below, the italicized value giving the frequency:

	Experiment					
	1	2	3	5	7	16
Maxima:	*11*	*1*	*31*	*6*	*3*	*7*
Minima:	*16*	*27*	*10*	*3*	*1*	*2*

The distribution of the maxima and minima differ significantly from the expected uniform distribution. That experiment 3 accounts for most of the maximum values and experiment 2 for the minimum values is further indication that the *modal* group still contains some systematic errors which are correlated with structural parameters.*

The low values found for the least-squares derived standard deviations are to be associated with the known systematic errors present in some, if not all, of the experiments. The formulas used to derive the internal standard deviations assume that only random errors are present in the observations. As this condition is increasingly violated, the apparent standard deviation, which is only a measure of the precision of fit between the model and the observations, becomes correspondingly unreliable as a measure of accuracy.

Conclusion

Systematic differences among structure factors from different experiments and different crystals are manifested in systematically different parameters when the data are subjected to least-squares refinement. Even if the parameters of an acceptable theoretical model refine without divergence, the derived parameters may be in error by several times the estimated standard deviations calculated from the goodness-of-fit achieved as a result of the least-squares refinement. Standard deviations on bond lengths and thermal parameters obtained in crystal structure refinements are realistic only if (1) there are no errors in the theoretical model and (2) if there are no systematic errors in the experiment. It is hoped that by projects such as this, the validity of (2) may be assessed so that we may direct our attention toward (1) – which includes all the questions of physical and chemical interest.

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* The large number of extrema for experiment 3 is partially influenced by the fact that, because of the smaller number of reflections, it has larger internally estimated standard deviations. On this basis, the number of extrema should be 3 to 4 times as great as for other members of the modal group.

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A Direct Method for the Determination of Polytype Structures. I. Theoretical Basis

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A direct method for the determination of polytype structures of SiC, ZnS and similar substances from X-ray data is described. It is based on the values of a Patterson-like function (the 'Pattersonian') which only depends on the stacking of the translationally equivalent layers of the structure. The way of obtaining the Pattersonian function from the experimental intensities is described and an algorithm given by which the sequence of layers may be deduced. This sequence is conveniently characterized by the sequence of the digits of a binary number. The influence of experimental errors in the intensities on the possibilities of determining the real sequence is discussed.

Introduction

It has been found recently that optical and electronic data of semiconducting substances, especially of ZnS and SiC, depend on the polytype present (Kholuyanov, 1964; Gobrecht, Nelkowski, Baars & Brandt, 1965; Hamilton, Patrick & Choyke, 1965; Patrick, 1965; Patrick, Choyke & Hamilton, 1965; Brafman & Steinberger, 1966; Farkas-Jahnke, Schanda & Kovacs, 1966). Quite a number of polytypes of both materials have been known to exist for a considerable time (see *e.g.* Verma & Krishna, 1966), and the process of discovering new polytypes and of determining the sequence of layers of particular polytypes does not seem to have come to an end as yet (see *e.g.* Krishna & Verma, 1964; Farkas-Jahnke, 1965; Gomes de Mesquita, 1965; Krishna & Verma, 1966; Daniels, 1966; Tokonami, 1966; Brafman, Alexander & Steinberger, 1967; Mardix, Alexander, Brafman & Steinberger, 1967; Mardix, Brafman & Steinberger, 1967; Mardix & Brafman, 1968).

Trial and error or semi-direct methods have so far been used to determine these structures. For polytypes with large periods, the sequence of layers is difficult, if not impossible, to determine unambiguously by these methods, because of the multitude of periodic sequences of the same period. Therefore it seemed to us worthwhile to work out a direct method for the determination of polytype structures, suitable for large periods as well; a short account of this has already been given (Farkas-Jahnke, 1966).

Only after the material for this paper had been prepared did we first notice the method of unravelling a periodic vector set proposed by Tokonami & Hosoya (1965) and Tokonami (1966). The theoretical basis of their method seems to have much in common with ours. The actual working of our method seems, however, very different from that proposed by these authors so that in our opinion a description of our own method is justified.

In this paper we consider only periodic structures of substances like ZnS or SiC which may be described as follows. The structure is built of translationally equivalent layers, *i.e.* any layer, L_p, may be brought into coincidence with any other layer, L_0, by a suitable translation. Each of these layers, taken by itself, possesses hexagonal symmetry, its structure being known. Consecutive layers, L_p, L_{p+1}, may be related by either of two translational vectors (referred to orthohexagonal basic vectors $\mathbf{a},\mathbf{b},\mathbf{c}$), the so called stacking vectors:

$$\mathbf{t}_p^0 = -\mathbf{b}/3 + \mathbf{c} \,.\, p/M \,, \quad \mathbf{t}_p^1 = \mathbf{b}/3 + \mathbf{c} \,.\, p/M \,, \tag{1}$$

where M is the number of layers per period, in the direction of the hexagonal axis of the single layer. Thus we may write the stacking vector in the form

$$\mathbf{t}_p = -(-1)^{\alpha_p}\mathbf{b}/3 + \mathbf{c} \,.\, p/M \,, \tag{2}$$

where α_p is the superscript 0 or 1 of $\mathbf{t}_p$ in equation (1). A generalization of these concepts is possible but outside the scope of this paper.

Either of these vectors leads to geometrically equivalent pairs of consecutive layers, *i.e.* the polytypes of such a substance belong to a family of OD-structures (Dornberger-Schiff, 1964, 1966). In the case of ZnS (or SiC) the coordinates of the atoms of L_0 may be given (in terms of orthohexagonal axes) as

$$\begin{array}{ll} \text{Zn (or Si) in } 0,0,0; & \tfrac{1}{2},\tfrac{1}{2},0 \\ \text{S (or C) in } 0,0,z_0/M; & \tfrac{1}{2},\tfrac{1}{2},z_0/M \,, \end{array} \tag{3}$$

with $z_0 \simeq \frac{3}{4}$, independent of the polytype. The structure factor $F(hkl)$ of such a polytype is then equal to

$$F(hkl) = F_0(hkl) \,.\, S(kl) \tag{4}$$

where $F_0(hkl)$ is the structure factor of a hypothetical structure which possesses the same periodicity as the real structure but contains only the atoms of layer L_0 within the unit cell, and where $S(kl)$ depends only on the stacking sequence of the layers.

A direct method for the determination of the polytype stacking sequence will thus have to give an algorithm by which the sequence of layers, *i.e.* the sequence of stacking vectors, may be obtained from the values $|S(kl)|^2$ which in their turn, may be deduced from the $|F_{\text{obs}}(hkl)|^2$ values (obtained from the experimental intensities) and the $|F_0(hkl)|^2$ values calculated for the known structure of the single layer (see below).

Any sequence of $p+1$ successive layers L_q to L_{q+p} may be characterized by a binary number with the superscripts of the stacking vectors $\alpha_q,\alpha_{q+1}\ldots\alpha_{q+p-1}$ in their proper sequence as its digits. In the following this characterization will be called the binary symbol of the sequence. The binary symbol of a periodic polytype (period N) would be a binary number, periodic after N digits, one period of which may be obtained from Hägg's or Frank-Nabarro's notation by substituting 0 for '$-$' or 'Δ', and 1 for '$+$' or '∇', respectively.

The binary symbol may be obtained from the classical *ABC* notation, by writing '0' for each pair *BA*, *CB*, or *AC*, and '1' for each pair *AB*, *BC*, or *CA*. It may be obtained from the Zhdanov symbol $\beta_1\beta_2\beta_3\ldots\beta_{2s}$ in the following way: first there are β_1 digits 1, then follow β_2 digits 0, and so on, and β_{2s-1} digits 1, and finally β_{2s} digits 0.

Such a binary notation has various advantages; each binary can be characterized by a very short abbreviated symbol; namely its decimal value. Thus complete sets of sequences of a given length can easily be written down. Furthermore, binaries are easily handled by computers and an algorithm using binaries may thus be fairly easily adapted to a computer program.

A (primitive) trigonal or hexagonal polytype is thus characterized by a periodic binary of M digits per period, and within a period the number of digits 1 differs by a multiple of 3 from the number of digits 0.

A binary characterizing a rhombohedral polytype repeats after $M/3$ digits, and within a period the difference between the number of digits 1 and the number of digits 0 within such a repeat is not a multiple of 3.

We shall in the following denote by N the number of digits per repeat, and by β the residue modulo 3 of the difference between the number of digits 1 and the number of digits 0 per repeat of N digits. Then:

for hexagonal and trigonal polytypes, $N=M$ and $\beta=0$;
for rhombohedral polytypes, $N=M/3$
in reverse description $\beta=1$
in obverse description $\beta=-1$.

Almost all the discussion below is applicable not only to polytypes of substances isomorphous with SiC but also to other polytype structures like graphite or closest packing of spheres, as long as they consist of translationally equivalent layers, with consecutive layers related by one of the stacking vectors given by (1). The only exception is the discussion of symmetry. Other hexagonal polytype structures like CdI_2 have to be considered as OD-structures consisting of two different kinds of layers and have to be treated in a different way.

Characteristic features of X-ray diagrams and of the $|S(kl)|^2$

As has previously been pointed out (Dornberger-Schiff, 1964) reflexions on X-ray diagrams of this kind of polytype belong to two classes:

'Family reflexions' with $k\equiv 0$ *(mod* 3*)*. Their intensities (per layer) are the same for the whole family of polytypes of a substance, including, *e.g.* in the case of ZnS, the simple sphalerite and wurtzite structures.

Reflexions with $k\equiv\pm 1$ *(mod* 3*)*. The position of these reflexions depends on the number of layers per period, on the value of β, and their intensities on the stacking sequence; only these reflexions can therefore be used to determine the polytype.

The electron density distribution $\varrho(x,y,z)$ of the structure is periodic and, within an orthohexagonal unit cell, may be regarded as the sum of the electron density distributions $\varrho_p(x,y,z)$ of the layers L_p (with $p=0,1,\ldots M-1$)

$$\varrho(x,y,z)=\sum_{p=0}^{M-1}\varrho_p(x,y,z)\,. \tag{5}$$

ϱ_p may be obtained from ϱ_0 by successive shifts according to the stacking vectors (2). This results in a total shift $\mathbf{T}_p$.

$$\mathbf{T}_p=\sum_{j=0}^{p-1}\mathbf{t}_j=-\sum_{j=0}^{p-1}(-1)^{\alpha_j}\mathbf{b}/3+p\mathbf{c}/M. \tag{6}$$

Therefore

$$\varrho_p(x,y,z)=\varrho_0(x,y-m_p/3,z-p/M)\,, \tag{7}$$

if we define

$$m_p\equiv-\sum_{j=0}^{p-1}(-1)^{\alpha_j}\ (\mathrm{mod}\ 3)\,, \tag{8}$$

and thus we may take m_p as equal to 0 or to ± 1. As can easily be seen, the following relations hold:

$$m_0=0\,, \tag{9}$$
$$m_{p+1}-m_p\equiv-(-1)^{\alpha_p}\ (\mathrm{mod}\ 3)\,.$$

The set of m_p values depends on the stacking sequence and, in its turn, characterizes this sequence.

The structure factor, $F(hkl)$, of the structure is equal to

$$F(hkl)=V\,.\iiint\varrho(xyz)\exp 2\pi i(hx+ky+lz)\,.\,dxdydz=F_0(hkl)\,.\,S(k,l)\,. \tag{10}$$

$F_0(hkl)$ denotes the structure factor of a structure with the same unit cell as the real structure having the electron density distribution $\varrho_0(x,y,z)$ of only a single layer; V is the volume of the unit cell:

$$F_0(hkl)=V\,.\iiint_v\varrho_0(xyz)\exp 2\pi i(hx+ky+lz)\,.\,dxdydz\,. \tag{11}$$

$S(h,k,l)=S(k,l)$ is the Fourier transform of a periodic function $\sigma(x,y,z)$ with the same unit cell, characterizing the stacking of the layers: it is different from zero only at the points corresponding to the vectors $\mathbf{T}_p$ [see equation (6)]; *i.e.* it possesses point scatterers at the coordinates of the Zn (or Si) atoms. It may be thought of as the sum of Dirac functions, so that the real electron density ϱ is equal to the convolution of ϱ_0 with σ (see the Appendix).

$S(k,l)$ is equal to

$$S(k,l)=\sum_{p=0}^{M-1}\exp 2\pi i(km_p/3+lp/M)\,. \tag{12}$$

Equation (12) leads to the following relations:

$$S(kl)=S(k'l'),\ \text{if}\ k\equiv k'\ (\mathrm{mod}\ 3)\ \text{and}\ l\equiv l'\ (\mathrm{mod}\ M)\,; \tag{13}$$

$$S(\bar{k}\bar{l})=\widetilde{S(kl)}\,; \tag{14}$$

$$S(3k',l)=0\quad\text{if}\ l\not\equiv 0\ (\mathrm{mod}\ M)\,, \tag{15}$$
$$S(3k',l)=M\ \text{if}\ l\equiv 0\ (\mathrm{mod}\ M)\,.$$

These S values were introduced by Tokonami (1966) and called 'unitary structure factors' $U(l)$. Their absolute square values may be obtained from the observed intensities according to

$$|S(kl)|^2=|F_{\mathrm{obs}}(hkl)|^2/|F_0(hkl)|^2\,, \tag{16}$$

which follows from (4).

From the $|S(kl)|^2$ values we shall calculate values of a function $\pi(m,p)$ which, by definition, can take on only non-negative integral values. These are related to the values v_j introduced by Tokonami.

The procedure described is, however, different from that suggested by Tokonami. In contrast to his procedure, its application to trigonal and hexagonal polytypes is as easy as its application to rhombohedral polytypes and can even be done without a computer. This will be clearly demonstrated when our method is applied to a practical example in part II of this paper (Farkas-Jahnke & Dornberger-Schiff, 1970). In spite of some similarity between our lines of thought and those of Tokonami, his statement – that accurate values of the intensities are not necessary for the determination of a polytype structure – seems to us open to doubt, unless the period is quite small. His 'rationalization procedure' led in the test example quoted by him (Tokonami, 1966) to a polytype in far worse agreement with the observed intensities than we need expect, even if errors in the observed intensities are allowed for. Particularly striking is the fact that for $l=70$ the calculated intensity is equal to zero, whereas the observed intensity is among the strongest (one half of the intensity of the strongest reflexion) (see part II).

The Pattersonian function π(m,p)

Let $\pi(m,p)$ be defined as the number of pairs of layers (generally not successive) L_r, L_{r+p} with differences $m_{r+p}-m_r \equiv m \pmod 3$ where $0 \le r < N$. It thus corresponds to a type of Patterson function and the name 'Pattersonian function' has been suggested for it. Its values are equal to the values of a Patterson function at the coordinates $v=m/3$ and $w=p/M$ of the structure $\sigma(x,y,z)$ consisting of M point scatterers per unit cell distributed at positions characterized by the set of vectors $\mathbf{T}_p$ of the polytype $(0 \le p < M)$.

The Pattersonian may be obtained from the $|S(kl)|^2$ values:

$$\pi(m,p)=\frac{N}{3M^2}\sum_{k=-1}^{1}\sum_{l=0}^{M-1}|S(k,l)|^2 \times \exp -2\pi i(km/3+lp/M) \,. \quad (17)$$

Using (14) and (15), this may be transformed into

$$\pi(m,p)=\frac{N}{3M^2}\left[\sum_{l=0}^{M-1}|S(0,l)|^2 \exp -2\pi ilp/M \right. \quad (18)$$

$$+\sum_{l=0}^{M-1}|S(1,l)|^2 \exp -2\pi i(m/3+lp/M)$$

$$\left.+\sum_{l=0}^{M-1}|S(\bar{1},l)|^2 \exp -2\pi i(-m/3+lp/M)\right]$$

$$=\frac{N}{3}+\frac{2N}{3M^2}\sum_{l=0}^{M-1}|S(1,l)|^2 \cos 2\pi(m/3+lp/M)$$

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

The scaling of the $|F_{\rm obs}|$ has to be done so that

$$\pi(0,0)=N, \text{ and thus } \sum_{l=0}^{M-1}|S(1,l)|^2=M^2 \,. \quad (19)$$

The following properties of the $\pi(m,p)$ result either from its definition or from the relations deduced above:

(i) $\pi(m,p)$ can have only integral non-negative values;

(ii) $\pi(m,p)$ is periodic in p:

$$\pi(m,p)=\pi(m+\beta,p+N)$$

where $\beta=0$ and $N=M$ for hexagonal or primitive trigonal polytypes and $\beta=1$ or -1 and $N=M/3$ for rhombohedral polytypes.

$\beta=1$ and $\beta=-1$ refer to the reverse and the obverse setting of the rhombohedral lattice, respectively. Accordingly it suffices to consider the $\pi(m,p)$ values for $0 \le p < N$;

(iii) $\pi(0,p)+\pi(1,p)+\pi(\bar{1},p)=N$ for any p;

(iv) $\pi(0,0)=N$ and thus $\pi(1,0)=\pi(\bar{1},0)=0$;

(v) $\pi(0,1)=0$;

(vi) The value of $\pi(\bar{1},1)$ denotes the number of vectors $\mathbf{t}_j^{(0)}$ amongst N consecutive vectors $\mathbf{t}_j$, and $\pi(1,1)$ the corresponding number of vectors $\mathbf{t}_j^{(1)}$. Thus

$$\pi(1,1)-\pi(-1,1)=\beta \,.$$

According to (ii) and equation (17):

$$\begin{aligned}
\text{(vii)}\ \pi(0,p)&=\pi(0,3N-p)=\pi(\beta,N-p)=\pi(\beta,N+p)\\
&=\pi(-\beta,2N+p)=\pi(-\beta,2N-p)\\
\pi(1,p)&=\pi(2\beta-1,2N-p)=\pi(-1,3N-p)\\
&=\pi(1+\beta,N+p)=\pi(1-\beta,2N+p)=\pi(\beta-1,N-p)\\
\pi(-1,p)&=\pi(1+\beta,N-p)=\pi(1-\beta,2N-p)\\
&=\pi(\beta-1,N+p)=\pi(2\beta-1,2N+p)=\pi(1,3N-p);
\end{aligned}$$

thus from (vii) and (v)

$$\pi(\beta,N-1)=0 \,.$$

From these relations and from (ii) and (iii) it follows that it suffices to consider $\pi(m,p)$ for $0<p<N$ and one particular value of m, provided m is chosen to make $m+\beta \not\equiv 0 \pmod 3$.

(viii) $\pi(0,2)$ denotes the sum of the number of pairs $\mathbf{t}_q^{(0)}\mathbf{t}_{q+1}^{(1)}$ and of the number of pairs $\mathbf{t}_q^{(1)}\mathbf{t}_{q+1}^{(0)}$ for $0 \le q < N$, and as these numbers are necessarily equal, $\pi(0,2)$ is even. Thus $\pi(0,2)$ is equal to the number of figures in the Zhdanov symbol, except for the trivial cubic case of the Zhdanov symbol (∞).

(ix) For symmetrical X-ray diagrams, *i.e.* if

$$|S(k,l)|^2=|S(k,\bar{l})|^2 \text{ for all pairs } (k,l) \,,$$

it follows that $\pi(1,p)=\pi(-1,p)$, and the binary contains as many digits 0 as digits 1. Thus N is even, and because of (iii), $\pi(0,p)$ is even for all values p.

$$\text{(x)}\ \pi(1,p)-\pi(-1,p)\equiv p[\pi(1,1)-\pi(-1,1)] \pmod 3$$

or

$$\pi(1,p)-\pi(-1,p)\equiv p\,.\,\beta \pmod 3 \,.$$

This relation* follows from the following consideration: $\pi(m,p)$ denotes the number of vectors $\mathbf{T}_p$ with component $m/3$ in the $\mathbf{b}$ direction. The total shift in the $\mathbf{b}$ direction produced by the N vectors $\mathbf{T}_p$ is equal

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* We are indebted to the referee for drawing our attention to this relation.

to $\frac{1}{3} . \sum_{m=-1}^{1} m . \pi(m,p)$. Each of these vectors is composed of p stacking vectors $\mathbf{t}_j$ and each of these stacking vectors $\mathbf{t}_j$ occurs in p vectors $\mathbf{T}_p$. Therefore the total shift of the N vectors $\mathbf{T}_p$ is congruent mod 3 to p times the shift produced by a set of N stacking vectors $\mathbf{t}_j$:

$$\sum_{m=-1}^{1} m . \pi(m,p) \equiv p . \sum_{m=-1}^{1} m . \pi(m,1) \pmod 3$$

or

$$\pi(1,p)-\pi(-1,p)\equiv p[\pi(1,1)-\pi(-1,1)] \pmod 3$$

and according to (vi)

$$\pi(1,p)-\pi(-1,p)\equiv p . \beta \pmod 3 .$$

Relation between the Pattersonian and the rate of occurrence of different sequences within a cycle of a given polytype

$\pi(m,p)$ gives, according to definition, the number of pairs of layers L_q, L_{q+p}, which are p steps apart and for which

$$m_{q+p}-m_q\equiv m \pmod 3 \tag{20}$$

holds, within one cycle, *i.e.* for N consecutive values

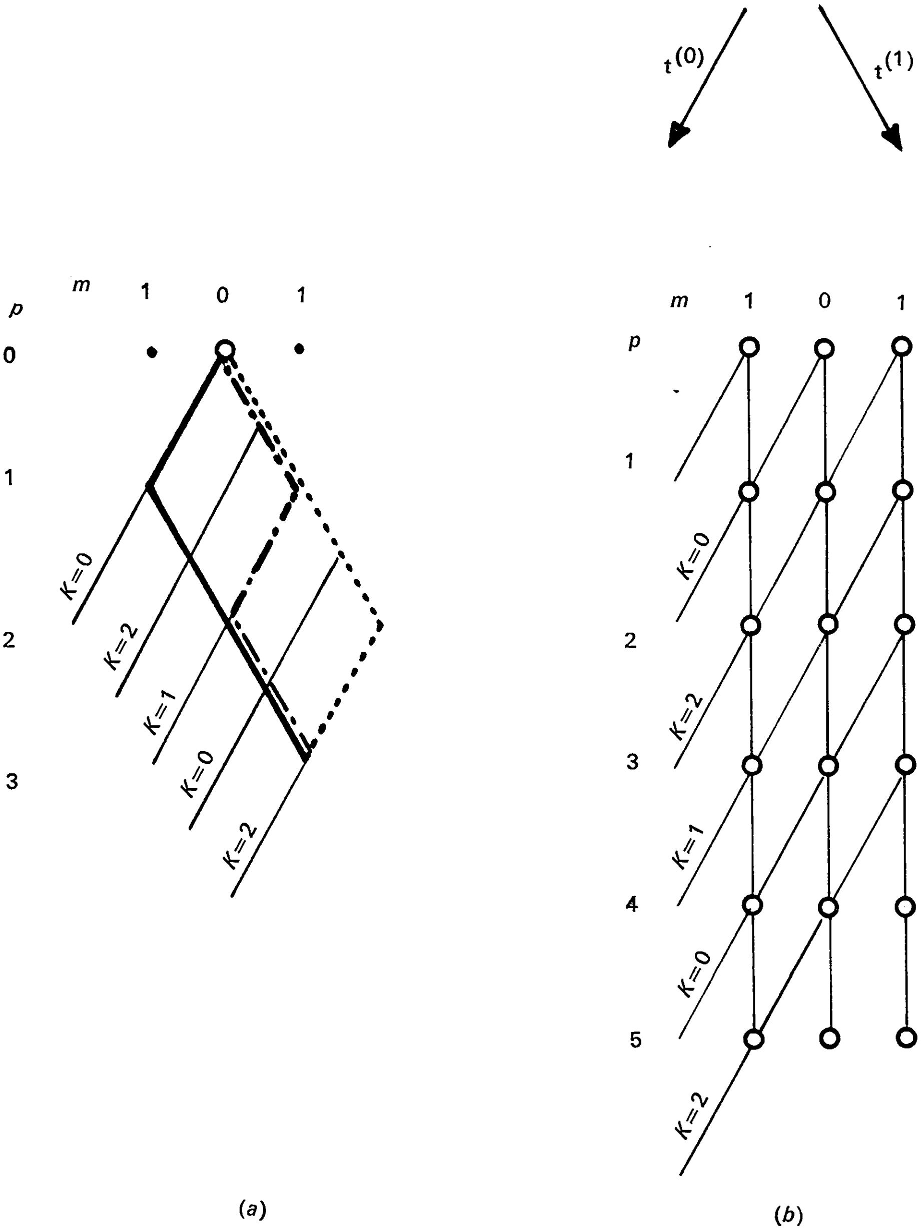

Fig. 1. Relation between the position (m,p) of a vector peak and the reduced digital sum K, of a sequence contributing to this peak. (*a*) the sequences contributing to the peak $\pi(1,3)$: ——— 011, –·–·– 101, -------- 110. (*b*) The positions of vector peaks characterized by m,p and K.

of q. According to equation (8)

$$m \equiv - \sum_{j=q}^{q+p-1} (-1)^{\alpha_j} \pmod 3 \tag{21}$$

for any pair of layers contributing to $\pi(m,p)$. Let us now consider the binary consisting of the digits $\alpha_q, \alpha_{q+1}, \ldots \alpha_{q+p-1}$, characterizing the stacking of the layers from L_q to L_{q+p}. If K' denotes the digital sum of the binary, *i.e.* the number of digits 1, then it follows from (20) that

$$m \equiv K' - (p - K') \pmod 3 .$$

The same relation holds for the 'reduced digital sum' $K \equiv K' \pmod 3$, which is taken as 0, 1, or 2.

The number $\pi(m,p)$ of pairs of layers p steps apart and shifted relative to one another by $m/3$ in the **b** direction is thus equal to the number $\psi(K,p)$ of sequences of p digits with reduced digital sum K, within a period of the periodic binary, where

$$m \equiv 2K - p \pmod 3 \tag{22}$$

or

$$m + p + K \equiv 0 \pmod 3 .$$

The suggested procedure for the structure determination of a polytype starts from the Pattersonian distribution calculated from the observed intensities. From this distribution ψ values are deduced. The subsequent procedure will be described below.

Example of a direct determination of a polytype

The mode of procedure for the direct structure determination of a polytype is best explained by applying it to a theoretical example. The $\pi(m,p)$ and $\psi(K,p)$ values of a hypothetical $27R$ polytype are given in Table 1. The structure is necessarily periodic after 9 layers, and because of the trivial centre of symmetry of $\pi(m,p)$, it is sufficient to give the Table up to $p=4$. In the following the binary symbol in square brackets $[\alpha_1, \alpha_2 \ldots \alpha_p]$ will represent the number of times the particular sequence denoted by the binary symbol $\alpha_1, \alpha_2, \ldots \alpha_p$ occurs within a cycle of the polytype, *i.e.* starting from N consecutive layers L_q (the rate of occurrence of the sequence). Because binaries with more than a few digits are rather clumsy to handle we shall, as a kind of shorthand, replace them by their decimal equivalent γ and indicate the number of digits of the binary by a subscript. Thus for example $[4]_3$ stands for [100], and $[4]_5$ for [00100].

Table 1. *Values of the Pattersonian function $\pi(m,p)$ and of $\psi(K,p)$ for a theoretical example 27 R*

$\pi(m,p)$

p \ m	$\bar{1}$	0	1
0	0	9	0
1	4	0	5
2	3	4	2
3	2	2	5
4	4	3	2

$\psi(K,p)$

p \ K	0	1	2
1	4	5	0
2	2	4	3
3	2	2	5
4	4	2	3

According to the first line of Table 1 there are four digits 0 and five digits 1 within a cycle, *i.e.*

$$[0]=4 \quad \text{or} \quad [0]_1=4$$
$$[1]=5 \quad \text{or} \quad [1]_1=5 .$$

Each digit 0 is followed either by a digit 0 or by a digit 1, *i.e.*

$$[00]+[01]=4 \quad \text{or} \quad [0]_2+[1]_2=4 , \tag{23}$$

and it is also preceded by either 0 or 1:

$$[00]+[10]=4 \quad \text{or} \quad [0]_2+[2]_2=4 . \tag{24}$$

Similar statements hold for the digits 1:

$$[10]+[11]=5 \quad \text{or} \quad [2]_2+[3]_2=5 \tag{25}$$

$$[01]+[11]=5 \quad \text{or} \quad [1]_2+[3]_2=5 . \tag{26}$$

Moreover, $\psi(0,2)$ gives the rate of occurrence of sequences [00] because this is the only sequence of length 2 with reduced digital sum zero, *i.e.* for which $K \equiv 0 \pmod 3$. Thus from Table 1:

$$[00]=2 \quad \text{or} \quad [0]_2=2 . \tag{27}$$

From equations (23) to (27) the rates for the other sequences of length 2 may be deduced:

$$\begin{aligned} [01]&=2 \quad \text{or} \quad [1]_2=2 \\ [10]&=2 \quad \text{or} \quad [2]_2=2 \\ [11]&=3 \quad \text{or} \quad [3]_2=3 . \end{aligned} \tag{28}$$

These values are in keeping with the values of $\psi(1,2)$ and $\psi(2,2)$ given in Table 1. To keep track of all the rates of occurrence of sequences deduced, they are summarized in Table 2, each sequence being characterized by its decimal equivalent. Using a similar argument, we obtain equations for the rates of the sequences of length 3 from those of length 2. Thus *e.g.* from (27):

$$[000]+[100]=2 \quad \text{or} \quad [0]+[4]=2 \tag{29}$$

and

$$[000]+[001]=2 \quad \text{or} \quad [0]+[1]=2 . \tag{30}$$

Moreover from Table 1:

$$[100]+[010]+[001]=2 \quad \text{or} \quad [4]+[2]+[1]=2 \tag{31}$$

$$[000]+[111]=2 \quad \text{or} \quad [0]+[7]=2 . \tag{32}$$

In this way the values for the rates of the sequences of length 3 listed in Table 2 are obtained.

From these values we proceed to $p=4$. By a similar argument each of these values gives two equations (partly identical). Besides from $[000]=1$ it follows that $[0000]=0$ by indirect proof: a sequence 0000 contains 2 sequences 000 and thus cannot be present, if $[000]=1$. Similarly, $[1111]=0$ follows from $[111]=1$. Without making further use of ψ values we obtain the rates listed in Table 2 under $p=4$.

In these deductions full use has to be made of the non-negative integral character of these rates.

Table 2. *Rates of occurrence* $[\gamma]_p$ *of binary sequences of length p with decimal equivalent* γ *for the polytype* $27R_{\text{th}}$

The reduced digital sum K is also given.

K	γ	p 1	2	3	4
0	0	4	2	1	0
1	1	5	2	1	1
1	2		2	0	0
2	3		3	2	1
1	4			1	0
2	5			1	0
2	6			2	1
0	7			1	1
1	8				1
2	9				0
2	10				0
0	11				1
2	12				1
0	13				1
0	14				1
1	15				0

The values obtained are again in keeping with the values in Table 1. From the different sequences of length four, only nine are present in the polytype, each occurring exactly once within a cycle. We may now proceed by building up the sequence of the whole cycle, at each step testing whether there are one or two ways of continuing the sequence. Starting *e.g.* with 1100 we obtain uniquely:

$$\begin{array}{l} 1100 \\ 1000 \\ 0001 \\ 0011 \\ \hline 1100011 \end{array}$$

For the next step there are two possibilities; but then for each of these the continuation is again fully determined until 9 digits (*i.e.* a period) are full. It is easy to verify that in each case the 9 sequences of 4 digits occur as determined:

Table 3. *List of some terms and some relations in binary and in decimal equivalent notation*

	Terms	Binary	Decimal equivalent
	Symbol of a sequence of length p	$\alpha_1\alpha_2\alpha_3\cdots\alpha_p$ with $\alpha_j=0$ or 1	γ_p
	Rate of occurrence of such a sequence	$[\alpha_1\alpha_2\alpha_3\cdots\alpha_p]$	$[\gamma]_p$
(*a*)	$\psi(0,1)$ $\psi(1,1)$ $\psi(0,2)$ $\psi(1,2)$ $\psi(2,2)$	$[0]$ $[1]$ $[00]$ $[01]+[10]=2\,.\,[01]$ $[11]$	$[0]_1$ $[1]_1$ $[0]_2$ $[1]_2+[2]_2=2\,.\,[1]_2$ $[3]_2$
Relations			
(*b*)		$[\alpha_1\alpha_2\cdots\alpha_p]=[\alpha_1\alpha_2\cdots\alpha_p0]+[\alpha_1\alpha_2\cdots\alpha_p1]$ $[\alpha_1\alpha_2\cdots\alpha_p]=[0\alpha_1\alpha_2\cdots\alpha_p]+[1\alpha_1\alpha_2\cdots\alpha_p]$	$[\gamma]_p=[2\gamma]_{p+1}+[2\gamma+1]_{p+1}$ $[\gamma]_p=[\gamma]_{p+1}+[2^p+\gamma]_{p+1}$
(*c*)		If $p>1$ and $[\underbrace{00\cdots0}_{p-1\text{digits}}]>0$ it follows that $[\underbrace{00\cdots0}_{p\text{ digits}}]<[\underbrace{00\cdots0}_{p-1\text{ digits}}]$ If $p>1$ and $[\underbrace{11\cdots1}_{p-1\text{ digits}}]>0$ it follows that $[\underbrace{11\cdots1}_{p\text{ digits}}]<[\underbrace{11\cdots1}_{p-1\text{digits}}]$	If $p>1$ and $[0]_{p-1}>0$ it follows that $[0]_p<[0]_{p-1}$ If $p>1$ and $[2^{p-1}-1]_{p-1}>0$ it follows that $[2^p-1]_p<[2^{p-1}-1]_{p-1}$
(*d*)		$[\underbrace{00\cdots0}_{p-1\text{ digits}}1]=[1\underbrace{00\cdots0}_{p-1\text{ digits}}]$ $[\underbrace{11\cdots1}_{p-1\text{ digits}}0]=[0\underbrace{11\cdots1}_{p-1\text{ digits}}]$ If $p>1$ and $[\underbrace{00\cdots0}_{p-1\text{ digits}}]>0$ it follows that $[\underbrace{00\cdots0}_{p-1\text{ digits}}1]=[1\underbrace{00\cdots0}_{p-1\text{ digits}}]>0$	$[1]_p=[2^{p-1}]_p$ $[2^p-2]_p=[2^{p-1}-1]_p$ If $p>1$ and $[0]_{p-1}>0$ it follows that $[1]_p=[2^{p-1}]_p>0$
(*e*)		If $p>1$ and $[\underbrace{11\cdots1}_{p-1\text{ digits}}]>0$ it follows that $[\underbrace{11\cdots1}_{p-1\text{ digits}}0]=[0\underbrace{11\cdots1}_{p-1\text{ digits}}]>0$	If $p>1$ and $[2^{p-1}-1]_{p-1}>0$ it follows that $[2^p-2]_p=[2^{p-1}-1]_p$

$$\begin{array}{r} 1100011 \\ 0110 \\ 1101 \\ \hline 110001101 \end{array} \qquad \begin{array}{r} 1100011 \\ 0111 \\ 1110 \\ \hline 110001110 \end{array}$$

These two sequences are closely related: one is the reversal of the other. As one can easily prove, both are in agreement with the ψ values of Table 1 of which actually only a part has been used. They constitute a homometric pair. (For a discussion of homometric pairs of polytypes of this kind, see Appendix). Their Zhdanov symbols are $(3321)_3$ and $(3312)_3$ respectively.

General procedure for the direct determination of a polytype

Following the procedure used in our example we may now formulate relations to be used in the general procedure. In Table 3, the various relations are given in binary notation, and in parallel with it, in decimal equivalent notation. The length p of the sequence is indicated by a subscript to the decimal equivalent where this is necessary to make it unambiguous.

Relations (*b*) denote that each sequence occurring within a period of our periodic binary is preceded (and followed) either by a digit 0 or 1. Relations (*c*) are concerned with the rates of occurrence of sequences consisting solely of digits 0 or of digits 1, respectively. It is sufficient to prove the relations for sequences of length p and $p-1$ consisting solely of digits 0 (decimal equivalent 0_p and 0_{p-1}). These sequences must occur within sequences of the type $1\underbrace{00\ldots0}_{q}1$ [decimal equivalent $(2^{q+1}+1)_{q+2}$] for $q \geq p-1$. The rates of these sequences are $[0]_p = q-p+1$ and $[0]_{p-1} = q-p+2$. Thus $[0]_p < [0]_{p-1}$ for every single sequence $(2^{q+1}+1)_{q+2}$, and thus also for the sums of the corresponding rates for all these sequences.

Relation (*d*) follows from (*b*): specifying $\alpha_j = \alpha_{j+1} = \ldots = \alpha_{j+p} = 0$ we obtain

$$[\underbrace{0\ldots0}_{p\text{ digits}}] = [\underbrace{0\ldots0}_{p+1}] + [\underbrace{0\ldots01}_{p}]$$

$$[\underbrace{0\ldots0}_{p\text{ digits}}] = [\underbrace{0\ldots0}_{p+1}] + [\underbrace{10\ldots0}_{p}]$$

thus

$$[\underbrace{0\ldots01}_{p\text{ digits}}] = [\underbrace{10\ldots0}_{p\text{ digits}}]$$

and in a similar way the relation with 0 and 1 interchanged.

For part of relation (*a*) we made use of $[01]=[10]$ which is a special case of (*d*).

The relations given in Table 3 may now be used for the following general procedure. Starting with the values for $p=2$ given by (*a*), the rates for sequences of length $p+1$ are deduced from those for length p using (*b*) and (*c*) and the ψ values, as shown in the example discussed above. This has to be continued until a sufficient number of sequences occurs with the rate zero. This should be the case for $p=N/2$ at the latest. Then, starting from any one sequence (length p), this sequence is continued by a sequence having as digits number 1 to $p-1$, the digits number 2 to p of the former sequence. If this continuation is ambiguous, both possibilities have to be discussed. In this way a closed cycle of binary digits is obtained (or several such cycles). Care has to be taken that each sequence is included in the cycle at its proper rate. In some cases closed cycles of less than N digits result. These cases have to be discarded. Any solution arrived at in this way has to be tested for consistency with ψ values of higher p.

If at a certain stage p, a unique determination of the rates is not possible, a sum of rates according to (*b*) or corresponding to a low ψ value is taken, and the cases compatible with this sum discussed one after the other. Thus if for example $[A]+[B]=2$, there are three cases to be discussed: $[A]$ may be equal to 0, 1 or 2. Then one of the following situations may arise:

(i) in one or more cases to be discussed we are led at a later stage to results contradictory to some of the relations (*a*) to (*c*) or to the ψ values. Such cases have to be discarded;

(ii) more than one of the cases discussed is in keeping with relations (*a*) to (*c*) and the ψ values. They may either constitute homometric polytypes, or different descriptions of the same polytype.

All binary cycles compatible with the set of ψ values should be tested by calculating $|S_{\text{calc}}|^2$ values and discrepancy factors, or by applying a similar test.

After the polytype sequence has been determined, the space group of the particular polytype structure follows. The fact that our method does not presuppose a knowledge of the space group is of importance because, in the case of the polytypes, the symmetry of the diffraction pattern does not allow the unambiguous distinction of hexagonal from trigonal polytypes (see Appendix.

In some cases the determination of the polytype may be shortened considerably. If, for example, $\psi(1,2)=2$, the binary symbol of the polytype has the following form: $11\ldots100\ldots0$, *i.e.* $M-q$ digits 1 followed by q digits 0. The number q is equal to $\psi(0,1)$. Thus no further work is needed if $\psi(1,2)=2$ and $\psi(0,1)$ is known.

Even in the general case the deduction of the polytype (and its homometric mates, if any) from correct ψ values takes only a day or two, working without a computer, and dealing with polytypes with N between 20 and 40.

On the determination of π- or ψ-values from experimental intensity data

As we have seen, a given set of correct integral non-negative ψ values allows us, by the method described, to obtain the real polytype structure or the real structure with all its homometric mates. If experimental errors lead to ψ values which may differ from the true ψ values by 1 or 2, it is still possible to apply our method and obtain *all* polytype structures compatible with the ψ values within their limits of error. This is done by discussing various sets of ψ values. Our experience shows that the number of cases to be discussed rises sharply with increasing errors, and that errors within about ± 2 at the most, and within ± 1 on average, are about the limit of what can still be handled by hand with a great amount of labour. We believe that even if a computer were used, the limits could not be extended much further. Besides, for wider limits of error, the number of compatible polytype structures will probably be so large that the result of such a determination would be of little interest. This is not due to the special method employed to obtain all polytypes compatible with the experimental data, but it is a property of the polytype structures themselves. If this has not become obvious to date, it is due to the fact that previously methods to obtain *all* compatible polytypes have not been applied, and that the calculation of structure factors for all polytype structures of a given length could not be carried out for N values of the order of magnitude considered here.

It follows from these considerations that the accuracy of the experimental data is important. In our opinion, the practice of indicating the intensities only as *vs*, *s*, *m*, *w*, *vw*, *a*, or of giving them only in big steps without proper corrections, is to be deplored. We wish to make a plea against this practice and for intensity measurements as accurate as possible, and on as many *hkl* reflexions as possible.

Then reflexions which, according to equations (13) and (14) ought to give the same $|S(k,l)|$ values may be used to obtain $|S|$ values less affected by absorption and other experimental errors than those obtained from one or two reflexions only.

As has been pointed out to us* it may be that the observed intensities are proportional to the $|F|$ values rather than to the $|F|^2$ values (Darwin, 1914). Generally speaking, the intensity is equal to

$$I(hkl) = K|F(hkl)|^{\tau} \frac{1+|\cos 2\theta|^{\tau}}{\sin 2\theta} \qquad (33)$$

where K is a constant, θ is the Bragg angle of the reflexion and $\tau=1$ for a perfect, and $\tau=2$ for a mosaic, crystal (Darwin, 1914). In our case we may, according to (4), replace $|F(hkl)|$ by $|F_0(hkl)| \,.\, |S(hkl)|$, and consider reflexions which, according to (13) or (14) ought to have the same $|S|$ value. Then for such a set of reflexions

$$\log I + \log \sin 2\theta - \log (1+|\cos 2\theta|^{\tau}) = \tau \,.\, \log |F_0| + K' \qquad (34)$$

and this relation may be used to test whether τ is approximately equal to 1 or 2 in any practical case.

If $\tau=1$, then $\log I + \log \sin 2\theta - \log (1+|\cos 2\theta|)$ plotted against $\log |F_0|$ will – except for experimental errors – give points lying on a straight line of slope 1.

If $\tau \simeq 2$, then $\log I + \log \sin 2\theta - \log (1+\cos^2 2\theta)$ plotted against $\log |F_0|$ will – except for experimental errors – give points on a straight line of slope 2.

After a decision has been made concerning the proper value of τ, the values of $|F(hkl)|^2$ may be deduced from the intensities, according to (33). Mean values of $|F(hkl)|^2/|F_0(hkl)|^2$ of a set of reflexions corresponding to the same $|S|$ value will then give the desired $|S|^2$ values.

Another way of testing which τ is the correct one is based on the relation

$$\sum_{l=0}^{M-1} |S(1,l)|^2 = |S(00)|^2 \qquad (35)$$

which follows from (15) and (19). The two sides of equation (35) are calculated for the assumption $\tau=1$ and $\tau=2$ respectively, using the mean values obtained as described for the $|S(1,l)|^2$ and mean values of $|F(hkl)|^2/|F_0(hkl)|^2$ for triples (h,k,l) with

$$\begin{aligned} k &\equiv 0 \pmod 3 \\ h+k/3 &\equiv 0 \pmod 2 \\ \text{and} \qquad l &\equiv 0 \pmod N \end{aligned}$$

i.e. the family reflexions.

These tests applied to the practical example reported in part II led to a value of τ which is certainly not larger than 1. If a similar value of τ holds for polytypes which have been investigated by other workers in the field, this fact may have discouraged them from quoting numerical values for their observed intensities.

APPENDIX

We assumed that any polytype [electron density $\varrho(xyz)$] is composed of translationally equivalent layers [of electron density $\varrho_p(xyz)$] according to equation (5). Then $\varrho(xyz)$ may be obtained as the convolution of $\varrho_0(xyz)$ with a function $\sigma(xyz)$:

$$\varrho(xyz) = \iiint \sigma(x'y'z') \,.\, \varrho_0(x-x',y-y',z-z')dx'dy'dz' \qquad (A1)$$

σ possesses the same periodicity as the structure itself; the triple integral has to be taken over the volume of one unit cell. The function σ characterizes the sequence of layers in the polytype; it is different from zero only at the positions characterized by the vectors $\mathbf{T}_p$ [defined by equation (6)] and those related to them by the translational vectors resulting from the periodicity of the polytype. σ corresponds to a sum of Ewald's peak functions of content 1 (see *e.g.* Luis & Amoros, 1968, p.40).

The space group of the polytype, the symmetry of the diffraction pattern and the existence or non-exis-

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* We are indebted to the referee for drawing our attention to this possibility.

Table 4. *Symmetry of the electron density $\varrho(xyz)$ and of the functions $S(hkl)$, $|S(hkl)|^2$, $|F(hkl)|^2$ and $|F_{\rm an}(hkl)|^2$, depending on the space group of the function $\sigma(xyz)$ which characterizes the stacking sequence*

The symmetry of $\varrho_0(xyz)$ has been assumed as $P(6)mm$. Under the heading 'Zhdanov symbol, general' letters with or without indices are used to indicate numbers of the Zhdanov symbol, equal letters and indices in one particular symbol indicating equal numbers. The function $\sigma(xyz)$ corresponds to a pure close-packing of spheres, and letters without indices in the Zhdanov symbol correspond to numbers enclosed in parentheses in the description of stacked closest-packed layers in *International Tables for X-ray Crystallography* (1962). The existence of homometric pairs is indicated by +. The value of $[1]_1-[0]_1=\beta'\equiv\beta$ (mod 3) is also given.

$\sigma(xyz)$	$\varrho(xyz)$	$S(hkl)$	$\|S\|^2$	$\|F\|^2$	$\|F_{\rm an}\|^2$	Zhdanov symbol General	Zhadanov symbol Example	β'	Condition	Homo-metric pair
$P3m1$	$P3m1$	$3m1$	$\bar3m1$	$\bar3m1$	$3m1$	$a_1b_1a_2b_2\cdots a_rb_r$	1235 or 5321	$\Sigma a_j-\Sigma b_j$	$\beta'\equiv0$ (mod 3)	+
$R3m1$	$R3m1$	$3m1$	$\bar3m1$	$\bar3m1$	$3m1$	$(a_1b_1a_2b_2\cdots a_rb_r)_3$	1234 or 4321	$\Sigma a_j-\Sigma b_j$	$\beta'\not\equiv0$ (mod 3)	+
$P3m1$	$P3m1$	$\bar3m1$	$\bar3m1$	$\bar3m1$	$3m1$	$a_1b_1a_2b_2\cdots a_rb_rcb_ra_rb_{r-1}\cdots b_1a_1d$	23(5)32(6)	$2(\Sigma a_j-\Sigma b_j)+c-d$	$\beta'\equiv0$ (mod 3)	
						or $a_1b_1a_2b_2\cdots a_rca_rb_{r-1}a_{r-1}\cdots b_1a_1d$	123(5)321(8)	$2(\Sigma a_j-\Sigma b_j)-c-d$		
$R\bar3m1$	$R3m1$	$\bar3m1$	$\bar3m1$	$\bar3m1$	$3m1$	$(a_1b_1a_2b_2\cdots a_rb_rcb_ra_rb_{r-1}\cdots b_1a_1d)_3$	23(4)32(6)	$2(\Sigma a_j-\Sigma b_j)+c-d$	$\beta'\not\equiv0$ (mod 3)	
						or $(a_1b_1a_2b_2\cdots a_rca_rb_{r-1}a_{r-1}\cdots b_1a_1d)_3$	123(5)321(7)	$2(\Sigma a_j-\Sigma b_j)-c-d$		
$P\bar6m2$	$P3m1$	$\bar6m2$	$6/mmm$	$6/mmm$	$3m1$	$a_1a_2\cdots a_{r-1}a_ra_ra_{r-1}\cdots a_2a_1$	123|321	0	—	
$P6_3\,mc$	$P6_3mc$	$6/mmm$	$6/mmm$	$6/mmm$	$6mm$	$a_1a_2\cdots a_ra_1a_2\cdots a_r$	123 123 or 321 321	0	$r=2n+1$	+
$P6_3/mmc$	$P6_3mc$	$6/mmm$	$6/mmm$	$6/mmm$	$6mm$	$a_1a_2\cdots a_ra_ra_{r-1}\cdots a_1ba_1a_2\cdots a_ra_ra_{r-1}a_1b$	123|321(4)123|321(4)	0	—	
$F43m$	$F43m$	$43m$	$4/m3m$	$4/m3m$	$43m$	∞				

tence of a homometric mate to the polytype depend on the space group of the distribution σ, and the eight possibilities are summarized in Table 4. Each of these possibilities* corresponds to a characteristic sequence of figures in the Zhdanov symbol which is also given in Table 4.

From (A1) it follows that the space group of $\varrho(xyz)$, *i.e.* of the polytype, contains at least those symmetry elements which are common to the space groups of $\sigma(xyz)$ and $P6mm$, *i.e.* the space group of $\varrho_0(xyz)$. The point group of $S(hkl)$ corresponds to the space group of $\sigma(xyz)$, and the point group of $|S(hkl)|^2$ results from the latter through an addition of a centre of symmetry (if not yet present). Because

$$|F(hkl)|^2=|S(hkl)|^2\,.\,|F_0(hkl)|^2\,, \qquad \text{(A2)}$$

the point group of $|F|^2$ necessarily contains all symmetry elements common to the point group of $|S(hkl)|^2$ and to $6/mmm$, the point group of $|F_0|^2$.

Thus, if $\sigma(xyz)$ has the space group $P\bar6m2$, the point group of $|F|^2$, *i.e.* the symmetry of the diffraction pattern, is hexagonal although the point group of F is only trigonal, as is the polytype itself. One particular example of this has been found by Ramsdell & Kohn (1951) who noticed the fact without commenting on the general aspect.

Quite recently, Sadanaga & Takeda (1968) proposed the term 'diffraction enhancement of symmetry' for a similar difference between the symmetry of the diffraction pattern and of the structure, which they came across in mica structures. They discuss a class of structures consisting of different kinds of layers which they show to exhibit this effect. If this term is generally accepted, it certainly should be applied to those polytypes of ZnS-like structures whose $\sigma(xyz)$ has the space group $P\bar6m2$.

As has been shown in the main part of this paper, our method for the determination of the polytype makes use of the Bravais lattice ($\beta=0$ for primitive, $\beta=\pm1$ for a rhombohedral lattice), but not of the trigonal or hexagonal symmetry of the structure. Actually, in the case of a hexagonal diffraction pattern a knowledge of the trigonal or hexagonal symmetry, if available, could be made use of. This knowledge does not, however, seem necessary for the determination of a polytype. If, however, an attempt is made to find the correct polytype by calculating structure factors for the whole class of polytypes of a certain periodicity compatible with the observed symmetry of the diffraction pattern, one has to include this class of trigonal polytypes in those cases where hexagonal symmetry of the diffraction pattern has been observed, whereas they need not be considered if the observed symmetry is trigonal.

It might be useful to discuss what possibilities arise, if X-radiation is used of a wave length which is scat-

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* See *International Tables for X-ray Crystallography* (1959).

tered anomalously by atoms present in the structure. Then

$$F_{\mathrm{an}}(hkl)=F(hkl)+iF'(hkl)$$
$$=S(hkl)\,.\,[F_0(hkl)+iF_0'(hkl)]\,, \quad \text{(A3)}$$

where $F(hkl)$ is the Fourier transform of the real part of the (complex) scattering function $\varrho_{\mathrm{an}}(xyz)$, and $F'(hkl)$ is the Fourier transform of the imaginary part of $\varrho_{\mathrm{an}}(xyz)$, and $F_0(hkl)$ and $F_0'(hkl)$ have corresponding meanings.

$$|F_{\mathrm{an}}(hkl)|^2/|S(hkl)|^2=|F_0(hkl)|^2+|F_0'(hkl)^2$$
$$-i\,|F_0(hkl)\widehat{)F_0'(hkl}) - \widehat{F_0(hkl)}F_0'(hkl)|\,. \quad \text{(A4)}$$

If $F_0'(hkl)\neq 0$ this expression has no centre of symmetry. Thus the diffraction pattern obtained with anomalous scattering can have no higher symmetry than $F_0(hkl)$. By using anomalous scattering it would therefore be possible to distinguish between polytypes with hexagonal symmetry in the normal diffraction pattern but a structure of trigonal symmetry (*i.e.* showing diffraction enhancement of symmetry) on the one hand, and truly hexagonal polytypes on the other hand.

Anomalous scattering cannot, however, be used to determine the polytype structure *via* a determination of phases. This method presupposes a knowledge of the position of the anomalous scatterers within the unit cell and this knowledge is available only when the polytype is already known.

To any polytype with a space group of $\sigma(xyz)$ which contains a polar axis (*i.e.* $P3m1$, $R3m1$ and $P6_3mc$) there exists an essentially different polytype giving exactly the same diffraction diagram, *i.e.* there exists a structure homometric* to it. Let us consider two polytypes and distinguish functions referring to them by superscripts. If we choose the crystal axes so that

$$\varrho_0^{(1)}(xyz)=\varrho_0^{(2)}(xyz), \quad \text{(A5)}$$

then, if

$$\varrho^{(1)}(xyz)=\varrho^{(2)}(\bar{x}\bar{y}\bar{z}) \quad \text{(A6)}$$

and if $\varrho^{(1)}(xyz)$ has a polar axis, the two polytypes form a homometric pair, because

$$|F^{(2)}(hkl)|^2=|F_0^{(2)}(hkl)|^2|S^{(2)}(hkl)|^2$$
$$=|F_0^{(1)}(hkl)|^2|S^{(1)}(hkl)|^2=F^{(1)}(hkl)|^2. \quad \text{(A7)}$$

Some of the polytypes which have been stated to be uniquely determined possess homometric mates from whom they certainly could not have been distinguished. Thus for example from 28 polytypes reported upon and referred to in a series of papers by Alexander, Brafman, Mardix and Steinberger, exactly one half possess homometric mates.

Anomalous scattering cannot help in this case, either, because $F_{0an}^{(1)}=F_{0an}^{(2)}$ and thus the argument of (A7) holds for anomalous scattering as well.

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* For a definition and discussion of homometric structures see *e.g.* Lipson & Cochran (1953) p. 145, 167 ff.

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