Acta Cryst. (1981). A**37**, 838–842

Application of Modulated Structure Analysis to Polytypes

By Akiji Yamamoto

National Institute for Researches in Inorganic Materials, Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, *Japan*

(*Received* 25 *September* 1980; *accepted* 16 *April* 1981)

Abstract

A new method is used to analyze polytypes of SiC and ZnS by regarding the polytype as a modulated structure with ideal electron-density modulation. To resolve a phase problem appearing in the density modulation, the square of the weighted R factor and a penalty function with some value outside the physically reasonable range of the occupation probability of atoms are minimized simultaneously by the least-squares method. The convergence was very smooth for known structures of $21H$ SiC and $66R$ ZnS polytypes, even though the starting point had large R factors (0·61 and 0·67), and the correct results were automatically obtained.

Introduction

Many polytype structures of SiC and ZnS have been reported so far and a considerable number of them are already known. (See, for example, Verma & Krishna, 1966; Shaffer, 1969.) However, there are many unresolved structures which have large periods. As is well known, the determination of the structure of a SiC (or ZnS) polytype is the problem of determining the stacking sequence of three SiC (ZnS) layers which consist of atoms located at $0,0,z$; $\frac{1}{3},-\frac{1}{3},z$; and $-\frac{1}{3},\frac{1}{3},z$ in the hexagonal unit cell. To analyze such a polytype structure, the trial-and-error or the direct method has so far been used (Verma & Krishna, 1966; Tokonami, 1966; Dornberger-Schiff & Farkas-Jahnke, 1970). For polytypes with long periods, it is not easy to determine the sequence of layers by these methods because of the multitude of sequences of the same period and considerable effort is necessary even in the direct method which is considered to be the most powerful method for the long-period polytypes. The method developed here is very simple and effective as shown in the following. The method is applied to known structures of $21H$ SiC and $66R$ ZnS polytypes to exemplify the analysis based on the new method for cases with space groups $P3m1$ and $R3m$ since almost all polytypes of SiC or ZnS with long periods have these space groups. The periods of these examples are comparatively long. Therefore, the success of automatic analyses for these examples encourages us to expect that analyses of polytypes with longer periods are performed more easily by the application of this method. In the following, the method is explained for the case of SiC. The same method is applicable to ZnS.

Polytype as a modulated structure

All polytypes of SiC have a fundamental hexagonal unit cell with $a = b = 3{\cdot}08$, $c = 2{\cdot}52$ Å except for the trivial cubic case of the Zhdanov symbol $[\infty]$. The coordinates of the atoms are given in terms of these hexagonal axes as

$$\begin{array}{ll} 0,0,\nu;\ \tfrac{1}{3},-\tfrac{1}{3},\nu;\ -\tfrac{1}{3},\tfrac{1}{3},\nu & \text{for Si} \\ 0,0,z+\nu;\ \tfrac{1}{3},-\tfrac{1}{3},z+\nu;\ -\tfrac{1}{3},\tfrac{1}{3},z+\nu & \text{for C} \end{array} \tag{1}$$

with ν and $z = \frac{3}{4}$ independent of the polytype. According to the usual notation, we call these three sites A, B, C in order. We can regard the structure as the modulated structure: Si and C atoms occupy all sites ($\nu = 0, \pm 1, \ldots$) but with the occupation probability of one or zero. Then we have a sequence of occupation probabilities for A, B and C sites. For example, for a simple structure of $6H$ with the stacking sequence $ABCACB\ldots$, the occupation probability for the A site is given by a periodic sequence 100100…, for the B site 010001…, and for the C site 001010…. In general, a structure with period M is designated by three sequences of M digits with one or zero for A, B and C sites. Therefore, this can be regarded as a special case of the density modulations.

Modulated structure analysis of polytypes

As shown by de Wolff (1974), the modulated structure is conveniently described in terms of four-dimensional space. According to his idea, a modulated structure with a long period is described by a structure with short period in the four-dimensional space. The unit vectors in this space are given by $\mathbf{a}_1 = \mathbf{a}$, $\mathbf{a}_2 = \mathbf{b}$, $\mathbf{a}_3 = \mathbf{c} - \mathbf{d}/M$, $\mathbf{a}_4 = \mathbf{d}$, where $\mathbf{d}$ is a unit vector perpendicular to the usual three-dimensional space. Therefore, a vector $\mathbf{x} = x_1\,\mathbf{a} + x_2\,\mathbf{b} + x_3\,\mathbf{c}$ in the three-dimensional space is described by $\mathbf{x} = x_1\mathbf{a}_1 + x_2\mathbf{a}_2 + x_3\mathbf{a}_3 + (x_3/M)\mathbf{a}_4$, that is, x_1, x_2, x_3 are the same as those referring to $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $x_4 = x_3/M$. In this notation, the sequence of occupation probability of the μth site ($\mu = A, B, C$) is

0567-7394/81/060838-05$01.00

represented by $P^\mu(x_4^\mu)$ as a periodic function of $x_4^\mu = (x_3^\mu + \nu)/M$ ($\nu = 1, 2, \ldots, M$, $x_3^\mu = 0$ for Si and $x_3^\mu = \frac{3}{4}$ for C). [We do not specify Si or C because $P^\mu(x_4^\mu)$ has the same value for Si and C in the same layer.]

In the four-dimensional description, the reflection appearing at $h = h_1\mathbf{a}^* + h_2\mathbf{b}^* + (h_3 + h_4/M)\mathbf{c}^*$ (h_4 is an integer within the range $\pm M/2$) in the three-dimensional space is regarded as the projection of a lattice point $h' = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^* + h_4\mathbf{a}_4^*$ in the four-dimensional space, where h_1, h_2, h_3, h_4 are integers and $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$, $\mathbf{a}_4^*$ are the unit vectors reciprocal to $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, $\mathbf{a}_4$ and are given by $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $(1/M)\mathbf{c}^* + \mathbf{d}$. The structure factor at the lattice point $\mathbf{h}'$ in the four-dimensional space is given by (de Wolff, 1974)

$$F'(h_1,h_2,h_3,h_4) = \sum_\mu \int_0^1 \mathrm{d}x_4^\mu f^\mu P^\mu(x_4^\mu) \times \exp 2\pi i \sum_{i=1}^{4} h_i x_i^\mu, \qquad (2)$$

where f^μ is the atomic scattering factor of the μth atom at h in the three-dimensional reciprocal space. When h' is projected onto the three-dimensional space, all the lattice points specified by h_1, h_2, $h_3 - m$, $h_4 + mM$ (m is any integer and h_4 is an integer within the range $\pm M/2$) are projected onto the same point h in the three-dimensional space. Therefore, to obtain the structure factor in the three-dimensional space, these contributions must be summed up. If we sum (2) over all these reflections, the projected structure factor is given by

$$F(h_1,h_2,h_3,h_4) = \frac{1}{M} \sum_\mu \sum_{\nu=1}^{M} f^\mu P^\mu(x_4^\mu) \times \exp 2\pi i \sum_{i=1}^{4} h_i x_i^\mu, \qquad (3)$$

where $x_4^\mu = (x_3^\mu + \nu)/M$ ($x_3^\mu = 0$ for Si and $x_3^\mu = \frac{3}{4}$ for C) and h_4 is an integer within the range of $\pm M/2$.

As mentioned before, $P^\mu(x_4^\mu)$ is a periodic function of x_4^μ, so that this can be expressed in terms of the Fourier series

$$P^\mu(x_4^\mu) = \frac{1}{2} \sum_n \{P_n^\mu \exp(2\pi i n x_4^\mu) + P_{-n}^\mu \exp(-2\pi i n x_4^\mu)\}, \qquad (4)$$

where P_n^μ is the complex amplitude of the nth-order harmonics and P_{-n}^μ is its complex conjugate. Since the structure factor (3) depends only on discrete values of $x_4^\mu = (x_3^\mu + \nu)/M$ ($\nu = 1, 2, \ldots, M$), n up to $M/2$ for even M or up to $(M - 1)/2$ for odd M must be included in (4).

In modulated structure analysis, the R factor is minimized by taking the complex amplitudes as variable parameters. Substituting (4) into (3) and taking the summation with respect to ν, we have the intensity for the reflection $h_1h_2h_3h_4$ except for $h_4 = M/2$ for the even M case with the following expression.

$$I(h_1,h_2,h_3,h_4) = |\sum_\mu f^\mu P_{-h_4}^\mu \exp(2\pi i \sum_{i=1}^{3} h_i x_i^\mu)|^2. \qquad (5)$$

This intensity is invariant for the uniform shift of P_n^μ. If we take different phase shifts for different n, we have different occupation probability giving the same intensity. Therefore, the analysis in which the square of the weighted R factor, $R_w^2 = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$, is minimized does not necessarily lead to correct occupation probability: the refinement may give a physically unreasonable result, that is, the occupation probability exceeds one or is less than zero. This is a general conclusion for the density (or substitutional) modulation (Yamamoto, 1981*a*). However, in the present case, $P^\mu(x_4^\mu)$ at $x_4^\mu = (x_3^\mu + \nu)/M$ ($\nu = 1, 2, \ldots, m$) must be zero or one. Such a restriction makes it possible to determine the phase of P_n^μ and therefore $P^\mu(x_4^\mu)$. One method to obtain the occupation probability (4) is to minimize R_w^2 and the penalty function $\mathrm{PF} = \sum_\nu \{[P^\mu(x_4^\mu) - 1]P^\mu(x_4^\mu)\}^2/M$ simultaneously by the least-squares method since the latter function takes minimum value zero when all the $P^\mu(x_4^\mu)$ ($\nu = 1, 2, \ldots, M$) take one or zero. Another penalty function (PF) takes a value $g^2|P^\mu(x_4^\mu)|^2/M$ for $P^\mu(x_4^\mu) < 0$ and $g^2|P^\mu(x_4^\mu) - 1|^2/M$ for $P^\mu(x_4^\mu) > 1$ and zero otherwise, where g designates the gradient of the penalty function which is taken to be two in the present analysis. Both functions prevent the occupation probability becoming non-physical. These two PF's were tested and the latter gave a good result: the convergence was very smooth and the correct results were automatically obtained. Therefore, the refinements mentioned later were performed with the latter penalty function.

Symmetry

Symmetry of a modulated structure is described by a space group in four-dimensional space. This is a supergroup of the three-dimensional space group (Janner & Janssen, 1977). Therefore, we can consider a four-dimensional space group including the three-dimensional one as a subgroup. In SiC polytypes, the only possible three-dimensional space groups are $R3m$, $P6_3mc$, $P3m1$ (Verma & Krishna, 1966). The four-dimensional space groups corresponding to these space groups are easily obtained with the method proposed by Yamamoto (1981*b*). Corresponding to $R3m$, we have a group generated by $(C_3^+|0,0,0,0)$, $(\sigma_{\nu 1}|0,0,0,0)$ and centering translations $(E|\frac{1}{3},-\frac{1}{3},0,-\frac{1}{3})$, $(E|-\frac{1}{3},\frac{1}{3},0,\frac{1}{3})$, where we use the same symbol for the rotation operator as in the three-dimensional space because the matrix elements of the first 3 × 3 part are the same as the usual matrix representation of the rotation operator, and the translation vector associated with this rotation operator is represented by its $\mathbf{a}_i$ components ($i = 1, 2, 3, 4$) (Yamamoto, 1981*b*). (For the symbol used here, see Bradley & Cracknell, 1972.) Similarly, for $P6_3mc$, we have the corresponding four-dimensional group generated by $(C_6^+|0,0,0,\frac{1}{2})$, $(\sigma_{v1}|0,0,0,0)$, and for $P3m1$ the group generated by $(C_3^+|0,0,0,0)$, $(\sigma_{v1}|0,0,0,0)$. Components of a vector in the four-dimensional space are transformed by a symmetry operator $(R|\tau)$ in the four-dimensional space group as

$$x'_i = \sum_{j=1}^{4} R_{ij} x_j + \tau_i \; (i = 1, 2, 3, 4), \tag{6}$$

where R_{ij} is the ij element of the 3 + 1 reducible matrix (de Wolff, 1974), the $4i$ and $i4$ ($i = 1, 2, 3$) elements of which are zero, and τ_i, the $\mathbf{a}_i$ component of the translation vector. On the other hand, the occupation probability is transformed as

$$P(x'_4) = P(x_4). \tag{7}$$

The symmetry operator transforms an atom into itself or another atom of the same kind. The former case generally restricts the shape of a function $P^{\mu}(x_4^{\mu})$ (though the examples treated here have no restriction) while the latter relates the occupation probability of an atom with that of the other atom (Yamamoto, 1981*b*).

For the case of $R3m$, the centering translation $(E|\frac{1}{3},-\frac{1}{3},0,-\frac{1}{3})$ transforms A, B, C sites into B, C, A sites, respectively. Therefore, from (4), (6), (7), we have

$$P^B(x_4^B) = P^A(x_4^B + \tfrac{1}{3}). \tag{8}$$

This leads to

$$P_n^B = P_n^A \,(\exp 2\pi i n/3) \quad \text{for any } n. \tag{9}$$

Similarly, we have

$$P_n^C = P_n^B \exp(2\pi i n/3) = P_n^A \exp(-2\pi i n/3) \quad \text{for any } n. \tag{10}$$

In particular, this gives $P_{3n}^A = P_{3n}^B = P_{3n}^C$ ($n = 0, 1, \ldots$). Other operators in the four-dimensional space group do not give any additional relation or restriction for the occupation probability.

From similar considerations for the case of $P6_3mc$ we have

$$P_n^C = (-1)^n P_n^B. \tag{11}$$

For $P3m1$, the P_n^{μ} ($\mu = A, B, C$) are independent and not restricted.

In addition to these relations derived from the space-group symmetry, another relation exists for SiC: the occupation probability satisfies the relation $P^A(x_4^A) + P^B(x_4^A) + P^C(x_4^A) = 1$ for all atoms in a layer, where $x_4^A = (x_3^A + \nu)/M$ ($\nu = 1, 2, \ldots, M$). This gives

$$P_0^A + P_0^B + P_0^C = 1 \tag{12}$$

and

$$P_n^A + P_n^B + P_n^C = 0 \quad \text{for } n \geq 1. \tag{13}$$

From (9), (10), (13), we have

$$P_n^A[1 + \exp(2\pi i n/3) + \exp(-2\pi i n/3)] = 0 \quad \text{for } n \geq 1. \tag{14}$$

These relationships give

$$P_0^A = \tfrac{1}{3} \tag{15}$$

and

$$P_{3n}^A = 0 \quad (n = 1, 2, \ldots) \tag{16}$$

for the case of $R3m$, and similar consideration leads to

$$P_{2n+1}^A = 0 \quad (n = 1, 2, \ldots) \tag{17}$$

$$P_{2n}^A + 2P_{2n}^B = 0 \quad (n = 1, 2, \ldots) \tag{18}$$

for $P6_3mc$. Therefore, in these two cases, P_n^A [$n \neq 0$ (mod 3)] and P_n^B ($n \geq 0$) are independent parameters, respectively. On the other hand, two of P_n^A, P_n^B, P_n^C ($n \geq 0$) are independent in the case of $P3m1$. With these parameters, the refinement is made as shown in the following.

Structure refinement

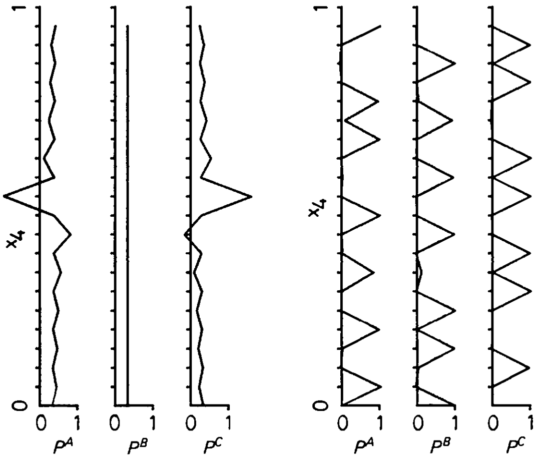
In the refinement of the polytype structure, we calculate, instead of $F(h_1,h_2,h_3,h_4)$, the periodic intensity distribution function $S(h_1,h_2,h_3,h_4)$ which is defined by

$$S(h_1,h_2,h_3,h_4) = \frac{F(h_1,h_2,h_3,h_4)}{F_0(h_1,h_2,h_3,h_4)} M, \tag{19}$$

where $F_0(h_1,h_2,h_3,h_4)$ is the structure factor of the structure consisting of one SiC layer with the period M, and is given by $f^{\text{Si}} + f^{\text{C}} \exp\{3\pi i h_4/2M\}$. $S(h_1,h_2,h_3,h_4)$ is the structure factor for the point atom with one electron located at the Si site and has complete information on stacking sequences. Therefore, this is obtained from (3) by setting $f^{\mu} = 1$. With this structure factor and the least-squares method mentioned before, two cases of $21H$ SiC with space group $P3m1$ and $66R$ ZnS with space group $R3m$ were refined using data given by Inoue, Komatsu, Tanaka & Inomata (1973) and Farkas-Jahnke & Dornberger-Schiff (1969).

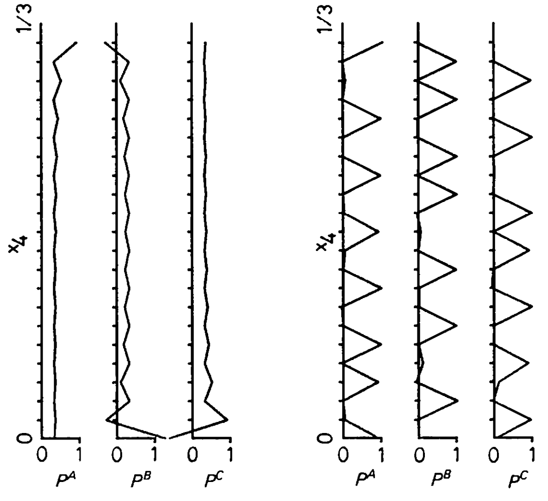
(*a*) $21H$ SiC. $21H$ SiC shows the extinctions $h_1h_2h_3h_4$ with $h_1 - h_2 \neq 0$(mod 3) and $h_4 = 0$. Therefore, from (5) and (12), we have $P_0^A = P_0^B = P_0^C = \frac{1}{3}$. In the least-squares fitting of S_o and S_c, we take the real and imaginary parts of $P_n^A - P_n^B$ and $P_n^A + P_n^B - 2P_n^C$ ($1 \leq n \leq 10$) as independent parameters and the starting point was selected so as to have a value 0·05 or −0·05 for all variable parameters. The usual R factor $R = \sum(|S_o| - |S_c|)/\sum|S_o|$ of this starting point was 0·61. After 20 cycles, we had $R = 0{\cdot}03$, PF = 0·03 and a result with Zhdanov symbol [534333], in agreement with the result of Inoue *et al.* (1973). The occupation probabilities of the initial and final results are shown in Fig. 1.

(*b*) 66*R* ZnS. In this case, $P_0^A = P_0^B = P_0^C = \frac{1}{3}$ and variable parameters are the real and imaginary parts of P_n^A up to $n = 32$ except for $n = 0 (\mathrm{mod}\ 3)$. In the real analysis, non-observed reflections owing to the centering translation are dropped. Then the structure factor can be obtained from atoms at only the *A* site because atoms at the *B* and *C* sites give the same contributions as the *A* site for all observed reflections. The initial parameters were taken as 0·05 or −0·05 for all variable parameters, which gave $R = 0{\cdot}67$. After 15 cycles, we had $R = 0{\cdot}04$, PF = 0·04. The final result showed a structure $[7753]_3$ in accordance with the result of Farkas-Jahnke & Dornberger-Schiff (1969). The initial and final occupation probabilities are shown in Fig. 2. The initial and final parameters of these two cases are given in Tables 1 and 2 and the structure factors are listed in Table 3.



(*a*) (*b*)

Fig. 1. Occupation probabilities of 21 *H* SiC: (*a*) starting point, (*b*) final result. This shows the stacking sequence of *BACBABCACBACBCABACBCA*... represented by the Zhdanov symbol [435333], which is equivalent to [534333] determined by Inoue *et al.* (1973).



(*a*) (*b*)

Fig. 2. Occupation probabilities of 66*R* ZnS: (*a*) starting point, (*b*) final result. This shows the stacking sequence of one third, which is given by *ACBACABCABCACBABCABCBA*. The rest is obtained from this by cyclic replacement of *A*, *B*, *C*. The structure is represented by the Zhdanov symbol $[7735]_3$ which is equivalent to $[7753]_3$ determined by Farkas-Jahnke & Dornberger-Schiff (1969).

Table 1. *The initial and final parameters of the* 21*H* SiC *polytype*

Parameter	Initial value	Final value
$P_0^A = P_0^B = P_0^C$	0·3333	0·3333
$P_1^A - P_1^B$	0·05 − *i*0·05	0·0034 + *i*0·0114
$P_2^A - P_2^B$	−0·05 + *i*0·05	0·0062 + *i*0·0008
$P_3^A - P_3^B$	0·05 − *i*0·05	0·0988 − *i*0·0580
$P_4^A - P_4^B$	−0·05 + *i*0·05	0·0695 + *i*0·0275
$P_5^A - P_5^B$	0·05 − *i*0·05	−0·0693 + *i*0·0445
$P_6^A - P_6^B$	−0·05 + *i*0·05	0·1108 + *i*0·0779
$P_7^A - P_7^B$	0·05 − *i*0·05	−0·4151 − *i*0·1543
$P_8^A - P_8^B$	−0·05 + *i*0·05	−0·1630 − *i*0·0582
$P_9^A - P_9^B$	0·05 − *i*0·05	−0·0857 + *i*0·0803
$P_{10}^A - P_{10}^B$	−0·05 + *i*0·05	−0·0598 + *i*0·1862
$P_1^A + P_1^B - 2P_1^C$	0·05 − *i*0·05	0·0343 − *i*0·0059
$P_2^A + P_2^B - 2P_2^C$	−0·05 + *i*0·05	−0·0097 − *i*0·0436
$P_3^A + P_3^B - 2P_3^C$	0·05 − *i*0·05	0·0181 − *i*0·0443
$P_4^A + P_4^B - 2P_4^C$	−0·05 + *i*0·05	0·0953 + *i*0·1166
$P_5^A + P_5^B - 2P_5^C$	0·05 − *i*0·05	0·0469 + *i*0·0047
$P_6^A + P_6^B - 2P_6^C$	−0·05 + *i*0·05	0·0557 − *i*0·0465
$P_7^A + P_7^B - 2P_7^C$	0·05 − *i*0·05	0·0962 − *i*0·0827
$P_8^A + P_8^B - 2P_8^C$	−0·05 + *i*0·05	−0·0570 + *i*0·1006
$P_9^A + P_9^B - 2P_9^C$	0·05 − *i*0·05	0·0937 − *i*0·0260
$P_{10}^A + P_{10}^B - 2P_{10}^C$	−0·05 + *i*0·05	−0·2008 + *i*0·0383

Table 2. *The initial and final parameters of the* 66*R* ZnS *polytype*

Parameter	Initial value	Final value
P_0^A	0·3333	0·3333
P_1^A	0·05 − *i*0·05	0·0002 + *i*0·0169
P_2^A	−0·05 + *i*0·05	0·0057 − *i*0·0350
P_4^A	0·05 − *i*0·05	−0·0102 − *i*0·0170
P_5^A	−0·05 + *i*0·05	0·0196 − *i*0·0068
P_7^A	0·05 − *i*0·05	−0·0062 + *i*0·0076
P_8^B	−0·05 + *i*0·05	−0·0414 + *i*0·0224
P_{10}^A	0·05 − *i*0·05	−0·0652 − *i*0·0475
P_{11}^A	−0·05 + *i*0·05	0·0411 + *i*0·0239
P_{13}^A	0·05 − *i*0·05	0·0719 + *i*0·0151
P_{14}^A	−0·05 + *i*0·05	−0·0290 + *i*0·0936
P_{16}^A	0·05 − *i*0·05	0·0073 + *i*0·0280
P_{17}^A	−0·05 + *i*0·05	−0·0027 − *i*0·1291
P_{19}^A	0·05 − *i*0·05	0·2120 − *i*0·0239
P_{20}^A	−0·05 + *i*0·05	−0·1024 − *i*0·1965
P_{22}^A	0·05 − *i*0·05	0·1607 + *i*0·0893
P_{23}^A	−0·05 + *i*0·05	0·1627 + *i*0·2742
P_{25}^A	0·05 − *i*0·05	0·2113 − *i*0·1187
P_{26}^A	−0·05 + *i*0·05	0·0446 + *i*0·0048
P_{28}^A	0·05 − *i*0·05	0·1653 + *i*0·0657
P_{29}^A	−0·05 + *i*0·05	−0·2232 − *i*0·0932
P_{31}^A	0·05 − *i*0·05	−0·0563 − *i*0·0825
P_{32}^A	−0·05 + *i*0·05	0·0310 − *i*0·0736

Summary and discussion

A new method for polytype analysis based on the theory of modulated structure is proposed. The method is easier than methods developed previously: the starting point seems to be arbitrary because the convergence was very smooth and the two cases gave the correct results starting from very large R factors. This method is therefore considered to be effective for the polytype analyses of SiC with longer periods or other polytypes.

The smooth convergence seems to be due to the linear dependence of $S(h_1, \ldots, h_4)$ on P_n^μ and a suitable choice of the penalty function. When the penalty function was dropped in the least-squares refinement, the weighted R factor in fact rapidly converged within two or three cycles. In this case, however, some skilled technique is necessary to avoid the coefficient matrix of the normal equation becoming singular because the intensity of the satellite reflection is invariant for the uniform phase shift of the nth-order harmonics in (4) for all the atoms. [This is realized by replacing P_n^μ by $P_n^\mu \times \exp(i\varphi_n)$, where φ_n is a real number independent of μ. It is clear from (5) that the intensity of the nth-order satellite reflections is invariant for such a replacement.] The method used here is as follows. The normal equation is normalized so that all the diagonal terms of the coefficient matrix are equal to one. After that, the damping factor is introduced by assigning the same value (0·01–0·5) to all the diagonal elements. This effectively functions to make a non-positive matrix positive and to turn the search direction towards the direction of steepest descent (see Kowalik & Osborne, 1968). By introducing this damping factor, it is possible to avoid the appearance of the singular matrix in the minimization of only R_w^2. In particular, if we take small amplitudes for all P_n^μ, $P^\mu(x_4^\mu)$ at all $x_4^\mu = (x_3^\mu + v)/M$ ($v = 1, 2, \ldots, M$) must be within the physical range, that is, $0 \leq P^\mu(x_4^\mu) \leq 1$. In that case, the penalty function is equal to zero, so that the introduction of the damping factor is inevitable to proceed with the refinement. In other cases, the penalty function may become zero at some step in the middle of the refinement. Therefore, it is desirable to introduce the damping factor in all the processes of the refinement for safety. Throughout the present analysis, a damping factor of 0·05 was used.

The present work gives a new method of analyzing SiC polytypes. The method is general, so that it is applicable to the other polytypes recognized as one-dimensionally modulated structures without displacive modulation. If the polytype includes the displacement modulation, the usual method of modulated structure analysis will be applicable (Yamamoto 1981*a*,*b*) because the phase of P_n^μ can, in principle, be determined owing to the presence of the displacive modulation.

The author thanks Dr Z. Inoue for drawing his attention to the properties of SiC.

Table 3. *The observed and calculated structure factors,* $|S(100h_4)|$ *of* 21 *H* SiC *and* $|S(010h_4)$ *of* 66*R* ZnS *polytypes* (×10)

21*H*			66*R*		
h_4	S_o	S_c	h_4	S_o	S_c
−10	38	37	−31	34	33
−9	45	45	−28	61	59
−8	70	68	−25	84	80
−7	50	49	−22	62	60
−6	48	47	−19	70	71
−5	27	27	−16	9	9
−4	44	42	−13	25	24
−3	35	32	−10	28	26
−2	16	15	−7	2	4
−1	13	13	−4	5	6
0	0	0	−1	4	6
1	10	9	2	11	12
2	13	13	5	6	7
3	17	17	8	16	15
4	57	55	11	16	16
5	13	13	14	34	33
6	6	6	17	44	43
7	119	117	20	75	73
8	6	8	23	105	105
9	31	28	26	14	15
10	99	97	29	85	80
			32	26	26

References

BRADLEY, C. J. & CRACKNELL, A. P. (1972). *The Mathematical Theory of Symmetry in Solids*, p. 37. Oxford: Clarendon Press.

DORNBERGER-SCHIFF, K. & FARKAS-JAHNKE, M. (1970). *Acta Cryst.* A**26**, 24–34.

FARKAS-JAHNKE, M. & DORNBERGER-SCHIFF, K. (1969). *Acta Cryst.* A**25**, 35–41.

INOUE, Z., KOMATSU, H., TANAKA, H. & INOMATA, Y. (1973). *Proceedings of the 3rd International Conference on Silicon Carbide at Miami, Florida*, edited by R. C. MARSHALL, H. W. FAUST JR & C. E. RYAN, pp. 119–196. Univ. of South Carolina Press.

JANNER, A. & JANSSEN, T. (1977). *Phys. Rev. B*, **15**, 643–658.

KOWALIK, K. & OSBORNE, M. R. (1968). *Methods for Unconstrained Optimization Problems*. New York: Elsevier.

SHAFFER, P. T. B. (1969). *Acta Cryst.* B**25**, 477–487.

TOKONAMI, M. (1966). *Mineral. J.* **4**, 401–423.

VERMA, A. R. & KRISHNA, P. (1966). *Polymorphism and Polytypism in Crystals*. New York: John Wiley.

WOLFF, P. M. DE (1974). *Acta Cryst.* A**30**, 777–785.

YAMAMOTO, A. (1981*a*). Submitted to *Acta Cryst.*

YAMAMOTO, A. (1981*b*). Submitted to *Acta Cryst.*