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The Structure of a New Silicon Carbide Polytype 105*R*

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A 105-layered rhombohedral polytype of silicon carbide has been discovered with unit-cell dimensions $a = b = 3{\cdot}078$ and $c = 264{\cdot}39$ Å as referred to hexagonal axes. By comparing the calculated relative intensities of $10.l$ reflexions with those observed on Weissenberg photographs, its structure has been confirmed to be $(333333333332)_3$ in Zhdanov's notation. This polytype thus belongs to the $[(33)_n\,32]_3$ series of structures whose existence is expected on the dislocation theory.

Introduction

Over 40 different polytypes of silicon carbide have been discovered, and their number is continually increasing. To understand how such a large number of modifications of the same substance occur the theories advanced are (*a*) the impurity theory (Zhdanov & Minervina, 1945*a*, *b*; Lundqvist, 1948), (*b*) screw dislocation theory (Frank, 1951), (*c*) polymer theory (Ramsdell & Kohn, 1952) and (*d*) thermodynamical theory (Jagodzinski, 1954). But because of the complicated nature of growth none of these attempts has been completely successful. Attempts are being made here to study the nature of growth of these polytypes and for this purpose we are searching for new polytypes and studying their detailed structure by X-ray diffraction to ascertain whether the data collected in relation to them can be explained on the basis of the above theories. During the course of above study a new 105-layered polytype was discovered, and we describe below its detailed structure.

Structure of the unit cell

The crystal under investigation was a small dark crystal of dimensions $1 \times 0{\cdot}5 \times 0{\cdot}5$ mm^3. From a 15° oscillation photograph about the c axis taken on a camera of radius 11·48 cm, the rhombohedral symmetry of the crystal was confirmed since the nearest spots (of the $10.l$ row) on either side of the zero-layer Laue streak were in the ratio of 1:2. The number of layers in the unit cell was approximately determined from the measured ζ value from Fig. 1. The number of layers was accurately determined on a zero-layer Weissenberg photograph taken about the a axis by the method of Krishna & Verma (1962*b*) where the exact number of layers is obtained by counting the number of spacings after which the intensity sequence begins to repeat in the $10.l$ row. Fig. 2 shows this Weissenberg photograph in which the above number of spacings was 35. Because of the rhombohedral symmetry the unit cell contains $35 \times 3 = 105$ layers.

The number of layers in the unit cell of the polytype 105*R* fits in the series of silicon carbide polytypes in the Ramsdell zigzag sequence $[(33)_n\,32]_3$. Indeed 105*R* was an undiscovered member of this series, the known members being 15*R*, 33*R*, 51*R*, 87*R*, 141*R* and 393*R*. It was therefore suspected that the structure of 105*R* was $[(33)_5\,32]_3$ (Zhdanov notation). This was further confirmed by comparing the characteristics of intensity in the 10 l row with an intensity plot given by Mitchell (1954) for five other members of this series. The structure $[(33)_5\,32]_3$ in the *ABC* notation is

ABCACBABCACBABCACBABCACBABCACB
ABCACBCABACBCABACBCABACB
↓
CABACBCABACBCABACABCBACABCBACAB
CBACABCBACABCBACABCB

which has a centre of symmetry for the silicon atoms at the atom marked by an arrow. Choosing the origin on this atom the interval sequence (Ott, 1925*a*, *b*) is

24242424242433333333333424242424242;

because of the centre of symmetry the intensity calculations are very much simplified. As is generally done in silicon carbide to establish the structure, it is sufficient to show an agreement between the calculated and observed relative intensities in the $10.l$ row up to $l = 105$ on the positive as well as the negative side (Ramsdell, 1944). The intensities of these 10 l reflections were calculated in the usual manner (Ramsdell, 1944) and multiplied by the Lorenz polarization factor.

For the estimation of observed intensities following Krishna & Verma (1962*a*, *b*), zero-layer Weissenberg photographs were taken for 10, 25, 50, and 100 oscillations of the crystal. A standard intensity scale was prepared by exposing a particular intense spot for 1, 2, ..., 100 oscillations of the crystal. All these films were processed under identical circumstances. Hence the intensity estimations were done with enough

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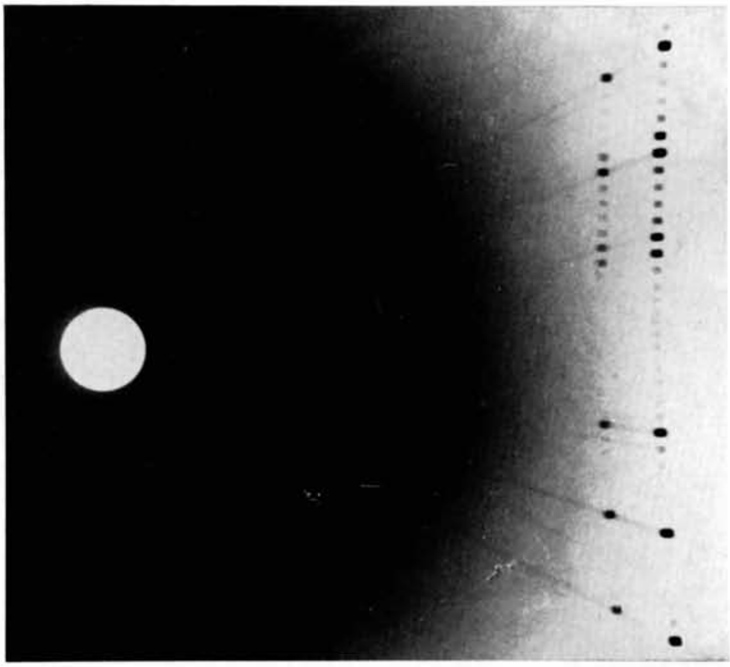

Fig. 1. The $10.l$ row of spots as recorded on a 15° c-axis oscillation photograph of the $105R$ crystal, on a camera of radius 11·48 cm. (× 1).

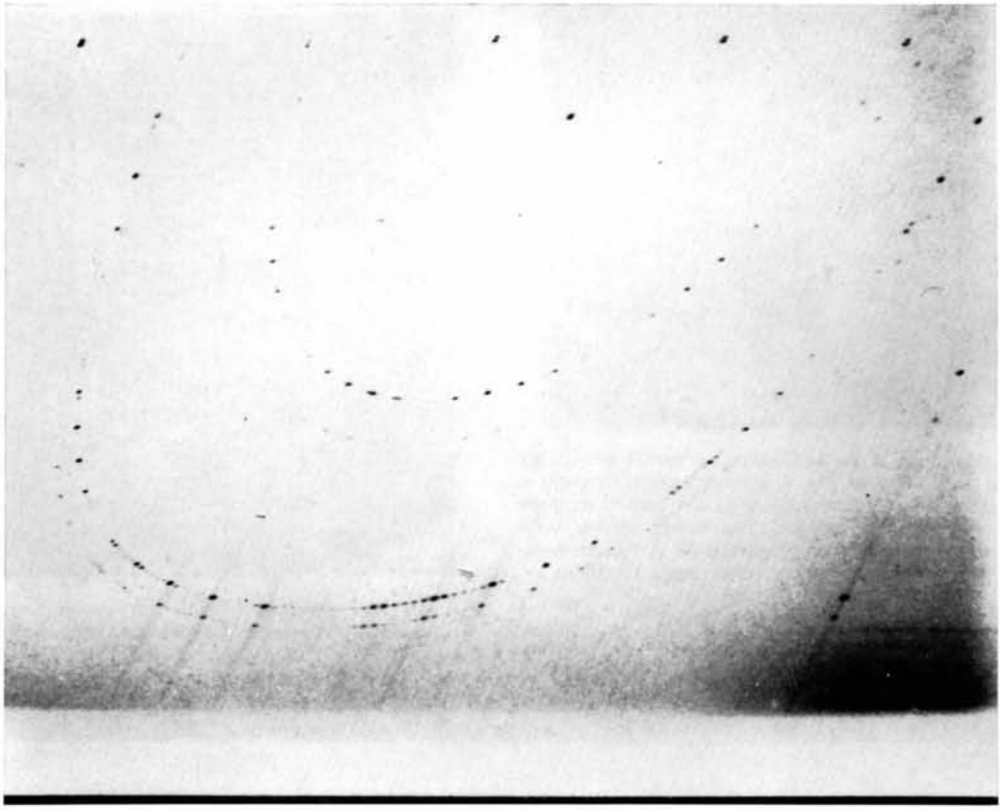

Fig. 2. Zero-layer a-axis Weissenberg photograph taken with unfiltered Cu $K\alpha$ radiation on a camera of diameter 5·73 cm. (× 1·5).

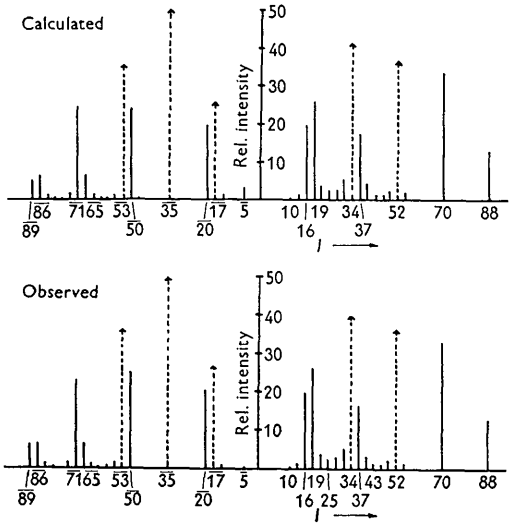

Fig. 3. Graphs of relative intensity of 10.*l* reflexions against their *l* values. Intensity values of different spots are plotted as percentages of the value for 10.$\overline{35}$. Dotted lines indicate very high intensities plotted to half the scale.

accuracy. Fig. 3 is the graph showing the calculated and observed relative intensities of the 10.*l* reflexions. The observed and calculated intensities for the 10.*l* row are listed in Table 1. The close agreement between these establishes the postulated structure. The reliability factor is found to be 0·14.

Table 1. *Intensities of* 10.*l reflexions*

l	*I* obs.	*I* calc.	*l*	*I* obs.	*I* calc.
1	0·0	0·19	$\overline{2}$	0·0	0·15
4	0·0	0·34	$\overline{5}$	0·5	3·60
7	0·0	0·32	$\overline{8}$	0·0	0·20
10	0·7	0·62	$\overline{11}$	0·0	0·37
13	1·9	1·80	$\overline{14}$	1·1	1·10
16	20·0	19·78	$\overline{17}$	53·3	51·20
19	26·6	25·60	$\overline{20}$	20·8	19·50
22	3·9	3·93	$\overline{23}$	0·0	0·40
25	2·8	2·52	$\overline{26}$	0·0	0·20
28	3·1	2·99	$\overline{29}$	0·0	0·10
31	5·6	5·84	$\overline{32}$	0·0	0·10
34	80·0	83·22	$\overline{35}$	100·0	100·00
37	16·7	17·60	$\overline{38}$	0·0	0·10
40	3·1	4·54	$\overline{41}$	0·0	0·13
43	1·7	1·54	$\overline{44}$	0·0	0·20
46	1·4	1·41	$\overline{47}$	0·0	0·50
49	2·8	2·50	$\overline{50}$	25·0	24·00
52	73·3	73·20	$\overline{53}$	73·3	71·50
55	1·9	2·00	$\overline{56}$	1·9	1·94
58	0·0	0·29	$\overline{59}$	1·0	0·90
61	0·0	0·11	$\overline{62}$	0·8	0·80
64	0·0	0·19	$\overline{65}$	1·3	1·30
67	0·0	0·04	$\overline{68}$	6·7	6·50
70	33·3	33·50	$\overline{71}$	23·3	24·10
73	0·0	0·03	$\overline{74}$	1·7	1·70
76	0·0	0·02	$\overline{77}$	0·6	0·70
79	0·0	0·03	$\overline{80}$	0·6	0·70
82	0·0	0·12	$\overline{83}$	1·1	1·10
85	0·0	0·43	$\overline{86}$	6·7	6·50
88	13·3	12·60	$\overline{89}$	6·1	5·10
91	0·0	0·30	$\overline{92}$	0·0	0·50
94	0·0	0·09	$\overline{95}$	0·0	0·20
97	0·0	0·08	$\overline{98}$	0·0	0·10
100	0·0	0·04	$\overline{101}$	0·0	0·05
103	0·0	0·09	$\overline{104}$	0·0	0·02

Unit-cell dimensions and atomic positions

The space group of 105*R* is $R3m$ with its cell dimensions based on hexagonal axes:

$$a = 3{\cdot}078,\quad c = 264{\cdot}39\ \text{Å}\ .$$

The zigzag sequence given above results in the following atomic positions in the hexagonal unit cell:

35 silicon atoms at $00t$, where

t = 0, $2z$, $6z$, $8z$, $12z$, $14z$, $18z$, $20z$, $24z$, $26z$, $30z$, $32z$, $36z$, $39z$, $42z$, $45z$, $48z$, $51z$, $54z$, $57z$, $60z$, $63z$, $66z$, $69z$, $73z$, $75z$, $79z$, $81z$, $85z$, $87z$, $91z$, $93z$, $97z$, $99z$, $103z$

where $z = 1/105$

35 silicon atoms at $\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$ plus the above coordinates;
35 silicon atoms at $\frac{1}{3}$, $\frac{2}{3}$, $\frac{2}{3}$ plus the above coordinates;
105 carbon atoms one above each silicon atom at $00p$ plus the coordinates of the 105 silicon atoms

where $p = 1/140$.

Discussion

The growth of 105*R* is expected on dislocation theory. As suggested by Krishna & Verma (1962*a*, *b*), rhombohedral polytypes grow only when the first and last layer of the exposed ledge is in the same orientation (*A*, *B* or *C*). Consider a screw dislocation ledge of 35 layers exposed in the basic 6*H* structure, *ABCACB*, *ABCACB*, . . ., with an arrangement

BCACBABCACBABCACBA
BCACBABCACBABCACB.

As growth proceeds, this would wind up spirally, creating a structure

BCACBABCACBABCACBABCACBABCACBA
BCACBABCBACABCBACABCBACABCBAC
ABCBACABCBACABACBCABACBCABACBC
ABACBCABACBCABAC .

Confirmation of the structure of 105*R* as $[(33)_5 32]_3$ (Zhdanov notation) shows the utility of Mitchell's method (1954) for detecting directly the structure of unknown polytypes of silicon carbide belonging to $[(33)_n 32]_3$ series. A similar intensity plot was made by Krishna & Verma (1962*a*, *b*) for the direct determination of structures of the unknown members of the series $[(33)_n 34]_3$. These suggestions have simplified the structure work in silicon carbide to a large extent. Similar attempts can be made for other series also.

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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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