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Electron Microscopy Studies of Long-Period Polytypes of SiC

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The structures of four long-period polytypes of SiC found in a sample of reaction-sintered material have been analyzed using transmission electron microscopy. Those structures which have been positively identified are $303R$ or $[(33)_{16}(32)]_3$, $180R$ or $[(23)_{11}(32)]_3$ and $222R$ or $[(33)_6(34)\ (33)_4(34)]_3$. The fourth structure is tentatively identified as $150R$ or $[(34)_5(23)_3]_3$. The lack of conclusive identification for this structure is due to structural irregularities throughout the very small size of this grain. The frequency of observing long-period structures in reaction-sintered SiC is quite high, especially when the grain size is small.

Introduction

In the course of an investigation of the sintering properties of SiC by transmission electron microscopy, we have found an indirect indication that the existence of long-period polytypes might be created by a solid-state transformation at high temperatures in the presence of external strain (Sato, Shinozaki & Yessik, 1974). It was found that the frequency of occurence of such long-period structures is far higher in fine grain ($<10\mu$m) reaction-sintered SiC than in larger grain material, possibly due to strains introduced in the pulverization process. After the finely powdered grains are exposed to temperatures of about 1500°C during the reaction-sintering process, many highly ordered long-period structures are observed, while the size and shape of the grains remains unaltered. Since it is extremely important to confirm whether a solid-state transformation can be considered as an origin of long-period polytypes or not, we have begun a program to investigate in detail the distribution and structures of the polytypes in these materials.

Since we have to deal with the analyses of many structures based on small particles ($<10\mu$m) in reaction-sintered materials, electron microscopy is the only practical approach. In a previous paper (Sato, Shinozaki & Yessik, 1974), we reported the advantages of electron microscopy in identifying long-period polytypes and reported briefly on the determination of the structures $303R$ and $222R$ [notation due to Ramsdell (1947)]. However, no detail was given of the structural analyses. Therefore, in this paper we shall describe the details of the analyses of four long-period structures, including the two mentioned above, illustrating both the advantages and disadvantages of this method. These four polytypes were found within one small region of a single sample prepared from the reaction-sintered SiC known as REFEL (Forrest, Kennedy & Shennan, 1972).

Experimental results

The samples were prepared by first diamond grinding to $\sim 75\ \mu$m thickness. Then 3 mm diameter discs suitable for mounting in the electron microscope were machined ultrasonically and these discs were reduced to the final thickness by ion-beam milling. The result is a small hole in the center of the discs surrounded by a small wedge-shaped region thin enough for transmission electron microscopy. The inhomogeneity and the small grain size of the sample result in large fluctuations in thickness throughout the observable area.

A Philips 200 electron microscope with 100 kV acceleration and with a wide-angle goniometer stage was used. In this case about 20–30 individual grains could be seen in one sample, although because of the variations in thickness the quality of the micrographs and diffraction patterns varied greatly. In order to increase the penetration depth and allow a wider area to be observed, a Hitachi 650 kV microscope at Case-Western Reserve University was also used. However, because of the small grain size of the specimen, complicated multiple diffraction effects were observed resulting from penetration through more than one grain. Thus the additional penetration of the beam did not result in a significantly greater area of observation.

Every polytype of SiC is simply a stacking variant of the close-packed structure and thus it is only necessary to consider the $10.l$ row of reflections in order to determine the structure uniquely.† Since the entire cross section of the reciprocal lattice perpendicular to the beam can be seen at once in electron diffraction, the sample is adjusted until the [01.0] direction of the crystallite being observed is along the beam. In this orientation all of the $h0.l$ reflections can be observed. It is not possible, of course, to obtain the desired orientation for all grains.

The diffraction patterns for the four polytypes being considered here are shown in Fig. 1. The inset for each

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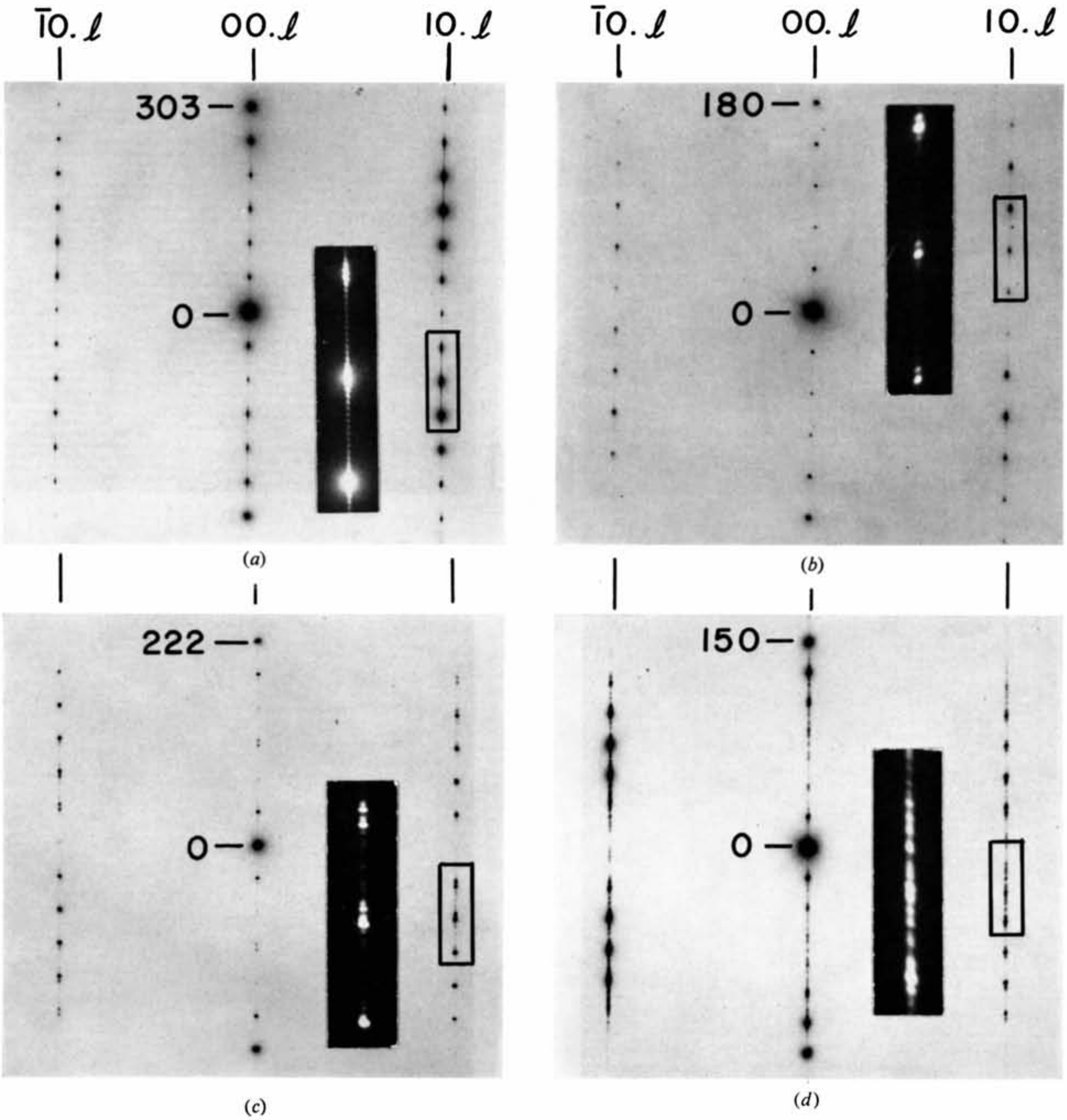
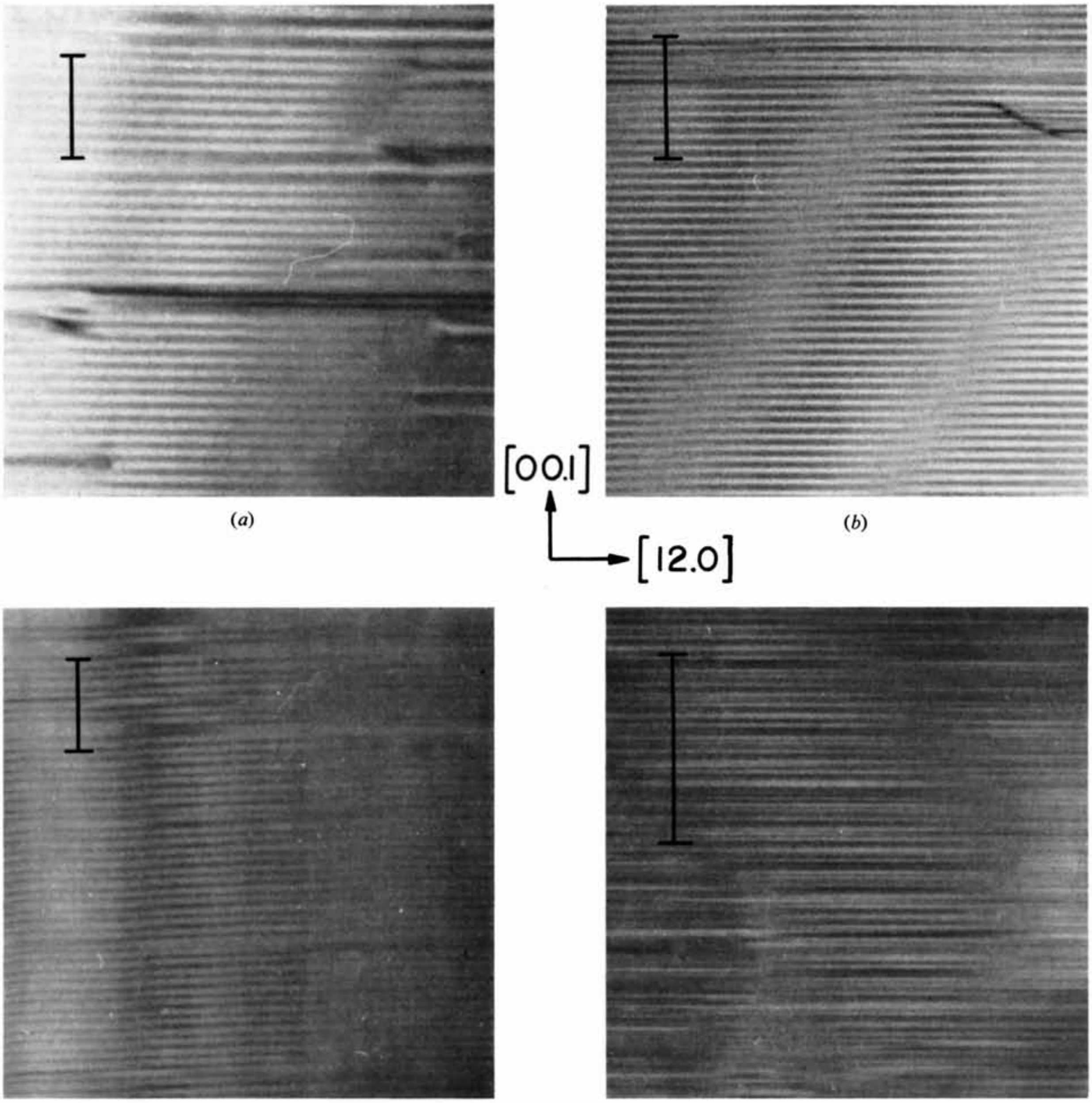
† In accordance with standard practice in discussions of SiC, all structures will be described based on a hexagonal unit cell and using hexagonal indices.



(a) (b) (c) (d)

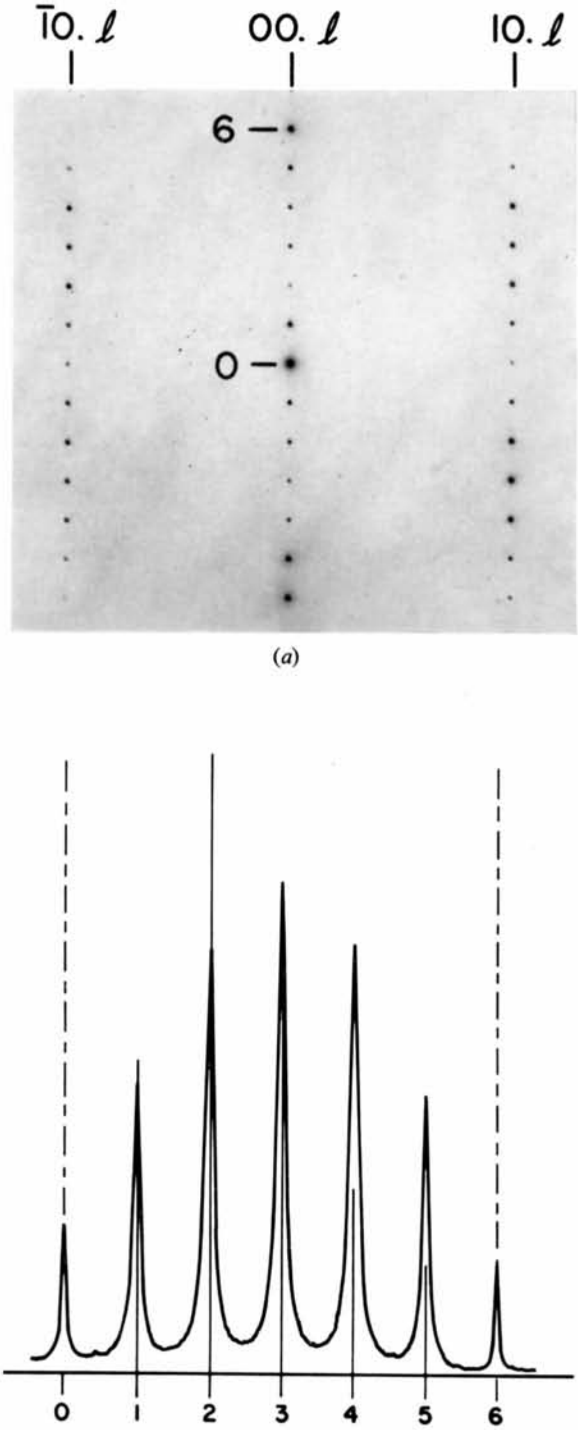
Fig. 1. Electron diffraction patterns of the (01.0) reciprocal-lattice plane showing the $h0.l$ rows of reflections. The insets show a region of the 10.l row expanded three times. (*a*) 303*R*, (*b*) 180*R*, (*c*) 222*R* and (*d*) 150*R*. All were taken with the 100 kV microscope.



(a) (b)

(c) (d)

Fig. 2. Bright-field micrographs for the same sample orientation as Fig. 1 showing direct resolution of the structural lattice periods. (*a*) 303*R*, (*b*) 180*R*, (*c*) 222*R*, and (*d*) 150*R*. (*a*) and (*d*) were taken at 100 kV; (*b*) and (*c*) at 650 kV. The bar in each micrograph is 2000 Å.



(a)

(b)

Fig. 3. The polytype 6*H*. (*a*) Electron diffraction pattern of the (01.0) reciprocal-lattice plane. (*b*) Intensity distribution along the 10.*l* row. The vertical lines indicate the calculated intensities.

pattern is a blow-up of a section of the 10.l row showing the closely spaced spots indicative of the very long periods of these structures. The bright-field micrographs corresponding to these diffraction patterns are shown in Fig. 2. The stripes whose spacing corresponds to the structural lattice period can be clearly seen in each case. The agreement between the lattice period measured from these stripes and that determined from analysis of the diffraction patterns is within the instrumental accuracy.

Structure determination

In the commonly used notation of Ramsdell (1947), the structures are designated as nH or nR, where n is the number of close-packed layers* in a hexagonal unit cell and H or R is used to designate whether or not the diffraction spots are spaced symmetrically with respect to the (00.1) plane. Thus the Ramsdell symbol can be given to a structure simply by counting the number of diffraction spots along the 10.l row and observing their symmetry with respect to the h0.0 row. In practice, this can be done quite readily for the shorter-period polytypes. However, for the long-period structures, when the number of spots is large, the spacing small, and the intensities low, this method is not always reliable. The exact number of spots and their symmetry can be stated reliably only when the corresponding calculations of the expected intensity distribution have been made. In addition, the Ramsdell notation does not describe a unique structure, and in general, there are a large number of possible structures corresponding to the same Ramsdell symbol. The Zhdanov notation is used to specify the exact stacking sequence of the structure (Zhdanov, 1945).

In order to determine the structures, intensities must be calculated for various trial structures and compared with the observed intensities. This only has to be done along the interval 10.0 to 10.n. The calculation of the structure factors has been described in detail by Verma & Krishna (1966). The intensities are read from photographic plates by means of a recording microdensitometer. However the dynamical effects inherent in electron diffraction make the exact interpretation of these intensities difficult. As an example, Fig. 3 shows the observed intensities for a 6H grain along with the calculated values for the 10.l row. It can be seen that there are peaks at the 10.0 and 10.6 positions although the structure factors are zero. In addition, there is a spot at each reciprocal-lattice point along the 00.l row although there are structural extinctions for all points except $l=0,6,12,\cdots$. Since the spacing between successive layers in the 6H structure is not exactly the same, these structure factors are not exactly zero (Gomes de Mesquita, 1967). However, estimates by Van Landuyt & Amelinckx (1971) show that the intensities of the extra 00.l spots, as seen in X-ray diffraction, are of the order of 10^{-3} of the intensity of the 00.6 spot. Thus the extra spots which appear in electron diffraction, as seen along the 00.l row in Figs. 1 and 3, must be due mostly to dynamical scattering. Although considerable faulting occurs in the stacking as evidenced by Fig. 2, this is not necessarily an indication of lattice strain in polytypical substances like SiC (Sato & Shinozaki, 1975) and so it is reasonable to assume strong dynamical effects. In general, there is some additional intensity of varying amounts at each reciprocal-lattice point due to dynamical scattering, which makes the difference in intensity between strong and weak spots far less than expected from the difference in structure factors. This makes the observation easier in the sense that both strong and weak spots can be observed clearly in the electron diffraction pattern.

As can be seen in Fig. 3, there is fair agreement between the observed and calculated intensities. Since the intensity distribution is very sensitive to the difference in stacking order among variants of the same Ramsdell designation, this type of qualitative agreement has proved to be sufficient to be able to distinguish among the various trial structures in the cases presented here. The qualitative agreement between calculated and observed electron diffraction intensities has previously been shown to enable stacking orders to be determined in the case of the long-period structures in metal alloys by Sato & Toth (1968).

In Fig. 1, we can see that the strong peaks in the diffraction patterns closely resemble the diffraction patterns of the simpler basic polytypes 6H, 15R, and 21R. This indicates that the long-period structures can be derived from these simpler structures by small periodic modifications. Thus the number of possible trial structures can be reduced to a manageable level.

Polytype 303R

A densitometer trace from 10.0 to 10.n of the diffraction pattern of Fig. 1(a) is shown in Fig. 4(a). This pattern closely resembles the intensity distribution for 6H as shown in Fig. 3. The stacking order of the 6H polytype of SiC is represented by the interval sequence (33). Therefore this structure must contain a large number of (33) units in the interval sequence. The main difference, aside from the large number of very small peaks, is the splitting of the major peaks near some of the 6H positions. In particular, the first major peak is nearly equally split, while the fourth peak appears entirely unsplit. By counting, the total number of peaks is found to be 101 although, as mentioned earlier, this is difficult to determine exactly. The lattice image for this structure in Fig. 2(a) shows a spacing of 255Å which can be determined to 1–2% accuracy. Since the spacing between adjacent Si (or C) layers is 2·52Å, this corresponds to 101 ± 2 layers in the primitive unit cell. The asymmetry in the positions of the spots with respect to the $l=0$ position indicates that the structure

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* It should be noted that the term 'layer' being used for SiC actually refers to a double layer of atoms, one of Si and one of C.

is rhombohedral and thus the Ramsdell notation for this structure is 303*R*.

The splittings of some of the major peaks allow us to draw some conclusions concerning the positions of these peaks relative to the 6*H* positions. It was first pointed out by Mitchell (1954) that for long-period polytypes based on 6*H*, the intensity of a spot is proportional to the distance away from the 6*H* positions. Thus if a 6*H* position falls midway between two reciprocal-lattice points, the intensities of the two peaks will be approximately equal. In Fig. 4(*a*) we see that the first major peak is nearly equally split and we can assume that the corresponding 6*H* position is halfway between. The peaks become more and more unevenly split, indicating uneven separation from the 6*H* positions, until at the fourth major peak there is complete coincidence. In fact, for each sixth of the RULS,* the corresponding 6*H* position shifts by one-sixth of the unit spacing for the observed peaks. This unit spacing is, of course, 1/101 of the RULS. The shift over the entire RULS is one unit spacing and thus the total number of peaks must differ by one from a multiple of six. This confirms our count of 101[=(6×17)−1] diffraction spots. The simplest structure based on 6*H* and having 101 peaks is given by the Zhdanov symbol $[(33)_{16}(32)]_3$. The subscript 3 indicates that the basic stacking sequence is repeated three times in a hexagonal unit cell and therefore this is *R* stacking. Intensities calculated for this structure are shown by the solid lines

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* The reciprocal unit layer spacing (RULS) is the reciprocal of the distance between two adjacent close-packed layers.

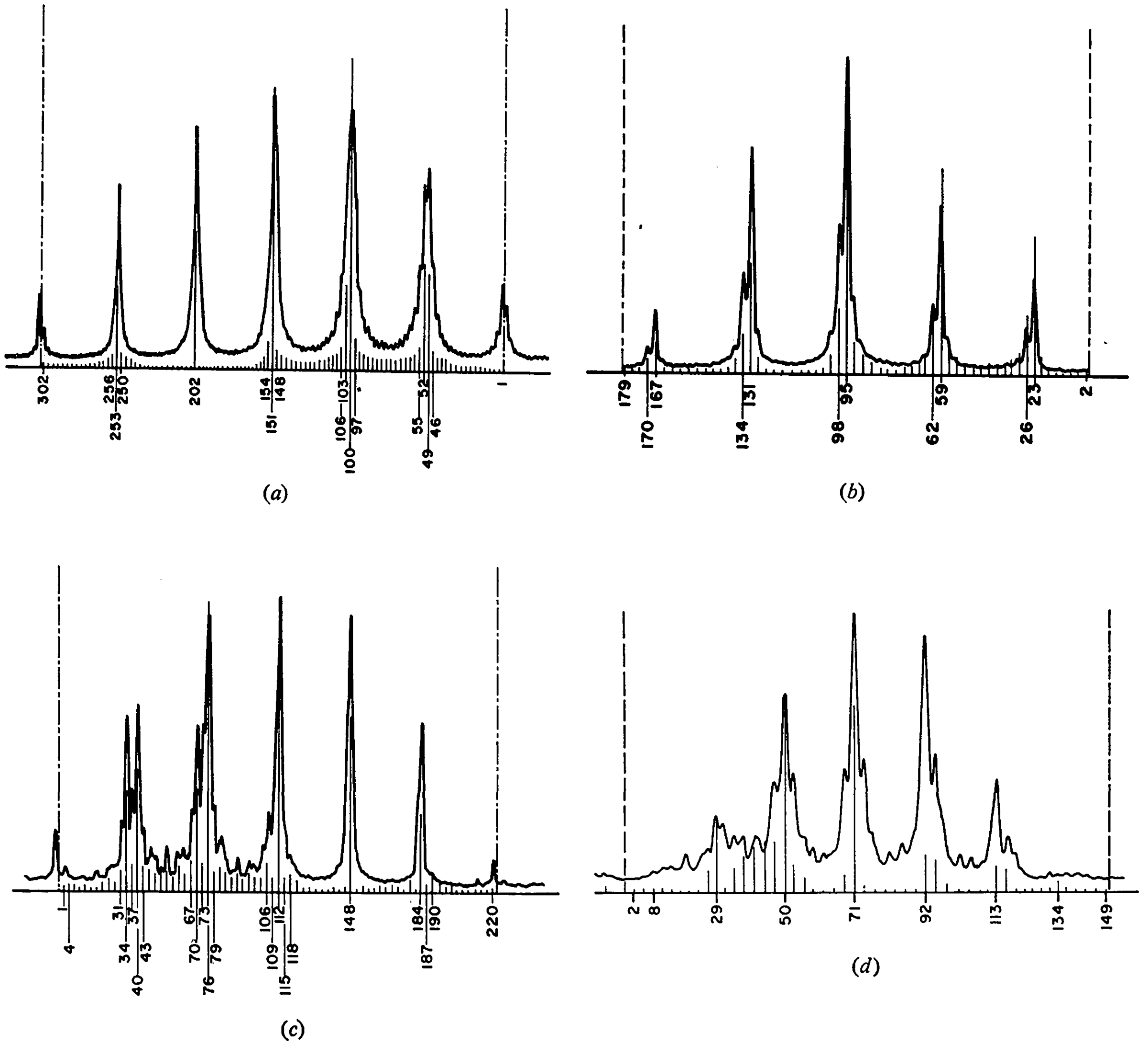

Fig. 4. Intensity distribution along the 10.*l* rows. (*a*) 303*R*, (*b*) 180*R*, and (*c*) 222*R* and (*d*) 150*R*. The vertical lines indicate the calculated values.

in Fig. 4(*a*) and it can be seen that there is reasonable agreement with the observed values. A large number of more complicated structures based on 6*H*, both with 101 peaks as well as with a slightly different number of peaks, have been calculated, but none of these have been found to have an intensity pattern similar to the observed peaks. This structure is a member of a series of structures first proposed by Ramsdell (1947) whose form is $(33)_m(32)$. So far members of this series have been reported with $m=1$, 2, 3, 4, 5, 7, and 21 and now 16 (Shaffer, 1969). It can be noted that, as first pointed out by Mitchell (1947), where the 303*R* peaks are furthest away from the 6*H* positions the intensities in the subsidiary peaks are the greatest while in the regions where the 303*R* peak coincides with the 6*H* position, the subsidiary intensities are very low. This can be clearly seen both in Fig. 1(*a*) and Fig. 4(*a*).

Polytype 180*R*

In the diffraction pattern of Fig. 1(*b*) and in its densitometer trace shown in Fig. 4(*b*) can be seen a long-period structure with five major peaks from 10.0 to 10.*n* which are very close to the positions of peaks in the 15*R* structure. We thus assume that this structure is based on 15*R* and consists primarily of (23) units in its interval sequence. Each of the major peaks is split into two peaks of unequal intensity whose relative values remain about the same for each pair. Also the spacing between the major peaks remains the same over the whole range. This indicates that there is only one periodicity involved in this structure and it is based on groups of five layers. The total number of peaks is approximately 60 which is a multiple of five as expected. The bright-field micrograph of this structure shown in Fig. 2(*b*) has a spacing of 150Å which is equivalent to 60 layers in the primitive unit cell. The spacing of the peaks relative to the $l=0$ position indicates that the structure is rhombohedral and the Ramsdell symbol is thus 180*R*. The simplest structure consisting of two different groups both of five layers is the general type given by the Zhdanov symbol $(23)_m(32)_n$, where in this case $m+n=12$. The only structure of this type which fits the observed intensity distribution is for $m=11$, that is, the structure $[(23)_{11}32]_3$. The comparison between measured and calculated values is shown in Fig. 4(*b*). There are two other structures known of this type, namely, 10*H* which is (2332) and 75*R* which is $[(23)_3(32)_2]_3$.

Polytype 222*R*

A densitometer trace along the 10.*l* row from 10.0 to 10.*n* is shown in Fig. 4(*c*) of the diffraction pattern of Fig. 1(*c*). It can be seen that the intensity distribution closely resembles that of the 6*H* structure as shown in Fig. 3, indicating that this structure is primarily made up of (33) units in its interval sequence. Some of the major peaks are split while some are not indicating that the structure consists of sub-units of differing periodicities. A closer examination, however, shows a very unusual pattern to the split peaks, namely, that there is a low-intensity peak in between two higher-intensity peaks. In the discussion of the intensity pattern of the 303*R* structure it was noted that the closer the reciprocal-lattice point to a 6*H* position the greater the intensity. Two equal intensity peaks in that case were equidistant from the corresponding 6*H* position. However, that principle does not suffice to explain the situation here. Near the 10.1 6*H* position there are two peaks of nearly equal intensity and therefore we expect the 6*H* position to be halfway between them. However, there is a reciprocal-lattice point of the long-period structure halfway between these two peaks and so we would expect the central peak to be of greatest intensity, whereas its actual intensity is quite small. This situation can be explained by the presence of two separate groups of (33) units out of phase with each other, *i.e.* separated by a group of different periodicity. The two groups of (33) units are in phase at the 10.4 6*H* position and out of phase at the 10.1 6*H* position. Thus there is a shift of one peak in half of the RULS relative to the 6*H* positions and the total number of spots in the RULS should differ by two from a multiple of six. By counting, the total number of spots is seen to be 74 which agrees with this expectation. The bright-field micrograph of this grain, shown in Fig. 2(*c*), has a series of stripes with a spacing of 185Å, which is equivalent to 74 layers in the primitive unit cell. The symmetry of the diffraction spots indicates rhombohedral symmetry and so this structure has the Ramsdell designation 222*R*.

The simplest structure based on two separate groups of (33) units is of the form $(33)_m(34)\ (33)_n\ (34)$ where $m+n=10$. Intensities calculated for all values of *m* and *n* show that a good fit is obtained for $m=6$, or in other words, for the structure with the Zhdanov designation of $[(33)_6\ (34)\ (33)_4\ (34)]_3$. The results of this calculation are shown as the solid lines in Fig. 4(*c*). None of the other structures of the above series, nor any of a number of other series also tried, had an intensity distribution which resembled the observed values. This is the first structure of this type that has been reported, although it is interesting to note that the very similar structure $[(33)_5\ (34)]_3$ has been observed by Krishna & Verma (1962). The latter structure is 111*R* and is essentially equivalent to the 222*R* structure with every other peak removed.

Polytype 150*R*

Fig. 1(*d*) shows the diffraction pattern for a long-period structure from which it can be seen that there are seven major groups of intensities. This structure should therefore be based on the 21*R* structure and contain primarily (34) units in its interval sequence. The total number of peaks is approximately 50 and the symmetry of the peaks indicates that the structure is rhombohedral, so the Ramsdell designation is tentatively given as 150*R*.

However, no long-period structure based on $21R$ could be found which gave as good a fit to the observed data as in the three previous cases. The best fit which could be found of a large number of trial structures is given by the stacking sequence $[(34)_5(23)_3]_3$ and the calculated values are shown in Fig. 4(*d*).

An examination of the corresponding bright-field micrograph shown in Fig. 2(*d*) reveals a highly irregular series of stripes with shifts in positions. The size of this particular grain is quite small, less than 2μm diameter, and no region could be found with sufficient uniformity for a regular lattice image to be obtained. It appears that this particular grain contains a higher proportion of stacking disorder or other structural irregularities than the other grains, which may be related to the small size of the grain and the particular stress field existing during the processing. Although the total amount of disorder is not large, as evidenced by the fairly sharp diffraction spots, it is sufficient to complicate the analysis, and therefore, the stacking sequence given above must be considered as tentative.*

Conclusions

The usefulness of transmission electron microscopy in determining the stacking arrangement in SiC structures has been demonstrated by the analysis of four structures of very long periods. Although dynamical effects make precise comparison of calculated and observed intensities very difficult, the sensitivity of the intensity distribution to minor changes in stacking order enables us to distinguish the correct structure from a number of trial structures in most cases. In addition, the ability to observe the lattice image gives additional confirmation to the existence of the long-period structures deduced from the diffraction patterns.

The examination of materials with grain size of the order of 10μm allows many different crystals to be observed in a short time. The smallness of the grain size, however, also creates certain difficulties. One of these is the presence of complicated multiple-diffraction effects which are more pronounced when a high-voltage electron microscope is used because its beam can penetrate farther and go through many grains. It has also been observed that very small grains may contain a higher proportion of stacking disorder, which complicates the analysis. Another problem in the identification of the observed long-period structures has been the difficulty in obtaining homogeneously thinned samples. However, improved thinning techniques have recently allowed the observation of considerably more grains per sample as well as more reliable diffraction patterns. A number of new long-period structures have already been observed and their structures are presently being determined. The results will be reported in the near future.

While small grains may contain a higher proportion of stacking disorder, a considerable degree of faulting is seen in all the samples. This fact has been used as an argument against the screw-dislocation theory of polytype growth (Verma & Krishna, 1967). The nature of these irregularities along with the observed stacking sequences should be indicative of the origin of polytypes. However, the data obtained so far are not sufficient to allow any reliable conclusions to be made, or to confirm the possibility of a solid-state transformation to create long-period structures from the simpler polytypes.

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* The existence of a polytype $150R$ has previously been noted by Kuo (1964), although no attempt was made then to determine the actual stacking sequence.