THE CRYSTAL STRUCTURE OF α-SiC, TYPE VI

LEWIS S. RAMSDELL,
Mineralogical Laboratory, University of Michigan, Ann Arbor, Michigan.

ABSTRACT

A structure has been determined for α-SiC, type VI, one of the new modifications of SiC recently reported by Thibault. He found the rhombohedral unit cell to contain 11 SiC, with the dimensions $a_{rh}=27.704$Å and $\alpha=6°21.5'$. Space group $R3m$. Referred to hexagonal axes, the unit cell contains 33 SiC, with $a=3.073$Å and $c=82.94$Å. Following a procedure similar to that used for type IV, the following atomic positions have been determined for type VI:

Hexagonal unit cell—
11 Si at 000, $0\,0\,2z$, $0\,0\,6z$, $0\,0\,8z$, $0\,0\,12z$, $0\,0\,15z$, $0\,0\,18z$, $0\,0\,21z$, $0\,0\,25z$, $0\,0\,27z$, $0\,0\,31z$.
11 C at $00p$, $0\,0\,2z+p$, $0\,0\,6z+p$, $0\,0\,8z+p$, $0\,0\,12z+p$, $0\,0\,15z+p$, $0\,0\,18z+p$, $0\,0\,21z+p$, $0\,0\,25z+p$, $0\,0\,27z+p$, $0\,0\,31z+p$.
11 Si and 11 C at 2/3 1/3 1/3 plus the above coordinates.
11 Si and 11 C at 1/3 2/3 2/3 plus the above coordinates.
$z=1/33$; $p=1/44$

In his investigation of silicon carbide, Thibault[1] discovered two new rhombohedral modifications of α-SiC, which he designated as types IV and VI. This brought to four the number of known types based on rhombohedral unit cells, namely, type I with 5 SiC in the unit cell, type IV with 7 SiC, type VI with 11 SiC, and type V with 17 SiC. Ott determined the structure of type I[2] and reported the existence of type V[3], but made no attempt at a structure determination of the latter. The author recently published an account of the structure of type IV,[4] and the present paper deals with the structure of type VI. The structure of type V has also been determined, and an account of this will appear in the near future.

In these structure determinations both Ott and the writer have made the assumption that in all of the types there is a common structural arrangement in which each silicon atom is surrounded tetrahedrally by four carbon atoms, and each carbon by four silicon. This assumption seems justified on two grounds; first, the very excellent agreement between the observed intensities and those calculated for such a tetrahedral arrangement, and second, the very close crystallographic relationships between

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[1] Thibault, N. W., Morphological and structural crystallography and optical properties of silicon carbide: *Am. Mineral.*, **29**, 249–278, 327–362 (1944).

[2] Ott, H., Das Gitter des Karborunds (SiC): *Zeits. Krist.*, **62**, 291–317 (1925).

[3] Ott, H., Eine neue Modifikation des Karborunds: *Probleme der modernen Physik.* Arnold Sommerfeld Festschrift. S. Hirzel, Leipzig, (**1928**).

[4] Ramsdell, L. S., The crystal structure of α-SiC, type IV: *Am. Mineral.*, **29**, 431–442 (1944).

the various types. The vertical heights of all of the unit cells are integral multiples of a common unit, while the horizontal dimensions remain constant. Certain forms are common to two or more types. *X*-ray photographs of the various types have certain reflections in common. All of these facts seem to point indisputably to a common basic structure. If this is true, then in each type all atoms are located on the vertical symmetry axes, and the types differ merely in the distribution of atoms along these axes. This relationship may be expressed in another way. All of the structures are built up of equally spaced, identical layers. The various types differ only in the relative horizontal displacement of these layers. There are three possible positions for a single layer, and the sequence in which these positions are successively occupied constitutes the distinguishing feature of each type.

In this investigation of the structure of type VI the tetrahedral arrangement has been taken for granted. However, even with this assumption the solution would still remain very difficult. As the size of the unit cell increases, the number of geometrically possible arrrangements increases very rapidly. For type I, Ott had to choose between two possible sequences. For type IV, only five arrangements had to be considered. But for type VI, there are 42 different arrangements geometrically possible, while for type V the number is in the thousands. Unless some additional simplifying assumption is made, the task of choosing among the various possibilities would be very great.

In all of the modifications whose structures are known, both in the hexagonal and the rhombohedral types (I, II, III and IV) the arrangements of silicon atoms along the vertical symmetry axes are such that adjacent atoms are separated by intervals of two, three and four layers only. Ott recognized this apparent limitation, and referred to it as the "Minimalprinzip." If it is assumed that this limitation holds for type VI, the number of possible arrangements is at once reduced from 42 to 5. The writer does not know why such a limitation might exist, but there seems to be nothing unreasonable about it. The justification for applying the limitation to type VI lies in the agreement between the observed intensities and those calculated for the proposed structure. This agreement is so excellent that it hardly seems possible that it could be due to chance, and that some more complex arrangement is the correct one.

The method used in determining the geometrical possibilities for type VI is similar to that used for types I and IV, and can be most easily described in terms of the hexagonal unit cell. This hexagonal unit is 33 layers high, with 11 silicon atoms on each of the three vertical symmetry axes, which pass through the points 000, 2/3 1/3 0 and 1/3 2/3 0. These three axes will be referred to as *A*, *B*, and *C*, respectively. Because of the tetrahedral arrangement, only one of the three axes may be occupied at any given level, and no axis may be occupied at two adjacent levels. Moreover, since the lattice is actually rhombohedral, the sequence of atoms along *A*, beginning at 000, must be identical with the sequence along *B*, beginning at 2/3 1/3 1/3, and with that along *C*, beginning at 1/3 2/3 2/3. This displacement of 1/3 and 2/3 along *B* and *C*, relative to *A*, means that for any silicon atom on *A* at the *n*th level, there will also have to be silicon atoms at $n+11$ and $n+22$ on *B* and *C*, respectively. Hence no two silicon atoms on *A*, *B* or *C* can be 11 or 22 layers apart. These restrictions are automatically taken care of by use of the following tabulation:

0	(1)	2	3	4	5	6	7	8	9	10
(11)	12	13	14	15	16	17	18	19	20	21
(22)	23	24	25	26	27	28	29	30	31	(32)

Permissible sequences will consist of 11 numbers, one to be chosen from each vertical column. Two cannot be chosen from the same vertical column because they are separated by intervals of 11 or 22. No two adjacent horizontal numbers may be chosen. Accordingly, if the sequence starts with 0, the numbers 11, 22, 1 and 32 may not be used. A possible sequence would thus be 0, 12, 2, 14, 4, 16, 6, 18, 8, 20, 10, which arranged in increasing order would become 0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 0. The intervals between the successive numbers are 2-2-2-2-2-2-2-2-2-2-13. It is the intervals between the numbers which are characteristic. The particular number with which a sequence starts is of no importance. There are 681 permissible sequences which can be derived from the tabulation, but when expressed as intervals, there are found to be only 42 different sets. These vary from the example given above, with a maximum interval of 13, down to five arrangements involving only intervals of 2, 3 and 4. These five arrangements are as follows:

(1) 32433333423
(2) 33432323433
(3) 22444234332
(4) 23343334332
(5) 24243334242

The theoretical intensities to be expected from each of these five arrangements have been calculated for a sufficient number of reflecting planes to determine whether or not there is any significant correlation with the actual observed intensities for type VI. The first four arrangements show marked discrepancies between observed and calculated intensities, and are accordingly discarded. The fifth arrangement shows excellent agreement, and is accepted as the correct one.

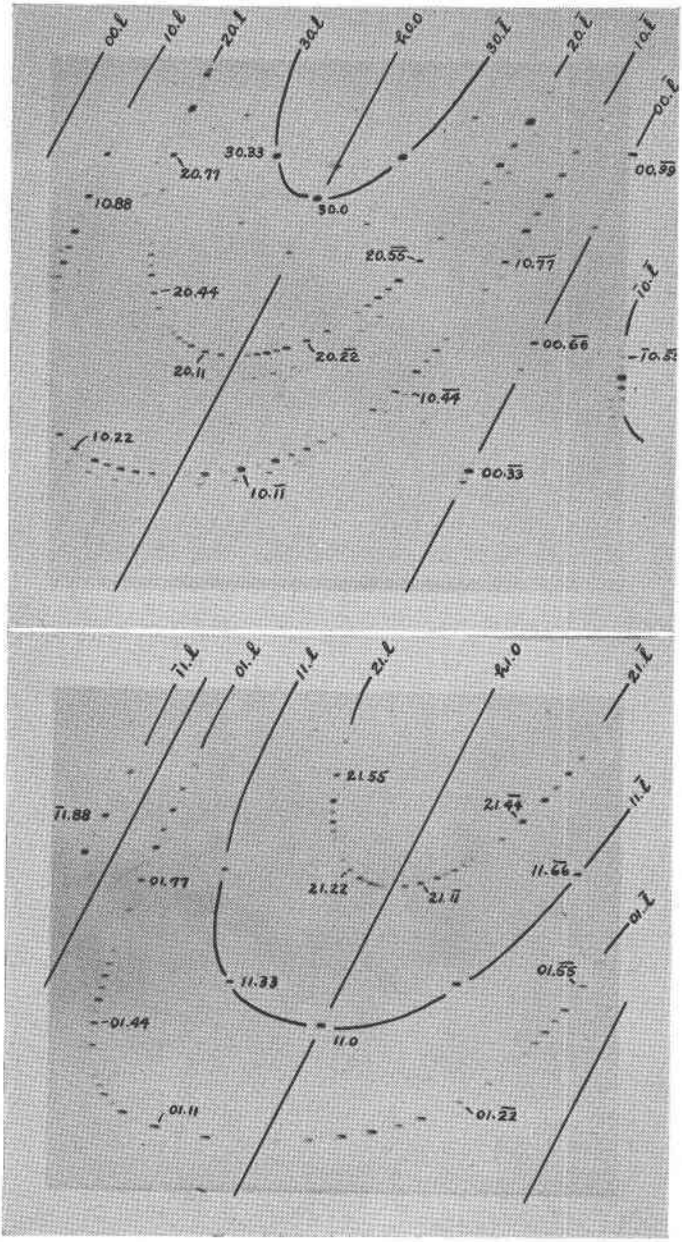

FIG. 1. Weissenberg photographs of α-SiC, type VI; *a*-axis rotation. Above—zero level; below—first level.

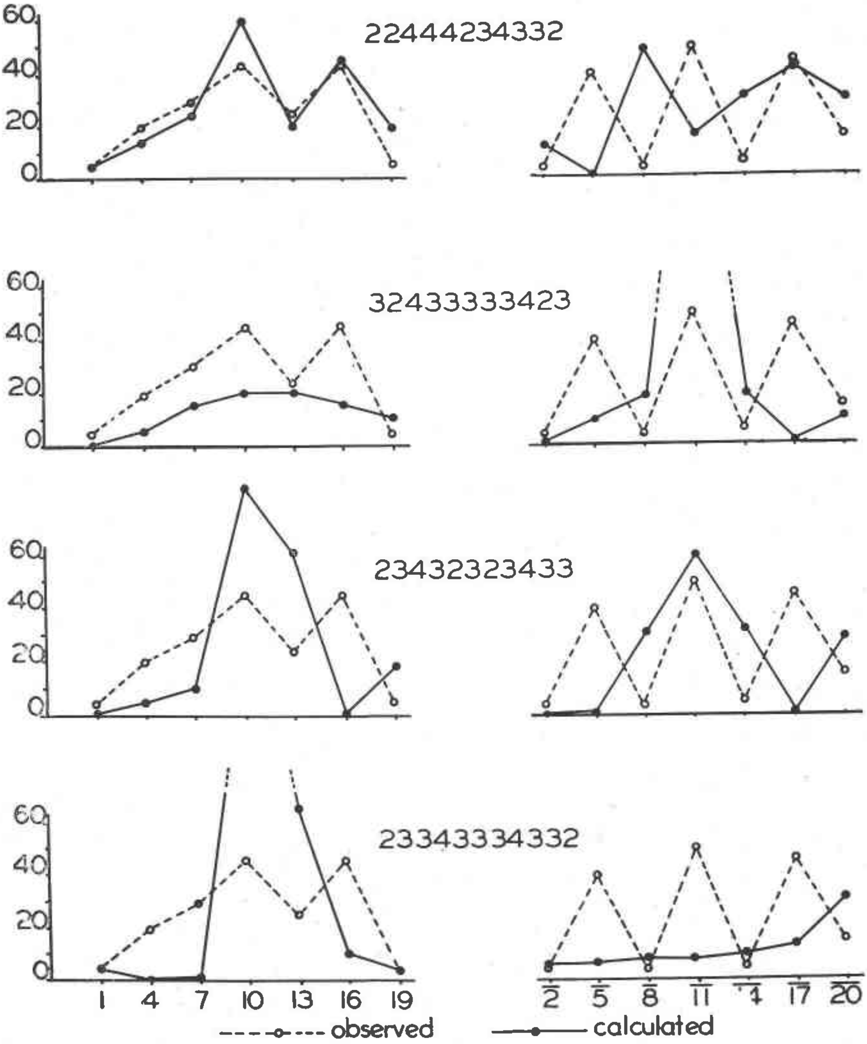

FIG. 2. Observed intensities compared with the calculated intensities for the first 14 reflections of the 10·*l* series of α-SiC, type VI, for the four discarded sequences. Relative intensities are plotted vertically, and values of *l* are plotted horizontally.

Three main series of reflections appear on the 0-level and 1-level Weissenberg photographs about an a-axis, namely, the $10\cdot l$, $20\cdot l$ and $21\cdot l$ series (Fig. 1). For these reflections the intensity calculations are relatively simple, the formula being

$$I\alpha[\Sigma f_0\,\mathrm{Si}\cos 2\pi(lz)+\Sigma f_0 C\cos 2\pi(lz+p)]^2+[\Sigma f_0 \sin 2\pi(lz)+\Sigma f_0 C \sin 2\pi(lz+p)]^2.$$

The results obtained with the use of this formula were multiplied by the Lorenz-polarization factor,

$$\frac{1+\cos^2 2\theta}{\sin 2\theta}.$$

It will be noticed that in the intensity formula the Miller indices h and k do not occur. The value of l is the determining factor, and except for differences in f_0 and the correction factor, the calculated values are alike for a given value of l, irrespective of h and k. Accordingly, there is such similarity in the intensities for the three series $10\cdot l$, $20\cdot l$ and $21\cdot l$ that calculations for only one series are sufficient to confirm or reject a possible structure. For the four discarded sequences, intensities were calculated for the first 14 reflections in the $10\cdot l$ series, while for the accepted sequence intensities were calculated for 34 reflections.

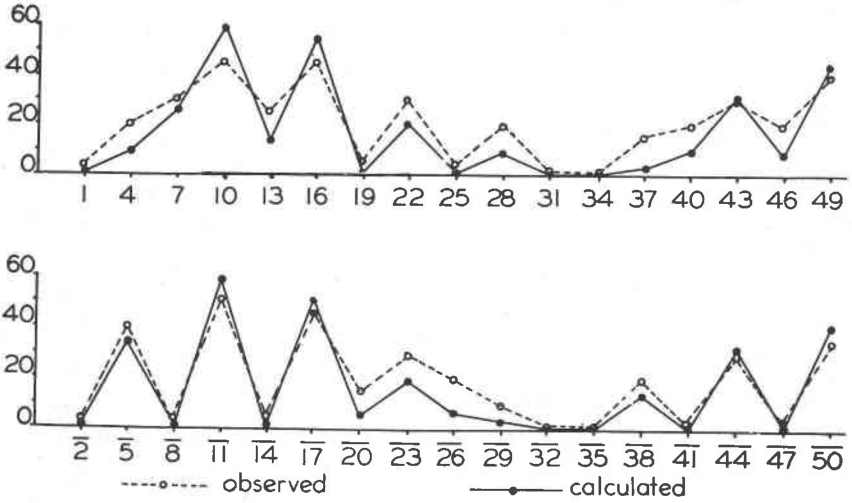

FIG. 3. Observed intensities compared with the calculated intensities for the first 34 reflections of the $10\cdot l$ series of α-SiC, type VI, for the accepted sequence 24243334242.

The results of the calculations are shown graphically in Figs. 2 and 3. Figure 2 shows clearly the marked discrepancies between the observed intensities and those calculated for the four discarded sequences, while Fig. 3 reveals the excellent correlation between the observed values and those calculated for the accepted sequence. The highest calculated value for the accepted sequence was 59,000, which was obtained for the $10\cdot\overline{11}$ reflection. In Fig. 3 this is plotted as 59, and the observed intensity for this same reflection is arbitrarily rated as 50. Two Weissenberg films, the 0-level and 1-level rotations about an *a* axis, were used for the intensity estimates. No corrections for absorption were made. The series $10.l$ and $01.l$, which should have identical intensities, show some minor differences. Accordingly, the intensity values as visually estimated from the films can only be regarded as approximate. However, the intensity variations are great, especially in consecutive reflections such as $10\cdot\bar{2}$, $10\cdot\bar{5}$, $10\cdot\bar{8}$, $10\cdot\overline{11}$, $10\cdot\overline{14}$, etc., where the reflections alternate from very weak to very strong. With such intensity contrasts, even approximate estimates of intensity are sufficient to make a choice between possible structures.

The atomic arrangement of α-SiC, type VI, corresponding to the accepted sequence 24243334242, is derived as follows. On the vertical axis *A* through the origin, 11 silicon atoms are placed on levels separated by the numbers of the sequence, as follows: 0, 2, 6, 8, 12, 15, 18, 21 25, 27, 31, 0. On the vertical axis *B*, through the point 2/3 1/3 0, a similar series begins with the 11th layer, with 11 silicon atoms on 11, 13, 17, 19, 23, 26, 29, 32, 3, 5, 9. On the vertical axis *C*, passing through the point 1/3 2/3 0, a similar series begins with the 22nd layer, with 11 silicon atoms on 22, 24, 28, 30, 1, 4, 7, 10, 14, 16, 20. Above each of the 33 silicon atoms is a carbon atom, at a vertical distance of 1.90Å. This distance represents 1/44 of the length of the *c* axis, while the distance between the silicon layers is, of course, 1/33 of the *c* axis. Accordingly the atomic coordinates for the structure of α-SiC, type VI are as follows:

Hexagonal unit cell; $Z=33$.
11 Si at 000, 0 0 $2z$, 0 0 $6z$, 0 0 $8z$, 0 0 $12z$, 0 0 $15z$, 0 0 $18z$, 0 0 $21z$, 0 0 $25z$, 0 0 $27z$, 0 0 $31z$.
11 C at 00p, 0 0 $2z+p$, 0 0 $6z+p$, 0 0 $8z+p$, 0 0 $12z+p$, 0 0 $15z+p$, 0 0 $18z+p$, 0 0 $21z+p$, 0 0 $25z+p$, 0 0 $27z+p$, 0 0 $31z+p$.
11 Si and 11 C at 2/3 1/3 1/3 plus the above coordinates.
11 Si and 11 C at 1/3 2/3 2/3 plus the above coordinates.

Rhombohedral unit cell; $Z=11$.
11 Si at 000; $2z$, $2z$, $2z$; $6z$, $6z$, $6z$; $8z$, $8z$, $8z$; $12z$, $12z$, $12z$; $15z$, $15z$, $15z$; $18z$, $18z$, $18z$; $21z$, $21z$, $21z$; $25z$, $25z$, $25z$; $27z$, $27z$, $27z$; $31z$, $31z$, $31z$.
11 C at ppp, $2z+p$, $2z+p$, $2z+p$; $6z+p$, $6z+p$, $6z+p$; $8z+p$, $8z+p$, $8z+p$; $12z+p$, $12z+p$, $12z+p$; $15z+p$, $15z+p$, $15z+p$; $18z+p$, $18z+p$, $18z+p$; $21z+p$, $21+p$, $21z+p$; $25z+p$, $25z+p$, $25z+p$; $27z+p$, $27z+p$, $27z+p$; $31z+p$, $31z+p$, $31z+p$.
For both hexagonal and rhombohedral unit cells, $z=1/33$, $p=1/44$.