

## STUDIES ON SILICON CARBIDE

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### ABSTRACT

This paper is divided into four parts. Part I describes a new system for naming the types of SiC based on the symmetry and number of layers in the unit cell. Part II presents several methods for describing the structures of the various types. These reveal definite progressive series, from which the possible existence of new types may be predicted. Part III discusses the structure of type 51R (old type V). Part IV describes the morphology and the crystal structure of the new type 87R.

### PART I. THE NAMING OF SiC TYPES

The discovery of another form of SiC, as reported in Part IV of this paper, and the probability that still others will yet be found makes it highly desirable that a new system of designating the types of SiC be introduced. The present system is based primarily on the order of discovery, and has no relationship with either the symmetry or contents of the unit cells.

When crystal structure determinations first began to be made, there were three known types of SiC, arbitrarily designated as I (15-layer rhombohedral), II (6-layer hexagonal), and III (4-layer hexagonal). When a cubic form was discovered, it became type IV, and the 51-layer rhombohedral type next found was designated type V (Ott, 1928). Thibault (1944) more recently found two new rhombohedral types, with 21 and 33 layers, respectively. He renamed the cubic form  $\beta$ -SiC, and called all of the others  $\alpha$ -SiC. The designation type IV (formerly cubic) he then applied to his new 21-layer structure and type VI to the 33-layer.

The author has recently found a crystal of SiC based on an 87-layer rhombohedral cell. Because of the very definite systematic relationships evident between the 15-, 33-, 51-, and 87-layer types, it seems certain that there is also a 69-layer rhombohedral cell yet to be found. Although the 21-layer rhombohedral (IV) has no companions so far, it is likely that it, too, is part of a series with still other types. It would seem rather ridiculous to go on naming these types VII, VIII, IX, etc., in the order of their discovery. Moreover, if any new scheme of naming appropriate to the actual structures is developed for new types yet to be found, it should logically be applied to the types already known.

There seems no likelihood of more than one cubic form. Since this has a structure corresponding to  $\beta$ -ZnS (sphalerite), the choice of  $\beta$ -SiC seems to be satisfactory. All remaining types ( $\alpha$ -SiC) so far found are based on either hexagonal or rhombohedral unit cells, and a proper

designation should certainly indicate which. All types have identical layers, but differ in the arrangement of these layers. Each type is uniquely distinguished either by the number of layers necessary for the arrangement to repeat itself, that is, the number of layers in the unit cell, or by the number of formula weights in the unit cell. Which of these two numbers is used is more or less a matter of choice. In the hexagonal types, or in the rhombohedral types referred to a hexagonal unit, the two numbers are identical. In the actual rhombohedral unit cell, the number of formula weights is  $\frac{1}{3}$  of the total number of layers included within the length of the  $c$  axis. However, since comparisons between types and descriptions of types are best made by using hexagonal unit cells throughout, it would seem a wiser choice to use the number of layers as the characteristic number. The designation for any type, then, would consist of the appropriate number, followed<sup>1</sup> by the letter "H" or "R", depending upon whether the unit cell is hexagonal or rhombohedral. Such a designation is simple, accurate, and descriptive. The 8 known types would be designated as follows:

| Cubic        | Hexagonal         | Rhombohedral                       |
|--------------|-------------------|------------------------------------|
| $\beta$ -SiC | 4H (old type III) | 15R (old type I)                   |
|              | 6H (old type II)  | 21R (old type IV)                  |
|              |                   | 33R (old type VI)                  |
|              |                   | 51R (old type V)                   |
|              |                   | 87R (new, no previous designation) |

All of the possible types which are predicted in Part II of this paper, would readily fit into this system of naming.

## PART II. THE DESCRIPTION OF SiC TYPES, AND THE PREDICTION OF TYPES AS YET UNDISCOVERED

In his report on the 15R type of SiC (old type I), Ott (1925) described the structure in terms of the sequence of silicon (or carbon) atoms along the symmetry axes. The five atoms on a given axis are separated by layer intervals of 2, 4, 3, 4, and 2, and thus the sequence 24342 describes the structure. For the 33-layer rhombohedral type (Ramsdell, 1945), the author used the same method of description, and found the structure to be based on an interval sequence of 24243334242, and for the 51-layer rhombohedral type (described in part III of this paper), the sequence was found to be 24242433333424242. This method of describing the atomic arrangement becomes increasingly unwieldy, for the 87-layer

<sup>1</sup> The *Strukturbericht* classifies general structure types as A, B, C, . . . followed by a number. Thus scheelite is type H4 and apatite H57. By having the number precede the letter H in the type designations for SiC, no confusion will result.

rhombohedral type (part IV of this paper) has an interval sequence of 242424242433333333334242424242. Moreover, this method is not equally applicable to the hexagonal structures, for in them the symmetry axes are not all alike, the sequence along the 6-fold axis being different from that along the 3-fold axes. A much superior type of description is available.

In  $\alpha$ -SiC, all atoms lie on the symmetry axes, and all symmetry axes lie in the  $11\bar{2}0$  plane; hence, a vertical section through the unit cell along  $11\bar{2}0$  gives an adequate representation of the structure (Fig. 1). If a Si (or C) atom lies on *A* in one layer, the next must either be to the right,

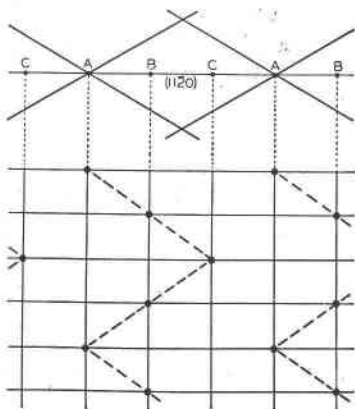


FIG. 1.  $11\bar{2}0$  cross-section of  $\alpha$ -SiC, showing zig-zag arrangement of Si (or C) atoms.

on *B*, or to the left, on *C*. If to the right, the third layer might have its atom continue to the right, or it might change direction and go to the left. Because of these repeated changes in direction, a zig-zag pattern results. Such an arrangement can be described in terms of the number of layers added in each direction in succession, and in this paper will be designated as the *zig-zag* sequence, in contrast to the *interval* sequence previously used.<sup>2</sup> Thus, type  $4H$  consists of two layers added to the right, then two to the left, etc., and can be described as 22. Type  $6H$  adds three to the right, then three to the left, or 33. Type  $15R$  has three right, then two left. This is repeated three times to form the unit cell, and the complete symbol would be 323232. Every symbol for a rhombohedral cell

<sup>2</sup> The author had used this method in determining the number of possible structures for  $51R$ , but is indebted to Dr. H. T. Evans, Jr., of the Massachusetts Institute of Technology, for his suggestion that the zig-zag sequence was a better method for description of types than the interval sequence. Recently, there has also appeared an article on "The Numerical Symbol of Close Packing of Spheres" (Zhdanov, 1945), in which this method was described.

would be of this triple character, and could easily be abbreviated to a single set of figures. The following list of rhombohedral types will illustrate this method of notation.

*3 . . . 2 series, rhombohedral*

|       |           |
|-------|-----------|
| 15R   | 32        |
| 33R   | 3332      |
| 51R   | 333332    |
| (69R) | 33333332  |
| 87R   | 333333332 |

Not only is this a concise method of describing the structure, but it clearly reveals the basis for predicting the existence of a 69-layer rhombohedral type. Moreover, only odd numbers of 3's occur in this tabulation, and the possibility of structures involving an even number of 3's arises. To complete a unit cell, the last layer must be directly above the initial layer. This is the reason the rhombohedral sequences must be repeated three times. Likewise, with an even number of 3's, the sequences would have to be repeated twice, and the following tabulation becomes evident.

*3 . . . 2 series, hexagonal*

|       |           |           |
|-------|-----------|-----------|
| 4H    | 2         | 2         |
| (16H) | 332       | 332       |
| (28H) | 33332     | 33332     |
| (40H) | 3333332   | 3333332   |
| (52H) | 333333332 | 333333332 |

Only the first of these represents a known structure, 4H, but the others represent possible hexagonal types as yet undiscovered. It might be noted here that the *interval* sequence originally used likewise predicts the existence of 69R, but does not suggest the possible hexagonal types. The complete hexagonal symbols are always doubled, and like the rhombohedral, could be abbreviated, except for the first one (4H). The symbol 2 alone would not be satisfactory.

The 21R type does not appear in the foregoing tabulations. Its zig-zag sequence is 343434, or, in abbreviated form, 34. Although no other structures of this type have so far been found, the following series is suggested:

*3 . . . 4 series*

|                    |                |                 |         |               |
|--------------------|----------------|-----------------|---------|---------------|
| Rhombohedral types | 34 21R         | Hexagonal types | 4       | 4 (8H)        |
|                    | 3334 (39R)     |                 | 334     | 334 (20H)     |
|                    | 333334 (57R)   |                 | 33334   | 33334 (32H)   |
|                    | 33333334 (75R) |                 | 3333334 | 3333334 (44H) |

In both the 3 . . . 2 and the 3 . . . 4 series, the larger cells have an increasing number of 3's. The sequence 33 is characteristic of 6H (old type II), which has been found to be the most abundant type present in commer-

cial silicon carbide. Thus, not only is the 33 structure the most common, but it occurs within most of the other structures. Whole blocks of the larger cells have the  $6H$  structure, and the larger cells become increasingly like  $6H$ . For this reason, it is quite certain that the above series extend indefinitely, with  $6H$  as the limiting case. However, the increasing resemblance to type  $6H$ , both with respect to  $x$ -ray diffraction effects and to morphology, may make proof of this difficult. This matter will be discussed later in part IV.

Although the sequence methods already discussed give adequate mathematical description of the structures, they do not give a completely satisfactory visual picture. A graphical 2-dimensional presentation is possible in terms of the atomic configurations represented in the  $11\bar{2}0$  cross-section. A remarkable simplification occurs when this is done, for it reveals that for all known types, including the cubic, there are only two basic arrangements of the atoms.

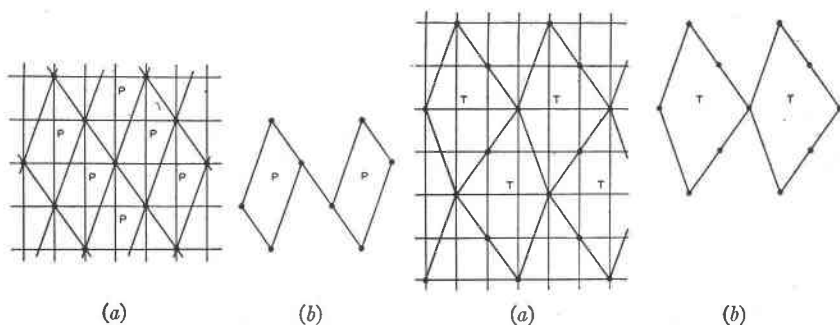


FIG. 2 (a). Typical parallelogram arrangement ( $P$ ) of Si (or C) atoms in  $11\bar{2}0$  cross-section through cubic  $\beta$ -SiC, in rhombohedral orientation. (b). Single horizontal  $P$  layer.

FIG. 3 (a). Typical trapezoidal arrangement ( $T$ ) of Si (or C) atoms in  $11\bar{2}0$  cross-section of SiC, type  $4H$ . (b) Single horizontal  $T$  layer.

The cubic form may be treated as a rhombohedron, with cubic  $[111]$  becoming hexagonal  $[0001]$ . In this orientation, the  $11\bar{2}0$  cross-section shows that the silicon (or carbon) atoms are so arranged that successive layers are all added in one direction, without change. The appropriate symbol would be  $\infty$  (Fig. 2). This arrangement consists of a series of identical parallelograms, and will be designated by the letter  $P$ . Single horizontal layers of  $P$  appear as shown in Fig. 2b.

Type  $4H$  has a  $11\bar{2}0$  plane arrangement of silicon (or carbon) atoms illustrated in Fig. 3. The repeated figure is a trapezium, and will be designated by the letter  $T$ . This arrangement occurs in single horizontal layers as shown in Fig. 3b.

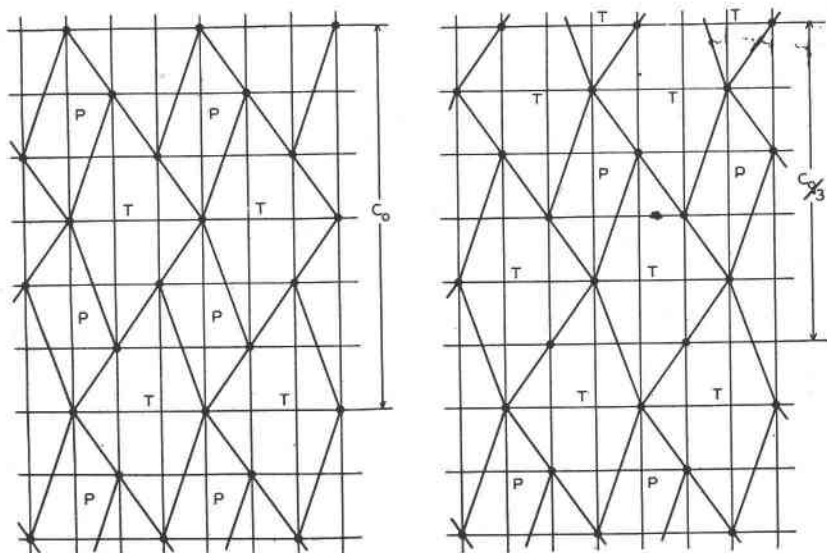


FIG. 4.  $11\bar{2}0$  cross-section through type  $6H$ , showing alternate  $T$  and  $P$  layers.

FIG. 5.  $11\bar{2}0$  cross-section through type  $15R$ , showing double  $T$  layers alternating with single  $P$  layers.

All other known types of  $\text{SiC}$ , as well as all of the undiscovered types predicted in the series previously described, are made up of horizontal layers of these two basic configurations,  $T$  and  $P$ , in various combinations. For example, the most common type,  $6H$ , is made up of alternate layers of  $T$  and  $P$ , Fig. 4. Such alternate layers always occur whenever the symbol  $33$  occurs, and in the  $3 \dots 2$  and  $3 \dots 4$  series, whole sections of the structures are made up of these alternating  $T$  and  $P$  layers. In addition, the  $3 \dots 2$  series is characterized by double  $T$  layers (Table 1). This feature is illustrated in Fig. 5, which shows the arrangement in type  $15R$ .

The  $3 \dots 4$  series is very similar to the  $3 \dots 2$ , but has double  $P$  instead of double  $T$  layers. No table is shown for this, but it would be similar to Table 1. The first vertical column would be  $\beta\text{-SiC}$ , with nothing but  $P$  layers, followed by the other members. Each succeeding column would have double  $P$  layers interspersed with increasing numbers of alternating  $T$  and  $P$  layers. In both series the increasing resemblance to type  $6H$  is very apparent.

It is quite possible that all types of  $\text{SiC}$  are limited to these two basic configurations,  $T$  and  $P$ , but the author knows no reason why this should be. Even if this limitation did hold, there are other extensive



photograph ( $a$  axis rotation), is reproduced in Fig. 6. A complete morphological study of this crystal will soon be published by Dr. Thibault.

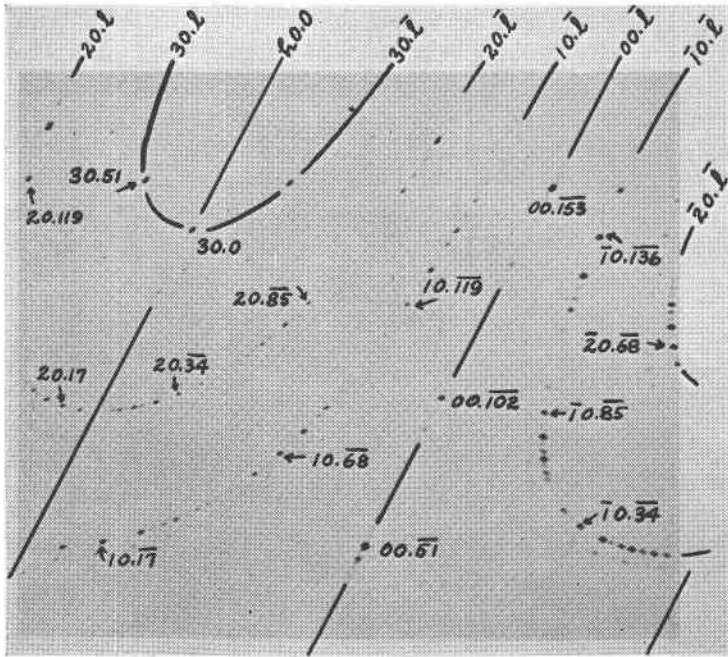


Fig. 6. Weissenberg photograph of crystal of SiC, type 51R. 0-level,  $a$  axis rotation.

Measurements from the Weissenberg photographs, together with the known relationship to the other types of SiC, give the following cell constants:\* hexagonal unit,  $a_0 = 3.073 \text{ \AA}$ ,  $c_0 = 128.17_s \text{ \AA}$ ; rhombohedral unit,  $a_r = 42.76_s \text{ \AA}$ ,  $\alpha = 4^\circ 07'$ . The coordinates of the Si and C atoms are as follows:

Hexagonal unit cell:

17 Si at  $000, 002z, 006z, 008z, 0012z, 0014z, 0018z, 0021z, 0024z, 0027z, 0030z, 0033z, 0037z, 0039z, 0043z, 0045z, 0049z$ .

17 C at  $00p, 002z+p, 006z+p, 008z+p, 0012z+p, 0014z+p, 0018z+p, 0021z+p, 0024z+p, 0027z+p, 0030z+p, 0033z+p, 0037z+p, 0039z+p, 0043z+p, 0045z+p, 0049z+p$ .

17 Si and 17 C at  $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$  + the above coordinates.

17 Si and 17 C at  $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$  + the above coordinates.

$$z = 1/51; p = 1/68$$

The unit cell of type 51R is so large that from a purely geometrical

\* In order to be consistent with the earlier articles on SiC, the unit cell dimensions are given in  $\text{\AA}$  units, although they should actually be designated as  $kX$  units.



standpoint an enormous number of structures exist which could fully satisfy the requirements as to symmetry and provide the basic tetrahedral arrangement of carbon atoms about the silicon atoms.<sup>3</sup> In determining the structure of type 33*R*, certain limiting assumptions were made (Ramsdell 1945), which reduced the number of possible atomic arrangements to five. Each of these five was tested, and the correct one determined. The same procedure applied to 51*R* leaves 44 possible structures, from which the correct one must be selected. The labor involved in calculating intensities for such a large number of structures would be very great. As reported at the 26th annual meeting of the Mineralogical Society of America (Ramsdell 1946), the existence of a progressive series of structures, consisting of types 15*R*, 33*R* and 51*R*, seemed apparent when their interval sequences were listed.

|             |                    |     |      |
|-------------|--------------------|-----|------|
| 15 <i>R</i> | 24                 | 3   | 42   |
| 33 <i>R</i> | 2424               | 333 | 4242 |
| 51 <i>R</i> | 242424333333424242 |     |      |

The third set of intervals is an extrapolation of the first two, and corresponds to one of the possible arrangements for type 51*R*. The intensities calculated for this arrangement were in such excellent agreement with the observed intensities that it was felt that it must be the correct one.

However, since no actual elimination of the remaining 43 possible structures had been made, further study seemed desirable. The possibility of a quite different arrangement producing the same diffraction effects was ruled out. Certainly, cumulative experience in the field of crystal structure determinations gives no support to the idea that two different structures can give rise to similar diffraction effects for any extended series of reflections.

There remained the possibility that a very similar structure might give approximately the same series of relative intensities as the chosen one. To test this, a structure was chosen from among the rejected ones which was very similar in arrangement. Its interval sequence was 24332433333423342. This represents a structure with the least change possible. Forty-five out of the original fifty-one atoms are unchanged. The remaining six form pairs, in which the only change is a reversal of position in the two structures in the  $11\bar{2}0$  plane. If these pairs slope to

<sup>3</sup> For type 51*R* the total number of interval sequences is 43,690, being equal to  $2^n/3$ , where  $n$  is the number of Si atoms on any vertical symmetry axis—in this case, 17. Actually many of these sequences are congruent, and the number of different sequences is much smaller than 43,690. So far, the author has found no means of predicting the number of different sequences, but it would undoubtedly be in the thousands.

the right in one, they slope to the left in the other. The intensities calculated for this slightly modified structure are so distinctly different as to completely eliminate it from consideration.

The use of the zig-zag sequence in describing the structures reveals more clearly than the interval sequence why this apparently very minor change just referred to results in such marked intensity changes. The abbreviated symbol for 51*R* is 333332, whereas the symbol for the modified structure is 3932. In other words, it changes the addition of successive layers from 3 right, 3 left, 3 right, to 9 in one direction. In terms of the 11 $\bar{2}$ 0 cross-section, as described in Part II, the structure is changed from TTPTPTPTPTTT to TTPTPPPPPTPTT. There is no reason known to the author why this latter structure is not a possible one, but it very definitely is not in the established 3 . . . 2 series, to which type 51*R* clearly belongs.

These computations would probably never have been made had the existence of type 87*R* been known at the time. The recent discovery of this new type, reported in part IV of this paper, establishes so firmly the existence of a progressive series of structures, that there should be no hesitancy in accepting the structure as valid, without any further study of the many rejected structures.

Recently, two Russian scientists have reported on an investigation of type 51*R*, and found the same structure (Zhdanov, Minervina 1945). The only types known to them were 4*H*, 6*H*, and 15*R*, whose structure symbols are 22, 33, and 32. On the assumption that the zig-zag sequence symbol for any other type of SiC must be limited to the numbers 2 and 3, they found for type 51*R* only two possible rhombohedral arrangements, 2222223 and 333332. The calculated intensities for the former did not correspond, while those for the latter agreed so well with the data published by Ott, that they accepted it as the correct structure. Even had they been familiar with the existence of type 21*R*, with the symbol 34, it would have made no difference, for there is no combination of 3 and 4 which can give rise to a rhombohedral 51-layer structure. Their determination was based on a restriction much more limiting in its character than that used by the author—namely, that the sequence intervals must be limited to 2, 3, and 4. This restriction limited the number of possible structures to 44, as contrasted with the two possibilities which they considered. Since 51*R* does belong to the 3 . . . 2 series, their limitation happened to be all right, and their determination turned out to be correct. However, it seems quite obvious that their restriction is not a general one, and cannot be applied to any type not in the 3 . . . 2 series.

If the type 21*R* had not been discovered, there would not be any sug-

gestion whatever of the possibility of a 3 . . . 4 series. For this reason, the author feels that it would be very unwise to propose any limitations as to further possible types. Various simple structures not included in the 3 . . . 2 and 3 . . . 4 series are geometrically possible, as well as an enormous number of more complicated arrangements.

#### IV. THE MORPHOLOGY AND STRUCTURE OF $\alpha$ -SiC, TYPE 87R

##### *Morphology*

The only example of the new type 87R so far found is a very small, dark blue crystal, about 0.4 mm. long, 0.25 mm. wide, and 0.15 mm. thick. It is tabular parallel to (0001) and elongated parallel to one of the *a* axes. The two pinacoids are the largest faces present. They are well developed and give excellent reflections on the goniometer. No attempt has been made to determine by etching which is the upper and which the lower pinacoid (Thibault, 1944). The remaining faces are much smaller, and in general less well developed. None gives as good signals on the goniometer as do the pinacoids, and for some the signals are diffuse, or spread over a considerable angular range. Of the six trigonal pyramid zones, only four have measurable faces. Seven trigonal pyramids have been definitely established, with one more probable, and several other quite doubtful. No evidence of second order faces has been found. The distribution of faces is shown in Table 2. Table 3 gives the morphological data, and the angle table is given in Table 4. With the exception of  $10\bar{1}1$ , the faces present correspond to planes whose *x*-ray reflections are very strong.

TABLE 2. DISTRIBUTION OF FACES ON CRYSTAL OF  $\alpha$ -SiC, TYPE 87R

| (10 $\bar{1}$ l)             | (01 $\bar{1}$ l) | ( $\bar{1}$ 10l)            | ( $\bar{1}$ 01l)             | (0 $\bar{1}$ 1l) | ( $\bar{1}$ $\bar{1}$ 0l)    |
|------------------------------|------------------|-----------------------------|------------------------------|------------------|------------------------------|
| 1.0. $\bar{1}$ .43           | —                | $\bar{1}$ .1.0.43           | $\bar{1}$ .0.1.44            | —                | —                            |
| 1.0. $\bar{1}$ .28           | —                | $\bar{1}$ .1.0.28           | $\bar{1}$ .0.1.29            | —                | 1. $\bar{1}$ .0.29           |
| 1.0. $\bar{1}$ .13           | —                | —                           | $\bar{1}$ .0.1.14            | —                | 1. $\bar{1}$ .0.14           |
| 1.0. $\bar{1}$ .1            | —                | $\bar{1}$ .1.0.1            | $\bar{1}$ .0.1. $\bar{1}$    | —                | 1. $\bar{1}$ .0. $\bar{1}$   |
| 1.0. $\bar{1}$ . $\bar{1}$ 4 | —                | —                           | $\bar{1}$ .0.1. $\bar{1}$ 6? | —                | —                            |
|                              |                  | —                           | $\bar{1}$ .0.1. $\bar{2}$ 8  | —                | —                            |
|                              |                  | $\bar{1}$ .1.0. $\bar{4}$ 4 | $\bar{1}$ .0.1. $\bar{4}$ 3  | —                | 1. $\bar{1}$ .0. $\bar{4}$ 3 |

On the crystals of types 21R and 33R, Thibault found faces which were characteristic, their angles being quite different from those of any other type. But for the crystal of 87R, the only measurable faces present are

TABLE 3. MORPHOLOGICAL DATA,  $\alpha$ -SiC, TYPE 87R

| Form               | No. Times Observed | Quality | Angle between Form and Base |                  |         |
|--------------------|--------------------|---------|-----------------------------|------------------|---------|
|                    |                    |         | Range                       | Weighted Average | Calcd.  |
| 0001               | 2                  | A       |                             |                  |         |
| 1.0. $\bar{1}$ .43 | 4                  | C-E     | 62°07'–62°25'               | 62°21'           | 62°22'  |
| 1.0. $\bar{1}$ .28 | 3                  | B-E     | 71°06'–71°42'               | 71°12'           | 71°11'  |
| 1.0. $\bar{1}$ .13 | 1                  | B       | 80°59'                      | 80°59'           | 81°02'  |
| 1.0. $\bar{1}$ .1  | 4                  | B-D     | 89°15'–89°23'               | 89°19'           | 89°18'  |
| 0.1. $\bar{1}$ .14 | 3                  | B-E     | 80°19'–80°34'               | 80°23'           | 80°21'  |
| 0.1. $\bar{1}$ .29 | 2                  | D       | 70°35'–70°44'               | 70°39'           | 70°33½' |
| 0.1. $\bar{1}$ .44 | 2                  | D-E     | 61°42'–61°51'               | 61°48'           | 61°52'  |

TABLE 4. ANGLE TABLE,  $\alpha$ -SiC, TYPE 87RHexagonal— $R$ , ditrigonal pyramidal— $3m$ 

$$a:c = 1:71.151_6 \quad \alpha = 2^\circ 25'$$

$$\rho_0:r_0 = 82.09:1 \quad \lambda = 119^\circ 59'$$

| Form   | $\phi$  | $\rho$  | $A_1$   | $A_2$   |
|--|---------|---------|---------|---------|
| $c-\bar{c}$ 0001                             | +30°00' | 0°00'   | 90°00'  | 90°00'  |
| $\zeta-\bar{\zeta}$ 1.0. $\bar{1}$ .43       | +30°00' | 62°22'  | 39°53½' | 90°00'  |
| $\epsilon-\bar{\epsilon}$ 1.0. $\bar{1}$ .28 | +30°00' | 71°11'  | 34°56½' | 90°00'  |
| $\beta-\bar{\beta}$ 1.0. $\bar{1}$ .13       | +30°00' | 81°02'  | 31°11½' | 90°00'  |
| $\alpha-\bar{\alpha}$ 1.0. $\bar{1}$ .1      | +30°00' | 89°18'  | 30°00½' | 90°00'  |
| $\tau-\bar{\tau}$ 0.1. $\bar{1}$ .44         | –30°00' | 61°52'  | 90°00'  | 40°12½' |
| $x-\bar{x}$ 0.1. $\bar{1}$ .29               | –30°00' | 70°33½' | 90°00'  | 35°15'  |
| $\nu-\bar{\nu}$ 0.1. $\bar{1}$ .14           | –30°00' | 80°21'  | 9°00'   | 31°22½' |

ones whose angles are very close to those commonly found on type 6H crystals, and careful measurement is necessary to make the distinction. The closeness of the angles is shown in the following list, which gives the calculated values for  $\rho$ . In cases where good goniometer signals can be obtained, this situation would present little difficulty, but where signals are poor, and possibly only a few faces present, the variation from type 6H might be overlooked. For higher members of the 3 . . . 2 series, this closeness of angles would become increasingly evident. Consequently, the discovery of new members of the series on the basis of goniometric measurements along will be increasingly difficult.

|      | 6H      |        | 87R     |
|------|---------|--------|---------|
| 10.0 | 90°00'  | 10.1   | 89°18'  |
| 10.1 | 79°59½' | 10.13  | 81°02'  |
|      |         | 14     | 80°21'  |
|      |         | 16     | 79°00'  |
| 10.2 | 70°33½' | 10.28  | 71°11'  |
|      |         | 29     | 70°33½' |
| 10.3 | 62°06'  | 10.43  | 62°22'  |
|      |         | 44     | 61°52'  |
| 10.4 | 54°47'  | 11.58* | 54°47'  |
|      |         | 59*    | 54°21'  |
| 10.5 | 48°34½' | 10.71* | 49°11'  |
|      |         | 10.73* | 48°23½' |

\* Not present on crystal, but possible.

$\rho$  values in italics are identical for both types.

### Crystal structure of 87R

Weissenberg photographs of excellent quality were obtained from the crystal of SiC, type 87R. Reproductions of the 0-level and 1-level photographs, with rotation about an  $a$  axis, are shown in Fig. 7*a, b*. The space group is  $R3m$ , and the unit cell dimensions as obtained from the 0-level films are as follows: Hexagonal— $a_0 = 3.073\text{\AA}$ ,  $c_0 = 218.657\text{\AA}$ ;  $Z = 87$ ; rhombohedral— $a_{rh} = 72.865\text{\AA}$ ,  $\alpha = 2^\circ 25'$ ;  $Z = 29$ .

As would be expected, certain reflections coincide exactly in position with those of the other rhombohedral types, as well as with type 6H. Since the length of the  $c$  axis in every case is an exact multiple of a common unit, certain planes must come at exactly the same angles. The reflections from these planes are the ones which have common positions on the Weissenberg films. In the rhombohedral types, the value of  $l$  for these planes is always a multiple of the number of formula weights in the unit cell. Some of these common planes are as follows:

| 15R   | 21R   | 33R   | 51R   | 87R    | 6H    |
|-------|-------|-------|-------|--------|-------|
| 10·5  | 10·7  | 10·11 | 10·17 | 10·29  | 10·2  |
| 10·10 | 10·14 | 10·22 | 10·34 | 10·58  | 10·4  |
| 10·20 | 10·28 | 10·44 | 10·68 | 10·116 | 10·8  |
| 10·25 | 10·35 | 10·55 | 10·85 | 10·145 | 10·10 |
| etc.  | etc.  | etc.  | etc.  | etc.   | etc.  |
| 00·15 | 00·21 | 00·33 | 00·51 | 00·87  | 00·6  |
| 11·15 | 11·21 | 11·33 | 11·51 | 11·87  | 11·6  |

The characterizing difference between the Weissenberg photographs of the successive rhombohedral types lies in the increasing number of  $hk \cdot l$  reflections occurring *between* the common reflections in fixed positions. This is illustrated in the diagrams of Fig. 8. These diagrams represent small portions of the rows of  $10 \cdot l$  reflections from the Weissenberg



photographs. For each type, two of the common reflections occurring in fixed positions are shown. These are the ones at the extreme right and left of each row. In between are the additional reflections characteristic of each type. Each reflection is designated by its  $l$  value, and the observed intensities are approximately indicated by the vertical height of the line, with a spot indicating a very weak or missing reflection.

The indexing of the films presents no serious difficulties. Since the unit cell is rhombohedral, the  $10 \cdot l$  reflections cannot have  $l = 3n$ . For 87R, the  $10 \cdot \overline{29}$  reflection must come at exactly the same position of the film as  $10 \cdot \overline{2}$  for 6H, and  $10 \cdot 58$  at the same position as  $10 \cdot 4$  of 6H. Although  $10 \cdot \overline{29}$  does coincide in position with  $10 \cdot \overline{2}$ ,  $10 \cdot 28$  is so close to the position of  $10 \cdot 2$  that it is very uncertain which is which at the start. Likewise,  $10 \cdot 58$  and  $10 \cdot \overline{59}$ , both strong reflections, are practically indistinguishable. The calculated values for the distances from the zero line of  $10 \cdot 28$  and  $10 \cdot \overline{29}$  differ by only 0.12 mm., those for  $10 \cdot 58$  and  $10 \cdot \overline{59}$  by 0.13 mm. However, for higher values of  $l$ , the separation of such pairs becomes increasingly greater, and no difficulty is encountered, for example, in distinguishing  $10 \cdot 217$  and  $10 \cdot \overline{218}$ , or  $10 \cdot 247$  and  $10 \cdot \overline{248}$ . From these identifiable reflections, it is easy to work back down to the lower values.

Although, as explained later, the characteristics of the x-ray pattern are such as to furnish definite proof of the fact that the structure must belong to the  $3 \dots 2$  series, intensities have been calculated for some of the reflections. A structure based on the zig-zag sequence 333333332 has theoretical intensities that agree with the observed intensities with the same high degree of correlation which has been found for the other types of SiC. A comparison of the observed and the calculated intensities for the first 30 reflections from type 87R is given in Table 5.

An interesting feature of the Weissenberg photographs of type 87R is the resemblance to photographs of type 6H. It is now apparent that this is also true, but to a much less extent, of the photographs of 51R and 33R, but it was not until the films of 87R were available that this was noticed. This is illustrated in Fig. 9, which shows diagrammatically some of the reflections of type 6H compared with the strongest reflections of 87R. The pairs of reflections joined by dashed lines come at identical positions, and the others at approximately the same positions. In some cases, single reflections of 6H are opposite pairs of 87R reflections. The variations in intensity in the comparatively few reflections of 6H are closely followed in the reflections of 87R which occur at the same position, while in between, where 6H has no reflections, the reflections of 87R are either comparatively weak or absent.

TABLE 5. COMPARISON OF OBSERVED AND CALCULATED INTENSITIES FOR SOME OF THE REFLECTIONS OF TYPE 87R

| $10 \cdot l$ | Calcd.<br>I | Obsr.<br>I | $10 \cdot \bar{l}$ | Calcd.<br>I | Obsr.<br>I |
|--------------|-------------|------------|--------------------|-------------|------------|
| 10·1         | 1.1         | vw         | 10·2               | 1.1         | vw         |
| 4            | 1.8         | vw         | 5                  | 1.4         | vw         |
| 7            | 3.2         | vw         | 8                  | 2.2         | vw         |
| 10           | 8.4         | w          | 11                 | 6.2         | vw         |
| 13           | 100         | vs         | 14                 | 262         | vvs        |
| 16           | 135         | vs         | 17                 | 10          | mw         |
| 19           | 24          | m          | 20                 | 2.5         | vw         |
| 22           | 19          | m          | 23                 | 1.0         | a          |
| 25           | 33          | m          | 26                 | 0.7         | a          |
| 28           | 515         | vvs        | 29                 | 417         | vvs        |
| 31           | 92          | ms         | 32                 | 0.7         | a          |
| 34           | 17          | m          | 35                 | 1.1         | vw         |
| 37           | 10          | w          | 38                 | 2.4         | vw         |
| 40           | 12          | w          | 41                 | 12          | w          |
| 43           | 390         | vvs        | 44                 | 365         | vvs        |

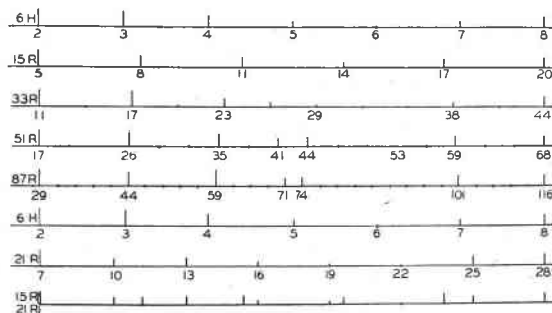


FIG. 8. Comparison of some of the  $10 \cdot l$  reflections from various types of SiC. The reflections at the extreme right and left of each row occur in identical positions for all types. In between are varying number of reflections, characteristic of each type. Heights of lines indicate approximate relative intensities for important reflections. Other reflections are either absent, or comparatively weak.

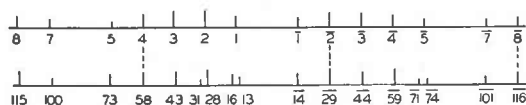


FIG. 9. Diagrammatic comparison of some type  $6H$  reflections with the strongest reflections of  $87R$ . Reflections from  $87R$  not indicated are comparatively weak or absent.



This situation is, of course, due to the fact that of the 87 layers in the unit cell of 87R, 81 correspond exactly to the 6H arrangement. Consequently, there are large blocks of the 87R structure which are identical to 6H. This close resemblance of the Weissenberg pattern of 87R to that of 6H implies membership in either the 3 . . . 2 or the 3 . . . 4 series. The fact that only in the former could an 87-layer rhombohedral cell occur clearly establishes the structure.

Types 51R and 33R include relatively smaller blocks of the 6H structure, and their resemblance to 6H, as revealed by the Weissenberg photographs, is not so pronounced (Fig. 8).

Since type 6H is the limiting case for the 3 . . . 2 series (and the 3 . . . 4 series as well), it would be expected that the higher members should increasingly resemble 6H, both morphologically and with respect to x-ray data. If single small crystals are available, consisting entirely of one type, recognition of several additional members of the series, such as 105R and 123R, might be possible. The Weissenberg patterns should offer a better opportunity for detection than a morphological study.

In the recognition of possible new types of SiC by means of Weissenberg photographs, care must be taken to avoid confusion with crystals which represent a coalescence of types (Thibault, 1944). Such crystals would likewise have extra reflections in between the common reflections in fixed positions. An example of this is illustrated in the bottom row of Fig. 8, which represents an imaginary coalescence of 15R and 21R. In such a case, the reflections  $10\cdot\bar{5}$  and  $10\cdot\bar{20}$  of 15R would coincide with  $10\cdot\bar{7}$  and  $10\cdot\bar{28}$  of 21R. In between would be  $10\cdot\bar{8}$ ,  $10\cdot\bar{11}$ ,  $10\cdot\bar{14}$ , and  $10\cdot\bar{17}$  of 15R, and  $10\cdot\bar{10}$ ,  $10\cdot\bar{13}$ ,  $10\cdot\bar{16}$ ,  $10\cdot\bar{19}$ ,  $10\cdot\bar{22}$ , and  $10\cdot\bar{25}$  of 21R. This would make a total of ten reflections in between the fixed positions. Type 33R likewise has ten reflections in between the corresponding fixed positions ( $10\cdot\bar{11}$  and  $10\cdot\bar{44}$  for 33R). But these two sets of ten reflections would be easily distinguishable. Those for 33R would be regularly spaced, while the coalescence of 15R and 21R would have an uneven distribution. This is clearly shown in the bottom line of Fig. 8.

This would hold true for any possible coalescence of types. Two sets of regular spacings of differing magnitude cannot combine to form a single set of smaller equal spacings. The reflections would form irregular groups. However, in the special case where one set of spacings was an exact multiple of the other, the larger spacings would all coincide with certain ones of the smaller, and the coalescence might be overlooked. This might be the case with a coalescence of  $\beta$ -SiC (which treated as rhombohedral

would be type 3R) with any other rhombohedral type, and might also occur in coalescences between possible hexagonal types.

The 3 . . . 2 series was first recognized when the structure of type 51R was determined. At that time, there seemed to be no evidence as to how far the series might extend. It now seems certain that it extends indefinitely. Indeed, type 6H is really the limiting case for the series, with the number of 3's in the symbol indefinitely large. Because of the increasing resemblance to 6H, both morphologically and with respect to x-ray data, the chances of discovering any large number of additional types in the 3 . . . 2 series seems remote.

#### SUMMARY

Like all of the other rhombohedral types of SiC, the space group of 87R is  $R3m$ . The unit cell constants are as follows:

Hexagonal— $a_0 = 3.073\text{\AA}$ ,  $c_0 = 218.657\text{\AA}$ ,  $Z = 87$ .

Rhombohedral— $a_r = 72.907\text{\AA}$ ,  $\alpha = 2^\circ 25'$ ,  $Z = 29$ .

The atomic positions for the hexagonal cell are:

29 Si at 000, 002z, 006z, 008z, 0012z, 0014z, 0018z, 0020z, 0024z, 0026z, 0030z, 0033z, 0036z, 0039z, 0042z, 0045z, 0048z, 0051z, 0054z, 0057z, 0061z, 0063z, 0067z, 0069z, 0073z, 0075z, 0079z, 0081z, 0085z.

29 C at 00p, 002z+p, 006z+p, 008z+p, 0012z+p, 0014z+p, 0018z+p, 0020z+p, 0024z+p, 0026z+p, 0030z+p, 0033z+p, 0036z+p, 0039z+p, 0042z+p, 0045z+p, 0048z+p, 0051z+p, 0054z+p, 0057z+p, 0061z+p, 0063z+p, 0067z+p, 0069z+p, 0073z+p, 0075z+p, 0079z+p, 0081z+p, 0085z+p.

29 Si and 29C at  $\frac{1}{3}$ ,  $\frac{2}{3}$ ,  $\frac{2}{3}$ +the above coordinates.

29 Si and 29C at  $\frac{2}{3}$ ,  $\frac{1}{3}$ ,  $\frac{1}{3}$ +the above coordinates.

$$z = 1/87; p = 1/116$$

The rhombohedral types of SiC, 15R, 33R, 51R, (69R, not yet discovered) and 87R belong to a definite series, in which the higher members become increasingly like the simple 6H type, both morphologically and with respect to x-ray data. This is because incorporated in the structures are increasing numbers of layers identical to 6H. Type 21R belongs to a different series, which likewise converges toward 6H as the limiting case. It is so far the only member of this series to be found. There seem to be no reason why others may not be found in either of the known series, or in yet other series.

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