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A Novel Determination of the Structure of An Anomalous Polytype of Silicon Carbide

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This paper describes an unusual silicon carbide crystal of special crystallographic interest. During the growth of this crystal there has occurred a change in the structure, from one region of the crystal to another, without a change of space group ($P3m$) or of the dimensions of the unit cell. The crystal has been identified as type $36H$ (Ramsdell notation) and its two structures, designated as $36H_a$ and $36H_b$, form respectively the upper and lower portions of a single crystal piece.

In addition to the usual extinctions inherent in all silicon carbide structures, the X-ray diffraction photographs of $36H_b$ show striking structural extinctions. In the $10.l$ row the reflexions $l=6n\pm2$ (n any positive or negative integer) have zero intensity; this imposes on the structure, the conditions

$$\sum_{z_A} \exp\,[2\pi i(6n\pm2)z] = \sum_{z_B} \exp\,[2\pi i(6n\pm2)z] = \sum_{z_C} \exp\,[2\pi i(6n\pm2)z] = 0\ .$$

From these, by working backwards in a novel way, the structure has been uniquely determined.

The polytype has an unexpected structure with the Zhdanov symbol (333334333332), which has been confirmed by the excellent agreement between the observed and calculated relative intensities of X-ray reflexions. The growth of this structure is discussed on the existing theories of polytypism, and it is concluded that none of them is able to provide a completely satisfactory explanation for the growth of the crystal.

Introduction

In a previous paper (Krishna & Verma, 1963) we reported on a group of silicon carbide structures which show anomalies that cannot be explained on Frank's screw dislocation theory of polytypism (Frank, 1951). One of the new polytypes discussed therein was $36H$; it was apparent that the structure of this polytype would have considerable significance on account of the fact that its unit cell is an integral multiple of the unit cell of the $6H$ structure on which it is based. However, no structure based on the usual considerations employed in silicon carbide structure work could account for the intensity distribution observed on the X-ray diffraction photographs of this crystal. Unlike other known structures of silicon carbide, this polytype does not fit into any of the expected structure series.

In addition, the crystal showed several features of special crystallographic interest. It was discovered that in the same parent single-crystal piece there coexist two different structures having the same space group and unit cell dimensions. Further, one of these structures revealed numerous and striking structural extinctions on its X-ray diffraction photographs. It was therefore considered that a clue to this structure might lie in these extinctions. We have succeeded in determining the structure by a novel method employing the structural extinctions. This is perhaps a unique case where the structure of a crystal has been worked out almost entirely from a consideration of the structural extinctions observed on its X-ray diffraction photographs. The structure so determined has been confirmed by comparing calculated relative intensities of X-ray reflexions with those observed on Weissenberg photographs. The structure and growth of this polytype are discussed below.

Experimental observations

The polytype $36H$ was discovered in a mass of commercial silicon carbide, as a single-crystal piece with

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a well-developed shining (0001) face about $1{\cdot}0 \times 0{\cdot}5$ mm^2 in size. The upper and lower parts of this crystal piece were found to have different structures. The $10.l$ row of spots as recorded on c-axis oscillation photographs taken from (1) the composite $36H$ crystal, (2) the upper part $36H_a$, and (3) the lower part $36H_b$ are reproduced in Figs. 1, 2 and 3 respectively and reveal the existence of two different structures within the same single-crystal piece without a change in the periodicity of the lattice. The shape of the spots obtained is discussed in a previous paper (Krishna & Verma, 1963) where it was shown that the two structures, designated $36H_a$ and $36H_b$, belong to the trigonal system with a space group $P3m$ and have the same unit cell dimensions

$$a = b = 3{\cdot}078 \text{ Å}, \quad c = 90{\cdot}65 \text{ Å}.$$

Figs. 4 and 5 show the complete $10\ l$, $20\ l$ and $30.l$ rows of spots as recorded on the zero-layer, a axis, Weissenberg photographs of $36H_a$ and $36H_b$ respectively. The number of layers of structure in the unit cell of each type can be confirmed by counting the number of spacings after which the sequence of relative intensities begins to repeat in the $10\ l$ row. It is, of course, necessary to take into account the absent reflexions as well. Details of this method have been described in the previous publication.

The oscillation and Weissenberg photographs of $36H_b$ show very unusual and interesting structural extinctions. Thus from the Weissenberg photograph of $36H_b$ (Fig. 5), considering the left side of the $10\ l$ festoon to correspond to l positive, we have the following extinctions for the $10.l$ reflexions

$$l = 36n, \quad 6n \pm 2 \quad \text{and} \quad 36n + 6$$

where $\pm n = 0, 1, 2, \ldots$.

The same may also be confirmed from the $01.l$ row recorded on the first-layer equi-inclination Weissenberg photograph (Fig. 6) where the spots are better resolved. The intensities $I_{10.l}$ and $I_{01.l}$ are identical for a SiC polytype.

Determination of structure

The structure factor

Assuming Ott's binary tetrahedral model of silicon carbide (Ott, 1925), the carbon atoms in all silicon carbide polytypes are displaced relative to the silicon atoms through $00p$, where $p = 3/4n$ for a polytype nH or nR. For such a close-packed structure all the Si and C atoms lie on the three symmetry axes A: $[00z]$, B: $[00z]\frac{1}{3}, -\frac{1}{3}$ and C: $[00z] -\frac{1}{3}, \frac{1}{3}$ (Niggli's notation). Consequently, the structure factor F for any SiC polytype nH or nR is given by

$$F = [f_{\mathrm{Si}} + f_{\mathrm{C}} \exp(2\pi i p l)][P + Q \exp(2\pi i \tfrac{1}{3}(h-k)) + R \exp(-2\pi i \tfrac{1}{3}(h-k))] \quad (1)$$

where

$$P = \sum_{z_A} \exp(2\pi i l z_A/n), \quad Q = \sum_{z_B} \exp(2\pi i l z_B/n),$$
$$R = \sum_{z_C} \exp(2\pi i l z_C/n)$$

and z_A/n, z_B/n, z_C/n are z coordinates of Si atoms along A, B, and C respectively.

It can be readily seen that when

$$h - k = 3r, \quad (r \text{ any integer}) \quad (2)$$

then

$$F = [f_{\mathrm{Si}} + f_{\mathrm{C}} \exp(2\pi i p l)] \left[\sum_{z=0}^{n-1} \exp(2\pi i l z/n)\right] = 0$$

except when $l = 0, n, 2n, \ldots$ *etc.* Hence the reflexions $00.l$, $11.l$, $30\ l$ *etc.*, satisfying the conditions (2) would be absent except when $l = 0, n, 2n, \ldots$ *etc.* These structural extinctions are, therefore, inherent in all silicon carbide structures and can be observed on the Weissenberg photographs of $36H_a$ and $36H_b$ also (Figs. 4, 5 and 6). The extinctions observed along the $10.l$ row of type $36H_b$ do not belong to this class and are peculiar to this polytype alone. It would also be noticed that the exponential part of F is the same for the reflexions $10.l$, $20\ \bar{l}$, $21.l$ *etc.*, for the same value of l (positive as well as negative). The only difference in the intensity of these spots would be due to a variation in f_{Si} and f_{C}. It follows that the relative intensities along these rows would be very similar. It would, therefore, suffice to compare the calculated and relative intensities of $10.l$ reflexions alone, to determine the validity of a proposed structure. This was first pointed out for a rhombohedral polytype, $21R$, by Ramsdell (1944).

The structure factor for the $10.l$ row of spots is given by

$$F_{10.l} = (f_{\mathrm{Si}} + f_{\mathrm{C}} \exp(2\pi i p l))[P + Q \exp(2\pi i/3) + R \exp(-2\pi i/3)]. \quad (3)$$

It has been shown (Krishna & Verma, 1963) that the sequence of relative intensities of $10.l$ reflexions for a polytype nH or nR is similar after a change of n in the l value. For this reason, and on account of the characteristic intensity variations in the $10.l$ row of a polytype, it suffices to compare the calculated and observed relative intensities of spots from 10.0 to $10.n$ alone. However, some of the spots in the larger θ range may not be recorded on the photographs owing to the small value of f_{Si} and f_{C}; hence it is advisable to compare the calculated and observed intensities of spots from 10.0 to $10.\overline{n}$ as well.

Derivation of probable structures

The polytype $36H_a$ appears to have a proportion of $36\mathrm{H}_b$ mixed in it since X-ray diffraction photographs taken from different fragments of $36H_a$ show slightly different relative intensities. The structure of $36H_a$ is therefore not discussed here. The polytype $36H_b$ held our interest on account of the unusual structural extinctions it displays. These extinctions show that

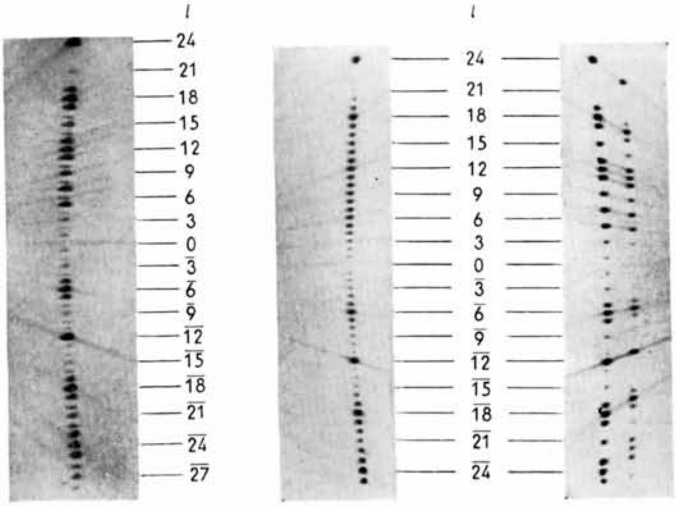

Fig. 1.
The parent $36H$ crystal.

Fig. 2.
Type $36H_a$.

Fig. 3.
Type $36H_b$.

Figs. 1, 2, and 3. The $10.l$ row of spots recorded on 15° c-axis oscillation photographs with Cu K radiation (filtered for Figs. 1 and 2) and a camera of radius 3 cm (all × 2).

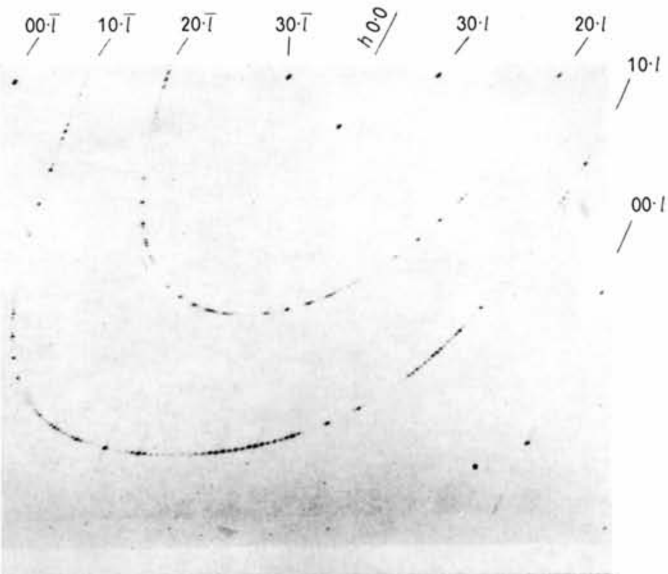

Fig. 4. Zero-layer a-axis Weissenberg photograph of $36H_a$ taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm. The lowest 'festoon' records the $10.l$ row of spots, the missing spot near the minima of the festoon being 10.0 (× 1).

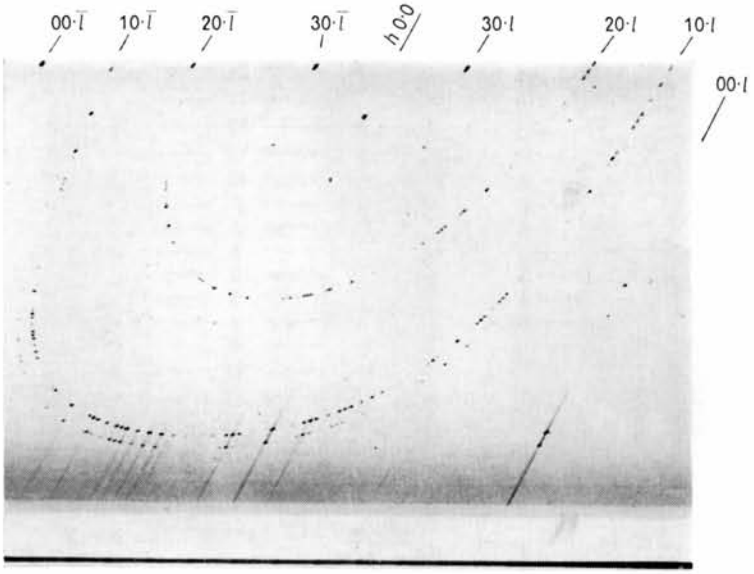

Fig. 5. Zero-layer *a*-axis Weissenberg photograph of $36H_b$ taken with Cu *K* radiation on a camera of diameter 5·73 cm. The lowest festoon records the $10.l$ row of spots, the four faint spots near the minima of the festoon being, from left to right, 10·3, 10·1, 10·1 and $10\cdot\bar{3}$ (× 1).

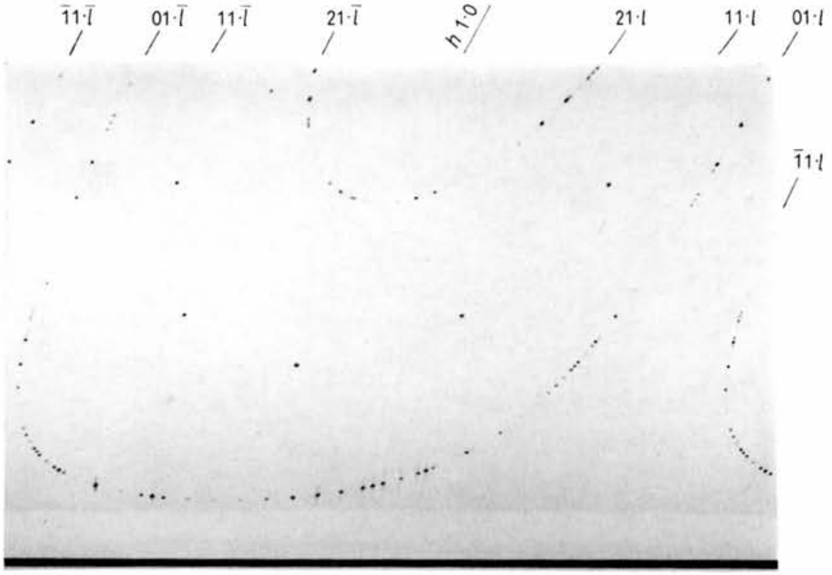

Fig. 6. First-layer *a*-axis equi-inclination Weissenberg photograph taken with Cu $K\alpha$ radiation on a camera of diameter 5·73 cm. The lowest 'festoon' records the $01.l$ row of spots, the four spots near the minima of the festoon being, from left to right, $01\cdot\bar{3}$, $01\cdot\bar{1}$, 01·1 and 01·3 (× 1).

the polytype $36H_b$ is a pure structure free from any $36H_a$. The absence of the reflexions $36n+6$ eliminates any possibility of a coalescence with $6H$ which would otherwise have been difficult to detect. The absence of any diffuse streak along the $10.l$ row of spots indicates the high degree of order present in this crystal.

The structure of this polytype was first attempted by the usual methods employed in silicon carbide structure work (Ramsdell, 1947; Zhdanov & Minervina, 1945; Krishna & Verma, 1962*a*, *b*). Almost all the known SiC structures have a Zhdanov symbol (Zhdanov, 1945) consisting of a number 33, 22 or 23 units with faults at the end. Considering that the X-ray diffraction photographs obtained from $36H_b$ (Figs. 3, 5 and 6) reveal intense reflexions in most $6H$ positions, a large number of structures based on the $6H$ phase, like $(33)_4 3432$, $(33)_3 242424$, $(33)_3 322344$, *etc.*, were tried. None of these could account for the intensity-distribution observed along the $10.l$ row of type $36H_b$. It thus became evident that the structure does not belong to any of the usual structure series. Attempts were therefore made to find a clue to the structure from the observed extinctions.

It is evident from (3) that for a $10.l$ reflexion to be absent

$$P+Q\exp(2\pi i/3)+R\exp(-2\pi i/3)=0$$

whence, equating real and imaginary parts to zero,

$$P=Q=R\,. \qquad (4)$$

The extinction of $10.l$ reflexions, when $l=36m$ requires

$$n_A=n_B=n_C \qquad (5)$$

where n_A, n_B and n_C denote the number of atoms on A, B and C respectively. Hence the structure has 12 silicon and 12 carbon atoms on each of the symmetry axes.

Now since the reflexions $10.(6m\pm2)$ are absent, we have from (4) by writing $6m\pm2=q$:

$$(P)_{l=q}=(Q)_{l=q}=(R)_{l=q}=\tfrac{1}{3}(P+Q+R)_{l=q}\,.$$

But

$$(P+Q+R)_{l=q}=\sum_{z=0}^{35}\exp(2\pi iqz/36)=0 \text{ since } q\neq36n\,.$$

Hence

$$\sum_{z_A}\exp(2\pi iqz_A/36)=\sum_{z_B}\exp(2\pi iqz_B/36)$$
$$=\sum_{z_C}\exp(2\pi iqz_C/36)=0\,. \qquad (6)$$

The problem of determining the structure, therefore, reduces to that of selecting three sets, z_A, z_B and z_C of 12 numbers each, from the 36 numbers $0, 1, 2, \ldots, 35$ such that condition (6) is satisfied. For this, z_A, z_B and z_C must be arranged in a partial periodic way; thus each must be given by a series of the kind

$$z_r,\ z_r+m,\ z_r+2m,\ \ldots,\ z_r+\nu_0 m\,.$$

Then the term $(P)_{l=q}$ may be represented as follows:

$$(P)_{l=q}=\sum_r\exp(2\pi iqz_r/36)\sum_{\nu=0}^{\nu_0}\exp[2\pi i\nu m(\tfrac{1}{6}n\pm\tfrac{1}{18})]=0\,.$$

This will be true for all values of n only if it is independent of n. For this we must have

$$m=6t \quad (t=\text{integer})$$

whence

$$\sum_{\nu=0}^{\nu_0}\exp(\pm2\pi i\nu t/3)=0\,.$$

This has two solutions*

$$(1)\ t=1,\ \nu_0=2; \quad (2)\ t=2,\ \nu_0=2\,.$$

The second one would require every layer to repeat after 12 layer spacings and, since 12 × 3 = 36, this would reduce the z period of the lattice by a factor of $\frac{1}{3}$. It, therefore, affords no solution. The first one requires three layers at z_i, z_i+6, and z_i+12. This is quite possible and means that each set z_A, z_B and z_C consists of 12 numbers of the kind $\alpha, \beta, \gamma, \delta, \alpha+6, \beta+6, \gamma+6, \delta+6, \alpha+12, \beta+12, \gamma+12$ and $\delta+12$; where α, β, γ and δ are different for the three sets.

We shall now assume the following limitations commonly used in silicon carbide structure work:

(i) That the interval between successive Si (or C) atoms along any of the three symmetry axes A, B or C is limited to 2, 3 or 4 layer spacings only (Ramsdell, 1945). This would mean that if the numbers in each set z_A, z_B or z_C are arranged in increasing order, no two consecutive numbers will differ by anything other than 2, 3 or 4. No structures of SiC so far known contradict this condition though no theoretical reason has yet been assigned for this limitation.

(ii) That the zigzag sequence, or Zhdanov symbol, does not contain the number 1. All structures so far known agree with this except type $2H$ with a sequence (11). But type $2H$ is not found in commercial silicon carbide and has been synthesized only by the method of gaseous cracking (Adamsky & Merz, 1959). Since the present crystal under investigation was found in a commercial sample it is reasonable to apply the above limitation.

Now the unit cell of type $36H_b$ is made up of 36 unit layers of structure, each layer occupying one of the three possible positions A, B or C, analogous to close-packed layers of spheres (Zhdanov & Minervina, 1945). Let the origin be chosen on a silicon atom at

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* We are grateful to Dr Behari Sharan who showed that with $\theta_n=2\pi(6n\pm2)r_n/36$

$$\sum_{n=1}^{3}\cos\theta_n=\sum_{n=1}^{3}\sin\theta_n=0\,,$$

if

$$r_3-r_2=r_2-r_1=6\,,$$

which suggested the proof given here. Dr Sharan's proof is given in the Appendix.

which there is a 'stacking reversal', so that the sequence of layers A, B and C changes from anticyclic to cyclic. Then since the smallest number in the Zhdanov sequence is 2, the 34th, 35th, 0th, 1st and 2nd layers in the unit cell may be written down as C, B, A, B, and C respectively. It is evident that the condition on the sets z_A, z_B and z_C, as derived from (6), would require the first 18 layers in the unit cell to be represented by a thrice repeated sequence of 6 letters starting with ABC. Similarly the next 18 layers would be represented by another sequence of 6 letters repeated three times.

To derive the possible ABC sequences for the first 18 layers, consider Table 1, which tabulates the numbers 0, 1, 2, ..., 17 along 3 rows and 6 columns. Each column is to be assigned one of the three letters A, B or C, subject to the conditions (i) and (ii) stated above. As discussed earlier the choice of origin assigns to the first three columns the letters A, B and C respectively. Since a letter cannot follow itself column VI cannot be A and column IV must be either A or B.

Table 1. *Possible ABC sequences: first* 18 *layers*

	Column						
	I	II	III	IV	V	VI	
	0	1	2	3	4	5	
	6	7	8	9	10	11	
	12	13	14	15	16	17	
(*a*)	*A*	*B*	*C*	*A*	*B*	*C*	Possible sequences
(*b*)	*A*	*B*	*C*	*A*	*C*	*B*	
(*c*)	*A*	*B*	*C*	*B*	*A*	*C*	

If it is A then two possibilities result: (*a*) and (*b*). If column IV is B then column V must be A since two A's cannot be separated by more than 4 layer spacings. Column VI then cannot be B as this would involve a number 1 in the zigzag sequence. Of the three possibilities (*a*), (*b*) and (*c*), the first one would cause the Zhdanov symbol to have a number 17 or more, and is, therefore, highly improbable. Thus only two possible arrangements for the first 18 layers need to be considered:

1. $(ABCACB)_3$ and 2. $(ABCBAC)_3$.

Now consider the next 18 layers in the unit cell. To derive the possible ABC sequences for these the numbers 18, 19, 20, ..., 35 are tabulated in Table 2, in a manner similar to Table 1. In the first 18 layers there are 6 A's, 6 B's and 6 C's and, therefore, from equation (5) we have that the next 18 layers must also consist of 6 A's, 6 B's and 6 C's. It follows that the six columns in Table 2 have to be filled with 2 A's, 2 B's and 2 C's. As discussed earlier, with the present choice of origin the 34th and 35th layers in the unit cell are C and B. Columns V and VI are filled accordingly. Proceeding in a manner similar to that in Table 1, only four different possibilities are obtained, (*a*), (*b*), (*c*) and (*d*), subject to the conditions (i) and (ii) cited earlier (see Table 2). Of these, (*c*) is highly improbable since it would involve a number 18 in the Zhdanov symbol. We are therefore left with the following probable sequences for the last 18 layers in the unit cell:

Table 2. *Possible ABC sequences: second* 18 *layers*

	Column							
	I	II	III	IV	V	VI		
	18	19	20	21	22	23		
	24	25	26	27	28	29		
	30	31	32	33	34	35		
(*a*)	*A*	*C*	*A*	*B*	*C*	*B*	*A*	Possible sequences
(*b*)	*C*	*A*	*B*	*A*	*C*	*B*	*A*	
(*c*)	*A*	*C*	*B*	*A*	*C*	*B*	*A*	
(*d*)	*A*	*B*	*C*	*A*	*C*	*B*	*A*	

1. $(ACABCB)_3$. 2. $(CABACB)_3$. 3. $(ABCACB)_3$.

To obtain the probable sequences for the whole unit cell, each of these has to be coupled with the two sequences derived for the first 18 layers. One obtains five possible combinations:

1. $(ABCACB)_3(ACABCB)_3$.
2. $(ABCACB)_3(CABACB)_3$.
3. $(ABCACB)_3(ABCACB)_3$.
4. $(ABCBAC)_3(ACABCB)_3$.
5. $(ABCBAC)_3(ABCACB)_3$.

Of these, (3) represents merely the $6H$ structure and (4) involves a number 1 in the zigzag sequence. Both these are therefore ruled out. The other three sequences have the Zhdanov symbols:

(1) 333334333332 ,
(2) 333332333334 and (3) 233333433333 .

It will be seen that all the three represent the same structure and differ only because of a shift of origin. There is thus only one probable structure for $36H_b$, namely, 333334 333332.

Calculation of intensities

The ABC sequence of the postulated structure is

ABCACBABCACBABCACB
↓
ACABCBACABCBACABCB

and it shows a centre of symmetry for the silicon atoms, at the atom marked by an arrow. Shifting the origin to this atom one obtains the sequence of layers in the new unit cell as

ABCBACABCBACABCBAC
ABACBCABACBCABACBC ,

for which

$$z_A = 0,\ 4,\ 6,\ 10,\ 12,\ 16,\ 18,\ 20,\ 24,\ 26,\ 30,\ 32$$

$$z_B = 1,\ 3,\ 7,\ 9,\ 13,\ 15,\ 19,\ 22,\ 25,\ 28,\ 31,\ 34$$

$$z_C = 2,\ 5,\ 8,\ 11,\ 14,\ 17,\ 21,\ 23,\ 27,\ 29,\ 33,\ 35$$

The intensity formula for a $10.l$ reflexion then simplifies to

$$I_{10.l} \propto (f_{\mathrm{Si}}^2 + f_{\mathrm{C}}^2 + 2 f_{\mathrm{Si}} f_{\mathrm{C}} \cos 2\pi l p)$$
$$\times \left[1 + \cos l\pi + 2 \sum_{z_A > 0}^{<18} \cos \frac{2\pi l z_A}{36} + 2 \sum_{z_B} \cos \frac{2\pi}{36} (l z_B + 12) \right]^2 .$$

The intensity values obtained from this were multiplied by the Lorenz-polarization factor $(1 + \cos^2 2\theta / \sin 2\theta)$ where θ is the Bragg angle.

The relative intensities so obtained are tabulated in Table 3 together with the visually estimated values.

Table 3. *Calculated and observed relative intensities* (I) *of* 10 l *reflexions*

l	I_c	I_o	l	I_c	I_o
1	2·0	2	$\bar{1}$	1·6	1·5
2	0	0	$\bar{2}$	0	0
3	4·9	5	$\bar{3}$	2·6	2·5
4	0	0	$\bar{4}$	0	0
5	51·7	60	$\bar{5}$	17·1	18
6	0	0	$\bar{6}$	117·6	110
7	85·5	86	$\bar{7}$	15·3	16
8	0	0	$\bar{8}$	0	0
9	26·8	30	$\bar{9}$	1·9	2
10	0	0	$\overline{10}$	0	0
11	107·4	95	$\overline{11}$	1·0	1
12	75·1	70	$\overline{12}$	300·0	300
13	87·6	80	$\overline{13}$	1·0	1
14	0	0	$\overline{14}$	0	0
15	15·2	14	$\overline{15}$	2·0	2
16	0	0	$\overline{16}$	0	0
17	34·3	32	$\overline{17}$	18·6	20
18	158·7	140	$\overline{18}$	158·7	150
19	14·9	15	$\overline{19}$	27·5	30
20	0	0	$\overline{20}$	0	0
21	1·1	1	$\overline{21}$	8·1	8
22	0	0	$\overline{22}$	0	0
23	0·4	0·5	$\overline{23}$	33·9	35
24	100·7	90	$\overline{24}$	25·2	25
25	0·3	0	$\overline{25}$	32·5	35
26	0	0	$\overline{26}$	0	0
27	0·5	0·5	$\overline{27}$	7·1	7
28	0	0	$\overline{28}$	0	0
29	3·9	4	$\overline{29}$	21·8	25
30	29·5	25	$\overline{30}$	0	0
31	4·3	4	$\overline{31}$	13·1	14
32	0	0	$\overline{32}$	0	0
33	0·7	0·5	$\overline{33}$	1·3	1
34	0	0	$\overline{34}$	0	0
35	0·5	0·5	$\overline{35}$	0·6	0·5
36	0	0	$\overline{36}$	0	0

The quantitative estimation of observed intensities was done from Weissenberg photographs, by the method described in an earlier publication (Krishna & Verma, 1962*b*). The excellent agreement between the calculated and observed relative intensities establishes the postulated structure.

Atomic coordinates

The coordinates of atoms in the unit cell of the polytype $36H_b$ are as follows:

12 Si at $0, 0, t/36$ where
$t = 0, 4, 6, 10, 12, 16, 18, 20, 24, 26, 30, 32$
12 Si at $\frac{1}{3}, \frac{2}{3}, t/36$ where
$t = 1, 3, 7, 9, 13, 15, 19, 22, 25, 28, 31, 34$
12 Si at $\frac{2}{3}, \frac{1}{3}, t/36$ where
$t = 2, 5, 8, 11, 14, 17, 21, 23, 27, 29, 33, 35$
36 C at $0, 0, \frac{1}{48}$ plus the coordinates of the 36 Si atoms.

Discussion

The polytype $36H$ is a unique crystal within which there has occurred a transition in the structure without affecting the periodicity of the lattice. This is similar to the observations of Edwards & Lipson (1942) and Wilson (1942) in cobalt, where 'the structure possesses a lattice in which the unit cells are all of the same size and shape but the distribution of atoms within the unit cell varies throughout the crystal,' with the difference that the distribution of atoms in this case appears to have changed more or less abruptly, across a certain (0001) plane. Any theory of growth must not only account separately for the growth of the two structures $36H_a$ and 36H$_b$ but also for the transition from the one to the other.

The structure of type $36H_b$ differs from the other known structures of silicon carbide in many important respects and this is perhaps the first instance where a structure could be determined almost entirely from a consideration of the structural extinctions noticed in its X-ray diffraction photographs. The structure (333334333332) does not fit into any of the silicon carbide structure series formulated by Ramsdell (1947), Mitchell (1957) and others. Almost all the silicon carbide structures known so far have a zigzag sequence consisting of a series of 33, 23 or 22 units with faults at the end of the sequence. The discovery of this structure with a sequence (333334333332) shows that faults may occur in the middle of a sequence as well, resulting in a series of structures of the type $[(33)_n 34 (33)_m 32]$. Tomita (1960) has reported a polytype $174R$ with a structure $[(33)_2 36 (33)_5 43]$ which also has faults in the middle of a 33 sequence. This increases considerably the configurations possible in silicon carbide and structure work in future should take these into consideration.

According to the polymer theory of the growth of silicon carbide polytypes (Ramsdell & Kohn, 1952) only two polymers can coexist at a time in a certain temperature range. The structure $[(33)_2 34 (33)_2 32]$ includes three different polymers 33, 34 and 32 and is thus at variance with the above theory. None of the silicon carbide structures determined so far has all the three numbers 2, 3 and 4 in its zigzag sequence; the discovery of the structure $36H_b$ shows that such structures, though rare, are actually possible. The zigzag sequence of the structure is, however, limited to 2, 3 and 4, like most other polytypes.

The X-ray diffraction photographs of $36H_b$ do not reveal any diffuse streak connecting the $10.l$ row of spots, indicating a high degree of order in the crystal. According to the disorder theory of polytypism (Jagodzinski, 1954) it is increasingly improbable for polytypes of larger periodicity to have a completely ordered structure. The larger the periodicity, the smaller is the contribution of the vibration entropy to the total entropy of the structure and the greater is the probability of random faults. Indeed as we have discussed in an earlier paper (Krishna & Verma, 1963), the creation of large polytypes like $36H$, $54H$, $66H$, $126R$, $111R$, $90R$, *etc.*, with a completely ordered structure is, therefore, contrary to the expectations of the disorder theory of polytypism.

Since the polytypes $36H$ give intense X-ray diffraction spots at the $6H$ positions they were believed to be based on the $6H$ phase. This has been confirmed by the predominance of the 33 group in the structure of $36H_b$. For the growth of a $36H$ structure from a single screw dislocation, according to the ideas of Frank (1951), the exposed ledge should consist of 36 layers; but a ledge of 36 layers, exposed in a $6H$ structure, would necessarily cause further growth of type $6H$ itself, the Burgers vector being an integral multiple of the basic unit. However, the structure (333334333332) can be considered to result from the cooperation of two sufficiently close screw dislocations, one with a Burgers vector 19 layers high and the other with a Burgers vector 17 layers high. The exposed ledges of the two dislocations should have the sequences 333334 and 333332 which by themselves would have created the already discovered types $57R$ (Krishna & Verma, 1962*a*) and $51R$ (Zhdanov & Minervina, 1945) respectively. But it is difficult to understand how such a system of cooperating dislocations could in the later stages generate a different structure, $36H_a$. Moreover, the (0001) face of $36H$ would be expected to show a growth spiral with a step height of the order of 90 Å, which ought to be easily observable; but a careful examination of the smooth, shining, plane (0001) face of this crystal under the Vicker's projection phase-contrast microscope failed to reveal any spiral markings on the surface. We are thus led to conclude that this crystal has not grown by the screw dislocation mechanism. None of the existing theories of polytypism is thus able to provide a completely satisfactory explanation for the growth of this crystal.

APPENDIX

By Behari Sharan

Let the conditions

$$\sum_{n=1}^{3} \cos (2\pi/36)qr_n = 0 \qquad (A1)$$

$$\sum_{n=1}^{3} \sin (2\pi/36)qr_n = 0 \qquad (A2)$$

be simultaneously true for a set of 3 integers, r_1, r_2, and r_3. It is required to find a relation between r_1, r_2 and r_3. Let

$$r_1 = \alpha,\ r_2 = \alpha + \beta_1 \text{ and } r_3 = \alpha + \beta_2 .$$

Then writing $2\pi/36 = 10°$, we get from (A1)

$$\cos 10q\alpha + \cos 10q(\alpha+\beta_1) + \cos 10q(\alpha+\beta_2) = 0 \qquad (A3)$$

or

$$2 \cos 10q(\alpha+\beta_2/2) \cos 10q\beta_2/2 + \cos 10q(\alpha+\beta_1) = 0 . \qquad (A4)$$

Similarly from the equation (A2)

$$2 \sin 10q(\alpha+\beta_2/2) \cos 10q\beta_2/2 + \sin 10q(\alpha+\beta_1) = 0 . \qquad (A5)$$

If the expressions on the left hand sides of (A4) and (A5) have a common factor which is zero, they would both vanish. They would have a common factor if, say,

$$2\beta_1 = \beta_2 = 2\beta .$$

For then (A4) and (A5) may be written respectively as

$$\cos 10q(\alpha+\beta)\{1 + 2 \cos 10q\beta\} = 0 \qquad (A6)$$

and

$$\sin 10q(\alpha+\beta)\{1 + 2 \cos 10q\beta\} = 0 \qquad (A7)$$

whence

$$1 + 2 \cos 10q\beta = 0$$

or

$$\begin{aligned} q \times \beta &= 2\times 6,\ 4\times 6,\ 8\times 6,\ \ldots\ etc. \\ &= (6n \pm 2)\times 6 . \end{aligned}$$

If $q = 6n \pm 2$ then $\beta = 6$ and relations (A1) and (A2) would be satisfied by a set of three numbers

$$r_1 = \alpha,\ r_2 = \alpha + 6, \text{ and } r_3 = \alpha + 12$$

where α may be any integer.

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The Structures of the Intermetallic Phases MoAl$_{12}$, ReAl$_{12}$ and TcAl$_{12}$

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X-ray methods have been used to refine the structures of MoAl$_{12}$, ReAl$_{12}$ and TcAl$_{12}$. The unit cell is *b.c.c.* and the structures are nearly the same as that of WAl$_{12}$. The interatomic distances of the three phases are compared and those of MoAl$_{12}$ are compared with distances in other Mo–Al phases.

1. Introduction

The molybdenum–aluminum phase diagram has recently been investigated at the aluminum-rich end by Clare (1961), who reported a new phase corresponding to the formula MoAl$_7$ and confirmed that the compound richest in aluminum had the formula MoAl$_{12}$.

The phase ReAl$_{12}$ was first reported by Savitskii, Tylkina & Povarova (1961) and was later confirmed by Alte da Veiga (1962), who gave $a = 7{\cdot}5280 \pm 0{\cdot}0005$ Å.

TcAl$_{12}$ has been reported as having a *b.c.c.* unit cell with $a = 7{\cdot}5270 \pm 0{\cdot}0003$ Å (Alte da Veiga & Walford, 1963). Powder photographs of all three phases were found to be similar.

2. Material

The MoAl$_{12}$ crystal used in the refinement was picked from several given by Mr J. W. H. Clare and Dr R. S. Harding of the British Aluminium Co. Ltd., Banbury. Crystals of the other phases were prepared by Mr L. M. d'Alte da Veiga in this laboratory.

The crystals chosen were approximately 0·1 mm cubes, so only the normal scaling correction for absorption was necessary. Extinction, although presumably reduced by the use of small crystals, was still found to be present in the most intense reflexions (see § 5).

3. Unit cell and space group

The cell dimension of each phase was measured by the method of Farquhar & Lipson (1946) with unfiltered Fe radiation. The values obtained were:

MoAl$_{12}$	$7{\cdot}5815 \pm 0{\cdot}0005$ Å
ReAl$_{12}$	$7{\cdot}5270 \pm 0{\cdot}0005$
TcAl$_{12}$	$7{\cdot}5255 \pm 0{\cdot}0005$

The space group is the same as that of WAl$_{12}$ (Adam & Rich, 1954), *viz. Im*3.

4. Density and composition

The densities of the Mo, Re and Tc phases were measured by the displacement method and found to be 3·20, 3·90 and 3·25 g.cm^{-3} respectively (all $\pm 0{\cdot}05$). The calculated densities are 3·23, 3·94 and 3·27 g.cm^{-3} respectively.

The composition of MoAl$_{12}$ has been determined by neutron activation analysis of small samples (*ca* 2 mg) of the crystals. This work was kindly undertaken by Mr H. Simpson of the Chemistry Group, Isotope Research Division, Wantage Radiation Laboratory of the United Kingdom Atomic Energy Authority (Simpson, 1964).

The samples were dissolved and irradiated with a comparator in the BEPO reactor for about 10 seconds, followed immediately by the counting of γ-radiation greater than 1·7 meV, resulting from the short lived aluminum isotopes. The molybdenum was measured by counting the 0·14 meV gamma peak due to ^{99}Tc (the decay product of ^{99}Mo) from the same samples two days later.

The results of this analysis gave

$$22{\cdot}6 \pm 0{\cdot}1 \text{ wt\% Mo}$$
$$77{\cdot}7 \pm 0{\cdot}3 \text{ wt\% Al}$$

which agrees well with the theoretical value of 22·7 wt% Mo for the formula MoAl$_{12}$. This determination corresponds to the formula MoAl$_{12{\cdot}2\pm0{\cdot}1}$.

5. Collection of intensities

Reflexions of the form (0*kl*) were collected on zero-layer normal-beam Weissenberg photographs, filtered