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Determination of the Cyclicity of Polytypes

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The difference between the number of cyclic displacements and the number of anticyclic displacements of neighbouring layers within one unit cell of a polytype is uniquely determined by the stacking sequence. The *a priori* knowledge of this difference greatly helps in establishing the structure of the polytype. It is shown that the 'cyclicity' of a polytype, a quantity closely related to this difference and defined in this paper, can be found in a simple way from an appropriate oscillation photograph.

Introduction

Polytypes known so far are all related to close-packed structures belonging to one of the eight appropriate space groups (Verma & Krishna, 1966) and are thus conveniently described in terms of hexagonal unit cells (which may be centred).

The various polytypes of a given substance are characterized by the number, n, of layers crossing each unit cell (the order of the polytype) and by the stacking sequence of the layers.

The equivalent positions $\mathbf{r}_{pm}$ of an atom of type p within the unit cell are given by

$$\mathbf{r}_{pm}=\mathbf{r}_{p0}+\alpha_m\mathbf{a}_1+\beta_m\mathbf{a}_2+\frac{m}{n}\mathbf{c}\,, \qquad (1)$$
$$m=0,1,2,\ldots n-1,\ \alpha_0=\beta_0=0\,.$$

$\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$ are the primitive translations of the hexagonal unit cell.

The distribution of the atoms in each layer (including the values of the vectors $\mathbf{r}_{p0}$) as well as the interlayer distance $\frac{1}{n}\mathbf{c}$ is characteristic for a given substance and is very nearly the same for all polytypes of the same substance.

The pairs $(\alpha_m;\beta_m)$ which determine the lateral displacement of layer number m can have the values $(0;0)$, $(+\frac{1}{3};-\frac{1}{3})$ or $(-\frac{1}{3};+\frac{1}{3})$ (which are referred to as the '*A*', '*B*' and '*C*' position respectively in the classical *ABC* notation), with the additional requirement

$$(\alpha_m;\beta_m)\neq(\alpha_{m+1};\beta_{m+1})\,. \qquad (2)$$

The displacement vector between any two neighbouring layers can thus have only the value

$$\tfrac{1}{3}(\mathbf{a}_1-\mathbf{a}_2)+\frac{1}{n}\mathbf{c}\ \text{or}\ \tfrac{1}{3}(\mathbf{a}_2-\mathbf{a}_1)+\frac{1}{n}\mathbf{c}$$

(for 'cyclic' or 'anticyclic' displacement respectively).

After ascertaining the order n of a certain polytype by standard methods from oscillation or rotation photographs, the structure determination involves essentially the determination of the sequence of pairs $\alpha_m\beta_m$, *i.e.* the stacking sequence.

This is usually done by comparing experimentally measured intensities with structure factors calculated for all possible stacking sequences of appropriate order and selecting the sequence giving the best fit. (See references given in Table 2).

If all possible layer combinations leading to a polytype of order n are considered, the number of resulting stacking sequences increases very rapidly with n and exceeds the capacity of computers even for moderate values of n. It is therefore essential to reduce the number of possible stacking sequences by introducing subsidiary conditions, as far as possible, before calculating the structure factors.

One such subsidiary condition, namely the determination of the percentage of hexagonality from an independent measurement (birefringence in the case of ZnS) has been dealt with previously (Brafman & Steinberger, 1966).

The present paper describes a simple method for obtaining an additional subsidiary condition, namely the determination of the total number of cyclic and anticyclic displacements between neighbouring layers within the unit cell. These numbers will be denoted by I and J respectively with $I+J=n$ (order of the polytype).

Specifically it will be shown that the quantity C, which will be called the cyclicity of the polytype and defined by

$$C=\frac{I-J}{I+J}=\frac{I-J}{n}\,, \qquad (3)$$

can be determined in a simple way from a rough estimate of reflected intensities obtained from an oscillation photograph.

Knowledge of C reduces the number of possible stacking sequences by an order of magnitude.

Outline of the method

In polytypes of substances containing two atoms per molecule, for instance ZnS, there are two non-equivalent atoms, thus $p=1$ and $p=2$, and if $\mathbf{r}_{10}$ is choosen to be 0, then $\mathbf{r}_{20} = \frac{\gamma}{n}\,\mathbf{c}$, with γ very close, or equal, to 3/4.

The structure factor $F_{hk.l}$ for these substances is given by

$$F_{hk.l}=f(l)\varphi_{hk.l} \tag{4}$$

$$f(l)=f_{\text{S}}+f_{\text{Zn}}\exp\left(2\pi i\,\frac{\gamma}{n}\,l\right) \tag{5}$$

$$\varphi_{hk.l}=\sum_{m=0}^{n-1}\exp\left[2\pi i\left(h\alpha_m+k\beta_m+\frac{m}{n}\,l\right)\right]. \tag{6}$$

It is easily seen that in general $|\varphi_{hk.l}|=|\varphi_{h'k'.l'}|$ if $h-k=h'-k'$ (mod 3) and $l=l'$ (mod n). Furthermore if $h=k$ (mod 3) then $\varphi_{hk.l}\neq 0$ for $l=0, n, 2n \ldots$ only. From this it follows that all the available information regarding the stacking sequence is contained in a set of n values $\varphi_{hk.l}$ with h,k constant and $h-k\neq 0$ (mod 3), and l ranging over n successive values, say from $-n/2$ to $\frac{n}{2}-1$.

Henceforth it will for simplicity be assumed that the polytype is of an even order, which may be achieved for a polytype of odd order by doubling the height of its unit cell.

The squares of the absolute values of φ are calculated from equation (6).

$$\begin{aligned}|\varphi_{10.l}|^2&=\sum_{m=0}^{n-1}\sum_{m'=0}^{n-1}\exp\left[2\pi i\left(\alpha_m-\alpha_{m'}+\frac{m-m'}{n}\,l\right)\right]\\&=n+\sum_{m=m'+1}^{n-1}\sum_{m'=0}^{n-1}\exp\left[2\pi i\left(\alpha_m-\alpha_{m'}+\frac{m-m'}{n}\,l\right)\right]\\&\quad+\exp\left[-2\pi i\left(\alpha_m-\alpha_{m'}+\frac{m-m'}{n}\,l\right)\right].\end{aligned} \tag{7}$$

It should be noted that expression (7) contains only the coordinate differences between pairs of positions. Each $\alpha_m-\alpha_{m'}$ can have only one of the values $+\frac{1}{3}$, $-\frac{1}{3}$, or 0. Equation (7) may thus be rearranged as follows:

$$\begin{aligned}|\varphi_{10.l}|^2=n+\sum_{p=1}^{n-1}&\left[X_p\exp\frac{2\pi i}{3}+Y_p\exp\left(-\frac{2\pi i}{3}\right)\right.\\&\left.+Z_p\right].\exp\left(\frac{2\pi ipl}{n}\right)+\left[X_p\exp\left(-\frac{2\pi i}{3}\right)\right.\\&\left.+Y_p\exp\frac{2\pi i}{3}+Z_p\right]\exp\left(-\frac{2\pi ipl}{n}\right)\end{aligned} \tag{8}$$

where $p=m-m'$ and X_p, Y_p, Z_p are the numbers of pairs of positions whose interpositional distances are $\frac{p}{n}\,\mathbf{c}$ along the c axis and $+\frac{1}{3}(\mathbf{a}_1-\mathbf{a}_2)$, $-\frac{1}{3}(\mathbf{a}_1-\mathbf{a}_2)$ or 0 respectively perpendicular to the c axis. Such pairs are called cyclic, anticyclic or zero pairs respectively. Clearly:

$$X_p+Y_p+Z_p=n-p\,.$$

Calculating the sum, T, of $|\varphi_{10.l}|^2$ over one period of l,

$$T=\sum_{l=-\frac{n}{2}}^{\frac{n}{2}-1}|\varphi_{10.l}|^2,$$

using equation (8), and observing that, p being an integer, $\neq 0$ (mod n)

$$\sum_{l=-n/2}^{\frac{n}{2}-1}\exp 2\pi ipl/n=0\,,$$

we obtain the result

$$T=n^2\,. \tag{9}$$

The difference, D, between the partial sums is defined as

$$D=\sum_{l=-\frac{n}{2}+1}^{-1}|\varphi_{10.l}|^2-\sum_{l=1}^{\frac{n}{2}-1}|\varphi_{10.l}|^2\,. \tag{10}$$

Substituting for $|\varphi_{10.l}|^2$ from equation (8) we obtain directly, on summing over l, the result

$$D=V_pU+V_p^*U_p^*$$

where

$$\left.\begin{aligned}V_p&=X_p\exp(2\pi i/3)+Y_p\exp(-2\pi i/3)+Z_p\\U_p&=\{-1-\exp(2\pi ip/n)+\exp(2\pi ip/2)\\&\quad+\exp[2\pi i\,.\,(p/n)-(p/2)]\}/[1-\exp(2\pi ip/n)]\end{aligned}\right|. \tag{11}$$

The asterisk indicates the complex conjugate.

Observing that U_p is zero for p even and equal to $2i$ cotg $\pi p/n$ for p odd, we have finally:

$$\left.\begin{aligned}D&=\sum_{p=1,3,5,..}^{n-1}2i\,.\,(Y_p-X_p)\\&\quad.\,[\exp(2\pi i/3)-\exp(-2\pi i/3)]\,.\,\operatorname{cotg}\pi p/n\\&=4\sin\frac{2\pi}{3}\,.\sum_{p=1,3,5..}^{n-1}(X_p-Y_p)\,.\,\operatorname{cotg}\pi p/n\\&=2\sqrt{3}\sum_{p=1,3,5..}^{n-1}[I(p)-J(p)]\,.\,\operatorname{cotg}p/n\end{aligned}\right\}. \tag{12}$$

The numbers $I(p)$ and $J(p)$ introduced in equation (12) are defined as

$$I(p)=X_p+Y_{n-p}\,,\quad J(p)=Y_p+X_{n-p}\,. \tag{13}$$

$I(p)$ is the number of cyclic pairs, within one entire unit cell, which are p interlayer distances apart along the c axis. Similarly $J(p)$ refers to the number of anticyclic pairs.

The numbers $I(1)$ and $J(1)$ are related to the numbers comprising the Zhdanov symbol. Let a certain polytype be characterized by its Zhdanov symbol

$$(I_1J_1I_2J_2 \ldots I_qJ_q) \qquad \sum_{k=1}^{q} I_k+J_k=n\,.$$

Then

$$\sum_{k=1}^{q} I_k=I(1)\equiv I\,, \quad \sum_{k=1}^{q} J_k\equiv J(1)=J\,. \tag{15}$$

Henceforth the Zhdanov symbol will always be written so that $I \geq J$.

Returning to equation (12), it is seen that the first term of the sum has the value $\mu_n\,.\,n\,.\,(I-J)$, where $\mu_n = \frac{2\sqrt{3}}{n} \operatorname{cotg} \frac{\pi}{n}$. The value of μ_n ranges 1 for $n=6$ to 1·1 for $n=\infty$, *i.e.* it remains close to 1 for all values of n which are of interest.

Regarding the remaining terms of the sum in equation (12) it is noted that $\operatorname{cotg} \frac{\pi p}{n}$ decrease with increasing n at a rate faster than $n/p\pi$. Also the differences $I(p)-J(p)$ are never more than n (or less than $-n$) and are generally of alternating sign. To a first rough approximation (which will however be shown to be sufficient) we may completely disregard all but the first term of the sum and write for equation (12)

$$\frac{D}{n} \simeq \mu_n\,.\,(I-J) \simeq I-J\,. \tag{16}$$

Substituting in equation (16) for n from equation (9) and using C defined in equation (3) we obtain

$$C=\frac{I-J}{n}=\frac{D}{T}\,. \tag{17}$$

Equation (17) has been derived in terms of the values $|\varphi_{10.l}|^2$, which can be obtained from experimental intensities by calculating first the squares of the structure factors $|F_{10.l}|^2$ and then using equations (4) and (5). [$f(l)$ is independent of the stacking sequence of the polytype]. However, in practice it turns out that owing to the particular form of equation (17) and because of the fact that $f(l)$ is symmetric in l, the expression $|\varphi_{10.l}|^2$ may be replaced simply by $|F_{10.l}|^2$. Similarly, the Lorentz, polarization and correcting factors connecting measured intensities $R_{10.l}$ with the structure

Table 1. *Permissible values of I–J for possible values of n and the various crystal systems*

	n odd	n even
Hexagonal: $I-J=0$ (mod 3)	$3+6m$	$6m$
Rhombohedral A: $I'-J'=1$ (mod 3)	$1+6m$	$4+6m$
Rhombohedral B: $I'-J'=2$ (mod 3)	$5+6m$	$2+6m$

$m=0,1,2,\ldots$

Table 2. *Comparision of values of (I–J) calculated from structure factors with actual values of (I–J) for all hitherto identified polytypes of ZnS*

A. Non-rhombohedral polytypes with asymmetric Zhdanov symbol

Polytype	$(I-J)$	$(I-J)$ calc.	Reference*	Polytype	$(I-J)$	$(I-J)$ calc.	Reference*
14*L*(5 4 2 3)	0	0·12	*d*	24*L*(15 9)	6	6·03	*h*
20*L*(8 7 2 3)	0	0·12	*j*	24*L*(9 5 6 4)	6	5·93	*h*
20*L*(7 6 3 4)	0	0·20	*j*	16*L*(14 2)	12	12·02	*g*
20*L*(5 3 3 4 2 3)	0	0·23	*f*	22*L*(17 5)	12	11·98	*i*
24*L*(9 8 3 4)	0	0·11	*h*	24*L*(16 4 2 2)	12	12·18	*h*
24*L*(10 7 2 5)	0	0·06	*h*	26*L*(17 3 2 4)	12	11·74	*d*
24*L*(5 3 3 3 2 4 2 2)	0	0·22	*h*	22*L*(20 2)	18	18·22	*i*
34*L*(7 5 3 5 5 5 2 2)	0	0·73	*l*	24*L*(21 3)	18	18·12	*l*
10*L*(8 2)	6	6·05	*d*	28*L*(23 5)	18	18·00	*j*
12*L*(9 3)	6	6·06	*j*	28*L*(21 3 2 2)	18	18·00	*j*
20*L*(13 7)	6	6·15	*i*	44*L*(17 4 17 6)	24	24·60	*j*
20*L*(6 2 2 5 2)	6	6·31	*f*	44*L*(37 7)	30	30·32	*j*

B. Non-rhombohedral polytypes with symmetric Zhdanov symbol

For all these polytypes $(I-J)$ calculated from structure factors equals zero exactly.

Polytype	Reference*	Polytype	Reference*	Polytype	Reference*
2*H*(1 1)		12*L* (4 2 2 4)	*l*	20*L*(7 3 3 7)	*i*
4*H*(2 2)		14*H*(7 7)	*e*	20*L*(5 3 2 2 3 5)	*i*
6*H*(3 3)	*a*	14*L*(4 3 3 4)	*l*	24*L*(7 5 5 7)	*e*
8*H*(4 4)	*b*	16*H*(8 8)	*d*	24*L*(3 3 4 2 2 4 3 3)	*h*
10*H*(55)	*b*	16*L*(5 3 3 5)	*g*	26*L*(7 3 3 3 3 7)	*i*
10*L*(3 2 2 3)	*l*	16*L*(3 3 2 2 3 3)	*g*	28*L*(9 5 5 9)	*c*
12*H*(6 6)	*j*	20*H*(10 10)	*j*	28*L*(3 3 3 3 2 2 3 3 3 3)	*l*

Table 2 (*cont.*)

C. Rhombohedral polytypes, category *A* $(I'-J')=1 \pmod 3$†

Polytype	$(I'-J')$	$(I'-J')$ calc.	Reference*
$30R(7\ 3)_3$	4	3·97	*i*
$36R(6\ 2\ 2\ 2)_3$	4	4·20	*e*
$42R(9\ 5)_3$	4	3·89	
$48R(10\ 6)_3$	4	4·08	*g*
$48R(8\ 4\ 2\ 2)_3$	4	3·91	*g*
$60R(12\ 8)_3$	4	4·08	*i*
$60R(5\ 3\ 2\ 2\ 5\ 3)_3$	4	4·65	*f*
$60R(6\ 3\ 3\ 3\ 3\ 2)_3$	4	4·03	*j*
$60R(5\ 4_5\ 2\ 2\ 2)_3$	4	5·39	*j*
$60R(8\ 4\ 2\ 2\ 2\ 2)_3$	4	3·78	*j*
$84R(7\ 3\ 3\ 3\ 3\ 3\ 3\ 3)_3$	4	3·00	*l*
$42R(12\ 2)_3$	10	10·23	*j*
$48R\ (13\ 3)_3$	10	10·12	*g*
$60R(9\ 3\ 6\ 2)_3$	10	10·30	*j*
$60R(10\ 3\ 5\ 2)_3$	10	10·71	*j*
$72R(17\ 7)_3$	10	10·30	*l*
$72R(7\ 3\ 5\ 2\ 5\ 2)_3$	10	10·70	*l*
$78R(13\ 5\ 5\ 3)_3$	10	10·19	*i*
$60R(18\ 2)_3$	16	16·33	*f*
$78R(17\ 3\ 4\ 2)_3$	16	16·19	*i*
$114R(21\ 9\ 6\ 2)_3$	16	16·25	*j*
$114R(13\ 5\ 2\ 2\ 6\ 2\ 6\ 2)_3$	16	16·34	*j*
$84R(25\ 3)_3$	22	22·23	*j*
$102R(31\ 3)_3$	28	28·25	*l*

D. Rhombohedral polytypes, category *B* $(I'-J')=2 \pmod 3$†

Polytype	$(I'-J')$	$(I'-J')$ calc.	Reference*
$18R(4\ 2)_3$	2	2·28	*e*
$24R(5\ 3)_3$	2	2·35	*d*
$30R(6\ 4)_3$	2	2·05	*l*
$30R(4\ 2\ 2\ 2)_3$	2	2·57	*l*
$36R(7\ 5)_3$	2	1·78	*k*
$36R(4\ 2\ 3\ 3)_3$	2	2·98	*k*
$36R(5\ 3\ 2\ 2)_3$	2	2·39	*k*
$48R(9\ 7)_3$	2	2·19	*f*
$48R(6\ 4\ 3\ 3)_3$	2	2·13	*l*
$48R(7\ 4\ 2\ 3)_3$	2	1·63	*f*
$48R(4\ 2\ 2\ 2\ 3\ 3)_3$	2	3·53	*f*
$54R(10\ 8)_3$	2	2·12	*j*
$60R(11\ 9)_3$	2	2·14	*i*
$60R(9\ 6\ 2\ 3)_3$	2	2·04	*k*
$60R(8\ 7\ 3\ 2)_3$	2	2·63	*k*
$60R(7\ 4\ 2\ 3\ 2\ 2)_3$	2	1·00	*i*
$66R(7\ 7\ 5\ 3)_3$	2	2·25	*i*
$66R(8\ 7\ 4\ 3)_3$	2	1·55	*i*
$66R(5\ 5\ 4\ 2\ 3\ 3)_3$	2	2·82	*i*
$66R(7\ 3\ 2\ 4\ 3\ 3)_3$	2	1·18	*c*
$72R(9\ 6\ 4\ 5)_3$	2	1·82	*h*
$72R(9\ 7\ 4\ 4)_3$	2	2·25	*l*
$72R(11\ 6\ 2\ 5)_3$	2	1·83	*h*
$72R(7\ 3\ 3\ 5\ 3\ 3)_3$	2	1·28	*l*
$72R(8\ 6\ 3\ 2\ 2\ 3)_3$	2	2·14	*l*
$78R(7\ 7\ 3\ 3\ 4\ 2)_3$	2	2·75	*i*
$84R(11\ 8\ 4\ 5)_3$	2	1·97	*j*
$36R(10\ 2)_3$	8	8·36	*l*
$48R(12\ 4)_3$	8	8·14	*f*
$60R(9\ 4\ 5\ 2)_3$	8	8·72	*j*
$60R(11\ 4\ 3\ 2)_3$	8	8·65	*f*
$66R(15\ 7)_3$	8	8·26	*i*
$72R(11\ 5\ 5\ 3)_3$	8	8·40	*l*
$72R(14\ 5\ 2\ 3)_3$	8	7·78	*l*
$78R(9\ 3\ 3\ 3\ 5\ 3)_3$	8	9·35	*j*
$60R(17\ 3)_3$	14	14·34	*j*
$72R(17\ 3\ 2\ 2)_3$	14	14·49	*l*
$96R(17\ 5\ 6\ 4)_3$	14	14·24	*l*
$120R(13\ 3\ 3\ 5\ 11\ 5)_3$	14	13·82	*l*
$72R(22\ 2)_3$	20	20·39	*l*
$114R(29\ 9)_3$	20	20·22	*j*
$120R(29\ 3\ 2\ 2\ 2\ 2)_3$	26	26·80	*l*
$114R(35\ 3)_3$	32	32·25	*j*

* References are to publications of identification of the polytype. (*a*) Frondel, C. & Palache, C. (1950). *Amer. Min.* **35**, 29. (*b*) Evans, H. T. & McKnight, E. T. (1959). *Amer. Min.* **44**, 1210. (*c*) Daniels, B. K. (1966). *Phil. Mag.* **14**, 487. (*d*) Brafman, O., Alexander, E. & Steinberger, I. T. (1967). *Acta Cryst.* **22**, 347. (*e*) Mardix, S., Brafman, O. & Steinberger, I. T. (1967). *Acta Cryst.* **22**, 805. (*f*) Mardix, S., Alexander, E., Brafman, O. & Steinberger, I. T. (1967). *Acta Cryst.* **22**, 808. (*g*) Mardix, S. & Brafman, O. (1967). *Acta Cryst.* **2** , 501. (*h*) Mardix, S. & Brafman, O. (1968). *Acta Cryst.* A**24**, 258. (*i*) Kiflawi, I. & Mardix, S. (1969). *Acta Cryst.* In the press. (*j*) Kiflawi, I., Mardix, S. & Steinberger, I. T. (1969). *Acta Cryst.* In the press. (*k*) Mardix, S., Kiflawi, I. & Kalman, Z. H. (1969). *Acta Cryst.* In the press. (*l*) Mardix, S. (1969). To be published.

† Owing to the fact that all vapour-grown ZnS polytypes are of even periodicity, the values of $I'-J'$ increase in steps of 6.

factors are symmetric in l and change only slightly for the n reflexion under consideration. We may write finally for the cyclicity defined in equation (3):

$$C=\frac{I-J}{n}=\frac{D'}{T'} \tag{18}$$

where

$$D'=\left[\sum_{l=-\frac{n}{2}+1}^{-1}(R_{10\,.\,l})^b\right]-\left[\sum_{l=1}^{\frac{n}{2}-1}(R_{10\,.\,l})^b\right],$$

$$T'=\sum_{l=-\frac{n}{2}}^{\frac{n}{2}-1}(R_{10\,.\,l})^b\,.$$

$R_{10\,.\,l}$ is the measured reflected intensity. The exponent b has the value 1 for reflexions from mosaic crystals (R proportional to $|F|^2$) and the value 2 for reflexions from perfect crystals* (R proportional to $|F|$). Intensities can be determined for example from an oscillation photograph of the $10\,.\,l$ row. It has been found practical to use for intensity scaling the reflexions obtained from an oscillation photograph of a known polytype.

The same arguments hold for any row of reflexions $hk\,.\,l$ with $h-k\neq0 \pmod 3$ and thus any such row may be used to determine C by means of equation (18).

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* In many of the vapour grown ZnS samples the polytype regions are in fact perfect crystals.

Rhombohedral polytypes

Frequently polytypes are found which can be indexed on a rhombohedral unit cell. Obviously in this case the number of layers per hexagonal unit cell must be an integral multiple of 3. The Zhdanov symbol of such a polytype is composed of three equal groups of numbers, each group being referred to as an 'elementary Zhdanov sequence':

$$(I_1J_1I_2J_2 \ldots I_eJ_eI_1J_1I_2J_2 \ldots I_eJ_eI_1J_1I_2J_2 \ldots I_eJ_e)\,, \quad e=n/3\,,$$

which is usually abbreviated to the form

$$(I_1J_1I_2J_2 \ldots I_eJ_e)_3\,. \tag{19}$$

Clearly

$$\sum_{k=1}^{e} I_k - \sum_{k=1}^{e} J_k \neq 0 \pmod 3\,. \tag{20}$$

Rhombohedral polytypes fall into two categories, depending on whether the value of the difference (20) equals 1 (mod 3) or 2 (mod 3) – category A or B respectively. This stipulation defines uniquely the category of any given polytype, as, by convention [see remark following equation (15)], the numbers I_k and J_k are chosen so that $I>J$.

Oscillation photographs of rhombohedral polytypes show characteristic absences, reflexions being permitted along the $10\,.\,l$ row if $l=2$ (mod 3) for category A and if $l=1$ (mod 3) for category B. [The same extinction rules hold for any row $hk\,.\,l$ with $h-k=1$ (mod 3)]. This particular classification is a consequence of the convention $I>J$.

The category of a rhombohedral polytype can be determined from an oscillation photograph of *e.g.* the $10\,.\,l$ row: the sum of the intensities of the reflexions of each of the two half-periods above and below the equator are always unequal (for rhombohedral polytypes), see equation (18), and from the definition of D' in equation (18) it is seen that the 'stronger' half-period must be assigned the negative l-indices (as $I-J>0$).

Having determined the signs of the indices on the oscillation photograph, it is now easily found whether reflexions of indices $=+2$, $+5$, *etc.* or those of indices $=-2$, -5, *etc.* are present, and thus whether the crystal belongs to category A or B respectively.

For determining I and J of a rhombohedral type the general procedure outlined before does hold. Obviously in these cases both I and J must be whole multiples of 3.

It is conceivable that, in some rhombohedral polytypes of high periodicity and lowest cyclicity, it may not be possible to determine experimentally which of the two half-periods in an oscillation photograph is the stronger. In such cases (which have not been encountered yet in practice) it may not be possible to categorize the polytype. Still, even in such a case there will be only two possible values for $I'-J'$, instead of the one obtained for the straightforward cases (see *Conclusion*) and thus even here the work required for a complete structure determination will be considerably reduced.

Conclusion

The foregoing considerations show that from a c axis oscillation photograph containing at least one well resolved row of reflexions, the cyclicity C can be obtained using equation (18). (In addition to the other information obtained from an oscillation photograph.) It should be noted that the intensities required for this calculation do not require high accuracy, owing to the fact that certain restrictions are imposed on the possible values of $I-J$. It is readily confirmed, by counting the various possibilities, that the permissible values for $I-J$ for different values of n and the three possible categories are as shown in Table 1.

In order to simplify the presentation, results for rhombohedral polytypes here and in Table 2 are given in terms of the numbers I' and J' of cyclic and anticyclic displacements per elementary Zhdanov sequence. They are related to I and J by the relations $I'=I/3$. $J'=J/3$.

This means that in calculating I and J from intensities a fairly large margin of error can be tolerated without affecting the final result. As both n and the value of $I-J$ (mod 3) are obtained independently and accurately, the value of $I-J$ must have one of the values shown in Table 1 (for any crystal the smallest possible difference $I-J$ value is 6). Thus after calculating, by means of equation (18), the approximate value of $I-J$, its correct value is found by choosing that integer both closest to the calculated (approximate) value and consistent with the limitations of Table 1.

In order to illustrate the applicability of the method the values of $I-J$ for all identified ZnS polytypes were compared with the values $I-J=C\,.\,n$ from equation (18), using calculated structure factors instead of intensities. The results are tabulated in Table 2.

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