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A Review of the Structure of Silicon Carbide

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The structure of silicon carbide and its polytypism are reviewed together with a brief discussion of the proposed mechanisms of crystal growth. The unit-cell parameters and stacking sequences are tabulated for 74 polytypes and the atomic positions listed for seven of the most common polytypes. A complete bibliography of the literature pertaining to the structure of silicon carbide is presented.

Introduction

The long-range structure of silicon carbide is extremely complex as a result of the one-dimensional disorder or polytypism. The short-range structure is simple, a four-coordinate, diamond-like arrangement of alternate silicon and carbon atoms. Since approximately 75 structures have been identified, and many completely determined, it seemed desirable to bring these data together for reference. While many are in the literature available to most researchers, a number of others are reported in Soviet and Chinese literature, and as such are less readily available.

Since no mechanism of crystal growth has been completely accepted, or has fully explained the formation of crystal structures having unit cells of the order of one thousand layers long, brief descriptions of several theories will be presented, without attempting to make a choice, merely to point out obvious failings and strong points of each.

The system of nomenclature used in this description of the various polytypes (Baumhauer, 1915) will, unless otherwise stated, be that of Ramsdell (1947). This convention is to assign a number corresponding to the number of layers in the hexagonal unit cell and a letter suffix designating the crystal symmetry: *C*, cubic; *H*, hexagonal; *R*, rhombohedral.

Description of the basic structure

Early work on the crystallography of SiC was devoted to goniometric studies of interfacial angles (Acheson, 1893; Baumhauer, 1912; Becke, 1895; Negri, 1906; Peacock & Schroeder, 1934; Peacock, 1934; Cortellezzi & Schroeder, 1934), which in the earliest studies showed at least two polytypes present in the first samples (Acheson, 1893). Morphological studies also showed the intergrowth of two or more polytypes within a single crystal (Baumhauer, 1915).

Early etching studies (Becke, 1895*a,b*) showed the different chemical behavior of the opposite basal planes (Figs. 1 and 2).

The first true structural studies were based on the work of Hull (1919, 1920), Ott (1925*a,b,c,d,e*. 1926, 1928) and others (Braekken, 1930; Espig, 1921; Hauer & Koller, 1916).

The structure of SiC can be described in several ways. For example the spatial location of each atom may be given. This is completely unambiguous, but for most purposes over complicated. The symmetry of a plane of atoms, resulting from the relative positions of the two adjacent layers can be designated; using this system the relation between layers of wider separation is not readily shown. Still other descriptions are based on the relative position of the various layers. One of the simplest is based on the relative orientation of layers of tetrahedra.

All silicon carbide structures are made up of a single basic unit, a plane of tetrahedra, arbitrarily either SiC_4 or CSi_4, shown in Fig. 3. Successive layers can arrange themselves in one of two ways: parallel or anti-parallel, as shown in Fig. 4(*a*) and (*b*).

Arbitrarily designating one orientation '*a*', the other '*b*', the parallel stacking of layers leads to an '*aa*' se-

quence while the anti-parallel yields an '*ab*' sequence. An infinite number of combinations of '*a*' and '*b*' layers probably exists; however, the structures thus far examined contain relatively few sequences having four or more adjacent layers of the same orientation. Two exceptions are β-SiC in which all layers have the same orientation and the polytype 174*R* in which six layers within the unit cell are similarly oriented (Tomita, 1960).

The common structures, those of 6*H*, 15*R*, 4*H* and β-SiC, have *aaabbb*, *aaabb*, *aabb*, and (*aaa*) layer sequences. By far the most predominant sequences, whose structures have been analyzed, contain two and three successive layers of similar orientation.

The description of structures on the bases of orientation of the tetrahedral layers is basically the same as that used by Wells (1950) in which he refers to the layers of alternate atoms. The layers to which he refers are the tetrahedral layers described above but without the apex atoms, which are shared with the next successive tetrahedral layer.

Similarly, descriptions based on the hexagonal silicon and carbon double layers are the same as the tetrahedral layers, with the three basal atoms removed to the preceding layer.

Wyckoff (1963) describes the SiC structures on a different basis. He describes them on the basis of the symmetry of packing of one of the two atom types.

'Each of these structures can be considered as having planes of carbon atoms (or of silicon atoms), viewed either as packed ions or as centers of tetrahedra stacked one above another in different arrays. For the simplest, β, modification, the second of these layers is obviously displaced with respect to one chosen as first by $\frac{1}{3},\frac{2}{3},\frac{1}{3}$ and the third layer by $\frac{2}{3},\frac{1}{3},\frac{2}{3}$; the fourth layer at $0,0,\frac{3}{3}$ is then directly over the first. If these three positions are designated as $\underline{0},\underline{1}$ and $\underline{2}$, then the vertical sequence in the β form, that of a cubic close packing is

$$\underline{0},\underline{1},\underline{2},\underline{0},\underline{1},\underline{2},\underline{0},\underline{1},\underline{2},\ldots$$

Expressing planar displacements in the vertical sequence in this fashion, it follows directly from the coordinates listed above that the other modifications can be represented as:

For III: $\underline{0},\underline{1},\underline{0},\underline{2},\underline{0},\underline{1},\underline{0},\underline{2},\ldots\ldots\ldots\ldots$

For II : $\underline{0},\underline{1},\underline{2},\underline{0},\underline{2},\underline{1},\underline{0},\underline{1},\underline{2},\underline{0},\underline{2},\underline{1},\ldots\ldots\ldots$

For I : $\underline{0},\underline{2},\underline{0},\underline{1},\underline{2},\underline{1},\underline{0},\underline{1},\underline{2},\underline{0},\underline{2},\underline{1},\underline{2},\underline{0},\underline{1},\underline{0},\underline{2},\underline{0},\underline{1},\underline{2},\ldots$

For IV : $\underline{0},\underline{2},\underline{1},\underline{2},\underline{0},\underline{1},\underline{0},\underline{2},\underline{1},\underline{0},\underline{1},\underline{2},\underline{0},\underline{2},\underline{1},\underline{0},\underline{2},\underline{0},\underline{1},\underline{2},\underline{1},\ldots$

For VI : $\underline{0},\underline{2},\underline{0},\underline{1},\underline{2},\underline{1},\underline{0},\underline{2},\underline{0},\underline{1},\underline{2},\underline{1},\underline{0},\underline{1},\underline{2},\underline{0},\underline{2},\underline{1},\underline{0},\underline{1},$
$\underline{2},\underline{0},\underline{2},\underline{1},\underline{2},\underline{0},\underline{1},\underline{0},\underline{2},\underline{1},\underline{2},\underline{0},\underline{1},\ldots\ldots\ldots$

Continuing to follow Chapter II by designating as *H* a plane that has the same, and by *C* a plane that has different displacements above and below it (corresponding to the hexagonal and cubic close packed distributions), the sequences in these forms of SiC can also be written:

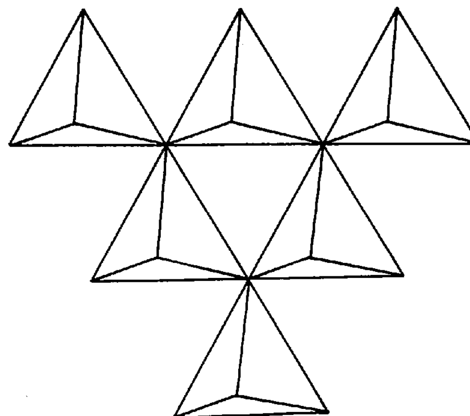
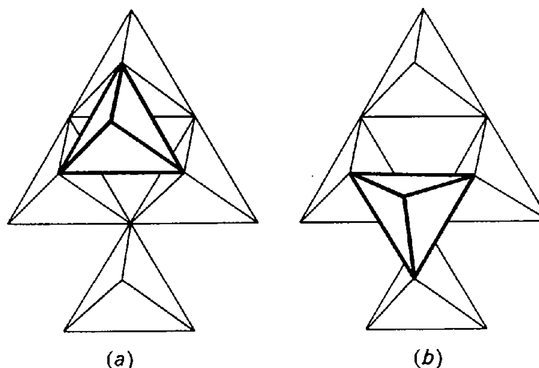


Fig. 3. Hexagonal layers of AB_4 tetrahedra.



(*a*) (*b*)

Fig. 4. Orientation of tetrahedra in successive hexagonal layers: (*a*) parallel, (*b*) antiparallel.

Table 1. SiC *polytype notation*

	Wells (1950)	Wyckoff (1963)	Zhdanov & Minervina (1946) and Mitchell (1957)
β	*a* ...	*CCC* ...	∞
4*H*	*aabb* ...	(*CH CH*) ...	22
6*H*	*aaabbb* ...	(*CCH CCH*) ...	33
15*R*	$(aaabb)_3$ ...	$(CCHCH)_3$ ...	$(32)_3$
21*R*	$(aaabbbb)_3$ ...	$(CCCHCCH)_3$ ...	$(34)_3$
33*R*	$(aaabbbaaabb)_3$ ...	$(CCHCCHCCHCH)_3$ ...	$(3332)_3$

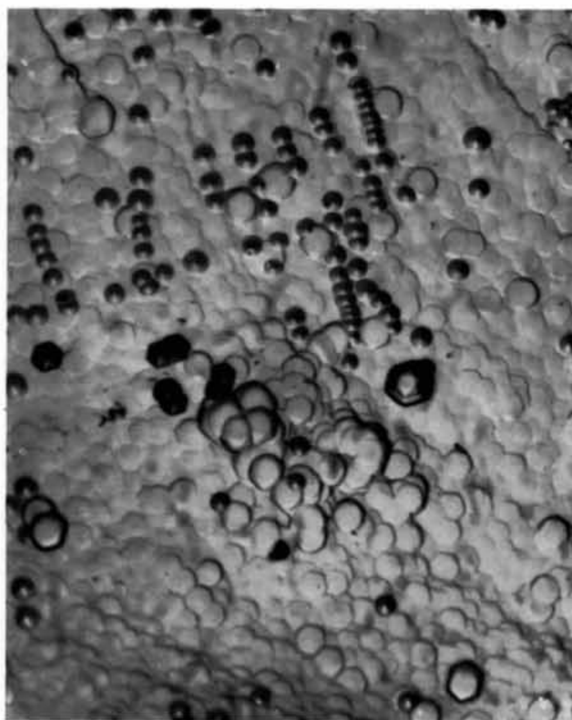


Fig. 1. SiC crystal etched at 800° in NaOH showing well developed etch pits associated with the 'bright' or silicon face.

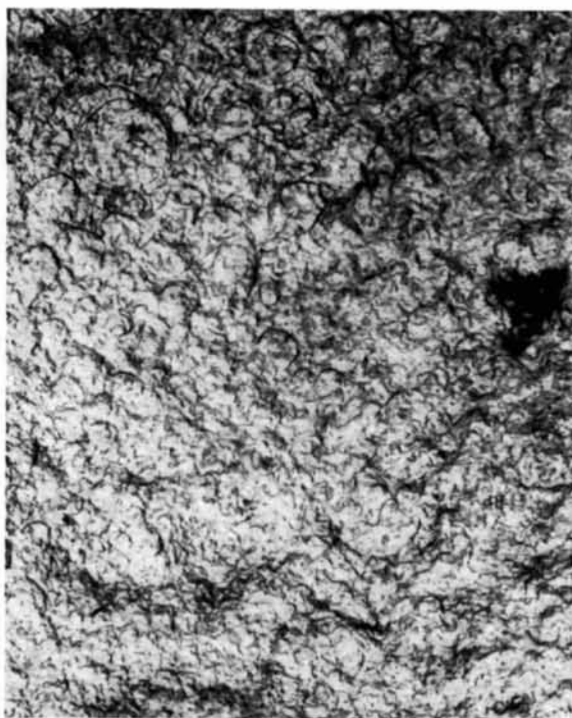


Fig. 2. Reverse side of crystal shown in Fig. 1, showing poor etch patterns associated with the 'dull' or carbon face.

For β:
0, 1, 2, 0, 1, 2, 0, 1, 2,
C C C C C C C C

For α-III:
0, 1, 0, 2, 0, 1, 0, 2, 0, 1, 0, 2,
H C H C H C H C H C H

Table 2. *Crystallographic data for* SiC *polytypes*

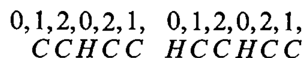
No. of layers and symmetry of unit cell[1]	Unit-cell dimensions: Hexagonal[2] c_0 (Å)	Rhombohedral a_0(Å)	Rhombohedral α	Layer sequence	Reference
2*H*	5·028				Sokhor & Glukov (1965)
2*H*	5·048			11	Adamsky & Merz (1959); Merz & Adamsky (1959); Merz (1961)
3*C*	4·349				Hull (1919; 1920); Mitchell (1957); Thibault (1944)
4*H*	10·053			22	Mitchell (1957); Ott (1926); Thibault (1944); Wyckoff (1963)
6*H*	15·079			33	Mitchell (1957); Ott (1925*a*, *b*); Thibault (1944);
7*H*	17·637				Kuo (1964*a*)
8*H*	20·1064			44	Mitchell (1957); Ramsdell & Kohn (1952)
9*H*	22·676				Kuo (1964*a*)
10*H*	25·133			3223	Gasilova (1957); Mitchell (1957); Ramsdell & Kohn (1951)
14*H*	35·182[3]			$(22)_2 33$	Yuasa, Tomita & Ohta (1966)
15*H*	37·794				Kuo (1964*a*)
15*R*	37·70	12·69	13° 54–½′	$(32)_3$	A.S.T.M. index; Mitchell (1957); Ott (1925*c*, *d*); Wyckoff (1963)
16*H*	40·208[3]			323323	Gasilova (1955; 1957)
18*H*	45·234[3]			$(22)_3 33$	Gliki (1954)
19*H*	47·753			$22(23)_3$	Ramsdell & Mitchell (1953)
21*R*	52·78	17·683	9° 58′	$(34)_3$	Mitchell (1957); Ramsdell (1944)
24*H*	60·312[3]				Gasilova (1955; 1957)
24*R*	60·47				Kuo (1964*a*)
27*R*	67·859	22·689	7046′	$(2223)_3$	Gasilova & Beletskii & Sokhov (1952); Mitchell (1957); Ramsdell & Kohn (1942
33*H*	82·929[3]				Mitchell (1954)
33*R*	82·94	27·704	6° 21′, 30″	$(3332)_3$	Mitchell (1957); Ramsdell (1945); Thibault (1944); Zhdanov & Minervina (1946; 1947)
36*H*[4]	90·65			$(33)_2 32(33)_2 34$	Krishna & Verma (1963; 1964)
39*H*	98·007[3]			$(33)_2 32(33)_2(32)_2$	Azuma, Ohta & Tomita (1963)
39*R*	98·007[3]			$(3334)_3$	Gasilova (1952; 1955)
48*H*	120·624[3]				Mitchell (1954)
48*R*	120·94				Kuo (1964*a*)
51*R*(*a*)[5]	128·178	42·763	4° 7′	$[(33)_2 32]_3$	A.S.T.M. index; Mitchell (1957); Ramsdell (1946; 1947); Thibault (1944; 1946; 1948); Zhdanov & Minervina (1945*a*)
51*R*(*b*)	128·163[3]			$[(22)_3 23]_3$	Mitchell (1957); Ramsdell & Kohn (1952)
54*H*	135·702[3]				Verma (1957)
55*H*	138·58				Kuo (1964*a*)
57*R*	143·52			$[(33)_2 34]_3$	Krishna & Verma (1962*a*, *b*)
57*R*	143·62				Kuo (1964*a*)
58*H*	146·14				Kuo (1964*a*)
60*R*	151·18				Kuo (1964*a*)
66*H*	165·858[3]				Verma (1957)
69*R*	173·85			$[(33)_3 32]_3$	Kuo (1964*a*)
72*R*	180·936[3]				
75*R*	188·497	62·857	2° 48′	$[(32)_3(23)_2]_3$	Mitchell (1957); Ramsdell & Kohn (1952)
78*H*	196·014[3]				Mitchell (1954)
80*H*	201·57				Kuo (1964*a*)
81*R*	204·09				Kuo (1964*a*)
84*R*	211·117	70·395	2° 30′	$[(33)_3(32)_2]_3$	Amelinckx (1952*a*); Mitchell (1957); Ramsdell & Kohn (1952)
87*R*	218·657	72·865	2° 25′	$[(33)_4 32]_3$	Mitchell (1957); Ramsdell (1957)
90*R*	226·6			$[(23)_4 3322]_3$	Krishna & Verma (1963)
93*R*	234·32				Kuo (1964*a*)
105*R*	264·56				Kuo (1964*a*); Singh & Verma (1964)
105*R*	264·54			$[(33)_5 32]_3$	Kuo (1964*c*)
111*R*	279·68			$[(33)_5 34]_3$	Krishna & Verma (1962*a*, *b*); Kuo (1964*a*); Singh & Verma (1964)

Table 2 (*cont.*)

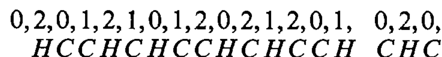
No. of layers and symmetry of unit cell[1]	Unit-cell dimensions: Hexagonal[2] c_0 (Å)		Rhombohedral a_0 (Å)	Layer sequence	Reference
120*R*	301·56[3]				Mitchell (1954)
123*R*	309·91				Kuo (1964*a*)
126*R*	316·638[3]				Verma (1957)
141*H*	355·26				Kuo (1964*a*)
141*R*	354·333	118·124	1°30′	$[(33)_7 32]_3$	Mitchell (1954)
144*R*	362·82				Kuo (1964*a*)
147*R*	370·38				Kuo (1964*a*
50*R*	377·94				Kuo (1964*a*)
153*R*	385·50				Kuo (1964*a*)
159*R*	400·62				Kuo (1964*a*)
168*R*	422·184[3]			$[(23)_{10} 33]_3$	Mitchell (1954)
174*R*	436·7			$[(33)_3 6(33)_5 4]_3$	Tomita (1960)
192*R*	482·496[3]				Ramsdell & Mitchell (1953)
216*R*	544·23				Kuo (1964*a*)
231*R*	582·03				Kuo (1964*a*)
249*R*	627·38				Kuo (1964*a*)
270*R*	680·29				Gasilova (1957); Kuo (1964*a*); Zhdanov &
	(may be 267, 270 or 273*R*)				Minervina (1946; 1947)
	If 267*R*			$[(23)_{17} 22]_3$	Gasilova (1957)
	273*R*			$[(23)_{17} 33]_3$	Gasilova (1957)
339*R*	854·14				Kuo (1964*a*)
354*R*	891·94				Kuo (1964*a*)
393*R*	987·609	329·208	0°32′	$[(33)_{21} 32]_3$	Mitchell (1954)
400*H*	1005·2[3]				Mitchell (1954)
	(may be 1200*R*)				Mitchell (1954)
417*R*	1050·7	350·4	30·4′		Mitchell (1954)
453*R*	1141·4	380·6	27·8′		Kuo (1964*a, b*)
513*R*	1292·6				Kuo (1964*a, b*)
595*R*	1491·72[3]				Kuo (1964*a*)
636*R*	1602·5				Honjo, Miyake & Tomita (1950)
1200*R*	3015·6[3]				Kuo (1964*a*)
	(may be 400*H*)				Mitchell (1954)

(1) *C* = cubic.
H = hexagonal.
R = rhombohedral.
(2) a_0 = 3·073 Å for all hexagonal polytypes.
(3) Calculated: *Zx* 2·513 Å.
(4) Two forms of 36*H* found, only one structure worked out.
(5) 51*R* (*a*) more common form of this polytype.
51*R* (*b*) less common form of this polytype.

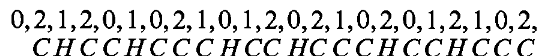
For α-II :



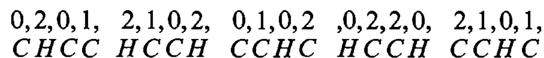
For α-I :

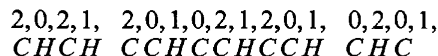


For α-IV :



For α-VI :





From this standpoint the various modifications of SiC appear as regularly repeated mixed sequences of hexagonal and cubic close packed ions or tetrahedra.'

The simplest method of notation to describe the stacking sequences is that of Zhdanov & Minervina (1946) and Mitchell (1957). This consists merely of applying a number corresponding to the number of adjacent layers of similar orientation. This notation is compared with Wyckoff's (1963) and Wells's (1950) in Table 1.

Summary of crystallographic data

The unit-cell dimensions and stacking sequences of the various SiC structures are summarized in Table 2. In Table 3 specific data, intensities, *etc.* for several of the more common polytypes are presented.*

* *Note added in proof*:— An article giving revised X-ray diffraction line intensities for silicon carbide polytypes will appear in *Journal of Applied Crystallography* (Hannam & Shaffer, 1969).

Table 3. *Intensities and spacings of various* SiC *polytypes*

1. $2H$ (wurtzite form) (*a*) (*b*) (*c*) (*d*) (*e*) (*f*) (*g*).

Space group: $P6_3mc$

Atomic positions[a]: Si at 0 0 0 $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$
C at 0 0 $\frac{3}{8}$ $\frac{2}{3}\ \frac{1}{3}\ \frac{7}{8}$

Unit cell: a_0 3·0763 ± 0·0010[a]
3·079[g]
c_0 5·0480 ± 0·0010[a]
5·028[g]

hkl	d_{exp}[g]	I_{exp}[g]	I_{exp}[a]	Corresponding β-SiC[g] reflection
10·0	2·667	59·6	6207	
00·2*	2·515	100·0	12178	111
10·1	2·353	57·9	8012	
10·2	1·826	11·2	2877	
11·0*	1·538	88·5	—	220
10·3	1·418	28·3	5866	
20·0	1·331	3·6	1554	
11·2*	1·308	77·5	—	311
20·1	1·286	20·2	2588	
00·4*	1·258	10·8	2531	222
20·2	1·180	2·6	843	
10·4	1·138	1·7	613	
20·3	1·043	14·5	3788	
21·0	1·005	19·2	—	
21·1	0·9842	25·5	—	
11·4*	0·9736	27·3	—	420
10·5	0·9425	10·0	3779	
21·2	0·9336	6·5	—	
20·4	0·9145	1·3	587	
30·0*	0·8867	46·0	5225	422
21·3	0·8626	26·5	—	
00·6, 30·2	0·8363	58·0	4216 (006)	
			4344 (302)	
10·6			640	
20·5			6097	

* Intensities may be somewhat shifted for certain lines since the samples contained β-SiC.

2. β ($3C$, sphalerite or zincblende form)

Space group: $F\bar{4}3m$

Atomic positions: Si at 0 0 0 0 $\frac{1}{2}\ \frac{1}{2}$
$\frac{1}{2}$ 0 $\frac{1}{2}$ $\frac{1}{2}\ \frac{1}{2}$ 0
C at $\frac{1}{8}\ \frac{1}{8}\ \frac{1}{8}$ plus Si position

Unit cell: a_0 4·349

hkl	d_{exp}(h)	I_{exp}(h)	I_{calc}(j)
111	2·51	10	70
200	2·18	1	12
220	1·54	6	53
311	1·310	6	44
222	1·256	1	5
400	1·087	2	13
331	0·998	5	31
420	0·772	3	11
422	0·888	8	62
333, 511	0·837	10	65

3. $4H$ (old type III)

Space group: $C6mc$

Atomic positions: Si at 0 0 0 0 0 $\frac{1}{2}$
$\frac{1}{3}\ \frac{2}{3}\ \frac{1}{4}$ $\frac{2}{3}\ \frac{1}{3}\ \frac{3}{4}$
C at 0 0 $\frac{3}{16}$ plus each Si position

Unit cell: a_0 3·073 Å
c_0 10·053 Å

Table 3 (*cont.*)

hkl	d_{exp}(h)	I_{exp}(h)
10·0	2·67	4
10·1	2·57	5
00·4	2·52	4
10·2	2·36	5
10·3	2·08	3
10·4	1·83	2
10·5	1·61	4
11·0	1·54	6
10·6	1·419	5
11·4	1·311	7
20·2	1·287	4
10·7	1·264	3
20·3	1·238	2
20·4	1·178	2
10·8	1·136	1
20·5	1·111	4
20·6	1·042	5
10·9	1·030	3
12·1	1·000	4
12·2	0·985	5
20·7, 11·8	0·973	4
12·3	0·963	3
10·10	0·941	5
12·4	0·933	2
20·8	0·912	1
12·5	0·899	4
30·0	0·887	6
10·11, 12·6	0·863	10
20·9	0·856	3
00·12, 30·4	0·837	8
12·7	0·824	4
20·10	0·803	9
10·12	0·798	1
12·8	0·786	3

4. $6H$ (old type II)

Space group: $C6mc$

Atomic positions: Si at 0 0 0 0 0 $\frac{1}{2}$
$\frac{1}{3}\ \frac{2}{3}\ \frac{1}{6}$ $\frac{1}{3}\ \frac{2}{3}\ \frac{5}{6}$
$\frac{2}{3}\ \frac{1}{3}\ \frac{2}{3}$ $\frac{2}{3}\ \frac{1}{3}\ \frac{1}{3}$
C at 0 0 $\frac{1}{8}$ plus each Si position

Unit cell: a_0 3·073 Å
c_0 15·079 Å

hkl	d_{exp}(h)	I_{exp}(h)
10·1	2·61	6
00·6, 10·2	2·51	7
10·3	2·36	5
10·4	2·19	4
10·5	2·00	3
10·7	1·67	3
10·8, 11·0	1·54	8
10·9	1·419	5
21·0	1·329	3
10·10, 11·6, 20·2	1·309	9
20·3	1·285	3
00·12, 20·4	1·253	3
10·11, 20·5	1·217	2
20·7	1·131	2
20·8	1·087	4
10·13	1·061	1
20·9	1·042	4
12·1	1·002	3
10·14, 20·10, 12·2	0·997	5
12·3	0·986	4
11·12, 12·4	0·972	5
20·11, 12·5	0·953	2
10·15	0·940	4
12·7	0·911	3
10·16, 12·8, 30·0	0·888	9
20·13	0·873	1
12·9	0·862	6
10·17	0·841	2
00·18, 20·14, 12·10, 30·6	0·837	10
12·11	0·811	3
20·15	0·802	5

5. $15R$ (old type I)

Space group: $R3m$

Atomic positions: Hexagonal system
Si at 0 0 u
$\frac{1}{3}\ \frac{2}{3}\ \frac{1}{3}+u$
$\frac{2}{3}\ \frac{1}{3}\ \frac{2}{3}+u$
$u=0\ \frac{2}{15}\ \frac{6}{15}\ \frac{9}{15}\ \frac{13}{15}$
C at 0 0 $\frac{1}{20}$ plus each Si position
Rhombohedral system

Unit cell: Hexagonal system
a_0 3·073 Å
c_0 37·70 Å
Rhombohedral system
a_r 12·69 Å
α 13°54−½′
Z 5

Table 3 (*cont.*)

hkl	d_{exp}[h]	I_{exp}[h]	*hkl*	d_{exp}[h]	I_{exp}[h]
10·1, 01·2	2·66	4	20·23	1·035	4
10·4	2·58	7	10·34	1·024	1
00·15, 01·5	2·51	7	01·35, 02·25, 21·4, 12·4	1·000	5
10·7	2·40	6	21·7	0·990	3
01·8	2·32	5	21·8	0·984	3
10·10	2·19	1	11·30, 21·10	0·974	5
01·11	2·11	3	12·11	0·965	1
10·13	1·97	1	10·37	0·952	4
01·17	1·70	2	01·38	0·930	4
10·19	1·59	5	12·17	0·917	1
01·20, 11·0	1·54	9	21·19	0·896	4
10·22	1·444	5	10·40, 12·20, 30·0	0·888	7
01·23	1·398	4	01·41, 21·22	0·868	6
02·4	1·320	2	12·23	0·858	5
10·25, 11·15, 20·5	1·311	8	02·23	0·851	1
02·7	1·297	2	00·45, 20·35, 21·25, 20·15	0·838	10
20·8	1·281	2	12·26	0·827	4
00·30, 02·10	1·257	2	02·37	0·809	5
20·11	1·246	1	20·38	0·796	6
20·17	1·143	1			
02·19	1·106	3			
20·20	1·089	2			
02·22	1·053	4			

6. 21*R* (old type IV)

Space group: *R*3*m*

Atomic positions: Hexagonal system[k]

Si at 000, 004*Z*, 009*Z*, 0012*Z*, 0015, 0017*Z* where $Z=\frac{1}{21}$

$\frac{2}{3}\frac{1}{3}\frac{1}{3}$ and

$\frac{1}{3}\frac{2}{3}\frac{2}{3}$ plus each of the above

C at 00 $\frac{1}{28}$ plus each Si position

Rhombohedral system[k]

Si at 0 0 0

4*Z* 4*Z* 4*Z*

6*Z* 6*Z* 6*Z*

9*Z* 9*Z* 9*Z*

12*Z* 12*Z* 12*Z*

15*Z* 15*Z* 15*Z*

17*Z* 17*Z* 17*Z* where $Z=\frac{1}{21}$

7C at $\frac{1}{28}\frac{1}{28}\frac{1}{28}$ plus each Si location

Unit cell: Hexagonal system

a_0 3·073 Å

c_0 52·78 Å

Rhombohedral system

a_r 17·68 Å

α 9°58′

Z 7

hkl	d_{exp}[h]	I_{exp}[h]	*hkl*	d_{exp}[h]	I_{exp}[h]
10·2, 10·4, 10·5	2·63	7	10·49, 20·35, 21·4, 12·5, 21·7, 12·8	0·999	5
00·21, 10·7	2·53	10	21·10, 12·11	0·986	2
01·8	2·47	2	11·42, 21·13, 12·14	0·973	4
10·10	2·40	2	20·38, 21·16	0·962	1
01·11	2·35	1			
10·13	2·23	1			
01·14	2·17	1			
10·16, 01·17	2·01	3			
10·25	1·66	1			

Table 3 (*cont.*)

hkl	d_{exp}[h]	I_{exp}[h]	*hkl*	d_{exp}[h]	I_{exp}[h]
01·26	1·62	1	10·52	0·948	2
10·28, 11·0	1·54	8	01·53	0·932	2
01·29	1·51	2	21·25	0·906	1
10·31	1·442	3	10·55, 12·26	0·902	3
01·32	1·407	2	01·56, 21·28, 30·0	0·888	7
10·34	1·337	1	12·29	0·881	2
01·35, 11·21, 20·5, 02·7, 20·8	1·311	7	21·31	0·867	3
02·10	1·293	1	10·58, 20·27, 12·32	0·858	4
00·42, 10·37, 20·14	1·259	3	21·34	0·844	2
01·38	1·229	1	00·63, 02·49, 12·35, 30·21	0·837	9
20·26	1·114	1	20·50	0·828	2
02·28	1·089	2	21·37	0·824	2
20·29	1·076	2	12·38	0·815	1
10·46, 02·31	1·050	2	02·52	0·807	3
01·47, 20·32	1·035	2	20·53	0·797	3
			02·55	0·779	5

7. 33*R* (type VI)

Space group: *R*3*m*

Atomic positions: Hexagonal system[l]

Si at 00*nZ* where

n = 0, 2, 6, 8, 12, 15, 18, 21, 25, 27 and 31

$Z=\frac{1}{33}$

$\frac{2}{3}\frac{1}{3}\frac{1}{3}$ and

$\frac{1}{3}\frac{2}{3}\frac{2}{3}$ plus each of the above

C at 00 $\frac{1}{44}$ plus each of the Si positions

Rhombohedral system[l]

11Si at *nZ*, *nZ*, *nZ* where

n = 0,2, 6, 8, 12, 15, 18, 21, 25, 27 and 31

$Z=\frac{1}{33}$

1C at $\frac{1}{44}\frac{1}{44}\frac{1}{44}$ plus each Si position

Unit cell: Hexagonal system[l]

a_0 3·073

h_0 82·94

Z 33

Rhombohedral system[l]

a_r 27·704

α 6°21′30″

Z 11

hkl	d_{exp}[h]	I_{exp}[h]	*hkl*	d_{exp}[h]	I_{exp}[h]
10·4, 01·5, 10·7	2·63	5	02·49, 20·50	1·044	3
00·33, 10·10, 01·11	2·53	10	01·77, 02·55, 12·5, 21·7, 21·10, 12·11	0·999	4
10·16, 01·17	2·38	6	21·16, 12·17	0·988	4
10·22, 01·23	2·18	3	11·66, 21·22	0·975	4
01·26	2·09	2	10·82	0·947	3
10·28	2·00	2	01·83	0·936	3
01·38	1·69	2	12·38	0·914	2
10·40	1·64	2	01·86, 21·40	0·905	2
10·43	1·56	3	21·43	0·891	2
01·44, 11·0	1·54	8			
10·46	1·497	1			

Table 3 (*cont.*)

10·49	1·434	3	10·88	0·888	5
01·50	1·410	3	12·44		
10·55	1·313	7	30·0		
11·33			01·89	0·880	2
02·10			21·49	0·867	4
20·11			12·50	0·860	4
01·56	1·291	3	02·76	0·844	1
02·16			00·99	0·838	7
00·66	1·260	3	10·94		
02·22			20·77		
02·43	1·091	2	21·55		
20·44			30·33		
01·71	1·072	1	02·82	0·806	2
02·46			20·83	0·793	3
			20·86	0·781	1

[a] Adamsky & Merz, 1959.
[b] Merz & Adamsky, 1959.
[c] Merz, 1961.
[d] Patrick *et al.* 1965.
[e] Patrick *et al.* 1966.
[f] Ryan *et al.* 1966.
[g] Sokhor & Glukhov, 1965.
[h] Thibault, 1944.
[j] Ott, 1926.
[k] Ramsdell, 1944.
[l] Ramsdell, 1945.

Mechanics of crystal growth

It seems appropriate at this point to describe briefly the actual mechanics of crystal growth by the various growth mechanisms. The most common case involves the collision of atoms with a crystal surface. They migrate around on the surface until they become attached to a growing front, or until several coalesce to form a growth nucleus on a crystal face or until the atom re-evaporates and leaves the surface. To insure that the adsorbed atoms will remain on a surface at a high enough concentration for sufficient time to nucleate a new layer, the activity of the atomic species in the vapor must be sufficiently greater than that of the surface; that is to say, the vapor must have a certain degree of supersaturation.

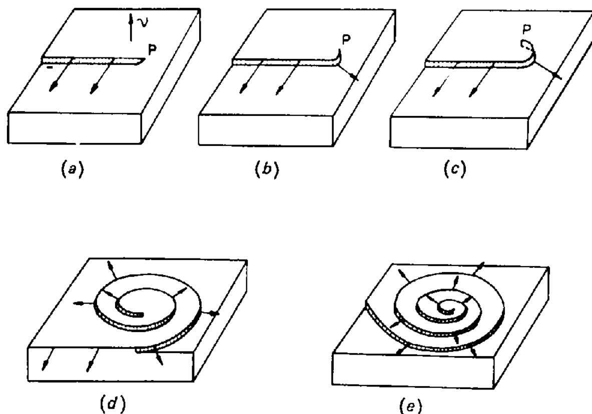


Fig. 5. Screw dislocation in successive stages of growth.

Once a new layer of greater than the critical size is formed, a lower degree of supersaturation is required to provide atoms to the growing layer at a rate sufficient for the layer to propagate. A mechanism which provides a continuous, constant growing front is the screw dislocation mechanism. Fig. 5 shows such a mechanism in successive stages of growth. Thus it is apparent that crystal growth by a screw dislocation mechanism proceeds at a lower supersaturation than will the ordinary layer nucleation mechanism.

A third mechanism of importance is the vapor-liquid-solid (VLS) mechanism. It differs from the layer nucleation mechanism in that a molten metal or alloy phase is present. Atoms are dissolved in the metal from the vapor and condense in turn from the liquid phase onto the crystal surface.

This brief description is intended only to define the various mechanisms. Complete detailed descriptions of each can be found in numerous texts on crystal growth and in technical papers such as those by Frank (1949, 1951) and Wagner (Wagner & Ellis, 1964; Wagner, Ellis, Jackson & Arnold, 1964; Wagner & Ellis, 1965).

Theories of polytype formation

As early as 1907, Tone (1907) reported the presence of spiral markings typical of large numbers of SiC crystals. His drawings (Fig. 6) show both right and left hand spirals, simple circular and hexagonal spirals and complex interacting spirals. A number of other investigators observed these figures but without explanation of their origin (Gliki, 1953; 1954; Kalt & Wittborg, 1951; Lemmlein, 1945; 1947; Lemmlein & Gliki, 1954; Mellor, 1924; Menzies & Sloat, 1929).

The presentation of the theory of the screw dislocation mechanism of crystal growth by Burton, Cabrera & Frank (1949, 1951) provided the necessary tool to stimulate renewed study of these markings on SiC. The first explicit description of the relationship between growth spirals, screw dislocations and polytypism in SiC was set forth almost simultaneously by Vand (1951*a*,*b*), Amelinckx (1951*c*) and Frank (1951). Earlier Zhdanov & Minervina (1945*b*) suggested that 'It (the long range periodicity in SiC) may be tentatively suggested to be bound with the formation of spirals ··· lately investigated by Lemmlein (1947).' Despite the nearness to the truth of Zhdanov & Minervina's observation it appears that the first explicit description was put forth by Amelinckx (1951*c*), Frank (1951) and Vand (1951*a*,*b*). Verma (1951, *a*,*b*,*c*,*d*, 1952*a*,*b*, 1953) and Amelinckx (1951*a*,*b*, 1952*a*,*b*, 1953) provided the greatest detailed study of this phenomenon, describing numerous forms and showing how they might interact.

Numerous measurements have been made on the step heights of various screw dislocations on SiC crystals. Lemmlein (1947) suggested that the step heights might be equal to multiples of the c_0 distances in the various unit cells. He later found step heights of the order of

10 Å ($c_0 = 10.053$ for 4*H* SiC) and concluded that growth steps of 2·5 Å probably exist, corresponding to a single 'layer' in the SiC structure.

Verma (1951*a*, *b*) confirmed Lemmlein's work when he found step heights of 15·1 and 15·2 Å on 6*H* crystals (c_0 = 15·079 Å). Amelinckx (1951*a*, *b*, *c*) reported the existence of step heights equal to unimolecular layers. He found step heights equal to fractions and multiples of the unit-cell c_0 dimensions and produced evidence for the formation of cubic SiC on a 6*H* substrate and of an unidentified rhombohedral type (~84*R*) on a 6*H* substrate (Amelinckx, 1952*a*).

Step heights corresponding to the unit-cell (c_0) dimensions of a number of polytypes have been measured by Verma (1957*c*, *d*, 1952*a*, *b*, 1953). Other less definitive measurements have been reported by Gliki (1954), Lemmlein & Gliki (1954), Buckley (1952) and Gevers (1953).

Mitchell (1957) approached the problem in detail on the basis of the crystal structure and showed that with a few basic assumptions, nearly all of the polytypes whose structures had been analyzed could be explained on the basis of screw dislocations. His assumptions were that:

1. There are three ideal structures for SiC – 6*H*, 4*H* and 15*R*.
2. There is a horizontal displacement associated with the vertical displacement along the *c* axis. Thus, horizontal displacement is necessary to maintain continuity in the Si–C zigzag 'chains'.

Based on these assumptions, the 6*H* structure, *aaabbb* layer sequence, leads to the layer sequences and polytypes shown in Table 4. Similarly, 4*H* and 15*R* structures lead to numerous polytypes also included in Table 4.

Mitchell, however, predicted that 2*H*-SiC should not exist because 'if is neither an ideal structure of the compound, nor can it be derived from dislocations in known phases of the compound'. This hypothesis was later proved to be incorrect by the discovery of the wurtzite (2*H*) polytype of α-SiC by Adamsky & Merz (1959) (Merz & Adamsky 1959; Merz, 1959).

Mitchell suggested that since several specimens of 8*H*-SiC had been reported and since the 44 sequence could not be easily derived from dislocations in the three SiC phases, 'this (8*H*) may also be a definite, but uncommon phase of SiC'. It might just as well be that the 2*H* polytype is yet another 'definite but uncommon phase of SiC.'

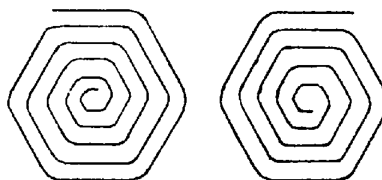


Fig. 6. Schematic drawings of growth terraces on basal planes of α-SiC, from Tone (1907).

Table 4. *Structures resulting from dislocations in* 6*H*, 4*H* *and* 15*R* *polytypes*

Burgers vector	6*H* Sequence	6*H* Polytype	4*H* Sequence	4*H* Polytype	15*R* (23) Sequence	15*R* (23) Polytype	15*R* (32) Sequence	15*R* (32) Polytype
1	∞	cubic	∞	cubic	∞	cubic	∞	cubic
2	*	*	*	*	*	*	*	*
3	*	*	21	9*R*	*	*	*	*
4	*	*	22	4*H*	22	4*H*	31	12*R*
5	32	15*R*	23	15*R*	23	15*R*	32	15*R*
6	33	6*H*	*	*	33	6*H*	24	18*R*
7	34	21*R*	2221	21*R*	*	*	*	*
8	*	*	2222	4*H*	*	*	*	*
9	*	*	2223	27*R*	2322	27*R*	2331	27*R*
10	*	*	*	*	2323	15*R*	3232	15*R*
11	3332	33*R*	$(22)_2 21$	33*R*	3233	33*R*	2324	33*R*
12	3333	6*H*	$(22)_2 22$	4*H*	*	*	*	*
13	3334	39*R*	$(22)_2 23$	39*R*	*	*	*	*
14	*	*	*	*	$(23)_2 22$	42*R*	$(32)_2 31$	42*R*
15	*	*			$(23)_2 23$	15*R*	$(32)_2 32$	15*R*
16	*	*						
17	$(33)_2 32$	51*R*						
18	$(33)_2 33$	6*H*						
19	$(33)_2 34$	57*R*						

* = unstable arrangements.

(*a*)

(*b*)

Fig. 10. Parallel or columnar growth in α-SiC crystal; (*a*) top view (*b*) side view.

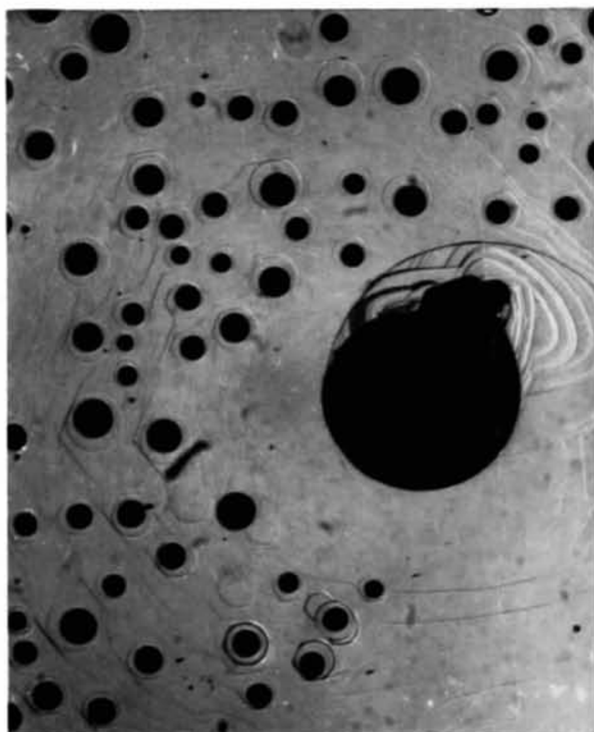


Fig. 11. Metal droplet associated with SiC crystal growth.

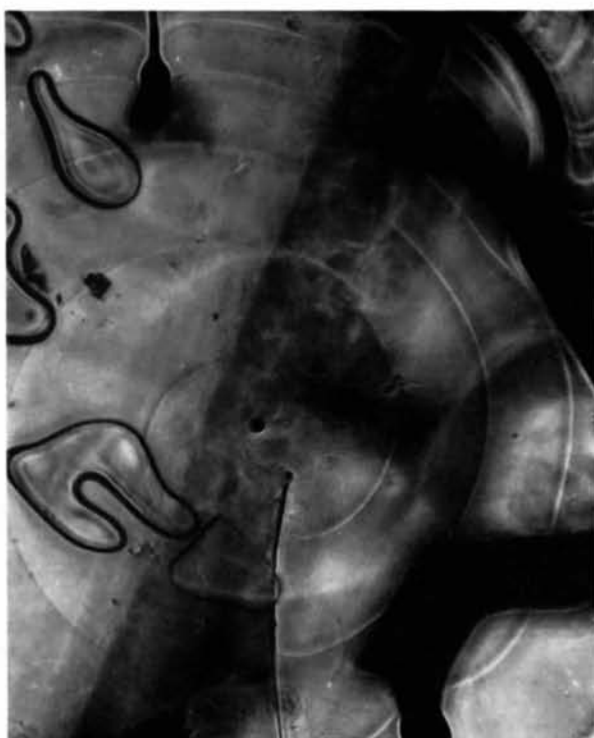


Fig. 12. Hollow core associated with the centeı of a screw dislocation.

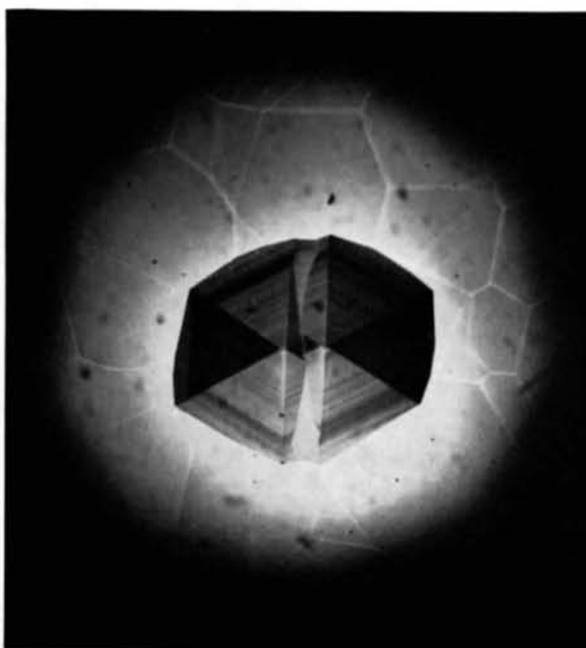


Fig. 13. Pyramidal etch pit, resulting from fused caustic etch of SiC containing a screw dislocation.

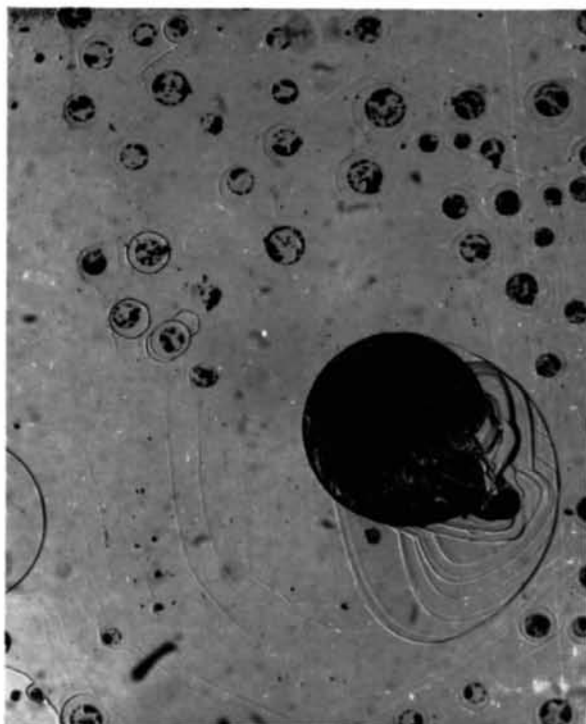


Fig. 14. Crystal shown in Fig. 11 after removal of the metal droplet with acid.

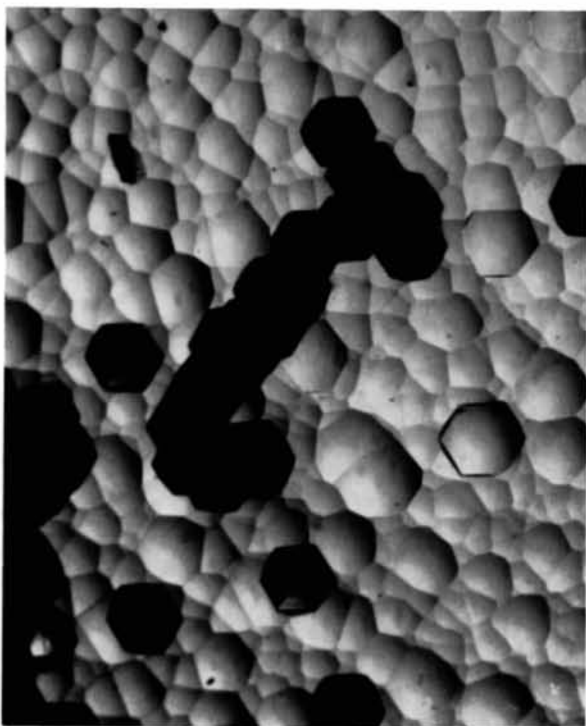


Fig. 15. Crystal shown in Figs. 11 and 14 after subsequent etch in fused NaOH at 800 °C.

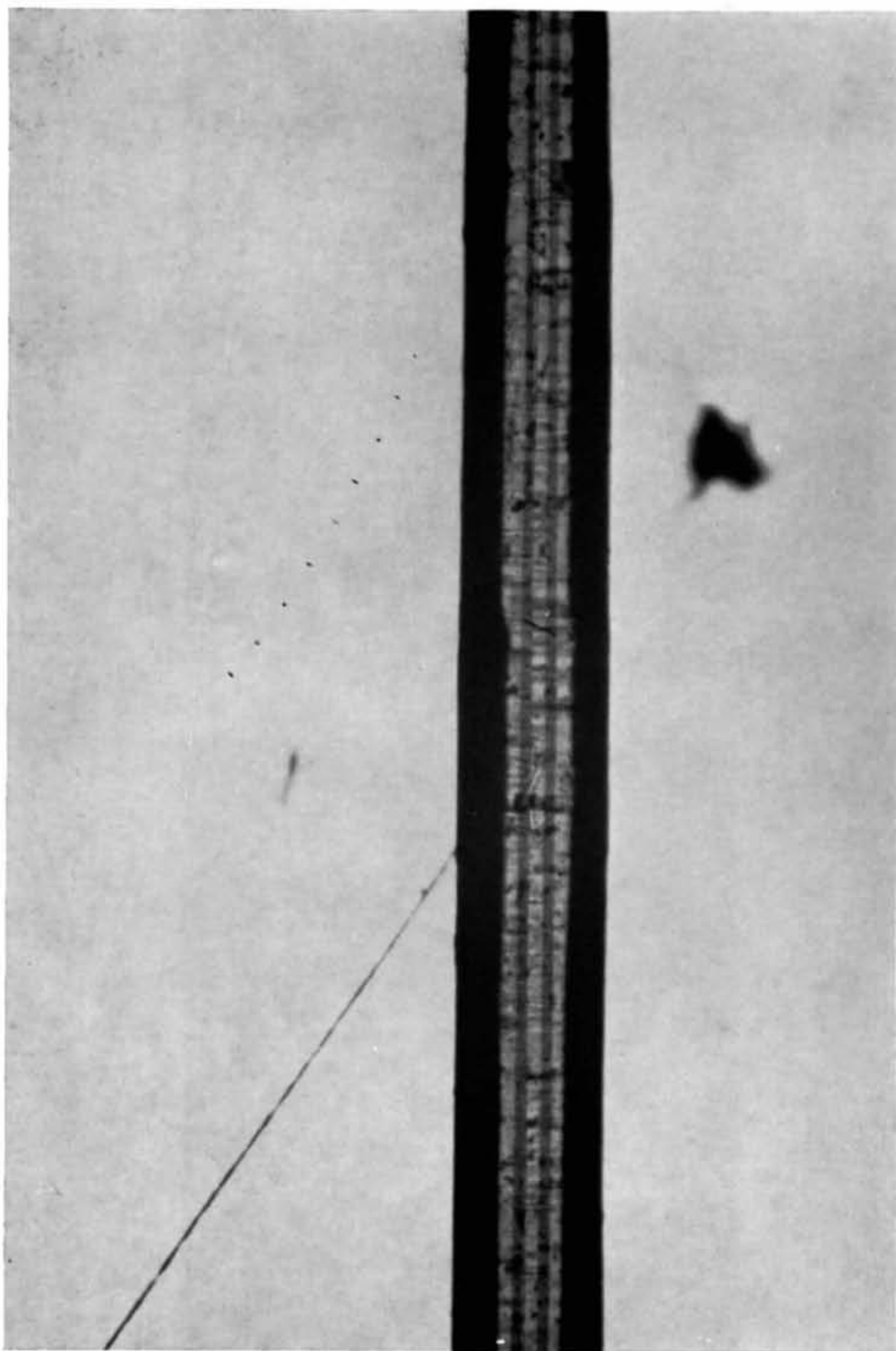
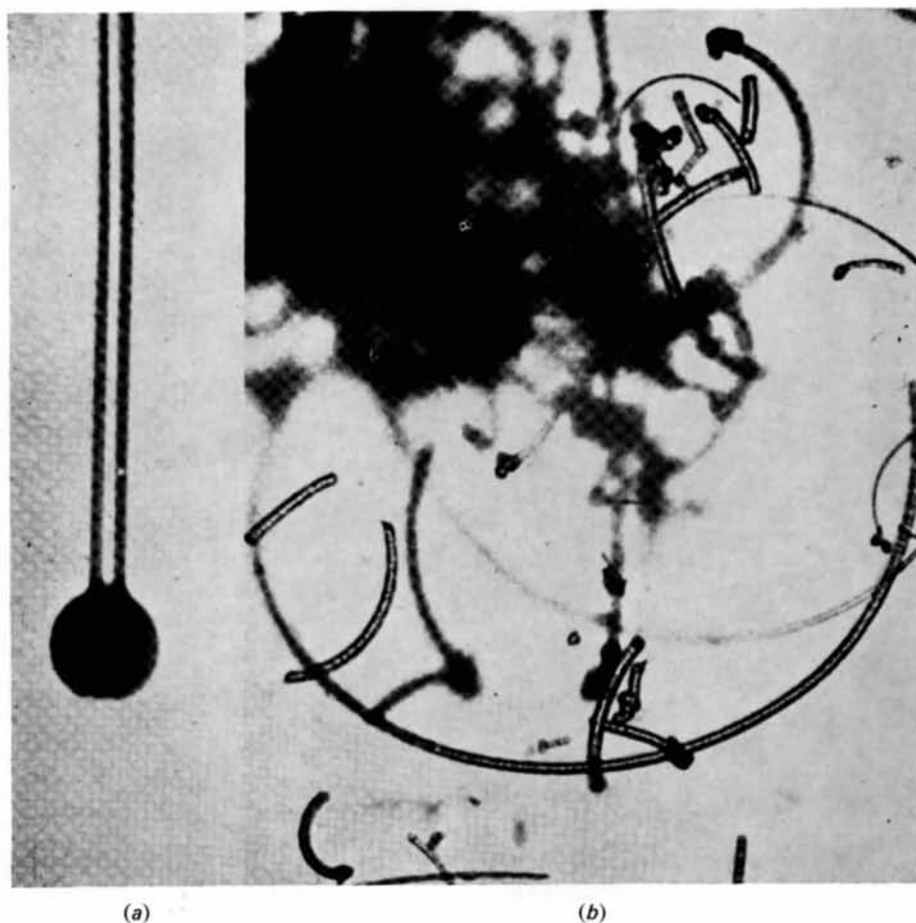


Fig. 16. Hexagonal SiC whisker grown by vacuum sublimation, showing axial discontinuities.



(a) (b)

Fig. 17. Droplet termination in a SiC whisker, from Merz (1959). (a) Ball termination on β-SiC whisker. (b) β-SiC fibers showing banded structure.

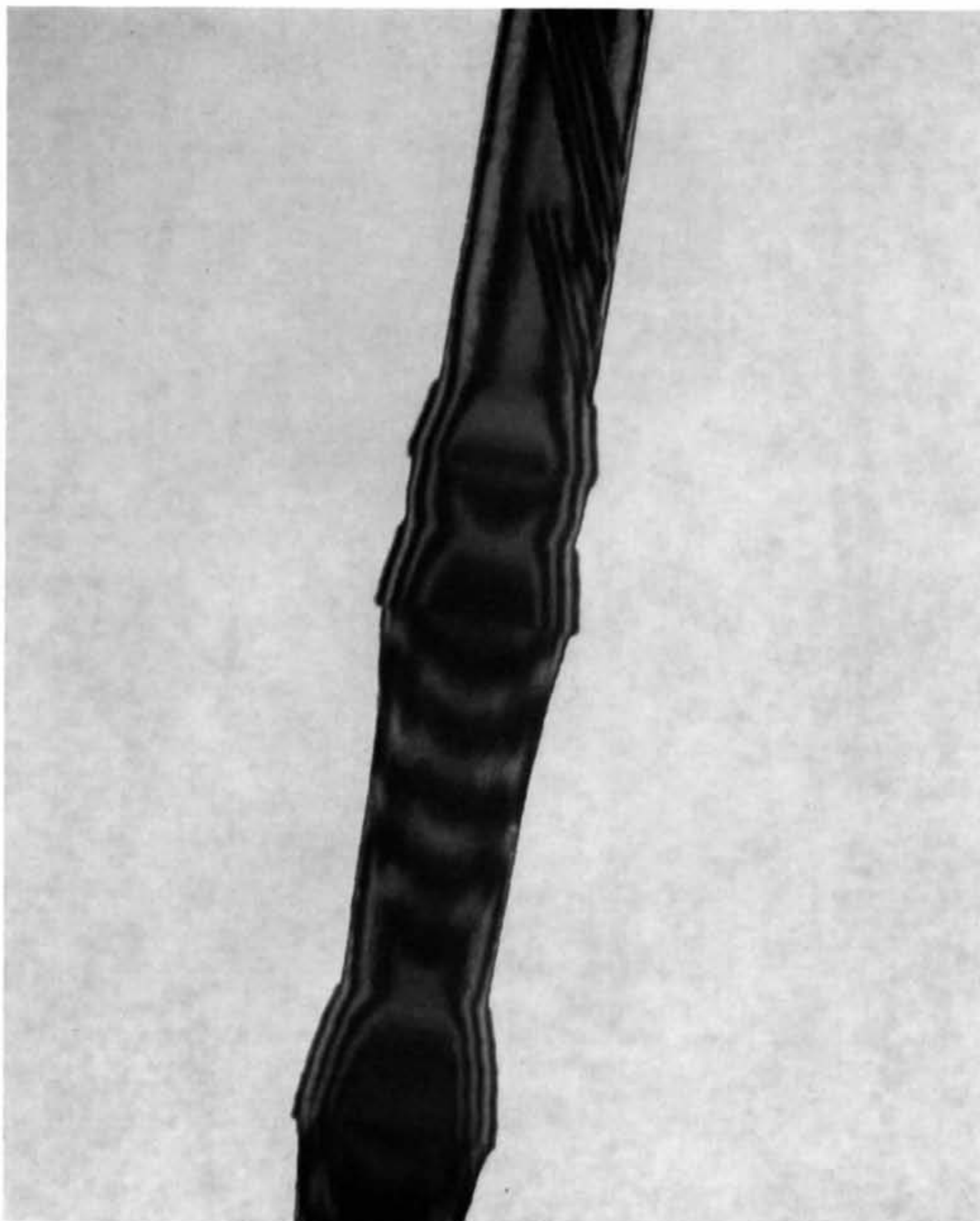


Fig. 18. SiC *c*-axis whisker.

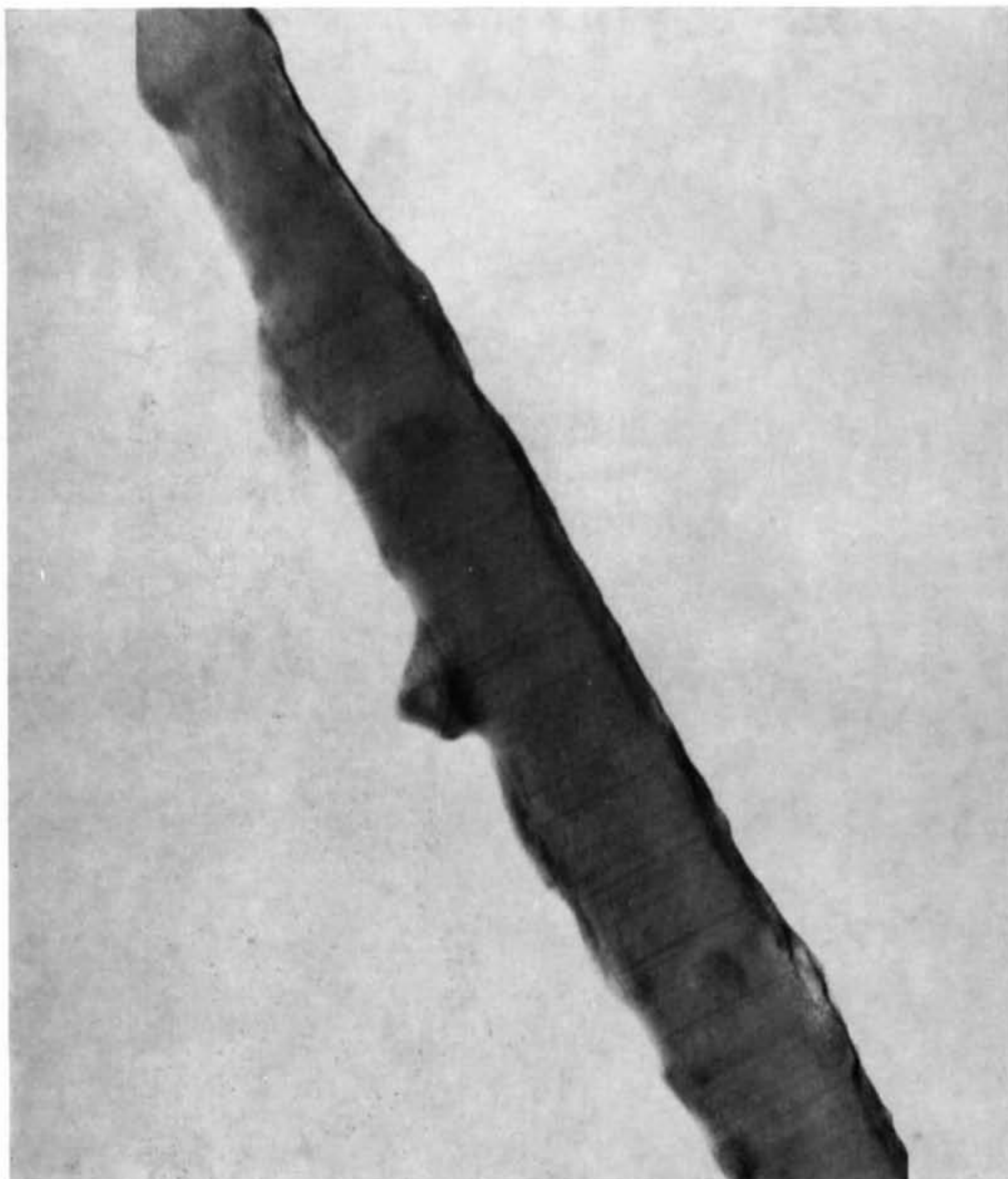


Fig. 19. Platinum shadowed *c*-axis whisker.

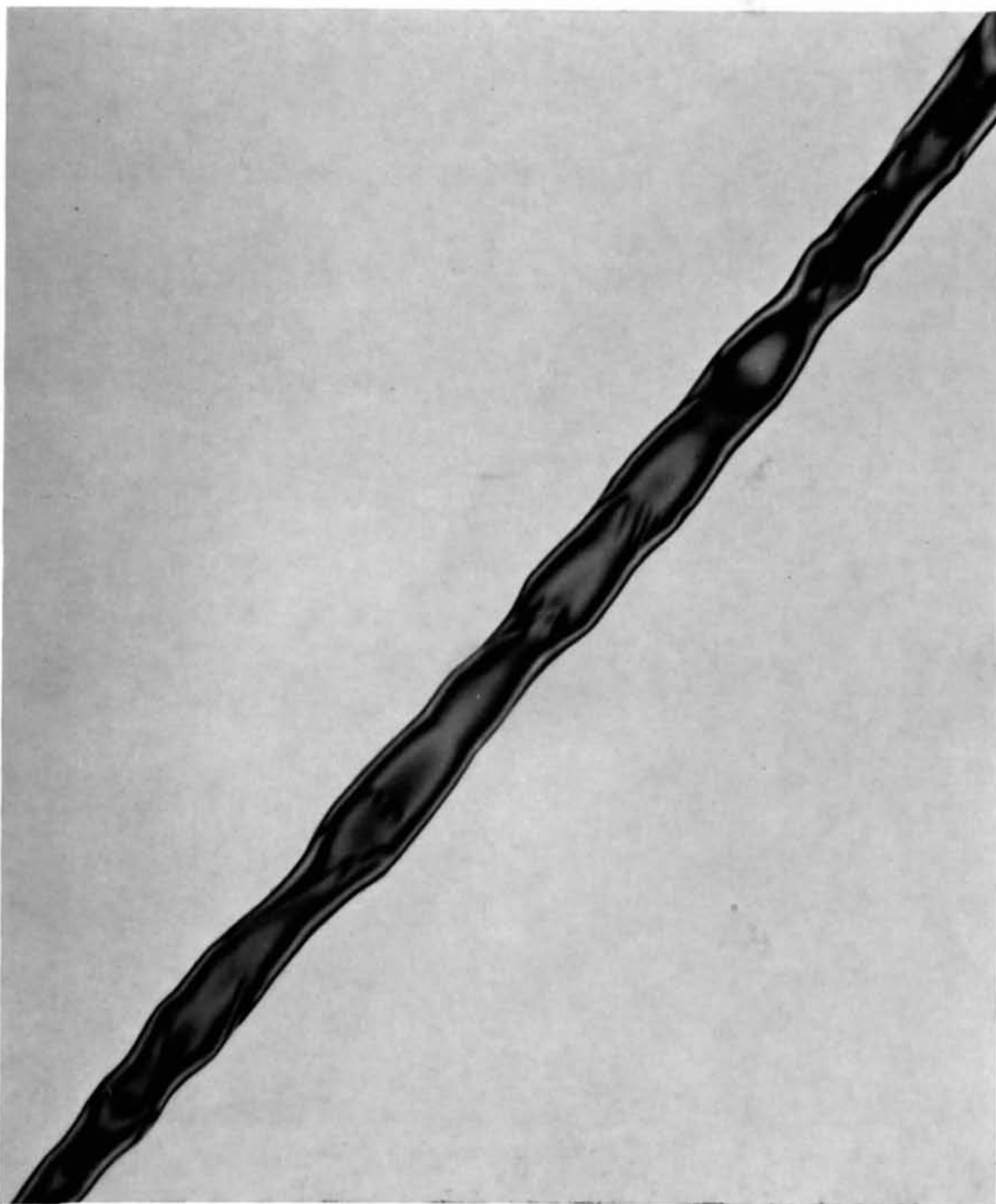


Fig. 20. *c*-Axis whisker showing non-parallel, non-linear extinction contours.

Mitchell theorized that, although β-SiC can be formed from other SiC structures by a screw dislocation mechanism of crystal growth, it is actually a stable form of SiC in itself and may be formed directly and independently.

Other mechanisms of polytype formation have been suggested but not generally accepted. Zhdanov & Minervina (1945*a*,*b*) and Lundqvist (1948) have suggested that polytypism was dependent on impurities This was not adequate in itself; however, a definite correlation at least exists. Ramsdell & Kohn (1951) suggested that polytypism might arise from so-called 'polymer' units stable over various temperature ranges. Zhdanov & Minervina (1945*a*,*b*) also suggest the possible influence of neighboring crystals on polytype formation. Jagodzinski (1954) proposed a transposition of layers based on vibrational entropy. None of these theories has received much support however.

Krishna & Verma (1963) cite much evidence for the non-universality of the screw dislocation mechanism. They cite such things as failure to observe screw dislocation helices on crystal surfaces, structures which do not appear to be based on smaller unit cells, and unit cells whose dimensions are multiples of the apparent smaller unit. They fail to consider the possible structural effects of multiple dislocations. For example, they suggest that the 36*H* polytype whose layered sequence is $(33)_2\,34(33)_3 32$ cannot be formed by a simple screw dislocation since its height is exactly six times that of the 6*H* basic structure. Two screw dislocations of 17 and 19 layers would satisfy such a structure. It is common for many screw dislocations to co-exist on a single crystal.

Recently Krishna & Verma (1965; Verma & Krishna 1966) re-evaluated Mitchell's hypothesis and detected an error in his reasoning. By modifying his original screw dislocation mechanism, not only can almost all the known polytypes be explained, but the occurrence of rhombohedral structures is explained. Briefly the reasoning is as follows.

The structure of SiC viewed parallel to the hexagonal axis consists of hexagonal double layers, each layer consisting of a single atomic species, and the alternate atoms located directly above one another. Since the bonding of both atoms in SiC is tetrahedral, additional double layers can attach themselves in only two positions. These three orientations, the only ones possible, can be designated *A*, *B* and C.

Mitchell based his considerations of the structure of SiC on two-layer arrangements of *a* and *b* and stacking sequences based only on the orientation of successive tetrahedral layers. The layers of tetrahedra can be arranged in space in three non-identical positions *A*, *B* and *C*, shown in Figs. 7 and 8. Mitchell neglected the fact that whereas a Burgers vector equivalent to one layer would result in an *a*,*a*,*a* stacking sequence, this would in reality not be stable since the layers would all

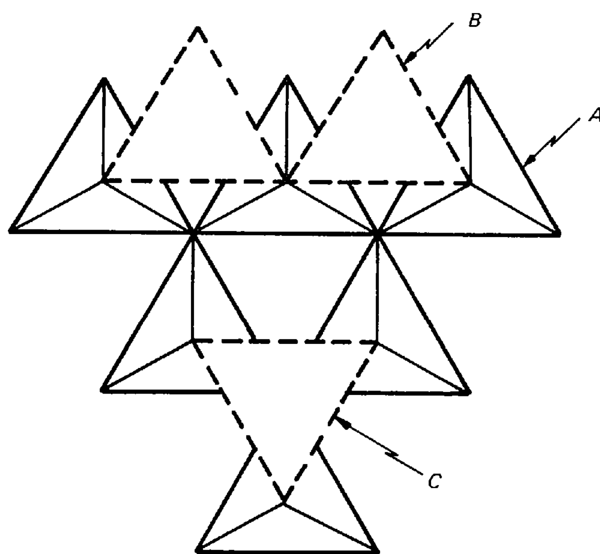


Fig. 7. Successive layers of tetrahedra showing non-equivalent positions.

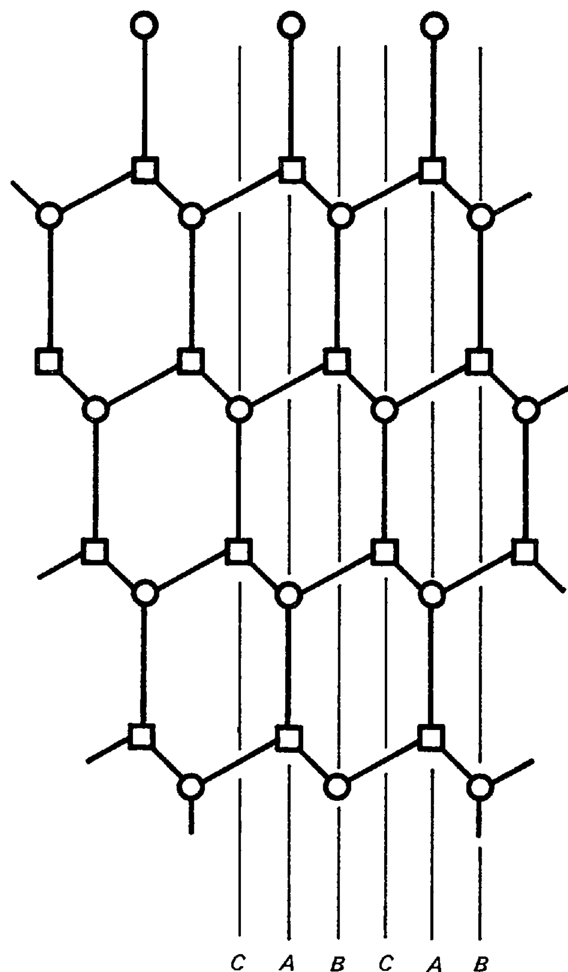


Fig. 8. Section through (11$\bar{2}$0) plane showing three non-equivalent positions.

have the same spatial position *AAA*..., *BBB*... or *CCC*..., *etc.* Since two adjacent layers in the case of tetrahedral bonding cannot have the same position *AAA*, *etc.*, each successive layer must undergo a translation parallel to the plane of the growth surface. Whatever forces 'cause it to occur in any particular direction, would cause it to occur in the same direction every time the stack moves through one pitch, since it comes back to an identical situation. Three shifts in the same direction would bring the stack back into its original position, completing one repeat period. It is easy to see that the resulting structure would have a rhombohedral lattice.'

Thus it appears that the long range order, or polytypism, in SiC is most easily explainable on the basis of the screw dislocation growth mechanism. Unusual cases may result from the interaction of more than one screw dislocation.

Crystal growth mechanisms

For a number of years the opinion seemed to be accepted that SiC had to grow by means of a screw dislocation mechanism and, for the larger more complex polytypes, this may be so. Recently evidence is being forwarded that the screw dislocation mechanism may be but one of several mechanisms of crystal growth. These recent findings are substantiated by earlier observations which seemed to have been overlooked in the concentrated study of screw dislocations.

Thibault (1944) observed a single crystal of β-SiC in which two lamellae of α-SiC had been formed (Fig. 9). These lamellae of α-SiC were oriented at an angle of 70° to one another, parallel to octahedral faces of the β crystal. It is hard to imagine to such a growth by screw dislocation mechanisms.

Frequently, large SiC crystals which appear at first glance to be well-formed single crystals are formed in the commercial Acheson furnaces. On closer examination, these large crystals are found to be growing as adjacent columnar growths surrounded by a six-sided shell. Fig. 10 shows such a crystal both in an as-grown state and after cross sectioning. Certainly a simple screw dislocation mechanism is not adequate to explain such a structure.

Recently Arrese (1965) showed that, with but a single exception, all the extremely pure crystals which he studied interferometrically were free of screw dislocations.

Knippenberg & Gomes de Mesquita (1965) found that columnar crystals usually consist of a single polytype while lamellar types frequently contain a number of polytypes within a single crystal. They conclude that polytypism and one dimensional disorder are determined by the kinetics of crystal growth.

The α-β transition postulated by Baumann (1952) represents another facet of the problem of the crystal structure of silicon carbide not yet answered satisfactorily. Baumann suggested that β-SiC was the low temperature form of SiC, stable to 2100–2200° at which temperature it changed to α-SiC. Recent findings show this to be incorrect. In fact, β-SiC might well be considered as merely the limiting case of SiC polytypism, the one in which all layers have the same orientation.

In our laboratory a number of epitaxic growths of β- on α-SiC have been discovered. Frequently screw dislocations and spiral growth forms are found exposed on the α-substrate crystal, but as yet such structures have never been observed on β-SiC crystal facets.

SiC grown rapidly from silicon, ferrosilicon or B_4C melts is generally of the β form, while slow, near-equilibrium cooling yields α-SiC.

Addamiano & Staikoff (1965) report that the reaction of pure carbon and silicon in atmospheres of greater than 500 torr ($\frac{2}{3}$ atm) of nitrogen yield β-SiC at temperatures even in exceess of 2600 °C. These β-SiC compositions may be heated to 2500 °C without conversion to α-SiC in atmospheres of 500 torr of nitrogen, yet they convert completely if heated to 2500° C in argon. Once converted to α-SiC the reverse recrystallization to produce β-SiC could not be achieved by reheating at 2050 or 2500 °C in nitrogen. This is in conflict with Lely's (1958) observation that α-SiC is stable at 2500 °C in 1 atmosphere of nitrogen. The author has grown large crystals of α-SiC by sublimation in a pure nitrogen atmosphere at 2450–2500 °C, which agrees with Lely's findings.

Slack & Scace (1965) converted α-SiC to β-SiC at 2450 °C and a pressure of 35 atmospheres of nitrogen. Kieffer and co-workers (1966) were able to transform the α and β forms from one to the other and back again by controlling nitrogen pressures.

In the Carborundum laboratory β-SiC crystals have been grown, by the author, by sublimation at tempera-

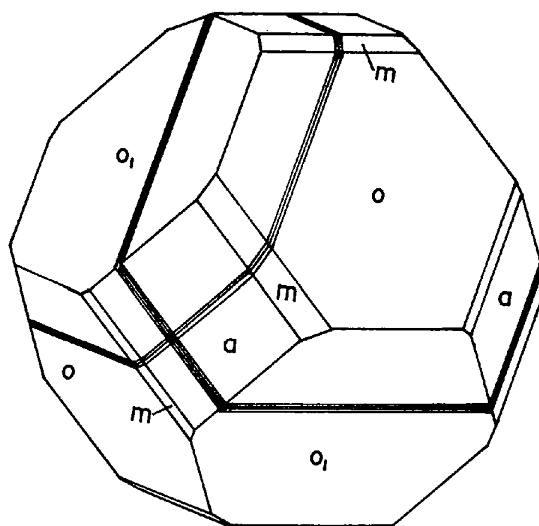


Fig. 9. Sketch of β-SiC crystal showing two intergrown lamellae of α-SiC parallel to (111) faces, from Thibault (1944).

tures from 2000–2200 °C in argon atmospheres under conditions of extreme purity. β-SiC crystals so grown have been shown to contain as little as 2 p.p.m. total detectible impurities. This seems to be contrary to several of the foregoing reports.

Recently Wagner (Wagner & Ellis, 1964; Wagner, Ellis Jackson & Arnold, 1964: Wagner & Ellis, 1965) has described a crystal growth mechanism by which crystals grow from vapors by way of a liquid intermediate (VLS mechanism). Certain evidence points to its applicability to SiC crystal growth.

In the laboratory many crystals of α-SiC have been prepared by sublimation in the presence of large excesses of silicon or aluminum. As grown, the surfaces contain numerous droplets of the solidified elements, each generally associated with a growth terrace such as that shown in Fig. 11. If these were growing by a screw dislocation mechanism they would show spiral growth terraces, hollow dislocation cores after the silicon or aluminum had been removed, or a pyramidal etch pit, after subsequent etching. Figs. 12 and 13 show typical evidence for screw dislocation growth. That none of these are present is shown by Figs. 14 an 15 which show the α-SiC crystal (Fig. 11) grown with condensed metal droplets after removal of the metal with acid and then after a fused caustic etch. No correlation between the metal droplets and evidence for screw dislocations exists.

While much as been written about the screw dislocation mechanism of whisker growth, even here it is far from universal. Certain mechanisms, such as simple sublimation, yield α-SiC whiskers containing screw dislocations (Hamilton, 1960) and the associated Eshelby (1953) twist. Fig. 16 shows such a whisker grown by vacuum sublimation. The two axial discontinuities are clearly visible because of their intense pleochroism.

Merz (1959) reported the presence of ball-like terminations on certain α silicon carbide whiskers which he grew by various gaseous reactions (Fig. 17). In recent papers by Patrick, Hamilton & Choyke (1965, 1966), it is suggested that the liquid droplets observed by Merz are incidental and in no way affect crystal growth of the $2H$ (wurtzite form) SiC needles. Ryan's results support the VLS mechanism (Ryan, Berman, Marshall, Considine & Hawley, 1966).

Smaller diameter whiskers, such as those comprising the commercial material do not display evidence for screw dislocation growth. Of the large number examined by electron microscopy, only isolated cases have been found which show evidence of a screw dislocation. Fig. 18 is an α-SiC whisker growing parallel to the c axis. That the cross section of such c axis whiskers is circular is shown by electron micrographs showing a whisker after platinum shadowing (Fig. 19) and showing non-linear, non-parallel extinction contours (Fig. 20). Fig. 21 is an α-SiC whisker growing parallel to an a axis, the major facets on this ribbon-like whisker being (0001) basal planes. Its orientation is clearly shown by the corresponding electron diffraction pattern, Fig. 22.

Summary

Two conclusions seem justified. The various forms of silicon carbide do not crystallize exclusively by any one mechanism. The available evidence indicates that a number of mechanisms may be operative: screw dislocations, simple layer nucleation and propagation, vapor-liquid-solid interactions, and surface diffusion and recrystallization structure tranformations.

The best explanation for the complex system of polytypes or long range order in SiC appears to be growth by means of screw dislocations, or some variation based on it.

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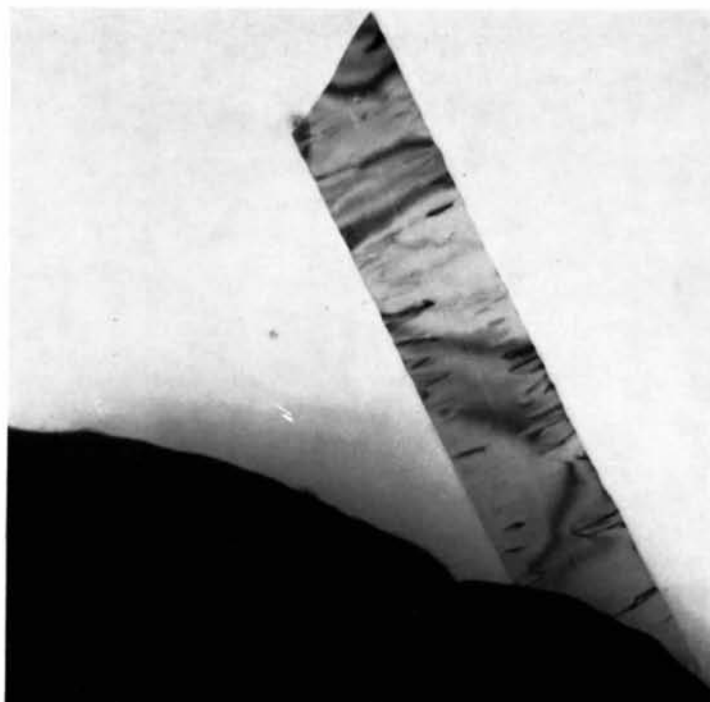

Fig. 21. *a*-axis whisker.

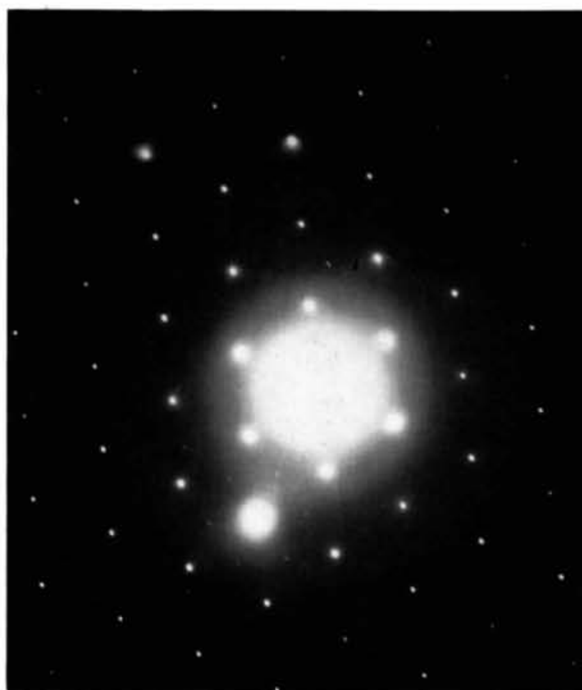

Fig. 22. Electron diffraction pattern of *a*-axis whisker shown in Fig. 21.

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