so that the maximum error of the approximation on the set of points $\bar{x}_1, \bar{x}_2, \ldots \bar{x}_Q$

$$E_{\max} = \max_{1 \le i \le Q} \{|P_M(\bar{x}_i) - G\bar{x}_i)|\} . \quad (31)$$

is a minimum. Then $G(x)$ is said to be at best Tchebycheff or minimax approximation to $P_M(x)$ on the set $\{\bar{x}_1, \bar{x}_2, \ldots \bar{x}_Q\}$. The N_p^q can most conveniently be determined using the flexible and powerful methods of linear programming (Rice, 1964).

The above approach has reduced the problem of extracting the periodic vector set from the Patterson function to a problem in linear approximation. There are many mathematical questions of a theoretical nature involved in the determination of the interpolatory and Tchebycheff approximations, and these cannot be treated adequately in this paper; the interested reader is referred to the excellent book of Rice (1964) for a thorough treatment. In any case, the application of (30) and (31) is not limited by theoretical considerations; the limitations are imposed by problems of numerical computation. Numerical difficulties may arise when the approximation problem is formulated in such a way that an extremely large system of equations results. For example, a three-dimensional interpolatory solution of the Patterson function, in which 30 divisional points were used along the *a*, *b*, and *c* axes, would require the solution of 27,000 equations in 27,000 unknowns! While such systems can be solved in practice (provided the system is mathematically stable), there would appear to be little reason for doing so; in the present method two- and three-dimensional solutions appear to offer no significant advantages over the one-dimensional formulations dealt with in this paper. The details involved in the practical computation of the interpolatory approximations have been briefly described in a previous paper (Goldak, 1969). The more powerful Tchebycheff methods will be dealt with in a following paper.

This work was supported by a National Research Council grant. The author is also grateful to Dean A. D. Booth for discussion and for his general support of the author's crystallographic work.

References

BUERGER, M. J. (1950). *Acta Cryst.* **3**, 87.
BUERGER, M. J. (1959). *Vector Space*. New York: John Wiley.
CHENEY, E. W. (1966). *Introduction to Approximation Theory*. New York: McGraw-Hill.
GOLDAK, G. R. (1969). *Acta Cryst.* A**25**, 367.
KITAIGORODSKII, A. I. (1961). *Theory of Crystal Structure Analysis*. New York: Consultants Bureau.
LANCZOS, C. (1966). *Discourse on Fourier Series*. London: Oliver & Boyd.
PATTERSON, A. L. (1935). *Z. Kristallogr.* **90**, 517.
RICE, J. R. (1964). *The Approximation of Functions*, Vol. 1. *Linear Theory*. Reading, Massachusetts: Addison-Wesley.
SIMPSON, P. G., DOBROTT, R. D. & LIPSCOMB, W. N. (1965). *Acta Cryst.* **18**, 169.
TOKONAMI, M. & HOSOYA, S. (1965). *Acta Cryst.* **18**, 908.
TOLSTOV, G. P. (1962). *Fourier Series*. Englewood Cliffs, New Jersey: Prentice-Hall.
WUNDERLICH, J. A. (1965). *Acta Cryst.* **19**, 200.

Acta Cryst. (1971). A**27**, 216

The Determination of Cyclicity, Hexagonality, and other Properties of Polytypes

BY K. DORNBERGER-SCHIFF AND H. SCHMITTLER
Deutsche Akademie der Wissenschaften zu Berlin, Zentralinstitut für physikalische Chemie, Berlin-Adlershof, Germany (DDR)

AND M. FARKAS-JAHNKE
Research Institute for Technical Physics of the Hungarian Academy of Sciences, Budapest, Hungary

(*Received* 17 *August* 1970)

The cyclicity of a polytype, the percentage of hexagonality, and the distribution of figures '1' among even and odd places of the Zhdanov symbol may be deduced directly from measured intensities. These values are given for a 66*R* polytype whose sequence has been determined earlier and for a hypothetical 114*R* polytype. A discussion is given of the errors in these values originating from the errors of the $|S|^2$ values used and of the errors produced, if instead of the exact formula for the cyclicity an approximation advocated by Mardix and his coworkers is used.

Introduction

A method for the direct determination of periodic polytypes of ZnS, SiC or similar substances from measured intensities of X-ray diagrams has been published by two of us (Farkas-Jahnke; 1966, Dornberger-Schiff & Farkas-Jahnke 1970) and successfully applied (Gomes de Mesquita, 1968; Farkas-Jahnke & Dornberger-Schiff, 1970). The method is applicable if rather accurate values $|S(kl)|^2 = |F(hkl)|^2/|F_0(hkl)|^2$ are ob-

tainable from the measured intensities $|F(hkl)|^2$ and from the Fourier transform $F_0(hkl)$ of the single layer. If these values possess too wide limits of error, then the method becomes rather time consuming, if the period of the polytype is fairly large. Four characteristic values for any polytype may, however, be determined directly and in a very simple way, even if the experimental values are not so accurate. On the theoretical basis underlying the method mentioned above, these characteristic values are the cyclicity, the percentage hexagonality, and the numbers of figures '1' on even and on odd places of the Zhdanov symbol, respectively. Depending on the margin of error of the experimental data these characteristic values may be determined unequivocally or with a certain margin of error (see below).

We characterize any periodic polytype by a periodic sequence of figures '1' and '0', *i.e.* by a periodic binary number. In this sequence of figures, '1' and '0' stand for shifts converting one layer into the next, either by a vector $\mathbf{b}/3+\mathbf{c}/M$ or by $-\mathbf{b}/3+\mathbf{c}/M$, respectively (this notation is similar to that introduced by Hägg, except that we use the figures instead of '+' and '−'). Here **b** and **c** are orthohexagonal basic vectors, M is equal to the number of layers traversing the lattice vector **c**. We denote further by $[\alpha_1,\alpha_2,\ldots,\alpha_p]$ the rate of occurrence within a period, of a partial sequence $\alpha_1,\alpha_2,\ldots,\alpha_p$. The 'Patterson function' $\pi(m,p)$ is defined as

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

($M=N$ for hexagonal, $M=3N$ for rhombohedral polytypes). The values $S(hkl)=S(kl)$ do not – except for experimental errors – depend on h and are equal to

$$S(kl)=S(k+3n',\ l+Mn'')=S(\bar{k}\bar{l})$$

for any pair of integral numbers n', n''. Thus for k not divisible by 3, there are N essentially different values of $S(kl)$. Sets of $|S(kl)|$ values may thus be obtained from $|F(hkl)|$ values with different indices h and/or k. The accuracy of the $|S(kl)|$ values obtained may be improved by taking mean values of $|S(kl)|$ which ought to be equal.

Cyclicity

The cyclicity C is defined as the difference between the number of figures '1' and the number of figures '0' per period, divided by the length N of the period, *i.e.*

$$C=\frac{[1]-[0]}{N}=\frac{\pi(1,1)-\pi(-1,1)}{N}.$$

As described earlier (Dornberger-Schiff & Farkas-Jahnke, 1970), the $\pi(m,p)$ values and thus the value of C may be obtained from the measured intensities.

Mardix, Steinberger & Kalman (1970) have recently proposed a method for the determination of the cyclicity. This method differs from our method only in the following points: they introduce an approximation, neglecting in the formula for the cyclicity C, a factor μ_n, for which $1\leq\mu_n\leq 1\cdot 1$ holds. They also regard it as satisfactory approximation, if the $|S(kl)|^2$ values are replaced by the $|F(hkl)|^2$ values for constant h. Besides, they state that a fairly large margin of error can be tolerated for the measured intensities, without affecting the final results. Unfortunately, although the authors have investigated a considerable number of polytypes and thus have sufficient experimental data at their disposal, they give not a single example of the determination of the cyclicity from quantitative intensity data, and do not discuss the influence of experimental errors on the results. When discussing examples (see below), the justification of the procedure advocated by Mardix *et al.* will also be discussed.

Hexagonality

The percentage hexagonality α is the number of figures in the Zhdanov symbol, divided by N. In our binary notation, this is equal to

$$\frac{[01]+[10]}{N},$$

because [01] denotes the rate of occurrence per period of a figure '0' followed by a figure '1', and so on. As has been shown earlier, $[01]+[10]=\pi(0,2)$ and thus

$$\alpha=\pi(0,2)/N.$$

For obvious reasons, α is always an even number.

Number of figures '1' in the Zhdanov symbol

Any figure '1' in the Zhdanov symbol gives rise either to a partial sequence '010', or to a partial sequence '101' in binary notation. From the relations between the rates of occurrence of partial sequences of length 2 and 3, earlier described, and from the meaning of the π values, it follows that

$$[010]=\pi(0,2)-\tfrac{2}{3}\cdot\pi(1,3)-\tfrac{1}{3}\cdot\pi(-1,3)$$
$$[101]=\pi(0,2)-\tfrac{1}{3}\cdot\pi(1,3)-\tfrac{2}{3}\cdot\pi(-1,3)$$

We may choose the direction of axes and the origin in such a way that $\pi(1,1)\leq\pi(-1,1)$ and that the first figure in the Zhdanov symbol refers to a sequence of figures '1'. Then [010] is the number of figures '1' in odd places in the Zhdanov symbol, [101] the number of figures '1' in even places of the symbol. The sum $[101]+[010]$ is thus the total number of figures '1' in the Zhdanov symbol; the values [101] and [010] taken separately show the distribution of these figures '1' on even and odd places of the symbol, respectively.

Examples

The π values calculated from mean values of the sets of $|S(kl)|^2$ values have been obtained for a $66R$ polytype (Farkas-Jahnke & Dornberger-Schiff, 1970), and

the polytype has been determined with the help of our method. This determination required the discussion of a number of sets of integral $\pi(m,p)$ values, before the correct polytype could be obtained. The characteristic values mentioned above, as computed from $\pi(0,2)$, $\pi(1,3)$ and $\pi(-1,3)$ are given in Table 1 (column 2). In column 4 the corresponding values are given which apply to the polytype present. In columns 5 to 8, values of the cyclicity calculated as advocated by Mardix *et al.* (1970) are given: columns 5 to 7 give the values calculated for three different sets of $|F|^2$ values; in the last column a mean value for $|S|^2$ was used.

Table 1. *Some characteristic values for the polytype with the Zhdanov symbol* $(7\ 7\ 5\ 3)_3$

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$C\,.\,N$	2·3	2	2	5·8	0·8	3·3	2·7
$\alpha\,.\,N$	4·8	4	4	–	–	–	–
[010]	0·3	0	0	–	–	–	–
[101]	0·5	0 or 1	0	–	–	–	–

Column (2) Values obtained from experimental $|S|^2$ values.
(3) Integral values compatible with values (2).
(4) Values for the polytype present.
(5), (6), (7) Values for the cyclicity obtained from one particular set of $|F|^2$ values, respectively, following the method described by Mardix *et al.*, $C\,.\,N \simeq I'-J'$.
(8) Value for the cyclicity obtained from mean values of the sets of $|S|^2$ values, using the formula given by Mardix *et al.*

In order to show the possible influence of experimental errors, we took as a second example a hypothetical polytype with Zhdanov symbol $(10\ 5\ 6\ 2\ 4\ 1\ 2\ 4\ 2\ 2)_3$ for which we calculated theoretical $|S|^2$ values as well as $|F|^2$ values for $(\bar{1}1l)$. Table 2 shows in rows 2 to 5 the result of the calculation of the values $C\cdot N$, $\alpha\cdot$N, [010] and [101] from the $|S|^2$ values. As 'case 1', the $|S|^2$ values were taken without errors. Thus the true values for $C\cdot N$, $\alpha\cdot N$, [010] and [101] result. As cases 2 to 5 statistical errors were introduced as follows: for case 2 and 3 the mean value of these errors was about 30%, for case 4 and 5 about half this value.

The value of $C\cdot N$ must be even, if N is even, and if only the reflexions with $1=3n-1$ are present, $C\cdot N=3n+1$. Thus in our case, only values ... 4, 10, 16, ... need be considered for $C\cdot N$. In case 2 we would be in doubt whether 4 or 10 is correct, in cases 3, 4, and 5 the conclusion $N\cdot C=10$ could have been drawn quite safely.

The last row was calculated in order to test the mode of procedure advocated by Mardix and coworkers. Although for the error-free calculation their approximation is certainly satisfactory, we see that, for example, in case 3 the correct value could not have been deduced unequivocally. Even in case 5, with a mean error of only 15% the true value might have been doubtful.

The figures of Table 2 seem to indicate that in order to obtain values within ± 2 for $C\cdot N$, a mean error of about 20% in $|S|^2$ may be tolerated, if the exact formula is used, whereas the same error in $C\cdot N$ would result from $(I'-J')$ values calculated from $|F|^2$ values with a mean error of only about 12%. If for example 16 sets of $|F|^2$ values are used to calculate the $|S|^2$ values (which is possible in most cases), a mean error of 50% in the $|F|^2$ values would lead to an accuracy in the mean value of $|S|^2$ well below what is required. In cases where the intensity corresponds to $|F|$ rather than $|F|^2$, the intensities would be required to have a mean error of not more than 35 to 40% which is well within possibilities with film methods. Following the procedure advocated by Mardix *et al.*, intensities with an accuracy of about 6% would be required. The accuracy required for an unequivocal determination of $N\cdot C$ rises with increasing N. Thus for smaller N ($N<38$) the margin of error to be tolerated is probably somewhat larger, for larger N it is still smaller.

Table 2. *Some characteristic values for a hypothetical polytype with the Zhdanov symbol* $(10\ 5\ 6\ 2\ 4\ 1\ 2\ 4\ 2\ 2)_3$

	case 1	case 2	case 3	case 4	case 5
$C\,.\,N$	10	6·8	11·7	8·5	10·8
$\alpha\,.\,N$	10	14·4	11·2	12·1	10·6
[010]	0	2·5	1·1	1·2	0·5
[101]	1	2·8	2·1	1·8	1·5
$I'-J'$	11·3	7·7	13·2	9·6	12·2

Case 1 Values obtained from $|S|^2$ values without errors.
2 and 3 Values obtained from $|S|^2$ values with statistical errors of about 30%.
4 and 5 Values obtained from $|S|^2$ values with statistical errors of about 15%.

From the values obtained for $\alpha\cdot N$ which must necessarily be even we may conclude that with a mean error of 30% the true value may be out by as much as 4 from the nearest even value obtained, with a mean error of 15% it still may be out by 2. The numbers of figures '1' in even or odd places of the Zhdanov symbol would obviously require a still more accurate determination of the $|S|^2$ values, because these numbers may take on any integral value. For mean errors of 30% these values may be out by 2 or even 3, with mean error of 15% by 1 or 2 at the most.

Conclusions

A unique determination of a polytype with fairly long period requires as good $|S|^2=|F|^2/|F_0|^2$ values as possible. For this purpose intensities should be measured with fair accuracy and for as many sets of reflexions as possible, so that mean values from several sets of $|S|^2$ values may be obtained. From these values the 'Pattersonian function' $\pi(m,p)$ may be directly calculated with the help of which the entire polytype sequence may be determined as described earlier. Even if the accuracy of the $|S|^2$ values is not sufficient to make this method applicable without a great amount of effort, the cyclicity C, the percentage of hexagonality α, and the

number of figures '1' in the Zhdanov symbol as well as their distribution among the even and odd places of the symbol may be directly obtained with certain limits of error from the values $\pi(0,2)$, $\pi(1,3)$, and $\pi(-1,3)$ obtainable from the set of $|S|^2$ values.

As the examples show, the application of the mode of procedure advocated by Mardix *et al.* may lead to erroneous conclusions for the cyclicity.

References

DORNBERGER-SCHIFF, K. & FARKAS-JAHNKE, M. (1970). *Acta Cryst.* A**26**, 24.

FARKAS-JAHNKE, M. (1966). *Acta Cryst.* **21**, A173.

FARKAS-JAHNKE, M. & DORNBERGER-SCHIFF, K. (1970). *Acta Cryst.* A**26**, 35.

GOMES DE MESQUITA, A. H. (1968). *Acta Cryst.* B**24**, 1461.

MARDIX, S., STEINBERGER, I. T. & KALMAN, Z. H. (1970). *Acta Cryst.* B**26**, 24.

Acta Cryst. (1971). A**27**, 219

A Neutron Diffraction Search for Non-centrosymmetric Thermal Oscillations in Germanium and Silicon*

BY ANTHONY C. NUNES†

Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, *U.S.A.*

(*Received* 2 *March* 1970)

A neutron diffraction study was made of the 222 reflection of germanium and silicon between the temperatures of 25 and 500°C. Care was taken to reduce effects of simultaneous and higher order reflections. Extinction effects were considered, as nearly perfect crystals were employed in the study. Within the sensitivity of the experiment, no 222 neutron intensity was detected. The resulting upper limit placed on β, the cubic atomic potential constant, is roughly one half of a previously suggested value.

Introduction

The inclusion of an anticentrosymmetric potential constant β as a perturbation in the usual Einstein model derivation of the Debye–Waller factor has been used to accurately describe the unique temperature dependence of the strengths of certain reflections of UO_2, CaF_2, and BaF_2 as observed in the neutron diffraction work of Willis (1963*a*,*b*, 1965). Dawson & Willis (1967) have further suggested that the anticentrosymmetric site symmetry of diamond structured crystals also allows the existence of such an anharmonic term in the binding potential experienced by each atom.

In such crystals, inclusion of this term in the derivation of the Debye–Waller factor results in a non-zero structure factor for the forbidden reflections ($h+k+l=4n+2$, $n=0,1,2,\ldots$) of the form

$$F_{hkl}\exp\{-M(T)\}=-i8b\left(\frac{\pi}{a_0}\right)^3\left(\frac{\beta}{\alpha^3}\right)(hkl)(\mathrm{k}T)^2\exp\left\{-\frac{\pi^2\mathrm{k}T}{\alpha}\left(\frac{h^2+k^2+l^2}{a_0^2}\right)\right\} \quad (1)$$

(where β is a small perturbation on the harmonic potential constant α). In the above equation, b is the nuclear scattering length of the atom, a_0 the cube edge, k Boltzmann's constant, T the absolute temperature, and h, k, l, the Miller indices of the reflection involved. The exponential is the harmonic Debye–Waller factor. This structure factor is purely imaginary (from symmetry considerations only; this does not imply an attenuation factor), and is directly proportional to the anticentrosymmetric potential constant β, the product of the Miller indices, and the square of the absolute temperature. The effect should thus be strongest at high temperatures in forbidden reflections of high order.

One may reproduce the above in the formalism of quantum mechanics, by tetrahedrally perturbing a spherical harmonic oscillator. Such an approach predicts a non-zero structure factor when $T=0$°K due to zero state motion. When T is greater than one quarter of the Debye temperature of the materials, however (the Debye temperatures of silicon and germanium reported by Batterman & Chipman (1962) are 543 and 290°K respectively), the classical and quantum mechanical predictions are indistinguishable.

Interaction of the neutrons with the anticentrosymmetrically distributed binding electrons of these materials would also produce Bragg scattering in otherwise forbidden reflections, Such interactions, however, are very weak (Krohn & Ringo, 1966; Obermair, 1967), and can safely be ignored here.

* Work supported by the United States Atomic Energy Commission.

† Present address: Department of Physics, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.