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Disagreement between Crystal Symmetry and X-ray Diffraction Data as shown by a New Type of Silicon Carbide, 10*H**

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The symmetry and characteristic extinctions observed on Weissenberg photographs of SiC, type 10*H*, indicate the space group $C6_3mc$, as with the other hexagonal types, 4*H* and 6*H*. However, no structure can be found in this space group which is in agreement with the observed intensities. Direct evidence of a 6_3 axis or a *c* glide is lacking, for the characteristic absences due to these symmetry elements are included in a larger group of absences inherent in the SiC structure. The calculated intensities for a structure based on the zigzag sequence 3223 are in excellent agreement with the observed intensities, but this arrangement falls in space group $C3m$. Before this structure can be accepted as correct, it is necessary to explain how the observed sixfold symmetry can result from an atomic arrangement with threefold symmetry.

In all known types of α-SiC the C atoms have an arrangement identical to that of the Si atoms, but displaced parallel to the *c* axis. It is shown that for any structure in which the zigzag sequence is symmetrical, such as 3223, the observed diffraction effects will show an apparent horizontal symmetry plane. A threefold axis, plus this horizontal plane, plus the center of symmetry always added by X-rays methods, results in an apparent sixfold axis of symmetry. Thus the seeming disagreement between the diffraction data and the crystal symmetry can be completely reconciled.

It is generally regarded as axiomatic that, except for the addition of a center of symmetry, if none be present, the X-ray diffraction data are in complete accord with the actual symmetry of the crystal. A situation in which this is not the case has been encountered in the determination of the structure of a new type of silicon carbide.

This new type is hexagonal, and since the unit cell is 10 layers high, it is designated as type 10*H* (Ramsdell, 1947). The crystal is an irregular fragment broken from a larger piece. The basal face (0001) is the largest face present. Pyramid faces are present on one side of the crystal, in three adjacent prism zones. Measurement on the two-circle goniometer of the angles between the base and the various pyramid faces indicated that the crystal did not conform to any of the known types, and Weissenberg photographs established it as being 10*H*. The crystallographic data obtained from the specimen are shown in Table 1.

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No etch tests have been made to establish whether the (0001) face is upper or lower (Thibault, 1944). The forms (10$\bar{1}$1), (10$\bar{1}$2) and (10$\bar{1}$3) were observed on both upper and lower halves, (10$\bar{1}$5) only on the side with the base, and (10$\bar{1}$4) only opposite the basal face. Owing to the incomplete development, no significance can be attached to these observations.

X-ray data

Excellent Weissenberg photographs were obtained with Cu $K\alpha$ radiation, with rotation about an *a* axis (Fig. 1). Complete series of 10.*l* reflections were recorded from 10.0 to 10.31; 20.*l* reflections from 20.0 to 20.26; and the three basal reflections 00.10, 00.20 and 00.30. Owing to the irregular shape of the specimen, there was variation in the size and shape of the reflected spots, and also some minor variation in the observed intensities of corresponding reflections, both on the same film and on different films with rotation about different *a* axes. The values used for the observed intensities in the structure determination were averaged from several films.

Table 1. *Crystallographic data*

Form	No. times observed	Quality	Observed	Calculated†
0001	1	A	0° 00′	0° 00′
10$\bar{1}$0	1	C	90° 03′	90° 00′
10$\bar{1}$1	2	E	83° 53′–84° 05′	83° 57′
10$\bar{1}$2	3	BC	78° 03′–78° 07′	78° 02½′
10$\bar{1}$3	4	BC	72° 17′–72° 24′	72° 22½′
10$\bar{1}$4	2	BD	67° 00′–67° 17′	67° 02½′
10$\bar{1}$5	2	D	62° 06′–62° 07′	62° 06′

† Calculated from the theoretical axial ratio for a 10-layer cell.

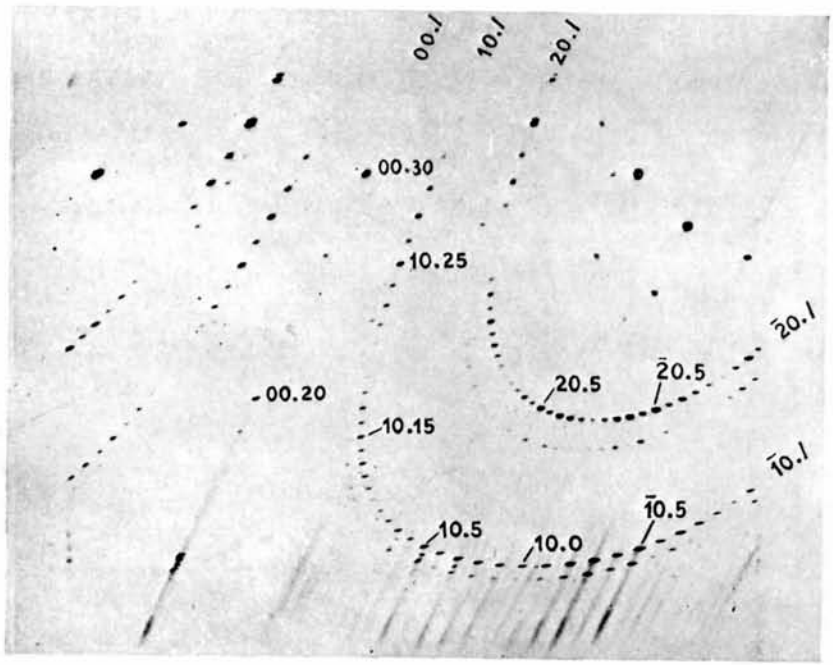

Fig. 1. Weissenberg photographs of SiC, type 10*H*. Zero level; rotation about an *a* axis.

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Until the discovery of type $10H$, the only hexagonal forms of SiC known were the $4H$ and $6H$. Hexagonal types $8H$ and $16H$ had been predicted (Ramsdell, 1947) as possible members of series indicated by known types, but nothing had suggested that a $10H$ might be encountered. A large number of structures are geometrically possible for a 10-layer unit cell. To avoid a solution based merely on trial and error, some systematic approach had to be developed. For a starting point it was assumed that the basic tetrahedral arrangement of carbon atoms about the silicon atoms (and vice versa) must be present. This tetrahedral arrangement of the atoms restricts possible structures to those in which any layer parallel to the basal plane of the unit cell contains only one silicon (or carbon) atom lying on one of the three vertical symmetry axes, and in which two silicon (or carbon) atoms in adjacent layers do not overlie each other. Also, the excellent Weissenberg photographs obtained from the crystal indicated sixfold symmetry about the c axis. A preliminary examination revealed that the above restrictions limited the structural possibilities to three, namely those having zigzag sequences (Ramsdell, 1947) of 55, 212212, and 131131. Each of these structures satisfies the sixfold symmetry requirement, and each has vertical symmetry planes characteristic of the space group $C6_3mc$. Since the two known hexagonal types, $4H$ and $6H$, also crystallize in the space group $C6_3mc$, it was felt certain that one of these three structures would prove to be correct. Moreover, since $4H$ and $6H$ have the sequences 22 and 33, respectively, it was concluded that the sequence 55 was the most probable for $10H$. However, neither the 55 nor the 212212 and 131131 arrangements gave calculated intensities which correlated at all with the observed intensities on the Weissenberg photographs of $10H$.

It has been observed that in all known structures of SiC the zigzag sequences never involve the number 1, or any number greater than 4*. It is not known whether this represents an actual limitation, or is merely an accidental feature. At any rate, all three of the above sequences violated this supposed limitation. Additional sequences can be found, both with and without this limitation, but none of these possesses a sixfold axis of symmetry—all are threefold. Likewise, none has the c glide in the plane of the a and c axes.

The X-ray evidence concerning the c-glide plane is unsatisfactory. This glide requires the absence of all $11.l$ reflections when l is odd. But the specific structure of SiC, in which all atoms lie on the three vertical symmetry axes, requires the absence of all $11.l$ reflections except those for which l is a multiple of the number of layers in the unit cell. Thus for $4H$, only 11.0, 11.4, 11.8, etc., are possible; and for $6H$, only 11.0, 11.6, 11.12, etc. Therefore the absences due to the structure are more extensive than, and include, those due to the glide plane. For $10H$, the only $11.l$ reflections on the films are 11.0, 11.10 and 11.20. These may be attributable to the structure alone and may not necessarily indicate a c-glide plane.

Likewise, the X-ray evidence concerning the presence of the vertical screw axis 6_3 is inconclusive. The structural arrangement limits the possible $00.l$ reflections to those with a value of $l=10n$, i.e. 00.10, 00.20 and 00.30. The screw-axis extinctions comprise those reflections with $l=2n+1$, which are already covered by the structural limitations. The sixfold axis of symmetry apparently revealed by the Weissenberg photographs of $10H$ thus becomes a factor of prime importance. Is the symmetry of $10H$ actually that of the space group $C6_3mc$, or is it possible that a $C3m$ structure could simulate the higher symmetry?

The SiC structures are all polar in character, with no horizontal plane of symmetry, and no center of symmetry. A vertical threefold axis requires that the reflections $10\bar{1}l$, $\bar{1}10l$ and $0\bar{1}1l$ be equivalent. The apparent center of symmetry, which is always added in X-ray reflections, requires that $\bar{1}01\bar{l}$, $1\bar{1}0\bar{l}$ and $01\bar{1}\bar{l}$, also be equivalent to the above three reflections. A vertical sixfold axis, plus the added center of symmetry, requires the equivalence of $10\bar{1}l$, $01\bar{1}l$, $\bar{1}10l$, $\bar{1}01l$, $0\bar{1}1l$ and $1\bar{1}0l$, and the six corresponding reflections with $\bar{l}$. The latter equivalence is the one observed on the Weissenberg films of $10H$. However, this same equivalence could be brought about by a threefold axis and a center, plus a horizontal plane of symmetry.

The additional possible sequences for $10H$ which have a threefold axis are of two kinds—those in which the sequence is symmetrical, namely 3223, 4114, 311113, 221122 and 21111112, and those in which the sequence is unsymmetrical, such as 7111 or 6121. In the first group, the arrangement of the silicon or carbon atoms, considered separately, is symmetrical with respect to the (0001) plane. When this occurs, the calculated intensities for $h0.l$ and $h0.\bar{l}$ are identical, even though no horizontal plane is actually present. Accordingly, such an apparent horizontal plane, plus the threefold axis, plus the center of symmetry, can give X-ray reflections corresponding exactly with those from the higher symmetry $C6_3mc$. This is not a general situation, but rather a specific one, brought about by the particular arrangements existing in the SiC structures. As far as the authors are aware, this is an unique situation, and it will be discussed later. At present we are concerned only with the result, which is that all those threefold sequences which are symmetrical represent possible structures for $10H$. These five sequences have been tested, and for only one of them, namely 3223, are the calculated intensities in harmony with the observed intensities. This falls within the apparent limitation of sequences to the values, 2, 3 and 4, the five discarded sequences all containing the value 1.

Fig. 2 shows the agreement between the intensities observed on the Weissenberg films and those calculated

* The values 2 and 3 only are found in six of the known types of SiC. Type $21R$ has the values 3 and 4.

for the 3223 sequence. It is so satisfactory that the 3223 structure must be regarded as the correct one for 10*H*.

Several unsymmetrical sequences were tested by calculating the intensities for selected pairs of $10.l$ and $10.\bar{l}$ reflections. No agreement at all was found in any case, and the unsymmetrical structures were accordingly eliminated.

A situation in which an atomic arrangement based on the space group *C*3*m* can give X-ray reflections apparently indicative of space group $C6_3mc$ is rather astonishing. The fact that such a situation actually

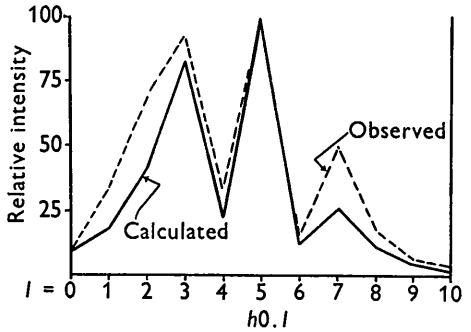

Fig. 2. Observed intensities for SiC, type 10*H*, compared with intensities calculated for structure based on the zigzag sequence 3223.

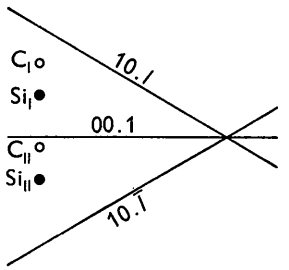

Fig. 3. Pair of symmetrical Si atoms, with displaced C atoms.

exists for the chosen structure of SiC, type 10*H*, depends upon the particular distribution of the Si and the C atoms required by the tetrahedral arrangement. The distribution of the Si and the C atoms is identical, except for a shift in the direction of the *c* axis. Every Si atom has a C atom directly above it, at a fixed distance.

The contribution of a particular atom to a given reflection can be expressed as a vector of length f_0 (scattering power) whose direction is defined by the angle $2\pi(hx+ky+lz)$. For any symmetrical sequence in SiC, the Si atoms will form pairs which are symmetrical to (0001). As seen from Fig. 3, such pairs must of necessity make identical contributions to $10.l$ and $10.\bar{l}$ reflections, since these pairs of planes are also symmetrical to (0001). The relationship of Si_I to $10.l$ and $10.\bar{l}$ corresponds exactly to that of Si_{II} to $10.\bar{l}$ and $10.l$, respectively. Thus the contributions of each pair to the $10.l$ and $10.\bar{l}$ reflections could be expressed by equal vectors at identical angles.

With respect to the Si atoms, each C atom is displaced through the same distance parallel to the *c* axis. For both C_I and C_{II} (Fig. 3) this displacement is as far *towards* the $10.l$ plane as it is *away* from the $10.\bar{l}$ plane. Thus the contributions of the pair of C atoms to the $10.l$ and $10.\bar{l}$ reflections are expressed by equal vectors, but with one rotated clockwise with respect to the Si vector and the other counterclockwise through an equal angle. The resultant of the Si_I and C_I vectors is hence equal to that of the Si_{II} and C_{II}, and differs only in direction. In the intensity formula these resultants would thus have different A and B terms, but would have equal values for A^2+B^2. This would hold for each symmetrical pair of Si atoms with the accompanying C atoms, and accordingly the $10.l$ and $10.\bar{l}$ reflections are of equal intensity.

This situation is not one involving pseudo-symmetry. Type 10*H* is in no sense pseudo-hexagonal—it is unequivocally *C*3*m*. If the ideal tetrahedral arrangement of carbon atoms around the silicon atoms actually exists, then the X-ray reflections from $10.l$ and $10.\bar{l}$ should be identical, and the films could not record anything other than hexagonal symmetry. It is probable, however, that there must be some deviation from the ideal tetrahedral arrangement. If so, it is so slight that it is undetectable by the X-ray methods used.

Summary

Types 4*H* and 6*H* of silicon carbide crystallize in the space group $C6_3mc$, but, because of the added center of symmetry, the films show the symmetry $6_3/mmc$. Type 10*H* belongs to space group *C*3*m*. The particular arrangement of the silicon and carbon atoms is such as to give equality to the $h0.l$ and the $h0.\bar{l}$ reflections, so the apparent symmetry is $3/mm$. The addition of a center of symmetry raises this to $6/mmm$, which is the symmetry revealed by the films.

Since the specific absences characteristic of the 6_3 screw axis and the *c* glide plane happen to be included in a larger group of absences attributable to the layered structural arrangement, no symmetry differences are revealed between the films of types 4*H* and 6*H* ($C6_3/mmc$) and of type 10*H* (apparently $C6/mmm$).

Structure of SiC, type 10*H*:

Hexagonal, *C*3*m*. Unit cell dimensions*:

$$a_0=3{\cdot}073, \quad c_0=25{\cdot}13_3\,\text{kX.}; \quad c/a=8{\cdot}178.$$

Atomic positions (corresponding to zigzag sequence 3223):

10 Si at $0,0,0$; $0,0,\frac{3}{10}$; $0,0,\frac{7}{10}$; $\frac{2}{3},\frac{1}{3},\frac{1}{10}$; $\frac{2}{3},\frac{1}{3},\frac{5}{10}$; $\frac{2}{3},\frac{1}{3},\frac{9}{10}$; $\frac{1}{3},\frac{2}{3},\frac{2}{10}$; $\frac{1}{3},\frac{2}{3},\frac{4}{10}$; $\frac{1}{3},\frac{2}{3},\frac{6}{10}$; $\frac{1}{3},\frac{2}{3},\frac{8}{10}$.

10 C at $0,0,\frac{3}{40}$; $0,0,\frac{15}{40}$; $0,0,\frac{31}{40}$; $\frac{2}{3},\frac{1}{3},\frac{7}{40}$; $\frac{2}{3},\frac{1}{3},\frac{23}{40}$; $\frac{2}{3},\frac{1}{3},\frac{39}{40}$; $\frac{1}{3},\frac{2}{3},\frac{11}{40}$; $\frac{1}{3},\frac{2}{3},\frac{19}{40}$; $\frac{1}{3},\frac{2}{3},\frac{27}{40}$; $\frac{1}{3},\frac{2}{3},\frac{35}{40}$.

References

RAMSDELL, L. S. (1947). *Amer. Min.* **32**, 64.

THIBAULT, N. W. (1944). *Amer. Min.* **29**, 274.

* These dimensions are given in kX. units to agree with the previously published values for the various SiC types. Previous results have been labelled as Ångström units, but actually were kX. units.