

Remarque

Dans les études faisant intervenir les rapports des pouvoirs rotatoires spécifiques, l'expression (3) a donné de bons résultats.

Cela tient à ce que les différences entre les valeurs mesurées et les valeurs calculées par la formule (3) étant systématiquement de même sens se compensent, au moins partiellement, dans les rapports.

Cette expression (3) est tout de même intéressante car elle met bien en évidence les facteurs principaux agissant sur le pouvoir rotatoire, à savoir: le pas et la biréfringence.

Conclusion

La théorie de Mauguin-de Vries donne une bonne représentation qualitative des phénomènes observés et une représentation quantitative présentant des écarts systématiques assez grands. Ces écarts avec les valeurs expérimentales pourraient être diminués en introduisant l'hypothèse d'une inclinaison des molécules de *p*-azoxyanisole sur l'axe hélicoïdal, variable avec la température. Cela introduirait des paramètres supplémentaires, qui pour être probants devraient être simultanément atteints par une autre voie.

Enfin la comparaison de nos résultats avec ceux de Cano (1967) pour une même longueur d'onde et un même titre montre que les valeurs du pouvoir rotatoire spécifique sont voisines, quels que soient la longueur d'onde et le titre, à condition de les comparer aux mêmes températures réduites – c'est à dire, pour nos mélanges, à des températures s'écartant également de la température de fusion isotrope du mélange.

Ceci serait en faveur d'une extension à l'état cholestérique de la théorie de Maier & Saupe (1959, 1960) faite pour l'état nématique.

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The Identification of High-Order Polytypes

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A practical and fast method for the determination of the layer sequence of high-order polytypes is described. Experimentally, the method involves only the determination of the relative order of reflexion intensities and does not employ actual intensity measurements. Auxiliary information, such as the percentage of hexagonality and the cyclicity of the polytype involved, considerably shortens the computer time needed. The method was used to identify a large number of ZnS polytypes and it is applicable to other polytypic material as well.

Introduction

The number of layers in the unit cell can be readily ascertained from an oscillation photograph of the polytype. The determination of the stacking sequence of the layers, on the other hand, is a far more involved problem, especially in polytypes having a large number of layers per unit cell. This is mainly due to the fact that there are approximately $2^{n-1}/n$ possible different structures in a polytype of order *n*, i.e. in a polytype having *n* layers in its elementary sequence.

The usual methods employed for the identification of polytypes are:

(a) Working out probable structures and arriving at the correct one by trial and error. Many SiC and CdI₂ polytypes were identified in this manner (Verma & Krishna, 1966). The method has been feasible in these cases since most polytypes in these materials are based on small basic types. For ZnS polytypes, however, which frequently have rather long elementary sequences and no small basic types, this method is generally not suitable, due to the excessively long time required, even if using a computer, for complete identification of higher order polytypes. Only one higher order ZnS polytype (of order 22) has been identified by this method (Daniels, 1966).

(b) Calculating, with the aid of a computer, the intensity distributions of all possible structures of given order and comparing them with the experimental intensity distribution. The advantage of this method over the former one is its applicability to computer work, where the bottlenecks are the input and output stages. A large number of ZnS polytypes could be identified in this manner.* For high order polytypes the method becomes impractical because of the very long time required both for computer compilation of the intensities of all possible structures as well as for the comparison process.

(c) Patterson's method as modified by Farkas-Jahnke (1966)† for the identification of polytypes. It seems that the need for a very accurate determination of experimentally obtained intensities is a serious limitation of this method.

In this paper a computer method is described which combines some of the principles underlying the three above mentioned methods whilst trying to decrease computer time as far as possible. The method is described here, and has been employed for the identification of more than 50 ZnS polytypes‡: it may also be adapted for the identification of polytypes of other materials.

Preliminary information and experimental data

Preliminary information about the polytype reduces the number of possible structures that must be considered in the course of the identification. The information available is as follows:

- (a) The number of layers in the unit cell of the polytype.
- (b) The polytype being rhombohedral or not.
- (c) The cyclicity of the polytype, defined as follows (Mardix, Steinberger & Kalman, 1969).

Let the Zhdanov symbol of a polytype of order n be $(I_1J_1I_2J_2 \dots I_mJ_m)$. Denoting

$$I = \sum_{k=1}^m I_k; \quad J = \sum_{k=1}^m J_k$$

(note that $I+J=n$ and that the Zhdanov symbol is written so that $I \geq J$), the cyclicity is defined as $C = (I-J)/n$.

The identification of ZnS polytypes is further simplified by the following facts:

(d) The number 1 does not occur in the Zhdanov sequence of vapour grown ZnS crystals.

* A list of identified ZnS polytypes appears in Table 2 of Mardix, Steinberger & Kalman (1969). Structures given in this Table under references (d) to (g) were identified by this method.

† A detailed description of the method is found in Dornberger-Schiff & Farkas-Jahnke (1970) and Farkas-Jahnke & Dornberger-Schiff (1970).

‡ Structures under reference h, i, j, k and l in Table 2 of Mardix, Steinberger & Kalman (1969).

(e) The number of Zhdanov numbers in the elementary sequence can be found from birefringence measurements (Brafman & Steinberger, 1966).

The information in (a) and (b) must be known in order to use the identification program. They are obtained from an oscillation photograph by measuring interlayer distances and observing systematic absences respectively. The information in (c), (d) and (e) are not essential, but reduce considerably the computer time needed.

Experimental data required for the identification proper are the relative reflected intensities of one row of reflexions $hk.l$ with arbitrary and constant h and k (subject to $h-k$ being non-divisible by 3) and $-n/2 \leq l \leq +n/2$ (n being the order of the polytype), as obtained for example from a c axis oscillation photograph.

From these reflexions a set of i ($i < n$) reflexion spots is chosen visually in such a way that no two spots should have equal or nearly equal intensities. Also the chosen spots should cover as wide an intensity range as possible.

The indices l of these reflexions are arranged as an ordered set l_1, l_2, \dots, l_i , so that their corresponding intensities I_{obs} are in decreasing order

$$I_{\text{obs}}(l_1) > I_{\text{obs}}(l_2) > \dots > I_{\text{obs}}(l_i).$$

The identification program

There are two different programs, one for rhombohedral polytypes and one for non-rhombohedral ones. Both programs consist of 4 sub-programs: classification, elimination, calculation of intensities and final identification.

A. Non-rhombohedral polytypes

It is supposed that the preliminary information given in (a) to (e) of the last paragraph is known; thus n, m, I and J are given.

The classification sub-program

The purpose of the program is twofold:

(a) To form all possible Zhdanov symbols compatible with the preliminary information.

(b) Since the Zhdanov symbols of a given polytype can be written in several equivalent ways [e.g. (3 2 2 3), (2 2 3 3), (3 3 2 2), (2 3 3 2)] this sub-program also selects one single Zhdanov symbol of the equivalent ones. Only this particular symbol is transferred to the next sub-program.

If the cyclicity of the polytype is not known, so that I and J are not given, classification begins with $I=J$ for n even (which incidentally is the case for vapour grown ZnS polytypes) or with $I=J+3$ for n odd. After forming all Zhdanov symbols for these values of I and J , I is increased and J decreased by 3. This procedure is discontinued for values $J < m$. If condition (d) holds, values $J < 2m$ need not be considered.

If the value of m cannot be determined by birefringence measurements, then the classification has to be

carried out for $m=1,2,\dots$. For $n>4$ no values $m\geq n/2$, and if condition (d) holds no values $m\geq n/4$ need be considered.

The elimination sub-program

Consider the selected set of reflexion spots, mentioned in the introduction, which comply with the conditions

$$I_{\text{obs}}(l_1) > I_{\text{obs}}(l_2) > \dots > I_{\text{obs}}(l_i) \quad (1)$$

The elimination sub-program has been designed to discard those Zhdanov sequences promoted from the classification sub-program, which do not comply with the above set of inequalities. In practice, the intensities $I_{\text{calc}}(l_1)$ and $I_{\text{calc}}(l_2)$ of the reflexions $hk.l_1$ and $hk.l_2$ are calculated* for the first Zhdanov sequence. If $I_{\text{calc}}(l_1) \leq I_{\text{calc}}(l_2)$, this particular Zhdanov sequence is discarded and another is promoted. If, however, $I_{\text{calc}}(l_1) > I_{\text{calc}}(l_2)$, then $I_{\text{calc}}(l_3)$ is calculated; again, $I_{\text{calc}}(l_3) \geq I_{\text{calc}}(l_2)$ causes the elimination of the sequence, while if $I_{\text{calc}}(l_3) < I_{\text{calc}}(l_2)$, the computer provides $I_{\text{calc}}(l_4)$ and so forth. All Zhdanov sequences successively promoted from the classification sub-program are tested in this manner, and only those are transferred to the next sub-program, which have the same hierarchy of intensities as the set selected from the diffraction photograph (equation 1). Some complication arises if the values of I and J are not known, or if $I=J$. In these cases the sign of the indices l are not known. For this reason the signs of the experimental indices l are reversed if $I_{\text{calc}}(l_1) < I_{\text{calc}}(l_2)$ and then calculation of intensities of the following indices l proceeds as described above.

The final determination of the structure

In most cases the output of the previous sub-program includes, after eliminating the non-fitting sequences, only one possible structure. In some cases however more than one structure passes the elimination. In either case the intensities for the entire range of l ($-n/2 \leq l \leq +n/2$) of all fitting structures are now calculated. This is necessary since the elimination program provided intensities of i reflexions only, where the number i is considerably smaller than n .

The final output of the computer is thus a small number (frequently only one) of possible Zhdanov sequences together with their sets of calculated intensities. These sets are easily compared with the entire set of observed intensities, and the Zhdanov sequence giving satisfactory fit is singled out as the one representing the structure of the polytype.

The same comparison between the entire sets of calculated and observed intensities is carried out, even if only one sequence passes the elimination process, as a final check.

The observed intensities are estimated by comparing the intensities of the reflexion spots with the aid of a

magnifying glass. It was found convenient to employ an oscillation photograph of a (preferably known) polytype for performing comparisons.

For this purpose intensities are arranged, as usual, in eight groups, from vs to a . If possible, further relations between intensities of the same group are determined.

It is noted that no ambiguities in polytype identification have been encountered so far by following this procedure.

B. Rhombohedral polytypes

The classification sub-program for these polytypes is somewhat different from that presented above, in that it deals separately with cyclic and anticyclic polytypes [$I-J=1(\text{mod } 3)$ and $I-J=2(\text{mod } 3)$ respectively]. The elimination sub-program is the same as for the other polytypes. The calculation of the intensities does not differ either, but it is performed only for $n/3$ reflexion spots, where n is the order of the polytype.

An example of the identification procedure

Table 1, column 2 shows the observed intensities of the 10. l row of a ZnS polytype, found in crystal 217/55 and identified by Kiflawi, Mardix & Steinberger (1969). (A photograph of the relevant row was published in that paper.) From the distances between the reflexion points along the row line it could be deduced that the elementary sequence contains 44 layers. This was ascertained by using a method, proposed by Krishna & Verma (1963), in which the numbers of reflexion points between two points having a similar intensity in relation to their neighbours were counted. The birefringence of the polytypic region was found to be 2.3×10^{-3} . The number $2m$ of Zhdanov symbols in the unit cell is determined by using the proportionality between the birefringence $\Delta\mu$ and the value of $2m$ (Brafman & Steinberger, 1966), given by

$$2m = \frac{\Delta\mu}{24 \times 10^{-3}} n.$$

In this case the value $2m = \frac{2.3 \times 10^{-3} \times 44}{24 \times 10^{-3}} = 4.2$ is obtained. As $2m$ is an even number it is clearly 4. The computer had now to eliminate all non-fitting elementary sequences of 44 layers having 4 Zhdanov numbers. Since the material was vapour-phase grown ZnS, Zhdanov symbols having the value 1 were discarded from the start. The set of l values of reflexion spots in a descending order of intensities included 8 values out of 44. They were $l_1 = -15$, $l_2 = -14$, $l_3 = -16$, $l_4 = -11$, $l_5 = -3$, $l_6 = 2$, $l_7 = 4$, $l_8 = 6$. After the elimination sub-program, nine structures were left as having the right hierarchy of intensities. They are given in Table 1 with their intensity distribution. It is easily seen that the only fitting sequence is (17 6 17 4). It should be noted that the number of remaining structures would have been reduced if more l values were introduced in the set of experimental l values given above. For exam-

* The formulae for the calculation of intensities are compiled in the Appendix.

ple from Table 1 it can be seen that the intensity of the reflexion spot with $l=16$ lies between the intensities of the reflexion spots having $l=-16$ and $l=-11$. Should this value be introduced into the l set, then the only possible structures would have been (21 17 4 2), (26 3 5 4) and (17 6 17 4). If also the intensity with $l=0$ would have been introduced between the values $l=4$ and $l=6$, thus having a set of 10 l values ($i=10$), there would remain, after the elimination, only one possible structure, namely (17 6 17 4), which indeed is the only fitting structure. Experience showed that in order to get only one structure after elimination, one should choose at the outset $i \approx n/3$. In the above example the value of the cyclicity was not used, though it is avail-

able from the diffraction photograph; if it were used, more elementary sequences would have been discarded before the use of the elimination sub-program proper.

Conclusion

The method described in this paper employs for identification of polytypes an ordered set of reflexions, arranged according to decreasing intensities, instead of the numerical values of relative intensities required in most other methods of structure identification. (The set of reflexions might have been arranged in order of increasing intensity as well.) This procedure is in principle justified by two considerations. First, the identifi-

Table 1. *Experimental distribution of intensities of a 44 order polytype and the calculated intensities of the nine structures left after eliminating the non-fitting ones*

The set of l values having intensities in a decreasing order was $l=-15, -14, -16, -11, -3, 2, 4, 6$. The calculated intensities given as 0.00 are not real absences, but they are less than 0.005.

l	Observed intensities	(20 16 2 6)	(21 17 4 2)	(19 17 6 2)	(17 16 2 9)	(26 9 5 4)	(24 9 7 4)	(25 6 9 4)	(17 7 17 3)	(17 6 17 4)
22	$vw (> 21)$	0.87	1.98	0.27	1.80	1.22	0.18	0.45	0.14	0.47
21	vw	1.43	1.45	0.23	3.02	0.03	2.41	1.39	0.69	0.23
20	m	0.66	6.41	3.81	0.33	1.26	1.42	1.01	1.68	2.99
19	a	8.50	2.44	2.46	2.33	0.57	2.70	0.67	0.00	0.00
18	s	7.91	12.35	14.54	7.60	4.45	2.26	6.87	5.70	7.38
17	$vw (\approx 13)$	14.21	1.30	5.29	14.46	12.81	2.44	4.55	0.81	0.23
16	s	29.19	26.49	32.98	40.48	7.32	19.27	0.97	10.29	11.46
15	$vw (> 13)$	25.65	61.46	36.18	12.86	4.63	15.12	10.79	1.82	0.49
14	$s (> 12)$	84.77	100.00	100.00	100.00	18.38	3.61	7.59	11.41	12.44
13	vw	34.11	11.41	19.64	30.50	16.66	15.22	0.44	1.29	0.36
12	s	4.63	13.74	11.75	4.93	2.32	9.64	7.26	7.82	9.48
11	a	6.65	1.42	1.99	1.29	0.87	0.16	5.14	0.13	0.04
10	m	0.17	4.13	1.94	1.34	1.73	1.51	0.02	2.98	4.66
9	vw	0.58	0.13	0.23	0.69	0.69	0.40	1.69	0.35	0.11
8	w	0.90	0.68	0.44	0.73	2.56	2.49	0.95	0.43	1.09
7	w	0.27	1.00	0.80	0.88	1.56	1.53	0.51	1.45	0.54
6	a	0.53	0.04	0.04	0.04	0.04	0.00	0.31	0.00	0.00
5	w	0.03	1.13	0.34	0.78	0.06	0.08	0.12	1.40	0.64
4	$vw (> 0)$	1.04	0.05	0.74	0.17	0.09	0.10	0.43	0.00	0.31
3	vw	0.27	0.41	0.44	0.04	0.40	0.26	0.30	0.36	0.21
2	$vw (> 4)$	1.70	0.10	1.40	1.57	0.10	0.38	0.48	0.07	0.50
1	a	0.13	0.49	0.22	0.23	0.29	0.63	0.10	0.03	0.02
0	vw	0.46	0.44	0.42	0.40	0.27	0.28	0.24	0.23	0.25
-1	$w (\approx 5)$	0.63	1.72	0.51	0.81	0.51	0.78	0.10	0.45	0.64
-2	a	0.23	0.73	0.26	0.43	1.46	0.04	0.68	0.07	0.02
-3	$w (> -1)$	2.20	2.41	2.20	2.16	0.56	0.76	1.09	0.45	1.31
-4	a	1.36	0.39	0.79	0.25	0.05	0.80	0.06	0.16	0.01
-5	w	1.36	1.53	2.03	0.13	0.17	0.22	0.48	0.09	0.92
-6	a	1.05	0.00	0.08	2.22	0.07	0.45	0.38	1.39	0.01
-7	vw	0.07	0.77	0.75	0.81	0.69	0.53	0.00	0.00	0.03
-8	a	1.10	0.61	0.86	2.53	0.46	0.66	0.06	2.50	0.01
-9	w	3.50	2.68	2.69	0.37	0.74	0.08	1.12	0.06	1.17
-10	$vw (> -7)$	1.65	1.55	2.64	0.05	0.51	0.51	0.73	1.41	0.06
-11	m	6.65	7.81	5.04	7.10	4.81	2.20	1.74	1.75	7.09
-12	a	0.48	0.71	0.52	0.59	13.16	16.46	12.61	0.08	0.01
-13	vs	5.66	18.34	7.97	11.13	3.74	10.65	8.85	14.37	25.12
-14	$vs (> -16)$	69.59	40.55	52.90	46.83	40.16	34.02	31.76	36.50	24.68
-15	vs	100.00	64.79	70.69	66.00	100.00	100.00	100.00	100.00	100.00
-16	vs	14.71	34.17	15.76	15.49	8.69	14.49	9.38	5.43	18.50
-17	w	0.35	0.43	2.24	2.97	9.25	9.65	6.13	1.50	1.00
-18	$w (> -17)$	6.02	4.50	1.95	5.28	1.93	1.62	1.84	0.01	2.67
-19	$w (> -21)$	1.03	0.19	4.91	1.45	0.45	0.37	1.40	3.71	1.84
-20	vw	4.83	0.75	1.18	0.84	0.27	0.61	0.09	0.01	0.09
-21	w	0.28	0.53	2.29	0.97	1.85	0.81	0.71	2.31	0.91
-22	vw	0.87	1.98	0.27	1.80	1.22	0.18	0.45	0.14	0.47

cation of the structure of a polytype of a given order entails basically the identification of the stacking sequence of a known number of identical layers, the structure of each layer being known and constant (at least to a very good approximation) whatever the order and the stacking sequence. Also the number of possible displacement vectors between two neighbouring layers is very small – namely two in the cases considered here. Second, the number of possible different stacking arrangements of n layers, about $2^{n-1}/n$, is much smaller than the number of possible ordered sets of n reflexions, which is $n!$. In most cases the number of possible stacking arrangements is further reduced by some additional information, such as the percentage of hexagonality (Brafman & Steinberger, 1966) or the cyclicity (Mardix, Steinberger & Kalman, 1969).

It is noted that the method described here is essentially a process of elimination: successively more and more structures are rejected as the ordered set of experimental intensities (used for comparison) is increased in size. Moreover, this process of elimination is efficient enough to turn out a reasonably small number of possible polytypes even if a relatively small set of ordered reflexions is used for comparison.

In the very unlikely case that two different polytypes should give identical sets of ordered reflexions, this method would leave both structures as possible answers, and in this case numerical values of relative intensities would have to be obtained to decide between the alternatives.

The main advantages of the method is the fact that normally no numerical values of relative intensities are required. This relieves not only the considerable experimental tedium of actual measurement of intensity values of often exceedingly small spots ($\sim 50\mu$) as obtained from very small polytype regions, but it also circumvents the necessity of determining, in a given sample, the exact dependence of reflected intensity on the structure factor.

An additional advantage of this method is its relative speed. If a set of m reflexions is considered for comparison, the number of eligible structures decreases by a factor of about $1/m!$. The number of structure factor computations to be carried out in this case, starting with N structures is about $2N + N/2 + N/3! + \dots + N/m!$. In practice the computer time required on an IBM 7040 for the elimination process for a polytype of order $n=40$, using $m=8$ reflexions, was found to be about 4 minutes.

Finally it is noted that the same method can be employed to identify polytypes of materials other than ZnS for example SiC and CdI₂.

APPENDIX

The calculation of intensities

The intensity $I_{hk.l}$ is given by

$$I_{hk.l} = |\varphi_{hk.l}|^2 K_{hk.l} \quad (2)$$

where

$$|\varphi_{hk.l}|^2 = \left[\sum_{t=1}^n \cos 2\pi \left(\frac{lt}{n} + \frac{\alpha_t}{3} \right) \right]^2 + \left[\sum_{t=1}^n \sin 2\pi \left(\frac{lt}{n} + \frac{\alpha_t}{3} \right) \right]^2$$

The summation is over all the layers in the unit cell; t is the cardinal number of the layer. α_t equals 0, 1 or 2 according to whether the layer in the t th place is an A , B , or C -type layer respectively. There are $3n$ possible different values of cosines and $3n$ different values of sines in equation (2). These $3n$ values are calculated and stored in the memory of the computer as two vectors $C(\mathbf{u}, \alpha)$ and $S(\mathbf{u}, \alpha)$, where $u = \frac{lt \pmod n}{n}$ and $\alpha = \alpha_t$.

The value of $|\varphi_{hk.l}|^2$ is then calculated by summing the appropriate values of $C(\mathbf{u}, \alpha)$ and $S(\mathbf{u}, \alpha)$. The factor $K_{hk.l}$ includes the atomic scattering factors and the Lorentz-polarization factor.

$$K_{hk.l} = f^2 L$$

$$f^2 = f_{Zn}^2 + f_S^2 + 2f_{Zn}f_S \cos \frac{3\pi l}{2n}$$

f_{Zn} and f_S are the atomic structure factors of Zn and S respectively and

$$L = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot \frac{\cos \theta}{(\cos^2 \theta - \sin^2 \psi)^{1/2}}$$

where θ is the Bragg angle and ψ is the angle between the reflecting plane and the axis of oscillation.

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