our contribution (Dornberger-Schiff & Farkas-Jahnke, 1970) the theoretical basis of a method for the direct determination of polytype structures of SiC- and ZnS-like polytypes from X-ray data was given, and the course of such a structure determination was demonstrated with the help of a hypothetical model. In this part we describe the application of this method to the determination of the stacking sequence in a real ZnS crystal.

Experimental

Fig. 1 shows the ZnS crystal under investigation. It is of irregular shape, and was grown from the vapour phase by a modified Frerichs-method (Kovács & Szabó, 1962). It was suspected that the clear region in the middle of the specimen which shows no streaks perpendicular to the *c* axis may be a region of one periodic polytype. This region has an extension of about 1 mm along the *c* axis of the crystal, occupying the whole cross-section.

X-ray oscillation diagrams with the *c* axis as oscillation axis were taken, with an X-ray tube (Cu-anticathode) with line focus and a collimator slit giving an X-ray beam of cross section 20 mm by 0·2 mm at the position of the crystal (Fig. 2). In order to test the uniformity of the stacking sequence along the total length of the region, we took a set of photographs with the same oscillation period, shifting the crystal parallel to the *c* axis by 0·1 mm after each exposure. The intensities of the reflexions were the same on each pattern, within experimental errors.

From the number and positions of the reflexions on the $02l$ row-line (orthohexagonally indexed) the polytype was found to have a periodicity of 66 layers in the **c** direction and to have a rhombohedral lattice (66*R*). (The rhombohedral character follows from the fact that reflexions with indices $k+l=3n\pm1$ are absent.)

The intensities of the reflexions on each oscillation pattern were obtained from the blackening measured by a single light path photometer with the help of intensity strips. In order to reduce the errors in $|S(k,l)|^2$,* the intensities of reflexions on the row-lines $02l$, $04l$, and $15l$ with l from -66 to $+66$ were measured. $|S(k,l)|^2$ values were calculated according to

$$|S(k,l)|^2 = |F(hkl)|^2/|F_0(hkl)|^2 \quad (16/\text{I})$$

[equation (16) of part I], where $F_0(hkl)$ denotes the structure factor of a hypothetical structure consisting only of one layer with Zn in 000 and S in $00z_S$ within the real unit cell. ($z_S \simeq 3/4M = 3/4 \,.\, 66$ in this case.) Mean values of $|S(kl)|^2$ which, according to equations (13) and (14) in part I, should be the same, were calculated. In this way it was hoped to reduce at least partly the influence of absorption which, because of the irregular shape of the crystal, could not be taken into account.

In spite of this it turned out that no polytype sequence was found by use of the method described in part I, which would be in agreement with the ψ values obtained from this set of $|S|^2$ values, unless frequent errors in ψ up to $|\psi_{\text{obs}} - \psi_{\text{calc}}| \simeq 2$, and some errors even >2 were allowed for. The best fitting polytype still gave a value of $R' = 0{\cdot}38$ for

$$R' = \frac{\Sigma\, \big||S_{\text{obs}}|^2 - |S_{\text{calc}}|^2\big|}{\Sigma\, |S_{\text{obs}}|^2} \quad (1)$$

and the sum of the squares of the differences in ψ was

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* For an explanation of the symbols used, see part I.

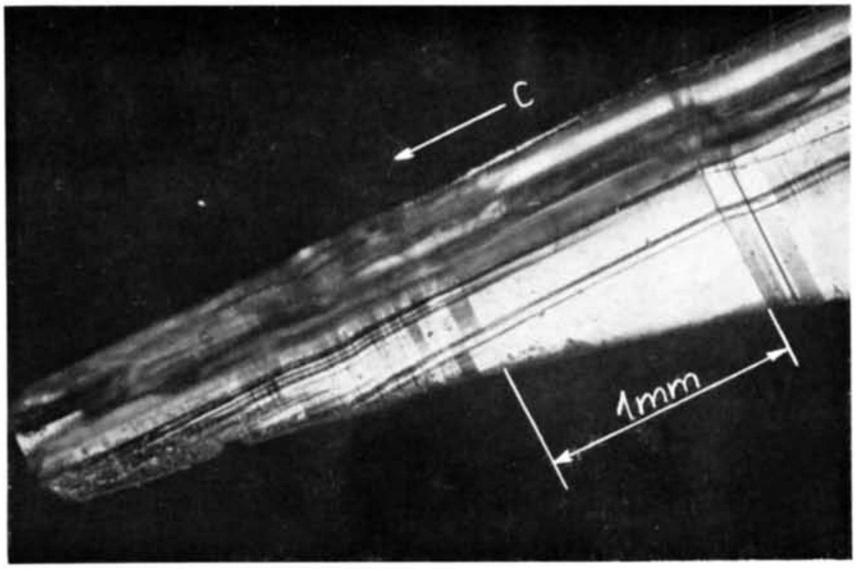

Fig. 1. The ZnS crystal investigated in polarized light the *c* axis is parallel to the arrow.

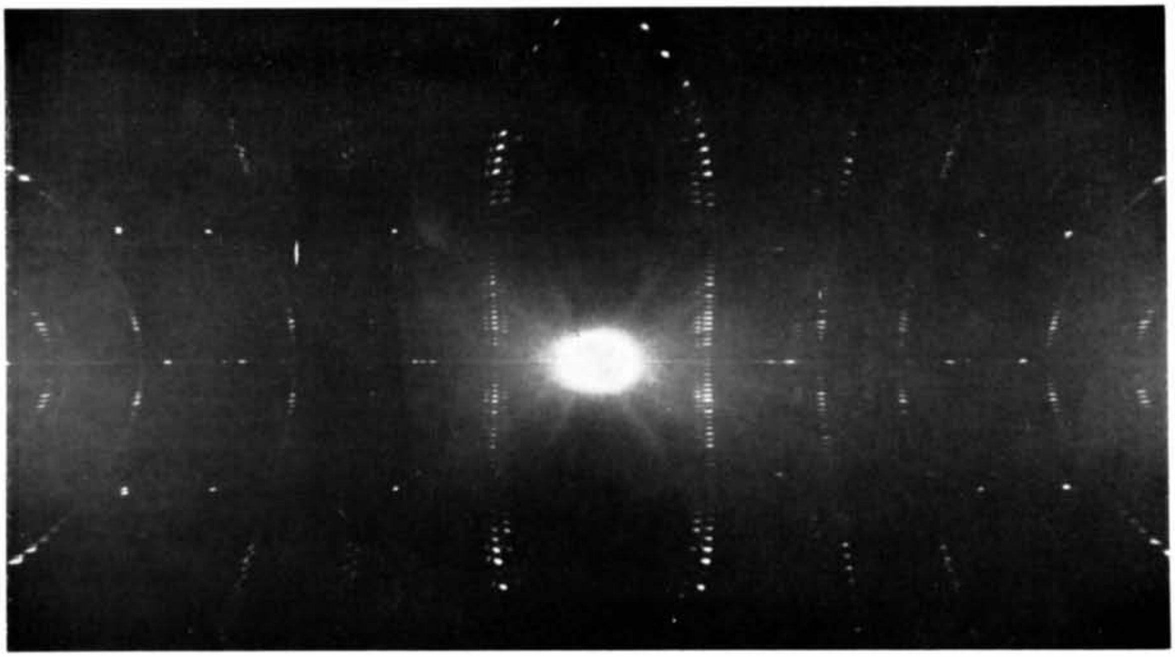

Fig. 2. Oscillation pattern from the part of the crystal marked on Fig. 1. Oscillation axis parallel to the *c* axis, Cu *K* radiation.

47·6, corresponding to a root-mean-square value of the differences in ψ of 1·2.

We then realized, as a result of a remark by the referee of part I, that the intensities in our case may be proportional to $|F|$ rather than to $|F|^2$.

To test which power of $|F|$ has to be taken as proportional to the intensities, sets of 4 intensity values corresponding to the same $|S|$ value were taken, one after the other, and the slope α of the straight line $y=\alpha x+K$ calculated, where

$$y=\log I+\log \sin 2\theta-\log (1+|\cos 2\theta|^{\delta})$$

and

$$x=\log |F_0|\,.$$

According to equation (34) of part I, the values α and δ ought to be $\simeq 1$, if the intensity is proportional to $|F|$, and $\simeq 2$, if it is proportional to $|F|^2$. This calculation was carried out for $\delta=1$ and for $\delta=2$ respectively, but the resulting slopes did not differ appreciably. For 4 different sets the α values obtained were 0·3, 0·7, 0·6 and 1·0 respectively. Thus α was assumed to be equal to 1.

From the $|S(kl)|^2$ values calculated with $\alpha=1$ a new set of $\psi(K,p)$ values was obtained, in the way described in part I; they were calculated from the corresponding π values according to

$$\psi(K,p)=\pi(m,p) \text{ for } m+p+K\equiv 0 \pmod 3\,, \qquad (2)$$

the $\pi(m,p)$ values being calculated from the $|S|^2$ values according to

$$\pi(m,p)=\frac{N}{3}\left[1+2\sum_{l=0}^{M-1}\frac{|S(1l)|^2}{M^2}\,.\cos 2\pi(m/3+lp/M)\right]. \qquad (18/\mathrm{I})$$

As has been shown in (viii/I), $\pi(0,2)$ must necessarily be even. Besides, according to (x/I, iii/I) and (vii/I), for $\beta=1$ (*i.e.* $|S(1,l)|\neq 0$ for $l=3n-1$)

$$-\pi(1,p)+\pi(1,N-p)\equiv p+N \pmod 3\,, \qquad (3)$$

or for $N=22$

$$-\pi(1,p)+\pi(1,N-p)\equiv p+1 \pmod 3\,. \qquad (4)$$

Thus, if we denote by π_0 the integral values chosen for π, and limit ourselves to pairs of values in agreement with (4) which lead to discrepancies

$$[\pi(1,p)-\pi_0(1,p)]^2+[\pi(1,N-p)-\pi_0(1,N-p)]^2<5$$

only those pairs of π_0 values listed in Table 2 need to be considered.

Table 1. *$\pi(m,p)$ values calculated from the observed intensities assuming $I\propto|F|$*

p \ m	-1	0	$+1$
1	12·37	−0·47	10·10
2	7·70	4·85	9·44
3	4·17	13·08	4·74
4	9·60	4·12	8·27
5	7·77	6·80	7·42
6	5·42	8·90	7·67
7	9·72	7·86	4·38
8	4·96	5·27	11·76
9	7·11	9·63	5·26
10	11·20	4·79	6·00
11	2·17	9·91	9·91

Table 2. *Sets of $\pi_0(m,p)$ and $\psi(K,p)$ values for $p=2,3,\ldots 5$, in accordance with the measured π values of Table* 1

	$\pi_0(m,p)$			$\psi(K,p)$		
p	m -1	0	$+1$	K 0	1	2
2	8	4	10	10	4	8
	7	6	9	9	6	7
3	4	14	4	14	4	4
	5	12	5	12	5	5
4	10	4	8	10	8	4
	8	5	9	8	9	5
5	7	6	9	9	6	7
	8	7	7	7	7	8
	6	8	8	8	8	6
	10	6	6	6	6	10

Determination of $[\gamma]_p$ values from the ψ values

As shown above, only the pair

$$\pi(1,2)=\psi(0,2)=10$$
$$\pi(1,20)=\pi(0,2)=\psi(1,2)=4$$

and the pair

$$\psi(0,2)=9$$
$$\psi(1,2)=6$$

need be considered; these two cases were treated in turn. We propose to describe the treatment of the first case in greater detail and then to report on the result of considering the second case.

For the first case it follows from Table 3(*a*) (part I) that

$$[0]_2=10\,,\ [1]_2=2\,,\ [2]_2=2\,,\ [3]_2=8\,.$$

For $p=3$ (using equations of type (*b*) of Table 3, part I)

$$[0]_3+[4]_3=10 \qquad [0]_3+[1]_3=10$$
$$[1]_3+[5]_3=2 \qquad [2]_3+[3]_3=2$$
$$[2]_3+[6]_3=2 \qquad [4]_3+[5]_3=2$$
$$[3]_3+[7]_3=8 \qquad [6]_3+[7]_3=8$$

From Table 3(*d*) and (*e*) (part I) it follows that $[1]_3=[4]_3>0$, and $[3]_3=[6]_3>0$.

Taking the sum of the rates of occurrence of numbers with reduced digital sum 0, 1, or 2, respectively, we obtain

$$\psi(0,3)=\ [0]_3+[7]_3 \tag{5}$$

$$\psi(1,3)=2[1]_3+[2]_3 \tag{6}$$

$$\psi(2,3)=2[3]_3+[5]_3\,. \tag{7}$$

The sets (14,4,4), (12,5,5) and (13,6,3) are the only sets of $\psi(K,3)$ in reasonable agreement with the π values obtained from the intensities (see Table 2) and the conditions discussed above.

For these three different sets of $\psi(K,3)$ values the discussion is summarized in Table 3. The $[\gamma]_3$ values are given which are in keeping with the set of $\psi(K,3)$ values indicated at the top of the column and with the condition given in the last column. Contradictions are indicated by a letter *c*. It follows that only the $\psi(K,3)$ values (14,4,4) do not lead to contradictions and the values of all $[\gamma]_3$ are uniquely determined as given in Table 5. From these values we obtain for the $[\gamma]_4$ the following relations:

$[0]_4+[8]_4=8$	$[0]_4+[1]_4=8$
$[1]_4+[9]_4=2$	$[2]_4+[3]_4=2$
$[2]_4+[10]_4=0$	$[4]_4+[5]_4=0$
$[3]_4+[11]_4=2$	$[6]_4+[7]_4=2$
$[4]_4+[12]_4=2$	$[8]_4+[9]_4=2$
$[5]_4+[13]_4=0$	$[10]_4+[11]_4=0$
$[6]_4+[14]_4=2$	$[12]_4+[13]_4=2$
$[7]_4+[15]_4=6$	$[14]_4+[15]_4=6$

Further, from Table 3(*e*) (part I) it follows that

$$[1]_4=[8]_4>0 \text{ and } [7]_4=[14]_4>0$$

and from the above relations:

$$[2]_4=[4]_4=[5]_4=[10]_4=[11]_4=[13]_4=0$$

and

$$[3]_4=2\,,\ [12]_4=2\,.$$

Using the values of $[\gamma]_4$ obtained already, the equations for the $\psi(K,4)$ values may be simplified:

$$\psi(0,4)=[0]_4+[7]_4+[11]_4+[13]_4+[14]_4=[0]_4+2[7]_4 \tag{8}$$

$$\psi(1,4)=[1]_4+[2]_4+[4]_4+[8]_4+[15]_4=2[1]_4+[15]_4 \tag{9}$$

$$\psi(2,4)=[3]_4+[5]_4+[6]_4+[9]_4+[10]_4+[12]_4 \\ =4+[6]_4+[9]_4\,. \tag{10}$$

For the $\psi(K,4)$ values the sets (10,8,4) and (8,9,5) should be discussed and this is summarized in Table 4.

Thus two sets of $[\gamma]_4$ values are in reasonable agreement with the $\psi(K,4)$ values obtained from the experimental data and from the $[\gamma]_p$ values, for $p\le 3$ deduced earlier.

In a similar way 4 sets of $[\gamma]_5$ values were deduced, being in agreement with the three sets of $\psi(K,5)$ values (9,6,7), (8,7,6) and (6,6,10). The $[\gamma]_p$ values thus obtained for $p=1,2,\ldots 5$ are summarized in Table 5. The two sets of $[\gamma]_4$ values are called I and II respectively and the four sets of $[\gamma]_5$ values are denoted *a* to *d*. In Table 6 the $\psi(K,p)$ values in agreement with the different cases are given.

All possibilities starting from the $\psi(K,2)$ set (9,6,7) with discrepancies <5 were also tested. The number

Table 3. *Determination of the $[\gamma]_3$ values in agreement with the three sets of $\psi(K,3)$ values given at the top of the columns and the conditions given in the last column*

$\psi(0,3)$	14		12		13	
$\psi(1,3)$	4		5		3	
$\psi(2,3)$	4		5		6	
$[\gamma]_3$						
$[1]_3$	1 or 2		1 or 2		1	equation (7) and $[1]_3>0$
$[2]_3$	2	0	3	1	1	equation (7)
$[3]_3$	*c**	2	*c*	1	1	$[2]_3+[3]_3=2$ and $[3]_3>0$
$[5]_3$	–	0	–	*c*	*c*	$[1]_3+[5]_3=2$ and equation (8)

* *c* indicates contradiction.

Table 4. *Determination of the $[\gamma]_4$ values in agreement with the two sets of $\psi(K,4)$ values given at the top of the columns and the conditions given in the last column*

$\psi(0,4)$	10	8		
$\psi(1,4)$	8	9		
$\psi(2,4)$	4	5		
$[\gamma]_4$				
$[6]_4$	0	0 or 1		equation (11)
$[9]_4$	0	1	0	equation (11)
$[7]_4$	2	2	1	$[6]_4+[7]_4=2$
$[1]_4$	2	1	2	$[1]_4+[9]_4=2$
$[0]_4$	6	*c**	6	$[0]_4+[1]_4=8$ and equation (9)
$[15]_4$	4	–	5	$[7]_4+[15]_4=6$ and equation (10)

* *c* indicates contradiction.

of these was considerably greater, and for those with the smallest values of

$$\sum_{p} \{[\pi(1,p)-\pi_0(1,p)]^2+[\pi(1,N-p)-\pi_0(1,N-p)]^2\}$$

the R' values were calculated. The best-fitting polytype still had an R' value of 0·5 which is still bigger than some of the discarded polytypes with $\psi(K,2)=(10,4,8)$.

The close correlation between the sums of discrepancies and R values justified those cases with large sums not being further pursued.

During the deduction of possible $[\gamma]_p$ sets we arrived at the following points:

(*a*) The values for $[\gamma]_{p-1}$ alone suffice for a unique determination of the $[\gamma]_p$ values. A trivial example is the determination of the $[\gamma]_2$ values from the $[\gamma]_1$ values. Non-trivial examples were actually found.

(*b*) The values for $[\gamma]_{p-1}$ and of $\psi(K,p)$ suffice for a unique determination of the $[\gamma]_p$. An example is the deduction of the $[\gamma]_3$ summarized in Table 3.

(*c*) More than one set of values $[\gamma]_p$ is compatible with the values for $[\gamma]_{p-1}$ and for $\psi(K,p)$. In this case all possibilities have to be pursued.

(*d*) No set of values $[\gamma]_p$ is compatible with the values for $[\gamma]_{p-1}$ and $\psi(K,p)$. Then either another set $\psi(K,p)$ must be chosen, or another set of $[\gamma]_{p-1}$ values.

Determination of polytypes in keeping with a given set of $[\gamma]_5$ values

Theoretically, this procedure for obtaining rates of occurrence $(\alpha_1,\alpha_2,\ldots \alpha_p)$ of longer and longer sequences could be continued until the length p of sequences reaches the value N. In practice, another mode of procedure is to be preferred, especially if the ψ values are known only within certain limits of error, therefore making it necessary to discuss several possibilities for any given p.

In part I we described how possible cycles could be built up from the knowledge of the $[\alpha_1\ldots\alpha_p]$ values.

Table 5. *Sets of* $[\gamma]_p$ *values for* $p=1,2,\ldots 5$

					Case	I	I*a*	I*b*	I*c*	II	II*d*
K	γ	p	1	2	3	4	5	5	5	4	5
0	0		12	10	8	6	4	5	4	6	4
1	1		10	2	2	2	2	1	2	2	2
1	2			2	0	0	0	0	0	0	0
2	3			8	2	2	2	2	2	2	2
1	4				2	0	0	0	0	0	0
2	5				0	0	0	0	0	0	0
2	6				2	0	0	0	0	1	1
0	7				6	2	2	2	2	1	1
1	8					2	0	0	0	2	0
2	9					0	0	0	0	0	0
2	10					0	0	0	0	0	0
0	11					0	0	0	0	0	0
2	12					2	0	0	0	2	1
0	13					0	0	0	0	0	0
0	14					2	1	0	0	1	0
1	15					4	1	2	2	5	1
1	16						2	1	2		2
2	17						0	1	0		0
2	18						0	0	0		0
0	19						0	0	0		0
2	20						0	0	0		0
0	21						0	0	0		0
0	22						0	0	0		0
1	23						0	0	0		0
2	24						2	2	2		2
0	25						0	0	0		0
0	26						0	0	0		0
1	27						0	0	0		0
0	28						2	2	2		1
1	29						0	0	0		0
1	30						1	2	2		1
2	31						3	2	2		4

Table 6. *Sets of* $\psi(K,p)$ *values corresponding to the sets of* $[\gamma]_p$ *values of Table* 5

Case				I	I*a*	I*b*	I*c*	II	II*d*
p	1	2	3	4	5	5	5	4	5
K									
0	12	10	14	10	9	9	8	8	6
1	10	4	4	8	6	6	8	9	6
2	0	8	4	4	7	7	6	5	10

We start from any arbitrary sequence $\alpha_1,\alpha_2\ldots\alpha_p$ with $[\alpha_1\alpha_2\ldots\alpha_p]>0$. It must necessarily be followed either by a sequence $\alpha_2,\alpha_3\ldots\alpha_p0$ or by a sequence $\alpha_2,\alpha_3\ldots\alpha_p1$. If one of the rates of occurrence $[\alpha_2\ldots\alpha_p0]$ or $[\alpha_2\ldots\alpha_p1]$ is equal to zero, then the next following sequence is uniquely determined. If both are $\neq 0$ then there are two possibilities; if p is sufficiently large, the number of sequences for which such ambiguities occur will not be very large.

Let us now describe this mode of procedure in terms of our decimal equivalent notation, γ. Let $\alpha_1\ldots\alpha_p$ correspond to a decimal number γ_0. If $\gamma_0<2^{p-1}$, then $\alpha_1=0$. Leaving this digit out, and shifting the sequence by one place to the left means multiplying γ_0 by a factor 2. Thus the two decimal equivalents which may follow γ_0 are $2\gamma_0$, and $2\gamma_0+1$. If, on the other hand $\gamma_0\geq 2^{p-1}$, then $\alpha_1=1$. Leaving this digit out and shifting the rest of the sequence one place to the left, means subtracting 2^{p-1} from γ_0 and multiplication by a factor 2. In this case the two decimal equivalents which may follow γ_0 are $2(\gamma_0-2^{p-1})$ and $2(\gamma_0-2^{p-1})+1$. If, therefore, $[\gamma_0]_p>0$, we may discuss the following cases:

	$[2\gamma']_p$	$[2\gamma'+1]_p$
I	0	0
II	0	+
III	+	0
IV	+	+

where $\gamma'=\gamma_0$ if $\gamma_0<2^{p-1}$ and $\gamma'=\gamma_0-2^{p-1}$, if $\gamma_0\geq 2^{p-1}$, and where '0' stands for equal to zero, and '+' for bigger than zero.

Case I would be in contradiction to the presupposed condition $[\gamma]_p>0$. In cases II and III the decimal equivalent of the sequence γ_1 following the sequence γ_0 is uniquely determined. For this sequence γ_1 we may again find out whether the sequence γ_2 following it is uniquely determined. In this way, we are led from γ_0 to γ_1 to $\gamma_2\ldots$ until either we arrive back at γ_0, or case IV occurs. In order to avoid using any sequence more often than is indicated by its rate of occurrence it is advisable to mark off any sequence as it is used. If we arrive back at γ_0 after N steps, the sequence of γ_ν obtained constitutes a solution to the problem. If, however, we arrive back at γ_0 after a smaller number of steps than N, then the set of γ_p values corresponds to two or more polytype structures with lengths of cycles $N_1,N_2\ldots$ where $\sum_j N_j$ is equal to N. Such sets of γ values thus do not constitute a solution to our problem, because the length N of the cyclic structure is known from the position of the X-ray reflexions.

We came across examples of this kind when trying to find a polytype in keeping with π values obtained under the assumption that the intensities are proportional to the $|F|^2$ values. Then we found that (among others) the sets of rates $[\gamma]_5$ given in Table 7 are in keeping with the $\psi(m,p)$ values for $p\leq 5$ (within given limits of error). Starting from $\gamma_0=4$ we obtain unambiguously the following series of γ_ν:

$$4\ 9\ 18\ (4)\,.$$

The last γ value, $\gamma_3=4$, is put in brackets to indicate that, because $[4]_5=1$, the decimal equivalent 4 has already been used for γ_0. Thus the series of γ_ν closes upon itself, and a closed cycle with $N_1=3$ results. Similarly, starting off from $\gamma_0'=13$ the closed cycle 13 27 22 (13) with $N_2=3$ results unambiguously. Thus the set of $[\gamma]_5$ values given in Table 5 is compatible only with a number of subcycles and cannot be the basis for the solution of the problem.

Table 7. *Set of* $[\gamma]_5$ *values leading to subcycles*

γ	$[\gamma]_5$	γ	$[\gamma]_5$
0	3	17	0
1	1	18	1
2	0	19	0
3	1	20	0
4	1	21	0
5	0	22	1
6	0	23	0
7	1	24	1
8	0	25	0
9	1	26	0
10	0	27	1
11	0	28	1
12	0	29	0
13	1		
14	0	30	1
15	1	31	5
16	1		

If at a certain γ_ν case IV occurs, *i.e.* the sequence $\gamma_{\nu+1}$ is not uniquely determined, we note the two possibilities for $\gamma_{\nu+1}$ and take each of them as a starting point for building up another part of the cycle.

As an example we take the sets of $[\gamma]_5$ values obtained from $|S|^2$ values after deciding to take $\alpha=1$, and given in Table 5, marked (*a*). Starting from the γ_0 value 1, the series (A) of γ_ν values is obtained

(A) $1, 3, 7, \binom{14}{15}$

where $\binom{14}{15}$ denotes the first ambiguity. Series (A) occurs twice. Starting from $\gamma_0''=14$ and $\gamma_0'=15$ we obtain the series (B) and (C) respectively

(B) $14, 28, 24, 16, \binom{0}{1}$ occurring once

(C) $15\ \binom{30}{31}$ occurring once.

Similarly

(D) $30, 28, 24, 16, \binom{0}{1}$ occurring once

and

(E) $31\ \binom{30}{31}$ occurring 3 times and

(F) $0\ \binom{0}{1}$ occurring 4 times.

Because (A) occurs twice, it is more convenient to start with (B), say. (B) may either be followed directly by (A) or by (A) after (F), or after up to 4 repeats of (F). After (A) only (C) can follow, because (B) (occurring only once) has already been used. (C) may either be followed directly by (D) or by (D) after (E) or up to 3 repeats of (E).

After (D) (A) may follow (of which only one has been used) either directly, or after up to 4 repeats of (F). Thus we obtain the following compound sequence: B F^{δ} A C E^{ε} D F^{χ} A with $0 \leq \delta \leq 4$, $0 \leq \varepsilon \leq 3$, $0 \leq \chi \leq 4$. The last sequence (A) may then be followed by the first sequence (B) to close the cycle.

All sequences are used up in one cycle if $\delta + \chi = 4$ and $\varepsilon = 3$. Thus 5 cases have to be discussed, corresponding to $\delta = 0, 1 \ldots 4$.

The deduction of a binary corresponding to a given succession of γ_p values is very simple indeed. Even γ values correspond to binaries whose last digit is 0 and odd γ values to binaries whose last digit is 1. We obtain the binary of the whole cycle of N digits if we put a digit '0' for any even, and a digit '1' for any odd, γ_p value.

In this way the following cyclic binaries and Zhdanov symbols are obtained:

for $\delta = 0$	000011111110000000111	$(4783)_3$
$\delta = 1$	000001111111000000111	$(5773)_3$
$\delta = 2$	000000111111100000111	$(6763)_3$
$\delta = 3$	000000011111110000111	$(7753)_3$
$\delta = 4$	000000001111111000111	$(8743)_3$

Those for $\delta = 0$ and $\delta = 4$ and those for $\delta = 1$ and $\delta = 3$ respectively, are homometric structures: there is no possibility of distinguishing between them by diffraction experiments, because they would lead to exactly the same $|F(hkl)|^2$ values (see Appendix to part I).

In a similar way other sets of $[\gamma]_5$ values which led to ψ values in reasonable agreement with those obtained from the intensities were used to obtain other possible polytype sequences. Tests were carried out for all of them to see whether the $\psi(K,p)$ values for $p > 5$ were also in agreement with the corresponding experimental ψ values and the homometric polytype pair with $\delta = 1$ and 3 was found to give the best all round fit. $|S|^2$ values were then also calculated for these polytypes and the R' values according to (1).

The Zhdanov symbols for some of the polytypes obtained in this way and the corresponding

$$\sum_{p=1}^{N} |\pi(1,p)_{\text{obs}} - \pi(1,p)_{\text{calc}}|^2 = \Sigma\, |\Delta\pi|^2$$

are given in Table 8, together with the R' values calculated according to (1).

Table 8. *Values of R' [calculated according to equation (1)] and of $\Sigma\,|\Delta\pi|^2$ for polytypes in keeping with the $[\gamma]_5$ values deduced*

Zhdanov symbol of polytype	R'	$\Sigma\,\lvert\Delta\pi\rvert^2$
$(4783)_3$; $(8743)_3$	0·39	33
$(5773)_3$; $(7753)_3$	0·176	18
$(6763)_3$	0·52	147
$(7339)_3$; $(9337)_3$	0·565	135

For all other polytypes (not given in this Table) the R' and $\Sigma\,|\Delta\pi|^2$ values were also larger than 0·35 and 30 respectively. As Table 8 shows, only the homometric pair $(5773)_3$ $(3775)_3$ gave the favourable R' and $\Sigma\,|\Delta\pi|^2$ values. Therefore one polytype of this pair has to be regarded as the polytype present in our crystal.

The conventional 'reliability index',

$$R = \Sigma\, \big||F_{\text{obs}}| - |F_{\text{calc}}|\big| / \Sigma\, |F_{\text{obs}}|\,,$$

calculated for this case was found to be equal to 0·147.

In Table 9 the $|S(k,l)|$ values obtained from the measured intensities are given alongside those calculated for the polytypes $(5773)_3$ and $(7834)_3$. As to be expected from the values of R, R' and $\Sigma\,|\Delta\pi|^2$, the polytype $(5773)_3$ shows very good agreement between calculated and observed values. Although for the polytype $(7834)_3$ there exist serious discrepancies, especially for the reflexions with l equal to 8, 38, 50 and 59, these discrepancies seem to us far less aggravating than those tolerated in some earlier polytype determinations carried out by trial and error or by the method described by Tokonami (1966). We may note that the reflexion with $l = 23$ (the strongest observed reflexion) also has the largest calculated $|S|$ value and that the six reflexions with $l = 20$, 23, 29, 41, 44 and 47, which are the only reflexions with observed $|S|$ values larger than 6·10, are the only reflexions with calculated $|S|$ values larger than 5·60.

Table 9. *$|S(1,l)|$ values obtained from observed intensities and calculated for two essentially different polytypes in order of decreasing $|S|_{\text{obs}}$ values*

l	$\lvert S\rvert_{\text{obs}}$	$\lvert S\rvert_{(7735)_3}$	$\lvert S\rvert_{(7834)_3}$
23	10·54	10·54	11·00
29	8·51	6·53	5·70
41	8·39	7·51	9·38
20	7·49	6·80	7·31
47	7·02	7·32	6·03
44	6·21	5·77	6·02
38	6·07	5·11	0·87
17	4·44	3·78	3·81
14	3·42	3·02	2·64
35	3·38	2·15	3·65
56	2·77	2·65	0·38
32	2·65	2·74	5·17
53	2·49	2·19	1·71
8	1·61	1·55	0·78
11	1·58	1·64	3·02
26	1·45	1·70	2·13
2	1·12	1·22	1·44
50	0·95	1·22	4·84
5	0·63	0·89	0·35
62	0·55	0·89	0·53
65	0·45	0·84	0·76
59	0·17	0·45	2·31

If, in our case, we had obtained the polytype $(7834)_3$ by trial and error methods but had failed to obtain the polytype $(7753)_3$, we might well have been content with the agreement achieved and taken this polytype as having been determined. Experience with this polytype has thus strengthened our opinion that:

(i) intensities measured quantitatively and with sufficient accuracy are needed for a reliable determination of a polytype unless its period is quite small (systematic errors have to be allowed for);

(ii) a method is needed which gives all polytypes in reasonable agreement with the observed data.

We believe that our method meets this requirement. These views are confirmed by Gomes de Mesquita (1969) who successfully applied our method to the determination of a 120R polytype of SiC. In this case the R value obtained was 6·6% and was further reduced to 5·9% by allowing for secondary extinction. For comparison, the observed and calculated intensities obtained by Tokonami (1966) in his test example of a 96R polytype are given in Table 10, with the intensities again arranged in order of decreasing observed values.

Table 10. *Intensity values observed and calculated by* Tokonami (1966) *for his test example, arranged in order of decreasing* I_{obs} *values*

l	I_{obs}	I_{calc}	l	I_{obs}	I_{calc}
22	128	22	28	16	8
31	96	60	82	16	6
79	96	72	88	16	1

Table 10 (*cont.*)

l	I_{obs}	I_{calc}	l	I_{obs}	I_{calc}
46	64	31	40	8	11
64	64	289	43	8	0
49	64	256	67	8	0·6
34	64	126	73	8	0·4
37	64	36	85	8	0
16	64	27	91	8	1
70	64	0	1	0	0·1
10	32	5	4	0	0·2
25	32	19	52	0	12
67	32	4	55	0	0·9
19	32	21	58	0	0·1
7	16	2	61	0	0·7
13	16	11	94	0	0·7

We would like to express our thanks to Mr P. Kovács and Mr E. Lendvay who kindly supplied the crystals used in our experiments.

References

DORNBERGER-SCHIFF, K. & FARKAS-JAHNKE, M. (1970). *Acta Cryst.* A**26**, 24.
GOMES DE MESQUITA, A. H. (1969). To be published.
KOVÁCS, P. & SZABÓ, J. (1962). *Acta Phys. Hung.* **14**, 131.
TOKONAMI, M. (1966). *Mineral. J. Japan*, **4**, 401.

Acta Cryst. (1970). A**26**, 41

Complex Lattice Potentials in Electron Diffraction Calculated for a Number of Crystals

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(*Received* 29 *January* 1969)

Structure potentials, V_g, and absorption potentials for 100 keV-electrons are given in tabulated form for almost all monatomic crystals with elements $Z=3$ to 90 and for a number of crystals of the rock-salt type. The absorption potentials are given in the form of the Fourier coefficients C^i_{0g} of the Yoshioka imaginary potential for excitation of crystal electrons and excitation of phonons at the temperatures 20, 93 and 293°K. All computations are based on numerical Hartree–Fock–Slater atomic radial functions by Herman & Skillman (*Atomic Structure Calculations*. Englewood Cliffs: Prentice Hall, 1963). The calculations show that the ratio $C^i_{0g}(\text{el})/V_g$, where $C^i_{0g}(\text{el})$ refers to excitation of single crystal electrons, lies between 0·005 and 0·012 for the lower reflexion vectors g and practically all Z. In contrast to this the ratio $C^i_{0g}(\text{phonon})/V_g$ is much larger and increases about linearly with Z, for a given g.

1. Introduction

The scattering of fast electrons in crystals can be understood in terms of a complex periodic potential by which the electrons are supposed to be diffracted. Its real part consists of the electrical potential of the crystal atoms plus their dynamical polarization induced by the passing external electrons, while the imaginary part represents the inelastic scattering suffered by these electrons during passage (Yoshioka, 1957).

Calculations of the imaginary crystal potentials have been done on the basis of the Thomas–Fermi atomic model for MgO (Yoshioka, 1957) and later, for Li, Be, Ne, Al and Cu by use of Hartree–Fock atomic functions (Whelan, 1956*a*). In these two papers the excitation of the tightly bound crystal electrons was dealt with. This mechanism, however, proved to be too weak to fully account for the experimental anomalous absorption effects, and it was soon found that the thermal diffuse scattering (phonon excitation) is the