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MORPHOLOGICAL AND STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE (SiC)*

PART II: STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES

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ABSTRACT

X-ray studies were made of β -SiC and five types of α -SiC by means of powder, rotation and equi-inclination Weissenberg photographs. The following data were obtained: α -SiC, a_0 of all types when referred to smallest hexagonal cell = 3.073 Å; c_0 of all types integrally related, type I = 37.70 Å, type II = 15.07₉ Å, type III = 10.053 Å, type IV = 52.78 Å,

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type VI = 82.94 Å. Formula weights in smallest hexagonal cell = 15, 6, 4, 21, 33, respectively. Calculated density of all α -SiC types = 3.217; observed density, type II = 3.218. Space group, types I, IV, VI = C_{3v}^5-R3m ; types II and III = C_6^4-C6mc . Beta SiC: $a_0 = 4.349$, formula weights in unit cell = 4, calculated density = 3.216, space group = $T_d^2-F\bar{4}3m$.

All α -SiC types are uniaxial positive. The dichroism varies considerably depending on the color, and both absorptions $\omega > \epsilon$ and $\epsilon > \omega$ were observed. The indices of refraction of all types are essentially the same, but some variation occurs within a given type: $\omega_{Na} = 2.6467-2.6487$, $\epsilon_{Na} = 2.6889-2.6930$. Dispersion (4360-6200 Å): $\omega = .0918$, $\epsilon = .1028$. Beta SiC was found to be transparent yellow to olive green, isotropic, n for red (essentially Li) light about 2.63.

The value of the study is not limited to SiC, for it may be considered the prototype of polytypic substances, many of which exist, but have not yet been studied in detail.

STRUCTURAL CRYSTALLOGRAPHY

REVIEW OF LITERATURE

Rinne (1915), (1916) published a Laue photograph of an unspecified type of SiC which was x -rayed perpendicular to the base. The presence of six-fold symmetry was said to be due to twinning, (0001) being the twinning plane.

Burdick and Owen (1918) investigated SiC of unknown type. They deduced an atomic arrangement whereby both the silicon and carbon atoms occupied face-centered rhombohedral lattices which were almost cubic, one displaced with respect to the other 0.36 of the (0001) spacing.

Hull (1919) stated that the structural arrangement of SiC was similar to that of the diamond except that half the carbon atoms, those of one of the face-centered lattices, were replaced by silicon.

Later Hull (1920) found that the powder photograph of an unknown type of SiC showed lines indicating a close-packed hexagonal structure as well as a diamond-type lattice. He concluded that there were, within the same crystal, both cubic and hexagonal close-packing of silicon atoms with carbon atoms at the centers of the tetrahedrons.

Hauer and Koller (1920) published Laue photographs perpendicular to the base of hexagonal (α) SiC, types I, II and III. Although each diagram was unique, there were many spots common to two, and a few common to all three of the SiC types. They also made a similar Laue photograph of a coalescence of types I and II. The diagram consisted of the type I pattern upon which was superposed the strongest spots of type II, equivalent spots being coincident.

Espig (1921) made Laue photographs perpendicular to (0001) and (10 $\bar{1}$ 0) of all three of the α -SiC types. Several very thin basal sections cut from different type II crystals were x -rayed perpendicular to (0001), but all showed hexagonal symmetry, disproving the assumption of Rinne that the hexagonal pattern was due to twinning. Rotation photographs were

made of type II α -SiC using Mo radiation. The smallest cell fulfilling the wave-length requirements of the Laue photographs was said to be hexagonal with: $a_0 = 6.2 \text{ \AA}$; $c_0 = 15.3 \text{ \AA}$. It contained 24 formula weights, and the most probable space group was given as C_{6v}^4 . Espig postulated the same unit cell for types I and III α -SiC but different arrangements within the cell, but no details were given.

Ott (1925*a*) gave complete structure data for type II α -SiC. The hexagonal unit cell dimensions obtained from rotation photographs using Mo radiation were: $a_0 = 3.09_5 \text{ \AA}$; $c_0 = 15.17 \text{ \AA}$. The $c_0:a_0$ ratio was thus 4.90 and the number of formula weights per cell was 6. Atomic co-ordinates were given as:

C: 0, 0, 0; 0, 0, $3/6$; $1/3$, $2/3$, $1/6$; $1/3$, $2/3$, $5/6$; $2/3$, $1/3$, $2/6$; $2/3$, $1/3$, $4/6$
 Si: 0, 0, p ; 0, 0, $3/6+p$; $1/3$, $2/3$, $1/6+p$; $1/3$, $2/3$, $5/6+p$; $2/3$, $1/3$, $2/6+p$; $2/3$, $1/3$, $4/6+p$; where $p=1/8$.

The structure was said to consist of an atom of one kind, for example C, surrounded exactly tetrahedrally by four atoms of the other kind, Si, the smallest C-Si distance being 1.9_0 \AA . The space group was given as C_8^6 .

Ott's second publication (1925*b*) discussed the structure of type I α -SiC. The dimensions of the smallest hexagonal cell as determined from rotation photographs were: $a_0 = 3.09_5 \text{ \AA}$, $c_0 = 37.9_5 \text{ \AA}$. The type actually was based on a rhombohedral cell containing five formula weights: $a_{rh} = 12.7_8 \text{ \AA}$ and $\alpha = 13^\circ 55'$. A possible space group was given as C_3^4 . Atomic co-ordinates in the hexagonal cell were:

C: 5 atoms at 0, 0, 0; 0, 0, $2/15$; 0, 0, $6/15$; 0, 0, $9/15$; 0, 0, $13/15$
 5 atoms in similar arrangement from $-1/3$, $1/3$, $1/3$
 5 atoms in similar arrangement from $1/3$, $-1/3$, $2/3$
 Si: 15 atoms at the C positions $+0$, 0, p , where $p=1/20$.

In a third paper, Ott (1926) reported on the structure of α -SiC, type III, and upon the so-called "amorphous" carbide. The unit cell of α -SiC, type III, was found to be hexagonal with $a_0 = 3.09_5 \text{ \AA}$ and $c_0 = 10.0_9 \text{ \AA}$ and to contain four formula weights. Within the limits of error of the measurements, both the c_0 value and the axial ratio were rationally related to similar values obtained for types I and II. Atomic co-ordinates of the structure were:

C: 0, 0, 0; 0, 0, $1/2$; $1/3$, $-1/3$, $1/4$; $-1/3$, $1/3$, $3/4$
 Si: 0, 0, p ; 0, 0, $1/2+p$; $1/3$, $-1/3$, $1/4+p$; $-1/3$, $1/3$, $3/4+p$, where $p=3/16$.

Gray aggregates of the "amorphous" carbide were studied by the x -ray powder diffraction method using copper radiation. They were found to be a mixture of a cubic ZnS-type substance with $a_0 = 4.37 \text{ \AA}$ —assumed to be cubic SiC—and a minor amount of α -SiC, type II.

Ott pointed out that the same exactly tetrahedral arrangement of C and Si atoms was the fundamental unit of all the SiC structures, and that the unit cells of the α -SiC types differed only in the manner in which these tetrahedrons were built up in the direction of the c -axis. The coalescence of types was readily explained since all the hexagonal modifications were similar in the plane of the a axes, the contact plane of the coalescences.

Becker (1927) gave $a_0 = 4.30 \text{ \AA}$ as the cell dimension of yellow cubic SiC.

Ott (1928) described α -SiC, type V. Rotation photographs indicated the unusual hexagonal cell: $a_0 = 3.09_6 \text{ \AA}$, $c_0 = 129.0_3 \text{ \AA}$; the type was actually based on a rhombohedral lattice with $a_{rh} = 41.1_5 \text{ \AA}$, $\alpha = 4^\circ 06'$, and contained 17 formula weights. No attempt was made to determine the atomic positions, but the relationship to the other types made it seem probable that the same tetrahedral arrangement of C and Si atoms existed here also.

Braekken (1930) examined a minute black "octahedral" crystal found in commercial SiC, and assumed to be cubic SiC. It had a ZnS-type structure with $a_0 = 4.348 \pm .005 \text{ \AA}$.

The data given by Ewald and Hermann in the *Strukturbericht I* (1931) and by Wyckoff (1931) agree with those given by Ott, except that they place α -SiC, type I, in space group C_{3v}^5 , and types II and III in group C_{6v}^4 .

Hengstenber and Garrido (1932) made a Fourier analysis showing the electron density normal to the basal pinacoid of an unspecified type of hexagonal SiC. The results were in harmony with the calculations of Ott that in the c direction carbon planes are about 2.53 \AA apart and that silicon planes lie about 1.90 \AA above the carbon.

Borrmann and Seyfarth (1933) gave the following data for type II SiC: $a_0 = 3.076 \pm 0.003 \text{ \AA}$; $c_0 = 15.07 \pm 0.015 \text{ \AA}$. The calculated density was 3.212 which the authors confirmed by the suspension method, although the value for the density determined in this manner was not given.

Hanawalt, Rinn and Frevel (1938) published powder photograph data for cubic and commercial SiC. The latter was said to be a mixture of cubic and hexagonal forms.

Tone (1938) stated that, in spite of the different known types of this substance, all lots of hexagonal crystals gave the same x -ray powder diffraction pattern irrespective of the source of the sample, and that lines of cubic as well as of hexagonal SiC were present in the pattern. He published a series of Laue photographs of α -SiC taken perpendicular to the base, and stated that the diagrams seemed to show a gradual transition from one type to another. No explanation was offered except that some of the differences were thought to be due to twinning.

Benner, Melton and Boyer (1940) gave 4.36_3 \AA as the lattice constant of a "typical" sample of cubic SiC , and stated that the constant varied with amount of impurity to a minimum of 4.35 \AA . No chemical data were given.

Baumann (1941) gave x -ray powder diffraction data for SiC (type or types not stated).

LAUE PHOTOGRAPHS

If the new method of notation used in connection with the observed crystal faces for the various α - SiC types (see Table 16) is applied to the Laue photographs of Hauer and Koller (1920), the relationship between the spots of the Laue photographs of the various types is immediately evident; again only those spots are common to two or more types whose indices are equivalent when referred to the greatest common divisor $c:a$ value.

From the Laue photographs published by Hauer and Koller, Espig, and Ott, and from the observations of coalescences of α - SiC types made by Baumhauer and the writer, it seems quite certain that the Laue patterns illustrated by Tone (1938) are "transitional" because they are from crystals consisting of coalescences of types I and II in different proportions. One of his patterns is apparently influenced by a type I twin in which the c axis is the twinning axis.

The numerous satisfactory Laue photographs reproduced in the literature clearly indicate that the centro-symmetrical crystal class of α - SiC , type I, is D_{3d} , and that of types II and III is D_{6h} . Because of this and the very close morphological relationship of the new types IV and VI to the well-known type I, no Laue exposures were made during the present study.

POWDER PHOTOGRAPHS

Introduction. Because of the common occurrence of coalescences and twinning of the various α - SiC modifications, extreme care was taken in the selection of crystals of each type to be prepared for the powder photographs. Well-developed, unstriated crystals of types I, II and III were employed, while small pieces were chipped from the edges of the large basal pinacoids of types IV and VI. It was not possible to select entirely isotropic individuals of β - SiC . Instead, masses containing a minimum amount of anisotropic material were crushed for the photographs. As additional checks, at least two powder photographs were made of each of the modifications, different samples being used in each case. The fact that in all cases the different powder photographs of the same type of α - SiC were identical indicates that a desired hexagonal modification can unequivocally be selected by careful goniometric study.

All the exposures were made with filtered Cu x -radiation using a camera of about 57.3 mm. diameter, a later modification of the type described by Buerger (1936). The camera was standardized with NaCl.

Pattern of Each SiC Modification. Data from the powder photographs of each SiC modification are given in Tables 18–23 inclusive. Values are for the $\text{CuK}\alpha_1$ lines where resolved, otherwise for $\text{CuK}\alpha_1$ and α_2 . The intensity values were derived from visual comparisons of the line intensities using an arbitrary scale in which the weakest line in each photograph was numbered 1 and the strongest, 10. In the case of α -SiC the planes giving rise to the lines on the powder photographs were ascertained by correlation with those giving Weissenberg spots on the zero and first levels of a -axis rotations. The films of β -SiC were indexed by the use of the chart published by Lukesh and Chesley (1941), as well as by correlation with Weissenberg data. The calculated values of $d_{hk.l}$ for the hexagonal modifications were derived from $a_0 = 3.073 \text{ \AA}$ and the $c:a$ ratios obtained from goniometric study; those for β -SiC were based on $a_0 = 4.349 \text{ \AA}$.

Figure 12 compares the powder photographs of the various SiC modifications. A few lines, indicated by asterisks, are due to quartz from the agate mortar used for final grinding of the specimens.

Cell Dimensions and Density. Because of the discrepancies in the literature concerning the cell dimensions and the calculated and observed densities of the hexagonal SiC types, it was thought worth while to make as precise determinations of these properties as equipment and samples available would permit, and to use analyzed material.

TABLE 18. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE I

Line No.	Intensity	$hk.l$	$d_{hk.l}$ (\AA)	
			Observed	Calculated
1	4	$\left\{ \begin{array}{l} 10.1 \\ 01.2 \end{array} \right\}$	2.66	$\left\{ \begin{array}{l} 2.65 \\ 2.64 \end{array} \right\}$
2	7	10.4	2.58	2.56
3	7	$\left\{ \begin{array}{l} 00.15 \\ 01.5 \end{array} \right\}$	2.51	$\left\{ \begin{array}{l} 2.51 \\ 2.51 \end{array} \right\}$
4	6	10.7	2.40	2.39
5	5	01.8	2.32	2.32
6	1	10.10	2.19	2.17
7	3	01.11	2.11	2.10
8	1	10.13	1.97	1.96
9	2	01.17	1.70	1.70
10	5	10.19	1.59	1.59
11	9	$\left\{ \begin{array}{l} 01.20 \\ 11.0 \end{array} \right\}$	1.54	$\left\{ \begin{array}{l} 1.54 \\ 1.54 \end{array} \right\}$

TABLE 18 (Type I, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
12	5	10.22	1.444	1.441
13	4	01.23	1.398	1.396
14	2	02.4	1.320	1.318
15	8	{ 10.25 }	1.311	{ 1.312 }
		{ 11.15 }		{ 1.311 }
		{ 20.5 }		{ 1.310 }
16	2	02.7	1.297	1.292
17	2	20.8	1.281	1.281
18	2	{ 00.30 }	1.257	{ 1.257 }
		{ 02.10? }		{ 1.255 }
19	1	20.11	1.246	1.241
20	1	20.17	1.143	1.141
21	3	02.19	1.106	1.105
22	2	20.20	1.089	1.087
23	4	02.22	1.053	1.051
24	4	20.23	1.035	1.033
25	1	10.34	1.024	1.023
26	5	{ 01.35 }	1.000	{ .998 }
		{ 02.25? }		{ .998 }
		{ 21.4 }		{ 1.000 }
		{ 12.5 }		{ .997 }
27	3	21.7	.990	.989
28	3	12.8	.984	.984
29	5	{ 11.30 }	.974	{ .973 }
		{ 21.10? }		{ .972 }
30	1	12.11	.965	.965
31	4	10.37	.952	.952
32	4	01.38	.930	.930
33	1	12.17	.917	.916
34	4	21.19	.896	.897
35	7	{ 10.40 }	.888	{ .888 }
		{ 12.20 }		{ .887 }
		{ 30.0 }		{ .887 }
		{ 01.41 }		{ .869 }
36	6	{ 21.22 }	.868	{ .868 }
37	5	12.23	.858	.857
38	1	02.34	.851	.852
39	10	{ 00.45 }	.838	{ .838 }
		{ 20.35 }		{ .837 }
		{ 21.25 }		{ .837 }
		{ 20.15 }		{ .837 }
40	4	12.26	.827	.826
41	5	02.37	.809	.809
42	6	20.38	.796	.795

TABLE 19. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE II

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	6	10.1	2.61	2.62
2	7	{00.6}	2.51	{2.51}
		{10.2}		{2.51}
3	5	10.3	2.36	2.35
4	4	10.4	2.19	2.17
5	3	10.5	2.00	2.00
6	3	10.7	1.67	1.67
7	8	{10.8}	1.54	{1.54}
		{11.0}		{1.54}
8	5	10.9	1.419	1.418
9	3	20.1	1.329	1.326
		{10.10}	1.309	{1.312}
10	8	{11.6}		{1.311}
		{20.2}		{1.310}
11	3	20.3	1.285	1.286
12	3	{00.12}	1.253	{1.257}
		{20.4}		{1.255}
13	2	{10.11}	1.217	{1.219}
		{20.5}		{1.217}
14	2	20.7	1.131	1.132
15	4	20.8	1.087	1.087
16	1	10.13	1.061	1.063
17	4	20.9	1.042	1.042
18	3	12.1	1.002	1.004
		{10.14}	.997	{.998}
19	5	{20.10}		{.998}
		{12.2}		{.997}
20	4	12.3	.986	.986
21	5	{11.12}	.972	{.973}
		{12.4}		{.972}
22	2	{20.11}	.953	{.955}
		{12.5}		{.954}
23	4	10.15	.940	.940
24	3	12.7	.911	.911
		{10.16}	.888	{.888}
25	9	{12.8}		{.887}
		{30.0}		{.887}
26	1	20.13	.873	.874
27	6	12.9	.862	.862
28	2	10.17	.841	.842
		{00.18}	.837	{.838}
29	10	{20.14}		{.837}
		{12.10}		{.837}
		{30.6}		{.837}
30	3	12.11	.811	.811
31	5	20.15	.802	.802

TABLE 20. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE III

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	4	10.0	2.67	2.66
2	5	10.1	2.59	2.57
3	4	00.4	2.52	2.51
4	5	10.2	2.36	2.35
5	3	10.3	2.08	2.08
6	2	10.4	1.83	1.83
7	4	10.5	1.61	1.60
8	6	11.0	1.54	1.54
9	5	10.6	1.419	1.418
10	7	11.4	1.311	1.311
11	4	20.2	1.287	1.286
12	3	10.7	1.264	1.264
13	2	20.3	1.238	1.237
14	2	20.4	1.178	1.176
15	1	10.8	1.136	1.136
16	4	20.5	1.111	1.110
17	5	20.6	1.042	1.042
18	3	10.9	1.030	1.030
19	4	12.1	1.000	1.001
20	5	12.2	.985	.986
21	4	{ 20.7? 11.8 }	.973	{ .976 .973 }
22	3	12.3	.963	.963
23	5	10.10	.941	.940
24	2	12.4	.933	.934
25	1	20.8	.912	.914
26	4	12.5	.899	.900
27	6	30.0	.887	.887
28	10	{ 10.11 12.6 }	.863	{ .864 .862 }
29	3	20.9	.856	.856
30	8	{ 00.12 30.4 }	.837	{ .838 .837 }
31	4	12.7	.824	.824
32	9	20.10	.803	.802
33	1	10.12	.798	.799
34	3	12.8	.786	.785

TABLE 21. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE IV

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1 broad	7	{ 01.2? }	2.63	{ 2.65 }
		{ 10.4 }		{ 2.61 }
		{ 01.5 }		{ 2.58 }
2	10	{ 00.21 }	2.53	{ 2.51 }
		{ 10.7 }		{ 2.51 }
3	2	01.8	2.47	2.47
4	2	10.10	2.40	2.38
5	1	01.11	2.35	2.33
6	1	10.13	2.23	2.23
7	1	01.14	2.17	2.17
8 broad	3	{ 10.16? }	2.01	{ 2.07 }
		{ 01.17 }		{ 2.02 }
9	1	10.25	1.66	1.65
10	1	01.26	1.62	1.61
11	8	{ 10.28 }	1.54	{ 1.54 }
		{ 11.0 }		{ 1.54 }
12	2	01.29	1.51	1.50
13	3	10.31	1.442	1.434
14	2	01.32	1.407	1.402
15	1	10.34	1.337	1.341
16	7	{ 01.35 }	1.311	{ 1.312 }
		{ 11.21 }		{ 1.311 }
		{ 20.5? }		{ 1.310 }
		{ 02.7 }		{ 1.310 }
17	1	{ 20.8? }	1.293	{ 1.304 }
		02.10		1.290
18	3	{ 00.42 }	1.259	{ 1.257 }
		{ 10.37 }		{ 1.257 }
19	1	{ 20.14? }	1.229	{ 1.255 }
		01.38		1.231
20	1	20.26	1.114	1.113
21	2	02.28	1.089	1.087
22	2	20.29	1.076	1.074
23	2	{ 10.46? }	1.050	{ 1.054 }
		{ 02.31 }		{ 1.048 }
24	2	{ 01.47? }	1.035	{ 1.035 }
		{ 20.32 }		{ 1.036 }
25	5	10.49	.999	.998
		20.35		.998
		{ 21.4? }		1.003
		12.5		1.001
		21.7		.997
		{ 12.8? }		.994

TABLE 21 (Type IV, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
26	2	{ 21.10 } { 12.11? }	.986	{ .988 } { .984 }
27	4	{ 11.42 } { 21.13? } { 12.14? }	.973	{ .976 } { .972 }
28	1	{ 20.38? } { 21.16? }	.962	{ .961 } { .962 }
29	2	10.52	.948	.948
30	2	01.53	.932	.933
31	1	21.25	.906	.908
32	3	{ 10.55 } { 12.26 } { 01.56 }	.902	{ .903 } { .901 }
33	7	{ 21.28 } { 30.0 }	.888	{ .888 } { .887 }
34	2	12.29	.881	.880
35	3	21.31	.867	.866
36	4	{ 10.58? } { 20.47 } { 12.32 }	.858	{ .861 } { .858 } { .859 }
37	2	21.34	.844	.844
38	9	{ 00.63 } { 02.49 } { 12.35 } { 30.21 }	.837	{ .838 } { .837 } { .837 } { .837 }
39	2	20.50	.828	.827
40	2	21.37	.824	.822
41	1	12.38	.815	.815
42	3	02.52	.807	.807
43	3	20.53	.797	.797
44	5	02.55	.779	.778

TABLE 22. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE VI

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1 very broad	5	10.4?	2.63	2.64
		01.5		2.63
2 broad	10	10.7	2.53	2.60
		00.33		2.51
		10.10		2.53
3 broad	6	01.11	2.38	2.51
		10.16		2.37
4 broad	3	01.17	2.18	2.34
		10.22		2.17
5	2	01.23	2.05	2.14
		01.26		2.04
6	2	10.28	2.00	1.98
7	2	01.38	1.69	1.69
8	2	10.40	1.64	1.64
9	3	10.43	1.56	1.56
10	8	01.44	1.54	1.54
		11.0		1.54
11	1	10.46	1.497	1.493
12	3	10.49	1.434	1.428
13	3	01.50	1.410	1.408
14	7	10.55?	1.313	1.312
		11.33		1.311
		02.10		1.314
		20.11		1.310
15	3	01.56	1.291	1.294
		02.16		1.289
16	3	00.66	1.260	1.257
		02.22?		1.255
17 broad	2	02.43	1.091	1.095
		20.44		1.087
18	1	01.71?	1.072	1.070
		02.46		1.071
19 broad	3	02.49	1.044	1.046
		20.50		1.038
		01.77		.998
20	4	02.55	.999	.998
		12.5?		1.004
		21.7?		1.002
		21.10		.999
21	4	12.11	.988	.997
		21.16		.987
22	4	12.17	.975	.985
		11.66		.973
		21.22?		.972

TABLE 22 (Type VI, continued)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
23	3	10.82	.947	.945
24	3	01.83	.936	.935
25	2	12.38	.914	.914
26	2	{01.86?}	.905	{.907}
		{21.40?}		{.905}
27	2	21.43	.891	.892
		{10.88}		{.888}
28	5	{12.44}	.888	{.887}
		{30.0}		{.887}
29	2	01.89	.880	.880
30	4	21.49	.867	.865
31	4	12.50	.860	.860
32	1	02.76	.844	.844
		{00.99}		{.838}
		{10.94?}		{.837}
33	7	{20.77}	.838	{.837}
		{21.55?}		{.837}
		{30.33}		{.837}
34	2	02.82	.806	.805
35	3	20.83	.799	.799
36	1	20.86	.781	.781

TABLE 23. DATA FROM X-RAY POWDER PHOTOGRAPHS OF BETA SiC

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	10	111	2.51	2.51
2	1	200	2.18	2.18
3	6	220	1.54	1.54
4	6	311	1.310	1.311
5	1	222	1.256	1.255
6	2	400	1.087	1.087
7	5	331	.998	.998
8	3	420	.972	.972
9	8	422	.888	.888
10	10	{333}	.837	.837
		{511}		

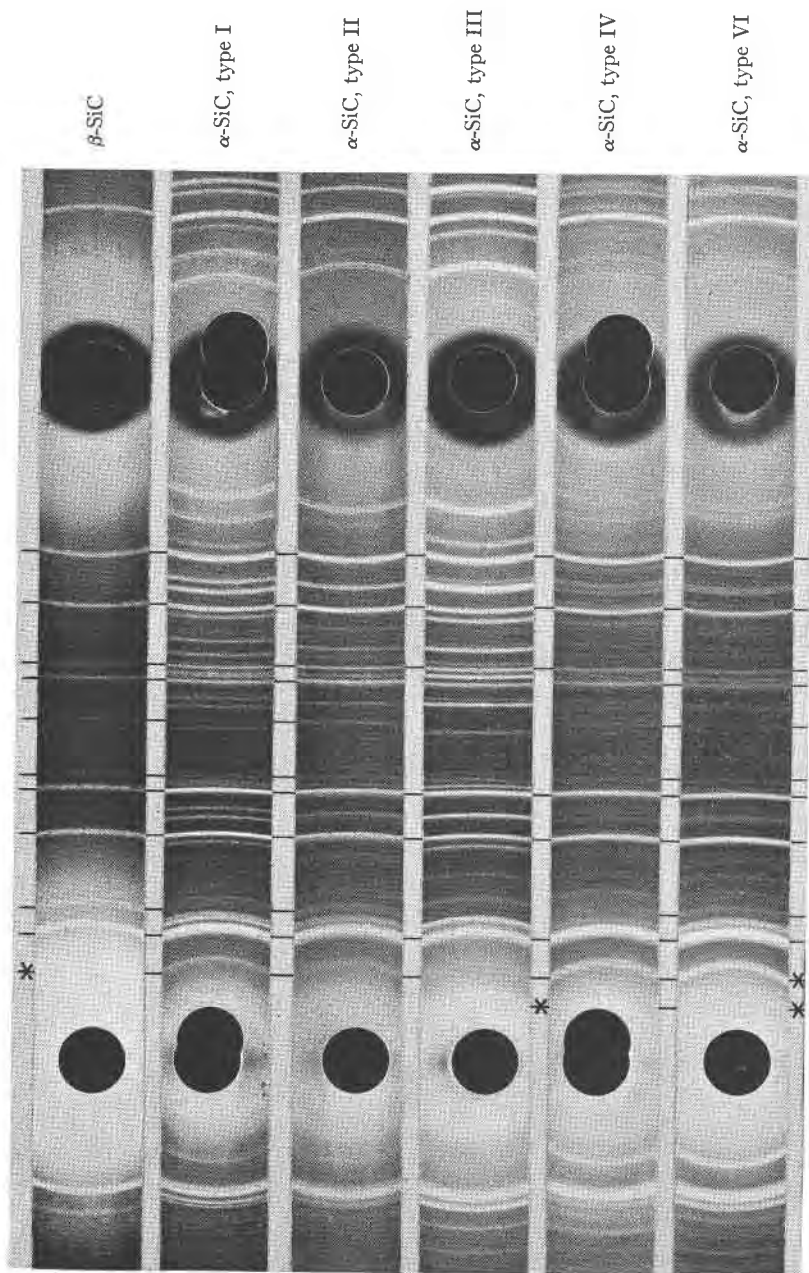


FIG. 12. X-ray Powder Photographs of the SiC Modifications. $\text{CuK}\alpha$ radiation; Camera diameter about 57.3 mm.

Accordingly, all the light green crystals of α -SiC, type II, whose crystal morphology was carefully studied and whose observed axial ratio is recorded in Table 8, were examined under a stereoscopic microscope at a magnification of 30. Those portions containing no visible impurities were segregated, crushed to -200 mesh in a steel mortar, and the magnetic portion removed. To further insure that impurities found in the analysis represented material actually within the SiC itself, either as microscopic or submicroscopic particles or in solid solution, the sample was ignited in an inclined tube furnace at 900°C . for 15 minutes in oxygen to remove any free carbon which might be present. Then it was treated with HF-HNO_3 to remove free SiO_2 , free Si, or iron introduced by powdering the sample, should these be present.

Mr. R. M. Rebert, Norton Worcester laboratories, determined the density, d at $30^{\circ}/4^{\circ}\text{C}$. = 3.218, using a 5 cc. pycnometer and xylene as the displacing liquid.

Mr. Rebert then analyzed the sample in duplicate according to the method outlined by Lamar (1939) and obtained:

		<i>Theoretical</i>
Si	69.78%	70.03%
C	29.99	29.97
Al	0.01	
Fe	0.10	
Ca	0.16	
Mg	0.01	
Total	100.05%	

From a portion of the analyzed SiC two powder photographs were prepared, one of the sample itself and another of the sample mixed with an equal portion of highest purity NaCl as a standard. The first indicated that within the limits of the method only type II was present. The second was used for a precise determination of the cell dimensions. a_0 was determined from planes 12.11 and 20.15, both of which gave well-defined doublets of medium to strong intensity in the back reflection position, and the axial ratio, 4.907, obtained from morphological study of the crystals used for the powder photograph and confirmed by equi-inclination Weissenberg photographs. The ratio, 4.907, is certainly correct to within ± 0.001 , and very likely to within ± 0.0005 . The average a_0 value calculated in this manner for type II is 3.073 \AA (see Table 24), and the c_0 value obtained by multiplying $a_0 \times c : a$ is 15.07_9 \AA (see Table 25). The calculated density is thus 3.217 which compares very favorably with the observed density of 3.218. Siegbahn's wave-lengths, 1940 International

atomic weights and the appropriate value for $1/N$, 1.6503×10^{-24} , were used in the x -ray calculations.

Similarly, from the back reflection planes of the other hexagonal SiC modifications their a_0 value was computed. The $c:a$ ratio used was the ap-

TABLE 24. CELL DIMENSION a_0 OF THE α -SiC MODIFICATIONS CALCULATED FROM THE $d_{hk,l}$ OF BACK REFLECTIONS ON POWDER PHOTOGRAPHS AND THE $c:a$ RATIO OBTAINED FROM MORPHOLOGICAL STUDY

α -SiC type	$hk.l$	$d_{hk,l}$	a_0	a_0 average
I	20.38	.7956	3.074	3.074
	02.37	.8092	3.074	
	12.26	.8271	3.075	
II	20.15	.8021	3.073	3.073
	12.11	.8106	3.072	
III	12.8	.7856	3.074	3.074
	20.10	.8025	3.075	
	12.7	.8236	3.074	
IV	02.55	.7787	3.074	3.073
	20.53	.7973	3.073	
	02.52	.8069	3.073	
VI	20.83	.7993	3.074	3.074
	02.82	.8055	3.074	

TABLE 25. CELL DIMENSIONS, FORMULA WEIGHTS PER CELL AND DENSITIES OF SiC MODIFICATIONS

Modifi- cation	Hexagonal Cell		Rhombohedral Cell		Formula Weights per Hexagonal Cell	Density	
	a_0	c_0	a_{rh}	α		Calc.	Obs.
α -SiC, I	3.073Å	37.70Å	12.69 ₁ Å	13°54½'	15	3.217	—
α -SiC, II	3.073	15.07 ₀	—	—	6	3.217	3.218
α -SiC, III	3.073	10.053	—	—	4	3.217	—
α -SiC, IV	3.073	52.78	17.68 ₃	9°58'	21	3.217	—
α -SiC, VI	3.073	82.94	27.70 ₄	6°21½'	33	3.217	—
<i>Cubic Cell</i>							
β -SiC (Cubic)	$a_0=4.349$				4	3.216	—

propriate rational multiple of 4.9070 as given in the next to the last column of Table 8 and confirmed by Weissenberg photographs. The results are indicated in Table 24. The a_0 values of all the α -SiC modifications are the same within the limits of error of the method, and 3.073 Å is retained for this dimension. The c_0 values of the other hexagonal modifications are obtained by multiplying 3.073 Å by the appropriate $c:a$ ratio, and are given in Table 25.

The cell dimension of β -SiC was determined from the average value obtained from lines 7–10 inclusive on two powder photographs of the substance. In each case, NaCl was mixed with the cubic SiC to furnish a standard. The calculated density is 3.216, remarkably close to that calculated for the hexagonal modifications.

Relationship of Modifications. It has previously been pointed out that certain planes on and within the crystals were common to two or more of the α -SiC types. Table 26 shows this relationship as derived from powder photographs. As is the case in Table 16, common planes would have the same indices if based on the greatest common divisor c_0 value; this could be obtained by dividing the “ l ” value of the indices of the α -SiC modifications of Table 26 by the number of formula weights per unit hexagonal cell for that modification.

Table 26 and Fig. 12 indicate that except for α -SiC, type III, all the hexagonal varieties contain lines which, within experimental error, are the same as those of β -SiC. This does not indicate, as many have concluded, that cubic SiC is present in the sample, but that all the planes giving powder photograph lines in β -SiC are very closely related to some of the planes of the α -SiC modifications.

The occurrence in the back reflection position of lines from equivalent planes in types II and III provided an excellent opportunity to determine whether the a_0 values of these types were the same and the c_0 values rationally related within the limits of error possible with the powder camera used, as all previous study had led the writer to conclude. A sample of the analyzed (green) type II SiC which was used for the powder photographs was intimately mixed with a sample of black type III whose powder photograph was at hand. As far as could be noted by careful examination of the film resulting from the x -raying of this mixture, all common lines were coincident and the single α_1 line due to both planes 20.10 (type III) and 20.15 (type II) was no broader than that on the photograph of either type alone. In a similar manner, other samples of the analyzed type II powder were mixed with powders of green type I, and with black type II with the same results, namely, that lines due to common planes were always strictly coincident on the photographs.

TABLE 26. X-RAY POWDER PHOTOGRAPH LINES COMMON TO THE SiC MODIFICATIONS

β -SiC <i>hkl</i>	α -SiC types				
	II	III	I	IV	VI
	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>
111	{00.6 10.2	00.4 —	00.15 01.5	00.21 10.7	00.33 01.11
—	10.3	10.2	—	—	—
200	10.4	—	10.10	01.14	10.22
220	{10.8 11.0	— 11.0	01.20 11.0	10.28 11.0	01.44 11.0
—	10.9	10.6	—	—	—
311	{10.10 11.6 20.2	— 11.4 —	10.25 11.15 20.5	01.35 11.21 02.7	10.55? 11.33 20.11
—	20.3	20.2	—	—	—
222	{00.12 20.4	— —	00.30 02.10?	00.42 20.14?	00.66 02.22?
400	20.8	—	20.20	02.28	20.44
—	20.9	20.6	—	—	—
331	{10.14 20.10 12.2	— — —	01.35 02.25? 12.5	10.49 20.35 21.7	01.77 02.55 12.11
—	12.3	12.2	—	—	—
420	{11.12 12.4	11.8 —	11.30 21.10?	11.42 12.14?	11.66 21.22?
—	10.15	10.10	—	—	—
422	{10.16 12.8 30.0	— — 30.0	10.40 12.20 30.0	01.56 21.28 30.0	10.88 12.44 30.0
—	12.9	12.6	—	—	—
333}	{00.18 20.14	00.12 —	00.45 20.35	00.63 02.49	00.99 20.77
511}	{12.10 30.6	— 30.4	21.25 30.15	12.35 30.21	21.55? 30.33
—	20.15	20.10	—	—	—

Tone's statement that every lot of hexagonal crystals wherever made will give the same *x*-ray diffraction pattern when examined by the powder method is nearly true in most cases because of the great predominance of type II in all commercial SiC. However, two different varieties of SiC manufactured commercially by the Norton Company give *x*-ray powder diffraction patterns which differ notably in several regions. One variety is a mixture of a large amount of type II and a small amount of type I, while

the other is predominantly type II with a smaller amount of type III.

The x -ray powder pattern of commercial SiC given by Hanawalt and co-workers (1938) and said to be of "cubic and hexagonal forms" is mainly of α -SiC type II with a small amount of type III. There was probably insufficient cubic SiC present to form any pattern. The pattern given by Baumann (1941) as characteristic for SiC contains some of the stronger lines of α -SiC, type II.

EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

Introduction. Alpha SiC, types I, II, III, IV and VI were studied with the aid of c -axis rotation photographs, and equi-inclination Weissenberg exposures of both c - and a -axis rotations, zero, first and sometimes second layer levels. In the case of β -SiC a zero level of an a -axis rotation, and zero and second layer levels of a dodecahedral axis rotation were made. Obviously not all these exposures were necessary for adequate determinations of the crystal symmetries. Exposures were made with unfiltered copper radiation. The general methods used have been described by Buerger (1942).

Because of the large c_0 cell dimensions of α -SiC, types IV and VI, and the consequent very close spacing of the layer lines of the first kind, rotation photographs were not satisfactory, and it was not always possible to screen out the first from the zero levels in c -axis rotation equi-inclination Weissenberg exposures. These difficulties were of no great consequence, however, because of the information given by a -axis Weissenberg exposures where no such ambiguities existed.

Crystal Classes. Table 27 summarizes the centro-symmetrical crystal classes indicated by plane point-group symmetries shown by the Weissenberg photographs. Actual crystal classes of α -SiC were determined by etching experiments as previously described: types I, IV and VI are $C_{3v}-3m$, and types II and III are $C_{6v}-6mm$. Morphological study of cubic SiC indicated class T_d-43m .

Cell Dimensions. The cell dimensions of all the SiC modifications were determined from the appropriate zero layer Weissenberg photographs, and aided in the precise determination of the lattice constants as discussed under the subject of powder photographs.

Space Groups and Space Lattice Types. The space groups of the various SiC modifications were obtained from characteristic absences noted on indexed Weissenberg photographs. Thus α -SiC, types I, IV and VI are C_{3v}^5-R3m , since:

$$\begin{aligned} (hk\bar{l}) & \text{ is present when } h-k-l=3n \\ (h\cdot h\cdot 2h\cdot l) & \text{ is present when } l=3n \\ (h\bar{h}0l) & \text{ is present when } 2h-l=3n. \end{aligned}$$

The space lattice is obviously rhombohedral as was predicted from the morphological study.

TABLE 27. CENTRO-SYMMETRICAL CRYSTAL CLASSES OF THE SiC MODIFICATIONS AS INDICATED BY PLANE POINT-GROUP SYMMETRIES OBTAINED FROM EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

SiC Modification	Rotation Axis	Level	Plane Symmetry	Centro-Symmetrical Crystal Class	
α , types I, IV, VI	c [00.1]	0	C_{6i}	D_{3d}	
		1	C_{3i}		
		a [11.0]	0	C_2	D_{3d}
			1	C_2	
α , types II, III	c [00.1]	0	C_{6i}	D_{6h}	
		1	C_{6i}		
		a [11.0]	0	C_{2i}	D_{6h}
			1	C_{2i}	
		β	dodecahedral [110]	0	C_{4i}
2	C_{2i}			O_h	

The space group of α -SiC, types II and III is $C_{6v}^4 - C6mc$, since:

- $(hki\bar{l})$ is present in all orders
- $(h \cdot h \cdot 2h \cdot l)$ is present when $l=2n$
- $(h\bar{h}0l)$ is present in all orders.

The space lattice of these types is, therefore, hexagonal as indicated by crystal morphology.

Beta-SiC is $T_d^2 - F\bar{4}3m$ from the following criteria.

- (hkl) present only when $h+k=2n$; $k+l=2n$; $l+h=2n$
- (hhl) present only when $h+l=2n$.

Relationship of Types. In Figs. 13-18 some of the common planes evident from the equi-inclination Weissenberg photographs have been indexed, and may be studied to advantage with the aid of Table 26 which shows most of the correlations to be expected.

The relationship of α -SiC and β -SiC is brought out very clearly in Fig. 18 which is an equi-inclination Weissenberg photograph of the well-developed crystal of β -SiC illustrated by Fig. 9. While this crystal was for the most part β -SiC, there were present within it two thin basal plates of α -SiC whose basal pinacoids were parallel to tetrahedral faces of the β -SiC modification. For the production of the photograph, Fig. 18, the β -SiC crystal was rotated about one of the dodecahedral axes. This was also an

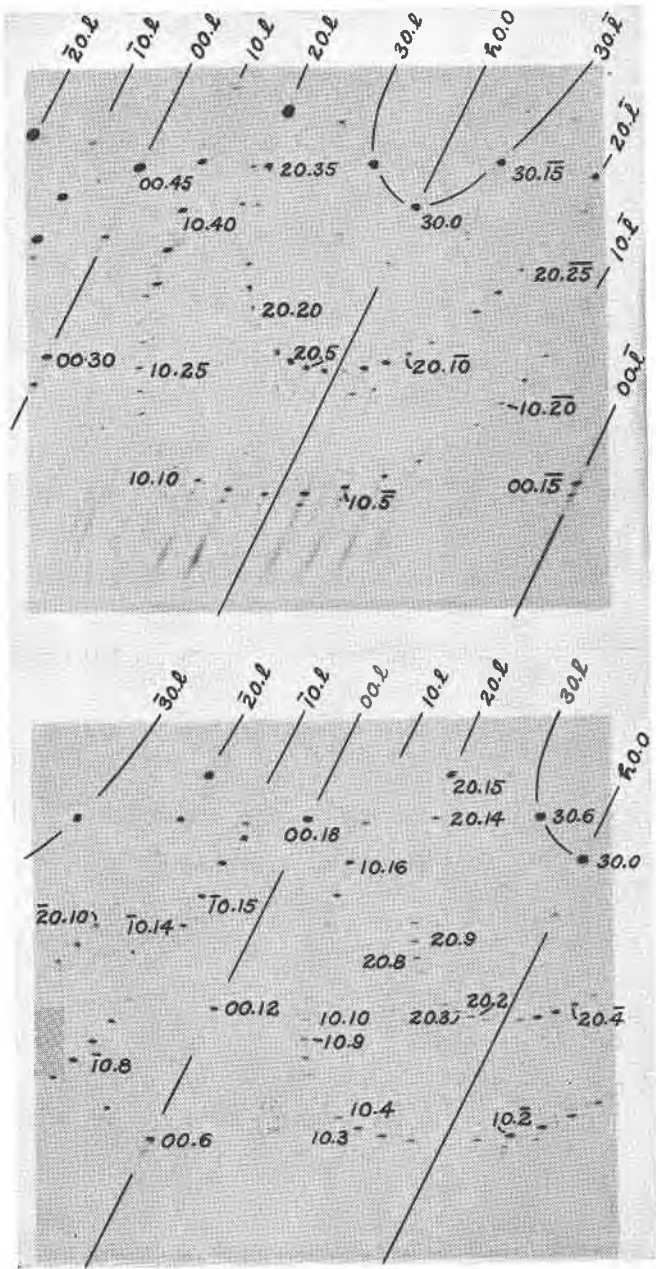


FIG. 13 (upper). Equi-inclination Weissenberg photograph of α -SiC, type I; a -axis rotation, zero level.

FIG. 14 (lower). Equi-inclination Weissenberg photograph of α -SiC, type II; a -axis rotation, zero level.

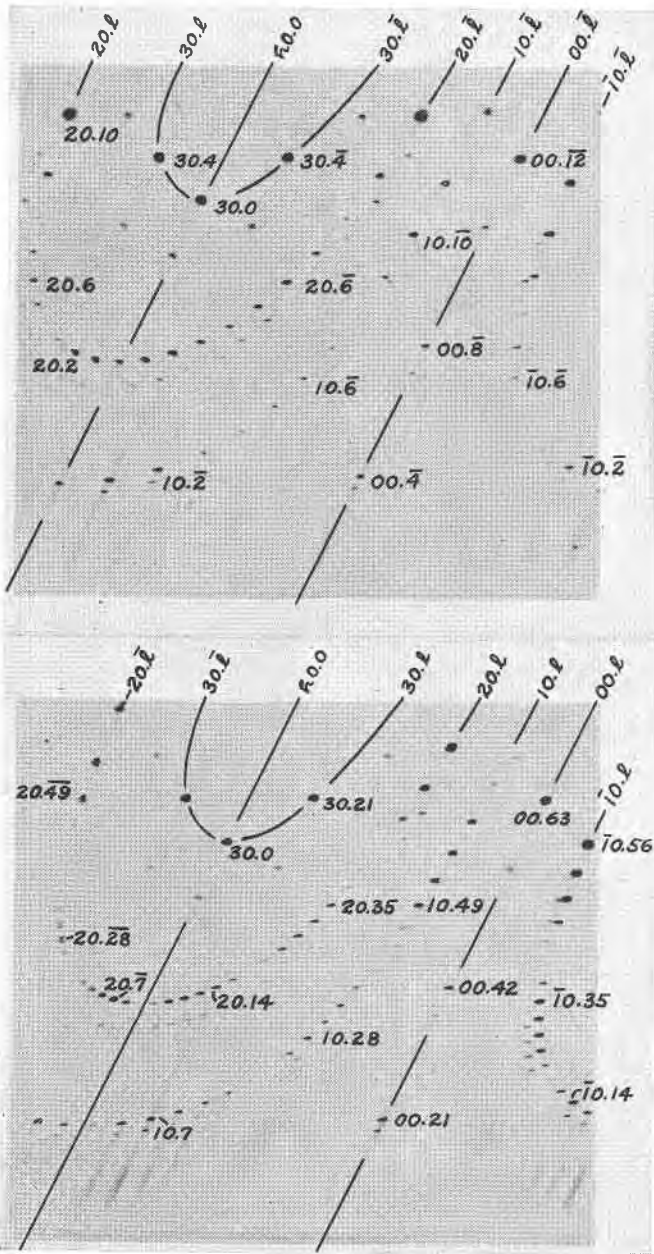


FIG. 15 (upper). Equi-inclination Weissenberg photograph of α -SiC, type III; a -axis rotation, zero level.

FIG. 16 (lower). Equi-inclination Weissenberg photograph of α -SiC, type IV; a -axis rotation, zero level.

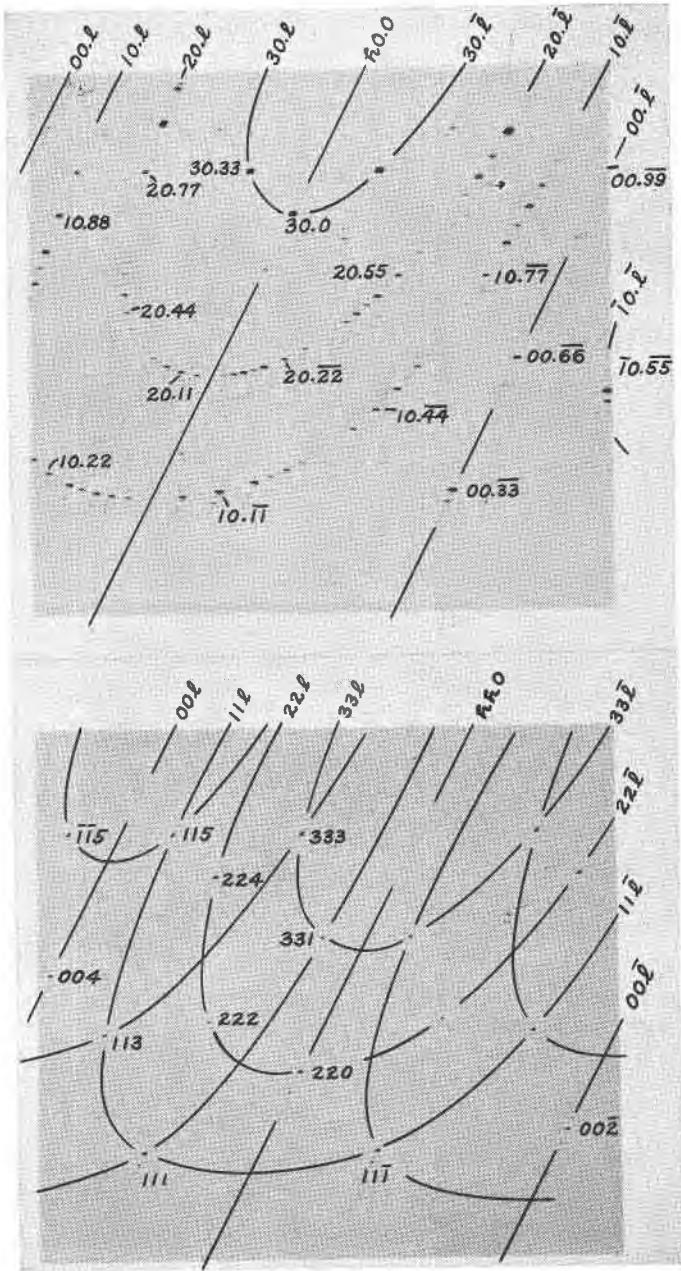


FIG. 17 (upper). Equi-inclination Weissenberg photograph of α -SiC, type VI; a -axis rotation, zero level.

FIG. 18 (lower). Equi-inclination Weissenberg photograph of the β -SiC crystal illustrated by Fig. 9. $[110]$ rotation, zero level.

a-axis of one of the included α -SiC plates. The resulting Weissenberg photograph was essentially of β -SiC, but with additional faint spots due to an *a*-axis rotation of α -SiC. These faint spots are very evident on the films in the zone $00\bar{2}$ - $11\bar{1}$ -220. Comparison of this figure with Fig. 14 not only indicates that the included α -SiC plate giving the pattern was type II, but that the following points are exactly coincident.

β -SiC	α -SiC
00 $\bar{2}$	10. $\bar{4}$
11 $\bar{1}$	10.2
220	10.8

Although the determination of the ultimate structure of the SiC modifications is beyond the scope of this paper, the data concerning the existing reflections and their intensities as obtained from Weissenberg exposures of α -SiC, types I, II and III during this study are in agreement with those published by Ott. It seems quite certain that the fundamental building block of all the α -SiC modifications is one slightly distorted tetrahedron of SiC, the differences between the types being due to differences in the manner in which these are turned with respect to one another in the direction of the *c*-axis. All the data are likewise consistent with the sphalerite structure of β -SiC.

OPTICAL PROPERTIES REVIEW OF LITERATURE

Frazier (1893) stated that SiC was uniaxial.

Becke (1895) obtained a uniaxial positive figure, and observed no pleochroism. The indices of refraction, determined by the Duc de Chaulnes method and measurements on interference figures, were said to be: $\omega_{\text{Na}} = 2.786$, $\epsilon_{\text{Na}} = 2.832$.

Tone (1908) published curves for the indices of refraction of SiC for various wave-lengths, the indices apparently having been calculated from interference phenomena. For sodium light the values obtained from the curves were approximately: $\omega = 2.83$, $\epsilon = 2.98$. SiC was said to be more transparent perpendicular to the *c*-axis than parallel to it.

Pirsson (1914) stated that SiC was uniaxial positive with weak double refraction, and that the indices for both rays were greater than 1.75. He observed some pleochroism: $\epsilon =$ deep indigo blue; $\omega =$ light blue.

Merwin (1917) determined the indices of refraction of the *o* ray for various wave-lengths by using the method of minimum deviation on two naturally occurring prisms found on a very pale green crystal of SiC, one face on each prism being somewhat curved. The values for the *e* ray were

obtained by measurements on the interference figure according to the method of Merwin (1914). The values for sodium light were: $\omega = 2.654$, $\epsilon = 2.697$. Merwin observed that bluish SiC was pleochroic light to dark blue, or olive green to greenish blue, but stated that the o ray was the more strongly absorbed.

Somewhat earlier Weigel (1916) published a paper including detailed observations on the indices of refraction of SiC for various wave-lengths and also for higher temperatures. For these purposes three prisms were very accurately ground and polished so that their refracting edges were parallel to the crystallographic c -axis. Two of the prisms were of clear, presumably light green, SiC, while the third was cut from black SiC. No determinations were made with sodium light, but interpolation gives: $\omega_{Na} = 2.6477$, $\epsilon_{Na} = 2.6934$ at about 22°C. Within experimental error, the values obtained on the black crystal were the same as those for the green crystals, so Weigel concluded that the impurity causing the color was admixed mechanically and did not exist in solid solution.

Many English-language reference texts, including Winchell (1931), Larsen and Berman (1934), and the *Handbook of Chemistry and Physics* (1943) quote Merwin's values for the indices of refraction. The *International Critical Tables* (1926) and Mellor (1924) give the values determined both by Merwin and Weigel. Winchell gives as the pleochroism formula: $X(\omega) > Z(\epsilon)$ while Larsen and Berman state: $\omega =$ light blue; $\epsilon =$ deep indigo blue, which would be equivalent to $Z > X$.

No optical data on cubic SiC have appeared in the literature.

ALPHA SILICON CARBIDE

Examination in Polarized Light. The normal interference figure of all the hexagonal SiC types throughout the visible spectrum is uniaxial positive. However, biaxiality due to strain, with $2V$ up to about 10°, may sometimes be observed, especially adjacent to opaque inclusions. Crystals of types I and II were examined for biaxiality but there was no evidence that it occurred more in one type than in the other.

Several pale green crystals of both types I and II up to 2 mm. in thickness were examined for optical activity in lithium, and mercury yellow, green and blue light, but there was no evidence of the rotation of the plane of polarization, nor was the interference figure that of an optically active crystal.

Color and Dichroism. Hexagonal SiC crystals are yellow, greenish-yellow, green, blue green, blue, gray, or black, the particular shade depending considerably upon the conditions of illumination, the size of the individuals and sometimes on the direction of view into the crystal. When

crushed to a fine size and observed by transmitted light, even the darkest silicon carbide will usually transmit some light and appear blue. Extremely pale green, almost colorless, crystals up to a millimeter in thickness have been found, but red SiC as reported by Winchell (1931) has not been observed by the writer. Crystals often show considerable color variation which may be irregular or zonal in nature.

The correlation between color and α -SiC type which Frazier, Baumhauer, and Espig have described was only partially substantiated. In a small sample of green crude forwarded by a foreign manufacturer there was apparently a perfect correlation between color and type, for in over 40 crystals measured from this specimen all the greenish yellow crystals were type I and all the green or blue green, type II. Moreover, when coalescences occurred, there was a sharp line of demarcation in color at the boundary between types, even when a thin plate of type I occurred between larger masses of type II. Each type was also characterized by its own dichroism as indicated by specimens 1*a* and 1*b* in Table 28.

TABLE 28. COLOR, DICHROISM AND ABSORPTION OF ALPHA SILICON CARBIDE TYPES

No.	SiC Type	Color of Crystal	Dichroism	Absorption	Remarks
1 <i>a</i>	I	greenish yellow	ϵ = light greenish blue ω = light lemon yellow	$\epsilon > \omega^2$	Coalescence of types I & II
1 <i>b</i>	II	blue green	ϵ = medium blue green ω = light green	$\epsilon > \omega$	
2 <i>a</i>	I	greenish yellow	ω = greenish blue ω = lemon yellow	$\epsilon > \omega^2$	Different parts of same crystal, same type
2 <i>b</i>	I	blue streak in above	ϵ = pale gray blue ω = gray blue	$\omega > \epsilon$	
3 <i>a</i>	I	greenish yellow	ϵ = light greenish blue ω = light olive green	?	Coalescence of types I & II
3 <i>b</i>	II	light blue	ϵ = light blue ω = very pale blue	$\epsilon > \omega$	
4 <i>a</i>	I	green	ϵ = medium greenish blue ω = light green	$\epsilon > \omega$	Different parts of same crystal, same type
4 <i>b</i>	I	blue streaks in above	ϵ = light gray blue ω = indigo blue	$\omega > \epsilon$	

TABLE 28—Continued

No.	SiC type	Color of Crystal	Dichroism	Absorption	Remarks
4c	II		same as 4a	$\epsilon > \omega$	4a and 4b (type I) coalesced with 4c and 4d (type II)
4d	II		same as 4b	$\omega > \epsilon$	
5	I	light yellow green	ϵ = light green ω = light buff	$\epsilon > \omega$	
6	I	blue black	ϵ = blue ω = very dark blue	$\omega > \epsilon$	
7	II	bluish green	ϵ = light blue ω = light blue green	?	
8	II	green	ϵ = blue green ω = yellow green	$\epsilon > \omega$	
9	II	light blue	ϵ = light blue ω = almost colorless	$\epsilon > \omega$	
10	II	dark blue	ϵ = light blue ω = dark blue	$\omega > \epsilon$	
11	II	black	ϵ = medium blue ω = very dark blue	$\omega > \epsilon$	From same small crude specimen
12	III	black	ϵ = medium blue ω = very dark blue	$\omega > \epsilon$	
13	IV	greenish yellow	ϵ = very pale green ω = very pale olive	$\epsilon > \omega?$	
14	VI	blue black	ϵ = medium blue ω = dark blue	$\omega > \epsilon$	
15	n.d.	blue	ϵ = pale purplish blue ω = medium blue	$\omega > \epsilon$	

A somewhat larger specimen of green SiC crude supplied by another foreign producer contained no greenish yellow or yellow crystals. Examination of over 60 crystals from this sample revealed that while most of the individuals were type II, there were a few of type I and a few coalescences. Specimens 4a, b, c, d, Table 28, are from this lot. It is to be noted

that there was no difference in color nor in dichroism between the type I and type II portions of this coalescence.

Because of the disagreement in the literature concerning the dichroism and especially the absorption formula for silicon carbide, a complete study of these properties for each of the hexagonal types was undertaken. The difficulty of obtaining satisfactory transmission of light through irregular fragments even when immersed in methylene iodide made it advisable to cut thin plates from the crystals parallel to the c axis with the aid of a suitable diamond cut-off wheel. Table 28 correlates the color, dichroism and absorption found for various crystals of the different α -SiC types.

The reason for the disagreement in the literature concerning the dichroism and absorption of hexagonal SiC no doubt is due to the variation in these properties in crystals from the same or different sources, variations which are probably caused by differences in accompanying impurities.

Indices of Refraction and Dispersion. Although the relationship between the different modifications of α -SiC clearly indicates that no differences in indices of refraction due to the structural differences between types are to be expected, it was nevertheless thought worth while to determine the indices of refraction and dispersion of two different α -SiC types. The purpose was three-fold: (1) to check the values published by Weigel and Merwin, (2) to determine experimentally whether different types were characterized by different refractive indices, and (3) to ascertain whether there were differences in indices due to material in solid solution or submicroscopic suspension in the crystal.

Prisms suitable for refractive index determinations were prepared in the following manner. A thick tabular crystal containing one large well-developed basal pinacoid was cemented to a suitable block of plate glass, the base of the crystal being in contact with the glass surface. Two cuts were then made through the crystal and into the glass with a diamond cut-off wheel such that a prism of about 40° was formed, the cut surfaces being essentially perpendicular to the basal pinacoid, and the prism edge, therefore, nearly parallel to the c -axis. For this operation the author is indebted to Dr. J. E. Burke, Norton Worcester laboratories. Each of the prism faces was polished by successively mounting in phenol formaldehyde plastic and polishing with 2 micron diamond on a lead lap, using the Graton-Vanderwilt polishing machine. The signals reflected from the prism faces on the goniometer were single, undistorted and perfectly sharp.

Three prisms were prepared in the above manner. Prism No. 1 was cut from a transparent, light green crystal of type II. It was free from flaws

and exhibited the dichroism, ϵ =medium greenish blue, ω =light green. Prism No. 2 was prepared from the same coalescence of types I and II as the plate whose dichroism is described in Table 28, specimens 1*a* and 1*b*. The purpose of cutting a prism from a coalescence was to permit a greater degree of precision in comparing the indices of refraction of the two types. If the indices of the types differed even slightly, it would be evident immediately when the minimum deviation angle was measured in monochromatic light, since four signals would be observed through the telescope of the goniometer, two from each type. This was found to be the case with prism No. 2 as is indicated by the values for the indices of refraction given in Table 29. Prism No. 3 was obtained from a green crystal of type I which varied greatly in color, and for this reason all but about one square millimeter of each prism surface was blocked off with opaque ink. The portion of prism No. 3 used to determine the indices of refraction showed the same dichroism as prism No. 1. Its identity as type I was checked by an x -ray powder photograph of the portion used for the optical examinations.

Each prism was set up on the same goniometer used for the morphological study. The prism angle was measured ten times on different parts of the scale, the average being used in the calculations. The minimum deviation angles for the ordinary and extraordinary rays through the prism were measured three times for each of the wave-lengths of light used. Finally the angle between each polished prism face and the basal pinacoid was measured five times, these measurements being necessary to determine the true ϵ value.

Omega and ϵ' were determined from the prism angles and the deviation angles by the usual formula for minimum deviation. The results appear under the columns headed " ω , 1st" and " ϵ' 1st" in Table 29. Subsequently, the prism and deviation angles were measured again, the results of these calculations appearing under the columns headed "2nd." Monochromatic light was supplied by a mercury vapor tube, hydrogen Geissler tube and sodium and lithium flames. The most precise measurements of indices of refraction given in Table 29 are indicated by asterisks. The absence of a symbol indicates average precision while less reliability is indicated by question marks. The reason for the latter was the weak signals, and therefore, somewhat uncertain deviation angles, afforded by some of the prisms for some of the wave-lengths. It is believed that the average values indicated by asterisks are correct to within ± 0.0003 .

The prisms were cut in such a manner that the refracting edges were approximately parallel to the c -axis. However, because of the methods employed, high precision could not be attained, and for that reason the index obtained for the extraordinary ray by the usual formula was the

TABLE 29. INDICES OF REFRACTION AND DISPERSION OF α -SiC, TYPES I AND II

Wave Length (Å)	Prism No. & SiC Type	ω			ϵ'			ϵ (calc.)
		1st	2nd	Avg.	1st	2nd	Avg.	
6708 (Li)	1, II	2.6264	2.6267	2.6266	2.6676??	2.6671??	2.6674??	2.6674??
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.6269	2.6265	2.6267	—	—	—	—
6563 (H)	1, II	2.6294*	2.6297*	2.6296*	2.6696	2.6695	2.6696	2.6696
	2a, I	2.6283	2.6285	2.6284	—	—	—	—
	2b, II	2.6307	2.6309	2.6308	—	—	—	—
	3, I	2.6294*	2.6288*	2.6291*	2.6700?	2.6692?	2.6696?	2.6697?
5895 (Na)	1, II	2.6474*	2.6476*	2.6475*	2.6889*	2.6888*	2.6889*	2.6889*
	2a, I	2.6465	2.6469	2.6467	2.6923	2.6928	2.6926	2.6930
	2b, II	2.6485	2.6489	2.6487	2.6905	2.6904	2.6905	2.6909
	3, I	2.6470*	2.6466*	2.6468*	2.6891*	2.6890*	2.6891*	2.6892*
5781 (Hg)	1, II	2.6509*	2.6513*	2.6511*	2.6931*	2.6934*	2.6933*	2.6933*
	2a, I	2.6502*	2.6505*	2.6504*	2.6963	2.6966	2.6965	2.6969
	2b, II	2.6522*	2.6527*	2.6525*	2.6946	2.6947	2.6947	2.6951
	3, I	2.6506*	2.6505*	2.6506*	2.6930*	2.6930*	2.6930*	2.6931*
5461 (Hg)	1, II	2.6629*	2.6632*	2.6631*	2.7062*	2.7065*	2.7064*	2.7064*
	2a, I	2.6622*	2.6624*	2.6623*	2.7094	2.7096	2.7095	2.7099
	2b, II	2.6640*	2.6644*	2.6642*	2.7071	2.7073	2.7072	2.7076
	3, I	2.6625*	2.6624*	2.6625*	2.7059*	2.7065*	2.7062*	2.7063*
4867 (H)	1, II	2.6923	2.6932	2.6928	2.7410??	2.7421??	2.7416??	2.7416??
	2a, I	2.6920	2.6918	2.6919	—	—	—	—
	2b, II	2.6941	2.6945	2.6943	—	—	—	—
	3, I	2.6931	2.6923	2.6927	2.7398?	2.7409?	2.7404?	2.7405?
4358 (Hg)	1, II	2.7304	2.7305	2.7305	2.7825	2.7822	2.7824	2.7824
	2a, I	2.7298	2.7302	2.7300	2.7852?	2.7860?	2.7856?	2.7860?
	2b, II	2.7319	2.7321	2.7320	2.7835?	2.7830?	2.7833?	2.7837?
	3, I	2.7301	2.7294	2.7298	2.7818	2.7822	2.7820	2.7821
4047 (Hg)	1, II	2.7652?	2.7650?	2.7651?	—	—	—	—
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.7635?	2.7640?	2.7638?	—	—	—	—

apparent value (ϵ') and not necessarily the true value (ϵ). The latter may be calculated from the true prism angle and the angle which each of the

prism faces makes with the basal pinacoid by the use of a series equations given by Born (1887). The writer is indebted to Mr. K. F. Whitcomb, Norton Worcester laboratories for some of the necessary calculations based on solid analytical geometry. Table 29, however, indicates that the maximum difference between ϵ' and ϵ hardly exceeds the experimental error of the best measurements of ϵ' .

Types I and II α -SiC are not characterized by different refractive indices since both ω and ϵ of prism No. 1 (type II) and prism No. 3 (type I) are the same within experimental error. From this we may conclude that the indices of refraction of all α -SiC types are fundamentally the same.

In disagreement with the conclusions of Weigel, however, differences in indices of refraction, presumably due to material in solid solution in the crystal, do occur within a single type as indicated by the differences found between the values obtained from prisms No. 1 and No. 2*b*, type II, or from prisms No. 2*a* and No. 3 both type I.

Additional proof of the influence of material in solid solution on the indices of refraction of α -SiC was afforded by prism No. 3. Although the polished prism surfaces reflected faultless signals on the goniometer, multiple signals accompanied by blurs were observed for both the ordinary and extraordinary rays passing through the prism. No indication of any biaxiality could be observed, so it seems improbable that the multiple signals were due to strains in the crystal. A marked variation in color was observed under the microscope. One area about 1 mm. square was uniformly light green, while the remainder of the prism varied from light green to medium blue. By permitting light to pass only through small portions of the prism at a time, it was found that the differently colored zones gave ordinary and extraordinary ray signals which varied slightly in position. This indicated differences in indices of refraction with color, which must be caused by variation in the amount or kind of material in solid solution or submicroscopic suspension. The indices given in Table 29 for this prism were obtained from the light green area which gave minimum values. The indices from the darker areas could not be determined satisfactorily but in some cases were certainly higher by at least 0.002.

Table 29 indicates that the following variations in indices for Na-light have been observed during the present study:

$$\omega = 2.6467-2.6487 \qquad \epsilon = 2.6889-2.6930$$

Similar variations were found for all other wave-lengths so that the dispersions of both ω and ϵ were the same for all prisms, the average values being:

$$\begin{aligned} \text{Dispersion of } \omega (4360-6200 \text{ \AA}) &= 0.0918 \\ \text{Dispersion of } \epsilon (4360-6200 \text{ \AA}) &= 0.1028. \end{aligned}$$

The data on the indices of refraction of SiC published by Becke (1895) and Tone (1908) are incorrect, since the methods used by them for the determination of the optical constants are not accurate. All of the indices of refraction determined during the course of the present study were 0.005 to 0.009 lower than the values given by Merwin for corresponding wave-lengths. This is probably due to inaccuracies resulting from the curved surfaces on Merwin's prism faces. The indices of refraction of the ordinary ray for all the prisms studied were within about 0.001 of the values given by Weigel (1916) for all wave-lengths. The ϵ of prism *2a* was within 0.0006 of Weigel's determinations for all wave-lengths, but the same values from the other prisms were 0.003 to 0.004 lower than reported by him. The dispersions agreed with the values reported by Weigel.

BETA SILICON CARBIDE

The cubic SiC encountered in the course of this study was transparent, yellow to olive green in color, and for the most part isotropic. In practically all cases, however, lamellae of an anisotropic substance were present as inclusions.

A study of β -SiC was made by embedding fragments of it in sulphur-selenium melts of known indices of refraction using fragments of a green crystal of α -SiC, type II, as control. The wave-length used was essentially equivalent to that of lithium because of the high index of the melts found necessary. The index of β -SiC for this wave-length is close to 2.63, about that of the *o* ray of α -SiC.

Petrographic examination of the cubic SiC crystal illustrated by Fig. 9 indicated that the anisotropic substance included within it was in the form of very thin basal plates parallel to tetrahedron faces of the β -SiC. These plates were found to be uniaxial positive with ω for Li about 2.63 and $\epsilon > 2.66$. These facts, together with similar spatial relationships found between crystals of β -SiC and macroscopic crystals of α -SiC, indicate that the lamellae are basal plates of α -SiC, confirming a conclusion already reached from *x*-ray studies.

OTHER POLYTYPIC SUBSTANCES

SiC was for a number of years the only known substance exhibiting the phenomenon of polytypism, and may today be considered the prototype of polytypic compounds because of the large number of types and the detail in which they have been studied. In recent years, however, data have appeared which clearly indicate that several other compounds are polytypic. For the most part the following descriptions have been taken from the literature.

Coquimbite and paracoquimbite, both with the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$, are two minerals which have been described as polytypic by Ungemach (1935*a*) and confirmed by Bandy (1938). The series of crystal forms of coquimbite is characteristic of a hexagonal substance while that of paracoquimbite is characteristic of a rhombohedral lattice. When the indices of the forms are simplified to the greatest extent, the indicated $c:a$ ratios are 1.5643 and 4.6928 respectively, the values being exactly rationally related as 1:3.

Rotation photographs of the two substances yielded the following cell dimensions, both being referred to the smallest hexagonal unit:

	<i>Coquimbite</i>	<i>Paracoquimbite</i>
a_0	10.8 ₅ Å	10.90 Å
c_0	17.0 ₃ Å	51.1 ₅ Å

Thus the a_0 values are probably the same, and the c_0 dimensions rationally related within the limit of error of the measurements.

Syntaxic intergrowths of coquimbite and paracoquimbite are very common, several examples of which are adequately illustrated by Ungemach's crystal drawings. The plane of contact between the individuals involved in the coalescences is always the basal pinacoid, the line of demarcation often being evident on the crystal by re-entrant angles or striations.

The similarity of the morphological and structural crystallography of coquimbite and paracoquimbite to that of the α -SiC types is so evident that no comments need be made.

In a paper on syntaxis and polytypism Ungemach (1935*b*) has shown that the minerals parisite and synchisite may very reasonably be divided into three modifications or types, all having the same composition $(\text{CeF})_2\text{Ca}(\text{CO}_3)_3$. The crystals of these minerals are not as well developed as are those of SiC or coquimbite-paracoquimbite, but it seemed possible to establish the three varieties with the following $c:a$ ratios:

α -parisite (hexagonal)	= 4.473
β -parisite (rhombohedral)	= 10.094
γ -parisite (hexagonal)	= 6.730

These three axial ratios are rationally related as 4:9:6. Again certain crystal forms are common to two or all three of the varieties which often form syntaxic intergrowths (coalescences).

For a number of years the x -ray powder photographs of several samples of natural graphites have been observed to show "extra" lines, apparently not due to impurities, but not indexed on the basis of the known graphite structure. Lipson and Stokes (1942*a*, 1942*b*) find that these lines may be accounted for on the assumption that there exists within these

samples about 14% of another form of graphite whose a_0 cell dimension is the same as that of ordinary graphite, but whose c_0 value is $3/2$ as great. This new structure is said to be based on a rhombohedral lattice and to belong to space group $R\bar{3}m$ whereas ordinary graphite is based on a hexagonal cell and belongs to $C6mc$. Again these appear to be polytypic compounds.

It seems quite certain that as more complete morphological and structural data concerning both minerals and artificial compounds become available, more polytypic substances will be found. The most fruitful field of search would seem to be compounds crystallizing in the hexagonal system, where polytypism might explain the appearance of two or more incompatible series of crystal forms, for example, a rhombohedral and a holohedral series, inconsistent x -ray patterns, or data seemingly showing transitions, etc. The crystal systems of lower symmetry should not be overlooked, however. The value of the optical goniometer in connection with the study of polytypic substances cannot be overemphasized, for the study of SiC has amply proven the rapidity and certainty with which the various types and the presence of syntactic intergrowths or coalescences may be determined with its aid. Entirely incorrect or inexplicable data might well result from the x -ray examination, without adequate morphological study, of a crystal which appeared to be single and well developed, but which actually was a syntactic intergrowth of two or more types.

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