THE CRYSTAL STRUCTURE OF α-SiC, TYPE IV

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ABSTRACT

A new modification of α-SiC, designated as type IV by Thibault, was found by him to have a rhombohedral unit cell, with $a_r = 17.68$Å and $\alpha = 9°58'$; space group $R3m$; $Z = 7$. For comparison with the hexagonal types, the rhombohedral unit can be referred to hexagonal axes, with $a_0 = 3.073$Å and $c_0 = 52.78$Å. This unit contains 21 formula weights.

There are shown to be only five possible atomic arrangements compatible with the rhombohedral space group and with the assumption that each Si atom is surrounded tetrahedrally by 4 C atoms, and each C atom by 4 Si atoms. Of these five arrangements, only one gives satisfactory agreement between the observed and the calculated intensities. This arrangement, referred to hexagonal axes, is as follows:

7 Si at 000, 0 0 4z, 0 0 6z, 0 0 9z, 0 0 12z, 0 0 15z, 0 0 17z.

7 C at 00p, 0 0 4z+p, 0 0 6z+p, 0 0 9z+p, 0 0 12z+p, 0 0 15z+p, 0 0 17z+p.

7 Si and 7 C at 2/3 1/3 1/3+the above coordinates.

7 Si and 7 C at 1/3 2/3 2/3+the above coordinates.

$$z = 1/21, \quad p = 1/28.$$

INTRODUCTION

The existence of five crystalline modifications of SiC has been known for some time. These five include one which is cubic, two which have hexagonal symmetry, and two with trigonal symmetry. Various studies of these modifications and their crystal structures have been made.[1] The cubic form has a β-ZnS type of structure, with each silicon atom surrounded tetrahedrally by four carbon atoms, and each carbon by four silicon. This same basic arrangement is found in all of the other modifications. In the two hexagonal types, all atoms lie on the vertical symmetry axes through the points A, B and C, which have the coordinates 000, 2/3 1/3 0 and 1/3 2/3 0, respectively (Fig. 1). It will be necessary to make frequent reference to these symmetry axes, and in the following discussion they will be designated simply as A, B and C. The two hexagonal types differ from each other in the number and sequence of atoms along A, B and C. The hexagonal symmetry is such that the arrangements along the trigonal axes B and C are identical, but differ from that along A. The two types with trigonal symmetry are based on rhombohedral unit cells. The sequence of atoms along A, beginning at 000, must be identical with the sequences along B and C, beginning at 2/3 1/3 1/3 and 1/3 2/3 2/3, respectively, since all three axes are alike.

In a comprehensive study of SiC, Thibault[2] has proved the existence

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[1] For a complete summary and list of references see the paper by Thibault in the preceeding issue of this Journal, pages 327–362.

[2] Thibault. N. W. Morphological and structural crystallography of SiC: *Am. Mineral.*, **29**, 249–278; 327–362 (1944).

of two additional types, both with rhombohedral unit cells. Contrary to previous usage, Thibault calls the cubic form β-SiC (isostructural with β-ZnS) rather than SiC, type IV. All the remaining forms, both hexagonal and trigonal, are called α-SiC, each one being designated by a type number. Thibault calls the two new modifications of α-SiC types IV and VI, leaving types I, II, III and V as originally designated by Ott. This usage is followed in the present paper.

No crystallographic data have been published for type V, but for the remaining α-SiC types, Thibault has shown the very remarkable morphological relationships, involving axial ratios which are multiples of a common fundamental unit, and characteristic form series for each type. Moreover, he established a complete correlation between the crystallographic data and the unit cells. However, no attempt was made by
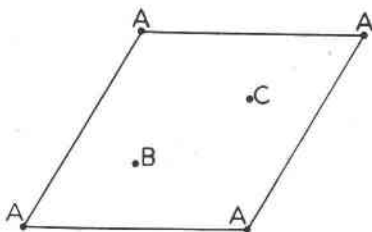

Fig. 1.   Basal projection of hexagonal unit cell, showing
the vertical symmetry axes *A*, *B*, and *C*.

Thibault to determine the actual atomic arrangements for either type IV or type VI.

In the course of this investigation of the crystal structure of type IV, the author needed several Weissenberg photographs, and he is greatly indebted to Dr. Thibault for the use of the crystal on which the type was established.[3]

Structure of α-SiC, Type IV

The data obtained by Thibault from the morphology, etch figures and x-ray study of type IV point unequivocally to a rhombohedral unit cell, with the space group $R3m$. Referred to hexagonal axes, the unit cell was found to have dimensions as follows: $a = 3.073$Å and $c = 52.78$Å. This cell is twenty one layers high. Because of the very definite interrelationship with the other types, it seems very certain that the same basic tetrahedral arrangement of silicon and carbon atoms must be present. If this is the case, the new type differs from the others solely in the manner in which successive layers of the structure are oriented with respect

[3] A report on the crystal structure of type VI is expected to appear in this Journal in the near future.

to each other, or in the sequence of the atoms along the vertical directions A, B and C (Fig. 1).

If a silicon atom is on A, with the coordinates 000, then a carbon atom must be directly above it at $00p$. The Si–C distance common to all of the types is 1.90 Å, which combined with the length of the c axis in type IV, gives a value of 1/28 for the vertical parameter p. In the next higher silicon layer, there are 2 equivalent positions, each equally probable, i.e., on B at 2/3 1/3 z, or on C at 1/3 2/3 z. Since there are twenty one layers of silicon atoms in the unit cell, the parameter z has a value of 1/21. If we arbitrarily choose the first of these two possibilities, on B, there would then have to be a carbon atom directly above it, at 2/3 1/3 $z+p$. In the third layer of silicon atoms, there would again be two choices, on C or A, with the vertical parameter equal to $2z$. This dichotomous relationship for each successive layer of silicon atoms would continue throughout the entire length of the unit cell. All silicon and carbon atoms would lie only on A, B and C, and would have vertical parameters involving only nz and $nz+p$, respectively. There would be 7 silicon and 7 carbon atoms on each of the vertical axes A, B and C, but no two could be occupied at the same horizontal level. It is evident that the carbon atoms would have an arrangement identical with that of the silicon atoms, only displaced a distance p in the vertical direction. Consequently, in discussing the atomic arrangement, it will be much simpler to refer in most cases only to the silicon atoms, keeping in mind the fact that above each silicon there must be a carbon atom.

There are two very definite restrictions controlling the sequence of silicon atoms along any one of the vertical directions A, B or C. First, the tetrahedral arrangement does not permit any two successive layers to be occupied along the same axis—the interval must be two or more. Second, the rhombohedral lattice requires that for any atom at nz on A, there must also be one at $1/3+nz$ on B, and one at $2/3+nz$ on C. Thus placing a silicon atom at 000 on A automatically places one on B at 2/3 1/3 $7z$, and another on C at 1/3 2/3 $14z$ ($7z=7/21=1/3$; $14z=14/21=2/3$). In more general terms this means that the interval between any two silicon atoms on A, B or C cannot be $7z$ or $14z$. The combined effect of these two restrictions is that the intervals between silicon atoms along A, B and C cannot be 1, 7 or 14, or any combination which adds up to 7 or 14, such as $5+2$, $4+3$ or $6+4+4$.

The determination of all the possible sequences along A, B or C which are compatible with these restrictions is easily carried out by a method used by Ott in his determination of the structure of type I.[4] In the following tabulation the numbers from 0 to 20 represent the 21 succes-

[4] Ott, H., Das Gitter des Karborunds: Zeits. Krist., **62**, 201–217 (1925).

0	(1)	2	3	4	5	6
(7)	8	9	10	11	12	13
(14)	15	16	17	18	19	(20)

sive silicon layers in the unit cell. If we arbitrarily place a silicon atom on A at 0, there cannot also be one on A at 1 (next layer above) or at 20 (next layer below). Neither can there be one on A at 7 or 14, for the rhombohedral lattice requires that B and C be occupied at these levels. Accordingly, if we always start the sequence on A at 0, we do not need the numbers 1, 7, 14 and 20 in the table. No two numbers may be chosen for A from any one vertical column of the table, for they would be separated by intervals of 7 or 14. Since there are 7 silicon atoms to be placed on A, one number must be chosen from each of the seven vertical columns. But no two successive numbers may be chosen from the same horizontal row. Following these rules, a possible sequence could be 0 8 2 17 4 12 6, or in ascending order, 0 2 4 6 8 12 17 0. A total of 43 such sequences can be derived. Two additional sets of 43 may be obtained by starting the sequences with 7 and 14, but these are exactly congruent with the original 43, and need not be considered. Of the 43 sequences, many are duplicates, either being the same sequence in reverse order, or differing only in the starting point of the sequence. For example, the sequence 0 2 6 11 15 17 19 0 has *intervals* between successive numbers of 2 4 5 4 2 2 2, and therefore is equivalent to the first sequence above, where the *intervals* are 2 2 2 2 4 5 4. It is the intervals which are the distinguishing feature. Of the 43 possible sequences, there are only 6 different series of intervals, as follows:

(1)	3	3	3	3	3	3	3
(2)	2	2	2	9	2	2	2
(3)	2	2	2	6	3	2	4
(4)	3	2	3	5	3	2	3
(5)	2	2	4	5	4	2	2
(6)	4	2	3	3	3	2	4

It will be noticed that the number 1 does not appear, and there are no groups of adjacent numbers such as 43, 223, 52, 644 and 8222, which add up to 7 or 14. Such forbidden combinations were all eliminated by the method used.

The above 6 sequences are all compatible both with the basic tetrahedral arrangement and with the rhombohedral lattice. However, the first one is not acceptable for type IV. It would consist merely of the repetition of an identical structure seven times in the direction of the c axis. The true unit would be only three layers high, and in fact would correspond to the structure of the cubic β-SiC, treated as a rhombo-
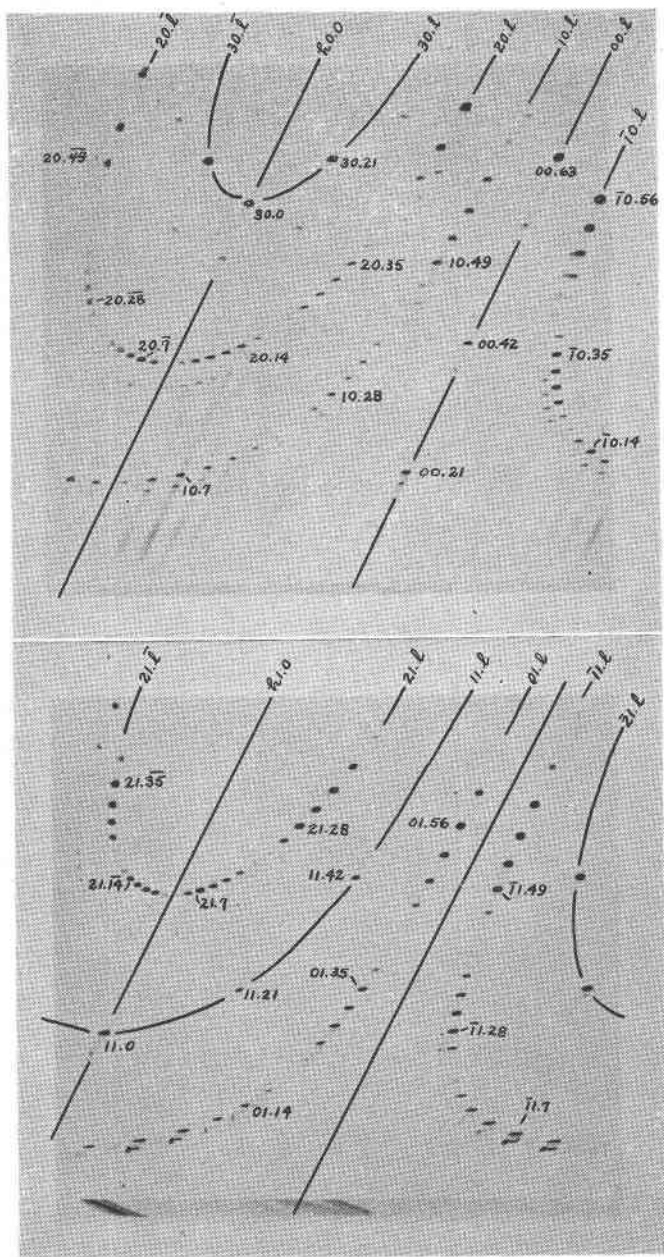
Fig. 2. Weissenberg photographs of α-SiC, type IV; a-axis rotation.
Above—zero level; below—first level.

hedron by making one of the cube diagonals the c axis. The remaining five sequences all have equal geometrical probabilities. The only apriori grounds for making a choice would be from the standpoint of structural uniformity. It could be argued that it would be highly improbable for silicon atoms to be distributed regularly along A at intervals of two, and then have the interval jump to nine, as in sequence (2). In his structure determinations of types I, II and III, Ott found intervals of 2, 3 and 4 only. Thus for the rhombohedral type I, with 15 layers, Ott[5] deduced three possible sequences: 33333, 22722 and 24342. The first was eliminated for a reason similar to that indicated for 3333333 above. The second sequence did not give proper calculated intensities, while the last one gave excellent agreement between calculated and observed intensities.

If we make the assumption here that only intervals of 2, 3 and 4 are possible, this would immediately eliminate the sequences (2), (3), (4) and (5), leaving only (6), 4233324. To test the validity of this assumption, intensity calculations have been carried out for all five sequences. The results are shown graphically in Figs. 3 and 4, and will be discussed later. They show quite clearly that only the final sequence 4233324 gives calculated intensities which are in satisfactory agreement with the observed intensities.

Calculation of Intensities

The general structure factor for the space group $R3m$ is rather complex,[6] but fortunately a very simplified form is possible in this case. On the Weissenberg films (Fig. 2) there are extensive series of reflections from trigonal and ditrigonal pyramidal planes. These include the $10 \cdot l$ series with 41 reflections, the $20 \cdot l$ series with 36, and the $21 \cdot l$ series with 26 reflections. This large number is ample for the structure determination, and for these particular series the structure factor can be expressed in a very simple form. For example, the $10 \cdot l$ planes all lie in a common zone, and the position of any atom with respect to any $10 \cdot l$ plane can be completely expressed by the term $2\pi(hx'+lz)$, where h and l are the Bravais-Miller indices, and x' and z are rectangular coordinates of the atom, with x' measured along the intermediate (b) axis and having only the values of 0, 1/3 and 2/3, while z is the usual vertical coordinate. Further simplification results because, although a hexagonal cell is being used for the description, the lattice is actually rhombohedral. Consequently, a given atom in the sequence on A has exactly the same position with respect to those planes which can reflect in a rhombohedral lattice as do the equiva-

[5] Ott, H., *loc. cit.*
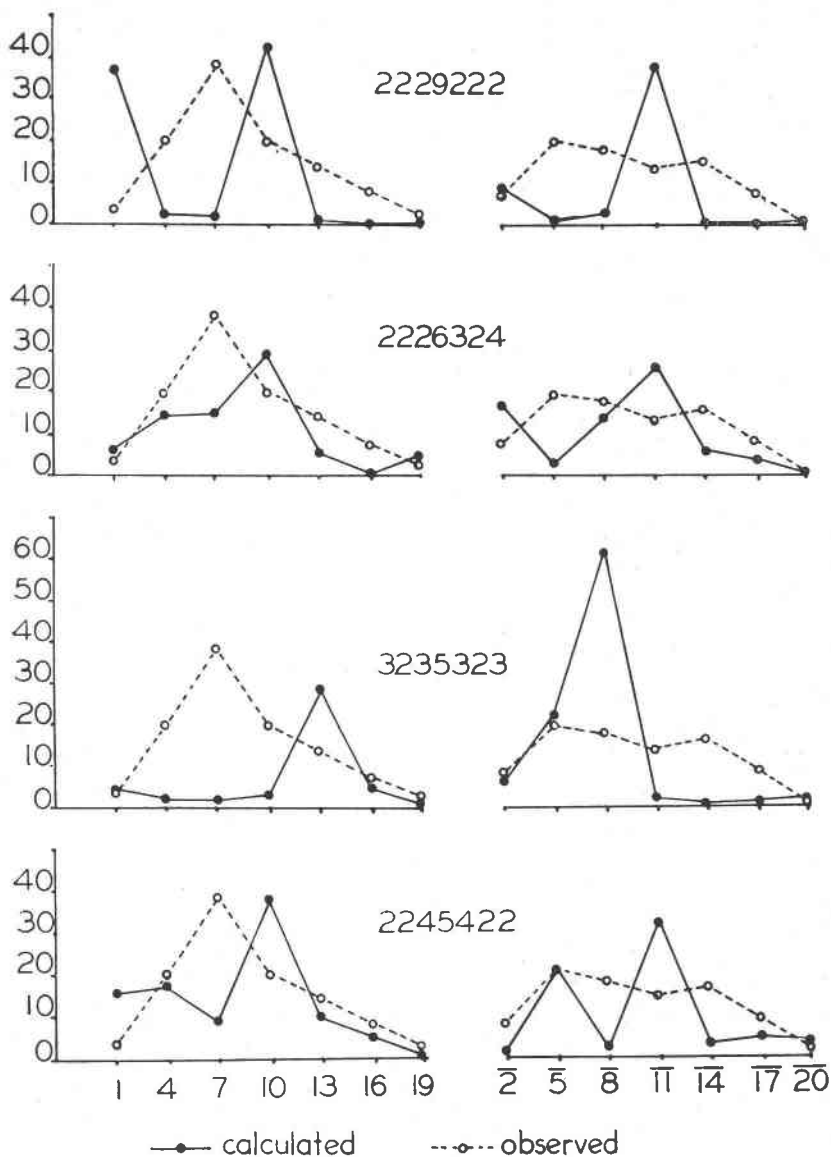
[6] *Inter. Structure Tables*, p. 242.

FIG. 3. Observed intensities compared with the calculated intensities for a portion of the 10 · *l* series of reflections from α-SiC, type IV, for the four discarded sequences. Relative intensities are plotted vertically, and values of *l* are plotted horizontally.
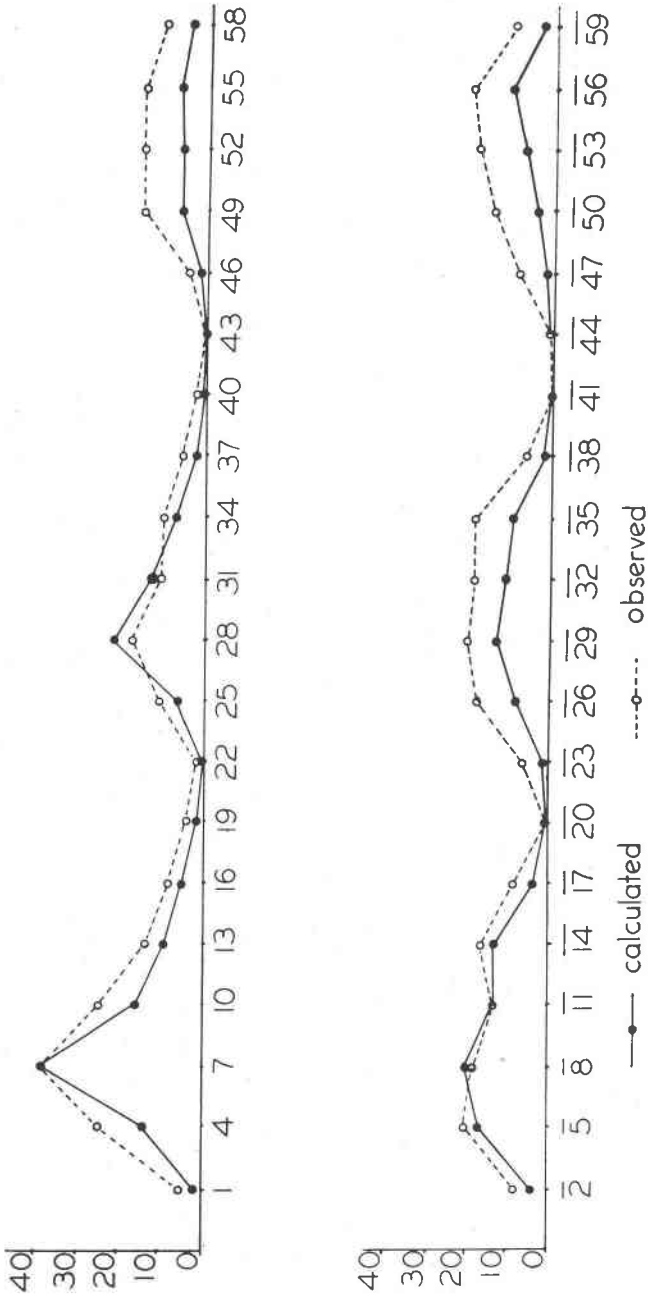
FIG. 4. Observed intensities compared with the calculated intensities for the entire series of 10·l reflections from α-SiC, type IV, for the sequence 4233324.

lent atoms on B and C. Hence instead of three terms involving the three values of x', only one term need be used. If the value $x' = 0$ be chosen, hx' drops out, and the term reduces to $2\pi(lz)$. The intensity formula then becomes

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

The summation must include the seven values of z for silicon, and the seven values of $z+p$ for carbon. Four of the five sequences for the silicon atoms are symmetrical, and for these the sine term is 0. Both the sine and cosine terms must be used for the unsymmetrical silicon sequence, and for all of the carbon atom sequences.

A similar situation is encountered in the series $20 \cdot l$ and $21 \cdot l$. In fact the trigonometrical portion of the formula is identical for planes with the same value of l, such as $10 \cdot 1$, $20 \cdot \overline{1}$ and $21 \cdot 1$, or $10 \cdot \overline{2}$, $20 \cdot 2$ and $21 \cdot \overline{2}$. The only difference is in the changed values of f_0 and of the correction factor. A comparison of the intensities for these three series of reflections on the Weissenberg films shows this similarity very clearly (Fig. 2). Not only are the three series very much alike, but variations in intensity tend to be repeated in each series. The contributions of the silicon atoms to the various reflections with l values from 1 to 20 are repeated in reverse order from 22 to 41, and then again directly from 43 to 62. Since the reflecting power of silicon is considerably greater than that of carbon, this repetition is impressed upon the series.

Because of this repetition, the calculated intensities for all sequences except the correct one (4233324) are shown only for values of l from 1 to 20 for the $10 \cdot l$ series. For the sequence found to be correct, they are shown for the complete $10 \cdot l$ series as recorded on the film, but are omitted for the $20 \cdot l$ and $21 \cdot l$ series, since these latter, although confirmatory, provide no additional information.

The numerical values plotted in Figs. 3 and 4 for the calculated intensities are derived from the formula by inserting the appropriate values of lz and p, and of f_0 for silicon and carbon, and then applying the Lorenz and polarization correction, $1 + \cos^2 2\theta / \sin 2\theta$. The highest value thus obtained was 38,000 for the $10 \cdot 7$ reflection. This is plotted as 38 in Figs. 3 and 4, and all other calculated values are reduced proportionally. Likewise, the strongest reflection on the film, also $10 \cdot 7$, has arbitrarily been given an estimated intensity of 38. On films with normal exposures, quite a number of spots have received exposures more than sufficient to develop maximum blackness, and hence appear of nearly equal intensity. To differentiate between these, a series of graduated exposures was made, varying from 4 hours to 20 minutes. From these films the rela-

tive intensities of the various reflections could be estimated more accurately. The β-reflections on the normal exposures of 0-level films can also be used in some cases to differentiate between planes whose α-reflections appear of equal intensity. Because of the irregular shape of the crystal, absorption effects are variable, and corresponding spots on different films may show some discrepancies in apparent intensities. In such cases an attempt has been made to use an averaged value for the estimated intensity. The most accurate intensity comparisons can be made on reflections adjacent to one another on the films, so the data have been divided into two sets, 10 · l and 10 · $\bar{l}$.

As seen is Fig. 3, there are marked disagreements between the calculated and observed intensities for the discarded sequences, while Fig. 4 shows the very satisfactory agreement for the accepted sequence 4233324. The observed intensities of the back reflections (high θ) are distinctly greater than the calculated values, but this is to be expected, since no correction for absorption was applied. The magnitude of this over-emphasis of back reflections can be seen by a comparison of the three orders of reflections from a single plane—10 · 7, 20 · 14 and 30 · 21 (Fig. 2). The calculated intensities for these three reflections are in the ratio of 38:9:8, while the observed intensity of 30 · 21 is distinctly greater than that of 20 · 14.

THE STRUCTURE OF α-SiC, TYPE IV

In order to obtain the structure indicated by the correct sequence, 4233324, it is only necessary to place 7 silicon atoms along A at heights corresponding to the sequence, namely, at 0, 4/21, 6/21, 9/21, 12/21, 15/21, and 17/21. A similar set of 7 silicon atoms is placed on B, beginning the sequence at a height of 1/3, and another similar set along C, beginning at a height of 2/3. One carbon atom is placed above each of the 21 silicon atoms at a distance $p = 1/28$. This is illustrated in Fig. 5a.

The rhombohedral arrangement is shown in Fig. 5b. This unit contains only 7 formula weights, and the distribution of Si and C atoms corresponds to that along A in the hexagonal unit.
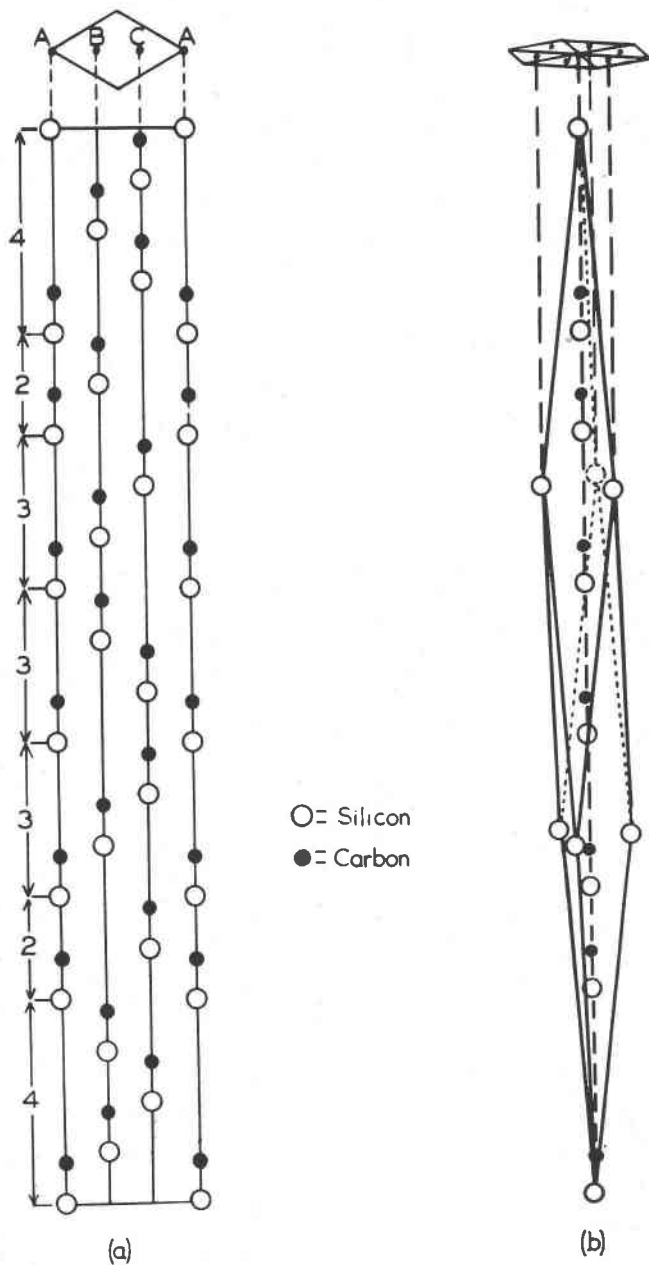
FIG. 5a. Vertical section along the (11·0) plane of the hexagonal unit cell of α-SiC, type IV.

FIG. 5b. Corresponding rhombohedral unit cell of α-SiC, type IV.

The atomic positions are as follows:

Hexagonal unit cell:

7 Si at 000, 0 0 4z, 0 0 6z, 0 0 9z, 0 0 12z, 0 0 15z, 0 0 17z.
7 C at 00p, 0 0 4$z+p$, 0 0 6$z+p$, 0 0 9$z+p$, 0 0 12$z+p$, 0 0 15$z+p$, 0 0 17$z+p$.
7 Si and 7 C at 2/3 1/3 1/3+the above coordinates.
7 Si and 7C at 1/3 2/3 2/3+the above coordinates.

Rhombohedral unit cell:

7 Si at 000; 4z, 4z, 4z; 6z, 6z, 6z; 9z, 9z, 9z; 12z, 12z, 12z; 15z, 15z, 15z; 17z, 17z, 17z.
7 C at ppp; 4$z+p$, 4$z+p$, 4$z+p$; 6$z+p$, 6$z+p$, 6$z+p$; 9$z+p$, 9$z+p$, 9$z+p$; 12$z+p$, 12$z+p$, 12$z+p$; 15$z+p$, 15$z+p$, 15$z+p$; 17$z+p$, 17$z+p$, 17$z+p$.

For both unit cells $z=1/21$, $p=1/28$.