Table 3 (cont.)

(c) involving the possible hydrogen bonds

O(7)–O(1)	2·865 (12)	2·865*
O(7)–O(8^{iv})	2·993 (13)	2·968
O(8)–O(8^{iii})	2·797 (16)	2·739
O(4)–O(8)	2·956 (12)	2·924
O(6)–O(9)	2·748 (13)	2·737
O(5)–O(8)	3·019 (14)	2·998

The superscripts refer to the following transformations of the atomic coordinates.

No symbol	x	y	z
i	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$-x$	$-y$	$1-z$
iii	$x-\frac{1}{2}$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	$-x$	$1-y$	$1-z$

* The data of Leclaire & Monier.

bonds joining the $Ca_2(H_2O)_8(NO_3)_4$ dimers are given in Table 3.

We have used the two sets of data to calculate a half normal probability analysis (Abrahams & Keve, 1971). The experimental values of Δ_j/σ_j (where Δ_j is the difference between the corresponding jth coordinate and σ_j is the pooled standard deviation) plotted against the expected values of Δ_j/σ_j (Hamilton & Abrahams, 1972) are given in Fig. 1. The plot is linear indicating that there are no systematic errors in either measurement. The slope of about 1·1 for all the points shows that the standard deviations are underestimated by about 10%. The average of the two sets of results should give a better estimate of the true data for $Ca(NO_3)_2 \cdot 4H_2O$.

Fig. 1. The half-normal probability plot of Δ_j/σ_j for the two sets of 39 positional coordinates.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). Acta Cryst. A27, 157–165.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.
LECLAIRE & MONIER, I. C. (1970). C. R. Acad. Sci. Paris, 271, 1555–1557
HAMILTON, W. C. & ABRAHAMS, S. C. (1972). Acta Cryst. A28, 215–218.

A new polytype of silicon carbide, 189R. Its structure and growth.

By M. DUBEY, U. S. RAM and G. SINGH, Department of Physics, Banaras Hindu University, Varanasi 221005, India

A new 189-layered rhombohedral modification of silicon carbide has been discovered. Its structure is based on the 21R phase instead of one of the usual basic structures 6H, 15R and 4H, and has been found to be $[(34)_843]_3$ in Zhdanov notation. The studies on this polytype provide new information regarding the growth of polytypic crystals.

Introduction

Usually silicon carbide structures are found to be based on one of the basic structures 6H, 15R and 4H. Recently we have found a number of structures which are based on other structures like 21R (33R, 147R, Ram, Dubey & Singh, 1973a, b) etc. instead of one of the basic phases. Although a large number of polytypes of SiC are known by now, 189R was found to be of special interest because it is one of the few newly found structures which are based on a structure (21R) other then the usual phases. The structure and growth mechanism of this polytype is reported in the present paper.

Experimental details

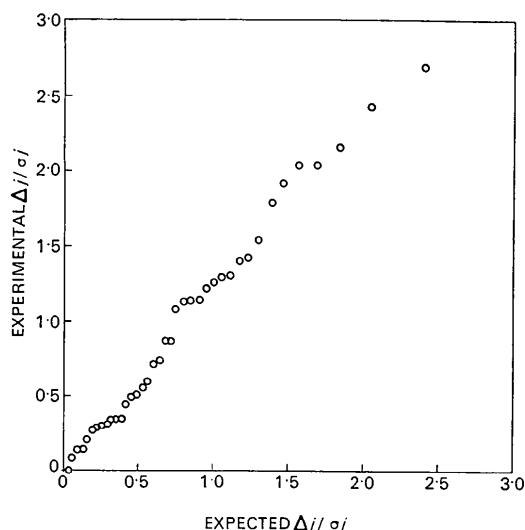The crystal containing 189R was a bluish-black piece of silicon carbide of size $3·0 \times 2·0 \times 1·5$ mm with a well devel-oped (0001) face. The crystal surface was examined under the optical microscope and spiral features were observed over a wide area of the surface.

Single-crystal X-ray diffraction patterns show that almost all the crystal is a well ordered 21R structure and only a small region parallel to (0001) near the top gives reflexions due to other polytypic structures. Two polytypes 189R and 259H or 777R were found in a small region of the specimen near two different corners, intergrown in parallel orientation with the 21R structure. Fig. 1(a) is a c-axis oscillation photograph of 189R and Fig. 1(b) shows the reflexions of 259H or 777R. Fig. 1(c) is another c-axis oscillation photograph in a different range which shows 189R spots, but a careful observation of these reflexions shows that each of these spots are split up into 3 or 4 finer spots. These fine spots correspond to an undefined high-period polytype whose structure is strongly based on the 189R phase.
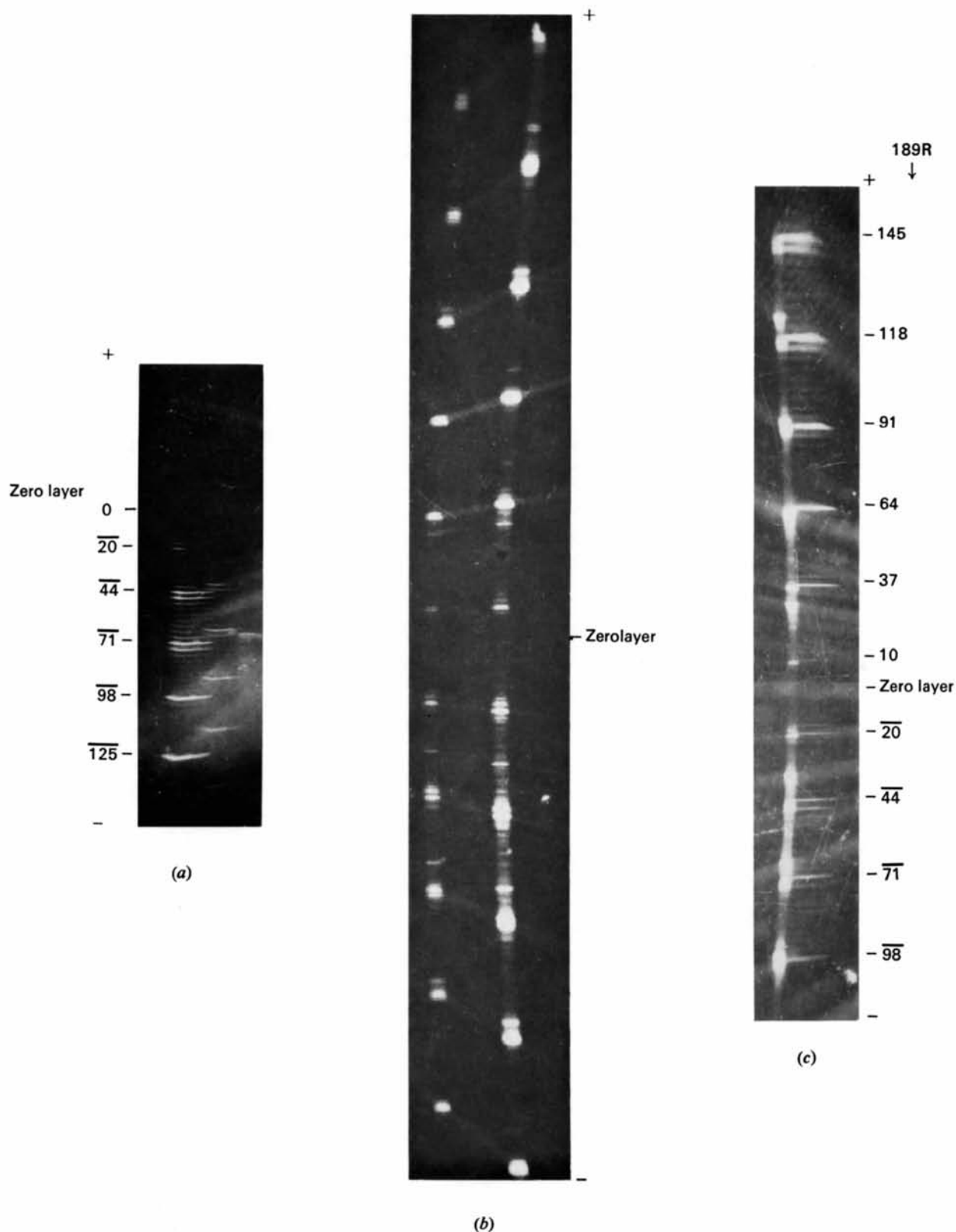
(a)

(b)

(c)

Fig. 1(a) The 10.*l* row of spots as recorded on a 15°, *c*-axis oscillation photograph of SiC crystal type 189*R* (mag. ×3). The intensities of 10.*l* reflexions have been absorbed. (b) A 15°, *c*-axis oscillation photograph of 259*H* or 777*R* based on the 21*R* phase (mag. ×7). More intense spots represent the positions of the 21*R* phase. (c) A 15°, *c*-axis oscillation photograph of the new high-period polytype with 189*R* and 289*H* or 777*R* (mag. ×5). The intensities of 10.*l* reflexions have been affected by absorption and are better represented in Fig. 1(a).

Table 1. *Calculated and observed intensities along the* 10.*l*
row of the 189*R* SiC *phase*

Observed intensities are derived from a large number of *c*-axis oscillation photographs recorded over different ranges, *e.g.* Fig. 1(*a*) and (*c*). In the Table, *a* stands for absent, *w* for weak, *vw* for very weak, *vs* for very strong, *s* for strong, *ms* for medium strong (*vs* > *s* > *ms*) and * represents a reflexion which is not recorded on the photograph.

l	I_{cal}	I_{obs}	*l*	I_{cal}	I_{obs}
1	6·6	*a*	2	4·4	*a*
4	11·2	*a*	5	3·0	*a*
7	37·2	*a*	8	1·8	*a*
10	63·0	*w*	11	1·3	*a*
13	4·2	*a*	14	5·9	*vvw*
16	4·5	*a*	17	242·2	*s*
19	6·4	*a*	20	123·6	*s*
22	9·0	*a*	23	33·8	*w*
25	13·4	*a*	26	20·4	*w*
28	22·3	*a*	29	16·0	*vw*
31	49·0	*w*	32	14·7	*vw*
34	264·1	*ms*	38	16·3	*vw*
37	968·5	*s*	38	24·4	*w*
40	86·3	*ms*	41	89·0	*ms*
43	28·1	*w*	44	1188·6	*vs*
46	22·4	*vw*	47	390·4	*s*
49	24·8	*vw*	50	88·5	*ms*
52	33·7	*vw*	53	50·9	*w*
55	55·9	*w*	56	40·7	*w*
58	128·9	*s*	59	39·4	*w*
61	726·7	*s*	62	44·7	*w*
64	2625·0	*vs*	65	63·6	*ms*
67	148·2	*ms*	68	137·7	*s*
70	44·6	*vw*	71	1604·5	*vs*
73	21·4	*vw*	74	306·7	*s*
76	14·1	*vw*	77	43·4	*w*
79	13·2	*vw*	80	18·4	*vw*
82	18·6	*vw*	83	13·3	*vw*
85	43·0	*w*	86	13·4	*vw*
88	266·8	*s*	89	17·2	*vw*
91	1096·0	*vs*	92	27·9	*w*
94	71·4	*ms*	95	69·8	*ms*
97	24·7	*vw*	98	920·7	*vs*
100	13·0	*vw*	101	190·9	*s*
103	8·8	*vw*	104	26·8	*w*
106	7·6	*vw*	107	10·1	*vw*
109	9·2	*vw*	110	6·3	*a*
112	19·2	*w*	113	6·0	*a*
115	121·4	*s*	116	8·0	*a*
118	568·4	*vs*	119	15·3	*a*
121	44·2	*w*	122	45·9	*a*
124	18·6	*vw*	125	745·2	*vs*
127	12·2	*vw*	128	191·3	*s*
130	10·0	*vw*	131	32·0	*a*
133	9·8	*vw*	134	13·3	*a*
136	11·6	*vw*	137	7·7	*a*
139	19·8	*w*	140	5·5	*a*
142	84·9	*mw*	143	4·9	*a*
145	255·5	*s*	146	6·0	*a*
148	14·2	*w*	149	13·7	*a*
151	5·2	*	152	206·7	*s*
154	3·5	*	155	56·3	*
157	3·2	*	158	10·6	*
160	3·5	*	161	4·8	*
163	4·3	*	164	3·0	*
166	7·5	*	167	2·0	*
169	28·1	*	170	1·5	*
172	56·2	*	173	1·1	*
175	1·4	*	176	1·0	*
178	0·3	*	179	15·2	*
181	0·4	*	182	9·2	*
184	0·7	*	185	2·8	*
187	1·1	*	188	1·7	*

Structure

A closer scrutiny of the intensity distribution of the 189*R* reflexions reveals that the spots corresponding to spot positions of 21*R* are conspicuously stronger than the others. This indicates that the 189*R* structure is strongly based on the 21*R* phase. Thus keeping in view that the correct structure is likely to have larger units of (34) and restricting the numbers in Zhdanov notation as usual to 2, 3 and 4 only, the following most probable structures were postulated:

(1) $[(34)_8 43]_3$ (2) $[(34)_7 (43)_2]_3$
(3) $[(34)_7 323222]_3$ (4) $[(34)_7 22(23)_2]_3$
(5) $[(34)_7 22(32)_2]_3$ (6) $[(34)_6 (33)_2 3222]_3$
(7) $[(34)_6 33322233]_3$ (8) $[(34)_6 3222(33)_2]_3$.

The intensities from all these structures were calculated for the 10.*l* row of reflexions and it was found that $[(34)_8 43]_3$ gave an intensity pattern matching well with the observed intensities. The calculated intensities were corrected with the Lorentz–polarization factor. The calculated and observed intensities are given in Table 1.

Discussion and conclusion

The 189*R* polytype of silicon carbide is one of the few cases where a polytype has a structure based on a phase other than the usual basic phases 6*H*, 15*R* or 4*H*. The somewhat similar case of 147*R* has been reported earlier by the same authors. An important conclusion which may be drawn from such observations is that it is not essential for one of the basic phases to nucleate first so that screw dislocations created in such nuclei give rise to different polytypic structures. Further, the experimental observations on these polytypes provide additional information which is helpful in understanding the growth mechanism of SiC polytypes. For example, in the same crystal a polytype of very high periodicity based on 189*R* has been found, 189*R* itself being based on 21*R*. Such observations indicate the possible existence of structures with extremely high periodicities, and X-ray diffraction spots from such crystals merge to form continuous streaks along *h*0.*l* rows. The observation of streaks is usually attributed to one-dimensional disorder, but this is not necessarily the case. This overcomes an important shortcoming of the screw-dislocation theory of polytypism.

On the basis of extensive crystal growth and phase transformation studies of silicon carbide (Schaffer, 1971; Inomata, Inoue & Kijima, 1969; Mardix, Kalman & Steinberger, 1968; Knippenberg & Verspui (1969) the growth of β-SiC nuclei seem to be more likely in the initial stages rather than those of 6*H*, 15*R* or 4*H*. This is because β-SiC has been found to grow in the entire temperature range 1400 to 2500 °C under varying supersaturations, whereas basic polytypes have a tendency to grow in preferred temperature ranges. Moreover, β-SiC is known to undergo a phase transformation to α-SiC. We will not go into the detailed mechanism of phase transformation (Krishna & Marshall, 1971; Powell & Will, 1972; Will & Powell, 1972) here but it can safely be assumed that initially β-SiC nucleates and undergoes a phase transformation to α-SiC, most probably by the introduction of stacking faults which are repeated regularly owing to screw dislocations created in the initial platelet (Ram *et al.*, 1973; Mardix *et al.*, 1968). Thus the structure units of any polytype may form the basic units of a high-period polytype.

Two of us (M.D. and U.S.R.) are grateful to the Council of Scientific and Industrial Research of India for financial assistance during the tenure of this work.

References

INOMATA, Y., INOUE, Z. & KIJIMA, K. (1969). *J. Ceram. Assoc. Japan,* **77,** 313–318.

KNIPPENBERG, W. F. & VERSPUI, G. (1969). *Mater. Res. Bull.* **4,** S45–S49.

KRISHNA, P. & MARSHALL, R. C. (1971). *J. Cryst. Growth,* **9,** 319–325.

MARDIX, S., KALMAN, Z. H. & STEINBERGER, I. T. (1968). *Acta Cryst.* A**24,** 464–469.

POWELL, J. A. & WILL, H. A. (1972). *J. Appl. Phys.* **43,** 1400–1408.

RAM, U. S., DUBEY, M. & SINGH, G. (1973*a*). *Z. Kristallogr.* To be published.

RAM, U. S., DUBEY, M. & SINGH, G. (1973*b*). *J. Cryst. Growth.* To be published.

SHAFFER, P. T. B. (1971). *Appl. Opt.* **10,** 1034–1038.

WILL, H. A. & POWELL, J. A. (1972). NASA Report TN *D*-6717.

Refinement of the structure of 11CaO.7Al₂O₃.CaF₂. By P. P. WILLIAMS, *Chemistry Division, DSIR, Petone, New Zealand*

A refinement is reported ($R = 6.7$ %) of the structure of the fluoride analogue of cubic hydrated 12CaO . 7Al₂O₃. It has been confirmed that the fluoride ion sites are only partially occupied and that calcium atoms adjacent to filled fluoride positions are displaced. No evidence has been found to indicate an ordered structure in a lower-symmetry space group.

Reports on the crystal structure of the cementitious compound 12CaO·7Al₂O₃ have appeared previously (Büssem & Eitel, 1936; Jeevaratnam, Dent Glasser & Glasser, 1962; Bartl, 1969) and the structure of the fluoride analogue of the monohydrate has also been reported (Williams, 1968, 1969). This communication details the results of further refinement of the latter structure.

The material used for the study, the data collection procedures, and an approximate structure have been previously described (Williams, 1968, 1969). The crystals are cubic,

$I\bar{4}3d$ (No. 220) with $a = 11\cdot970$ Å, $Z = 2$. Full-matrix least-squares refinement of the structure, including site-occupancy parameters for calcium and fluorine atoms led to the parameters in Table 1. The conventional R at this stage for 213 'observed' $[F > 3\sigma(F)]$ reflections was 0·067. The scattering factors used were those given for Ca⁺, Al⁺, O⁻, F⁻ in *International Tables for X-ray Crystallography* (1962). The structure factors are listed in Table 2, and Table 3 gives interatomic distances and bond angles.

The structure is disordered in that there are two sites,

Table 1. *Atom parameters*

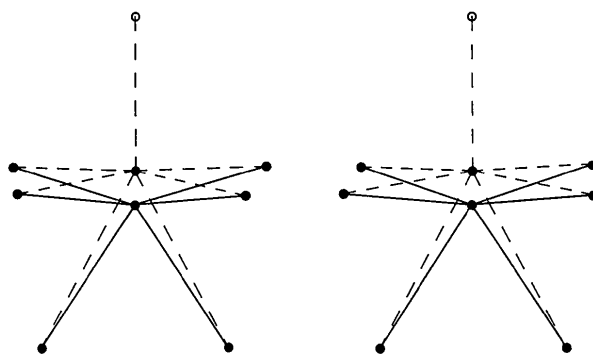|	x	y	z	Occupancy	B
Ca(1)	0·1103 (6)	0	0·25	0·74 (3)	0·57 (11)
Ca(2)	0·0682 (15)	0	0·25	0·28 (3)	0·35 (25)
Al(1)	0·375	0	0·25		0·19 (9)
Al(2)	0·2306 (2)	0·2306 (2)	0·2306 (2)		0·27 (9)
O(1)	0·1919 (6)	0·2857 (6)	0·0991 (6)		0·80 (11)
O(2)	0·3139 (6)	0·3139 (6)	0·3139 (6)		0·80 (19)
F	0·875	0	0·25	0·33 (7)	2·2 (13)

Fig. 1. Stereoscopic representation of the possible coordination shells for the calcium atoms. The central atom is calcium; bold lines denote six coordination contacts from the Ca(1) site, fine lines are the seven contacts in the Ca(2) site.