41 Published Papers

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Ph.D
Spiral Growth on Carborundum Crystal Faces

In 1949 Frank pointed out the possibility that growth of crystals at low supersaturations, essential for good crystals, could take place because of the formation of dislocations in the crystal so that any real crystal should have a number of dislocations with a screw component, terminating on the face. When growth takes place on these exposed molecular terraces, the edges of these layers develop into spirals centred on the dislocation. Griffin has observed these 'monomolecular' layers on the (1010) face of a beryl crystal, and has shown by multiple-beam interferometry that the height of these steps is less than 34 A., that is, less than four unit cells of the crystal. It was inferred that these steps are only one unit cell high.

In the present investigation, numerous 'growth spirals' have been observed on the faces of carborundum and measured with the aid of phase-contrast microscopy and multiple-beam interferometry.

Carborundum occurs in at least eight known types, one of which is cubic, whereas the rest are either hexagonal or rhombohedral and have identical layers but differ in their arrangement and are uniquely distinguished by the number of layers in the unit cell. The crystals studied here are of type I (rhombohedral, fifteen layers, with lattice parameter \( c = 37.7 \) A.), and type II (hexagonal, six layers, \( c = 15.1 \) A.).

These spirals were studied by coating the crystal faces with a thin film of silver of reflectivity nearly 90 per cent, deposited by thermal evaporation, and then examining these faces in reflexion.

Theory shows that for growth taking place from vapour, the ledge extending from the point of emergence of the dislocation to the crystal boundary has a rate of advance independent of the crystallographic orientation, thus forming a simple Archimedean spiral which can be calculated and from which the constant of spacing between turns can be predicted. These predictions have been completely confirmed numerically by the circular spirals shown in Fig. 1.

The dependence of the rate of advance of a growth front on the orientation of the step line should impose a characteristic distortion of the growth of spirals, exhibiting the crystal symmetry. In accordance with this, Fig. 2 shows a hexagonal spiral (crystal type II). The straight edges correspond to a sharp minimum in the growth-rate as a function of orientation.
The complex growth patterns predicted for two or more screw dislocations ending on a crystal face and depending on the property of growth fronts which annihilate each other where the two edges meet are illustrated in Fig. 1. Thus for two screw dislocations of opposite hand, with the unfolding of the two spirals the ledges starting from one terminate on the other, generating closed loops.

Various other growth patterns for two, three and larger numbers of dislocations ending on crystal faces of type I and type II have been photographed and explained.

Interlacing of hexagonal spirals observed on a crystal face of type II is illustrated in Fig. 3.

The observed density of dislocations varies widely on different specimens, ranging from a few to a maximum of $\sim 10^4$ per sq. cm. On any crystal they are predominantly of one hand.

The calculated radius of the critical nucleus is $2 \mu$ and the supersaturation $0.2$ per cent.

To measure the step height of these spirals, multiple-beam interference (Tolansky) has been employed. Fig. 4 shows the Fizeau fringes for $\lambda 5,461$, passing over a circular spiral, in which the height can be accurately measured; and as the number of turns is readily visible, the height of each single step can be deduced with precision. Analogous measurements
have been made also with fringes of equal chromatic order. The step heights on a type II crystal measured from two different spirals are respectively 15.2 Å and 15.1 Å, with a maximum uncertainty of 2 Å. It is already known from X-ray analysis that, for type II, \( c = 15.1 \) Å. Thus it has been proved here that the step is a single unit-cell high.

The observation of spiral markings on carborundum has already been reported\(^6\). The observed shapes of these spirals are in accordance with the predictions of theory, and their step height is equal to that of a unit cell, showing that these are growth spirals originating from screw dislocations.

A more detailed account of this work has been communicated elsewhere. I am grateful to Prof. S. Tolansky for his interest and encouragement in the course of this work, and to the British Council for the award of a scholarship.

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Observations on Carborundum of Growth Spirals Originating from Screw Dislocations.

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[Plates XXV.-XXVIII.]

ABSTRACT.

Numerous growth spirals with shapes ranging from circular to regular hexagonal have been observed on carborundum crystals of types I. and II., by coating the crystal faces with a thin film of silver of reflectivity nearly 90 per cent and then working in reflection, using phase contrast illumination. The shapes of these spirals, in relation to the crystal structure, are shown to be in accordance with the predictions of Frank’s theory. On a type II. crystal, hexagonal interlaced spirals have been observed. The annihilation of growth fronts where they meet, and other properties of growth fronts are illustrated and hence the observed patterns for two or more screw dislocations are explained. The observed density of dislocations ranges from small values up to a maximum of $10^4$ per sq. cm. For a typical circular spiral the calculated values of the radius of the critical nucleus is $2\mu$ and supersaturation is 0.2 per cent. By the application of multiple-beam interference, using both Fizeau fringes and fringes of equal chromatic order, the step heights in spirals have been measured accurately for type II. crystal and found to be 15 A. This is equal to the height of the unit cell, proving that these are growth spirals originating from screw dislocations, in exact accordance with theoretical prediction.

§1. INTRODUCTION.

According to Burton, Cabrera and Frank (1949) growth of crystals at low supersaturations can take place only in the presence of dislocations. A crystal should, therefore, have a number of dislocations with a screw component terminating on the crystal face. Frank (1949) showed that when growth takes place on the molecular terraces so exposed, the edges of monomolecular layers develop as “growth spirals” centred on the dislocation. Experimental evidence supporting this was found on beryl by Griffin (1950). The present paper deals with dislocations and “growth spirals” found on the faces of carborundum crystals.

* Communicated by Professor S. Tolansky.
§ 2. THE CRYSTAL STRUCTURE AND TYPES OF CARBORUNDUM.

Carborundum, a strongly homopolar crystal, occurs in at least eight known types. One of these is cubic, sometimes called \( \beta \)-SiC. All other types (\( \alpha \)-SiC) are based on either hexagonal or rhombohedral unit cells. All types have identical layers, but differ in their arrangements. Each type is distinguished by the number of layers in the unit cell. The basal pinacoid is predominantly developed, and it is on this that these growth spirals have been observed.

The crystals studied were either pale green, dark green or black. Some, which have a few well developed faces, have had their structural types determined by a goniometric method (Thibault 1944). X-ray diffraction methods will be required for the others.

No cubic crystal has been studied. Most of the crystals examined were of the commonest type, carborundum II. Its unit cell is hexagonal with six layers, and in Ramsdell’s notation is 6 H (Ramsdell 1947). The lattice parameters are

\[
a = 3.073 \text{ Å}, \quad c = 15.079 \text{ Å}.
\]

In this work the only other type available was carborundum I. This has a rhombohedral unit cell and referred to the hexagonal axes consists of fifteen layers. In Ramsdell’s notation it is 15 R with

\[
a = 3.073 \text{ Å}, \quad c = 37.70 \text{ Å}.
\]

§ 3. VISIBILITY OF GROWTH SPIRALS.

Numerous "growth spirals" have been observed on the faces of carborundum (SiC) crystals. These spirals are well developed; over thirty turns of the spiral can be traced in some cases. The spirals are centred on a dot which must mark the point of emergence of a screw dislocation on the crystal face.

The clean surface of the crystal when examined by a metallurgical microscope, using bright field illumination, does not show up these features, the surface appearing smooth. A little amount of impurity makes these features slightly visible (fig. 8, Pl. XXVI. has been taken by this method). Breathing lightly on the crystal face, while it is under observation, increases the visibility and the "lines" flash out, but soon disappear when the water re-evaporates. The "lines" seen by breathing are dotted and slightly diffuse, but the visibility obtained by this method is high. Though convenient for visual observations, the procedure is not suitable for photography.

Following Griffin’s technique, contrast was increased by deposition of a thin film of silver on the crystal face using thermal evaporation. This was improved by the use of phase contrast illumination. The photographs have been taken using positive phase contrast, the absorption of the phase plate being 80 per cent and phase retardation equal to \( 4\pi \). With this equipment many features are often still faint and only
just visible. Usual photographic methods for increasing the contrast have been employed in some of the photographs given.

In fig. 13 (Pl. XXVIII.), it is seen that the visibility and contrast is high compared with other photographs. The surface of this crystal was not very clean when it was silvered. The silver deposit was not uniform, the surface appearing mottled. Examination with phase contrast illumination gave high visibility. This suggests that impurity can make the steps more visible.

§4. Shape of the Spiral for a Single Screw Dislocation.

The growth spiral will have a shape depending upon the rate of advance of a growth front in different crystallographic directions.

For growth taking place in accordance with Frank’s ideas two cases arise:

(a) when the Frenkel kinks on the step (exchange sites) are close together and the distance moved by an adsorbed molecule before it hits a step is large;

(b) when the kinks are few or the distance moved by the adsorbed molecule is small.

When the former conditions exist, which are more likely to occur in growth from vapour, the molecule will have a high probability of adhering to the step if adsorbed near it, irrespective of the crystallographic orientation of the step. Thus for growth from the vapour, taking the rate of advance of the ledge to be independent of direction, the ledge will form a simple spiral under steady uniform supersaturation. The form of the spiral can be represented by the Archimedian equation

$$r = 2\rho_0\theta,$$

and the constant spacing between turns is

$$\delta r = 4\pi\rho_0,$$

where \( \rho_0 \) is the radius of critical nucleus, equal to \( \alpha d/2kT \ln z \), and where \( z \) is the supersaturation ratio, \( \alpha \) is the interatomic distance and \( \phi \) is the neighbour-neighbour binding energy of the crystal.

These predictions are confirmed by the circular spirals shown in figs. 1, 2, 3 and 8 (Pls. XXV., XXVI.). It is to be noted, however, that the spiral turns are more closely spaced at the centre, and the spacing gradually increases on going away from the centre until it becomes nearly constant. This is in accordance with the prediction of theory (Burton, Cabrera and Frank 1951).

Any dependence of the rate of advance of a growth front on the orientation of the step-line could impose a distortion of the growth spirals, so that they exhibit the symmetry of the crystal face. Such an effect has been found in fig. 4 (Pl. XXVI.), where the spiral is nearly circular at the centre, and gradually takes on the hexagonal symmetry of the
crystal face (carborundum type II). In fig. 7 (Pl. XXVI.) is a hexagonal spiral observed on a crystal identified to be of type II. This is a regular hexagonal spiral, showing clearly the dependence of the growth rate on the crystallographic orientation. The step-lines very near the centre show a curvature, which, as predicted by theory, decreases with distance from the centre. However, soon the straight step-lines start rounding off at the corners and become gradually curved on moving away from the centre. These step-lines do not meet the line of discontinuity sharply, but tend to curve away from it, as shown in fig. 7, for the outer five or six step-lines.

The straight edges show that under certain conditions there is a sharp minimum in the growth rate as a function of orientation.

In figs. 10 and 11 (Pl. XXVII.) further spirals are shown. Fig. 10 has been observed on a rhombohedral crystal type I.

§ 5. Properties and Behaviour of Growth Fronts.

The growth pattern for two or more screw dislocations ending on a face is complex and depends on the properties of the growth fronts. The growth fronts starting from a single screw dislocation will spread on the surface of the crystal face in regular shapes, but the presence of a boundary or an obstruction will distort its regular shape. When the advancing growth fronts meet an obstruction they can propagate round corners, as shown at the upper end of the obstruction in fig. 4; this point behaves almost as a source of secondary growth fronts.

The growth fronts emitted by two sources of opposite sign annihilate each other where they meet. Numerous examples of this can be seen in figs. 2 and 3 (Pl. XXV.). When there are several screw dislocations actively emitting growth fronts, a point on the crystal face will be in the dominant field of only one of these, and this alone determines the number of growth fronts passing through it. This is exemplified in fig. 2 where there are five screw dislocations. By choosing the point of observation, say, near the bottom screw dislocation, the number of growth fronts passing through it is solely determined as if this alone were active.


In fig. 17 is drawn schematically the growth pattern for two screw dislocations A and B of the same hand. The ledge starting from A goes on rotating and generating the spiral until it meets at \( p_1 \) the ledge originating from B where it terminates. At \( p_1 \) the two ledges fuse with one another. As the spirals unfold themselves the ledges meet at \( p_1, p_2, p_3 \ldots \) in the upper half and at \( p_2, p_4, p_6 \ldots \) in the lower half of the figure. The locus of points of intersection for two equal spirals has been shown to be a cartesian oval (Burton, Cabrera and Frank 1951). Between \( p_1 \) and \( p_2 \) (\( p_3, p_4 \)), etc., the missing parts of the two spirals are shown by the dotted lines. The resultant figure is the solid line curve.
Starting from A and going round the spiral we descend by one step in each complete turn till we come to the point \( p_1 \). From \( p_1 \) we go round the spiral B to the point \( p_2 \) and then again on the spiral A to the point \( p_3 \). Thus in going round the resultant curve once, we descend by two steps from \( p_1 \) to \( p_2 \), to \( p_3 \), and so on. Similarly, starting from B and going round we will descend by two steps, from \( p_2 \) to \( p_4 \), etc. . . . As the curves gradually smooth out at the points of contact, the figure will appear to be two spirals alternately spaced. Fig. 17 has been drawn for circular spirals, and the case for spirals with straight edges can similarly be drawn where the behaviour will be the same. In fig. 3 (Pl. XXV.) the case for circular spirals is illustrated.

Fig. 17.

Fig. 8 (Pl. XXVI.) illustrates a unique example in which the spiral is doubled with the members strictly "parallel". It may be that the twin form arises from two close-by dislocations of the same sign, cooperating closely.

In fig. 9 (Pl. XXVII.) is illustrated the case of two screw dislocations of the same sign close to each other. The spirals are circular and developed for two or three turns after which the ledges from other neighbouring dislocations interact with them.

In fig. 10 (Pl. XXVII.) is shown another case of two similar screw dislocations close to each other, so that growth starts from both of them. The spirals are circular at the centre for one or two turns after which they settle down as spirals with straight edges. The meeting of the growth fronts
from the two screw dislocations results in small kinks in the innermost straight edges. As in the case of circular spirals, here also by going round we descend by two steps, and the figure has the appearance of two spirals alternately spaced. However, the step height between successive lines in any particular direction is just one unit.

Fig. 11 (Pl. XXVII) shows the case in which the central screw dislocation has developed several turns before reaching the point where the second small screw dislocation emerges. They quickly accommodate each other and the behaviour is similar to the previous cases. The central screw dislocation is dominant and would determine the rate of crystal growth of the face. Near the edge of the figure it is seen that some more screw dislocations emerge on the crystal face, and are situated in the same direction from the central screw dislocation as the second one. These new screw dislocations yield within a short while to the domination of the central one and quickly fall in line, passing on the growth fronts with slight delay and in slightly modified form.

Now consider two screw dislocations of opposite hand terminating on the crystal face. The ledge starting from one terminates on the other, and with the unfolding of the spirals the two arms join together generating closed loops. This is exemplified in fig. 3 (Pl. XXV.), where one of the spirals has developed several turns before the other starts growing.

The growth pattern for three screw dislocations of the same hand observed on a crystal of type II. is illustrated in fig. 12 (Pl. XXVII.). Here, again, the spirals are circular at the centre and soon change into hexagonal spirals. It can easily be seen that, for three screw dislocations cooperating with each other, by following any one of the edges, the resultant curve descends three units in each turn. It should again be emphasized that the step height in the successive lines will be just one unit.

At the centre the ledges are closely spaced and, once they have settled down, the ledges are more widely spaced.

Fig. 2 (Pl. XXV.) illustrates the interaction of five screw dislocations. The growth fronts emitted by the screw dislocation at the top of the figure meet, first, the growth fronts advancing from the screw dislocation on the left of the figure and then, later, the growth fronts advancing from the bottom screw dislocation. Annihilation occurs over portions of the resultant growth fronts which assume characteristic shapes composed of arcs of circles with these dislocation points as centre. Near the centre of the figure, due to the interaction of different growth fronts a crowding occurs. Here the compound growth fronts are not arcs of circles with the different dislocation points as centres, but instead there is a gradual change in curvature.

§ 7. HEXAGONAL INTERLACED SPIRAL.

These features observed on a crystal face of carborundum type II. are shown in figs. 13 and 15 (Pl. XXVIII.). In each of these hexagonal spirals the edges fork out at the corners and meet the two neighbouring edges.
This interlacing gives the hexagonal spiral the "spider web" structure shown clearly in fig. 13 which shows the interlinking of four such spirals.

A double interlaced spiral is shown in fig. 14 (Pl. XXVIII.) in which the edges do not meet each other. The lines are broad with inner edges sharp and the outer diffuse.

An explanation of this interlacing has been given by Frank (1951).


The step height has been measured by the use of multiple-beam interference fringes using both Fizeau fringes of equal thickness and the fringes of equal chromatic order (Tolansky 1948).

A rounded spiral, effectively a spiral conical hill, may be considered as a circular conical hill made of a series of concentric steps with a constant spacing \( d \) and step height \( h \). It can be shown that if a Fizeau fringe passing over the peak of such a hill appears to bend through an angle \( 2\theta \), and if \( X \) is the dispersion, i.e., the distance between successive fringes, then the step height \( h \) is given by

\[
h = d \lambda \sin \theta / 2X.
\]

By measuring \( X \), \( \theta \) and \( d \), \( h \) can be evaluated. Fig. 5 (Pl. XXVI.) shows the Fizeau fringes passing over the spiral of fig. 4 (\&5461).

For examination with fringes of equal chromatic order, the image of the peak of the hill is projected on to the spectrograph slit. This was arranged to produce a system of fringes of equal chromatic order parallel to the spectrum line in one half of the field and sloping towards the red in the other (fig. 6, Pl. XXVI.).

Since the step height is obtained from the mean of all those contributing to form the peak, irregularities of the optical flat and the lack in faithfulness of silver contouring are averaged out.

In one case another determination of the step height has been possible. In fig. 4 (Pl. XXVI.) starting from the centre of the spiral we can reach any point \( A \) on the line of discontinuity, either by going round the "fish-like" obstruction in a clockwise or an anti-clockwise direction. In the former, we encounter, say, \( N_1 \) steps. Therefore the point \( A \) is \( N_1 \) steps lower with respect to the centre of the spiral. In the latter case we go down, say, \( N_2 \) steps from the peak of the hill in order to arrive at \( A \). Thus at \( A \) the difference in level on the two sides of the line of discontinuity is that corresponding to \( (N_2 - N_1) \) step heights. This difference is quite large (over 50) and is therefore capable of being measured accurately and easily either by Fizeau or fringes of equal chromatic order. Knowing this, the step height has been evaluated, but is subject to uncertainty due to the possible presence of hidden dislocations in the obstacle and discontinuity surfaces.
§ 9. Result of Measurement of Step Height.

It is seen below that the step height measured in the cases so far is equal to just one unit cell.

<table>
<thead>
<tr>
<th>Fizeau fringes</th>
<th>Fringes of equal chromatic order</th>
<th>Method by counting No. of steps</th>
<th>Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-2 Å</td>
<td>17-1 Å</td>
<td>14-8 Å</td>
<td>Spiral in fig. 4, Type II.</td>
</tr>
<tr>
<td>14-1 Å</td>
<td></td>
<td></td>
<td>Spiral in fig. 4, Type II.</td>
</tr>
<tr>
<td>14-5 Å</td>
<td></td>
<td></td>
<td>Circular spiral, right of fig. 2.</td>
</tr>
<tr>
<td>15-0 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15-3 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

§10. Discussion of Results.

From fig. 2 (Pl. XXV), which is at magnification $\times 90$, the spacing between the successive arms of the circular spiral when it is nearly constant is approximately 2-5 mm. Using $\delta r=4\pi \rho_0$, we have

$$\rho_0=\frac{2.5}{90 \times 4\pi} \text{mm.} \approx 2\mu.$$  

From $\rho_0=\alpha \phi/2kT \ln \phi$ and using Trouton's rule to estimate $\phi/kT$ according to which $\phi/kT=3.5T_0/T=6$ at an absolute temperature of 0-6 of the boiling point of the material we get

$$\alpha \approx 0.2 \text{ per cent.}$$  


The density of dislocations varies widely on different specimens of carborundum. In fig. 4 (Pl. XXVI.) there is only one which dominates the growth of the face. In figs. 1, 2, 3, 11 and 12 (Pls. XXV., XXVII.) there are several. The largest density of dislocations observed is shown in fig. 16 (Pl. XXVIII.). Here there are nearly $10^4$ screw dislocations per square centimetre.

Another noteworthy point is that in fig. 16 (Pl. XXVIII.) there are nearly twenty screw dislocations, most of which are of the right-handed type. It is characteristic that in any one region there is a large predominance either of right-handed or of left-handed screw dislocations.

§12. Summary.

Numerous growth spirals starting from points of emergence of screw dislocations have been photographed on the surfaces of carborundum crystals. These spirals have characteristic shapes. The shape is discussed in relation to the crystal structure. The behaviour and properties of
growth fronts and the growth patterns for two and more screw dislocations are illustrated. From the observations on the photographs it is shown that the type of information that can be derived is the determination of the radius of the critical nucleus, the supersaturation and density of dislocations.

The step height has been measured accurately by multiple-beam interference fringes. The step height at the edges of these growth spirals is found to be one unit cell.

Acknowledgments.

I am grateful to Professor S. Tolansky for his kind interest and encouragement in the course of this work. Thanks are due to Dr. F. C. Frank for his valuable suggestions on the subject, and also to B. T. M. Willis and H. E. Rahbek for useful discussion. I am indebted to Sir K. S. Krishnan, F.R.S., and Dr. J. T. Kendall for the supply of the crystals, to the British Council, for the award of a scholarship, and to the University of Delhi for granting the study leave. This work has been carried out with instruments made available by grants by the Royal Society and the D.S.I.R.

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Growth Spirals on Carborundum Crystals

The observation of growth spirals on carborundum crystals has been reported earlier. These growth spirals can be divided into two classes: (1) those in which the step-height between the successive edges of the spiral is equal to the height of a unit cell; and (2) those in which the step-height is a multiple of it. The latter type of multi-stepped spiral will result from a dislocation the strength of which is a multiple of the repetition period, the Burger's vector being a multiple of the height of the unit cell. Such spirals have been found to originate at a large hole (see Fig. 2); they have a much higher optical visibility because of the relatively large step-height, being therefore easily observed with a microscope using bright-field illumination. Of the numerous spirals of this kind seen, two typical examples are shown here. The steps of these spirals can break up into their component steps under certain conditions. In Fig. 1, showing only one half of the spiral, the various components advance together in different directions for some twelve turns, after which they break up into five or six close branches. In Fig. 2 is illustrated a case where the dissociation takes place quite near the centre and growth can be regarded as taking place from the multiple dislocations.

Carborundum is a polytypic crystal. In the hexagonal types or the rhombohedral types referred to the hexagonal axes, the number of layers necessary for the arrangement to repeat itself is also the number of 'formula weights' in the unit cell. However, in the actual rhombohedral unit cell, the number of formula weights is one-third of the total number of layers included within the c-axis. The measurement of the step-height of the growth-spirals on the different types should be able to show this point.

On the hexagonal type II crystal (6H in Ramsdell's notation) the step-height measurements have already been given and shown to be equal to the height of the unit cell (c = 15 Å). Further measurements of the step-height, by the application of multiple-beam interferometry on the growth spirals on the different rhombohedral types, are now reported here.

On a type I crystal (15H in Ramsdell's notation) the measured step-height is 12 ± 2 Å. This is equal to one-third of the lattice parameter c of the unit cell referred to the hexagonal axes, and is in agreement with experimental error with the predicted X-ray value of \( a_{2h} = 13 \) Å of the rhombohedral cell. The visibility of this growth spiral is consistent with this measurement of step-height.
On a type VI crystal (33$R$ in Ramsdell's notation), the measured step-height is 28 ± 2 A., which again is very close to $a_{rh}$ of the rhombohedral cell, and within experimental error is identical with it.

Fig. 3 shows a hexagonal spiral with step-height nearly 130 A., and it may be concluded that it is one of the types with giant unit cells. If $a_{rh}$ is indeed equal to the step-height of 130 A., then the classification is probably 159$R$.

Thus, it seems established that the step-height is equal to the height of the actual unit cell. This gives another physical confirmation of the existence of the X-ray unit cell.

I wish to express my thanks to Prof. S. Tolansky for his interest in the work, and to the British Council for the award of a scholarship.

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Growth Spiral Patterns on Carborundum Crystals

Observations on growth spirals on carborundum crystals have been reported earlier, affording experimental evidence of Frank's theory of crystal growth depending upon dislocations. Some new and unpredicted features of these growth spirals are reported here.

In Fig. 1 is shown part of an interlaced spiral in which in any one orientation seven steps are seen to group together. On following these steps to the other side of the interlaced portion, the same sequence of spacing repeating itself has been observed (not shown in Fig. 1). Under low magnification these grouped steps give an appearance resembling optical band-spectra.

On another crystal a similar grouping of five steps has been observed. In addition, on one face of a crystal the number of steps grouped together has been observed to change in certain regions.

These features can be explained thus. The different polytypes of carborundum have the Ramsdell's zig-zag sequence or Zhdanov symbol of [(33)n32]. Using Frank's notation, the structure can be written as [(V>V>A>A)M>V>A>. Whichever layer has the slowest velocity of growth in any one orientation—say, the first V after a series of A's—then it will repeat itself after six such layers, making the growth steps 15 A. high, until we reach the last layer V>V>A, which will be only 12.5 A. high. After this the whole sequence will go on repeating itself. Thus, depending upon the number n, we will have a certain number of steps grouping themselves together. The observation of the changing number of grouped steps together suggests a change in type from one part of the crystal to another. This may account for the disagreement between crystal symmetry and X-ray diffraction data sometimes observed.

The observation of this grouping of steps is another visual confirmation by crystal growth patterns of the repeat sequence predicted by X-ray phenomena.

Fig. 2 shows a spiral in which spots are seen just on the edges of the steps. Their size generally increases as we go away from the centre.

Fig. 3 shows a number of hexagonal spirals originating from screw dislocations, the point of emergence of which is marked by a somewhat hexagonal spot. A large number of similar spots with no spirals attached to them are also seen. These
are sometimes linearly arranged. At the Bristol Summer School (1951), where some of these pictures were presented, it was suggested by Dr. F. C. Frank that these may be the ends of edge dislocations.

I wish to express my thanks to Prof. S. Tolansky for his interest, and to the British Council for the award of a scholarship.

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Further Observations of Growth Patterns on Silicon Carbide (Si-C) Crystals

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Abstract
This paper reports further observations of growth patterns on silicon carbide crystal faces using techniques previously described. In addition to the simple types of spirals in which the step height was shown to be equal to the height of an x-ray unit cell, spirals originating from dislocations of multiple strength, the step height being a multiple of the height of an x-ray unit cell, are reported. More complex geometrical growth patterns of groups of dislocations are illustrated. The conditions for the interaction of growth fronts issuing from a number of dislocations are discussed and shapes of the loci of points of intersection of such growth fronts are calculated and illustrated. It is observed that in any one region of the crystal, the screw dislocations are not only predominantly of the same sign but have also the same strength.

§ 1. Introduction
Observations of 'growth spirals' on silicon carbide (Si-C) crystals have been reported earlier (Verma 1951) affording experimental support for the theory of growth of crystals depending upon the presence of dislocations (Burton, Cabrera and Frank 1951). The present paper deals with further observations on the more complex geometrical growth patterns of groups of dislocations and the interaction of a number of dislocations. Also spirals originating from dislocations of multiple strength are reported.

§ 2. Spirals Originating from Dislocations of Multiple Strength
The step formed by the emergence of a screw dislocation on to the crystal face will have a height corresponding to the differences in the amounts of slip between neighbouring regions of the crystal. Because of the existence of discrete atomic structure in the glide plane, this will be limited to the value of the x-ray unit cell of the crystal or in some lattices a small multiple or fraction of this. The spirals reported earlier (Verma 1951) were mostly of the simple type and the measured step height was shown to be equal to the height of the x-ray unit cell (in type 11=15 Å). Because of the small step height visibility was low.

Some of the spirals now observed have a much higher visibility and interferometric measurement shows that they have a relatively large step height; indeed, they can often be seen simply with a microscope using

* Communicated by Professor S. Tolansky.
bright field illumination without the need for silvering the crystal. The figures reproduced here have been taken by the technique used previously (Verma 1951).

As silicon carbide (Si-C) is a polytypic crystal, a large step height may be due to its being equal to (1) the height of a large x-ray unit cell, (2) a multiple of a smaller x-ray unit cell. The latter type of spiral results from a dislocation of multiple strength, the Burgers' vector being a multiple of the x-ray unit cell.

Fig. 1 (Plate XVIII) illustrates such a spiral originating from a dislocation of multiple strength, observed on a crystal of type II (determined goniometrically). The step height between the successive arms of the spiral is nearly 620 Å as determined by the shift of the multiple-beam Fizeau fringes over these steps. The rate of advance of a multiple step will be controlled by the deposition rate at the bottom of the step (Frank 1951) and as long as the bottom of the step is not privileged with respect to the diffusion of the molecules from the gas, the multiple step will not dissociate into its component steps. In fig. 1 (Plate XVIII) the edges do not remain straight after three or four turns from the centre and become irregular. This behaviour continues for a few more turns after which the steps dissociate into five visible components. The edges of these multiple steps will not be close packed. The Fizeau fringes are observed to be continuous over the edges of the steps while climbing them. This indicates that the edges are not steep and vertical. Furthermore the crystal face between the successive edges is not close packed. This is shown in fig. 2 (Plate XVIII) where some faint step lines can be seen between successive edges.

The dissociation of a step into its components is seen to take place preferentially in certain orientations. In figs. 1 and 2 (Plate XVIII) it is seen that the dissociation has taken place preferentially in one orientation and at 60° to this direction this dissociation is much less marked. Fig. 3 (Plate XVIII) is another example showing this better, where the dissociation is observed on the three alternate sides of the hexagonal spiral. This is easily comprehensible since in Si-C a growth layer which is fastest in any one orientation becomes slowest in orientations at 60° to it; the faster moving steps will overtake it and pile up behind it.

Dissociation is seen to take place quite near the origin for a further example (fig. 4, Plate XVIII). Here amongst the dissociated steps, in three orientations the outermost edges (which will correspond to the bottom layers of the group) are straight and parallel to each other in the successive arms of the spiral, whereas in the inner edges the usual irregularity is observed.

Fig. 5 (Plate XVIII) shows a case of multiple dislocations. In contrast to fig. 4 (Plate XVIII) the growth is faster at the six corners, the rate increasing towards the outer (or bottom) layer in the group. At some of these corners crosslacing of the step lines is observed and this might be responsible for the faster growth, or alternatively there may be other explanations.
§3. Pairs of Dislocations of Opposite Sign

When two dislocations of opposite sign emerge on the crystal face, they attract each other with a force which is inversely proportional to the distance between them and increases with the strength of the dislocation (Taylor 1934). There is however a constraining force anchoring these dislocations to their equilibrium positions between the lattice rows, and this force depends upon the elastic constants of the medium (Peierls 1940, Nabarro 1947). This force should also depend in some way upon the strength of the dislocation. At a certain distance of separation between the two dislocations these forces will balance each other. During the process of growth of Si–C, when the temperature is high, the two dislocations of opposite sign will draw towards one another and will finally coalesce, joining to form a common hollow core, unless the distance of separation is more than the above equilibrium value. Experimentally, pairs of dislocations of opposite sign are seldom observed. Amongst all such pairs observed so far on Si–C, a pair of dislocations of opposite sign close to each other such that the two spirals are equally developed (i.e. the first, second etc. arms of the spiral from one dislocation meet the corresponding arms from the other) has not yet been observed for the dislocations of elementary Burgers vector (e.g. 15 Å for type II). However for a comparatively large Burgers vector one pair of closely spaced and equally developed dislocations has been observed. Fig. 7 (Plate XVIII) shows this rare case in which the step height is nearly 120 Å as measured by the shift of the multiple-beam Fizeau fringes over these steps (fig. 6, Plate XVIII).

Fig. 8 (Plate XIX), which is a bright-field photograph of an unsilvered crystal, shows two dislocations of opposite sign each giving rise to a hexagonal spiral. When the successive arms of the two spirals meet each other they generate closed loops. At the points of intersection an edge can be observed, indicating that the levels of the two steps joining together are not the same.

Another rare case is shown in fig. 9 (Plate XIX) which consists of closed hexagonal sheets with no trace of the dislocations at the centre. The closed hexagonal figures might have originated from two dislocations of opposite sign, alternatively there may be some other mechanism. (No new closed loops are generated at the centre after the dislocations are drawn close to each other compared to $p_c$.)

The possible 'neutralization' of pairs of dislocations of opposite sign will leave only the surplus of one kind to be observed. This may explain the observation that in any one region of the crystal the dislocations are predominantly of one type. Further, after this 'neutralization' the surplus left behind will be much less than the original value. (For $N$ dislocations randomly formed, the probable excess will be $\sim N^1$.) Thus the observed maximum density of dislocations $\sim 10^6$/cm$^2$ (in fig. 18 (Plate XX), all of the same type) is much less than the theoretically predicted value $\sim 10^8$/cm$^2$. 
§4. GROUPS OF DISLOCATIONS

Quite often groups of dislocations arranged in different ways emerge to the surface of the crystal. A group of some 50 dislocations of the same sign arranged along a line of length \( L \) is seen in fig. 10 (Plate XIX), to generate a spiral system of \( s \) branches. The resultant activity of the group will be \( s/(1+L/2\pi \rho_c) \) times that of a single dislocation (Burton, Cabrera and Frank 1951) where \( \rho_c \) is the radius of the critical nucleus. Fig. 11 (Plate XIX) illustrates another such group of dislocations where steps are seen to group together giving a repeat pattern.

In the general case of a group of like dislocations Burton, Cabrera and Frank (1951) predict that a pit may be developed on the crystal face if the growth fronts have difficulty in penetrating the group itself. This prediction is confirmed by the case illustrated in fig. 12 (Plate XIX) where over 50 circular step-lines originate from an elliptical hole. Obviously at such a source pairs of dislocations of opposite sign will neutralize each other leaving the excess of only one type to promote growth.

§5. GROWTH FROM A NUMBER OF INTERACTING DISLOCATIONS

Interaction of Growth Fronts and Curves of Intersection

Very often a group of dislocations, instead of originating from one source, spread on the surface of the crystal. The growth fronts spreading from the various sources meet each other producing complicated growth patterns in accordance with their properties. The general principles that govern their interaction and the shape of the locus of points of intersection are as follows:

The successive arms of the spirals originating from any two dislocations can go on joining with each other only if the two dislocations are of the same strength, i.e. the two step heights are equal. Conversely, if successive steps from two dislocations join and fuse together, it can be concluded that the step heights of the two spirals are equal. Since this joining together of steps is observed in figs. 15 and 18 (Plate XX) for the successive steps from all the interacting dislocations, the step height must be a fixed unit and its measurement on any one of them will give the value of all the rest. Thus in any one region of the crystal, the dislocations are not only predominantly of the same sign but also have the same strength.

If then the \( n \)th step from one source \( O_1 \) meets the \( m \)th step from the other source \( O_2 \), they will join together if they are at the same level. Thereafter pairs of steps that can join together are \((n+1)\)th with \((m+1)\)th; \((n+2)\)th with \((m+2)\)th etc. such that the order difference between these steps fusing with one another is always constant and equal to \((n-m)\). Macroscopically speaking, on either side of the locus of points of intersection, the portions of the two pyramids should slope in the same direction, i.e. on travelling along this locus of points of intersection we will be moving from a higher to a lower level, or vice versa, for both the pyramids. Examples of this can be seen in fig. 15 (Plate XX).
Further, if the spacing between the \(n\)th and the \((n+1)\)th arms of one spiral is \(d_1\) and between the \(m\)th and the \((m+1)\)th arms of the other is \(d_2\), the two pairs of steps will meet the locus of points of intersection at angles \(\theta_1\) and \(\theta_2\) respectively, such that \(\sin \theta_1 / \sin \theta_2 = d_1 / d_2\). The value of \((\theta_1 + \theta_2)\) at a particular point of intersection is fixed by the initial conditions of the distance of this point from the two sources, the distance between the two sources, and the shapes of the two spirals.

In the more general case \(d_1\) and \(d_2\) are the lengths of perpendiculars dropped from the point where the \((n+1)\)th and \((m+1)\)th arms meet each other, upon the tangents drawn to the \(n\)th and \(m\)th arms of the two spirals at the point where they meet. The tangents to the \(n\)th and \((n+1)\)th arms of one spiral may not be parallel to each other, so that not only the spacing between the successive arms changes, but also their directions may change, in which case the locus of points of intersection will have to turn suitably in order to satisfy the above sine condition. This is illustrated in fig. 13 (Plate XIX) where with the change of direction by the steps through an angle about \(60^\circ\), the locus of points of intersection also turns through a similar angle. Other examples of the interaction of growth fronts and the loci of their points of intersection in accordance with the above conditions are seen in figs. 15 and 18 (Plate XX), where a large number of polygonal spirals with varying spacings are interacting with one another. Another example of the interaction is seen in fig. 14 (Plate XIX), where as a result of the meeting of the growth fronts from three dislocations closed triangular loops are formed. (The figure includes only two dislocation centres. The third one will be on the left side.)

If the two series of steps originating from two dislocations, on reaching the same region of the crystal, are unable to satisfy any of the above conditions, e.g. sine condition, they will not join with one another. These steps will then terminate in such a region. The points where the steps terminate will be at the ends of screw dislocations or at discontinuities in level. Such behaviour is seen in fig. 15 (Plate XX) along a line running from left to right nearly in the middle of the figure, with a small gap in the centre, over which region four steps of the two spirals are seen to join together. We can reach any one of these steps (say the second from the left) from a point \(A\) in a number of ways. In going from \(A\) to the chosen step we have to go down 30 steps, this number being independent of the path taken. A direct path can be traversed or one involving the crossing of different hexagonal spirals by going round the right hand end of the line of discontinuity. This is what is expected since the different spirals are of the same strength.

§6. Special Case: Circular Spirals

By introducing the approximation used for the interferometric measurements of step heights, according to which these spirals may be regarded as composed of circles of constant spacing \(\Delta r = 4\pi \rho_d\), the condition \((n-m) = \text{constant}\) directly gives the locus of the point of intersection \(P\) of the two
rounded spirals originating from the two source centres \( O_1 \) and \( O_2 \). Thus \((n-m) \delta \tau \) will be a constant from which we have \( O_1 P - O_2 P = \text{constant} \). This gives the locus of the point of intersection, a hyperbola which reduces to a straight line perpendicular to \( O_1 O_2 \) and passes through its middle point when \( n-m = 0 \) (Burton, Cabrera and Frank 1951).

A locus of points of intersection, which is hyperbolic, is illustrated in fig. 16 (Plate XX) for two circular spirals unequally developed. The condition \((n-m)=0\) corresponds to the symmetrical case of two spirals equally developed and is illustrated in fig. 17 (Plate XX) where the locus of points of intersection is seen to be approximately a straight line, perpendicular to the line joining the two dislocations and passing through the middle point. Here the two series of steps with equal spacing (i.e. \( d_1 = d_2 \)) meet the locus of points of intersection at equal angles (i.e. \( \theta_1 = \theta_2 = 0 \)). In fig. 16 (Plate XX), as the spacings of the two spirals become equal (i.e. \( d_1 = d_2 \)), in accordance with the sine condition \( \theta_1 = \theta_2 \), and in this case the steps tend to be parallel to each other at the points of intersection (i.e. \( \theta_1 = \theta_2 = 0 \)).

As shown by Burton, Cabrera and Frank (1951) a small influence is transmitted along each step from the points where the two spirals meet, into the respective centres. This will tend to increase the rate of rotation of the spiral whose centre is nearer the points of contact (the upper one in fig. 16, Plate XX), trying to synchronize the two in phase. This will smooth out the corners formed by the meeting of the two series of steps. This is observed in all the interacting spirals.

Acknowledgments

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New Observations of Crystal Overgrowth on Silicon Carbide

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ABSTRACT. On the faces of some silicon carbide crystals showing 'growth spirals' superimposed oriented overgrowths can sometimes be observed. These oriented overgrowths which took place during the process of manufacture consist of stepped triangular pyramids with craters at their peaks, the pyramids having heights up to a few wavelengths of light, and built sometimes on platforms of similar heights. These conclusions have been arrived at by the application of the techniques of multiple-beam interferometry and light-profile microscopy. In addition to the pyramids some trigonal, hexagonal and their compound figures have also been observed, which by the application of multiple-beam interference fringes are shown to be molecular oriented layers. These oriented molecular layers, the existence of which is revealed from the observation of the above overgrowths on silicon carbide crystals, may be silica deposit or possibly the growth of silicon carbide on itself.

§1. INTRODUCTION

Recently several workers have studied oriented overgrowth of crystals on different substrates. A substrate flat to molecular dimensions is required for this study and usually a cleavage face of a crystal is chosen for this purpose. Thus Schultz (1951) has studied the overgrowths of alkali halides on a cleavage face of mica, Lucas (1951) has studied the thin layers of ZnO, grown on a cleavage face of Zn, and Pashley (1952 a, b) has used cleavage faces of crystals and electrolytically polished silver surfaces as substrates.

In these experiments the thickness of the overgrowth layers deposited on the substrate is only a few Ångström units thick. Therefore it becomes increasingly important to know the flatness of the substrate for drawing reliable conclusions.

As has recently been shown by the author (Verma 1951), growth spirals are sometimes observed on the basal planes of silicon carbide crystals. The step height between the successive arms of the spiral has been shown to be equal to the height of the x-ray unit cell, and for type II crystals this step height is only 15 Å.
The area between successive steps is molecularly plane. Thus silicon carbide crystal surfaces, which are flat and plane to this extent provide a good substrate on which to study overgrowths.

§2. OVERGROWTHS ON SILICON CARBIDE CRYSTALS

Triangular Pyramids

We have not yet studied the overgrowth of crystals deposited artificially on silicon carbide crystals as substrate. However by using techniques previously described (Verma 1951), the examination of some of these silicon carbide crystals themselves reveals oriented overgrowths which took place during the process of manufacture. Figure 1 (Plate I) shows six trigonal pyramids observed on the basal plane of a silicon carbide crystal. On the rest of the crystal face faint step lines of an interlaced spiral of the type described previously (Verma 1951) can be seen as background. The step height between the successive edges of such a spiral would be 15 Å. Thus the scale of flatness of the substrate is superimposed on the picture.

The two pyramids at the top left corner in fig. 1 are oriented at 60° with respect to the remainder. It can also be seen that the three edges of the pyramids are rounded and are more or less similarly oriented to the edges of the interlaced spiral. Sometimes these overgrowths overlap and are 'twinned'. In fig. 2 are shown two such cases of overlapping. On the right-hand side the overlapping pyramids are similarly oriented, whereas in the middle of the figure showing the overlapping of three pyramids, the pyramids are alternately Δ and V in orientation. The pyramids are seen to have a stepped structure. The steps are nearly triangular in their contour but at the three corners a characteristic dimple can be seen for all of them. At the peak of every pyramid there appears to be a crater. Similar craters can be observed at the edges of some of the pyramids and elsewhere on the crystal surface.

Interferometric and Light Profile Microscopic Examination

To study the triangular overgrowths the techniques of multiple-beam interferometry (see Tolansky 1948) and light-profile microscopy (Tolansky 1952) have been applied. In multiple-beam interferometry both the Fizeau fringes and fringes of equal chromatic order have been utilized. Figure 3 shows the multiple-beam Fizeau fringes passing over these features. To obtain fringes of equal chromatic order shown in fig. 4, the image of a Fizeau fringe passing over the peak of a pyramid was projected on the slit of a spectrograph. The fringes so obtained are seen to be convex towards the violet end of the spectrum showing clearly that these triangular features are hills, i.e. pyramids. The heights of these pyramids range from a few hundred Angström units to a few wavelengths of light; the particular pyramid studied in fig. 4 is approximately 1000 Å high. The discontinuity of the fringes in figs. 3 and 4 at the edges of the pyramids shows that the pyramids are built on platforms whose heights vary and may be as much as a few light wavelengths.

The light-profile microscope (recently developed by Tolansky (1952)) demonstrates these facts vividly. In this technique the field of view of the microscope is crossed by a dark profile line which is the image of the opaque fine line placed at the field iris and projected on the surface of the specimen by an off-centre illumination. The profile gives the line contour of the surface of the
Fig. 4. (×85)

Fig. 6. (×45)

Fig. 7. (×45)

Fig. 8. (×15)

Fig. 9. (×45)

PLATE II.
New Observations of Crystal Overgrowth on Silicon Carbide

specimen where the changes in level are registered as lateral shifts of the profile. It is seen in fig. 5 that the profile line shifts towards the left after crossing the edge of the pyramid showing it to be an elevation above the general level of the crystal. By the interferometric calibration given by Tolansky, this shift corresponds to a change in height of about 1 Å, which is the height of the platform on which the pyramid is built in this particular case. At the peak of the pyramid the shift of the profile towards the right shows it to be a crater. Over a small area the bottom of the crater is nearly flat and its depth is nearly equal to the total height of the pyramid.

Behaviour of the Growth Fronts

The step lines of the successive growth fronts are seen in figs. 1 and 2 to be slightly deformed after they have travelled past these overgrowths, which act as obstacles. This deformation of the step lines indicates that the surface of the crystal had continued to grow after the formation of the overgrowths. In fig. 2 the growth fronts, which are advancing from the top to the bottom, break up into two halves on arriving at the overgrowths. After crossing these obstacles they rejoin and fill up the shadow region. The step lines in doing so fork out leading to interlacing of step lines of the type described previously (Verma 1951, fig. 14).

§3. ORIENTED MOLECULAR LAYERS ON SILICON-CARBIDE CRYSTALS

A different type of overgrowth observed on silicon carbide crystals is shown in figs. 6, 7 and 9. Triangular, hexagonal and compound figures formed by the overlapping of the former with the edges slightly rounded are seen in these figures. In fig. 9 a plainly visible dot can be observed at the centre of some of the figures. Figure 8 shows the multiple-beam Fizeau fringes passing over the areas of figs. 6 and 7. Under this high dispersion there appears to be a very small kink when the fringes cross the boundary of these figures (the third fringe from the top passes over the hexagonal figure and the fourth and the fifth fringes over the triangular figure shown in fig. 6. The eighth and the ninth fringes pass over the lower and the upper figures of fig. 7 respectively). The kink has been measured to correspond to a change in height of 35 ± 5 Å. Thus one can assume that the triangular and hexagonal figures are molecular layers since for silicon carbide type II the height of the unit cell is 15 Å.

The edges of these molecular layers have a dotted appearance which may be due to the deposition of some impurity. This will then explain the rather high visibility of the edges.

§4. CONCLUSIONS

The observations of figs. 6, 7 and 9 show that a molecular layer is initially deposited on the crystal face. These monolayers which take definite orientations and shapes are fairly large in extent and form the nucleus for further oriented overgrowth. The dots observed in the centres of the figures in fig. 9 may be some foreign matter which acts as the nucleus for the laying down of the first molecular layer on the crystal face. These dots may develop into the craters observed at the peaks of the pyramids of figs. 1 and 2. The further observations of figs. 1 and 2 that some of the pyramids are built on a platform may mean that this oriented monolayer could grow up to the height of the platform by a
repetition of the process of the formation of the first monolayer. This will happen if the atomic pattern of the 'embryo' and hence that of the substrate resembles the atomic pattern of a plane, in the normal lattice of the deposit (van der Merwe 1949).

In the manufacture of silicon carbide the different elements present inside the furnace are silicon, carbon and oxygen, so that these overgrowths may consist of any of these elements in combination. As is well known silica deposits are often observed on silicon carbide crystals and from the symmetry of the figures it is thought that these may be the overgrowth of silicon carbide on itself. If this is so, it demonstrates an interesting mode of crystal growth, of a crystalline substance growing on itself. Even in such a case, the configuration of a surface layer of the crystal is different from that of an interior layer by reason of Verwey displacements (Frank 1951). It will, however, be interesting to apply electron diffraction techniques to study these overgrowths.

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I wish to express my thanks to Professor S. Tolansky for his interest. This work has been carried out during the tenure of a scholarship by the British Council while on study leave from the University of Delhi.

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Growth Spirals on Hæmatite (Fe₂O₃) Crystals

The observation of 'growth spirals' on silicon carbide (Si—C) crystals was reported by me recently. It was shown that the observations are in accordance with the theory of crystal growth put forward by Burton, Cabrera and Frank.

Similar observation of growth spirals on hæmatite (Fe₂O₃) crystals are now reported. Hæmatite, which is isomorphic with corundum (Al₂O₃), may be referred to the rhombohedral axes making an angle of 85° 42' with each other, or to hexagonal axes with a : c = 1 : 1.36. X-ray measurements show that the oxygen atoms are arranged in approximately hexagonal close-packing. Between two successive layers of oxygen atoms there are positions for cations. The distance between successive layers of oxygen atoms is nearly 2.3 A. along the trigonal axis, which is perpendicular to the (111) plane. The structure when projected on the (111) plane shows that it will repeat itself after six such layers, giving the repeat distance equal to nearly 14 A. along the trigonal axis. The growth spirals observed on hæmatite illustrate these facts very well.

The accompanying photograph shows a spiral originating from a right-handed screw dislocation. The spiral is triangular in the centre, but soon becomes hexagonal. After about two turns, the spiral is seen to terminate on a left-handed screw dislocation.
Thereafter successive closed loops are generated in accordance with theory.

The measurement of step height between successive arms of the spiral, by the application of multiple-beam interference fringes, shows it to be nearly $16 \pm 3$ A. This, within experimental errors, confirms the X-ray measurements.

Besides this elementary type of spiral, several other more-complicated growth patterns have also been observed, some of which give interesting comparison with similar observations on silicon carbide crystals. One feature seen clearly in the present photograph is that, unlike silicon carbide, the point of emergence of screw dislocation on the crystal surface is not marked by a hole, showing that in this case the core is not hollow.

A detailed account of this work is being communicated elsewhere.

I wish to express my thanks to Prof. S. Tolansky for his interest and suggesting that haematite be examined. I am grateful to the authorities of the British Museum (Mineralogical Department) for the loan of the crystals, and to the British Council for a scholarship.

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Observations on Growth and Etch Phenomena on Haematite (Fe₂O₃) Crystals

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ABSTRACT. New observations of growth and etch features on haematite (Fe₂O₃) crystals are reported. Of the many growth patterns observed, the simplest are the elementary 'molecular growth spirals' in accordance with the theory of Burton, Cabrera and Frank. The step height between the successive arms of an elementary spiral has been measured by the application of multiple beam interference fringes and is shown to be equal to the x-ray value of the repeat distance. More complex growth patterns are illustrated and discussed. The etch figures reported are also of molecular thicknesses and consist of a very large number (~10⁸/cm² of the crystal surface) of similarly oriented small triangular figures, and some more complex shapes.

§1. INTRODUCTION

According to the theory of crystal growth developed by Burton, Cabrera and Frank (1951), when a crystal grows due to the presence of dislocations, the steps exposed on the crystal face by screw dislocations wind themselves into spiral forms giving rise to 'molecular growth pyramids'. The observation of numerous 'growth spirals' on the faces of silicon carbide crystals has been reported earlier and shown to be in accordance with theory (Verma 1951). Similar observations of 'growth spirals' on haematite (Fe₂O₃) crystals were reported in a preliminary note (Verma 1952 b), and in the present paper a fuller account of the observations of growth and etch phenomena is given.

§2. TECHNIQUE OF OBSERVATION

Most of the observed features are of molecular height and are consequently faint. The technique found most suitable for their observation is that previously employed for silicon carbide crystals (Verma 1951) and consists of depositing a highly reflecting layer of silver on the crystal surface by thermal evaporation and then examining it in reflection using phase-contrast microscopy.

§3. STRUCTURE OF HAEMATITE AND ITS MODE OF GROWTH

The structure of haematite may be referred to rhombohedral axes making an angle of 85° 42' with each other or to hexagonal axes with an axial ratio c/a = 1:36. The structure assigned to haematite by x-ray measurements (Bragg 1924, Pauling and Hendricks 1925) may be pictured as follows. A series of rhombic cells is formed by slightly extending cubic cells along a trigonal axis so that the angle between the edges meeting in this axis is 85° 42' instead of 90°. At every cell corner is placed a unit consisting of two Fe atoms and three O atoms. The two Fe atoms are separated by a distance of about 2:88 Å and lie at equal distances from the cell corner along the trigonal axis which passes through it. The three oxygen atoms surround each cell corner at a distance of about 1:47 Å and lie in a plane through the corner at right angles to the trigonal axis, i.e. in the (111) plane. The equilateral
triangles formed by the three O atoms are oriented at 60° to each other in successive layers, i.e. are Δ and V in orientation. The distance between successive oxygen layers is nearly 2-3 Å. Figure 11* shows the structure projected on the (111) plane. The structure repeats itself along the trigonal axis after six such (111) layers, giving the repeat distance equal to nearly 14 Å. The rhombic unit cell is outlined by joining the Fe pairs '1' to '3'; '3' to '5'; '5' to '7'; '7' coinciding in projection with '1'. This structure gives an approximate hexagonal close packing for oxygen atoms.

Haematite, which is formed in various ways and is found in rocks of all ages, is considered to occur in connection with volcanic activities as a sublimation product, often as small thin crystal plates which are parallel to the c axis (Dana 1948). At a temperature of about 2000 °C, at which ferric oxide can be sublimed in crystalline form, it becomes dissociated into a magnetic oxide and consequently it will be the magnetic rather than the ferric oxide that will volatilize at these temperatures. Haematite is probably produced by the action of water vapour upon ferric chloride with the generation of HCl. The HCl vapour, if not removed, can act strongly on the haematite crystals formed, and most of the surfaces will easily etch.

§4. OBSERVATIONS ON GROWTH FEATURES ON HAEMATITE

Simple or Elementary Type of Spiral

On the haematite crystals many growth patterns have been observed, some of which are of the simple type. Figure 1 shows such a spiral with elementary Burgers' vector (see §5) observed on the basal plane of a thin hexagonal plate of haematite. Originating from a right-handed screw dislocation, the spiral is seen to terminate on a left-handed one after about two turns. Thereafter successive closed loops are generated in accordance with theory.

This spiral with straight edges indicates that the rate of growth depends strongly upon the crystallographic directions, the straight edges marking the directions of minimum growth. According to Burton, Cabrera and Frank's theory (1951) the conditions of growth for a polygonal spiral are such that the 'Frenkel kinks' or exchange sites are few and far between, whereas the distance moved by the adsorbed molecule is small.

The trigonal symmetry of the spiral in fig. 1 follows from fig. 11, since for spirals on the basal planes (111) we are looking on the edges of 'monomolecular layers' along the triad axis. Further, the spiral (fig. 1) is observed to be triangular at the centre, becoming hexagonal after one or two turns. This is represented in fig. 12, which is a projection on the (111) plane, remembering that the successive arms of the spiral lie on successive 'molecular layers'.

Figure 2 is another example, of which the central growth pyramids are shown enlarged in fig. 3. Here two right-handed screw dislocations close to one another each give rise to a growth pyramid with very close spacing, indicating that the growth of these pyramids took place at quite a high supersaturation. (That these features are elevations, i.e. pyramids, has been confirmed by the application of multiple-beam fringes of equal chromatic order.) These two step lines join together after about one turn (fig. 2) to form a common spiral. Furthermore, the step lines are broad and kinked and the corners concave. This is to be attributed to the subsequent etching of the crystal giving rise to a general retreat of the step lines and rounding off the corners.

* All the figures in this paper are plates, printed at the end of the issue.
Fig. 7. X 400

Fig. 8. X 300

Fig. 9. X 1000

Fig. 10. X 60

Fig. 11. Structure of haematite (Fe₂O₃) projected on (111) plane. Bigger circles represent Fe atoms and smaller circles oxygen atoms. The numbers inside the circles refer to the plane in which the atoms lie.

PLATE II.
Interaction of Growth Fronts originating from Elementary Dislocations

A striking example of the interaction of the growth fronts from a number of dislocations emerging on the face of a haematite crystal is illustrated in fig. 4. This interaction contrasts with similar observations on silicon carbide crystals. Among the points to be specially noticed are: (i) the meeting of the three edges at an angle of 120° to each other at the centre; (ii) the way in which close pairs of dislocations give rise to peninsula-like plateaus at two places round the central part; (iii) in a total of about 20 dislocations, only two or three are of the right-handed type, the remainder being left-handed; (iv) by going round the compound growth pattern once we shall descend or move up by as many steps as the effective number of dislocations enclosed within the circuit.

Curvilinear and Bunched Spirals

On one crystal face a large number of growth hills were observed to be arrayed along the edge of the crystal. These growth hills were bunched and their spiral form could not be resolved clearly. If these growth hills have originated from screw dislocations this would be the simplest case of an assembly of dislocations, and would then form a complex transition surface (Burgers 1937, 1940). On the rest of the crystal face similar spiral features (see fig. 5) have been observed. These growth spirals appear to originate from multiple dislocations and might have been expected to take on hexagonal shapes with straight edges if left undisturbed. Further, in these spirals on the three alternate edges the steps dissociate into several components, giving an appearance analogous to that found in similar observations on silicon carbide crystals (Verma 1952 a, fig. 3). This observation, together with the curvilinear and bunched spirals of high visibility (see fig. 6), shows that, like Si-C crystals, it is also possible in haematite for spirals to originate from dislocations of multiple strength, which suggests that small portions of haematite crystals may exist as polytypes.

In a few cases rounded spirals which are heavily bunched have also been observed. Figure 6 is an example in which the spiral starts at the centre as a single step line of high visibility. Over small segments of the spiral the step lines have nearly straight edges, especially near the origin; further from the origin the steps dissociate into several components. In the lower half of the figure over a dozen elementary faint step lines with the edges straight bunch together, leading to curved step lines of high visibility. This suggests that the high visibility rounded spiral of fig. 6 may be considered to originate from a dislocation of multiple strength.

In another case a very large number of dislocations (over 100), all of the same hand, originate in one region of the crystal. Groups of these step lines bunch together, leading again to steps with high visibility.

The circular type of spiral could be formed when the growth rate does not depend upon the crystallographic directions. Bunching of steps seems to facilitate the generation of curvilinear spirals.

§5. MEASUREMENT OF STEP HEIGHT

Multiple-beam interference fringes (Tolansky 1948) have been utilized for the measurement of step heights. The individual steps are rather close, and step heights are too small to be detected by the shift of the Fizeau fringes at each step.
However, as in previous work (Verma 1951), measurements were obtained by allowing a Fizeau fringe under high dispersion to pass over the peak of the pyramid, and, from the angle through which the fringe appears to bend at the peak, the average step height can be determined. Consider a pyramid formed of a series of parallel steps with straight edges, having a constant spacing \( d \) and step-height \( h \): if a Fizeau fringe passes perpendicular to the series of steps on one side of the peak, it will appear to bend through an angle \( \theta \) such that

\[
h = \frac{d \sin \theta}{(1 + 3 \cos^2 \theta)^{1/2} X} \frac{1}{2} \lambda
\]

where \( X \) is the distance between the successive Fizeau fringes for wavelength \( \lambda \). For small values of \( \theta \) (which usually correspond to small values of \( h \)) as a first approximation this reduces to \( h = \frac{1}{2} d \sin \theta/\lambda X \), which is identical with the relation used for circular spirals.

This method was used for the measurement of the step height of the spiral in fig. 1. Since the separation between the successive steps in fig. 1 gradually decreases on going away from the centre, the Fizeau fringes passing on these steps were observed to be slightly curved. For the evaluation of step height in this case the Fizeau fringe picture and the microphotograph at the same magnification were superposed, so that the exact position of the fringe was known with certainty. For measuring \( \theta \), two straight portions of the Fizeau fringe, one on either side of the centre of the spiral, were chosen and their corresponding spacing of steps \( d \) was used.

Using this method, the step height measurements for different independent trials were 12.4, 16.3, 11.2, 12.9, 17.2, 13.3, 16.0 Å.

Another measurement of average step height is possible with the fringes of equal chromatic order formed when the slit of the spectrograph was adjusted to pass over the centre of the image of the pyramid (fig. 3). This determination gave an average value of nearly 11.5 Å step height, but is subject to the error that if the slit does not pass exactly over the centre of the pyramid the value of step height will appear to be low.

These measurements, within experimental errors, show the step height to be equal to the x-ray value of the repeat unit along the trigonal axis. This spiral, therefore, is an elementary growth spiral, originating from a dislocation of unit Burgers' vector.

§6. MOLECULAR ETCH FIGURES

Very often on haematite crystal surfaces a variety of etch figures is observable. Figure 7 is an enlargement of one part showing a very large number of similarly oriented triangular figures covering the whole crystal surface. (For this observation the crystal surface was not silvered.) Sometimes, due to the overlapping of several smaller triangles, a much bigger triangular figure can be formed. Also some hexagonal figures, with a stepped structure and sometimes with a dot at the centre, can be observed in fig. 7. This observation of discrete triangular figures at different points is in accordance with the general observation that solution does not act uniformly over the whole face, but begins only at isolated points, proceeding more easily in certain directions, giving rise to regular figures. In the present case the triangular figure indicates three preferred directions of solution inclined to each other at 120°. The triangular shape of the etch figure conforms to the trigonal symmetry of the crystal face.
Growth and Etch Patterns on Haematite (Fe₃O₄) Crystals

If etch begins favourably at certain isolated points in an otherwise continuous lattice surface it would seem that there are small scale lattice irregularities at these points, since solution takes place favourably at ridges, steps, etc. The small cracks of possibly near molecular dimension assumed by Smekal can explain the appearance of etch pits at such spots. According to the ideas of Frank, dislocations which provide steps for the growth of the crystal should also promote the development of etch pits. If, indeed, these etch pits have originated on the ends of dislocations, the surface density of these pits would give the density of dislocations. In Fig. 7 this density is of the order of 10⁷/cm², which may be compared with the largest density of dislocations of the order of 10⁶/cm² observed on silicon carbide crystals (Verma 1952 a).

These triangular figures are the elementary etch figures with shallow depths, possibly of near molecular depth, a conclusion suggested by the fact that these features are not normally observable with usual bright field illumination, and some of the triangular features have a low visibility, even under phase-contrast illumination. However, because of the smallness of these features, it is not possible to apply interferometric techniques for their study. A hollow, which may be a different type of etch pit, is shown in Fig. 8. This consists of a series of roughly circular steps some of which are seen to interlace with one another. The step height is approximately 100 Å. Fringes of equal chromatic order over this feature show it to be a pit whose total depth is about 1000 Å.

Figure 9 is a further illustration; here an anticlockwise triangular spiral is surrounded by the rugged and irregular broad step lines produced by solution. The kinks in these broad step lines have again triangular or probably hexagonal contours which may be due to some local growth taking place at these step edges.

§7. GROSS FEATURES

The elementary spiral and other molecular growth features were only rarely found on the haematite crystals studied. The majority of the growth features observed were gross, consisting of triangular pyramids (Fig. 10) with broken and irregular steps of heights of a few microns with a flat triangular top with rounded corners. Three crystallographic directions inclined to each other at 120° appear as three directions of differential growth along the lines joining the three corners of the triangular feature to its centre. Similar observations have been reported previously (Maurice 1932).

§8. COMPARISON WITH SILICON CARBIDE CRYSTALS

Unlike the spirals on silicon carbide crystals, in haematite the point of emergence of the screw dislocation on the crystal surface, whence the spiral originates, is not marked by a hole, showing that in this case the core of the dislocation is not hollow. According to Frank (1951) a dislocation of Burgers' vector exceeding about 10 Å is only in equilibrium with an empty tube at its core, which gives rise to a crater at the point of emergence of the dislocation on the crystal surface. This conclusion will follow when the large strain energy near the dislocation is insufficient to overcome the surface energy which tends to close up the tube. However, for crystals where a complete dislocation is readily dissociated into a cluster of weak partial dislocations the core will not be hollow. Such is the case for the dislocations 47 Å high observed on paraffins by Dawson and Vand (1951). In haematite this does not seem to be a possible explanation. It is
likely that the magnitudes of the surface and strain energies depending upon the elastic constants of the crystal are such that the core closes up.

Whereas in most cases of silicon carbide the spirals are more closely spaced near the centre than further out, in the spiral of fig. 1 the separation between the successive arms gradually decreases with increased distance from the centre. This is attributed, not to the gradually decreasing supersaturation, but to the limitation placed by the triangular boundary enclosing the spiral. Further, in accordance with the theory, the step lines of the polygonal spirals on silicon carbide are observed to have a curvature near the centre, whereas in fig. 1 the step lines are observed to be quite straight and the corners quite sharp at the centre. The gradual rounding off of the corners and of the step lines takes place only away from the centre.

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I wish to express my thanks to Professor S. Tolansky for his interest and for first suggesting that haematite might exhibit spirals. I am grateful to the authorities of the Mineralogical Department of the British Museum for their kind loan of the crystals. This work has been carried out during the tenure of a British Council Scholarship while on study leave from the University of Delhi.

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Growth Spirals and Polytypism of Silicon Carbide Crystals

By Ajit Ram Verma
**Growth Spirals and Polytypism of Silicon Carbide Crystals**

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(Vorgetragen auf der Diskussions- und Sondertagung der Deutschen Bunsengesellschaft in Berlin am 10. Januar 1951)

The different growth features observed on the faces of silicon-carbide (Si–C) crystals are illustrated and explained. These can be divided into (A) Growth Spirals, which are of three types (1) Elementary spirals, with step heights equal to the size of the X-ray unit cell, (2) Spirals originating from dislocations of multiple strength, the step heights being a multiple of the X-ray unit cell, (3) interlaced spirals in which the step heights are a fraction of the unit cell. The microscopic studies illustrate the information about the shape of the spirals, interaction of the growth fronts and the growth pattern for a number of dislocations, density of dislocations etc. The interferometric studies of the measurement of step heights lead to an understanding of polytypism of silicon-carbide crystals. (B) Oriented overgrowths, which consist of either oriented triangular pyramids of heights up to a few wavelengths of light or oriented triangular and hexagonal molecular layers. (C) Holes, Hollows and Spots. Holes at the origin of the spirals and certain other spots observed on the step lines are illustrated.

**Introduction**

Frank (1949) pointed out that the theory as developed by Volmer, Kossel, Stranski, Becker and Döring and others for the growth of a perfect crystal face from vapour by the formation of two-dimensional nuclei would give a growth rate negligibly small at low supersaturations. This is contrary to experimental observation. This discrepancy has been explained by the theory developed by Burton, Cabrera and Frank (1949, 1951). According to this theory at finite growth rates, dislocations will be formed in a crystal and the surface of any real crystal must contain a certain number of dislocations with a screw component, terminating on the face. The crystal face, then, always has exposed molecular terraces on which growth can continue, and the need for fresh two-dimensional nucleation never arises. The theory shows that during the process of growth, the edges of these "monomolecular" layers will curl up and form a spiral centred on the dislocation. Thus on the surfaces of crystals, which have grown by this process, molecular growth pyramids should be observed.

An ideally long enough anneal would get rid of these dislocations. But in practice some may be expected to remain. Griffin (1950) was the first to observe on the prism faces of beryl, spiral marking and other complex line markings. It was shown that the step-height at these lines was less than 34 Å. Further from the behaviour of these steps he concluded that these steps are unit cell high, thus interpreting the observed spiral to be a growth spiral in accordance with Burton, Cabrera and Frank’s theory.

Silicon-carbide crystals offer excellent observational examples for the growth features of this type. Spiral markings on silicon-carbide crystals have been observed for some time past. Mennie and Sloot (1929) reported these spirals and, more recently Padurrow (1949) and Kalb and Wittborg (1951). But none of these workers have tried to offer any explanation as to the spiral formation, nor has any measurement of the step height been made.

Simultaneously with the author (1951a), Amelineckx (1951) also observed spirals on silicon-carbide crystals. Amelineckx could show that the step heights of some spirals was up to 35 Å and some probably of unimolecular steps, but no exact measurements were reported. The present paper deals with the author’s observations on these growth spirals some of which have already been reported elsewhere (1951a, b, c, d).

**Observation of the growth features on Si–C Crystals**

Many of these growth features have very small step heights (e.g. for type II crystal 15 Å see p. 272), and therefore are necessarily very faint to observe. The technique found most suitable for this observation is described elsewhere (Verma 1951d). This consists first in depositing a highly reflecting (about 90%) layer of silver on the crystals, and then examining them in reflection using phase contrast illumination.

In this paper we shall present largely the experimental observations of the different features and the details of the explanations will be found in the references indicated.

The different growth features observed on various silicon-carbide crystals can be divided as follows:

- **(A) Growth Spirals**
- **(B) Oriented overgrowths**
- **(C) Holes, Hollows and Spots**

**I. Elementary spirals**

These spirals which are usually faint to observe because of the small step heights are seldom seen with the ordinary microscope. It is therefore unlikely that this type of spiral had been seen by previous workers. As we shall see presently (see p. 272), the step heights between the successive arms of these spirals is equal to the height of
the X-ray unit cell, therefore, spirals belonging to this type originate from dislocations of unit Burgers' vector. For the study of these spirals two distinctly different techniques have been employed. These are (1) Microscopy and (2) Multiple beam interferometry. We begin first with the microscopic study.

Microscopic Study: From the microscopic studies we can derive the following information about these growth spirals:

(a) Shape of the spirals:

We consider first, the simple case of the shape observed for the growth spiral when a single screw dislocation emerges on the face of the crystal. These spirals have been observed to have shapes ranging from circular to hexagonal ones, depending possibly upon the conditions under which the growth of the crystal took place. According to Burton, Cabrera and Frank's theory when the conditions of growth are such that the "Frenkel kinks" or the exchange sites are close together and the distance moved by the adsorbed molecule large, the rate of growth would be independent of crystallographic orientation giving rise to circular spirals exemplified in Fig. (1). Polygonal spirals will be generated when the "Frenkel kinks" are few and far between and the distance moved by the adsorbed molecule small, the straight edges marking the directions of minimum growth. Figs. (2, 4) illustrate such spirals which also demonstrate the symmetry of the crystal face.

(b) Interaction of Growth Fronts: Growth Pattern for a Number of Dislocations

The growth pattern for two or more screw dislocations ending on a crystal face, is complex and depends on the properties of the growth fronts. The growth fronts starting from a single screw dislocation will spread on the surface of the crystal face in regular shapes, but the presence of a boundary or an obstruction will distort its regular shape. When the advancing growth fronts meet an obstruction, they can propagate round corners as shown in Fig. (5) at the upper end of the obstruction; this point behaving almost as a source of secondary growth fronts.

The growth fronts emitted by two sources annihilate each other where they meet, with the fusing of the two ledges. Numerous examples of this can be seen in Figs. (1), (9). When there are several screw dislocations actively emitting growth fronts, a point on the crystal face will be in the dominant field of only one of these and this alone determines the number of growth fronts passing through it. This is exemplified in Figs. (1, 9).

Sometimes among the group of dislocations emerging on the face, one of them may dominate the rest. Such a dominant dislocation, shown in the centre of Fig. (4), would determine the rate of crystal growth of the face, the other screw dislocations merely passing on the growth fronts with slight delay and in slightly modified form.

Growth patterns for two or more screw dislocations can now be explained. Considering the case of two screw dislocations of the same sign and close to each (compared to $g_s$, the radius of critical nucleus) we will have two spirals cooperating with each other giving a double spiral illustrated in Fig. (3). With the increase of distance between the two dislocations of the same sign, the
growth pattern will have the appearance of two spirals alternately spaced, so that by going round it once we shall descend by two steps.

For two dislocations of opposite sign emerging on the crystal face, the ledge starting from one terminates on the other and with the unfolding of the two spirals closed loops are generated. This is illustrated in Figs. (1, 6).

The growth pattern for three screw dislocations of the same sign cooperating with each other is shown in Fig. (7). Here, by going round the resultant curve once, we shall descend by three steps.

The growth patterns for a larger number of screw dislocations can thus be similarly explained.

The microscopic study also gives information about the curves of intersections of spirals interacting with one another, which in the simple case of two equal circular spirals is a cartesian oval as illustrated in Fig. (1). More complex cases can be seen in Fig. (9).

(c) Density of Dislocations

The density of dislocations varies widely on different specimens of silicon-carbide crystals. The largest density of dislocations observed is shown in Fig. (9) where there are $\sim 10^5$ screw dislocations per square cm.

A noteworthy point in Fig. (9) is that all the dislocations are of the same hand. Further the successive arms of any two neighbouring dislocations go on joining and fusing with one another. This will be possible only
if the step heights of the two spirals are the same i.e. the dislocations have the same strength. Thus it is characteristic that in any one region of the crystal, the dislocations are predominantly of the same sign and have also the same strength.

The relation of a step into its components is seen to take place preferentially orientations at 60° to each other. This behaviour is in accordance with the structure of silicon-carbide where the fastest layer in one orientation becomes the slowest in orientations at 60° to it.

2. Spirals Originating from Dislocations of Multiple Strength

These spirals have a much higher visibility and interferometric measurement shows that they have a relatively large step height; indeed they can often be simply seen with a microscope using bright field illumination without the need for silvering the crystal: Fig. (8) (showing only one half of the spiral) illustrates such a spiral observed on a crystal of type II. The step height between the successive arms of the spiral is nearly 620 Å as determined by the shift of the multiple-beam Fizean fringes over these steps. In Fig. (8) the edges become irregular after three or four turns from the centre. This behaviour continues for a few more turns after which the steps dissociate into five visible components. This disso-

3. Interlaced Spirals

This new type of spiral which was not predicted by theory is shown in Figs. (10), (11), (12). In each of these hexagonal spirals, at the six corners the edges fork out and meet the two neighbouring edges. This interlacing of the edges gives the hexagonal spiral a spider web structure. An explanation of this has been given by Frank (1951 a). According to this, in the stack of monolayers forming the unit cell of silicon-carbide crystals, a monolayer will be the slowest growing. Behind this monolayer, the faster growing monolayers will pile up. Since this slowest growing monolayer will be different in orientations at 60°, interlacing will occur. Further, the step height in the interlaced portion will be only
half the size of the unit cell, since over this portion each step has split up into two.

A point of special interest in Fig. (11) is that the growth fronts on moving away from the centre do not appear to remain convex, but become rather concave with a cusp in the middle. This is due to the fact that the six corners grow faster.

In some of the interlaced spirals a grouping of a certain number of steps takes place. The number of steps grouping together depends upon the number of layers in the X-ray unit cell. In the Fig. (12) grouping of seven steps together is illustrated. These seven steps together will form the complete X-ray unit cell. Thus the step height at the successive edges is only a fraction of the unit cell. An explanation of this is given elsewhere (Verma 1951 c).

Interferometric Study and Polytypism of Si—C Crystals

Multiple beam interference fringes (see Tolansky 1948) have been employed for the measurement of step heights (Verma 1951 d). Some examples of these are shown below. Fizeau fringes for \( \lambda \) 5461 passing over the spiral steps of Figs. (2), (5) are shown in Figs. (13), (14) respectively. Fig. (17) shows the fringes of equal chromatic order corresponding to Fig. (14). A study of the measured step heights leads to the understanding of 'polytypism' of silicon-carbide crystals which occur in different types — over 12 in number have now been discovered. Of these types, one is cubic; all others being based on either hexagonal or rhombohedral unit cells. All types are composed of identical layers and it is only the arrangement and number of layers in the unit cell that uniquely distinguishes them. These growth spirals demonstrate the X-ray predictions and confirm them.

As shown below in Table 1 the step heights of the growth spirals observed on the different types have a direct correspondence with the size of the X-ray unit cell. Thus these crystals, growing in the form of helicoids, have the X-ray unit cell as the crystal building unit, giving rise to the different polytypes. These spirals in which the step height is equal to the size of the X-ray unit cell are the elementary spirals, originating from dislocations with unit Burgers' vector.

Table 1

<table>
<thead>
<tr>
<th>Type of Si—C Crystal</th>
<th>Ramsdell's notation (Ramsdell 1947)</th>
<th>Lattice parameter 'c' of the unit cell</th>
<th>( a ) of the actual rhombohedral unit</th>
<th>( h ), the measured step height</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>6H; (33)</td>
<td>15.1 A</td>
<td>—</td>
<td>15 ± 2 A</td>
</tr>
<tr>
<td>I</td>
<td>5R; (32)</td>
<td>15.95</td>
<td>15.78 A</td>
<td>14 ± 2 A</td>
</tr>
<tr>
<td>VI</td>
<td>33R; (3342)</td>
<td>15.94</td>
<td>25.7 A</td>
<td>28 ± 2 A</td>
</tr>
</tbody>
</table>

(B) Oriented overgrowths on Si—C Crystals

On the faces of some silicon-carbide crystals, showing growth spirals sometimes oriented overgrowths superimposed on them can be observed. These oriented overgrowths which took place during the process of manufacture may be silica deposits or possibly the growth of silicon-carbide on itself. Fig. (16) shows one case of oriented overgrowth where two pyramids at top right corner are oriented at 60° with respect to the remainder. For the study of these overgrowths two techniques have been employed: (1) multiple beam interferometry, (2) light profile microscopy (see Tolansky 1952). Multiple beam fringes of equal chromatic order shown in Fig. (19), when the slit of the spectrograph was adjusted to pass over one of these triangular features, prove them to be elevations, i.e. pyramids. Fig. (18) shows the light profile microscope picture of another pyramid. The shift of the profile line towards the left after crossing the edge of the pyramid shows it to be an elevation above the general level. These pyramids which are seen to have a stepped structure with a crater at the top, have heights up to a few wavelengths of light and are sometimes built on platforms of similar heights. In addition to these pyramids some trigonal, hexagonal and compound figures observed on some crystals are shown in Fig. (17). By the application of multiple beam interference fringes it is shown that these figures are oriented layers of molecular thicknesses.

(C) Holes, Hollows and Spots

In general the point of emergence of the dislocation from where the spiral originates is marked by a hole.
showing that there is a hollow tube at this point. This is to be expected for dislocations of Burgers' vector exceeding about 10 Å (Frank 1951 b). Further, at the centre of the spiral originating from dislocation of multiple strength there is usually a large hole. Some of these holes are not deep and have a flat bottom (cf. Frank 1951 b). A light profile picture [see Tolansky, 1952, Fig. (8)] over one such hollow shows it to be only a few microns deep.

A group of dislocations of the same sign can develop a pit on the crystal face if the growth fronts have a difficulty in penetrating the group itself. Such a case is exemplified in Fig. (20), where over 50 hexagonal step lines originate from a large hole. The hole is too deep for measurement by light profile microscopy.

In addition to these holes, sometimes, certain spots are seen on the faces of silicon-carbide crystals. Fig. (21) shows certain spots observed on the step lines. These spots vary in size and give the step lines a kinked appearance.

Yet another type of spot can be seen in Fig. (9). The centre of every spiral is marked by a somewhat hexagonal spot. Similar spots unattached by spiral step lines and sometimes arranged along a line are seen in Fig. (9).
Frank (private communication) suggests that these may be ends of edge dislocations.

It is a pleasure for me to express my thanks to Professor S. Tolansky for his interest and encouragement in the course of the work. This work has been carried out during the tenure of a British Council Scholarship while on study leave from the University of Delhi.

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Transmission-like Reflexion Fringes in Birefringent Crystals

It has long been known that the suppression of the first beam in multiple-beam reflexion interference fringes produces a transmission-like pattern. This was established in 1907 by Lummer\(^1\), and was recently applied by Bruce\(^2\), who cut out the first beam by a knife edge. In high-magnification studies, this obscuration of the lens may lead to diffraction anomalies (Tolansky\(^3\)).

In the special case of thin birefringent crystals, transmission-like systems can be obtained in reflexion by a simple optical device. If a birefringent tabular crystal is grown on a silvered optical flat and the upper surface is then silvered, we have a birefringent medium between silvered surfaces capable of producing familiar multiple-beam localized Fizeau fringes, and in reflexion such a system gives dark fringes on a bright background. Fig. 1 gives an example using the crystal stearic acid. Owing to birefringence the fringes are double, the components being mutually perpendicularly plane-polarized. However, if illuminated with plane-polarized light and the reflected system is viewed through an analyser, it is clear that, without any change of the numerical aperture, the first reflected beam can easily be cut out, since this is the only beam in the interference system which does not go through the crystal, and hence its

![Image of fringes](image-url)
plane of polarization differs from that of the complete multiple-beam system. Fig. 2 shows the appearance of the pattern obtained by thus suppressing the first beam. Here the two components are polarized in the same plane. It is clear that this simple technique permits not only the total suppression of the first beam but also its partial suppression if wished. Hence it is possible to study systematically the continuous change in the appearance of the fringe pattern as the contribution of the first beam is successively varied.

Detailed analysis of the system will be published elsewhere.

I wish to thank Prof. S. Tolansky for his interest and Miss P. M. Reynolds for valuable discussion. This work is being done during the tenure of an I.C.I. Fellowship while on study leave from the University of Delhi.

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Interferometric Studies of the Growth of Stearic Acid Crystals and their Optical Properties

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Abstract. On the basal planes of stearic acid crystals, grown from solution, growth spirals observed by optical and phase contrast microscopic techniques are reported. These growth spirals are in accordance with the theory of Burton, Cabrera and Frank. For the measurement of spiral step-heights multiple-beam interference methods were used, including a modified multiple-beam interference method, which is described. The minimum step-height found was 46.3 ± 0.8 Å, which agrees with the x-ray repeat unit. In addition, step-heights which were integral, as well as half integral, multiples of this unit were found. By interferometric methods the refractive index was found to be 1.42 ± 0.04 and for the two types of crystal rhomb observed the birefringence for directions of vibration parallel to the 'a' and 'b' axes was approximately 0.018 and 0.015 respectively for λ = 5461 Å.

§1. Introduction

Since Burton, Cabrera and Frank (1949, 1951) proposed a screw dislocation mechanism for the growth of crystals from vapour, observations of the related growth spirals have been reported on several ionic, homopolar, molecular and metallic crystals. Among these observations measurements of growth spirals with step-heights equal to a parameter of the x-ray unit cell have been reported on beryl (Griffin 1950), the long chain paraffins (Dawson and Vand 1951, Dawson 1952), silicon carbide (Verma 1951 a, b, Amelinckx 1951), and haematite crystals (Verma 1952). On cadmium iodide (Forty 1952) all the measured spiral step-heights were found to be multiples of the x-ray unit, whilst on other crystals, e.g. gold (Amelinckx 1952), the existence of dislocations of multiple strength has been inferred from the visibility of the steps. The only crystal upon which dislocations of both unit and multiple strength have been measured is silicon carbide.

In previous observations upon the growth of long chain organic molecules only an electron microscopic technique has been applied. The spiral step-heights were found to be only equal to the x-ray unit. In the present study upon the growth of crystals of the long chain molecule stearic acid [CH₃(CH₂)₁₇COOH], optical and interferometric techniques have been applied. A preliminary account has already been given elsewhere (Reynolds and Verma 1953). The following is a detailed account, in part I of the growth properties, and in part II of the optical properties, of small, nearly perfect crystals.
PART I

§ 2. PREPARATION OF STEARIC ACID CRYSTALS

The crystals were grown from a dilute benzene solution of stearic acid (B.D.H. pure laboratory reagent, concentration 0.3% by weight). Thin crystal plates formed if a small drop of this solution was placed upon a cooled glass flat and the rate of evaporation suitably restricted by enclosing it. At higher rates of evaporation dendritic chains of small crystals were obtained, whilst if the droplet evaporated rapidly from a warmed glass plate, features resembling circular spirals were obtained (fig. 1)*. An examination of a line section across these features by the dark slit profile microscope (Tolansky 1952) has shown that the edges of the circular spirals are ridges of material, and that the surface between successive turns of the spiral is not plane, but has an appreciable curvature. These are, therefore, 'evaporation figures', and are to be distinguished from growth spirals.

When the crystals were grown upon a silvered glass surface for interferometric examination it was found that the solvent, benzene, did not appreciably increase the absorption of the silver layer.

§ 3. CRYSTAL STRUCTURE

Stearic acid is polymorphic (Piper, Malkin and Austin 1926) and forms monoclinic prismatic crystals. The crystal molecule has a chain of carbon atoms arranged in a zigzag manner, the number of carbon atoms in this chain being equal to that in the chemical molecule. The chain axes all lie in the symmetry plane (ac plane), parallel to the c-axis and inclined to the basal plane (ab plane) at an angle 48° 38'. Müller (1927) reported one form with lattice parameters a = 5.546 Å, b = 7.381 Å, c = 48.84 Å, β = 63° 38' so that c sin β = 43.76 Å. Other forms have been reported with the longer layer spacings equal to 46.6 Å, 43.75 Å, 39.75 Å (Francis, Collins and Piper 1937), 41.5 Å (Thibaud and Dupré la Tour 1930).

§ 4. MICROSCOPIC OBSERVATIONS OF GROWTH FEATURES

For the observation of growth features the crystals were silvered by thermal evaporation under high vacuum, and examined with bright field illumination, or with a positive phase contrast equipment. All the growth spirals were observed on the basal planes of the crystals, but there were many crystals upon which there was no evidence of any surface structure. Numerous examples of growth features originating from one and a larger number of screw dislocations were observed, including the interaction of their growth fronts (e.g. formation of closed loops in fig. 7). Their behaviour is similar to features already reported on other crystals, therefore observations were concentrated upon growth features which are peculiar to stearic acid.

The observed growth spirals could be divided into two types, firstly, rectilinear spirals having the symmetry of the crystal face and secondly curvilinear spirals.

Figure 2 shows a spiral of the first type. In such a rectilinear spiral the growth edge is parallel to the edges of the crystal plate which correspond to the close-packed [110] directions. This is shown diagrammatically in fig. 3, which

* For figs. 1, 2, 4, 5, 6, 7, 8 see Plate.
represents the projection of a layer of long chain molecules on the \((ab)\) plane (neglecting the inclination \(\beta\)). Figure 4 is another example. In fig. 2 the successive turns of the growth edge are more widely spaced towards the centre yet remain parallel to the edges of the crystal plate. This indicates that the last phase of growth occurred under lower supersaturation or at a higher temperature. The final section of the growth edge is almost parallel to the \(a\)-axis, which after the [110] is the next most close-packed direction. It is probable, therefore, that some movement of the dislocation occurred after growth had ceased.

In the second type of spiral the obtuse, and also sometimes the acute, angle between the growth edges became rounded, giving the spiral a 'leaf' shape. Opposite diagonals of these spirals were not generally collinear but were inclined at an angle usually less than 10° (see fig. 5). Numerous growth spirals were observed in which the spiral step-edges were not only curved but also inclined at a fairly large angle to the boundary of the crystal plate, which indicates that although growth spirals may take the symmetry of the crystal face, they do not necessarily control it.

A characteristic feature observed on these crystals was that the growth edges on opposite sides of the spiral with respect to the \(b\)-axis (bisectrix of acute angle of rhomb) were dissimilar; on one side the edges were generally regular and smooth, whilst on the other side they were irregular, as illustrated in fig. 5. This effect is understandable since the axes of the long chain molecules are inclined at an angle to the basal plane and the \(a\)-axis, so that in one half of the crystal with respect to the \(b\)-axis the exposed molecular ledge makes an acute angle with the basal plane, whilst in the other half of the crystal this angle becomes obtuse. The van der Waals binding forces between neighbouring chains are therefore not the same for every growth edge in the [110] directions, and preferential etch may occur.

The visibility of the multimolecular steps on stearic acid was markedly less than that of steps of similar heights on silicon-carbide crystals, in which the edges are very much more regular.
In almost every case it was observed that the point of emergence of the dislocation was at the centre of the crystal plate; this is to be expected in an isolated single crystal since a dislocation line is effectively under tension (Frank 1949). The point of emergence of the dislocation was occasionally marked by a regular dot which is probably due to the nucleation of the crystal by an impurity.

The existence of oriented overgrowth on certain crystal plates was also established.

§ 5. INTERFEROMETRIC METHODS

(i) Multiple-Beam Fizeau Fringes

An external optical flat could only be used with a few of the larger crystals on which the growth steps could be clearly resolved at magnifications less than \( \times 200 \). Using multiple-beam Fizeau fringes (Tolansky 1948), it was convenient to adjust the tilt of the silvered optical flat until the fringes contoured the edges of the growth spiral. Assuming that the steps were all of equal height \( h \), the step-height is then given by

\[
h = \frac{\lambda}{2n_1},
\]

where \( \lambda \) is the wavelength of the monochromatic light, and \( n_1 \) (not necessarily integral) the number of growth steps between the intensity peaks of two successive fringes. Entry 1 in table I is an example of the application of this method, and is the most accurate value obtained in this study.

Since the crystals were usually small it was necessary to examine them at higher magnifications. A thin film technique (Tolansky and Omar 1952) was therefore used which indicated that certain step-heights were multiples of the x-ray repeat unit.

(ii) Multiple-Beam Internal Interference Fringes

For a more accurate determination of step-height interference fringes formed by internal reflection between the two surfaces of the crystal were used. Forty (1952) has used the two-beam internal interference fringes for CdI\(_2\) crystals. This method has been improved utilizing multiple-beam fringes by silvering opposite faces of the crystal, a method similar to that used by Tolansky (1948) for mica. Therefore the crystals of stearic acid were grown on a silvered optical flat (\( \lambda/40 \)), and their upper surfaces were also silvered. It was found that the crystal surface in contact with the flat did not generally acquire any growth features, and spirals only developed on the exposed surface; only such crystals were selected for the measurement of step-height. The Fizeau fringes formed between the flat base and ‘vicinal faces’ of any growth pyramids contour the growth steps and, if these fringes are sufficiently sharp, appear double, due to the birefringence of the crystal (see fig. 6), a feature which cannot be seen in two-beam fringes. Formula (1) now becomes

\[
h = \frac{\lambda}{2n_2},
\]

where \( n_2 \) is the number of steps between any two successive fringes having the same plane of vibration, and \( \mu \) is the corresponding refractive index for light of wavelength \( \lambda \). Since the peak of the Fizeau fringe may not occur on a step along a selected radial line \( n_2 \) will not necessarily be integral. It is then necessary to add to (or subtract from) the integral number of steps between two successive fringes a small fraction, as done by Forty (1952). However, multiple-beam fringes have shown that the surface of the stearic acid crystal is not perfect to within a few ångströms.
§ 6. DISCUSSION OF THE MEASURED STEP-HEIGHTS

A large number of measurements of step-heights have been made; of these the most accurate and important ones are given in table 1. Many higher steps have been measured, but in these cases, for step-heights greater than four times the x-ray repeat unit, the error in neglecting the fractional part of \( n \) is greater than 10\%, and it cannot be established whether these steps are an integral multiple of a unit.

### Table 1

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \mu )</th>
<th>( h (\AA) )</th>
<th>( \psi )</th>
<th>Multiple</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 58 &lt; n &lt; 60 )</td>
<td>1.0</td>
<td>46.3 ± 0.8</td>
<td>—</td>
<td>( 1 \times 46.3 )</td>
<td>Air film</td>
</tr>
<tr>
<td>( 29 &lt; n &lt; 30 )</td>
<td>1.42</td>
<td>65.2 ± 0.9</td>
<td>74\°</td>
<td>( 1 \frac{1}{2} \times (43.5 ± 0.6) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 2 \times (49.3 ± 1.2) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 2 \frac{1}{2} \times (39.5 ± 1) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 3 \times (32.9 ± 0.8) )</td>
<td></td>
</tr>
<tr>
<td>( 19 &lt; n &lt; 20 )</td>
<td>1.42</td>
<td>98.7 ± 2.5</td>
<td>74\°</td>
<td>( 2 \frac{1}{2} \times (46.5 ± 4) )</td>
<td>Fig. 4</td>
</tr>
<tr>
<td>( 32 &lt; 2n &lt; 33 )</td>
<td>1.42</td>
<td>118 ± 2</td>
<td>74\°</td>
<td>( 3 \times (39.3 ± 1) )</td>
<td></td>
</tr>
<tr>
<td>( 20 &lt; n &lt; 21 )</td>
<td>1.0</td>
<td>133 ± 3</td>
<td>—</td>
<td>( 3 \times (44.3 ± 1) )</td>
<td>Air film</td>
</tr>
<tr>
<td>( 10 &lt; n &lt; 11 )</td>
<td>1.42</td>
<td>183 ± 9</td>
<td>74\°</td>
<td>( 4 \times (45.7 ± 2.3) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 4 \times 49 ; 4 \frac{1}{4} \times 43.6 ) Fringes of equal chromatic order</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 5 \times 39.2 )</td>
<td></td>
</tr>
</tbody>
</table>

The step-heights in table 1 may be divided into three types: (i) those equal to the x-ray unit, (ii) a multiple, and (iii) an odd half-integral multiple of this unit.

The occurrence of step-heights equal to an integral multiple (including unity) of the x-ray repeat unit are readily understood as follows: in stearic acid there is an active carboxyl group at the end of the molecular chain which results in the association of the molecules in pairs and gives rise to a double-layer crystal structure as shown:

\[
\text{CH}_3 \cdot \text{CH}_2 \ldots \cdot \text{CH}_2 \cdot \text{C} = \text{O} | \text{OH} \quad \text{OH} \quad \text{O} \quad \text{CH}_3 \cdot \text{CH}_2 \ldots \cdot \text{CH}_2 \cdot \text{CH}_3.
\]

Although the binding forces between the carbon atoms in a chain are homopolar, the parallel chains are bound laterally by relatively weak van der Waals forces. Dislocations of integral multiple strength are therefore readily created by the slipping of long chain molecules past one another.

The most interesting step-heights are entries 2, 3, 4, and 7 in table 1, which may be interpreted either as integral multiples of different polymorphs or as half-integral multiples of a known x-ray unit. But in entry 2 the step-height is

\[
(65.2 ± 0.9) \AA = 1 \frac{1}{2} (43.5 ± 0.6) \AA = 2 (32.6 ± 0.45) \AA.
\]

No polymorph of stearic acid with long layer spacing equal to 32.6 \( \AA \) is known, and it is unlikely for a fatty acid with carbon content C_{16}. Furthermore it has been observed that stearic acid crystals grown from benzene always had the long layer spacing of 43.75 \( \AA \) (Francis, Collins and Piper 1937), which therefore supports the conclusion that the step-heights are odd half-integral multiples of the x-ray unit. It may be interpreted, then, that under certain circumstances single molecules can occur without pairing, but so far no step-height equal to half the x-ray unit has been found.
PART II
§ 7. Optical Properties

Stearic acid, which is monoclinic, will be expected to be an optically biaxial crystal. Of the three directions of vibration of the optical ellipsoid, one coincides with the symmetry axis $b$, the other two lying in the symmetry plane $ac$ (Thibaud and Dupré la Tour 1930). When examined between crossed nicols, the rhomb-shaped crystals show mutually perpendicular extinction directions.

The refractive index of a small crystal (size $\sim 200\mu$) has been determined interferometrically: comparing eqns. (1) and (2), $\mu = n_1/n_2$. In one growth feature (entry 1 in table 1) it was found $59 < n_1 < 60$ and the corresponding internal interference fringes gave $41 < n_2 < 42$, from which $\mu = 1.42 \pm 0.04$.

Two types of crystal rhombs of stearic acid were observed: (i) with the acute angle $\psi$ between $[110]$ and $[1\bar{1}0]$ measured in the $(001)$ plane equal to $74^\circ$, and (ii) with this acute angle $\psi$ equal to $56^\circ$ (fig. 7). These crystals differ in their optical properties.

(i) $\psi = 74^\circ$.

The refractive index for a vibration parallel to the $b$-axis (called $\mu_b$) is less than $\mu_a$. This is concluded from the doubled Fizeau fringes (fig. 6) in which the $b$ vibration corresponds to the component nearer to the centre of the growth hill, and hence to a larger interferometric gap and a smaller refractive index. It is confirmed by fringes of equal chromatic order in which the vibration parallel to $b$ (marked as $b$ in fig. 8) is the component which is towards the shorter wavelength end of the spectrum. This is to be expected since the $b$ vibration is perpendicular to the chain length, and should therefore give the minimum refractive index.

(ii) $\psi = 56^\circ$.

In contrast to the above, the refractive index for the vibrations parallel to the acute bisectrix is greater than for the vibration perpendicular to it.

The birefringence $d\mu$ is obtained directly from the fringes of equal chromatic order and, as shown by Tolansky (1948), is given by $d\mu/\mu = d\lambda/\lambda$, where $d\lambda$ is the wavelength separation between the two components of the same order. In table 2 the fractional birefringence $d\lambda/\lambda$ (for the shorter wavelength vibration) and an approximate value of the birefringence $d\mu$ is given for the two types of crystal. It was assumed that $\mu = 1.42$.

<table>
<thead>
<tr>
<th>Crystal type</th>
<th>$\lambda (\AA)$</th>
<th>$d\lambda/\lambda$</th>
<th>$d\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi = 74^\circ$</td>
<td>5703</td>
<td>0.013</td>
<td>0.0185</td>
</tr>
<tr>
<td></td>
<td>5614</td>
<td>0.014</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>5548</td>
<td>0.013</td>
<td>0.0185</td>
</tr>
<tr>
<td></td>
<td>4700</td>
<td>0.015</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>4543</td>
<td>0.013</td>
<td>0.0185</td>
</tr>
<tr>
<td>$\psi = 56^\circ$</td>
<td>5870</td>
<td>0.010</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>4425</td>
<td>0.011</td>
<td>0.016</td>
</tr>
</tbody>
</table>

It can be calculated from the fringes of equal chromatic order shown in fig. 8 that the thickness of the crystal is of the order of five wavelengths of green light, and in a few cases we have measured the birefringence of even thinner crystals,
but then the fringe width in terms of wavelengths is increased, so that the accuracy
deprees. It is interesting to compare these values of birefringence with the
value of $1.535 - 1.510 = 0.025$ reported by Thibaud and Dupré la Tour (1930).

§ 8. CONCLUSION

It is shown that stearic acid crystals can grow in the form of a spiral originating
from a screw dislocation. Multiple-beam interference techniques have been
applied which show that the spiral step-heights are equal to integral or half-
integral multiples of the x-ray repeat unit, within the limits of experimental
error. These interferometric techniques have also given the refractive index
and birefringence of crystals having a thickness of only a few wavelengths of
light.

ACKNOWLEDGMENTS

We have great pleasure in thanking Professor S. Tolansky for his kind
interest and for the facilities of his laboratory during this work. One of us
(A. R. V.) wishes to take this opportunity of expressing his thanks for the Imperial
Chemical Industries Fellowship of the University of London, and to the University
of Delhi for an extension of study leave.

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Growth and Optical Properties of Stearic Acid Crystals

We have applied optical and interferometric techniques to stearic acid crystals \((\text{CH}_3(\text{CH}_2)_n\text{COOH})\) which were grown from a dilute solution in benzene of the compound. Tabular crystals were produced by slow evaporation of a drop of this solution placed upon a clean, cooled microscope slide. Many spiral features have been observed upon the basal planes by examining the silvered crystals under phase-contrast illumination. These are growth spirals in accordance with the dislocation theory of Burton, Cabrera and Frank.

Fig. 1 (top) shows a growth spiral and a terminated line which can be interpreted as a ledge between the point of emergence of the screw dislocation on the underside of the crystal and the crystal boundary.

In addition, by the rapid evaporation of a drop of solution upon a warmed glass plate, circular spiral patterns have been obtained. These 'evaporation figures' have not been identified as growth spirals. The existence of oriented overgrowth has also been established.

Stearic acid is a monoclinic crystal with lattice parameters \(c = 48.84 \text{ Å} \); \(\beta = 63^\circ 38'\). Since the crystals were small (approximately 200 μ), the multiple-beam surface topography interference fringes generally obtained by matching the silvered crystal against a silvered optical flat could not easily be employed to determine the spiral step-height. It was found satisfactory to use the interferometric techniques formerly used with thin sheets of mica. The multiple-beam interference fringes produced by the internal reflexion between the two silvered surfaces of the crystal were thus found more convenient and accurate for the measurement of step-heights. We have made a large number of measurements and found that most of the step-heights are small integral multiples of \(45 \pm 5 \text{ Å}\), which within experimental errors agree with the predicted X-ray repeat unit.

Fig. 2 (middle) illustrates the multiple-beam reflexion Fizeau fringes given by a doubly silvered crystal plate. The fringes are contouring a spiral so that they are parallel to the growth edges and, being very sharp, appear double owing to the birefringence of stearic acid. The two components are polarized at right-angles to each other. In Fig. 3 (bottom), the fringes of equal chromatic order for a line section across the peak of this growth spiral are shown; the birefringence of the crystal is again obvious. These fringe patterns permit an accurate determination of the birefringence and also other optical properties of the crystal, in a manner already established.
A more detailed account of these investigations has been communicated elsewhere. We thank Prof. S. Tolansky for his interest and encouragement in this work. One of us (A. R. V.) wishes to express his thanks for the Imperial Chemical Industries Fellowship of the University of London, and to the University of Delhi for an extension of study leave.

Note added in proof. Since then, in addition to a step-of unit height equal to 46.3 ± 0.8 Å, we have measured steps which are odd-half integral multiples of the X-ray repeat unit.

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LETTERS TO THE EDITOR

A Further Note upon the Growth and Optical Properties of Stearic Acid Crystals

In a recent paper (Verma and Reynolds 1953) two types of stearic acid crystals were reported which differed in their optical properties and their edge (or profile) angle. It is possible to identify these two types as the B and C polymorphs (after Piper et al. 1926) as a result of the determinations of the $a$ and $b$ axial dimensions by Schoon (1938) and Anderson and Dawson (1953). The reported optical properties can also be clarified.

For the B polymorph Anderson and Dawson give $a = 5.64\AA$, $b = 7.59\AA$, whilst for the C form $a = 9.11\AA$ and $b = 4.82\AA$. The angle between the [110] and [110] directions is $2\tan\left(\frac{b}{a}\right)$ which for the B form of the acid leads to a profile angle (acute) $73^\circ 14'$ and for the C form $55^\circ 45'$. These profile angles agree, within experimental error, with the values reported by us, and also with the observations of Müller (1927), Thibaud and Dupré la Tour (1930) and Schoon (1938).

It then becomes apparent that in the B form the $b$ direction bisects the acute angle between the edges of the (001) face and in the C form the obtuse angle. Therefore in both the B and C forms of the crystal the vibration parallel to the $b$ axis, which is the symmetry axis, has a smaller refractive index than the vibration parallel to the $a$ axis. This is to be expected since the $b$ direction is perpendicular to the chain-length. The small difference in the magnitude of the birefringences, namely 0.018 and 0.015, is due to the change in the axial ratios and the monoclinic angle.

From their study of growth steps on stearic acid and other long-chain compounds using the electron microscope Anderson and Dawson (1953) conclude that in stearic acid the spiral steps are bimolecular, in accordance with the nature of this acid in solution. Using an optical microscope we have reported growth steps which are integral multiples of the bimolecular unit. These may be considered to be due to a group of bimolecular steps which were not resolved. However, steps which were odd half-integral multiples of the bimolecular unit, i.e. $(65.2 \pm 0.9)\AA = 1.5 (43.5 \pm 0.6)\AA$, were also found. These cannot be interpreted as any grouping of unit steps. Further step-height measurements are being undertaken to clarify this.

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9th July 1953; in final form 4th Sept. 1953.


*A.C.I. Research Fellow.
Interferometric Studies of the Slip Phenomena in the Growth of Palmitic Acid Crystals

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Palmitic acid crystals grown from solution have been studied by the application of multiple-beam interferometry and phase-contrast microscopy. Joining with one another of crystal monolayers and other crystal plates having a series of growth steps have been illustrated. Of special interest are the patterns which show that the internal slip of molecular layers which has been reported by Anderson & Dawson for only monomolecular layers can take place over distances ~ 1000 Å. The dislocations taking part in this slip would be those with multiple Burgers vector and thus these observations are evidence of the movement of large dislocation groups.

Introduction

In a series of papers Dawson & Vand (1951), Dawson (1952) and Anderson & Dawson (1953) have studied, by the electron-microscopic techniques, the spiral growth of long-chain organic molecules, in accordance with the dislocation theory (Burton, Cabrera & Frank, 1951). Some micrographs of n-nonatriacontane, C_{36}H_{74}, showed a striking feature that an internal slip of paraffin layers had taken place when the crystal settled on the surface of the microscope mount. As a result, when a thin crystal monolayer settled on another crystal plate having a series of growth steps the underlying growth steps were found to be imprinted on the monolayer. However, this transmission of the lower growth pattern through the crystal was observed to occur only for unimolecular layers and not for any thick layers. The spiral growth steps were also found to be equal to the molecular units of the substance in solution, and no multimolecular growth steps were encountered. Using interferometric techniques Verma & Reynolds (1953) reported the existence of spiral growth steps which are integral multiple (including unity) of the X-ray unit cell. This therefore suggested that by using optical techniques the multimolecular internal slip of layers could possibly be observed for substances exhibiting multimolecular growth steps. For this purpose palmitic acid, CH_{3}(CH_{2})_{14}COOH, was chosen. This optical study of the growth of palmitic acid, with evidence of the slip over large distances, is reported here.

Observations and discussion of results

On the basal planes (a b face), which develop predominantly, growth spirals could be observed. Of particular interest were the patterns which arise when two crystals are in contact with one another. These observations are divided into two types: (1) 'crystal layers' with uniform thickness showing no visible growth structure; (2) 'crystal plates' with a series of growth steps. The different possibilities for the joining of the crystals are (a) a crystal layer meeting or touching another layer, (b) a crystal layer settling on another layer, (c) a crystal layer settling on a crystal plate and vice versa, and finally (d) a thick crystal plate falling on another, a case which is trivial since one merely obstructs the view of the other. The following figures illustrate these possibilities.

The simplest case of crystal layers meeting one another is exemplified in Fig. 1. As growth edges advancing on the glass substrate touch each other, they fuse with one another, leaving an unbroken crystal level without any steps. This is possible only if all the layers are monolayers. Hence it may be concluded that nucleation of palmitic acid crystals takes place as monolayers which take up crystallographic shapes. At the time when growth ceased, advancing growth fronts enclose figures, e.g. a triangle. Observations of 'growth trigons' on octahedral diamond faces have been explained similarly by Tolansky & Wilcock (1946).

The next case (b) is illustrated in Fig. 2, which shows a phase-contrast micrograph of two partly superimposed crystal layers (doubly silvered). The crystal layers coincide exactly in orientation when settling on one another; such parallel orientations should be favoured on energy considerations.

The cases of a crystal layer falling on a crystal plate and vice versa are to a very large extent equivalent, and are shown in Figs. 3 and 4. Fig. 3 shows the...
multiple-beam Fizeau fringes formed by internal interference for the crystal which has been silvered on both sides. Here a small crystal layer has settled down on a crystal plate having a series of growth steps several hundred Ångström units high. The fringes are contouring the growth steps which shows that the crystal plate is sitting flat on the glass substrate. The step structure of the underlying crystal plate has been imprinted on to the layer, showing that it has taken the contours of the growth steps. From the shift of the series of fine Fizeau fringes running across the boundary of the crystal layer, it is seen that its thickness is about 1000 Å. Another very clear example of this is shown in Fig. 4. Here one crystal has fallen partly covering another. The crystal in the right half of the figure is a crystal layer of uniform thickness, since it shows uniform tint, and its thickness is about 800 Å, as deduced from the shift of the fringes across the boundary of the crystal layer. The growth steps on the crystal plate are about 250 Å high, as shown by the fringes for λ = 5461 Å. Assuming that the crystal layer has fallen on the crystal plate, then it has acquired the step structure of the underlying crystal surface.

Consider now the alternative that in Fig. 4 the crystal plate with the step structure has fallen on the crystal layer. Since the interference fringes are contouring the growth edges, that part of the crystal plate not superimposed on the crystal layer is lying flat on the glass substrate. This could have happened only if the crystal plate has slipped down the thickness of the crystal layer (≈ 800 Å) over the superimposed part along the three edges of the underlying crystal layer. Thus in both the cases, whether the crystal layer is on top of the crystal plate or vice versa, owing to the internal slip of the molecular layers, the same configuration of the compound crystal is left behind. Since the density of the crystal is less than that of the solution, either alternative is permissible, since the crystal monolayer will not sink down as soon as it is formed.

A similar transmission of growth layers through a monomolecular layer of n-nonatriacontane was reported by Anderson & Dawson (1953). This transmission of growth layers arises owing to the internal slip of the molecular layers. These authors, however, found that the process of slipping was confined only to monomolecular layers, but the above interferometric observations show that slip of molecular layers can be transmitted through fairly thick (~ 1000 Å) crystal layers.

The model used to explain the slip in real crystals is the movement of dislocations. The dislocations that take part in the unit slip are those with the unit Burgers vector, and only unit dislocations were observed in the electron-microscopic studies. Examples of unit slip on silver crystals have been explained similarly (Forty & Frank, 1953). Obviously the slip through these comparatively large distances observed on palmitic acid crystals is due to the dislocations with multiple Burgers vector. A study of the spiral growth pattern and the measurement of step heights by the multiple-beam interference fringes has shown the step heights to be integral multiple of the X-ray unit cell, so that the dislocations of multiple Burgers vector are actually formed on palmitic acid crystals. Thus these observations afford the evidence of the movement of large dislocation groups. The stresses under which this movement occurs are not well understood but it appears that the movement of even large dislocation groups can take place comparatively easily for long chain organic molecules.

It is a pleasure for me to express my thanks to Prof. S. Tolansky, F.R.S., for the facilities of the laboratory and the encouragement during the course of the work. I am indebted to my friend Dr R. C. Mehrotra for a supply of redistilled palmitic acid and to Messrs Price’s (Bromborough) Limited for the supply of very pure palmitic acid. This work has been carried out during the tenure of an Imperial Chemical Industries Research Fellowship of the University of London, while on study leave from the University of Delhi.

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Fig. 1. Phase-contrast micrograph of doubly silvered crystals showing the fusing of the advancing monolayers. × 340.

Fig. 2. Phase-contrast micrograph of doubly silvered crystals in which one crystal layer has settled on another. × 230.
Fig. 3. Multiple-beam Fizeau fringes for \( \lambda = 5461 \text{ Å} \), where a crystal layer \( \sim 1000 \text{ Å} \) thick, after settling on a crystal plate, has taken the contours of the underlying growth steps. \( \times 150 \).

Fig. 4. Fizeau fringes for \( \lambda = 5461 \text{ Å} \), illustrating the joining of a crystal layer showing uniform tint and a crystal plate with a series of growth edges each 250 Å high. \( \times 180 \).
Interferometric Observation of Mosaic Structure on the (111) Face of a Single Crystal of Germanium

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MS. received 25th November 1953

Recently Avery and Clegg (1953) have measured the optical constants of a highly perfect single crystal of germanium grown from the melt at Marconi Wireless and Telegraph Co. Limited, Chelmsford. It was therefore thought to be of interest to study the surface of the same crystal by interferometric techniques, and the author is indebted to Dr. I. Cressell for making available the crystal for this study.

The ingot of this germanium crystal has an exceptionally well developed large sized (nearly 5 mm across) hexagonal-shaped (111) face which appears quite smooth and plane when viewed under a metallurgical microscope using bright field illumination. This natural (111) face, without any polishing or chemical etching, was therefore examined by a vertical positive phase-contrast microscope. The appearance of the surface is shown in figure 1†, where the entire crystal face is seen to be covered with a mosaic structure, the figures being hexagonal in shape, varying in size, and also observed sometimes to be arranged along a row. To study these features interferometrically, the crystal surface was matched against a silvered glass flat. However, to save the crystal face from subsequent cleaning by hydrogen peroxide, which may etch the surface, it was not silvered. The multiple-beam interference fringes so obtained are, however, fairly sharp, due to the high reflectivity of the germanium crystal. Figure 2 shows the multiple-beam Fizeau fringes passing over the crystal face. Due to the high sensitivity of these fringes to reveal the surface topography, the mosaic structure is clearly visible within the width of the fringes. In order to decide whether these features are elevations or depressions over the general level of the crystal, and to get the magnitude of the height or depth, a line section was selected by a spectrograph slit and the fringes of equal chromatic order (Tolansky 1948) were utilized. Figure 3 shows such a line section, which was adjusted so that at

* I.C.I. Research Fellow.
† Figures 1, 2, 3 are printed in Plate, at end of issue.
its middle part it passed over one of the deepest hexagonal mosaic figures. The V-shaped fringes, convex towards the red end of the spectrum, indicate the hexagonal figure to be a depression, and in this particular case the depth is approximately 900 Å. Other shallower features over which the line section passes give the fringe a wavy appearance. These depressions are not flat-bottomed but are formed by sloping faces; in the above case the slope is about 10°. Indeed, in the micrograph (figure 1) it can be seen that these hexagonal figures have a structure with a point at the centre from whence the sloping surfaces radiate.

The mosaic boundaries can be interpreted in terms of dislocations as a row or lattice of dislocations as was first proposed by Burgers (1940). Evidence that the lineage boundaries consist of a row of dislocations has recently been produced by Vogel et al. (1953) who studied the boundaries between nearly perfect crystals of germanium grown from the melt, the growth direction being (110). But the crystal had to be etched in a suitable reagent to reveal the end points of the edge dislocations which serve as nuclei for etch pits (Lacombe and Beaujard 1947). However, it is possible to see the mosaic structure on the natural surfaces of a highly perfect germanium crystal by interferometric techniques without the need for etching the surface.

ACKNOWLEDGMENT

The author wishes to thank Professor S. Tolansky for the facilities of the laboratory and his interest.

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Figure 1. $\times 100$. (Note. The scratches visible in the photograph are due, not to polishing, but to continuous handling of the crystal by different observers.)

Figure 2. $\times 30$.

Figure 3. $\times 45$. 

4358 Å $\rightarrow$ 5461 Å
A phase-contrast microscopic study of the surface structure of blende crystals

BY

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A phase-contrast microscopic study of the surface structure of blende crystals.

(With Plates III and IV.)

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[Communicated by Dr. G. F. Claringbull; taken as read 26 January 1956.]

Summary.—The surface structure of blende crystals from Joplin, Jasper County, Missouri, U.S.A., has been explored by the application of phase-contrast microscopy and light-profile microscopy. Attention has been specially directed to the small-scale features with thicknesses (or depths) of molecular dimensions.

Some growth features of special interest were observed. A large number of beautifully developed growth spirals were observed on the tetrahedral face of a blende crystal. These are in accord with the dislocation theory of Burton, Cabrera, and Frank. The high visibility of these growth spirals is possibly due to the preferential deposition of some impurity, or etching, which also gives a mottled appearance to the entire surface. In addition, an extensive microscopic structure has been observed on some crystal faces. Triangular growth terraces and markings are seen, both orientated parallel to the edges of the crystal. Some triangles, inverted with respect to the latter, have been explained on similar lines to the well-known ‘growth trigons’ on the octahedral faces of diamond as arising from imperfect dislocations.

An attempt has been made to explain the growth features in the light of known theories of crystal growth.

The surface structure of mineral and other crystals has been studied from time to time by several workers, and these observations have helped us to understand the mode of growth of crystals. Most of the work has been done microscopically, using bright field illumination or polarized light. Recently Seager (1953) examined the surfaces of a large number of mineral crystals for the study of growth structures but utilized only a metallurgical type of microscope using low powers (usually 1 inch objective). Improved optical and interferometric techniques are now available. Tolansky (1948) and his co-workers have used multiple-beam interference fringes extensively for the study of the surface topography of crystals such as quartz, mica, diamond, silicon carbide, &c. Until recently phase-contrast microscopy has received only slight attention for the study of minerals, but some uses have been described by Bennett, Jupnik, Osterberg, and Richards (1946), and by Smithson (1946, 1948), the latter confining himself mainly to thin sections of rocks. But lately, mainly

1 Now at the University of Delhi, India.
because of the interest stimulated by the dislocation theory of crystal growth (Frank 1949a; Burton, Cabrera, and Frank, 1951), a closer examination of surface structure has been carried out for a large number of crystals and minerals by several workers. Over the past few years the author has also been carrying on a study of the topography of crystals, including minerals, utilizing a combination of multiple-beam interferometry and phase-contrast microscopy, with high magnifications. The different minerals that have been studied have been chosen mainly from the collection at the British Museum (Natural History). The choice of crystals has often been dictated by the demands of interferometry which requires crystals with almost perfectly plane faces. Attention has particularly been directed to the study of small-scale features with thicknesses of only molecular dimensions. A phase-contrast microscopic study of zinc-blende crystals is now presented. The multiple-beam interferometric study of some minerals will be described in a later communication.

Experimental methods.

Phase-contrast microscopy is a well-established technique and it is not proposed to give any detailed account here. Its principles were enunciated by Zernicke (1934), and recently an account of this branch of microscopy, including its applications and an extensive bibliography, has been given by Bennett, Jupnik, Osterberg, and Richards (1951). We give below some of the special features pertaining to the present investigation.

The microscopic study of the crystal surfaces has been carried out on phase-contrast equipment which can be fitted on to a Vickers projection microscope manufactured by Cooke, Troughton, and Simms. Since the crystals studied were opaque, only the reflection type of equipment has been used, which has an additional advantage that for two features differing in level by \( t \) the path difference becomes \( 2t \) in reflection and hence has a greater sensitivity as compared with transmission. A diagrammatic scheme of the general arrangement is shown in fig. 11. An annular diaphragm \( D \) serves as the entrance pupil of the optical system consisting of the field lens, the microscope objective, and the reflecting surface of the specimen. The field lens and the objective form an image \( D_1 \) of the field diaphragm just below the surface of the specimen. The reflected light passes through the objective and forms a real image \( D_2 \) (shown by solid lines) of the diaphragm \( D \). Image \( D_2 \) is the exit pupil and the place where the phase plate is placed. In the present equipment the optical assembly, consisting of the microscope objective lenses, 45° inclined beam splitter, and the phase plate, is all mounted on the objective. Objectives of focal
length 25 mm., 16 mm., 8 mm., 4 mm., and 2 mm. (oil immersion) were available. The equipment used was a positive phase contrast with the phase retardation of $\pi/2$, the absorption of the phase plate being equal to 80%. Whenever permission could be obtained for silvering the surface of the specimen this was always done, since silver truly contours the surface and does not impose any topography of its own, but cuts down the exposure time and thus reduces the background fogging of the photographic plate. The same silvered crystal can then also be used for multiple-beam interferometric studies or light-profile microscopy. The thin layer of silver deposited on the crystal is usually 400–500 Å thick, giving a reflectivity of 80–90%. The silvering is done \textit{in vacuo} in a commercial evaporating unit manufactured by Edwards & Co.

When dealing with rough surfaces, as in the present case of blende crystals, the interferometric techniques cannot be adequately applied. For such specimens having surface features of heights (or depths) ranging from a fraction of a micron to a few microns and requiring the use of high-power or even oil-immersion objectives, the technique of light-profile microscopy is specially suitable (Tolansky, 1952).

\textit{Results of observation (pls. III and IV).}

Of a large number of blende crystals examined, one group was found to show several interesting surface features, and all the following illustrations refer to them. They all come from Joplin, Jasper County, Missouri, U.S.A., and form a part of the Trechmann collection of the British

![Diagrammatic sketch of the arrangement for phase-contrast microscopy by reflected light.](image)
Museum. The Pb-Zn ores of Joplin are of low-temperature metasomatic origin. On the matrix of some of the specimens small crystals of pyrite were observed. The first crystal (crystal no. 1) has one fairly well-developed face of a tetrahedron of which the sign was not determined, together with a face of the form \{100\}. The appearance of this tetrahedral face is shown in pl. III, fig. 1, which is a low-power photomicrograph taken with bright field illumination using the green line, \(\lambda 5461\), of a mercury arc. To the naked eye the face shows somewhat dark metallic lustre, the surface appearing quite polished and smooth but showing some interference colours; some interference fringes can be seen in fig. 1. On examining this tetrahedral face by the phase-contrast microscope without silvering it, the whole surface appeared mottled, though according to Miers (1929) this mineral is exceptionally free from tarnish. However, on this messy background several surface features could be observed and are discussed below. Crystal no. 2, which also showed some interference tints, has one prominently developed cube face nearly 7 mm. \(\times\) 8 mm., together with faces of \{111\} and \{\overline{1}1\}. Pl. III, figs. 4 and 5, refer to crystal no. 2, all others to crystal no. 1.

The observed surface structures may be summarized as follows:

The commonly observed triangular growth terraces and lines may be seen in pl. III, figs. 3, 4, and 6; the triangular shape of these hills on tetrahedral faces is in conformity with the general observation that growth layers show the same degree of symmetry as the face on which they grow.

Growth spirals on the tetrahedral face of crystal no. 1 are observable on the mottled background in pl. IV, figs. 7, 8, and 10.

Small triangular markings can be seen at the bottom of fig. 7, and are shown enlarged, using high power, in fig. 9; these triangular markings are, throughout the surface of the crystal, orientated in the same direction as the edges of the tetrahedral face of fig. 1.

A hexagonal area (see fig. 2, which shows a part of fig. 1 under high power) is completely free from the messy background. This hexagonal area does not appear to be orientated in any simple crystallographic direction with respect to the edges of the growth terraces, which continue into or right across the figure. To decide whether this smooth hexagonal area is an elevation above or a depression below the general level of the crystal surface around it, a light-profile photomicrograph was taken; the shift of the profile line showed it to be a depression. Thus the possibility that it is an overgrowth can be ruled out. Perhaps a small adherent crystallite protected the surface underneath during the last
phase of growth and was dislodged afterwards; it may have been an inclusion of calcite or galena.

An extensive system of substructure was seen on the tetrahedral faces of crystals 1 and 2 (figs. 6 and 4). It appears as if these figures were produced as a result of solution, but it is not possible to verify this since permission could not be obtained to etch these crystals. However, according to Gebhardt (1933), etching experiments give sharply defined triangular or hexagonal pits on (111) and no figures on (111).

Fig. 5 shows several deep triangular pits on a tetrahedral face on crystal number 2.

*Perfect screw dislocations and growth spirals.*

The formation of a perfect screw dislocation in a crystal creates on the surface a terminated step with a height equal to (or an integral multiple of) the X-ray unit cell. When growth proceeds on this step it winds itself into a spiral shape, giving rise to growth spirals with molecular step heights (Burton, Cabrera, and Frank, 1951). These predicted growth spirals have been observed on several crystals (for a detailed list of references see Verma, 1953). A growth spiral originating from a unit dislocation in a blende crystal would not be easy to observe because of the small size of the unit cell \((a = 5.42 \text{ Å})\). However, it has been observed that a deposit of a suitable impurity along the growth edges can often lead to a remarkably high visibility (Verma, 1951; Vand, 1951; Forty and Frank, 1953). The growth spirals of figs. 7 and 10, which have possibly unimolecular step heights, may have been revealed by this 'decoration effect' of the impurities. However, it is not possible to measure the step heights of these growth spirals by multiple-beam interferometry because of the extensive background on the surface of the crystal. Applebe and Kaye (1953) attributed the exceptional visibility of small steps on beryl crystals to etching, since they found a high concentration of pits along the step edges.

To discover the nature of the surface layer of the crystal it was examined by electron diffraction methods; it was found to be amorphous. It is possible that this amorphous impurity layer was formed on the surface of the crystal in the last phase of growth, or it could be due to chemical alteration after growth, either by natural processes underground or by atmospheric attack after it was mined. Indeed, the surface of the crystal, though highly reflecting, shows interference colours, and these interference fringes with monochromatic light can be seen in fig. 1;

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1 The author is indebted to Dr. H. Wilman for this examination.
they are proof of the presence of a thin layer on the crystal surface. But it is at once clear that the growth spirals are not built of the impurity atoms since a regular arrangement of the impurity atoms over the extension of the growth spirals would give them a crystalline arrangement. Moreover, the growth spirals take crystallographic shape, the spiral edges tending to become straight lines that are orientated at simple crystallographic angles (e.g. 90°) with respect to the edges of the triangular growth hills. The structure of the underlying ZnS and the growth spirals thus appears to be alike.

The behaviour of the spiral growth steps originating from different dislocations is similar to that observed on other crystals. A compound growth pattern, from two dislocations of the same hand close to each other, is illustrated at the bottom right of fig. 7 (pl. IV). Another noteworthy observation, which is in striking similarity to an observation on silicon carbide crystals (Verma, 1951), is that in any one region of the crystal the dislocations are usually of the same sign. Thus in fig. 7 there are some twenty growth spirals, all of which appear to be right-handed. Different parts of the crystal were therefore searched and, as seen in fig. 10, the top left corner contains several left-handed growth spirals: this region being separated from the rest of the crystal by a boundary marking a region containing triangular markings of the type shown in fig. 9. Examples of two dislocations of opposite hand close together can also be seen in fig. 10. The predominant occurrence of dislocations of the same sign in any one region of the crystal has been explained by Frank (1951) on an hypothesis about the mechanism of the creation of the dislocations. According to this the initial crystal plate formed by the nucleation process gets self-stressed, through inhomogeneous distribution of impurities. When this stress reaches the yield stress, the plate will buckle and shear, raising terminated steps that will not be of constant height all along, and macroscopically speaking will taper away. Every time the step height is reduced by one unit cell a dislocation will be left behind, and these will obviously be all of the same hand. During growth these dislocations will repel each other and spread over the surface of the crystal. The above observation on zinc-blende crystals thus lends support to Frank's hypothesis about the creation of dislocations. Few other crystals have shown a large density of individual dislocations on the same crystal plate.

**Imperfect dislocations and growth trigons.**

The triangular growth terraces of fig. 3 represent a triangular growth hill, as is easily seen from the positive phase-contrast image showing a
white border on the edge of the step towards the higher level side. In addition to this, a closer examination of the step edge shows some ‘trigons’ in different stages of formation. These trigons are pits, oppositely orientated to the triangular growth hills. A small completed trigon can be seen nearly in the right middle of the bottom growth layer (it is indicated by arrows). Several incomplete trigons, which were still in the process of formation when growth ceased, can be seen at the top right-hand end of the figure. The formation of several oppositely orientated trigons can be seen in fig. 4 also. These trigons closely resemble similar features on diamond. Indeed, this is to be expected since the structure of blende and diamond are very similar: the Zn and S atoms are each arranged on a face-centred cubic lattice, and by replacing both Zn and S by C we get a structure like that of diamond. As was shown by Tolansky and Wilcock (1946, 1947), these oppositely orientated triangular pits on the octahedral faces of diamond are not the result of an etching but are ‘growth trigons’ arising from the meeting of the three systems of growth layers advancing at 60° to each other. Halperin (1954) has put forward a theory about the formation of trigons and has explained them on the basis of the presence of imperfect dislocations, which arise by the transfer of atoms from lattice positions to twin lattice positions (Frank, 1949b). The strength of these dislocations, i.e. the displacement of the atoms, is only a fraction of the lattice unit, and imperfect steps result. These steps are thought by Halperin (loc. cit.) to be formed as a result of accumulations of interstitial faults in the lattice. It is therefore possible to explain the formation of oppositely orientated trigons in zinc-blende arising from imperfect dislocations, since stacking faults can be easily created in the $ABC$ sequence of the hexagonal close-packed layers which form the face-centred cubic blende crystal. It should be noted that the triangular growth hills are not of this origin. If growth takes place on imperfect dislocations zinc-blende may also be thought to exhibit ‘polypytism’ of the type shown by silicon carbide crystals (Thibault, 1944). This has recently been reported by X-ray diffraction studies (Strock and Brophy, 1955; Buck and Strock, 1955). The step lines originating from two imperfect dislocations cannot fuse with one another crystallographically, and a surface of lattice discontinuity marking out a fault surface should be formed; some of the markings separating growth spirals in figs. 7 and 10 may be of this origin.

The creation of dislocations by buckling and slip mechanism may also create some slip steps on the surface of the crystal. Votava, Amelinckx, and Dekeyser (1953) have carried out microscopic studies of (111) faces
of deformed blende crystals from Trepča (Yugoslavia) to which they assign a pegmatitic-pneumatolytic origin with growth at elevated temperature and pressure. They reported the observation of some slip-step lines in addition to poorly developed growth spirals. In the extensive substructure on some crystal faces one can occasionally see step lines running along certain crystallographic directions and cutting across the growth steps. Two such lines parallel to a crystallographic direction can be seen in fig. 5, running from the pit at the left edge of the figure to the edge of the crystal on the bottom right of the figure. Several other such faint lines can be seen in other photographs, e.g. fig. 6. Votava et al. have in addition observed some faint lines, which are rows of etch pits, and which they have interpreted as polygonization lines (rows of Taylor dislocations).

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EXPLANATION OF PLATES III AND IV.

PLATE III.

Fig. 1. The entire tetrahedral face of a zinc blende crystal under low power using bright field illumination and mercury green light \( \lambda 5461 \), showing a series of growth edges on which some broad and diffuse interference fringes due to a layer on the surface can be seen. \( \times 10 \).

Fig. 2. A phase-contrast picture of a part of fig. 1, showing an hexagonal area which is remarkably smooth compared with the mottled crystal surface around it. \( \times 75 \).

Fig. 3. The triangular growth terraces on the tetrahedral face of blende, using the phase-contrast microscope. Some inverted triangles in different stages of formation can be seen, e.g. one completed ‘trigon’ in the right middle of the bottom growth layer. \( \times 75 \).

Fig. 4. A phase-contrast picture of another blende crystal, showing an extensive system of substructure which is quite shallow in depth (or height). \( \times 45 \).

Fig. 5. A phase-contrast picture of another tetrahedral face of the same crystal as fig. 4, showing triangular pits in addition to the growth edges. \( \times 30 \).

Fig. 6. A phase-contrast picture of the extensive substructure on a tetrahedral face of a blende crystal. \( \times 60 \).

PLATE IV.

Fig. 7. A phase-contrast picture of a part of fig. 1, showing on the tetrahedral face of the blende crystal a number of growth spirals on the mottled background. Note that the spirals are all of the right-handed type. At the bottom of the figure small triangular markings can also be seen. \( \times 140 \).

Fig. 8. A phase-contrast picture of a part of fig. 7 under higher power, showing a growth spiral. \( \times 270 \).

Fig. 9. A phase-contrast picture of a portion of the bottom of fig. 7, showing the triangular markings under higher power. \( \times 440 \).

Fig. 10. A phase-contrast picture of another part of the tetrahedral face of fig. 1, showing a system of both left- and right-handed growth spirals together with the triangular markings on the mottled background. \( \times 100 \).
A. R. Verma on Phase-Contrast Microscopy of Blende
A. R. Verma on Phase-Contrast Microscopy of Blende
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There are at least four meetings of the Society each year, on Thursdays, in January, March, June, and November. They are held (by kind permission) in the Apartments of the Geological Society, Burlington House, Piccadilly, London, W. 1. Titles of papers to be read at these meetings, with a view to subsequent publication in the Magazine, and of exhibits, should be sent with a short abstract to the Secretary at least three weeks before the meeting. Authors alone are responsible for the views set forth in their respective papers. They are allowed, free of charge, fifty separate copies of their papers published in the Magazine.
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Interferometric and X-ray investigation of the growth of long-chain fatty acid crystals

I. Polymorphism and polytypism in palmitic acid crystals

By Ajit Ram Verma
Interferometric and X-ray investigation of the growth of long-chain fatty acid crystals

I. Polymorphism and polytypism in palmitic acid crystals

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[Plates 1 to 3]

Two polymorphic forms of palmitic acid crystals grown from dilute solutions at approximately 0°C have been observed. These polymorphs grow as small rhomboidal (or related hexagonal shaped) crystal plates parallel to the (001), the acute angle between the adjacent edges, which are parallel to (110) directions, being 74° for one polymorph and 56° for the other. Hexagonal plates corresponding to these rhomboidal plates are derived by cutting them with a pair of edges parallel to the a- or b-axis.

The lattice constants of these small single crystals, which are nearly 100 μ in size and only a few microns thick, have been measured by the application of a fine focus X-ray tube of the Ehrenberg–Spears type, and a specially designed oscillation cylindrical camera of 1 cm radius. For the polymorph with edge angle 74° the constants are

\[ a = 5.63 \text{ Å}, \quad b = 7.39 \text{ Å}, \quad c \sin \beta = 40.20 \text{ Å}, \quad \beta = 62^\circ 2', \]

the b-axis being a screw axis. For the other polymorph with the edge angle 56° the unit cell constants are

\[ a = 9.68 \text{ Å}, \quad b = 5.05 \text{ Å}, \quad c \sin \beta = 36.43 \text{ Å}, \quad \beta = 51^\circ 3', \]

the b-axis not being a screw axis. The dimensions of the basal planes of the two monoclinic forms can be derived from the rectangular prism of the orthorhombic paraffin crystals by taking oblique sections at the appropriate angle β.

Palmitic acid crystals grow by the screw dislocation mechanism showing growth spirals. The measurement of spiral heights by the application of multiple-beam internal interference fringes has been carried out for the polymorph with the edge angle 74°, and it is found that steps which are integral multiples (including unity) of the X-ray repeat distance for this polymorph are formed. In addition, steps which are half-integral multiples of this X-ray unit have been measured. The interlaced type of growth spiral has also been observed. These observations can be explained only by recognizing that in addition to polymorphism, these long-chain acids exhibit polytypism, which, however, has not yet been found by X-ray diffraction experiments.

Several cases of the formation of large dislocations, their movement, macroslips and cleavage of extremely thin crystals have been illustrated.

The birefringence of very thin crystals of the two polymorphs has been measured for different wave-lengths in the visible region by the use of multiple-beam fringes of equal chromatic order on doubly silvered crystals.

1. INTRODUCTION

Long-chain organic compounds including the fatty acids form an important group of chemical compounds and have been the subject of a large number of investigations. Müller (1923, 1927, 1928), Piper, Malkin & Austin (1926), Francis, Piper & Malkin (1930), Francis, Collins & Piper (1937), Thibaud & Dupré La Tour
Growth of long-chain fatty acid crystals. I

(1930), Dupré La Tour (1936), Vand, Morley & Lomer (1951) and others have studied the structure of these compounds by using X-ray techniques. Recently the growth of these long-chain organic molecular crystals has stimulated considerable interest. These crystals are found to grow by the spiral mechanism in accordance with the dislocation theory of crystal growth (Burton, Cabrera & Frank 1951). For these studies two techniques have been used: (a) the electron microscopic and (b) the optical and interferometric techniques. Using the electron microscope, Dawson & Vand (1951), Dawson (1952), and Anderson & Dawson (1953) have examined the long-chain paraffins \( n\)-hexatriacontane, \( C_{36}H_{74} \); \( n\)-heptane, \( C_{100}H_{202} \); \( n\)-nonatriacontane, \( C_{38}H_{80} \), and stearic acid, \( CH_3(CH_2)_{18}COOH \). Optical and interferometric techniques have been applied by Verma & Reynolds (1953a) for a similar study of the growth of crystals of stearic acid.

The electron microscopic and interferometric studies appear to differ in one important observation. Dawson & Vand and Dawson found that in the paraffins with an even number of carbon atoms (namely, \( C_{36}H_{74} \) and \( C_{100}H_{202} \)) which have unimolecular units in solution and a unimolecular \( c\)-axial translation, the spiral growth steps are also of unimolecular height. Paraffins with an odd number of carbon atoms, which have a bimolecular \( c\)-axial translation but only a unimolecular unit in solution, were found to give only unimolecular spiral growth steps. In stearic acid, because of the polar attraction between the end carboxyl groups, both the unit in solution and the \( c\)-axial translation are bimolecular, and Anderson & Dawson reported only bimolecular spiral growth steps. Thus in the electron microscopic studies the growth steps for all these substances were found to be equal to their molecular units in solution and no multimolecular growth steps were encountered. From these observations Anderson & Dawson (1953) concluded that their observations are at variance with Frank's generalization (Frank 1951) according to which the growth steps are determined by the Burgers vector of the dislocation originally formed in the crystal; an observation which had been supported by the studies of growth spirals on SiC (Verma 1951, 1952), and CdI\(_2\) (Forty 1952). However, in contrast to the electron microscopic observation the interferometric studies by Verma & Reynolds (1953a, b) on stearic acid crystals suggested the existence of spiral growth steps which were integral and also half-integral multiples of the X-ray unit cell parameter. It was therefore thought desirable to see whether other long-chain organic crystals would also grow with multimolecular spiral growth steps. For this purpose, palmitic acid, \( CH_3(CH_2)_{14}COOH \), which is known to be dimeric in solution (Broughton 1934), was chosen.

The fatty acids are well known to exhibit polymorphism. Piper et al. observed that the different polymorphs differ in their long layer spacing. However, they carried out the X-ray studies on layers of acid obtained on a glass slide. ‘Single crystals of fatty acids have been rarely examined, and in spite of the large amount of work that has been carried out on the long-chain fatty acids, the data concerning them continue to be confusing’ (Wyckoff 1953). Therefore in the present investigation of the growth of single crystals of palmitic acid, an X-ray study of their polymorphism was also undertaken, attention being specially directed to
a consideration of the growth, optical and other properties in relation to polymorphism.

It is hoped to investigate later the detailed structure of the polymorphs of palmitic acid crystals.

2. Experimental

Preparation of crystals

Very pure samples of palmitic acid supplied by Messrs Price (Bromborough) Ltd and a sample of redistilled acid supplied by Dr R. C. Mehrotra were used. Crystals were grown from dilute solutions on cooled glass plates at approximately 0°C and were suitably enclosed during the growth. The step-height measurements are all upon crystals grown from a benzene solution. Crystals were also grown from an ethyl alcohol solution (figure 10, plate 2) and CS₂ solution (e.g. figure 11, plate 2). The crystals were highly perfect but usually occurred as small plates about 100 to 200 μ across and only a few microns thick. Such small crystals necessitated the use of special interferometric and X-ray techniques, described below.

X-ray techniques

The standard oscillation or rotation cylindrical cameras of 3 cm radius with the usual X-ray tubes could not be applied for the study of these minute and thin crystals of palmitic acid. Professor J. D. Bernal suggested to the author the use of a fine-focus tube of the type developed at Birkbeck College by Ehrenberg & Spears (1951). It was tried and found quite suitable for these microcrystals. Its particular advantage is that it provides a very intense X-ray beam (the specific loading of the target is over 50 times that of a normal tube) focused over a spot nearly 40 μ in size, giving a foreshortened width of only 4 μ at 6°. Because of the small size of the focal spot high resolution can be obtained with small cameras, but the geometrical, and therefore the mechanical, requirements are more stringent than with normal tubes, so that new designs of cameras are required. Jeffery (1952) has described powder cameras suitable for such a tube. A specially designed oscillation camera also developed at Birkbeck College was employed. This camera has a cylindrical film holder of 1 cm radius. Since the source is a part of the collimating system and the collimator hole is only about 100 μ, the camera is rigidly attached to the tube after all the adjustments for collimation have been done. The crystal can be mounted on a standard goniometer head. This was done by attaching, under a microscope, the crystal to the end of a thin glass fibre with a trace of shellac. Greater convenience in the adjustment of the crystal is obtained if a thin lead wire (1 mm diameter) is used for supporting the glass fibre and crystal, since the wire may be readily bent and twisted. With CuKα radiation filtered through nickel foil this arrangement required an exposure time of only 1 to 2 h for a 15° oscillation photograph, because of the small focus-window distance. No moving-film type of camera was used, since as yet no such camera has been produced for the fine-focus X-ray tube.
Growth of long-chain fatty acid crystals.

Optical and interferometric techniques

For the study of the surface topography of the crystals of palmitic acid, multiple-beam interference fringes (Tolansky 1948) were utilized. The usual method of producing these fringes by matching the silvered crystal against a silvered optical flat could not be applied to these minute crystals which require a high power for their study. Therefore the internal interference fringes, which were already found useful for the study of stearic acid crystals (Verma & Reynolds 1953a) were employed. This procedure consisted in growing the crystals on a glass cover-slip which has already been silvered. After growth had finished and the crystals had dried, their top surface was silvered in situ, thus producing doubly silvered crystals, between the end-faces of which multiple-beam internal interference fringes can be formed. These fringes were used for the measurement of growth steps and the birefringence of the crystals, and have an additional advantage in so far as they help to reveal the edges of growth layers by the sensitive interference tints. Reflecton positive-phase contrast was also employed for the observation of surface features.

3. Morphology and X-ray study of polymorphism

The shape of the crystal plates of palmitic acid grown from solution at once makes it clear that palmitic acid occurs in at least two polymorphs at ordinary temperatures. The crystals form rhomboidal or hexagonal plates, the flat face being the basal plane, i.e. (001). A measurement of the edge angles, i.e. the acute angle between the adjacent edges of the crystal plates, showed that the crystal could be divided into two types, though sometimes a small variation in the magnitude of angles was observed. For one type the rhomboidal plate has the edge angle 56° (see figure 7, plate 1) and for the other 74° (see figures 8 or 11). The hexagonal plates are simply related to these two rhomboidal plates. Only the first type (i.e. the 56° polymorph) has been observed by previous workers, while no hexagonal plates of palmitic acid have been reported.

Two modifications of palmitic acid called the B and C form by Piper et al. are known. An attempt was made therefore to see if the observed two types could be identified with the B and C forms. This could not be done on the known data, and it was only after an actual measurement of the a, b axial dimensions and the long-layer spacing for the single crystals of the two types that it was uniquely possible to identify them.

The unit-cell dimensions for the polymorph with edge angle 74°

The a- and b-axes lie in the plane of the crystal flake and are found to be parallel to the bisectors of the edge angles. These directions therefore can conveniently be adjusted parallel to the oscillation axis of the instrument. A series of 15° oscillation photographs about the a- and b-axes was taken. Figure 2, plate 1 (enlarged about 3 times in the print so as to correspond to the usual Bernal chart), shows a 15° oscillation photograph about the a-axis, the normal to the crystal plate being inclined nearly 18° to the X-ray beam in the middle of the oscillation range.
From the layer-line spacings of the oscillation photographs the $\xi$ values and hence $a$ and $b$ axial dimensions were calculated and are
\[ a = 5.63 \text{ Å}, \quad b = 7.39 \text{ Å}. \]

A rotation photograph about the $a$-axis (figure 1, plate 1) shows only a few strong reflexions, the majority of other spots being relatively faint. Following Müller (1927), a value of $\beta$ can be chosen so as to give small indices to all the strongly reflecting planes. Taking the strong reflexions in the first layer line as 110 and 111, it is easily calculated that
\[ \beta = 62^\circ 2' \]
(or $117^\circ 58'$ in the usual convention). The strong reflexion on the zero layer of figure 1 is 020 and the reflexions on the zero layer of figure 2 are 020 and 040, showing that most likely the $b$-axis is a screw axis.

For the measurement of the long-layer spacing, i.e. $c \sin \beta$, the special oscillation technique useful for crystals with large unit cells was employed. According to this the densest reciprocal lattice fine, i.e. the $c^\ast$-axis, is initially placed normal to the X-ray beam. This can be easily done in practice for palmitic acid crystals, with $a$ (or $b$) as oscillation axis, by adjusting the plane of the crystal flake parallel to the X-ray beam, since $c^\ast$ is perpendicular to the basal plane. When the crystal is allowed to oscillate through $15^\circ$ from this position, the closely spaced reciprocal points along the $c^\ast$-axis pass through the sphere of reflexion. These points project from the centre of the sphere on to the film near the centre, and, because of the small distortion in this region, are recorded as a series of nearly equidistant spots. These reflexions are 00l reflexions. Owing to the great disparity between $a$ (or $b$) and $c \sin \beta$ the reflexions corresponding to the non-zero lattice rows, i.e. $h0l$ (or $0kl$) reflexions, are farther away from the centre and no confusion arises in the indexing of the spots near the centre. In figure 4, plate 1, is illustrated such a $15^\circ$ oscillation photograph about the $a$-axis; the $c^\ast$-axis being perpendicular to the X-ray beam somewhere in the middle of the oscillation range, giving rise to reflexions on both sides of the centre. From these reflexions the position of the centre of the beam can be fixed very accurately. Because the crystal plate is only a few microns thick, these spots consist of extremely fine and sharp lines—indeed, the spots are so sharp that the record on the front and back of the film can be resolved and the spots appear distinctly double when viewed obliquely. Therefore the back of the film was scraped off and the distances of these spots from the centre were measured by using a Hilger measuring micrometer (type L50) reading up to 0.0001 cm. In the calculation of $\xi$ values from these spots, the thickness of the film and the black paper was taken into account so that the effective radius of the cylindrical camera is 0.992 ± 0.002 cm. The accuracy in the values of $c \sin \beta$ is nearly 0.3 %, neglecting the shrinkage factor of the film. For taking the mean value of $c \sin \beta$ only higher order reflexions were considered, since for them the error of measurement is proportionately smaller.

The long-layer spacing $c \sin \beta$ was determined for six different crystals of which two are illustrated in figures 4 and 5 (enlarged nearly 8 times). Three results have
been chosen and are given in Table 1. The mean value for crystal no. 1 is 40.33 Å, while for crystal no. 2 it is 40.22 Å. Crystal no. 3 (figure 5) was morphologically a polymorph with edge angle 74° but items 1, 3, 6 and 9 of Table 1 correspond to the spacing of Table 2. It may be concluded from this relationship that another small crystal of the polymorph with edge angle 56° had grown in parallel orientation with it, showing that it is possible for the crystals of two polymorphs to grow in parallel orientation. The mean values for the other four crystals are

40.2 Å, 40.0 Å, 40.2 Å, 41.7 Å,

which agree closely with the values of the crystals nos. 1 and 2 of Table 1, except for the higher values of \( c \sin \beta \) for the last crystal, which has the same \( a \) and \( b \)

### Table 1

<table>
<thead>
<tr>
<th>Item</th>
<th>Crystal no. 1</th>
<th>Crystal no. 2</th>
<th>Crystal no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>( \xi )</td>
<td>( c \sin \beta ) (Å)</td>
<td>( \xi )</td>
</tr>
<tr>
<td>1</td>
<td>0.151</td>
<td>004</td>
<td>40.7</td>
</tr>
<tr>
<td>2</td>
<td>0.113</td>
<td>003</td>
<td>41.0</td>
</tr>
<tr>
<td>3</td>
<td>0.113</td>
<td>003</td>
<td>41.0</td>
</tr>
<tr>
<td>4</td>
<td>0.152</td>
<td>004</td>
<td>40.4</td>
</tr>
<tr>
<td>5</td>
<td>0.190</td>
<td>005</td>
<td>40.5</td>
</tr>
<tr>
<td>6</td>
<td>0.267</td>
<td>007</td>
<td>40.3</td>
</tr>
<tr>
<td>7</td>
<td>0.281</td>
<td>unaccounted</td>
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<tr>
<td>8</td>
<td>0.305</td>
<td>008</td>
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<td>9</td>
<td>0.345</td>
<td>009</td>
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<tr>
<td>10</td>
<td>0.380</td>
<td>0010</td>
<td>40.5</td>
</tr>
<tr>
<td>11</td>
<td>0.460</td>
<td>0012</td>
<td>40.2</td>
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<td>12</td>
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</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>40.33</td>
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<td>40.22</td>
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<tr>
<td>SD</td>
<td>±0.13</td>
<td></td>
<td>±0.12</td>
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</tbody>
</table>

axial dimensions as the other crystals. This may be due to a small variation in the chain length of carbon atoms or possibly a small variation in the tilt of the chains to the basal plane or to some undetected experimental error. It may be recalled that Piper et al. (1930) also observed a polymorph called by them the \( A \) form which had a very similar long-layer spacing.

**Unit-cell dimensions for the polymorph with edge angle 56°**

By exactly similar methods \( a, b \) and \( \beta \) have been found out for this polymorph and are

\[
a = 9.68 \text{ Å}, \quad b = 5.05 \text{ Å}, \quad \beta = 51° 3'.
\]

The \( \xi \) values for the different 00\( l \) reflexions (illustrated in figure 6) are given in Table 2. The long-layer spacing \( c \sin \beta \) for this polymorph has a mean value of 36.43 ± 0.18 Å.
It may, however, be seen from figure 3 which is a 15° oscillation photograph about the \( a \)-axis that on the zero layer both 010 and 020 reflections are present, so that in this polymorph the \( b \)-axis is not a screw axis. Thus the two polymorphs differ in their space group also.

This polymorph has been studied by Schoon (1938), who applied electron-diffraction methods for the determination of \( a, b \) and \( \beta \), and Müller spectrogram for the long-layer spacing measurement. His values are

\[
\begin{align*}
a &= 9.54 \text{ Å}, & b &= 4.99 \text{ Å}, & c \sin \beta &= 35.45 \text{ Å}, & \beta &= 53.4°.
\end{align*}
\]

These may also be compared with the values

\[
\begin{align*}
a &= 9.41 \text{ Å}, & b &= 5.00 \text{ Å}, & c \sin \beta &= 35.6 \text{ Å}, & \beta &= 51° 10'\text{.}
\end{align*}
\]

for the so-called \( \alpha \)-form of palmitic acid (Dupré La Tour 1936).

**Table 2. Polymorph with edge angle 56°**

<table>
<thead>
<tr>
<th>( \xi )</th>
<th>0.298</th>
<th>0.211</th>
<th>0.168</th>
<th>0.125</th>
<th>0.125</th>
<th>0.211</th>
</tr>
</thead>
<tbody>
<tr>
<td>reflection</td>
<td>007</td>
<td>005</td>
<td>004</td>
<td>003</td>
<td>003</td>
<td>005</td>
</tr>
<tr>
<td>( c \sin \beta (\text{Å}) )</td>
<td>36.2</td>
<td>36.5</td>
<td>36.7</td>
<td>36.7</td>
<td>37.1</td>
<td>36.6</td>
</tr>
</tbody>
</table>

**Identification of the two polymorphs**

The two polymorphs called by Piper et al. (1926) and Francis et al. (1937) the \( B \) and \( C \) forms had long-layer spacings of 35.5 and 39.08 Å respectively. It is therefore likely that the crystal polymorphs with edge angles 56° and 74° are the \( B \) and \( C \) forms. However, it may be remembered that Piper et al. studied a layer of the acid obtained either by pressing a crystal on to the glass slide, allowing a solution to evaporate, or by melting the acid and letting it solidify. The first two methods usually gave the \( B \) spacing for even-numbered acids. But in the present

**Description of Plate 1**

**Figure 1.** Rotation photograph about the \( a \)-axis of the polymorph of palmitic acid with edge angle 74°. (Magn. \( \times 3 \).)

**Figure 2.** 15° oscillation photograph about the \( a \)-axis of the crystal of palmitic acid (polymorph with edge angle 74°), the normal to the crystal plate being inclined to the X-ray beam at 18° in the middle of the oscillation range. (Magn. \( \times 3 \).)

**Figure 3.** 15° oscillation photograph about the \( a \)-axis of the 56° polymorph with the \( b \)-axis normal to the X-ray beam nearly in the middle of the oscillation range.

**Figure 4.** 15° oscillation photograph about the \( a \)-axis (crystal no. 1, table 1), 74° polymorph with the \( c^* \)-axis nearly normal to the X-ray beam giving (00l) reflections. The \( l \) values are marked. (Magn. \( \times 8 \).)

**Figure 5.** Same as figure 4 for the crystal no. 3, table 1.

**Figure 6.** 15° oscillation photograph for the palmitic acid crystal polymorph with edge angle 56°, showing (00l) reflections.

**Figure 7.** A doubly silvered crystal plate of palmitic acid with the edge angle 56°, showing also a difference in shade on either side of the \( b \)-axis. (Magn. \( \times 200 \).)

**Figure 8.** Internal interference fringes in a crystal plate of which a triangular section has slipped out. (Magn. \( \times 240 \).)

**Figure 9.** A phase contrast photomicrograph of an extremely thin crystal layer (doubly silvered) showing a perfect cleavage. (Magn. \( \times 270 \).)
Verma

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(Facing p. 49)
Description of Plate 2

Figure 10. Phase contrast photomicrograph of a silvered crystal of palmitic acid showing two growth spirals of opposite hand interacting with each other, together with a fault line. (Magn. x 270.)

Figure 11. Phase contrast photomicrograph showing a pair of non-intersecting growth spirals. (Magn. x 375.)

Figure 12. A phase contrast photomicrograph of a crystal of palmitic acid (silvered opaque) showing the dissociation of steps along the diagonals. (Magn. x 190.)

Figure 13. Phase-contrast micrograph of a silvered crystal plate showing growth steps equal to $1\frac{1}{2}$ the bimolecular unit. (Magn. x 350.)

Figure 14. An internal interference photograph of a doubly silvered crystal plate showing the Fizeau fringes contouring the growth steps. To bring out the edges of growth steps the print has been overexposed. (Magn. x 200.)
study it was found that both the polymorphs grow simultaneously from solution at approximately 0°C, though crystals of the 74° polymorph were better developed.

The shapes of the rhomboidal crystals and their related hexagonal plates can now be easily explained. The angle between \([110]\) and \([110]\) directions in the \((001)\) plane is \(2 \tan^{-1}(b/a)\). For \(a = 9.68\,\text{Å}\), \(b = 5.05\,\text{Å}\) the value of \(2 \tan^{-1}(b/a) \approx 55°\) and for \(a = 5.63\,\text{Å}\) and \(b = 7.39\,\text{Å}\) it is approximately equal to 74° 40'. The observed hexagonal plates along with their interior angles can be derived from the two types of the rhomboidal plates by cutting them with a pair of edges parallel to the \(a\)- and \(b\)-axes of the 74° and 56° polymorphs respectively.

The lattice constants of the two polymorphs of palmitic acid are collected in table 3, and for comparison the unit cell constants of stearic acid and the paraffin \(C_{29}H_{58}\) crystals taken from Müller (1927, 1928) are also given.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Polymorph</th>
<th>Edge Angle</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c \sin \beta) (Å)</th>
<th>(\beta) (°)</th>
<th>(c) (Å)</th>
<th>(ab \sin \beta) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic Acid</td>
<td>74°</td>
<td>5.63</td>
<td>7.39</td>
<td>40-20</td>
<td>62° 2'</td>
<td>45-51</td>
<td>36-8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>56°</td>
<td>9.68</td>
<td>5.05</td>
<td>36-43</td>
<td>51° 3'</td>
<td>46-86</td>
<td>38-0</td>
<td></td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>74°</td>
<td>5.546</td>
<td>7.381</td>
<td>43-76</td>
<td>63° 38'</td>
<td>48-84</td>
<td>36-65</td>
<td></td>
</tr>
<tr>
<td>Paraffin (C_{29}H_{58})</td>
<td>4.97</td>
<td>7.45</td>
<td>77-2</td>
<td>90°</td>
<td>77-2</td>
<td>37-0</td>
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</tbody>
</table>

It is seen that the chain length in the two polymorphs of palmitic acid differ by 1:35 Å, and that the carbon chain length 45.51 Å for the 74° polymorph of palmitic acid is shorter by 3.33 Å than the chain length in the similar polymorph in stearic acid. As is to be expected the cross-section (\(ab \sin \beta\)) of the unit cell is nearly the same for both the polymorphs and is equal to the cross-section of the orthorhombic paraffin crystal. Further, the \(b\)-axial dimensions of the two polymorphs of palmitic acid are approximately equal to the \(a\) and \(b\) dimensions of the paraffin crystal. Starting from an orthorhombic arrangement with the rectangular

**Description of Plate 3**

**Figure 15.** Internal interference fringes for \(\lambda 5461\) with a thin crystal layer lying on another crystal plate having growth edges. (Magn. \(\times 310.\))

**Figure 16.** A phase contrast micrograph of the same crystal as figure 15 after resilvering the top surface opaque. (Magn. \(\times 250.\))

**Figure 17.** A crystal plate of palmitic acid with the internal interference fringes (for \(\lambda 4358\)) contouring the growth steps. The lower part of the figure has been exposed slightly less in the print. (Magn. \(\times 110.\))

**Figure 18.** A phase contrast photograph which is an enlargement of a part of figure 17 showing interlacing of steps. (Magn. \(\times 250.\))

**Figure 19.** Fringes of equal chromatic order of a doubly silvered crystal of palmitic acid with edge angle 74°, showing the birefringence of this polymorph. (Magn. \(\times 44.\))

**Figure 20.** Fringes of equal chromatic order of a doubly silvered crystal of palmitic acid with the edge angle 56°, showing the birefringence of this polymorph. (Magn. \(\times 44.\))
section having its edges equal to 5.0 and 7.4 Å, it is therefore possible to derive the two monoclinic polymorphs by tilting the carbon chains to one of the two edges of the rectangle at the appropriate angle \( \beta \), while keeping it perpendicular to the other edge. Thus the two sections of the rectangular prism obtained by cutting it with a plane inclined to the axis of the prism at the angle \( \beta \) and parallel to one of the edges of the cross-section (figure 21) will yield the dimensions of the basal plane (i.e. \( a \) and \( b \)) of the polymorphs, within limits of error of about 1%.

Schoon (1938) has discussed the different possible values of \( \beta \) on a similar model by starting from an orthorhombic cell and considering the displacement of the carbon chains in the \( c \)-direction, the glide planes in the rectangular cell being either \( ac \) or \( bc \) planes. On energy considerations it should be expected that the displacement of the chains will be an integral multiple of the distance \( \text{CH}_3-\text{CH}_2 \) along the \( c \)-axis. Therefore

\[
\cot \beta = n(1.27)/d_0,
\]

where \( d_0 \) is equal to 7.4 or 5.0 Å, depending upon whether the glide plane is \( bc \) or \( ac \) plane. From the measured values of the lattice constants of palmitic acid crystals it may be calculated that the chains are displaced by 2.5 Å, i.e. \( n = 2 \) for the 74° polymorph, and for the 56° polymorph it is nearly 6 Å, i.e. \( n \) lies between 4 and 5, indicating that this geometrical model is only an approximate one. The concept of slipping of carbon chains is used in the next section for the creation of dislocations.
Growth of long-chain fatty acid crystals. I

4. OPTICAL AND INTERFEROMETRIC STUDIES

Growth spirals and step heights

When the doubly silvered crystals of palmitic acid were examined with a phase-contrast microscope, growth spirals could be observed on the basal planes of some crystals. This indicates that palmitic acid crystals can grow by the dislocation mechanism (Burton et al. 1951). The conditions of growth were such that the majority of large crystal plates with well-developed growth steps consisted of the polymorph with edge angle 74°; the study of spiral growth and step-height measurement was therefore confined to this polymorph.

The height of spiral growth steps has been measured by the application of multiple-beam fringes formed by internal interference between the two silvered surfaces enclosing the crystal. A knowledge of the refractive index \( \mu \) of the crystal is required. The value 1.52, the mean of 1.533 and 1.508 reported by Thibaud & Dupré La Tour (1930), has been adopted. As discussed previously (Forty 1952; Verma & Reynolds 1953a) the step height \( h \) is given by

\[
h = \frac{\lambda}{2\mu n},
\]

where \( n \) is the number of steps between two successive Fizeau fringes which contour the growth edges, formed by monochromatic light of wave-length \( \lambda \). Here \( h \) is the mean step height, assuming all the steps between the two successive Fizeau fringes to be of the same height and that there is no growth structure on the back surface of the crystal. The number \( n \) is not necessarily an integer and for an accurate determination of step heights, the fractional part should be found, especially when the steps are large multiples of the unit cell. Using two beam fringes, Forty (1952) has calculated the fractional part graphically by measuring the photographic density of different steps. With multiple-beam fringes, for the same change in interferometric gap there is a considerably greater change in the photographic blackening over successive steps and a fraction less than \( \frac{1}{2} \) (probably \( \frac{1}{4} \)) can be judged visually; e.g. a fraction \( \frac{1}{4} \) will lead to two successive steps with the same intensity.

A large number of spiral step heights were measured. Step heights which are small multiples of the X-ray unit cell can be measured accurately and are given in table 4 together with the limiting error. Much higher steps were also observed.

<table>
<thead>
<tr>
<th>Item</th>
<th>( n )</th>
<th>( \lambda (\text{Å}) )</th>
<th>direction of growth steps</th>
<th>step height (Å)</th>
<th>multiple</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42 &lt; ( n ) &lt; 44</td>
<td>5461</td>
<td>[110] and [100]</td>
<td>42 ± 2</td>
<td>1(42 ± 2)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>31 &lt; ( n ) &lt; 33</td>
<td>5461</td>
<td>[110] and [100]</td>
<td>56 ± 2</td>
<td>1\frac{1}{2}(39 ± 2)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>21 &lt; ( n ) &lt; 23</td>
<td>5461</td>
<td>[110] and [100]</td>
<td>82 ± 4</td>
<td>2(42 ± 2)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>17 &lt; ( n ) &lt; 18</td>
<td>4358</td>
<td>[110] and [100]</td>
<td>82 ± 2</td>
<td>2(41 ± 2)</td>
<td>figure 13</td>
</tr>
<tr>
<td>5</td>
<td>18 ± 2</td>
<td>5461</td>
<td>[110]</td>
<td>100 ± 3</td>
<td>2\frac{1}{2}(40 ± 2)</td>
<td>figure 17</td>
</tr>
<tr>
<td>6</td>
<td>14 &lt; ( n ) &lt; 15</td>
<td>5461</td>
<td>[110]</td>
<td>129 ± 9</td>
<td>3(43 ± 3)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>15 ± 2</td>
<td>5461</td>
<td>[110] and [100]</td>
<td>119 ± 8 ± 2</td>
<td>3(39 ± 9 ± 7)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>11 &lt; ( n ) &lt; 12</td>
<td>5461</td>
<td>[110]</td>
<td>156 ± 6</td>
<td>4(39 ± 9 ± 5)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9 &lt; ( n ) &lt; 10</td>
<td>5461</td>
<td>[110]</td>
<td>190 ± 10</td>
<td>5(38 ± 2)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5 ( 1/2 ) &lt; ( n ) &lt; 6</td>
<td>5461</td>
<td>[110]</td>
<td>327 ± 15</td>
<td>8(40 ± 9 ± 2)</td>
<td></td>
</tr>
</tbody>
</table>

Dupper La Tour (1930), has been adopted. As discussed previously (Forty 1952; Verma & Reynolds 1953a) the step height \( h \) is given by

\[
h = \frac{\lambda}{2\mu n},
\]

where \( n \) is the number of steps between two successive Fizeau fringes which contour the growth edges, formed by monochromatic light of wave-length \( \lambda \). Here \( h \) is the mean step height, assuming all the steps between the two successive Fizeau fringes to be of the same height and that there is no growth structure on the back surface of the crystal. The number \( n \) is not necessarily an integer and for an accurate determination of step heights, the fractional part should be found, especially when the steps are large multiples of the unit cell. Using two beam fringes, Forty (1952) has calculated the fractional part graphically by measuring the photographic density of different steps. With multiple-beam fringes, for the same change in interferometric gap there is a considerably greater change in the photographic blackening over successive steps and a fraction less than \( \frac{1}{2} \) (probably \( \frac{1}{4} \)) can be judged visually; e.g. a fraction \( \frac{1}{4} \) will lead to two successive steps with the same intensity.

A large number of spiral step heights were measured. Step heights which are small multiples of the X-ray unit cell can be measured accurately and are given in table 4 together with the limiting error. Much higher steps were also observed.
An analysis of the measured step heights shows that they are multiples of a unit. This unit, within the errors of experimental observation, can be identified as 40.2 Å, the long-layer spacing characteristic of the 74° polymorph. Thus it may be concluded that spiral growth steps which are multiples of the X-ray unit cell occur frequently for the long-chain palmitic acid crystals also. This supports the hypothesis that the height of the growth step is determined by the Burgers vector of the dislocation originally formed in the crystal (Frank 1951). The observation that no multimolecular steps were encountered in the electron-microscopic studies may be due to the fact that multimolecular steps usually occur on the large macroscopic crystals which would not normally be examined by the electron microscope. Alternatively, it is possible that the multimolecular steps may consist of a group of closely piled up monomolecular steps unresolved by the optical microscope. Indeed, the edge of a multimolecular step is not expected to be close-packed (Frank 1951).

Items nos. 2 and 5 of table 4, illustrated in figures 13 and 14, plate 2, respectively, are commented upon in the next section.

Shape of growth patterns: polytypism

Palmitic acid shows the same properties of growth steps (e.g. interaction of growth fronts originating from different dislocations) as SiC, CdI₂ and various other long-chain molecules. Figure 10, plate 2, shows two simple hexagonal growth spirals of opposite hand interacting with each other, together with a fault line. A pair of non-intersecting spirals originating from two close dislocations which appear to have different strengths is illustrated in figure 11. Many complex examples originating from a number of dislocations were also encountered.

A few cases of hexagonal spirals on palmitic acid crystals showed the cross-laced type of growth pattern exhibited so far only by SiC crystals (Verma 1951), CdI₂ (Forty 1952) and biotite (Amelinckx 1952). Figures 12, 17 and 18, plates 2 and 3, show this pattern. In figure 12 (the crystal opaquely silvered) this dissociation and the cross-lacing of steps is clearly illustrated where the steps break up into components along all the four corners marking the [100] directions. Figure 17 shows the cross-lacing of steps along with the internal interference fringes for λ4358, which gives the step height to be 82 Å, i.e. twice the bimolecular value. A portion of figure 17 showing interlacing is shown enlarged in figure 18. These steps break into single bimolecular value over the cross-laced part; on either side of the cross-laced region they pile up again. The interlacing of growth steps arises if the relationship between the growth rates of the different monolayers that compose a step, varies in different orientations of the crystal.

These observations indicate that 'polytypism' of the kind observed on SiC crystals (Baumhauer 1911, 1915; Thibault 1944) should be observed on palmitic acid crystals also. Polytypism might be usefully redefined as the special case of polymorphism, in which the crystal lattices of different modifications differ only along one dimension (e.g. c-axis in SiC) and are obtained by stackings of layers of identical structure. As is known palmitic acid crystals (and also other long-
Growth of long-chain fatty acid crystals. I

Chain acids) consist of zigzag chains of carbon atoms, with a carboxyl group at the end, the forces between the C atoms being homopolar. The hydrogen bonding between the carboxyl groups leads to the formation of a bimolecular unit due to the association of two such chains. The double chains pack as straight rods in layers with weak van der Waals forces between them. According to the ideas of Frank (1951), a crystal plate grown initially without dislocations by surface nucleation, may become self-stressed through non-uniform distribution of impurities. Ultimately, when the stress reaches the yield stress, the crystal plate will buckle and shear, thereby raising terminated steps. Thus in a crystal plate of palmitic acid, dislocations can be created by the slip of the double chains in the [001] directions, the strength of the dislocations depending upon the amount of slip. Slip in the [001] direction will lead to a number of positions at which the energy will show subsidiary minima, of which two positions of low energy are of special interest and are discussed below.

(a) When the slip is an integral multiple of the double-chain length (it may be termed an 'even' dislocation using the terminology of Forty (1952)), the energy minimum will be the same as the absolute minimum characteristic of perfect crystal. Further growth on the exposed step due to an even dislocation produces the normal bimolecular layer structure of the crystal. (b) When the amount of slip is equal to a half-integral multiple of the double-chain length, the dislocation created is an imperfect dislocation and the crystal growing on this will be a polytype of palmitic acid. Figure 22 shows diagrammatically a step $\frac{1}{2}$ times the bimolecular unit, created on a crystal plate whose exposed surface has been taken as CH$_4$ end of the chain. The slip plane marked PQR in the figure is now a unique plane and is a misfit surface; the CH$_4$ ends of the chains on the left side of the slip plane lie in the same level as the COOH groups on the right. Because of this misfit such dislocations should be expected to occur less frequently, and experimental observation showed only two such cases out of nearly fifty measurements.

When the crystal grows on this ledge it is easily seen that if the bottom of the step is more favourable for deposition the total step will separate into a layer of thickness equal to the height of the bimolecular unit which will grow quite fast (since bimolecular units exist in the solution), and a slowly growing half-integral step. The faster moving integral step will advance round the dislocation point one complete turn and overtake the half-integral step, thereby re-creating the original ledge of $1\frac{1}{2}$ times the unit cell, but the crystal will thicken by only one bimolecular unit every time. But spiral step heights (items 2 and 5, table 4) equal to half-integral multiples of the bimolecular unit are actually formed so that it is concluded that the step formed by the imperfect dislocation is able to advance on the initial surface as one unit. Two arrangements of the molecules for their deposition on to the crystal are possible. One grouping of each of these two arrangements, which may be called the A and B arrangements, is shown in the right-hand end of figure 22. When the molecules are added in the A arrangement along the ledge, they fit with the molecules in the exposed ledge, but misfit takes place with the chains of molecules beneath it. Therefore the arrangement leaves a fault line running from the edge of the crystal to the centre, and as the crystal
grows this fault line sweeps a helical fault surface. The exposed surface of the growing crystal has everywhere the CH\textsubscript{3} end of the molecular chains. However, if the first row of molecules added along the ledge is in the \textit{B} arrangement (a mixture of \textit{A} and \textit{B} arrangements along the ledge is left out), these fit with the chains beneath them but misfit with the chains on the ledge, i.e. along the slip plane. When one layer has been laid down, the exposed surface of the crystal will have COOH groups on the top. In order to maintain the same type of fault, the next layer that will be laid down will be of the \textit{A} type and so on, and the fault surface will be a continuation of the original slip plane. The exposed surface of the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure22.png}
\caption{Diagrammatic representation of a crystal plate of fatty acid with an imperfect dislocation exposing a terminated step equal to \(1\frac{1}{2}\) times the bimolecular unit. The zigzag chains CH\textsubscript{3}, CH\textsubscript{2}, COOH—COOH, CH\textsubscript{2}, CH\textsubscript{2}, CH\textsubscript{2} have been represented by \(\hat{\gamma}\) and the tilt of the chains to the basal planes has been neglected for simplicity. The slip plane is marked PQRS in the figure and is a surface of misfit.}
\end{figure}

successive loops of the spiral will, however, have alternately CH\textsubscript{3} and COOH groups at the top. It is not possible to say with certainty which of these two processes of growth is favoured. An electron-diffraction study of such a surface may possibly settle this. The first process may be more likely, as it creates a misfit along the length of bimolecular units, which should be easier to create since lateral binding of chains appears to be stronger, as is shown by the cleavage of crystal plates parallel to the \textit{ab} plane (see figure 9). In any case the crystals growing on the imperfect dislocations will differ only in the \(c\) parameter and thus will be different polytypes. It may be pointed out that the observed interlaced spiral has step height equal to twice the bimolecular unit. Thus, all crystal plates of palmitic acid with half-integral steps are the different polytypes of palmitic
Growth of long-chain fatty acid crystals. I

acid. There are few other known examples of the growth of crystals on imperfect dislocations.

Though no such polytypism has yet been found by X-ray analysis, the measurement of step height and the cross-laced patterns give the first direct experimental indication of polytypism in palmitic acid crystals. Half-integral steps have also been measured on stearic acid crystals (Verma & Reynolds 1953a), and in general all long-chain molecules with an active group, e.g. carboxyl or hydroxyl group at one end, may be expected to show polytypism.

**Slip patterns**

The formation of large steps and other patterns have already indicated that slip can take place comparatively easily in palmitic acid. The observation of growth patterns shows a variety of such phenomena. In addition to the simple unit slip, often macroslips are observed, the simplest examples of which are discussed below.

Figure 8 shows a crystal plate in which a triangular sector with two of its edges parallel to the [110] directions and the third to an axial direction [100], has slipped out. The shift of the Fizeau fringes towards the peak of the growth pyramid shows that this triangular strip is lower by about 600 Å. Fringes of equal chromatic order have been utilized to confirm this. Thus there is no possibility of a triangular crystal plate having settled on it. Instead, slip along the two glide planes parallel to [110] and [100] has raised two steps which terminate on the surface of the crystal, at the tip of triangular sector. These are therefore macroscopic dislocations with slip steps having crystallographic orientation. On this triangular sector, growth steps are visible which follow the direction of growth steps on the rest of the crystal face. From this it may be concluded that this catastrophic slip happened after the primary growth had taken place.

A different observation of slip is illustrated in the interferometric picture (figure 15). The crystal on the top right of the figure is a crystal layer showing uniform tint, and over the part where it lies on the other crystal plate it has taken up the contours of growth steps. Both the growth steps and crystal layer are several hundred ångströms high. In order to make sure that we are not seeing through the layer, the top surface was resilvered opaque, and as the micrograph (figure 16) shows the step structure is clearly imprinted on the layer and a small crack can be seen at the beginning of each step line on the layer. The resulting appearance of the composite crystal will be the same whether the uniformly thick crystal layer lies on the crystal plate or vice versa, since if slip takes place, in the second case it will be the slip along the edges of the crystal layer buried underneath the crystal plate. Thus in either case the internal slip of layers takes place over fairly large thicknesses. In a similar observation it was found to extend to a thickness ~1000 Å (Verma 1954).

Unit slip lines have been observed by Forty & Frank (1953) on silver crystals and by Anderson & Dawson (1953) on n-nonatriacontane crystals and have been explained as the movement of unit dislocations. These macroslips are evidence of the movement of large dislocation groups, which will play an important part in the mechanical properties of the crystal if they can glide easily.
Figure 9 exemplifies a case of an extremely thin crystal with a perfect cleavage and glide along the basal plane. Here two crystal layers show uniform tint (the crystals are doubly silvered) and are rotated with respect to each other by about 10°. Since both the layers are identical in shape and size and possibly in thickness also, this could hardly have happened by the formation of two separate layers which settle on each other at that orientation. It appears that a single-crystal layer was formed which cleaved along the basal plane. The two cleaved parts are subsequently rotated slightly with respect to each other.

**Birefringence**

Multiple-beam fringes of equal chromatic order (Tolansky 1948) formed by doubly silvered crystals were used for the determination of the birefringence of the palmitic acid crystals in the (001) plane. As shown by Tolansky the birefringence \( d\mu \) is given by

\[
d\mu = \frac{d\lambda}{\lambda},
\]

where \( d\lambda \) is the wave-length separation between the two polarized components of a fringe of the same order. Figures 19 and 20 illustrate this for the 74° and 56° polymorphs respectively where each fringe has split up into two components polarized in perpendicular planes. As is to be expected the two polymorphs with edge angles 74° and 56° differ in their birefringence as well as in the direction of greater refractive index. The fractional birefringence \( d\lambda/\lambda \) and \( d\mu \) for the two polymorphs assuming \( \mu = 1.52 \) is given in table 5 for the different wave-lengths in the visible region.

<table>
<thead>
<tr>
<th>crystal polymorph with edge angle 74°</th>
<th>crystal polymorph with edge angle 56°</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda (\text{Å}) )</td>
<td>5745</td>
</tr>
<tr>
<td>( d\lambda/\lambda )</td>
<td>0.0145</td>
</tr>
<tr>
<td>( d\mu )</td>
<td>0.019</td>
</tr>
<tr>
<td>( \lambda (\text{Å}) )</td>
<td>5800</td>
</tr>
<tr>
<td>( d\lambda/\lambda )</td>
<td>0.013</td>
</tr>
<tr>
<td>( d\mu )</td>
<td>0.019</td>
</tr>
</tbody>
</table>
Growth of long-chain fatty acid crystals. I

It was made on stearic acid (Verma & Reynolds 1953). Indeed, the direction of the symmetry axis is often exhibited as a difference in shade of the two halves of the crystal with respect to the b-axis both for the 74° and 56° polymorphs; an example for the latter is illustrated in figure 7. Since these observations are interferometric, this difference in shade is due to the small change in thicknesses of the two halves, which would not normally be detected without the multiple-beam interference tints which provide a great sensitivity.

This birefringence of very thin crystals measured interferometrically may be compared with the value (1.533 - 1.508 = 0.025) reported by Thibaud & Dupré La Tour (1930) for the α form (i.e. the 56° polymorph). This is not one of the principal birefringences, since only one principal refractive index parallel to the symmetry axis b lies in the (001) plane. It has, however, a practical value since the crystals form plates parallel to (001).

It is a pleasure for me to express my thanks to Professor J. D. Bernal, F.R.S., for his kind interest in the work and the facilities of the Birkbeck College Research Laboratory for the X-ray investigation, and to Professor S. Tolansky, F.R.S., in whose laboratory at Royal Holloway College the interferometric studies were done, for his encouragement. My sincere thanks are due to Dr J. W. Jeffery for his most valuable advice and help during the X-ray studies. I am indebted to my friend Dr R. C. Mehrotra for a supply of redistilled palmitic acid and to Messrs Price (Bromborough) Ltd. for the supply of a very pure sample of palmitic acid. This work has been carried out during the tenure of an Imperial Chemical Industries Research Fellowship of the University of London, while on study leave from the University of Delhi.

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Dislocations in silicon carbide crystals:
Interferometric and X-ray study of polytypism

BY AJIT RAM VERMA
Dislocations in silicon carbide crystals: Interferometric and X-ray study of polytypism

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[Plates 14 and 15]

A number of silicon carbide crystals, some new polytypes, have been studied. Phase-contrast microscopic and multiple-beam interferometric techniques have been used to study the growth spiral structure on (0001) and for the measurement of spiral step heights. X-ray methods gave the lattice constants. The various silicon carbide crystals can be divided into the following categories by expressing the relationship between the step height of the growth spirals on (0001) and the measured height of the unit cell along the c axis:

(i) crystals in which there is direct correlation between the step height and the unit cell;
(ii) those in which the step height is a multiple or submultiple of the unit cell;
(iii) a very large unit cell size originating from a complicated growth pattern showing no direct correlation between the step height and the unit cell size;
(iv) crystals consisting of a mixture of polytypes and exhibiting an interlaced type of growth spiral;
(v) a gradual transition to crystals with unresolved structure and disordered types.

Rhombohedral silicon carbide crystals growing from two dislocations, one positive and the other negative, are shown to lead to the creation of a positive and negative rhombohedron (i.e. obverse and reverse positions).

INTRODUCTION

The phenomenon of polytypism which was first pointed out by Baumhauer (1915) and Thibault (1944) to occur in silicon carbide crystals, has in the last few years been shown to be a widely occurring property in crystals. Zinc sulphide, which has a similarity with silicon carbide, has at least three polytypes (Strock & Brophy 1955; Buck & Strock 1955). From the observation of growth patterns on the (001) faces of long-chain organic molecules, Amelinckx (1953) and Verma (1955) have concluded that these substances also are polytypic. However, no crystal appears to show such a large number of stable polytypes as silicon carbide. Up to now over twenty have been reported (Ramsdell & Kohn 1952; Mitchell 1954). Several of the polytypes have exceptionally large unit cell size, e.g. one reported by Honjo, Miyake & Tomita (1950) has $c \approx 1500 \text{Å}$, consisting of 594 layers. The origin and cause of the stability of the many-layered structures is not fully clear yet. Frank (1951) has tried to explain the origin of polytypism in silicon carbide in terms of screw dislocations, since it has been established by interferometric studies that the spirals originating from screw dislocations on silicon carbide have growth steps which are simply related to the size of the X-ray unit cell (Verma 1951 a, b). Recently Jagodzinski (1954) has investigated the faulty order phenomenon in silicon carbide crystals and has put forward arguments against Frank's interpretation of polytypism, suggesting that the cause of the stability of the many-layered structures of long periods is to be found in the vibration entropy.

[462]
In the present work a large number of silicon carbide crystals were selected which showed growth spiral patterns. They were examined by phase-contrast microscopy, multiple-beam interferometry (Tolansky 1948), and X-ray diffraction. A combination of interferometric and X-ray methods has been found to be very suitable for the study of polytypism. In this paper is presented the synthesis between these two studies. A more exhaustive interferometric examination of silicon carbide crystals was also undertaken, since the most direct evidence for dislocations is obtained by optical and interferometric techniques. This has enabled us to support the dislocation mechanism and also to suggest the modifications needed in the theory.

**Polytypism in silicon carbide crystals and spiral growth steps**

It had already been realized that the step heights of the growth spirals which are observed on (0001) of silicon carbide, would be related to the c-lattice parameter. Since the different polytypes of silicon carbide, though composed of identical layers, differ in the arrangement of these layers, the number of layers necessary for the arrangement to repeat itself determines the c parameter. In a previous study (Verma 1951 b) in which a relationship between the spiral growth steps and X-ray unit cell had been demonstrated, the identification of some of the polytypes with small numbers of layers in the unit cell was possible by the optical goniometric method of Thibault (1944), but this has a limited value for polytypes with a large number of layers in the unit cell. Hence X-ray diffraction is employed. It has now become possible to confirm the previous results and to extend them to other polytypes.

**Dislocations of unit Burgers vector and their spiral growth patterns**

The relationship between the growth spiral steps and the c parameter for silicon carbide is different for the hexagonal and rhombohedral polytypes. It has been shown (Verma 1951 a) that the growth steps of hexagonal crystals are equal to the height of the unit cell along the c axis. For this purpose the most commonly occurring crystal denoted as 6H (Ramsdell’s (1947) notation) had been chosen. The average step height \( h \) was found by interferometric methods to be

\[
h = 15 \pm 2 \text{Å}.
\]

The c-lattice parameter is 15·078 Å. Thus such growth spirals originate from dislocations of unit Burgers vector. To find if this is true for other hexagonal crystals with a larger number of layers, a silicon carbide crystal (serial no.*33) showing a growth spiral (figure 1†) with step height 168 ± 5 Å, as measured by multiple-beam fringes of equal chromatic order was chosen. A 15° X-ray oscillation photograph about the c axis of this crystal (figure 2) exhibits a mirror plane perpendicular to the c axis; thus it is a hexagonal crystal. There are eleven diffraction spots between the successive 10H spots of the 6H type. Hence the value of

\[
c = 11 \times 15·078 = 165·85 \text{Å},
\]

* A serial number has been given to the various crystals studied in the present investigation.
† Figures 1 to 10 are on plate 14, facing p. 466, and figures 11 to 23 on plate 15.
which is in agreement with the optical step height, within experimental errors. This
result will therefore be generalized for all hexagonal crystals.

In the case of silicon carbide crystals based on the rhombohedral unit cells, it
has been found for the polytype $15R$ that the step height $h$ is $12 \pm 2\text{Å}$. As the unit
cell height $c = 37.7\text{Å}$, the step height appears to be only one-third the height of the
unit cell referred to the hexagonal axes. It is thus equal to the side $a_{\text{th}}$ of the
rhombohedral unit cell and so corresponds to the number of layers in the Zhdanov
(1945) symbol, or Ramsdell’s (1947) zigzag sequence.

This interesting result, the consequences of which are explained later, has now
been confirmed on silicon carbide crystals of type $33R$. The step height $h$ measured
by interferometry is

$$h = 27 \pm 3\text{Å}.$$ 

The lattice constant is $c = 82.9\text{Å}$. A similar result has also been confirmed in poly-
type $21R$. Thus again the step height is one-third the $c$ parameter and is equal to
the projection of $a_{\text{th}}$ on the trigonal axis.

Figure 3 is a phase-contrast micrograph of (0001) of crystal no. 31. The two spirals,
clockwise and anti-clockwise, originate from two dislocations of opposite hand, and
equal strength, since the growth steps do not leave any fault surface when they fuse.

For the measurement of step height both multiple-beam Fizeau fringes and fringes
of equal chromatic order were employed, the latter being illustrated in figure 4.
Fizeau fringes gave $h = 109 \pm 5\text{Å}$, and fringes of equal chromatic order $103\text{Å}.$
A $15^\circ$ X-ray oscillation about the $c$ axis was taken to record $10\overline{1}1$ row on a $3\text{cm}$ and
$10\text{cm}$ camera (figure 5), which shows that the crystal is based on a rhombohedral
unit cell and $c = 105.8 \times 3 = 317.4\text{Å}$. The crystal therefore is a new polytype
$126R$, and does not belong to the $[(33)_632]_3$ series. This crystal establishes con-
clusively that the step height is one-third the $c$ spacing for the rhombohedral
crystals.

**Growth spiral with step heights which are a multiple
or submultiple of the Burgers vector**

The first example is the silicon carbide crystal (serial no. 124), whose phase-
contrast microphotograph (figure 6) shows a regularly developed single hexagonal
spiral with a step height $h = 88.7\text{Å}$ given by fringes of equal chromatic order
(figure 7). A $15^\circ$ single oscillation photograph (figure 8) shows the crystal to be of
$6H$ type, which indicates that the step height is $6 \times 15.078\text{Å}$ and is thus a multiple
of the unit Burgers vector. A similar result was verified on a silicon carbide crystal
(serial no. 137) with a much larger step height $h = 610 \pm 10\text{Å}$. Several other such
cases have now been confirmed. The above examples represent the category in
which the step height has a fixed value without any variation or dissociation, the
structure consisting only of $6H$ type.

We consider next a crystal belonging to the type $6H$ but showing growth steps of
different heights in different parts of the crystal (serial no. 138). The step height was
measured to be 264 and $624\text{Å}$ at two places, but an oscillation photograph gave
spots corresponding to $6H$ type only. It must therefore be interpreted that the
structure of both the growth steps is that of $6H$ type.
No case has been encountered so far in which the growth steps may be regarded to be multiples of the Burgers vector for a polytype other than 6H. Two cases have been noted in which the growth steps are a submultiple of the Burgers vector. Crystal serial 134 has a series of growth steps of height \( h = 68 \text{Å} \). A 15° oscillation photograph about the \( c \) axis obtained from a small chip broken from this crystal is shown in figure 9. By taking the known 6H reflexions 10\(1\bar{1} \) and 10\(\bar{1}\bar{2} \) as references, the size of the unit cell has been determined to be

\[
9\frac{1}{3} \times 15.08 = 140.75 \text{Å}
\]

(for 3 times this value if it is a rhombohedral crystal). Within experimental error the step height is half the Burgers vector. However, when a 15° oscillation photograph was taken of the whole crystal, it was noted that diffraction spots \( \frac{43}{4} \) in number were also present between 10\(1\bar{1} \) and 10\(\bar{1}\bar{2} \) reflexions of the 6H type. The unit cell size \( 4\frac{3}{4} \times 15.08 = 70.37 \text{Å} \) is within error in agreement with the observed step height. These polytypes if they are rhombohedral will be 84\(R \) and 168\(R \), and it is significant that two polytypes, one twice as big as the other, occur in the same crystal block.

In the second example (serial no. 139) the growth steps are of height 62.6 Å. A small chip broken from one corner gave a 15° oscillation photograph on a 10 cm camera shown in figure 10. The unit cell is exactly 9 times the 6H unit cell and \( c = 9 \times 15.08 = 135.7 \text{Å} \). Thus the step height is one-half the size of the unit cell. However, crystal chips broken from other parts of the crystal gave only 6H diffraction spots, and thus only one part of the crystal appears to be the above polytype.

**Mixed ordered and disordered crystals, and syntactic coalescence of different polytypes**

Crystal 135 shows a series of growth step (figure 11) of heights ranging from 18 to 434 Å with intermediate steps of 40, 100, 177 and 298 Å, as shown by the multiple-beam Fizeau fringes (figure 12). A 15° oscillation photograph taken about the \( c \) axis on a 10 cm camera is shown in figure 13. Between the 10\(1\bar{1} \) and 10\(\bar{1}\bar{2} \) reflexions for 6H type, one can count 15 or 16 diffraction spots. But the spacing between successive spots is not constant, and it cannot be taken as a single polytype with a \( c \) parameter some 16 times bigger than that of 6H. It may be regarded as a mixture of the possible polytypes corresponding to the heights of different growth steps of which one or two types are dominant; this conclusion is supported by the growth features.

Other examples of gradually increasing disorder or unresolved structures are illustrated by the following three cases. Crystal 140 shows growth steps of height \( h = 414 \text{Å} \). A 15° oscillation photograph about the \( c \) axis on a 10 cm camera (figure 14) shows big and strong spots corresponding to the 6H structure, but between the successive 6H spots are 8 to 9 fainter spots which are unevenly spaced. Crystal 136 shows growth steps of height \( h = 186 \text{Å} \), and its corresponding 15° oscillation photograph about the \( c \) axis (figure 15) shows extended 6H spots and a series of imperfectly resolved spots connected by a streak. Finally, the last stage is shown by crystal 32 which shows a rounded growth spiral on (0001). The growth steps do not remain single in different parts of the crystal, and the step heights measured at two different parts were 268 and 305 Å. The 15° oscillation photograph taken about
the c axis (figure 16) shows strong 10l1 spots corresponding to the 6H structure connected by continuous streaks without any indication of its breaking into discrete spots. The intensity of the continuous streaks falls gradually between the successive 6H spots.

The case of mixture of polytypes which are in syntactic coalescence is shown by crystal 120. Figure 17 shows a 15° oscillation photograph about the c axis on a 3 cm camera. There are discrete spots corresponding to types 6H, 15R and a new polytype which is 72R. A phase-contrast micrograph of the (0001) of this crystal (figure 18) shows a series of interlaced growth spiral patterns originating from two or three sources.

Another example of mixture of polytypes, crystal 37, shows on (0001) two spirals of steps height 404 and 270 Å respectively. A Weissenberg photograph taken from a small chip of this crystal confirms it to be a mixture of the polytypes.

COMPICLICATED GEOMETRICAL GROWTH PATTERN AND A LARGE POLYTYPE

The (0001) of crystal 141 shows the growth pattern illustrated in figure 19. An extremely thin flake (thickness ~ 0.05 mm) nearly parallel to (0001) was taken from this crystal, and a 15° oscillation photograph about the c axis was taken on a 10 cm camera and is shown in figure 20, of which an enlarged region is given in figure 21. The unit cell has a c parameter which is at least 26 x 15.08 = 392.0 Å (3 times this value if it is a rhombohedral lattice). The fine spacing of the spots is resolved only because of the thinness of the crystal. It may perhaps be emphasized that in order to have the successive 10l1 diffraction spots separately resolved, the size of each individual spot should be less than the distance between the successive spots as determined by the length of the unit cell size. On a 3 cm camera the distance between 10l1 and 10l2 reflexions for 6H is about 3 mm, and in order to be able to resolve diffraction spots from a unit cell 26 times bigger (e.g. crystal 141) the size of the spot (considering it to be the projected image of the crystal and neglecting absorption, focusing effects, etc.) should be less than \( \frac{3}{26} \) mm, and thus for a crystal of thickness

---

**DESCRIPTION OF PLATE 14**

**Figures 1 to 10**

**Figure 1.** Phase-contrast microphotograph of (0001) of silicon carbide crystal 33. x 60.

**Figure 2.** Enlargement of a 15° oscillation photograph about c axis, 3 cm camera, of crystal 33 using unfiltered X-ray from copper target. It shows 10l1 row.

**Figure 3.** Phase-contrast microphotograph of (0001) of crystal 31 showing growth spirals from two dislocations of opposite hand and of equal strength. x 60.

**Figure 4.** Fringes of equal chromatic order on growth steps of crystal 31. x 20.

**Figure 5.** 15° oscillation photograph about c axis, 10 cm camera of crystal 31; Cu Kα. It shows 10l1 row.

**Figure 6.** Microphotograph of (0001) of crystal 124. x 60.

**Figure 7.** Fringes of equal chromatic order on growth steps of crystal 124. x 20.

**Figure 8.** 15° oscillation photograph about c axis of crystal 124; 3 cm camera; Cu Kα lines.

**Figure 9.** Enlargement of a part of 15° oscillation photograph about c axis (with superimposed Laue photograph) of crystal 134; 3 cm camera.

**Figure 10.** 15° oscillation photograph about c axis, crystal 139; 10 cm camera; Cu Kα. It shows 10l1 row.
much greater than 0.1 mm, the spots corresponding to this big unit cell could hardly be expected to be resolved. It was actually verified that by taking another piece of the crystal of thickness slightly greater than 0.1 mm from the same specimen, spots begin to overlap and a crystal thicker still would make matters worse because of absorption and other factors leading to the smearing between successive $6H$ spots. Thus an unresolved spot structure of a crystal with a fairly long period would be partly due to this cause, and it would be difficult to say that an unresolved structure of the streak similar to that observed by Jagodzinski (1954) is wholly due to disorder unless sufficiently thin and small crystals are used for X-ray diffraction.

**DISCUSSION**

*Origin of polytypism: Frank’s theory and Jagodzinski’s comments*

The correlation between the spiral growth steps and the measured c spacing for the different polytypes lends support to Frank’s (1951) theory of the origin of polytypism by a dislocation mechanism. If we accept the growth spiral as evidence of a screw dislocation, we find that the Burgers vector of the dislocation is equal to the repeat period of the polytype as determined by X-rays. The identity period of the crystal is then a consequence of the dislocation whose pitch determines the repeat unit, and thus it provides us with a mechanism for the formation of the various polytypes including those with giant cells with periods far greater than the range of any conventional atomic forces. However, one has to explain the formation of the initial crystal plate of the size of (0001) and the creation of dislocation by some

---

**DESCRIPTION OF PLATE 15**

**FIGURES 11 TO 23**

**Figure 11.** Phase-contrast microphotograph; crystal 135. $\times 60$.

**Figure 12.** Fizeau fringes on growth steps; crystal 135. $\times 30$.

**Figure 13.** $15^\circ$ oscillation photograph showing $10\overline{1}I$ row; 10 cm camera; about c axis; crystal 135; $Cu K\alpha$.

**Figure 14.** $15^\circ$ oscillation photograph showing $10\overline{1}I$ row; 10 cm camera; about c axis; crystal 140; $Cu K\alpha$.

**Figure 15.** $15^\circ$ oscillation photograph showing $10\overline{1}I$ row; 10 cm camera about c axis of crystal 136; $Cu K\alpha$.

**Figure 16.** $15^\circ$ oscillation photograph showing $10\overline{1}I$ row; 10 cm camera about c axis; crystal 32; $Cu K\alpha$.

**Figure 17.** $15^\circ$ oscillation photograph about c axis; crystal 120; 3 cm camera; $Cu K\alpha$.

**Figure 18.** Phase-contrast microphotograph of (0001) crystal 120, showing interlaced spiral from two sources. $\times 60$.

**Figure 19.** Phase-contrast microphotograph of (0001) crystal 141. $\times 60$.

**Figure 20.** $15^\circ$ oscillation photograph showing $10\overline{1}I$ row about c axis; crystal 141; 10 cm camera; unfiltered X-rays, copper target.

**Figure 21.** Enlargement of a part of figure 20.

**Figure 22.** Laue photograph; X-ray beam at right angles to the c axis; crystal no. 31.

**Figure 23.** Enlargement of the extreme left part of figure 22, showing characteristic Laue spots.

*Note.* In figures 2, 5, 10, 13 to 16 and 20, an arrow has been drawn to indicate the zero layer. All the figures have been reduced 4 on reproduction.
mechanism. Assuming the initial crystal to have $6H$ structure and the slip to be an integral multiple (i.e. a perfect dislocation), the ledge exposed will have $6H$ structure and the crystal growing on it will be of $6H$ type. The growth steps which will be equal to the initial ledge will be a multiple of 15 Å, thus accounting for the observation of growth spirals with steps which are a multiple of the unit Burgers vector. In contrast with this, Cabrera (1953) has concluded, from considerations of supersaturation, that the macroscopic spirals observed on silicon carbide crystals show on rhombohedral type and not hexagonal.

It is easy to explain the growth of hexagonal crystals on pure screw dislocations by the accretion of hexagonal units on the vertical ledge created by a slip. The growth of rhombohedral crystals, with spiral steps equal to one-third of the repeat distance along the c axis, cannot be explained by the model of pure screw dislocations but can be satisfactorily explained by introducing inclined dislocations, i.e. a combination of screw and edge dislocations.

It was pointed out by Jagodzinski that the Burgers vector of edge dislocations equal to $\frac{1}{2}a + \frac{2}{3}b$ (or its multiple) is only a fraction of the Burgers vector of the screw dislocation and hence edge dislocations are more favourable. Moreover, growth by screw dislocation should produce a crystal elongated along [0001], but in practice crystals occur in tabular form. Thus the screw dislocations would appear to play a role in the last stages of growth, the more because if their high energy of formation is to be supplied by the lattice, this can only be possible when the crystal has grown to considerable volume, by which time the crystal has already settled down to a certain structure. Hence Jagodzinski concludes that under these assumptions the long-period structures can no longer be understood. According to him the cause of the stability of the many-layered structures, in part, of the long periods is to be found in vibration entropy. He has investigated by X-ray diffraction methods 150 silicon carbide crystals taken at random and found that some are ordered crystals while others are 'faulty ordered' or mis-ordered, the $6H$ structure being commonest. All mis-ordered crystals of silicon carbide showed sharp X-ray diffraction spots superimposed on diffuse background. He noted that all long-period structures belong to the mis-ordered type. This cannot be interpreted by screw dislocation growth because then there should exist only sharply limited reflections without essential 'smears'. Further, by considering the energy distribution of eigen-vibrations as a function of the state of order, Jagodzinski has given a simple qualitative interpretation of mis-order distribution in silicon carbide crystals. However, in the present investigation we have the following results which are at variance with Jagodzinski's.

Crystal 31 is a tabular crystal with a fairly well-developed (0001) of size nearly 10 sq.mm. on which two growth spirals of opposite hand of step height $h \approx 105 \text{Å}$ appear. The crystal is of $126R$ type. A $15^\circ$ oscillation photograph was taken from the entire crystal, showing that the whole crystal belongs to the type $126R$ without the commonest $6H$ type occurring in syntactic coalescence. The creation of two dislocations of opposite sign but of equal strength, which is easily understandable on the dislocation mechanism, at the two terminated ends of a slip line, would be difficult to explain otherwise.
Dislocations in silicon carbide crystals

Again crystal 141 gives sharp X-ray diffraction spots corresponding to the long-period structure, without any streaks connecting them. Thus it is possible for a long-period structure to exist without any mis-order in it. However, it remains to explain the relation between its growth pattern observed on (0001) (figure 19) and its X-ray unit cell. The growth pattern consists of a group of dislocations arranged along a line giving a repeat pattern. Therefore, in this case the highly ordered polytype has resulted from a group of neighbouring dislocations and not a single dislocation of a large Burgers vector as one would have expected on Frank's ideas of the origin of polytypism on dislocation mechanism. In addition, some evidence for the existence of the growth steps which are a submultiple of the Burgers vector has also been given (crystals 134 and 139).

The observation of mixed order and increasing mis-ordered crystals (crystals 140, 136 and 32) can perhaps be understood by introducing edge dislocation which changes A, B and C layers into one another, and the need for violating the strong covalent binding would not arise. It may be emphasized that in the continuous streak observed in crystal 32 (figure 16) the intensity falls gradually between two successive 6H spots. This will result when the main structure is of Z(33) type in Zhdanov symbols and the contribution of layers decreases the more they are removed from the Z(33) arrangement. When variation of polytypes can take place along a growth step, a mixture of polytypes over a scale revealed only by a microscope would take place. This will explain the observation of mixed ordered and mis-ordered crystals. According to Jagodzinski, crystals with high fault order have without exception a tendency to grow mixed superperiods; where the structure of 6H and 15R occur close together the two reflexions blur into one another. However, in constrast, crystal 120, which is a mixture of 6H, 15R and 72R, gave spots which were sharply defined. This may be regarded as a case of syntactic coalescence.

Positive and negative rhombohedra (obverse and reverse positions)
as a result of dislocations of opposite hand

The diffraction spots from crystal 31 show some peculiarities. In a 15° oscillation photograph taken on a 3 cm camera, the diffraction spots have a criss-cross appearance in the upper half and are tilted in the lower half of the figure. A similar 15° oscillation photograph on the 10 cm camera reveals that the diffraction spots immediately on either side of the equatorial line consist of a more or less circular spot and a small tail tilted to the equatorial line by about 30°. Higher-order reflexions in the upper half show clearly that the reflexions consist of a diffuse spot with a sharp horizontal line at its top but slightly separated from it. The 15° oscillation photograph from the entire crystal also clearly showed that the diffraction spots are tilted, though the horizontal zero-layer line indicated that the crystal was fairly well set with the c axis parallel to the oscillation axis. It was at first attempted to explain the anomalies as arising from the helicoidally arranged lattice due to the dislocation. The slope of the spiral growth terraces on (0001) of a screw-dislocated crystal is equal to \( \frac{h}{2\pi} \) per radian, where \( h \) is the step height, and is far less than the above tilt of the diffraction spots, even for large Burgers vector. It is proposed that this crystal consists of a positive and negative rhombohedron (i.e.
obverse and reverse positions) arising from two dislocations of opposite sign. Thus
a crystal chip containing both the positive and negative rhombohedra will give in
the (10\ell) row two series of diffraction spots vertically displaced from each other by
one-third the spacing of successive spots. When these two series of spots are dis-
placed sideways also and are not resolved, the compound spot will appear as a
tilted spot. The fact that this crystal does in fact consist of a positive and negative
rhombohedron is clearly shown by the characteristic spots seen as a vertical row
of spots in the Laue photograph (figure 22, extreme left), with the X-ray beam
perpendicular to the c axis. The relevant part is shown enlarged in figure 23, which
shows that there are two rows of double spots vertically displaced from each other
by one-third of the spacing. The doubling of spots is due to the Cu Kα₁ and Kα₂
components. It is therefore inferred that this crystal consists of positive and
negative rhombohedra, the simultaneous presence of which makes it possible to
distinguish between them. Thus we conclude that a pair of positive and negative
dislocations, the existence of which is shown conclusively by the observation of
growth spirals on (0001), lead to the formation of a positive and negative rhombo-
hedron for a silicon carbide crystal of rhombohedral type. This is explicable on
dislocation mechanism since the lattice is helicoidally arranged, but will be difficult
to understand on other mechanisms. It is interesting to compare it with a similar
result in quartz crystals in which the right-handed and left-handed varieties result
from the spirally arranged SiO₄ tetrahedra in a right-handed or left-handed fashion.
Willis (1952) found that the growth pyramids on the major rhombohedron faces
also reveal the right- and left-handed character of quartz.

A noteworthy point which is observable from the oscillation photograph (figure
17) of crystal 120 which consists of 6\ell, 15\ell and 72\ell types in syntactic coalescence
is that the rows 10\ell (and also 20\ell, etc.), both for 15\ell and 72\ell, have the reflections
of order 1, 4, 7, ..., etc. (or 2, 5, 8, ..., etc.) on the same side of the equatorial line.
This shows that in this crystal both the rhombohedra are of the same sign, i.e. both
either in obverse or reverse positions. The observation on (0001) of interlaced growth
steps originating from two or three sources suggests that the interlacing of growth
steps arises from the mixture of different rhombohedral and hexagonal structures
when the mutual arrangement is such that both are either in obverse or reverse
positions. This is further supported by the observation that it is possible to analyze
an interlaced spiral into a pair of growth spirals of similar hand. The original
explanation for interlacing given by Frank (1951), made it obligatory for growth
layers on crystals of 6\ell type to cross-lace. According to him 6\ell type consisting of
ABCACB structure in classical layer notation may be written in Nabarro–Frank
notation (Frank 1951) as ΔΔΔ VVV. Since a Δ layer changes into a V layer by a
rotation of 60°, whatever monolayer in this stack of six layers is the slowest growing
in [1010] orientation, the monolayer three layers later is slowest in [0110] orienta-
tion. This alternation of slowest and fastest rate for a particular monolayer by change
in orientation of 60° will lead to cross-lacing, which will be a necessity for 6\ell types
and is also a possibility for rhombohedral types. This conclusion is, however, not
borne out by experimental observations, since crystals of 6\ell type often show simple
hexagonal spiral without any interlacing. Similarly, growth spirals observed on
obverse and reverse positions) arising from two dislocations of opposite sign. Thus a crystal chip containing both the positive and negative rhombohedra will give in the (1011) row two series of diffraction spots vertically displaced from each other by one-third the spacing of successive spots. When these two series of spots are displaced sideways also and are not resolved, the compound spot will appear as a tilted spot. The fact that this crystal does in fact consist of a positive and negative rhombohedron is clearly shown by the characteristic spots seen as a vertical row of spots in the Laue photograph (figure 22, extreme left), with the X-ray beam perpendicular to the c axis. The relevant part is shown enlarged in figure 23, which shows that there are two rows of double spots vertically displaced from each other by one-third of the spacing. The doubling of spots is due to the Cu Kα₁ and Kα₂ components. It is therefore inferred that this crystal consists of positive and negative rhombohedra, the simultaneous presence of which makes it possible to distinguish between them. Thus we conclude that a pair of positive and negative dislocations, the existence of which is shown conclusively by the observation of growth spirals on (0001), lead to the formation of a positive and negative rhombohedron for a silicon carbide crystal of rhombohedral type. This is explicable on dislocation mechanism since the lattice is helicoidally arranged, but will be difficult to understand on other mechanisms. It is interesting to compare it with a similar result in quartz crystals in which the right-handed and left-handed varieties result from the spirally arranged SiO₄ tetrahedra in a right-handed or left-handed fashion. Willis (1952) found that the growth pyramids on the major rhombohedron faces also reveal the right- and left-handed character of quartz.

A noteworthy point which is observable from the oscillation photograph (figure 17) of crystal 120 which consists of 6H, 15R and 72R types in syntactic coalescence is that the rows 1011 (and also 2021, etc.), both for 15R and 72R, have the reflexions of order 1, 4, 7, ..., etc. (or 2, 5, 8, ..., etc.) on the same side of the equatorial line. This shows that in this crystal both the rhombohedra are of the same sign, i.e. both either in obverse or reverse positions. The observation on (0001) of interlaced growth steps originating from two or three sources suggests that the interlacing of growth steps arises from the mixture of different rhombohedral and hexagonal structures when the mutual arrangement is such that both are either in obverse or reverse positions. This is further supported by the observation that it is possible to analyze an interlaced spiral into a pair of growth spirals of similar hand. The original explanation for interlacing given by Frank (1951), made it obligatory for growth layers on crystals of 6H type to cross-lace. According to him 6H type consisting of ABCACB structure in classical layer notation may be written in Nabarro–Frank notation (Frank 1951) as ΔΔΔ VVV. Since a Δ layer changes into a V layer by a rotation of 60°, whatever monolayer in this stack of six layers is the slowest growing in [1010] orientation, the monolayer three layers later is slowest in [0110] orientation. This alternation of slowest and fastest rate for a particular monolayer by change in orientation of 60° will lead to cross-lacing, which will be a necessity for 6H types and is also a possibility for rhombohedral types. This conclusion is, however, not borne out by experimental observations, since crystals of 6H type often show simple hexagonal spiral without any interlacing. Similarly, growth spirals observed on
Dislocations in silicon carbide crystals

crystals which have been identified to be 15R and 33R and other polytypes with much bigger unit cells, e.g. silicon carbide crystal serial numbers 31 and 33 (figures 3 and 1), do not show any interlacing.

Table. Summary

<table>
<thead>
<tr>
<th>serial no. of crystal</th>
<th>crystal type</th>
<th>interferometric data: h (Å)</th>
<th>X-ray data: c (Å)</th>
<th>Unit Burgers vector</th>
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<td>6H</td>
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<td>15R</td>
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<td>33R</td>
<td>27 ± 3</td>
<td>27.5 x 3 = 82.5</td>
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<td>126R</td>
<td>102 ± 8, 109 ± 5</td>
<td>106.8 x 3 = 317.4</td>
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<td>11 x 6 = 66H</td>
<td>168 ± 3</td>
<td>15.08 x 11 = 165.88</td>
<td>known polytypes</td>
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<td>both positive and negative rhombohedra are present simultaneously in the crystal piece</td>
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Multiple Burgers vector

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Submultiple Burgers vector

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<td>68</td>
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<td>9 x 6 = 54H</td>
<td>63</td>
<td>135 ± 7</td>
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Complicated growth pattern and no correlation between Burgers vector and c spacing

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Mixture of polytypes

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Unresolved structure or disordered types

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It is a pleasure for me to express my sincere thanks to Professor S. Tolansky, F.R.S., and Professor J. D. Bernal, F.R.S., for their very kind interest and encouragement and for affording the facilities of their laboratories during my tenure at Royal Holloway College, as an I.C.I. Fellow at the University of London when this work was done.
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Movement of dislocations and polytypism in silicon carbide

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With 13 Figures
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Abstract

The surface structure of a number of SiC crystals, some of which have been identified by x-rays as a mixture of two or more polytypes, have been studied with phase-contrast microscopy and multiple-beam interferometry. In addition to the movement of unit dislocation causing unit slip, evidence for the movement of giant dislocations, in keeping with the observation of multimolecular spirals, has been obtained. The experimental evidence for the operation of a modified cone source as an alternative to the Frank-Read source, which is also common in SiC, is revealed. In this type of source the slip plane of a sweeping dislocation rotates as the dislocation spirals.
This study has revealed the nature of dislocations present in SiC. In addition to the pure screw dislocation with Burgers vector perpendicular to the growing surface, inclined dislocations which can be resolved into edge and screw components have been observed. A modification to Frank's theory of polytypism is suggested which explains the production of almost all the rhombohedral polytypes without invoking periodic breaks in the stacking sequence.

Introduction

A comparison of the crystal structure and the growth spirals observed on (0001) face of SiC suggested that the step height of the growth spiral is either equal to, or is a multiple of, the x-ray repeat distance along the c axis. The spiral growth patterns on SiC and on several other crystals have been explained on the screw-dislocation theory of Burton, Cabrera and Frank. Since it is established that the centre of the spiral is the point of emergence of a dislocation, it is now possible to identify various properties of individual dislocation.

Dislocations are known to play a significant part in the deformation of crystals by their movement. Griffin has observed certain growth features on prism faces of beryl from which a movement of dislocation could be inferred. Frank and Forty and Anderson and Dawson have also observed similar changes in the growth patterns on crystals of silver and on crystals of n-nonatriacontane respectively. In these cases, only unit slip has been inferred to have taken place. SiC exhibits a variety of spiral markings which are monomolecular as well

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as multimolecular, circular as well as polygonal, interlaced and also with straight edges, and is thus eminently suited for the study of the movement of dislocations. This study which we have undertaken has revealed the nature of dislocations present in SiC and has also suggested that the concept of pure screw dislocation cannot explain all the growth features. By introducing a combination of screw and edge dislocation, it has been possible to provide an explanation for some of the growth features. This idea has been used to explain the phenomena of polytypism in terms of the dislocation theory of crystal growth.

**Movement of dislocations**

The dislocation theory of crystal growth\(^8\),\(^9\) suggests that a growing crystal can only increase in thickness (except when the supersaturation is large) by the reasons of dislocations it contains. If a dislocation moves across a crystal surface, a slip step will be raised. This would cause rearrangement of the growth steps in the form of kinks along the slip step provided the structure of the growth step and the moving dislocation are identical. An example of such a mechanism operating in SiC is

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shown in Fig. 1. In view of the perfect kinking of the growth steps on one side of the slip step with the neighbouring layer on the other side it appears that the slip step is equal to the growth step. Multiple beam Fizeau fringes passing over the crystal are shown in Fig. 2. The main step across which kinking takes place is 434 Å, although at certain places steps of 18, 40, 100 and 298 Å are recorded. It is thus clear that the slip step is 434 Å. This affords evidence of the movement of a giant dislocation in keeping with the observation of multimolecular spiral steps on SiC. Another example of the movement of a dislocation causing kinks in the growth steps is shown in Fig. 3, the arrow indicating the direction of the slip step. In this case the dislocation taking part in the slip process has a Burgers vector equal to 75 Å, five times the x-ray repeat distance. Numerous such cases, and also those involving unit dislocations, have been observed on crystals of SiC.

Movement of dislocation causing spiral growth

Various kinds of geometrical patterns may be expected on a growth surface after a dislocation has moved through the crystal. A simple spiral of the kind shown in the Fig. 4 indicates that the dislocation is at its centre. If this dislocation moves, a slip step will be raised between the centre of the spiral and its new position. The slip step would obviously follow the trace of the plane in which the dislocation moves and would have a height equal to the Burgers vector of the dislocation. From the micrograph the slip step is not clearly visible,
but the multiple beam Fizeau fringes (Fig. 5) show the existence of the slip step over a short distance of about 30 μ. The slip vector is equal to the step height of the spiral, 420 Å, and is therefore assumed to be due to the movement of the active dislocation at the centre of the spiral.

![Fig. 4 (210 ×)](image1)

![Fig. 5 (140 ×)](image2)

**Movement of an inclined dislocation**

In the above case, the dislocation moved in a plane perpendicular to the crystal surface and hence the slip took place in a plane normal to the growth surface. It can be inferred from this that the dislocation which caused the slip step is purely screw. If the dislocation were one with its Burgers vector inclined to the growing face, the slip
step caused by the movement of such a dislocation would also be in a plane similarly inclined to the crystal surface. Such a case is illustrated in Fig. 6 which shows multiple beam FIZEAU fringes. The slip step indicated by the bend in the FIZEAU fringes in the first loop of the spiral extends up to the second loop of the spiral. The fringes of equal chromatic order\textsuperscript{10} corresponding to a line section perpendicular to the trace of the slip plane on the (0001) face are shown in Fig. 7 from which the angle of inclination of the slip plane to the general level of (0001) face, and also the normal slip component can be calculated. These correspond to 89°48′ and 399 ± 2 Å respectively. It is of interest to note that the normal slip component is equal to the step height of the spiral. This observation of an inclined slip step having a vertical component equal to the step height of the spiral suggests that it must have been caused by the movement of an inclined dislocation. Such an inclined dislocation can be resolved into screw and edge components, and as discussed later, play an important part in the phenomena of polytypism.

**Evidence for the operation of Frank-Read source**

Slip caused by the operation of a Frank-Read source is common in SiC. In this process, it is assumed that a dislocation line is anchored at two points. Under a suitable stress, this line moves outwards in the slip plane to encompass a larger area and in doing so eventually touches itself and so creates a series of dislocation loops in a way similar to the behaviour of two dislocations of opposite hand. The operation of such a source in SiC is shown in Fig. 8 and 9. In the former, there are 13 dislocations of both signs while in the latter there are 14 pairs.

The interaction of a Frank-Read source with the existing system of layers is shown in a typical case in Fig. 10 where it is possible to trace the kinking of steps, suggesting that the Frank-Read source operated just before or soon after the cessation of growth. The perfect kinking of steps of 75 Å suggests that the sweeping dislocation was also of the same strength. This slip line makes an angle of $120^\circ$ with the edge of the crystal, and thus lies in the prism face of this hexagonal crystal. An interferrogram reveals a slight tilt of $30'$ of arc between the two portions of the crystal on either side of the slip line.

**Slip due to a cone source**

Our observations provide evidence for the operation of the cone source suggested by Cotterell and Bilby\(^\text{11}\) as an alternative to the Frank-Read source. Cotterell and Bilby pointed out that the multiplication mechanism outlined by Frank-Read source is only one example of a topological property of a dislocation node. In the Frank-Read mechanism the dislocation sweeps in the same plane, each revolution causing unit slip. If the sweeping dislocation climbs as it rotates, as is envisaged in the cone source, it will produce a multiple slip, but the slip step will not be in the same plane. Such a slip step will not be perpendicular to the crystal surface.

Fig. 11 is a multiple beam interferrogram over a crystal which shows a growth pattern which can be explained on the operation of a modified cone source. Between the loops of the spiral (shown by dotted lines) the crystal is not molecularly flat in a triangular region having its vertex on the dislocation line and its base on the edge of the crystal, the angle between its arms being nearly $30^\circ$. In addition to the small change in the surface level in a direction perpendicular to the radius vector caused by the slope of the spiral of

step height 480 Å, it can be seen from the bend in the Fizeau fringes that the portion of the crystal below $OB$ is higher than the portion above $OA$. This change in level takes place gradually in the triangular region and is, in a sense, opposite to the initial slip which developed into a spiral. This difference in level between two portions on either side of the triangular region was determined along various sections with the help of fringes of equal chromatic order. Over all the sections, the difference in level was found to be the step height of the spiral.

This triangular region could not have arisen through an external triangular plate settling on this crystal. This difference in level must have resulted because of the slip of one portion with respect to the other. The two facts viz., that the normal slip component is equal to the step height of the spiral and that this slip is in a sense opposite to the initial slip which developed into a spiral, lead us to believe that it is due the propagation to the upper surface of the slip step left on the underside of this crystal. This propagation must have taken place after the growth of the spiral ceased since the step lines of the spiral do not show any discontinuity.

The above triangular region could not have originated due to the propagation of the step in one plane, nor could it have been caused by the dissociation of a giant dislocation of Burgers vector 480 Å. It can, however, be explained by a mechanism similar to that of a cone source. The structure of the triangular region is shown in Fig. 12. $OP$ is an axis of the spiral while $OA$ and $O'B$ mark the boundaries of the triangular region. The change in level between $OA$ and $O'B$
along any section is constant. Such a slip can not be due to the operation of a Frank-Read source nor could it be due to a pure cone source. If, however, the sweeping plane of the rotating dislocation rotates about the line AB as shown in the Fig. 13, the intersection of the sweeping plane, with the growing surface will successively take place along XY, X'Y', X''Y'' etc. This would give rise to the type of slip observed in the present case. The rotation of the sweeping plane may arise out of the spiralling of the other dislocation in a plane parallel to the growing surface. All that is necessary for the operation of this modified cone source, as in the Frank-Read mechanism or a Cottrell-Bilby cone source, is adequate anchoring of the point A.

**Polytypism in silicon carbide**

Polytypism can be explained as a special case of polymorphism in which crystal structures of different modifications differ along one direction, as for example the c-axis in SiC, and are obtained by stacking of identical layers, sometimes referred to as ABC close packing. The structures of SiC can be broadly classified into three categories (1) cubic, (2) hexagonal and (3) rhombohedral. Some of the crystals in the rhombohedral class have very large repeat distances. Frank has tried to explain polytypism in terms of the dislocation mechanism. The production of the rhombohedral class of crystals is explained on the basis of uniform but abruptly terminated slip of the 6H structure by nonintegral multiples of the unit cell. Thus, for example, starting with Z(33) structure (Zhdanov’s symbol), a terminated slip of five layers will give rise to a pure screw dislocation whose Burgers vector will be equal to the thickness of five layers. The crystal that will grow in the presence of such a dislocation will have a 15R structure. There are however various difficulties in explaining the rhombohedral structures on the above considerations, as pointed out by Bhide. It was shown that, instead of pure screw dislocation, one will have an inclined dislocation made up of screw and edge components, but leading to the same screw vector as required for a particular crystal. These inclined dislocations eliminate the possibility of a fault line emanating from the dislocation in all

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rhombohedral polytypes which would be otherwise present had the dislocation been purely screw.

On the basis of these inclined dislocation for which experimental evidence has been presented earlier, the production of all the rhombohedral polytypes of SiC becomes comprehensible. Consider an example of 15R. In the Z(33) structure, the arrangement of layers is ABCABCABABC... A terminated slip of this structure by five layers in a plane normal to the basal plane will give rise to a pure screw dislocation with an exposed ledge having the structure ABCABC. The arrangement of layers in the slipped and the unslipped portions of the crystal is different and hence the system is unstable. The top layers of the slipped and the unslipped portions can be brought in register by a unit edge dislocation. Three such components of screw dislocation of Burgers vector of five layers and unit edge dislocation will cause the structure of the slipped portion to be similar to the original structure with top layers in perfect register. Such a dislocation will be inclined to the growing (0001) face. The ledge that will be exposed by such a dislocation will have a structure ABCABCABABCABABC. The crystal that will grow in the presence of such a dislocation will have a structure similar to that of an exposed ledge and will therefore be 15R. This mechanism shows why layers in a 15R crystal can be grouped into three equal parts each one being represented by Zhdanov's symbol which denotes the arrangement of layers in the unit cell. Similar considerations would show that Z(43) or 21R is a possible polytype. In this case the inclined dislocation is made up of three components of screw dislocation of Burgers vector of seven layers and a unit edge dislocation. The condition that seems to emerge for the production of a particular polytype is 3 (number of layers indicated by Zhdanov's symbol) + 3 = 6N, where N is an integer and 6 is the number of layers in the parent structure Z(33). In addition to the Z(32) and Z(43) structures one can thus have Z{(33)n, 32} and Z{(33)n, 43}. This accounts for the large number of known polytypes 15R, 33R, 51R, 87R etc. and 21R, 57R, 75R etc. The above condition eliminates the possibility of Z{(33)n, 31} and Z{(33)n, 35} and explains Ramsdell's observation that in the zigzag sequence 1 and 4 normally do not occur. This mechanism is based on the assumption that 6H is the parent structure while all the rhombohedral structures are its derivatives. This would involve a possibility of a mixture of

14 L. S. Ramsdell, The crystal structure of alpha-SiC, type VI. Amer. Mineralogist 30 (1945) 519–525.
polytypes which are in syntaxic coalescence. It is interesting to note that such a case is exemplified by crystal No. 120 (see 1) which have three polytypes 6H, 15R and 72i? in syntaxic coalescence with spots of 6H predominant. That rhombohedral polytypes are indeed the derivatives of 6H is revealed by the fact that no multiple steps have been observed on rhombohedral crystals; they are only observed on 6H crystals.

The concept of an inclined dislocation leading to rhombohedral polytypes is also helpful in explaining the stacking of rhombohedral units to give a close packed structure. In hexagonal crystals the unit cell has the c axis perpendicular to a and b. This unit cell can be stacked on to a vertical ledge left behind by a pure screw dislocation. In the case of rhombohedral crystals, however, the unit cell is a rhombohedron whose edges are equally inclined to each other and to the triad axis. These units can be stacked on to an inclined step left behind by an inclined dislocation. In a 15R crystal the edges of the rhombohedron make an angle of about 9°30' with the vertical. The ledge left behind by an inclined dislocation giving rise to a 15R crystal is also inclined to the vertical by an angle \( \tan^{-1} \frac{5 \times 2.54}{\frac{5}{3} \times 0.07} \approx 9°30' \).

In the case of an inclined dislocation actually observed and described above, the step height and one third the c lattice parameter is 405 Å, and if this is in accordance with the mechanism outlined above, the angle of inclination of such an inclined dislocation should be \( \tan^{-1} \frac{405}{\frac{5}{3} \times 0.07} \approx 89°42' \). It is stricking to note that the actual angle of inclination is 89°48' which is in good agreement with the theory.

Further, as has been detailed in an earlier paper, the concept of an inclined dislocation removes the necessity of postulating periodic breaks in the stacking sequence which is otherwise necessary. It may be pointed out that Mitchell has also postulated inclined dislocations without giving any experimental proof.

Our grateful thanks are due to Professor S. Tolansky, F.R.S. for facilities of work and kind encouragement.

Fig. 1. 15°-oscillation photograph about c-axis, taken with unfiltered Cu K radiation. It shows the 1,0−l row of spots, recorded on a film of radius 11.48 cm. Magnification 1:9:1.

Fig. 2. Zero-layer, c-axis Weissenberg photograph taken with unfiltered Cu K radiation. The lower ‘festoons’ shows the 1,0−l row of spots. The five consecutive faint spots near the minimum of the ‘festoons’ are, from left to right, 1,0−5, 1,0−2, 1,0−1, 1,0−4 and 1,0−7. The I values of successive spots differ by 3. Magnification 1:1.
A New Polytype of Silicon Carbide, 57R. Its Structure and Growth

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A 57-layered modification of silicon carbide, having rhombohedral symmetry has been discovered. It is shown to have the structure (33 33 34) in Zhdanov's notation. The close agreement of calculated relative intensities of diffracted X-rays with those observed on a Weissenberg photograph establishes the postulated structure. Its growth is discussed.

Introduction

The interesting property of polytypism is prominently exhibited by silicon carbide, of which over 30 stable modifications have already been discovered, and there appears to be no upper limit to their number. It is still not fully understood how so many modifications form or grow. Explanations have been attempted on the basis of

(i) The impurities present during the process of growth (Zhdanov & Minervina, 1945; Landqvist, 1948).
(ii) The accretion of polymers of SiC with a stacking reversal inherent in their structure and stability governed by temperature (Ramsdell & Kohn, 1952).
(iii) The influence of a neighbouring crystal with an orientation different from that of the growing crystal (Zhdanov & Minervina, 1945).
(iv) Spiral growth from screw dislocations (Frank, 1951).
(v) Layer transposition caused by vibration entropy (Jagodzinski, 1954).

None of these has been able to explain all the observed features. The first three theories are unable to explain large polytypes like 141R, 594R, etc. The screw dislocation mechanism has received a lot of attention and a large amount of experimental work has been done to bring forth evidence in support of it. It easily explains the growth of the (0001) face and the formation of polytypes. Verma (1951, 1952) photographed growth spirals on the (0001) face of some SiC crystals by the use of phase contrast microscopy and measured their step heights by means of multiple-beam-interferometry. The growth steps were found to be simply related to the size of the X-ray unit cell. Though it is one of the important mechanisms causing growth, it has not yet been able to explain several observed facts. Jagodzinski (1954) has questioned it while working out the thermodynamics of layer structures with one dimen-

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Experimental details

The specimen in which the new polytype was discovered is a small, light green crystal about 1 x 1.5 x 0.5 mm., with a shining (0001) face which does not show any spiral markings.

Measurements made on a 15°-oscillation photograph taken on a 3 cm. cylindrical camera indicated a 57-layered unit cell with rhombohedral symmetry. Fig. 1 shows the 1,0-t row of spots on a c-axis oscillation photograph taken with a camera of radius 11.48 cm. using a very narrow, collimated beam of Cu K radiation. The rhombohedral symmetry was confirmed by taking an over-exposed oscillation photograph which showed the Laue streak along the zero layer line. The = values of the nearest 1,0-t spots on either side of this streak are in the ratio of 1:2.

A weak, diffuse and continuous streak can be seen along the 1,0-t row of spots. This streak could not be resolved into spots by increasing the camera radius or collimating the X-ray beam further. This indicates a certain random disorder of layers in the crystal. For the structure determination, discrete spots alone have been considered, disregarding the streak. Further, there are some diffuse spots on the streak that do not belong to the 57R structure. No regularity was found in these spots, but they might well be the more intense spots of a very large polytype, the other
unresolved spots of which give rise to the 'continuous' streak.

Fig. 2 shows a zero-layer Weissenberg photograph taken with the crystal rotated about the $a$-axis. The photograph has been indexed on hexagonal axes. The indices show the systematic absences of the space group $R3m$.

**Structure of the unit cell**

We shall assume, with Ramsdell (1944, 1945), Mitchell (1954), and others, that the structure consists of identical layers of atoms spaced successively at intervals of 2.518 Å along the $c$-axis. This assumption is more than amply justified by:

(i) The close agreement of observed and calculated intensities for structures worked out on this basis.
(ii) The $c$-dimension of all unit cells being integral multiples of 2.518 Å* while the $a$ and $b$ dimensions remain constant in all polytypes.

There are $2^{18}$ possible ways of stacking the first 19 layers on each other. The positions of the next 38 layers are determined by rhombohedral symmetry. To seek the correct structure from this formidable number by trial and error would be impossible. However, all structures known so far, with the exception of $2H$ and cubic SiC, have only the numbers 2, 3, and 4 in Ramsdell's zig-zag sequence. Expecting this to hold for the present polytype also and using Zhdanov's notation the problem reduces to finding the ways in which the number 19 can be split into a sum of twos, threes and fours. Since the number of stacking reversals has to be even, the only ways are:

1. $4 \times 0 + 3 \times 3 + 2 \times 5$
2. $4 \times 1 + 3 \times 1 + 2 \times 6$
3. $4 \times 1 + 3 \times 5 + 2 \times 0$
4. $4 \times 2 + 3 \times 3 + 2 \times 1$
5. $4 \times 3 + 3 \times 1 + 2 \times 2$

Working out the various permutations possible under each of the above combinations 15 different $57R$ structures are obtained:

(1) (33322222)$_3$
(2) (33232222)$_3$
(3) (32232222)$_3$
(4) (33223222)$_3$
(5) (43222222)$_3$
(6) (42232222)$_3$
(7) (433333)$_3$
(8) (443333)$_3$
(9) (433333)$_3$
(10) (434323)$_3$
(11) (434323)$_3$
(12) (224443)$_3$
(13) (224433)$_3$
(14) (244243)$_3$
(15) (244343)$_3$

These can be easily transformed into the classical $ABC$ notation, or the interval sequence, or Nabarro-Frank's stacking operator-sequence.

The Weissenberg and oscillation photographs show that the spots lying nearest to the position of $6H$ spots are very intense and their relative intensities are similar to those of $6H$. Of the structures listed above the 7th is nearest to the $6H$ phase and was thus thought to be the most probable structure. It is (333334)$_3$ and is thus a member of the [(33)$_n$(34)$_3$]$_n$ series with $n=2$. A polytype with this structure was predicted by Ramsdell (1947). The interval sequence of the structure is

3242424242333333

Fig. 3. Graph plotting the calculated relative intensities ($I_c$) of spots in the $1,0$ row against their $l$ values, ranging from $-47$ to $+178$ at successive intervals of 3.
The intensity values calculated from this formula were multiplied by the Lorenz polarization factor $(1+\cos^2 2\theta)/\sin 2\theta$.

Table 1 shows the values obtained for the $1,0l$ reflections from $l=47$ to $l=178$ and the intensity values are plotted to scale against $l$ in Fig. 3. Comparison of the table or graph with the Weissenberg photograph reveals the remarkable extent to which the results match, proving the correctness of the proposed structure. As a check, the intensities for a few typical $1,0l$ spots were calculated for the other 14 structures. They showed no agreement with observed variations in intensity.

Unit cell dimensions and atomic positions

On hexagonal axes:

$a=3.078, c=143.522 \text{ Å}; Z=57$.

The hexagonal unit cell has:

- $19 \text{ Si}$ at $0,0,0$, $0,0,4z$, $0,0,8z$, $0,0,12z$, $0,0,16z$, $0,0,18z$, $0,0,21z$, $0,0,24z$, $0,0,27z$, $0,0,30z$, $0,0,33z$, $0,0,36z$, $0,0,39z$, $0,0,42z$, $0,0,45z$, $0,0,47z$, $0,0,51z$, $0,0,53z$.

- $19 \text{ Si}$ at $\frac{3}{2}, \frac{1}{2}, \frac{1}{2}$ plus the above co-ordinates.

- $19 \text{ Si}$ at $\frac{3}{2}, \frac{1}{2}, \frac{1}{2}$ plus the above co-ordinates, where $z=1/57$.

- $57 \text{ C}$, one above each Si, at a distance $p=1/76$ having co-ordinates $00p$ plus the co-ordinates of the 57 Si atoms.

Discussion of results: Mode of growth

The fact that the arbitrary assumption of the zig-zag sequence not containing any numbers other than 2, 3 or 4 yielded a successful determination of the structure adds further weight to this being a genuine limitation.
and not merely an accidental feature. A theoretical explanation for this limitation ought to be provided by some theory of growth.

The formation of this crystal is easily understood, and in fact anticipated by Ramsdell & Kohn's (1952) idea of accretion of polymers. Thus if growth occurred at a temperature at which the polymers 33 and 34 coexist in the proportion of 2:1, then the resulting structure would be (33 33 34). The continuous streak observed along the 1,0,0 row of spots would be explained by the random disorders introduced by the fluctuating conditions in the furnace. But so far, the existence of such polymers, as the theory assumes, has not been experimentally demonstrated.

On the screw dislocation mechanism it is easy to picture the growth of hexagonal structures from a pure screw dislocation. But for the growth of rhombohedral structures a horizontal displacement has to be introduced. This was done by Mitchell (1953) and followed up by Bhide & Verma (1959) in their idea of an inclined dislocation. The mechanism causing this horizontal displacement is not yet understood. We wish to suggest a possible mechanism for the same.

The growth of any structure by the screw dislocation mechanism is really the winding up of the exposed ledge into a very flat spiral whose pitch is the same as the height of the ledge, thus producing a close-packed structure. Any one layer is not really in one plane, but is winding upwards very gradually, so that over fairly large areas (of several unit cell dimensions) any layer might be taken to be in one plane. Hence the structure may also be described by the close packing of plane A, B, C layers, a model that has been used in determining the structure. Now when the first and last layers of an exposed ledge are in different orientations it is easy to picture its winding over itself in a close-packed manner. But this will not be possible if the first and last layers of an exposed ledge are in identical orientation (A, B or C); for then the first layer cannot grow over the last one without slipping the whole stack of layers. Frank (1951) has shown that the layers of the stack shall maintain their interrelationship undisturbed. Thus every time the stack moves through one pitch there would be a horizontal displacement or slip, shifting the layers of the stack in a cyclic manner (A → B, B → C, C → A or vice versa). Three such shifts in the same direction would bring the stack back into an identical position, thus creating a structure with a unit cell thrice as high as the exposed ledge. This mechanism implies that rhombohedral structures grow only when the exposed ledge has the first and last layers in the same orientation.

It has been conclusively established (Verma, 1957) from observations of spiral step heights on the (0001) face of 15R, 21R, 33R and 126R that the Burgers Vector of the dislocation for rhombohedral structures is only one-third the c-dimension of the X-ray unit cell. Thus the screw dislocation creating 57R would have a Burgers Vector 19 layers high. There are 6 different ways in which a 19-layered screw dislocation ledge can be exposed in the 6H structure ABCACBABCACB, but in each case the first and last layers of the exposed ledge are in the same orientation. Consider one such ledge ABCACBABCACB ABCACBA. When the first layer tries to grow on the last one it shall slip into a neighbouring site, say C, and the next 19 layers would be CABCACABCRACA BCBAC; and again since a C layer cannot grow on another C layer, the stack shall slip as before and produce the structure BCABACBCABACBCABACB.

This time the slip would bring back the ledge into its initial position, thus completing a unit cell with the structure

\[
\text{ABCACBABCACBACRA} \\
\text{CABCACABCBACABCBAC} \\
\text{BCABABCABCBACBACB},
\]

which has the Zhdanov symbol (33 33 34).

All rhombohedral structures can be similarly explained to have grown from a ledge, exposed in an initial structure (usually 6H, 4H or 15R), with the first and last layers in the same orientation. A consequence of this idea would be that polytypes belonging to the series \((6n+1)H\) would not be based on the 6H phase since a ledge of \((6n+1)\) layers in the 6H structure would necessarily have the first and last layers in the same orientation. Indeed the only member of this series so far known is 19H, whose structure has been reported by Ramsdell & Mitchell (1953) to be (23232322), based on the 157? phase. Similarly polytypes \((4n+1)H\) and \((15n+1)H\) cannot be based on the 4H or 15R phase respectively. In general, a structure \((pq+1)H\) could not have grown from an initial structure with a \(p\)-layered unit cell. No structures known so far contradict this.

The screw dislocation mechanism is unable to explain the continuous streak along the 1,0,0 row of spots or the random spots obtained in places on the streak. It also does not tell anything about the formation of the initial plate. Only a very few SiC crystals show the spiral markings and that too only on the (0001) face. A single dislocation would produce needle-shaped crystals whereas the observed crystals are usually flat platelets.

Edge dislocations need much less energy for their creation than screw dislocations and would destroy any order created by the screw dislocations (Jagodzinski, 1954). Also a screw dislocation can originate only when the crystal lattice is large enough to provide sufficient energy and so screw dislocations could only cause growth in the later stages. Jagodzinski therefore suggested the layer transposition mechanism caused by vibration entropy. This does explain the continuous
streak so often observed. He has also shown from potential energy considerations that the $15\overline{R}$ structure is the most stable next to $6\overline{H}$, but the question still remains how such extremely improbable structures with large identity periods grow into stable forms.

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References


An x-ray diffraction study of silicon carbide structure types $[(33)_{n}34]_{3}R$

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With 3 figures

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Introduction

Numerous polytypic modifications of silicon carbide have so far been discovered, with unit cell heights ranging from $c = 5.048 \text{Å}$, in type

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2 \( H \) to 2\( c \approx 1500 \) Å in type 594 \( R \) and to more in many of the unidentified types. Ott\textsuperscript{3–8}, Ramsdell\textsuperscript{9–11} and Zhdanov and Minervina\textsuperscript{12–14} were among the first to investigate the detailed atomic structures of some of these. They described the structures in terms of the sequence of close-packed layers in the unit cell. Ramsdell\textsuperscript{9} first classified these structures into structure series which are conveniently described in the Zhdanov-Ramsdell notation\textsuperscript{9,15}. Since then the existence of the following structure series has been established by different workers:

<table>
<thead>
<tr>
<th>Zhdanov symbol</th>
<th>Polytypes known to be members</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (33),32</td>
<td>( 15 R^{6,7}, 33 R^{11}, 51 R^{14,9}, 87 R^9, 141 R^{17}, 393 R^{17} )</td>
</tr>
<tr>
<td>2. (33),34</td>
<td>( 21 R^{10}, 39 R^{18}, 57 R^{19}, 111 R )</td>
</tr>
<tr>
<td>3. (22),23</td>
<td>( 15 R, 27 R^{20,21}, 51 R^{20} )</td>
</tr>
<tr>
<td>4. (23),22</td>
<td>( 4 H^4, 19 H^{22}, 27 R )</td>
</tr>
<tr>
<td>5. (23),32</td>
<td>( 15 R, 10 H^{20}, 90 R^{14} )</td>
</tr>
<tr>
<td>6. (23),33</td>
<td>( 6 H^{3,4}, 168 R^{17}, 273 R ) (not sure)\textsuperscript{14}.</td>
</tr>
</tbody>
</table>

\textsuperscript{3} H. Ott, Die Gitterstruktur des Karborunds (SiC) I. Z. Kristallogr. 61 (1925) 515–531.
\textsuperscript{4} H. Ott, Die Gitterstruktur des Karborunds (SiC). Naturwissenschaften 13 (1925) 76.
\textsuperscript{5} H. Ott, Das Gitter des Karborunds (SiC) III. Z. Kristallogr. 63 (1926) 1–18.
\textsuperscript{6} H. Ott, Das Gitter des Karborunds (SiC) II. Z. Kristallogr. 62 (1925) 201–217.
\textsuperscript{7} H. Ott, Die Gitterstruktur des Karborunds (SiC). Naturwissenschaften 13 (1925) 319.
\textsuperscript{9} L. S. Ramsdell, Studies on silicon carbide. Amer. Mineralog. 32 (1947) 64–82.
\textsuperscript{10} L. S. Ramsdell, The crystal structure of \( \alpha \)-SiC type IV. Amer. Mineralog. 29 (1944) 431–442.
\textsuperscript{11} L. S. Ramsdell, The crystal structure of \( \alpha \)-SiC type VI. Amer. Mineralog. 30 (1945) 519–525.
An x-ray diffraction study of silicon carbide structure types

For the rhombohedral types the sequence is repeated thrice before completing a unit cell.

Many other structure series are expected but do not have sufficient identified members as yet. This is because the detailed structure of only a few polytypes has been determined. The structure analysis becomes increasingly more difficult for polytypes with larger number of layers in the unit cell. The usual method of listing the more probable structures and determining the correct one by trial and error becomes prohibitively tedious. Such large polytypes are quite common and their structure and growth cannot be easily analysed.

It has been realized by Ramsdell, Mitchell and others that a classification of all known polytypes into structure series and a study of their characteristic intensity distribution would make it considerably easier to analyse larger polytypes. The structures of large polytypes can then be predicted, and conversely, large new polytypes can be studied by fitting them into one or other of the structure series, without performing any intensity calculations. Mitchell has investigated the characteristic intensity distribution of the \([33]^3 R\) series of structures, and has framed empirical rules for the direct identification of its higher members. This series has so far the largest number of known members.

The series \([33]^3 R\) had, till recently, only two known members, \(21R\) and \(39R\), and hence a complete study of this series was not possible.

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16 This polytype has been recently analysed by us and has not yet been reported.


The discovery of two more members of this series, 57\(R^{18}\) and 111\(R\), has enabled us to make a detailed study of this series of structures. It is the purpose of the present work to determine the characteristics of intensity distribution in the 10\(·\)l row line of this series of structures and to frame empirical rules for the identification of its higher members. The probable mode of growth of these structures is also discussed.

The detailed atomic structure of the new polytype 111\(R\) is reported and it is shown to be the largest known member of the \([(33)_{n}^{34}R]_{h}\) series of structures. The structure has been confirmed by comparing the calculated and observed relative intensities of the 10\(·\)l reflections which, by now, is a standard procedure in silicon carbide structure work.

The origin and growth of various series of structures have been investigated by Mitchell\(^24\) on the basis of Frank's screw dislocation theory of polytypism\(^25\) and by Ramsdell and Kohn\(^26\) on their theory of the growth of silicon carbide by the accretion of polymers. In the present work the origin and growth of the \([(33)_{n}^{34}R]_{h}\) series of structures is discussed.

**Discovery and structure of 111\(R\)**

The new modification has been discovered in the form of a small, light-green crystal nearly 2\(×\)1\(×\)0.5 mm\(^2\) with a well developed and shining (0001) face. The 10\(·\)l row of spots, as recorded on an oscillation photograph taken on a 3 cm camera with the crystal oscillated about the c axis, is reproduced in Fig. 1. The spots are clearly resolved and well defined, with no continuous streak connecting them. This shows a high degree of order in the structure, which is rather remarkable for a crystal with such a large unit cell. The unsymmetrical arrangement of spots about the zero layer line indicates a rhombohedral lattice. The reflections 10\(·\)37 and 10\(·\)74 of this polytype coincide with the 10\(·\)2 and 10\(·\)4 reflections of type 6\(H\) respectively. Hence the number of layers in the unit cell is 74 + 37 = 111. This was further confirmed from the zero-layer Weissenberg photograph taken with the crystal rotated about the a axis (Fig. 2). The lowest "fostoon" records the 10\(·\)l row of spots. The polytype was thus identified as 111\(R\) confirming that it belongs to the space group \(R3m\).


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For a large polytype such as this it becomes very laborious to follow the usual method of working out all possible structures involving only 2, 3 and 4 in their zig-zag sequence and then finding out the correct one by calculating the 10·l intensities for each of them. Moreover the assumption that the zig-zag sequence contains only 2, 3 and 4 is no longer valid after the discovery\(^1\) of type 2\(H\) with a structure (11). The structure was anticipated as follows. The spots lying near 6\(H\) positions are more intense than the rest, showing the polytype is based on

\[\text{Fig. 1. 15° oscillation photograph about c axis, taken with CuK}\alpha\text{ radiation.}
\]

\[\text{Shows the 10·l row of spots recorded on a camera of radius 3 cm (×2.5)}\]

the 6\(H\) phase. Of the structure series based on the 6\(H\) phase, 111\(R\) could belong to the \([(33)_{n}, 34)]\ series with \(n = 5\). To confirm this possibility it was proposed to estimate visually the relative intensities of the 10·l reflections and to compare the observed intensity distribution with that of the other known members of the series.

For the visual estimation a standard scale of relative intensities was prepared by selecting a single 10·l reflection and then recording it on different portions of the same Weissenberg film. The exposure time for
successive recordings was measured in terms of complete oscillations of the crystal. For estimating the spots in different intensity ranges, Weissenberg films of different known exposures were used. For these films also the exposure time was reckoned by counting the number of complete oscillations of the crystal. The values obtained for the

Fig. 2. Zero-layer, a-axis Weissenberg photograph taken with unfiltered CuK radiation on a camera of diameter 5.73 cms. The lower ‘festoon’ shows the 10·l row of spots. The eleven faint spots near the minimum of the ‘festoon’ are, from left to right 10·14, 10·11, ... 10·2, 10·1, ... 10·13 and 10·16. The l values of successive spots differ by 3 (×1.5)

estimated intensity of different 10·l spots are tabulated in Table 1 as percentages of the value obtained for the 10·37 reflection, which is the most intense. We found that, for estimating intensities over such a large range as that obtained on the Weissenberg photograph of this crystal, the above method yielded more consistent results than the usual multiple-film method.
An x-ray diffraction stu d y of silicon carbide stru ctu re types
T a b le 1. Calculated and observed intensity values of different 1 0 ■ I spots
1

b ale.

bba .

1

b ale.

1

^oba.

b ale.

bba.

1

0.1

0.0

58

2.9

2.0

-

2

0.1

0.0

4

0,1

0.0

61

0.7

0.0

64

0.7

5
8

0.0

0.1

-

0.1

7
10

0.9
0.6

0.3

0.2

0.2

0.2

67

0.7

- 11

0.5

13
16

0. 4

0. 5
2.0

70

1.9

19
22

44 .9

43 .0

0.9

1. 0

25
28

0.3
0.15

0.3
0.0

31

0.1

34

1

0. 1

0.0

0 .0 5
0.0

0.0

- 14

1.7
18 .3

2 0 .0

- 74

5.0

22 .5

23 .0

- 23
- 26

3.7

3 .7

- 77
- 80

0.6

0.9
0.6

2.1

2.3

0.6

0.5

- 29

2.2

2.3

0.0

85
88

0.9

0.7

- 32

3.8

0.1

0.0

91

5.5

5. 0

- 35

18. 0

4.3
20.0

37

100.0

100 .0

94

- 38

6 3 .4

0.1

0.0

4.0

0.1

0.0

0.1

0.3
0.0

- 41

43
46

97
100

4 .5
0 .4

4.0

40

-

0.15

0.0

49

0.3

52

1.1

0.3
1.0

55

59 .0

5 3. 0

21.9

1.3
23 .0

5.6

79
82

1.1

0.8

- 65
- 68

- 17
- 20

73
76

bba.

0.9
0.2

0.5
2 .0

0.7
1. 6

bale.

- 59
- 62

- 71

0.0

0.0

3 3. 7
0.0

3 3. 3
0.0

0.0

0.0

- 83
- 86

0.0

0 .0

o.r

0.0

- 89

0.2

0.2

- 92

11 .3

10.0

6 7 .0

- 95

4.0

- 98

0.5
0. 1

0.3
0.0
0.0

44

1. 9

2.0

-101

0.05

103
106

0.1

0.0

- 47

1.1

1 .3

-104

0.0

0.0

0.0

0.0

- 50

1 .9

1 .7

0.0

0.0

109

0.0

0.0

- 53

3.5

3.7

-10 7
-11 0

0.0

0.0

- 56

57.5

5 3. 0

F ig u re 3 (/) p lo ts th e e s tim a te d re la tiv e in te n s itie s o f d ifferen t sp o ts
in th e 1 0 -Z ro w a g a in s t th e ir Z-values. T h is g ra p h w as c o m p a re d w ith
th e in te n s ity g ra p h s o f 217?, 397?, 577? a n d 757? [Figs. 3 (a, 6 , c, cZ)]
a lre a d y p re p a re d fo r a s tu d y o f th is series o f s tru c tu re s . T h e in te n s ity
d is trib u tio n w as fo u n d to be v e ry sim ilar, show ing t h a t 1117? w as
also a m e m b e r o f th is series. T o confirm th is conclusion, d e ta ile d in te n ­
s ity c a lc u la tio n s w ere m a d e for th e s tru c tu re [( 3 3 )5 3 4 ]g b y th e u su a l
m e th o d o u tlin e d b y R a m s d e l l ^®. F o r e sta b lish in g th e s tru c tu re , it
m o re th a n suffices to c o m p are th e in te n s itie s o f 1 0 *Z reflectio n s fro m
1 0 - 1 1 0 to 1 0 - 1 1 1 . T h e c a lc u la tio n s h a v e b e en d o n e o n ly fo r sp o ts ly in g
in th is ra n g e . F ig u re 3 (e) p lo ts th e c a lc u la te d re la tiv e in te n s itie s
ta b u la te d in T a b le 1 , a g a in s t Z. T h e v a lu es a re g iv e n as p e rc e n ta g e s o f
th e v a lu e o b ta in e d fo r th e m o st in te n se re fle c tio n 1 0 - 37. A c o m p ariso n
o f th e tw o gra%]hs in F igs. 3 (e) a n d 3 (/), o r o f th e ta b le s g iv in g th e c a lc u ­
la te d a n d e s tim a te d re la tiv e in te n sitie s, show s c o m p le te a g re e m e n t,
th u s e sta b lish in g th e p o s tu la te d s tru c tu re as c o rre ct. T h e d e ta ile d
s tr u c tu r e o f 1117? is th e re fo re as follow s:
S p ace g ro u p

: 7? 3 m

Z h d a n o v sy m b o l : [( 3 3 )5 3 4 ]g
H R esequence

:


Interval sequence:
\[333333333242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242424242
An x-ray diffraction study of silicon carbide structure types

111 C: one above each Si at a distance \( p = 1/148 \), having coordinates 00\( p \) plus the coordinates of 111 Si atoms.

Characteristics of the \([(33),34]\) series

The polytype 111\( R \) is the sixth member of this series, the first five being 21\( R \), 39\( R \), 57\( R \), 75\( R \) and 93\( R \) with \( n = 0, 1, 2, 3 \) and 4 respectively. The types 75\( R \) and 93\( R \) of this series have not yet been discovered but are expected to exist.

The positions of 10\( \cdot \frac{2}{3} \) reflections, for the different polytypes \( xR \) of this series, coincide, and this reflection is the most intense in each polytype. They have been made arbitrarily equal in plotting the graphs in Fig. 3. The \( l \) values for the different polytypes have been plotted on the same reciprocal scale along the \( x \) axis. The values for 21\( R \) have been taken from Ramsdell\(^{10} \). The structure of 39\( R \) was reported by Gasilova\(^{18} \) but all the intensity values have not been given by her and were therefore calculated. The values for 57\( R \) are the same as those reported by us\(^{19} \) in an earlier publication. In addition calculations have been made for 75\( R \), one of the yet undiscovered types. Those for 93\( R \) were not considered very necessary. Figure 3(\( g \)) plots the relative intensities of 10\( \cdot l \) reflections for 6\( H \) as the limiting member of the series. The intensity of 10\( \cdot 2 \) reflection of 6\( H \) has been made arbitrarily equal to that of the 10\( \cdot \frac{2}{3} \) spots of the \( xR \) types, since positions of the two coincide.

Calculations have been made in each case for all the spots lying between 10\( \cdot 6 \) and 10\( \cdot 6 \) positions of 6\( H \). As is well known, the 10\( \cdot l \) row lines of all the different polytypes of silicon carbide coincide because the \( a \) axis has the same repeat unit = 3.078 Å in each polytype. Further, the range from 10\( \cdot 0 \) to 10\( \cdot x \) for every \( xR \) or \( xH \) type is the same since it corresponds to the basic stacking unit = 2.518 Å. Therefore the range for any polytype \( xR \) from 10\( \cdot \frac{2}{3} \) to 10\( \cdot x \) is the same as that for 6\( H \) from 10\( \cdot 6 \) to 10\( \cdot 6 \).

It is evident that for a polytype \( xR \) to belong to this series \( x = 3(6n + 7) \). But all polytypes for which \( x = 3(6n + 7) \) do not necessarily belong to this series, an example being the 75\( R \) discovered by Ramsdell and Kohn\(^{26} \) with a structure (2323232323)\(_3\). Now since a structure belonging to this series contains a large number of 33 units, large blocks of it have the 6\( H \) structure, and hence its intensity distribution would resemble that for the 6\( H \) structure. Thus the spots falling near 6\( H \) positions would be more intense than the rest, except where the 6\( H \)
spot itself has zero intensity. For higher members the contribution to intensity from the few layers causing deviation from the $6H$ structure would become increasingly negligible, till for very large polytypes of this series only the spots near $6H$ positions would be recordable, the rest being very weak. As already pointed out by Ramsdell\(^9\), the $6H$ structure would be a limiting case of such a series.

As noticed by Mitchell\(^17\) for the $(33)_n32$ series of structures, the ratio of intensities of the nearest neighbours on either side of a $6H$ position depends upon their relative proximity to the $6H$ position, the nearer neighbour being more intense than the farther one. This relative intensity of spots around $6H$ positions is characteristic for the series. The $10\cdot p$ position of $6H$ will lie at $10\cdot q$ on the $10\cdot l$ reciprocal lattice row of a polytype $xR$ where $q = \frac{px}{6}$. For the $(33)_n34$ series of structures, $x = 3(6n + 7)$, and hence $q = \frac{p(6n + 7)}{2}$. Bearing in mind that for the $10\cdot l$ reciprocal lattice row of a rhombohedral lattice only those reciprocal lattice points are present for which

\[ l = 3r + 1 \text{ where } \pm r = 0, 1, 2, \ldots \text{ etc.} \]

the fractional distance of any $6H$ position between its $xR$ neighbours can be easily worked out.

The $10\cdot 0$, $10\cdot 6$ and $10\cdot 3$ reflections of $6H$ have zero intensity and hence the $xR$ neighbours of these positions are all very weak. The $6H$ positions $10\cdot 1$, $10\cdot 3$, $10\cdot 3$ and $10\cdot 5$ lie between two $xR$ reflections at a point $\frac{1}{6}$ or $\frac{3}{6}$ the way between them. In each case the nearer neighbour would be more intense than the farther one by a large ratio. The $6H$ positions $10\cdot 2$ and $10\cdot 6$ coincide with $xR$ reflections and hence these $xR$ reflections are strong, with very weak neighbours on either side of them. The $6H$ positions $10\cdot 4$ and $10\cdot 2$ lie $\frac{1}{6}$ or $\frac{3}{6}$ the way between two $xR$ reflections. The nearer neighbour would again be stronger than the farther one but by a ratio smaller than that for the neighbours of $10\cdot 1$, $10\cdot 3$, $10\cdot 3$ and $10\cdot 5$. The $6H$ positions $10\cdot 5$ and $10\cdot 6$ lie midway between two $xR$ reflections and hence the two $xR$ reflections are of nearly equal intensity. The resulting characteristics of intensity distribution for spots near $6H$ positions are tabulated in Table 2. To illustrate the same by a specific example, the intensities of $111R$ reflections lying near $6H$ positions are tabulated in Table 3 with other relevant data.

The weaker reflections lying far from $6H$ positions may now be considered. It would be noticed from Fig. 3 that these fall in clusters of moderate intensity around the $6H$ positions $10\cdot 1$, $10\cdot 2$, $10\cdot 4$ and $10\cdot 5$. 
Table 2

<table>
<thead>
<tr>
<th>$6H$ reflection</th>
<th>Neighbouring $xR$ reflections $x = 3(6n + 7)$</th>
<th>Fractional distance of $6H$ spot between its $xR$ neighbours</th>
<th>Intensity of $6H$ reflection</th>
<th>Characteristics of the intensity ($I$) of the neighbouring $xR$ reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>10.2</td>
<td>$\frac{2}{3}; \frac{4}{3}$</td>
<td>0</td>
<td>Both reflections very weak</td>
</tr>
<tr>
<td></td>
<td>10.1</td>
<td>$\frac{3}{8}; \frac{7}{8}$</td>
<td>47.8</td>
<td>$I_{10.3n+4} \gg I_{10.3n+1}$</td>
</tr>
<tr>
<td>10.2</td>
<td>10.6n + 7</td>
<td>Coincide</td>
<td>100</td>
<td>10.6n + 7 most intense reflection. Neighbours very weak</td>
</tr>
<tr>
<td>10.3</td>
<td>10.9n + 10</td>
<td>$\frac{1}{6}; \frac{5}{6}$</td>
<td>64.0</td>
<td>$I_{10.9n+10} \gg I_{10.9n+13}$</td>
</tr>
<tr>
<td></td>
<td>10.9n + 13</td>
<td></td>
<td></td>
<td>$I_{10.9n+10} \gg I_{10.9n+13}^4$</td>
</tr>
<tr>
<td></td>
<td>10.9n + 13</td>
<td></td>
<td></td>
<td>$I_{10.9n+10} \gg I_{10.9n+13}^4$</td>
</tr>
<tr>
<td>10.4</td>
<td>10.12n + 13</td>
<td>$\frac{1}{3}; \frac{5}{3}$</td>
<td>31.1</td>
<td>$I_{10.12n+13} &gt; I_{10.12n+16}$</td>
</tr>
<tr>
<td></td>
<td>10.12n + 16</td>
<td></td>
<td></td>
<td>$I_{10.12n+13} &lt; I_{10.3n+4}$</td>
</tr>
<tr>
<td>10.5</td>
<td>10.15n + 16</td>
<td>$\frac{1}{2}; \frac{1}{2}$</td>
<td>13.0</td>
<td>$I_{10.15n+10} \approx I_{10.15n+10}$ and $&lt; I_{10.12n+13}$</td>
</tr>
<tr>
<td>10.6</td>
<td>10.18n + 19</td>
<td>$\frac{2}{3}; \frac{1}{3}$</td>
<td>0</td>
<td>Both reflections very weak</td>
</tr>
<tr>
<td>10.1</td>
<td>10.3n + 2</td>
<td>$\frac{1}{2}; \frac{1}{2}$</td>
<td>47.8</td>
<td>$I_{10.3n+2} \approx I_{10.3n+5}$ and $&gt; I_{10.15n+10}^4 &gt; I_{10.15n+19}$</td>
</tr>
<tr>
<td>10.2</td>
<td>10.6n + 5</td>
<td>$\frac{2}{3}; \frac{1}{3}$</td>
<td>100</td>
<td>$I_{10.6n+8} \gg I_{10.6n+5}$</td>
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<tr>
<td></td>
<td>10.6n + 8</td>
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<td></td>
<td>$I_{10.6n+7} &gt; I_{10.6n+8}$</td>
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<tr>
<td></td>
<td>10.9n + 11</td>
<td>$\frac{3}{6}; \frac{9}{6}$</td>
<td>64.0</td>
<td>$I_{10.9n+11} \gg I_{10.9n+8}$</td>
</tr>
<tr>
<td>10.3</td>
<td>10.9n + 8</td>
<td>$\frac{3}{6}; \frac{9}{6}$</td>
<td></td>
<td>$I_{10.9n+11} \approx I_{10.9n+13}$</td>
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</table>
Table 2. (Continued)

<table>
<thead>
<tr>
<th>Neighbouring $xR$ reflections $x = 3(6n + 7)$</th>
<th>Fractional distance of $6H$ spot between its $xR$ neighbours</th>
<th>Intensity of $6H$ reflection</th>
<th>Characteristics of the intensity ($I$) of the neighbouring $xR$ reflections</th>
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</thead>
<tbody>
<tr>
<td>$10 \cdot 4$ 10 $\cdot 12n + 14$</td>
<td>Coincides</td>
<td>31.1</td>
<td>Neighbours of $10 \cdot 12n + 14$ very weak</td>
</tr>
<tr>
<td>$10 \cdot 5$ 10 $\cdot 15n + 17$</td>
<td></td>
<td>13.0</td>
<td>$I_{10 \cdot 15n + 17} &gt; I_{10 \cdot 15n + 20}$</td>
</tr>
<tr>
<td>$10 \cdot 6$ 10 $\cdot 18n + 20$</td>
<td></td>
<td>0</td>
<td>Both reflections very weak</td>
</tr>
<tr>
<td>$10 \cdot 7$ 10 $\cdot 21n + 23$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Neighbouring $111R$ reflections</th>
<th>Fractional distance of $6H$ spot between its $111R$ neighbours</th>
<th>Intensity of $6H$ reflection</th>
<th>Calculated intensities for the neighbours</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10 \cdot 0$ 10 $\cdot 2$ -10 $\cdot 1$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>0.0</td>
<td>0.1—0.1</td>
</tr>
<tr>
<td>$10 \cdot 1$ 10 $\cdot 16$ -10 $\cdot 19$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>47.8</td>
<td>1.9—44.9</td>
</tr>
<tr>
<td>$10 \cdot 2$ 10 $\cdot 37$</td>
<td>Coincides</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$10 \cdot 3$ 10 $\cdot 55$ -10 $\cdot 58$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>64.0</td>
<td>59.0—2.9</td>
</tr>
<tr>
<td>$10 \cdot 4$ 10 $\cdot 73$ -10 $\cdot 76$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>31.1</td>
<td>21.9—5.6</td>
</tr>
<tr>
<td>$10 \cdot 5$ 10 $\cdot 91$ -10 $\cdot 94$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>13.0</td>
<td>5.5—4.5</td>
</tr>
<tr>
<td>$10 \cdot 6$ 10 $\cdot 109$ -10 $\cdot 112$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>0.0</td>
<td>0.0—0.0</td>
</tr>
<tr>
<td>$10 \cdot 7$ 10 $\cdot 17$ -10 $\cdot 20$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>47.8</td>
<td>18.3—22.5</td>
</tr>
<tr>
<td>$10 \cdot 8$ 10 $\cdot 55$ -10 $\cdot 38$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>100</td>
<td>18.0—63.4</td>
</tr>
<tr>
<td>$10 \cdot 9$ 10 $\cdot 53$ -10 $\cdot 56$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>64.0</td>
<td>3.5—57.5</td>
</tr>
<tr>
<td>$10 \cdot 10$ 10 $\cdot 74$</td>
<td>Coincides</td>
<td>31.1</td>
<td>33.7</td>
</tr>
<tr>
<td>$10 \cdot 11$ 10 $\cdot 92$ -10 $\cdot 95$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>13.0</td>
<td>11.3—0.5</td>
</tr>
<tr>
<td>$10 \cdot 12$ 10 $\cdot 110$ -10 $\cdot 113$</td>
<td>$\frac{1}{3}$ : $\frac{1}{3}$</td>
<td>0.0</td>
<td>0.0—0.0</td>
</tr>
</tbody>
</table>

These are regions where the $6H$ positions lie between two $xR$ reflections at $\frac{1}{3}$, $\frac{1}{3}$ or $\frac{1}{3}$ the way between them. In those regions where the $6H$ position coincides with an $xR$ reflection, or lies $\frac{1}{3}$ or $\frac{1}{3}$ the way between them,
the reflections other than the closest neighbours are very weak. These observations are in accordance with those of MITCHELL\textsuperscript{17} for the $[(33)_n32]_3$ series of structures.

Thus it may be concluded that a polytype $xR$ belongs to this series of structures if—
(i) $x = 3(6n + 7)$
(ii) the spots near $6H$ positions are more intense than the rest and their relative intensities conform to those laid down in Table 2, and
(iii) the remaining weaker reflections fall in clusters of moderate intensity around $6H$ positions $10 \cdot 1, 10 \cdot 2, 10 \cdot 4, 10 \cdot 5$.

**Discussion: Origin and growth of the series**

The formation of this series of structures is expected both from RASMUSSEN and KOHN's\textsuperscript{26} idea of the growth of silicon carbide by the accretion of polymers as well as FRANK's\textsuperscript{25} dislocation theory of polytypism.

Thus when growth occurs in a temperature range in which the polymers 33 and 34 exist in different proportions, it would give rise to different structures of this series. But it would be expected, especially for structures with large unit cells, that there would be some amount of random disorder introduced by the fluctuating conditions in the furnace. This would produce, on the oscillation and Weissenberg photographs, a diffuse but continuous streak joining the discrete x-ray diffraction spots. Many large polytypes of silicon carbide do exhibit such a streak; but the polytype $111R$ discovered by us has a magnificently ordered structure in spite of having such a large unit cell. It appears improbable that thousands of unit cells, each of 111 layers, should be formed by the accretion of small polymers under the fluctuating conditions of the furnace with such a high degree of order. Even highly overexposed photographs have not revealed any disorder of layers. Moreover, the existence of such polymers has yet to be experimentally demonstrated.

The growth of this series of structures can be quite well understood on the screw-dislocation mechanism. VERMA\textsuperscript{27} has demonstrated experimentally that the spiral step height, and therefore the BURGER's vector of the screw dislocation, is one third the height of the unit cell for rhombohedral polytypes. Therefore the growth of rhombohedral polytypes is not possible on a pure screw dislocation. MITCHELL\textsuperscript{24} introduced the idea of a horizontal displacement coupled with a screw dislocation for the generation of such structures. In a previous paper\textsuperscript{19}
we have suggested a possible mechanism causing this slip. It requires the first and last layers of the exposed ledge to be in the same orientation \((A, B \text{ or } C)\) for the growth of rhombohedral polytypes. This fits in excellently for the \((33)_n34\) series of structures as the screw dislocation ledge for these necessarily has the first and last layers in the same orientation. For, the exposed ledge in any member \(xR\) of this series, \(x = 3(6n + 7)\), would consist of \((6n + 7)\) layers, and a ledge of \((6n + 7)\) layers exposed in any manner in a \(6H\) structure would necessarily have the first and last layers in the same orientation. The growth of this series of structures is thus very much to be expected on the screw-dislocation theory. It follows as a corollary that a hexagonal structure of the type \((6n + 1)H\) cannot grow from the \(6H\) phase, and any polytype with \(3(6n + 7)\) layers, based on the \(6H\) phase, must belong to this series of structures. The existence of \(19H\) with a structure \([23]_{22}\) and of \(75R\) with a structure \([23]_{3232}\) is in accordance with this.

The screw-dislocation mechanism is not able to explain the existence of random disorder of layers observed in many silicon carbide structures (Jagodzinski). It is, however, found (Verma) that often what appears initially to be a streak gets resolved into a large number of spots on employing techniques that provide higher resolution. In such cases the streak is not due to a random disorder of layers in the structure but due to a very large periodicity. As discussed in the earlier sections, a very high member of the above series of structures would give intense spots near the \(6H\) positions but very weak and closely spaced spots in between. These, if unresolved, would produce a weak continuous streak joining dark spots near \(6H\) positions. This streak can be distinguished from that due to a random disorder of layers as it will be darker round those \(6H\) positions which fall \(\frac{1}{3}, \frac{2}{3}\) or \(\frac{3}{3}\) the way between two reflections of the polytype, and very faint or absent around \(6H\) positions which coincide with a reflection of the polytype or are \(\frac{1}{6}\) or \(\frac{2}{6}\) the way between two of them. X-ray diffraction photographs showing dark spots in \(6H\) positions connected by a continuous streak are quite common. The absence of any streak connecting the reflections from \(111R\) favours its growth by the dislocation mechanism and points to the purity of its structure.

JAGODZINSKI\textsuperscript{29-31} has studied, theoretically, the phenomenon of one-dimensional fault order in crystals. He has applied this to the case of silicon carbide\textsuperscript{28} and suggested a layer-transposition mechanism based on the vibration entropy of the structure. He has been able to account for the presence of random disorder of layers in the structure but has not explained the origin and growth of structure series in silicon carbide. Indeed no single theory has been able to account for all the observed facts.

**Acknowledgement**

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Interferometric and X-ray Investigation of Polytypism in Cadmium Iodide Crystals in Relation to Crystal Growth

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A combined optical and X-ray diffraction study has been undertaken of the phenomenon of polytypism in cadmium iodide crystals, which grow by a dislocation mechanism. 88 CdI₂ crystals have been investigated to study Frank's ideas of a 'buckle followed by slip' mechanism in the creation of dislocations and subsequently of polytypes. A correlation between the spiral step height and X-ray unit cell is found for a few 2H and 4H structure types. However, for polytypes with larger unit cells no such correlation was observed. This is at variance with previous observations and with Frank's theory and cannot yet be fully explained. Some X-ray diffraction photographs show 'diffuse background' and 'smearing of diffraction spots', with spots elongated along streaks, similar to Jagodzinski's observations on silicon carbide crystals. 13 (possibly 18) new polytypes of CdI₂ are described. In addition, several crystals resembling 2H and 4H types, but having either intensity differences or conspicuous absences of certain reflections, have been found.

1. Introduction

It is now well established that polytypism is a widely occurring phenomenon in crystals. Silicon carbide (Verma, 1953), cadmium iodide (Mitchell, 1955), cadmium bromide (Mitchell, 1958), zinc sulphide (Buck & Strock, 1955; Strock & Brophy, 1955), etc., are known to be polytypic. These polytypic crystals, especially SiC and CdI₂, often exhibit growth spirals on their faces. This observation led Frank (1951) to explain polytypism in terms of dislocations. However, Jagodzinski (1954) has advanced an alternative theory of polytypism based on the vibration entropy of crystals. Mitchell (1956), by combining his X-ray diffraction results on CdI₂ crystals with the measurements of step heights of growth spirals previously published by Forty (1952), has supported Frank's 'buckle followed by slip' mechanism for the creation of dislocations. However, for an unequivocal verification of Frank's theory it is essential to perform the interferometric and X-ray diffraction studies upon the same crystals, as done by Verma (1957) for silicon carbide. In the present investigation we have carried out this combined optical and X-ray study on cadmium iodide to study its polytypism. For measurement of step height, we need crystals with well-developed growth spirals, and a simple method of growing such crystals was followed. These crystals were isolated for X-ray diffraction work. A preliminary study on a few crystals has been reported earlier (Trigunayat, 1959). A detailed study on 88 crystals has now been completed. These results are reported in the present paper and are discussed in relation to the ideas of Frank & Jagodzinski. This investigation has further resulted in the discovery of 13 (possibly 18) new polytypes in addition to those already found by Mitchell (1956).

2. Experimental methods

Details of the various experimental techniques employed in this investigation have been described earlier (Trigunayat, 1959). Briefly they consist of the following:

(i) Crystal growth
A drop of aqueous solution of CdI₂ saturated at about 90 °C was placed on a cooled glass slide. Nucleation of several small crystal platelets took place immediately due to the sudden change of temperature and consequent high supersaturation. The drop was then suitably enclosed and crystals allowed to grow at reduced temperature till they dried out in about 10-12 hr. Crystals exceeding 0.1 mm. across and a few microns thick were formed. The few crystals showing well-developed growth spirals on their (0001) faces were selected for investigation.

(ii) Microscopic examination
The crystals were studied both by transmitted and reflected light employing bright field illumination using a narrow pencil, a procedure which considerably improves the visibility of growth steps as demonstrated by Griffin (1951).

(iii) Interferometric measurement of step height
For step height measurement, the fringe methods used by Forty (1952) and by Verma & Reynolds...
(1953), which involve the interference of light between the two basal surfaces of the crystal platelet, were utilized. These fringes contour the growth steps and can be observed simultaneously with them in the field of view of the microscope when using a monochromatic light source. In order to distinguish between two successive polytypes it is necessary to measure the step height, \( h \), to within \( \frac{1}{4} M \), where \( M = 6.84 \, \text{Å} \) is the thickness of the basic layer or 'minimal sandwich' as referred to by Forty (1952). Since these two-beam fringes are much broader than the multiple-beam fringes, Forty's microphotometric method of 'successive differences of photographic density', which leads to considerable accuracy, was employed. To be conservative the errors in step height measurements, quoted in Table 1, have been taken to be four times as much as calculated mathematically by Forty, in order to take account of the presence of dust particles and other impurities on the surface which might cause irregularities in the microphotometric records.

(iv) X-ray diffraction methods

Taking advantage of the findings of Mitchell (1956) that practically all \( \text{CdI}_2 \) polytypes are hexagonal with polytypes differing only in \( c \)-spacing, a simplified diffraction method was evolved. This enabled identification of the crystal type, unique indexing of most of the diffraction spots, and evaluation of the unit-cell dimensions from one 15°-oscillation, \( a \)-axis photograph by preselecting the range. In fact by a suitable choice of the range of oscillation, a series of ten consecutive (1012) spots, which were taken by Mitchell for the determination of the stacking sequence of various polytypes, could be obtained on the zero layer-line for a type 4H crystal \((c=13.67 \, \text{Å}, \text{see Fig. 9})\). All the X-ray photographs reproduced are 15°-oscillation, \( a \)-axis photographs using \( \text{Cu Kx} \) radiation.

3. Experimental results

Upon \((0001)\) a wide range of growth patterns of familiar shapes was observed. Thus single spirals with hexagonal, trigonal or circular symmetry, spirals due to cooperating dislocations, cross-hatched spirals, closed loops due to dislocations of opposite hands, etc., have all been photographed. These patterns are familiar and will not be discussed here. Only certain representative examples relevant to polytypism will be described, along with their corresponding X-ray diffraction patterns.

Fig. 1 shows a single hexagonal spiral on the surface of a crystal (Table 1, No. 47) with clear internal interference fringes contouring the step structure. Fig. 2 is the corresponding 15°-oscillation photograph, in which the diffraction spots resemble those of type 2H but are not identical with them. In this and other similar cases there are either conspicuous absences of certain reflections or there exist intensity differences. This crystal has therefore been classified as 'resembling 2H'.

Fig. 3 shows a typical case (Table 1, No. 46) of one crystal lying over the other, each with its own growth spiral. Both series of growth steps, which are not visible in the figure, are of similar magnitude in height, and only their fringes can be observed. The corresponding X-ray photograph (Fig. 4) shows diffraction spots due only to one type, namely 10H\(_{a}\) (see Section 5), and thus both crystallites have the same structure.

Fig. 5 exhibits as many as eight rounded growth spirals with at least three different step heights (Table 1, No. 26). The corresponding X-ray photograph (Fig. 6) shows spots similar to those of 4H and has been classified as 'resembling 4H'. Thus it is a case of interacting spirals having different step heights but with the crystal structures being the same.

Fig. 8 illustrates the spiral steps and the contouring fringes due to a number of cooperating dislocations upon crystal No. 51. The central part is shown enlarged in Fig. 7. The 15°-oscillation photograph corresponding to this is given in Fig. 9, which shows it to be clearly of type 4H without any deviation. This is to be expected, since a number of dislocations lying close to, and cooperating with, one another will naturally be elementary dislocations.

Two separate crystal platelets lying adjacent to each other are shown in Fig. 10. The crystal on the left (Table 1, No. 55) has a thickness of nearly 15 microns and exhibits a hexagonal spiral which acquires increasing circular symmetry on going away from the centre. The crystal on the right (Table 1, No. 56) has a thickness of nearly 20 microns and shows a spiral with trigonal symmetry upon its surface. As seen in Table 1 and indeed revealed by the contouring fringes the step heights for the two crystals are widely different. The corresponding X-ray photographs (Figs. 11 and 12) show the crystals to be of type 38H\(_{a}\) and 16H, respectively.

Fig. 13 is the X-ray photograph of a crystal (Table 1, No. 59) which had a growth pattern of closed hexagonal loops due to dislocations of opposite hand on its surface. It shows a confused series of diffraction spots due perhaps to a coalescence of crystals which cannot be identified.

The growth sequence of crystal No. 85 was watched throughout its growth. Its 15°-oscillation photograph, shown in Fig. 14 consists of two series of diffraction spots, one due to 4H and the other to 6H. This case may therefore be classified as coalescence of two identified types.

Fig. 15 shows the micrograph of crystal No. 43 whose steps, on going away from the centre, begin to dissociate and interlace with one another in certain orientations. Its X-ray photograph (Fig. 16) shows it to be of type 4H but the spots are elongated along powder pattern arcs.

A close examination of the X-ray diffraction photo-
Fig. 1. Micrograph of (0001) with the interference fringes contouring the step-structure of crystal No. 47. Mag. ×320.

Fig. 2. 15° X-ray oscillation photograph about axis, showing the zero layer-line with 10H diffraction spots, along with the first layer lines (3 cm. camera, Cu Kα). Crystal No. 47. Mag. ×1.

Fig. 3. Micrograph of (0001) with contouring fringes of crystal No. 46. Mag. ×110.

Fig. 4. 15°-oscillation photograph about a axis of crystal No. 46 (Cu Kα, 3 cm. camera). Mag. ×1.

Fig. 5. Micrograph of (0001) with interference fringes on crystal No. 26. Mag. ×320.

Fig. 6. 15°-oscillation photograph about a axis of crystal No. 26 (Cu Kα, 3 cm. camera). Mag. ×1.

Fig. 7. Micrograph of (0001) with interference fringes of crystal No. 51. Mag. ×320.
Fig. 8. Micrograph of the entire crystal No. 51. Mag. x 162.

Fig. 9. 15°-oscillation photo about a axis of crystal No. 51 (Cu Kα, 3 cm. camera). Mag. x 1.

Fig. 10. Combined micrographs of crystals No. 55 and 56 with the contouring interference fringes visible on (0001). Mag. x 90.

Fig. 11. 15°-oscillation photo about a axis of crystal No. 55 (Cu Kα, 3 cm. camera). Mag. x 1.

Fig. 12. 15°-oscillation photo about a axis of crystal No. 56 (Cu Kα, 3 cm. camera). Mag. x 1.

Fig. 13. 15°-oscillation photo about a axis of crystal No. 59 (Cu Kα, 3 cm. camera). Mag. x 1.

Fig. 14. 15°-oscillation photo about a axis of crystal No. 85 (Cu Kα, 3 cm. camera). Mag. x 1.

Fig. 15. Micrograph of crystal No. 43. Mag. x 400.

Fig. 16. 15°-oscillation photo about a axis of crystal No. 43 (Cu Kα, 3 cm. camera). Mag. x 1.
graphs reveals that, besides showing the various polytypes through appropriate spacing of spots, these photographs also differ in their fine details and characteristics and may be classified in the following categories:

(i) The diffraction photographs show clear X-ray reflections, so that the corresponding polytypes can be identified without ambiguity, e.g., Figs. 4 and 9.

(ii) The distribution of diffraction spots is similar to that of a particular type, e.g., 2H, 4H or 8H, but there exist either conspicuous absences of certain reflections or intensity differences. These have been classified as 'coalescence identified', an illustration of which is Fig. 2.

(iii) The diffraction spots can be resolved into series of spots, each of which can be identified separately with a particular polytype. Such have been designated as 'coalescence unidentified', an illustration of which is given in Fig. 14.

(iv) The photographs show a confused series of diffraction spots, in which separate constituent types are indistinguishable, and have been classified as 'coalescence unidentified'. An example of this is shown in Fig. 13.

(v) A random distribution of diffraction spots appears. These have been classified as 'unidentified'.

(vi) Lastly, on many oscillation photographs diffraction spots on the zero and other layer-lines are connected by horizontal streaks (e.g., Figs. 2 and 14). These are not Laue streaks and are similar to the 'diffuse background' observed by Jagodzinski in silicon carbide along row lines for oscillation about the c axis. The 'smearing' of diffraction spots described by Jagodzinski (1954) has also been observed here and is illustrated by Figs. 2, 6, and 12. Apart from these two effects an unusual phenomenon has been found to occur on a large number of photographs in which the X-ray reflections are drawn into small arcs of a circle which do not lie along lines of constant \( \xi \)-value in the Bernal chart, but along powder lines of the substance, e.g., Figs. 2, 6, and 16. This would indicate that successive layers of the crystal plate are randomly oriented about the c axis through a certain range. Sometimes the arcs are clearly split into a string of two or more spots (e.g., Fig. 14), showing that the crystal is made up of two or more groups of layers rotated slightly with respect to each other about the c axis. The 'powder effect' might be due partly to strain, but in several cases it was certainly not so: some of the crystal plates appeared perfect under polarized light. Thus it is significant to note that during growth, successive layers of the crystal plate could be rotated through a small range with respect to one another, and there must be several stable positions of the stacking of the thin layers on each other. The elongation of the spots, however, did not present any difficulty in the identification of the crystal.

The X-ray and optical measurements are collected in Table 1. Step height measurements have been expressed in Angstrom units and also as multiples of \( M = 6.84 \text{ \AA} \); fractional parts of \( M \) are indicated only where it has been possible to measure the height to within \( \frac{1}{2} M \), i.e., nearly 3 \( \text{\AA} \). The c dimension, as found by X-ray diffraction has been shown as the nearest integral multiple of \( M = 6.84 \text{ \AA} \), the observed differences being very small. The symbols used for denoting the various polytypes are in accordance with the general scheme introduced by Ramsdell (1947) and Ramsdell & Kohn (1952). The polytypes having the same number of layers but differing in their arrangement have been distinguished by a subscript, e.g., \( H(a) \), \( H(b) \). Whether or not the step height, \( h \), has a direct correlation with the X-ray unit cell height (the c dimension), i.e., \( h \) is either equal to or an integral multiple of \( c \), has been indicated in Table 1 under 'remarks'. The proportional numbers of the various categories of crystals mentioned above are listed in Table 2.

4. Discussion

From the examples given in Table 1, it is evident that in CdI\(_2\) crystals it is not always possible to find a correlation between the step height of the growth spiral and the X-ray unit cell. This is at variance with the observations of Verma (1957) on silicon carbide and with the ideas of Frank (1951). According to the latter, a dislocation would be created in the silicon carbide crystal plate, which may have initially grown by a nucleation mechanism, when it becomes self-stressed, through non-uniform distribution of impurities or thermal stresses, up to its theoretical yield stress; it will then buckle and shear, exposing a ledge. The dislocations created in this process will be of different strengths, and since the crystal subsequently growing on these dislocations will necessarily have the structure of the ledge, it will lead to the formation of different polytypes. Forty (1962) extended these ideas to CdI\(_2\) crystals by taking the basic structure to be 4H, which has a structural sequence of layers (22) in Ramsdell's notation or \((A+yB)/(C\times B)\) in the classical \(ABC\) notation, where the Roman letters represent iodine ions and the Greek letters represent cadmium ions. The creation of an 'even' dislocation of any strength in the 'ideal' structure during the early stages of growth leaves the layers in perfect fit with each other, i.e., in a stable configuration, so that the same 4H structure is retained throughout the subsequent growth. This explains the growth steps observed on crystals of type 4H being an integral multiple of its c parameter. However 'odd' dislocations of various strengths leave a misfit in the structure at the initial step, so that the subsequent growth leads to formation of various polytypes of the \((22)_{a11}\) series. A method for the creation of polytypes with a stacking sequence of layers differing from \((22)_{a11}\) has been suggested by Mitchell (1956), who postulated a combination of dislocations close enough to cooperate.
<table>
<thead>
<tr>
<th>Crystal no.</th>
<th>Step height ($h$) in Å</th>
<th>$h$ expressed in multiples of $M$</th>
<th>Crystal type determined by X-rays</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>500 or greater</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>235-2 ± 1-6</td>
<td>34±4 ±0-023</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>221-2 ± 1-4</td>
<td>32±3 ±0-020</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>256-2 ± 0-0</td>
<td>~ 30</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>195-7 ± 1-0</td>
<td>27±5 ±0-15</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>184 ± 3 ± 3-7</td>
<td>~ 20</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>295±4 ± 9-0</td>
<td>~ 43</td>
<td>coalescence (identified 2H+10H)</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>303±1 ± 2-4</td>
<td>44±36 ±0-34</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>324±2 ± 4-0</td>
<td>~ 47</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>270±0 ± 2-9</td>
<td>~ 40</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>184±7 ± 5-8</td>
<td>~ 27</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>170±2 ± 3-0</td>
<td>24±88 ±0-46</td>
<td>resembles 34H(a)</td>
<td></td>
</tr>
<tr>
<td>17.</td>
<td>123±2 ± 3-4</td>
<td>17±20 ±0-49</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>18.</td>
<td>357±9 ± 2-8</td>
<td>52±33 ±0-40</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>19.</td>
<td>246±3 ± 5-9</td>
<td>~ 36</td>
<td>coalescence (unidentified)</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>164±6 ± 9-2</td>
<td>~ 24</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>190±8 ± 6-2</td>
<td>~ 28</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>124±1 ± 4-3</td>
<td>~ 18</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>82±3 ± 4-6</td>
<td>~ 12</td>
<td>18H</td>
<td></td>
</tr>
<tr>
<td>24.</td>
<td>132±2 ± 1-8</td>
<td>19±23 ±0-26</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>260±9 ± 7-8</td>
<td>~ 38</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>26.</td>
<td>$h_1$ = 296±1 ± 14-8</td>
<td>~ 43</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>$h_2$ = 176±9 ± 0-9</td>
<td>25±86 ±0-13</td>
<td>resembles 4H</td>
<td>Fig. 5</td>
</tr>
<tr>
<td>28.</td>
<td>234±3 ± 11-9</td>
<td>~ 34</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>29.</td>
<td>155±6 ± 2-7</td>
<td>22±73 ±0-39</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>175±8 ± 1-6</td>
<td>25±69 ±0-23</td>
<td>resembles 23H(a)</td>
<td></td>
</tr>
<tr>
<td>31.</td>
<td>429±2 ± 4-8</td>
<td>~ 63</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>32.</td>
<td>261±6 ± 15-4</td>
<td>~ 35</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>33.</td>
<td>214±3 ± 2-4</td>
<td>31±33 ±0-35</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>34.</td>
<td>$h_1$ = 298±1 ± 2-7</td>
<td>33±34 ±0-38</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>35.</td>
<td>$h_2$ = 151±8 ± 3-4</td>
<td>22±19 ±0-49</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>36.</td>
<td>164±3 ± 1-4</td>
<td>24±02 ±0-20</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>37.</td>
<td>88±1 ± 1-5</td>
<td>12±00 ±0-22</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>38.</td>
<td>92±4 ± 2-9</td>
<td>13±31 ±0-42</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>39.</td>
<td>80±6 ± 1-8</td>
<td>13±09 ±0-26</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>40.</td>
<td>184±8 ± 5-8</td>
<td>~ 27</td>
<td>10H(b)</td>
<td></td>
</tr>
<tr>
<td>41.</td>
<td>405±0 ± 3-3</td>
<td>59±21 ±0-48</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>42.</td>
<td>246±6 ± 10-3</td>
<td>~ 36</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>43.</td>
<td>410±1 ± 1-1</td>
<td>59±94 ±0-16</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>44.</td>
<td>64±8 ± 1-5</td>
<td>13±31 ±0-22</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>45.</td>
<td>305±6 ± 1-7</td>
<td>32±43 ±0-25</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>46.</td>
<td>266±3 ± 0-9</td>
<td>38±92 ±0-14</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>47.</td>
<td>369±3 ± 7-7</td>
<td>~ 54</td>
<td>6H(c)</td>
<td></td>
</tr>
<tr>
<td>48.</td>
<td>247±9 ± 20-7</td>
<td>~ 36</td>
<td>10H(a)</td>
<td>Fig. 3</td>
</tr>
<tr>
<td>49.</td>
<td>116±3 ± 0-4</td>
<td>17±01 ±0-05</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>50.</td>
<td>135±6 ± 1-4</td>
<td>23±92 ±0-20</td>
<td>resembles 30H</td>
<td></td>
</tr>
<tr>
<td>51.</td>
<td>205±2 ± 0-8</td>
<td>30±02 ±0-11</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>52.</td>
<td>198±8 ± 1-1</td>
<td>29±06 ±0-16</td>
<td>resembles 38H(a)</td>
<td></td>
</tr>
<tr>
<td>53.</td>
<td>246±3 ± 6-9</td>
<td>~ 36</td>
<td>4H</td>
<td></td>
</tr>
<tr>
<td>54.</td>
<td>263±7 ± 3-6</td>
<td>~ 39</td>
<td>coalescence (unidentified)</td>
<td></td>
</tr>
<tr>
<td>55.</td>
<td>$h_1$ = 169±7 ± 4-2</td>
<td>~ 25</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>56.</td>
<td>$h_2$ = 169±7 ± 4-2</td>
<td>~ 25</td>
<td>unidentified</td>
<td></td>
</tr>
<tr>
<td>57.</td>
<td>160±0 ± 1-3</td>
<td>23±38 ±0-19</td>
<td>resembles 34H(b)</td>
<td></td>
</tr>
<tr>
<td>58.</td>
<td>245±6 ± 3-1</td>
<td>35±99 ±0-46</td>
<td>resembles 38H(b)</td>
<td></td>
</tr>
<tr>
<td>59.</td>
<td>76±4 ± 1-7</td>
<td>10±29 ±0-25</td>
<td>resembles 16H</td>
<td></td>
</tr>
<tr>
<td>60.</td>
<td>164±6 ± 3-8</td>
<td>~ 24</td>
<td>4H</td>
<td></td>
</tr>
<tr>
<td>61.</td>
<td>371±1 ± 2-0</td>
<td>54±23 ±0-28</td>
<td>resembles 38H(c)</td>
<td></td>
</tr>
<tr>
<td>62.</td>
<td>184±7 ± 2-9</td>
<td>27±01 ±0-42</td>
<td>coalescence (unidentified)</td>
<td></td>
</tr>
<tr>
<td>63.</td>
<td>328±8 ± 3-0</td>
<td>47±34 ±0-43</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>64.</td>
<td>338±3 ± 2-0</td>
<td>48±27 ±0-30</td>
<td>resembles 2H</td>
<td></td>
</tr>
<tr>
<td>65.</td>
<td>124±4 ± 0-8</td>
<td>18±19 ±0-12</td>
<td>coalescence (identified 2H+14H)</td>
<td></td>
</tr>
</tbody>
</table>
the unit cell height. However, from the examples in type 4H happens to be a very common polytype of is not exactly identified or the error in the measure­
ment is too large. It is observed that in all these 18 cases no such correlation has been found to exist. It is easy to explain the correlation for the 2H and 4H types. Every step height should be a multiple of the 2H unit cell, since type 2H corresponds to a slip. If this slip happened to take place in the con­
cluding stages of growth, a non-correlation between the step-height and the c dimension will be explicable because, then, the measured height of the growth steps upon the end surface will not be a true represen-
tative of the structure of the main bulk of the crystal. The last dislocation will have helped the crystal to grow in thickness inappreciably, so that it will be the structure of the main body of the crystal alone that will dominate the X-ray photograph.

It was therefore decided to study the growth se­quence of crystals by observing them continuously during growth. Nine crystals (Table 1, Nos. 80 to 88) were subjected to this examination. The step heights given in Table 1 for these crystals are those corre­
sponding to the first of the several spirals originating upon their surface and were estimated from visibility. Consider the example of crystal No. 85. It started growing in thickness by the operation of a growth spiral with a step height greater than 500 Å. Within a few minutes the crystal had grown to a thickness of nearly 15 microns; then two more growth spirals appeared with step heights ~ 500 and 100 Å, respec­
tively, which completely overshadowed the previous one and thickened the crystal to about 25 microns in about an hour. At this stage, growth started by the advancement of certain long ‘steps’ and ‘blocks’ of trigonal and hexagonal shapes, which appeared on the crystal surface such that the existing growth spirals, although visible till the end, were rendered absolutely inactive. This mode of growth is very much similar to the one described by Williams (1957) on lead nitrate crystals and by Reynolds & Greene (1958) on cadmium sulphide, and most likely the occasional mode of growth observed by Tolansky & Emara (1955) is also similar. The crystal went on to grow to a thickness of nearly 50 microns till it dried out, when its X-ray

<table>
<thead>
<tr>
<th>Crystal no.</th>
<th>Step height (h) in Å</th>
<th>h expressed in multiples of M</th>
<th>Crystal type determined by X-rays</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>155±0.2 ± 3.2</td>
<td>22.85±0.39</td>
<td>resembles 4H</td>
<td>c = 13.7 Å; no correlation</td>
</tr>
<tr>
<td>64</td>
<td>309.5±0.6 ± 1.5</td>
<td>18.94±0.32</td>
<td>resembles 8H</td>
<td>c = 75.2 Å; no correlation</td>
</tr>
<tr>
<td>65</td>
<td>129.6±2.2 ± 1.5</td>
<td>15.66±0.23</td>
<td>resembles 22H (60)</td>
<td>4H</td>
</tr>
<tr>
<td>66</td>
<td>107.8±1.6 ± 1.3</td>
<td>6.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>278.0±17.3 ± 1.7</td>
<td>18.00±0.37</td>
<td>unidentifed</td>
<td></td>
</tr>
<tr>
<td>68</td>
<td>123.3±2.6 ± 1.7</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>nearly 140 Å</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>nearly 240 Å</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>228.9±1.6 ± 1.3</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>288.9±0.8 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>73</td>
<td>102.6±4.0 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>138.9±7.7 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>296.1±14.8 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td>298.8±15.4 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>260.6±7.8 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>246.9±13.8 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H (identified 6H + 4H)</td>
<td>4H</td>
</tr>
<tr>
<td>79</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>81</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>85</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>86</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>87</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
<tr>
<td>88</td>
<td>231.8±1.3 ± 0.8</td>
<td>16.30±0.31</td>
<td>resembles 4H</td>
<td></td>
</tr>
</tbody>
</table>

From energy considerations 'even' dislocations are more likely, which explains the abundant occurrence of type 4H.

According to the above one should therefore expect a direct correlation between the spiral step height and the unit cell height. However, from the examples in Table 1 it is seen that such a correlation exists only for all the cases of 2H and two cases of 4H types (Nos. 9 and 43). This relationship could be tested in 18 more cases with larger unit cells (Nos. 16, 23, 24, 29, 38, 48, 50, 54, 55, 56, 58, 63, 66, 72, 76, 77, 78, and 79); in the rest of the cases either the polytype is not exactly identified or the error in the measure­ment is too large. It is observed that in all these 18 cases no such correlation has been found to exist. It is easy to explain the correlation for the 2H and 4H types. Every step height should be a multiple of the 2H unit cell, since type 2H corresponds to
examination showed it to be a combination of types 4H and 6H. At no stage in the growth were the elementary growth spirals of step heights 13-7 and 18.5 Å, corresponding to types 4H and 6H, observed. These small steps would not be visible under the microscope but would have been noted by their contouring fringes. Only multiple steps were observed. Now multiple steps corresponding to the 4H structure are easily explained on the basis of Frank's ideas. An 'odd' dislocation and then a further slip in this polytype would be needed to explain the observation for type 6H. It is likely that the non-correlation between the step height and X-ray unit cell height in CdI₂ crystals in contrast to silicon carbide may be due most likely to high disorder (the crystals were perfect optically), shows that fault-order of high degree postulated by Jagodzinski does occur in CdI₂ crystals. Thus, it appears highly desirable to extend the experimental verification of his theory to the case of CdI₂ crystals by evaluating the fault-order degree of every crystal by his method and then analyzing the statistics.

5. New polytypes

This study has resulted in the finding of 13 new polytypes. All the polytypes of CdI₂ are composed of identical layers but differ only in their arrangement and in the number composing the unit cell. Using Ramsdell's notation, the new polytypes found in addition to the 29 reported by Mitchell (1956) and one reported by Pinsker (1941) are 6H(α), 10H(α), 12H(α), 18H(α), 22H(α), 22H(β), 24H(α), 34H(α), 34H(β), 36H, 38H(α), 38H(β), 38H(c), and 52H, after excluding types 2H and 4H. As noted earlier, when several varieties of a particular type are found in which there is the same number of layers in the unit cell but a difference in their arrangement, we have differentiated them by attaching a small letter as subscript, e.g., 38H(α), 38H(β), and 38H(c). We have found five polytypes with the same number of layers in the unit cell as found by Mitchell, but these have not been differentiated by a subscript letter though they may differ by virtue of their arrangement. However, two polytypes of 18H were encountered as against one by Mitchell, and the new one has been labelled 18H(α). Similarly, two type 10H crystals were encountered, one of which had the same stacking sequence as found by Mitchell; accordingly this has been designated 10H(α) and the other 10H(β). The polytypes 16H, 18H, 20H, 32H, and 50H have ambiguous identity.

This work has been carried out with assistance from the Council of Scientific and Industrial Research of India.

References

Multiple Beam Interferometric Study of ‘Built-up’ Films of Barium Stearate

BY V. K. SRIVASTAVA† AND AJIT RAM VERMA‡

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Multiple Beam Interferometric Study of ‘Built-up’ Films of Barium Stearate

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Abstract. A direct determination of the metrical thickness of mono- and multi-molecular films of barium stearate has been carried out with the use of multiple beam interferometry. The thickness of the unimolecular film, as obtained from measurements on a four-layer film, is $25.7 \pm 0.3$ Å which is in excellent agreement with the length of the molecular chain of barium stearate ($=25.75 \pm 0.25$ Å) as obtained from Fankuchen’s x-ray data. The technique employed eliminates differential phase change effects and does not involve the refractive index of the films. The result confirms the monomolecular spreading of stearic acid on a water surface.

§ 1. INTRODUCTION

Barium stearate films of mono- and multi-molecular thicknesses can be built up by the Blodgett and Langmuir technique (Blodgett 1935, Blodgett and Langmuir 1937). It has been shown by them that these films consist of superposed sheets of oriented molecules and form a positive uniaxial crystal with the optic axis at right angles to the plane of the film. Electron diffraction studies have further shown that these films actually form hexagonal crystals with the symmetry axis perpendicular to the plane of the film (Germer and Storks 1938). The films deposited may be of X or Y type depending upon the orientation of adjacent layers. X-ray diffraction investigations indicate that the lattice spacing is independent of the type of film deposited (Holley 1937, Fankuchen 1938). According to Fankuchen, the lattice spacing of barium stearate film is $51.5 \pm 0.5$ Å and hence the length of the molecular chain is $25.75 \pm 0.25$ Å.

Several attempts have been made to estimate the thickness of barium stearate films. Interference of monochromatic light reflected by the film has generally been used for this determination (Blodgett 1935, Blodgett and Langmuir 1937, Blodgett 1937). In another method a Michelson interferometer was utilized (Holley 1937). More recently an interference reflector of barium stearate itself was used (Mattuck 1956) to determine the thickness by Hartman’s method (Hartman 1954), utilizing white light interference fringes. These interference methods essentially yield the optical thickness. For an exact correlation with x-ray data an accurate knowledge of the refractive index of the molecular films is therefore required, apart from the elimination of the spurious effects due to differential phase changes. A direct determination of the actual metrical thickness of barium stearate film has not yet been reported. In the present work the standard thin film multiple beam interferometric technique (Tolansky 1948) has been used to determine accurately the thickness of mono- and multimolecular barium stearate films. As is well known, the method is independent of the optical properties of the film and since differential phase changes have been eliminated, as described later, it yields the true metrical thickness.

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‡ Now at the Department of Physics, Banaras Hindu University, India.
§ 2. EXPERIMENTAL

2.1. ‘Building up’ of Films

Using the Blodgett and Langmuir technique, films were built up by depositing successive monolayers of barium stearate on suitably conditioned glass slides. A monolayer of stearic acid dissolved in benzene (concentration commonly $3 \times 10^{-4}$ by weight) was spread on the surface of doubly distilled water (in a Langmuir Perspex trough heavily waxed from inside) containing $0.3 \times 10^{-4}$ M BaCl$_2$, the pH of the solution having been held at about 7.0 by adding a small concentration ($4.0 \times 10^{-4}$ M) of potassium bicarbonate. The layer was transferred from the water surface to the slide by a continuous dipping and withdrawal process, the stearic acid film being kept under suitable two-dimensional pressure, with oleic acid as the ‘piston oil’. Under these conditions a layer is transferred every time the slide is dipped or withdrawn, and the built-up film is expected to be Y type in which the molecules in adjacent layers in the crystal lattice are oppositely oriented.

2.2. Interferometric Technique

It has been found that uniform and well-adhering films of barium stearate can be deposited better on silvered microscope slides than on the glass surface itself. Therefore, on a clean glass slide, first a thin layer of silver is deposited in vacuum by thermal evaporation. Then over the entire surface of this silvered glass slide, a suitable number of barium stearate layers, say twenty, are deposited to form the base film. Over a part of this slide is deposited a film of the required number of barium stearate layers, the thickness of which is to be measured. This forms a sharp step the height of which is obviously the film thickness to be measured. The base film provides the same material structure on both sides of the step and thus avoids any differential phase changes in reflection from the two sides of the step. For the standard method of multiple beam interferometry an almost opaque coating (reflectivity > 90%) of spectroscopically pure silver is then deposited, by thermal evaporation in vacuum (better than $10^{-5}$ cmHg), over an area including the step. This silvered film is now matched, at a small angle, against a reference optical flat which is silvered with a low absorption coating of about 80% reflectivity. This leads to fringes with good contrast. The interference system is illuminated with normally incident, collimated, white light to obtain fringes of equal chromatic order (called in abbreviation FECO) which were observed in reflection by the usual method (Tolansky 1948, Scott et al. 1950). With proper manipulation of the system in a suitably constructed jig, the image of the step is projected on the slit of a spectrograph so that the slit crosses the image of the step perpendicularly. This results in discontinuities in the FECO, corresponding to the step height or film thickness. To obtain higher sensitivity and precision, low-order fringes are studied by reducing the optical gap.

For the measurement of film thickness the FECO have been preferred to the Fizeau fringes since, as is well known, any effects due to irregularities of reference flats over small areas are considerably reduced. This is because the slit of the spectrograph selects a very narrow area of the interference plates, particularly at high microscopic magnifications. Indeed, in place of a reference optical flat one can use, with advantage, microscope slides which, having been rolled or fire polished, have local areas much smoother than those of optical flats polished by an abrasive (Tolansky 1955). Comparatively smoother areas can be chosen with reference to FECO which, in these areas, would be straight and practically smooth.
The step height or film thickness $h$ is given by

$$ h = \Delta t = \frac{\Delta \lambda}{2} $$

where $\Delta \lambda$ is the discontinuous shift in wavelength due to the step, for a fringe of order $n$. The order is given by

$$ n = \frac{\lambda_{n+1}}{\lambda_n - \lambda_{n+1}} $$

in which $\lambda_n$ and $\lambda_{n+1}$ are the wavelengths corresponding to fringes of order $n$ and $n+1$ respectively on the same side of the discontinuity.

§3. RESULTS AND DISCUSSION

Steps were formed on different microscope slides by depositing one, two or more layers of barium stearate, by the method described. The fringes of equal chromatic order corresponding to these steps were produced and their step heights measured. The measured thickness of the one-layer film is 31.3 Å and 35.2 Å corresponding to fringes (FECO) of order number 12 and 13 respectively. With the two-layer film the thickness obtained is 58.3 Å and 46.1 Å corresponding to fringes (FECO) of order number 14 and 15 respectively. Owing to wriggle in these fringes, high accuracy could not be attained. However, a more accurate measurement was possible with a four-layer barium stearate film, the FECO for which are illustrated in the figure, which shows successive orders 18, 19, 20, 21... etc. The values of the wavelengths at the shifts at these orders are respectively 6332.06 Å and 6320.57 Å ($\Delta \lambda = 11.49 \text{ Å}$), 6001.44 Å and 5990.58 Å ($\Delta \lambda = 10.86 \text{ Å}$), 5700.20 Å and 5689.90 Å ($\Delta \lambda = 10.30 \text{ Å}$), 5429.69 Å and 5419.95 Å ($\Delta \lambda = 9.74 \text{ Å}$). The thickness of the film, as measured from the successive orders 18, 19, 20 and 21, is 103.4 Å, 103.2 Å, 103.0 Å and 102.3 Å respectively. The mean value is therefore 102.9 ± 1 Å. The thickness of the unimolecular film (i.e. one fourth of the thickness of a 4-layer film) is therefore 25.7 ± 0.3 Å. This result is in excellent agreement with the length of the molecular chain of barium stearate, which is 25.75 ± 0.25 Å as obtained from Fankuchen’s x-ray data (Fankuchen 1938).
Such an agreement is, in fact, to be expected in view of the direct nature of the interferometric method yielding the true metrical thickness. Incidentally this agreement confirms the exact contouring properties of the evaporated silver coatings. From the result it can also be inferred that molecules in the transferred layers are oriented with their hydrocarbon chains almost at right angles to the substrate.

Comparison of the above measured metrical thickness of a unimolecular film of barium stearate with the length of the molecular chain of stearic acid (\(\approx 24.42\) Å, Müller 1927) leads to direct and independent evidence in favour of the hypothesis of monomolecular spreading of stearic acid on aqueous substrates. Indeed the aqueous substrate does not seem to produce any long-range surface effects bringing about the attachment and orientation of polymolecular chains.

Similar conclusions were drawn by Courtney-Pratt (1950, 1952), who first applied multiple beam interference technique to molecular films and studied the molecules of fatty acids spread by the droplet retraction technique on mica cleavage surfaces. However, the method of measurement with doubly-silvered mica, forming the interference system, does not directly yield the metrical thickness since it requires a knowledge of the refractive index of the film. Moreover, the differential phase changes upon reflections at mica–silver and monolayer–silver interfaces are involved, which are not unambiguously known, leading to a slight variation in his result. Also, fairly low orders are not conveniently obtained with such an interference system. All these limitations have been overcome by the method employed in the present work.

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REFERENCES

Anomalies in silicon carbide polytypes

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Anomalies in silicon carbide polytypes

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Frank's dislocation theory of the origin of polytypism received direct experimental support from the observation of a correlation between the step height of growth spirals on silicon carbide polytypes and the heights of their X-ray unit cells (Verma 1952, 1957). A detailed X-ray diffraction and microscopic investigation of silicon carbide structures has revealed anomalies that cannot be explained on the dislocation theory.

Three new unusual polytypes 36Hg, 36Hj, and 90R are described in detail. The structures 36Hg and 36Hj were found in a single crystal piece and have identical lattices with \( a = b = 3.078 \, \text{Å} \) and \( c = 90.65 \, \text{Å} \). Both structures belong to the space group \( \text{P}3\text{m} \). The polytype 90R belongs to the space group \( \text{R}3\text{m} \) with hexagonal unit cell dimensions \( a = b = 3.078 \, \text{Å}, c = 226.6 \, \text{Å} \). The detailed atomic structure of type 90R has been worked out and has a Zhdanov symbol \( \{23\}_{3}\{(322)\}_{3} \). It is shown that the polytypes 36Hg and 36Hj are based on the QH phase while type 90R is based on the 15R phase.

The creation of such polytypes requires a screw dislocation with a Burgers vector which is an integral multiple of the \( c \) spacing of the basic structure, and is therefore not understood on Frank's theory. A surface examination of the faces of these crystals does not reveal any growth spirals, showing that they have not grown by the dislocation mechanism. The growth of the different polytypes of silicon carbide is discussed and it appears that screw dislocations determine the surface structure but not the contents of the unit cell and therefore the cause of polytypism needs to be reconsidered.

INTRODUCTION

Among the various theories put forward to explain the phenomenon of polytypism (Lundqvist 1948; Frank 1951; Ramsdell & Kohn 1952; Jagodzinski 1954) our attention has mainly been directed towards Frank's dislocation theory. It provides a simple explanation of polytypism in silicon carbide, in support of which experimental evidence was put forth in a previous publication (Verma 1957). The direct correlation observed between the step height of growth spirals on silicon carbide, and the height of the X-ray unit cell (Verma 1952, 1957) left little doubt about the validity of the theory. The theory was able to explain the origin of structure series in silicon carbide and it was, therefore, felt that the phenomenon of polytypism had been satisfactorily explained.

However, doubts have been expressed by different workers regarding some aspects of the dislocation theory (Buckley 1952; Jagodzinski 1954). According to Jagodzinski the structure of a polytype is determined by thermodynamic considerations. He has suggested a layer transposition mechanism based on the vibration entropy of the structure. Recently Trigunayat & Verma (1962) have reported, from their interferometric and X-ray diffraction study of cadmium iodide polytypes, a non-correlation between the step height of the observed growth spiral and the height of the X-ray unit cell. It has thus become increasingly evident that

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the screw dislocation mechanism does not fully explain the formation of all the different polytypes. Other mechanisms suggested for silicon carbide have also not been able to explain all the observed facts.

We have, therefore, carried the investigation a stage further by working out the detailed atomic structure of different silicon carbide polytypes, to examine if the structure conforms with the dislocation theory. A large number of silicon carbide single crystals were examined by X-ray diffraction and microscopic techniques. Three new polytypes of special interest, \(36H_a\), \(36H_b\), and \(90R\), are described in detail. The atomic structure of type \(90R\) has been worked out. It is shown that the structure of these and some other polytypes have anomalies that cannot be explained on the dislocation theory. A critical review of the growth of the different polytypes of silicon carbide is given along with the existing experimental evidence.

**New and unusual polytypes**

Of the many new polytypes discovered in the course of the present investigation, special attention was given to two unusual structures. Figure 1, plate 15, shows the c-axis oscillation photograph taken from a parent single-crystal piece of silicon carbide, grown commercially. The 10.1 row of spots alone is shown in figure 2, plate 15, as magnified from figure 1. The polytype was identified by usual methods (Krishna & Verma 1962a, b) to be \(36H\). The crystal piece had a well-developed smooth shining (0001) face, which when examined under a Vicker’s projection phase-contrast microscope revealed no spiral markings.

The photographs in figures 1 and 2 show spots with two different shapes. The spots of one kind have the shape of a thick line while the others have a composite shape consisting of a rounded spot with a line touching it. The shape of the latter agrees with that of the projected image of the crystal but the cause of the line spots was not understood, to begin with. In an attempt to break a small fragment off the crystal, for finer X-ray diffraction study, the crystal piece split into two big pieces along a plane nearly parallel to the (0001) face, though silicon carbide has no cleavage parallel to (0001). The plate containing the shining (0001) face gave X-ray diffraction spots with intensities completely different from those of the remaining piece, while their spacings showed both pieces to be \(36H\). To differentiate between the two structures the upper plate containing the (0001) face would be designated as \(36H_a\) and the remaining lower portion as \(36H_b\). In figure 2 the spots with a line shape are due to \(36H_a\) while the rounded spots are due to \(36H_b\). The composite spots result from the superimposition of the reflexions from the two structures, and wherever the reflexions of \(36H_a\) are absent the spot reduces to a line.

Figures 3 and 4, plate 15, show the 10.1 row of spots recorded on c-axis oscillation photographs obtained from small fragments of \(36H_a\) and \(36H_b\), respectively. They reveal the markedly different intensity distribution along the 10.1 row of the two structures. The c-axis rotation photographs of \(36H_a\) and \(36H_b\) are shown in figures 5 and 6, plate 16, respectively, and confirm that both structures have hexagonal lattices with the same unit cell dimensions \(a = b = 3.078\,\text{Å}, c = 9.065\,\text{Å}\).
The space group for both the structures is $P3m$. This is an unusual instance wherein there has occurred, during growth, a change in the structure, from one region of a crystal piece to another, without a change of space group or of the dimensions of the unit cell. This is similar to the observations of Edwards & Lipson (1942) and Wilson (1942) in cobalt where, ‘The structure possesses a lattice in which the unit cells are all of the same size and shape but the distribution of atoms within the unit cell varies throughout the crystal’, with the difference that the distribution of atoms in this case appears to have changed more or less abruptly, across a certain (0001) plane.

The X-ray diffraction photographs taken from different fragments of $36H_a$ showed slightly different relative intensities, indicating that they have different proportions of $36H_a$ mixed with them. On account of the uncertainty of isolating a pure $36H_a$ crystal its structure will not be discussed here. Moreover, it is the polytype $36H_b$ that held our interest on account of the numerous and striking structural extinctions it displays on its X-ray diffraction photographs. In addition to the structural extinctions inherent in all silicon carbide polytypes, type $36H_b$ has the $10l$ reflexions missing when

$$l = 36n, \ 6n \pm 2, \ 36n+6, \ \text{where} \ \pm n = 0, 1, 2, \ldots$$

These extinctions show that the crystal piece has no $36H_a$ structure mixed in it. The possibility of a coalescence with $6H$, which would otherwise be difficult to determine, is also ruled out by the absence of the reflexions $10(36\% - 1 - 6)$. This crystal piece is therefore a pure $36H_b$ structure.

The structure of this polytype was first attempted by the usual methods employed in silicon carbide structure work (Ramsdell 1944, 1947; Zhdanov & Minervina 1945; Krishna & Verma 1962a, b). Almost all silicon carbide structures known so far have a zigzag sequence consisting of a series of 23, 33 or 22 units with faults at the end (Mitchell 1957). It is evident from the photographs shown in figures 4 and 6 that the structure $36H_b$ is based on the $6H$ phase, since it gives intense X-ray diffraction spots in most of the $6H$ positions. Assuming, therefore, that the structure has many 33 units in its zigzag sequence and that the latter is restricted to the numbers 2, 3 and 4, over 30 probable structures were postulated from usual considerations. However, many of these were discarded outright since the absence of the $10.36\%$ reflexions requires, as shown later, that the number of silicon (or carbon) atoms on $A:00z$, $B:1\frac{3}{4}z$ and $C:1\frac{1}{4}z$ axes be equal. Intensity calculations were performed for the following probable structures conforming with the above condition:

1. $(33)_a3432$
2. $(33)_b242424$
3. $(33)_b322344$
4. $(33)_a234432$
5. $(33)_b234234$
6. $(33)_a423423$
7. $(33)_a432234$
8. $(33)_b323334$.  

The calculated intensities for none of them matched with the observed intensity distribution. The failure of these attempts made it evident that this structure was not of the usual type and would not be based on any of the existing structure series.
**Figure 1.** A 15°, c-axis, oscillation photograph of the parent 36H crystal, recorded on a 3 cm camera with CuKα radiation. (Magn. x 1.)

**Figure 2.** The 10.l row of spots magnified from the oscillation photograph shown in figure 1. (Magn. x 3.)

**Figure 3.** The 10.l row of spots, as recorded on a 15° c axis oscillation photograph of type 36Hg, taken on a 3 cm camera with CuKα radiation. (Magn. x 3.)

**Figure 4.** The 10.l row of spots, as recorded on a 15° c axis oscillation photograph of type 36Hg, by means of a 3 cm camera and unfiltered CuK radiation. (Magn. x 3.)

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Figure 5. The c axis rotation photograph of type 36H. Camera radius 3 cm; CuKα radiation. (Magn. x 1.)

Figure 6. The c axis rotation photograph of type 36H. Camera radius 3 cm; CuKα radiation. (Magn. x 1.)
**Figure 7.** The 10.1 row of spots, as recorded on a 15° c axis oscillation photograph of type 90R. Camera radius 3 cm; CuKα radiation. (Magn. × 3.)

**Figures 10 and 11.** The 10.1 rows of two disordered polytypes as recorded on 15°, c axis oscillation photographs, taken on a 11.46 cm camera with unfiltered CuKα radiation (Magn. × 1.)

**Figure 12.** Enlargement of a part of figure 11.
Figure 8. Zero-layer, $a$ axis, Weissenberg photograph of type 90R, taken with unfiltered CuK radiation, on a camera of diameter 5.73 cm. The lowest 'festoon' records the 10.$l$ row of spots. The ten faint spots near the minimum of the festoon are, from left to right, 10.19, 10.16, ..., 10.8, 10.11. The $l$-values of successive spots differ by 3. (Magn. $\times$ 1.5.)
It was then felt that a clue to the structure might be found from the structural extinctions. Now, the intensity of a 10.l reflexion from any silicon carbide polytype nH or nR may be written down as

\[ I_{10.1} \propto (f_A^2 + f_B^2 + 2f_{sl} f_C \cos 2\pi lp) (A_{sl}^2 + B_{sl}^2) \]  

with

\[ A_{sl} = \sum_{z_A} \cos 2\pi lz + \sum_{z_B} \cos 2\pi (lz + \frac{1}{2}) + \sum_{z_C} \cos 2\pi (lz - \frac{1}{2}) \]  

and

\[ B_{sl} = \sum_{z_A} \sin 2\pi lz + \sum_{z_B} \sin 2\pi (lz + \frac{1}{2}) + \sum_{z_C} \sin 2\pi (lz - \frac{1}{2}), \]

where \( z_A, z_B \) and \( z_C \) denote the \( z \) co-ordinates of silicon atoms on the \( A: 0 \ 0 \ z, B: \frac{1}{2} \ \frac{1}{2} \ z \) and \( C: \frac{1}{2} \ \frac{1}{2} \ z \) symmetry axes, respectively, and \( p = \frac{1}{2}n \) is the height of each carbon above a silicon. Therefore, for the intensity to be zero we must have

\[ A_{sl} = B_{sl} = 0. \]

Since the reflexions 10.36m (±m = 0, 1, 2, ...) are absent we have from (2) and (3)

\[ n_A - \frac{1}{2}n_B - \frac{1}{2}n_C = 0 \]

and

\[ n_B \sin \frac{3\pi}{4} - n_C \sin \frac{3\pi}{4} = 0, \]

or

\[ n_A = n_B = n_C, \]  

(4)

where \( n_A, n_B \) and \( n_C \) denote the number of atoms on \( A, B \) and \( C \) symmetry axes. The structure therefore has 12 silicon and 12 carbon atoms on each of the symmetry axes, in the unit cell. Now since the reflexions 10.(6m ± 2) are absent (±m = 0, 1, 2, ...) we have, from (2) and (3), the following series of equations to which the structure must conform

\[ \sum_{z_A} \cos 2\pi ((6m \pm 2)z) + \sum_{z_B} \cos 2\pi ((6m \pm 2)z + \frac{1}{2}) + \sum_{z_C} \cos 2\pi ((6m \pm 2)z - \frac{1}{2}) = 0, \]  

(5)

\[ \sum_{z_A} \sin 2\pi ((6m \pm 2)z) + \sum_{z_B} \sin 2\pi ((6m \pm 2)z + \frac{1}{2}) + \sum_{z_C} \sin 2\pi ((6m \pm 2)z - \frac{1}{2}) = 0. \]  

(6)

We have actually succeeded in determining the detailed atomic structure of type 36H6, by solving the above equations in a novel manner. The structure is shown to have a Zhdanov symbol \((33)_p34(33)_q32\). Details of the structure determination are being reported in another paper (Krishna & Verma 1963). The fact that the polytypes 36H6 and 36H8 are based on the 6H phase and have a unit cell exactly 6 times as high as that of 6H is significant and is discussed later.

The 10.l row of the other new polytype 90R, as recorded on a c-axis oscillation photograph, is shown in figure 7, plate 17. The non-symmetrical arrangement of spots about the zero layer line indicates rhombohedral symmetry. The number of layers in the unit cell was determined, first approximately, by measurement on the oscillation photograph. The exact number of layers was determined from the Weissenberg photograph (figure 8, plate 18) by counting the number of spacings in the 10.l row, after which the sequence of relative intensities begins to repeat. For any polytype \( nH \) or \( nR \) the sequence of intensities of 10.l reflexions is similar after every change of \( n \) in the \( l \) value, i.e. the sequence of the relative intensity of spots
The relative intensity of the spots \( (Z_{+n}) \) is similar to that of the spots \( (l) \), \( (l+n+1) \), etc., is similar to that of the spots \( (l) \), \( (l+1) \), etc. This is because the values of \( A_{Si} \) and \( B_{Si} \) in the expression \((1)\), for the relative intensity of a \( 10.l \) reflexion from any silicon carbide polytype, are the same for the reflexions \( 10.l \) and \( 10.(l+n) \). The difference in the intensity of these spots is due to a change in the factor \( (f_{Si}^2 + f_{C}^2 + 2f_{Si}f_{C} \cos 2\pi \rho) \). But since \( f_{Si} \) and \( f_{C} \) vary monotonously with \( \theta \) and the atomic scattering factor for silicon is much greater than that for carbon \( (f_{Si} \approx 3f_{C}) \), the variation in \( \cos 2\pi \rho \) does not have much effect, and the sequence of relative intensities of \( 10.l \) spots is similar after a change of \( n \) in the \( l \) value. This repetition of relative intensities was first noticed by Ramsdell (1944) in type \( 21R \) and provides a simple method of determining the exact number of layers in the unit cell. It is particularly useful for large polytypes for which measurements on the oscillation and Weissenberg photographs provide only an approximate value of the repeat period. It, however, requires that the \( 10.l \) spots be both present and well resolved in the entire range of counting. In order that the width of successive \( 10.l \) spots be less than the distance between their centres, it is imperative to choose extremely small crystal pieces for X-ray diffraction. The photographs shown in figures 3 to 8 were taken with crystal pieces having dimensions of the order of 0.1 mm.

In the Weissenberg photograph of type \( 90R \) (figure 8), taken about the \( a \) axis, the relative intensities of \( 10.l \) reflexions are similar after every 30 spacings. Since the structure is rhombohedral, every spacing corresponds to a change of 3 in the \( l \)-value and hence the polytype is \((30 \times 3)R\). This method was also used for the identification of types \( 36H, 126R, 66H, 111R, \) etc., where the relative intensities are similar after 36, 42, 66 and 37 spacings, respectively.

The polytype \( 90R \) gives very well defined, sharp X-ray reflexions without any diffuse streaks connecting them. This indicates the high degree of order present in the structure. This polytype, like \( 36H \), is also of special interest as it is found to be based on the \( 15R \) phase and has therefore a unit cell which is an integral number of times as high as the unit cell of the basic structure. Moreover, not many structures based on the \( 15R \) phase are known and hence this polytype adds to a comparatively rare group of crystals.

**Structure of Type \( 90R \)**

To establish the structure of this polytype, a list of probable structures was worked out in a manner similar to that employed for type \( 57R \) (Krishna & Verma 1962a). Since X-ray diffraction spots near the position of \( 15R \) spots are distinctly more intense than the rest, the structure must contain a large number of \( '23' \) units in its zigzag sequence. As observed by Ramsdell (1947) and others, the zigzag sequence usually consists of twos, threes, and occasionally fours. The only exceptions to this are (i) cubic or \( \alpha-SiC \) with Zhdanov symbol (\( \infty \)); (ii) type \( 2H \) with the Zhdanov symbol (11) (Adamsky & Merz 1959); and (iii) type \( 174R \) with a structure \([33)_3(63)_{15}(13)_{15}] \) (Tomita 1960). Of these, the polytype \( 2H \) does not occur in commercial samples and has been grown by the method of gaseous cracking, while \( \alpha-SiC \) is known to be a low-temperature modification distinct from the rest. It was therefore assumed that type \( 90R \) would also, most probably, have only the
numbers 2, 3 and 4 in its zigzag sequence. Further, zigzag sequences reverse of each other were treated as identical, though in one the carbon atoms would be at a distance of 1.9 Å above each silicon and in the other below. Thus the sequences \((23)_5^2\) and \(23(32)_5\) have been regarded as identical as they are indistinguishable for X-ray diffraction purposes, on account of Friedel’s law. The following is the list of probable structures in the order of decreasing probability:

(a) With five ‘23’ units

(i) \([(23)_5^32]_3\).

(b) With four ‘23’ units

(ii) \([(23)_4^322]_3\),

(iii) \([(23)_4^2232]_3\),

(iv) \([(23)_4^2242]_3\),

(v) \([(23)_4^2222]_3\).

(c) With three ‘23’ units and no fours

(vi) \([(23)_3^33232]_3\),

(vii) \([(23)_3^232332]_3\),

(viii) \([(23)_3^333222]_3\),

(ix) \([(23)_3^333332]_3\),

(x) \([(23)_3^33332]_3\),

(xi) \([(23)_3^332232]_3\),

(xii) \([(23)_3^33223]_3\).

For a rhombohedral polytype of silicon carbide (space group \(R3m\)), the expression (1) for the relative intensity of 10.1 reflexions reduces to

\[
I_{10.1} \propto (f_{\overline{1}}^2 + f_{\overline{3}}^2 + f_{\overline{4}} f_{\overline{3}} \cos 2\pi l) \left( \sum \cos 2\pi l z \right)^2 + \left( \sum \sin 2\pi l z \right)^2.
\]

The calculated relative intensities for the first structure gave a fairly good qualitative match with observed intensities and therefore it was initially thought to be the correct structure and was mentioned in an earlier publication (Krishna & Verma 1962b). Subsequently the intensities for other structures were worked out to confirm that none other fits in. Surprisingly, we found that the second structure listed above gave a better fit than the first one. The rest of the structures gave no fit at all. Figure 9 plots the calculated relative intensities for the two structures along with the estimated value for the observed intensities. The visual estimation was done by the method described in an earlier publication for 111.R (Krishna & Verma 1962b). Table 1 gives the estimated intensities as percentages of the most intense reflexion 10.43, together with the calculated relative intensities for the two structures. A comparison of the observed and calculated values shows that the correct structure is \([(23)_4^3322]_3\). The corresponding \(ABC\) sequence of layers is

\[
ABCBACABACBCABCBACCBACABCBACABCA,
\]

\[
CABACBACABBCBACABCAABCBACBCACBAC\]

\[
BCBACABCBACABCBACBCACBACBCACBACBCABCB
\]

and the interval sequence is

\[
42243424222243422424342243334.
\]

The atomic co-ordinates can easily be worked out from these.
The above instance shows that it is not quite correct to accept a structure of silicon carbide from a mere qualitative fit. A quantitative estimation of observed intensities must be carried out and the intensities for a number of probable structures calculated, before a structure can be definitely accepted; especially when two or more structures give fairly similar intensity distributions.

**Table 1. The Relative Intensity \( (I) \) of 10.1 Reflexions for Type 90R**

<table>
<thead>
<tr>
<th>( l ) (obs.)</th>
<th>( I ) (calc.) ([[(23)<em>{3322}]</em>{5}])</th>
<th>( I ) (calc.) ([[(23)<em>{322}]</em>{5}])</th>
<th>( l ) (obs.)</th>
<th>( I ) (calc.) ([[(23)<em>{3322}]</em>{5}])</th>
<th>( I ) (calc.) ([[(23)<em>{322}]</em>{5}])</th>
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<td>17</td>
<td>7.0</td>
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<td>20</td>
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<tr>
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<tr>
<td>82</td>
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<td>0.64</td>
<td>83</td>
<td>2.0</td>
<td>1.62</td>
</tr>
<tr>
<td>85</td>
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<td>0.64</td>
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<td>0.3</td>
<td>0.30</td>
<td>89</td>
<td>0.3</td>
<td>0.36</td>
</tr>
</tbody>
</table>

**Disordered Structures**

In contrast with the long-period ordered structures like 111R, 36H and 90R silicon carbide also forms crystals with considerable one-dimensional disorder. Figures 10 and 11 show the 10.1 row of spots, as recorded on c-axis oscillation photographs, from two such crystals (\( r = 11.46 \) cm, CuK\( \alpha \) radiation). The more intense spots in figure 10 correspond to 6H reflexions and in figure 11 to 15R reflexions.

Though the continuous diffuse streak along the row indicates a random disorder of layers in the structure, there can be noticed a tendency towards long-range order. Thus between the 10.1 and 10.4, 6H positions in figure 10, there can be seen closely spaced spots corresponding to a periodicity about 15 times greater.
than that of 6H (45 times, if it is a rhombohedral structure). Similarly in figure 11, the region between the 10.2 and 10.8 reflexions of 15R shows a series of finely resolved spots. This is clearer in the enlargement shown in figure 12. There are about 33 spacings between successive 15R reflexions, corresponding, roughly, to a periodicity of \((33 \times 5)H\) or \((33 \times 15)R\).

![Graphs plotting the relative intensity of 10.l reflexions against their l-values.](image)

However, even where the spots appear resolved, the diffuse streak persists, though it is definitely fainter. This indicates that the diffuse streak is not entirely due to a lack of resolution of spots corresponding to a very large periodicity, as suggested earlier (Verma 1957). A method for distinguishing between streaks due to a lack of resolution and those due to a random disorder of layers has been discussed elsewhere (Krishna & Verma 1962b). There is a definite evidence of a random disorder superposed over the order in some silicon carbide crystals. The significance of this observation is discussed later.

**Discussion: Growth of Polytypes**

According to Frank's dislocation theory, the different polytypes of silicon carbide grow from basic structures like 6H, 15R and 4H, by the creation of a screw dislocation with a Burgers vector which is a non-integral multiple of the height of the parent unit cell. When the Burgers vector is an integral multiple of the
height of the parent unit cell, then the resulting structure is the same as the basic structure. It follows from these considerations that:

1. Crystal faces should exhibit growth spirals whose step-height is directly related to the height of the unit cell of the structure;

2. The large polytypes should have a structure based on one or other of the basic structures, i.e. a major portion of the unit cell of large polytypes should have the same structure as one of the basic structures, so that the Zhdanov symbol is made up of a number of 33, 23 or 22 units with faults at the end of the sequence;

3. The Burgers vector of the screw dislocation (=c for hexagonal polytypes and \( \frac{1}{3}c \) for rhombohedral ones) should be a non-integral multiple of the repeat unit of the basic structure, along c; and

4. The resulting polytype should have a completely ordered structure.

The experimental evidence, both against and in favour of each of these is discussed below.

Most of the crystals examined during the present investigation were flat plates with well-developed faces. As pointed out by Vand (1951) such crystals would require, for their growth, three non-coplanar screw dislocations. However, growth spirals are observed only on the (0001) face of some silicon carbide crystals, while most of the crystals show no spiral markings at all. Moreover, a single screw dislocation would form needle-shaped crystals. The step height of growth spirals observed on the (0001) face is found to be directly related to the height of the X-ray unit cell, being equal to it for hexagonal types and one-third of it for rhombohedral ones (Verma 1957); but a similar study of cadmium iodide, by Trigunayat & Verma (1962) has revealed the absence of such a correlation in this substance.

Most of the large polytypes of silicon carbide, so far discovered, are found to be based on one of the basic structures, and have a zigzag sequence consisting of a number of 33, 23 or 22 units with faults at the end. They therefore have an intensity maxima distribution similar to that of the basic structure. However, the intensity distribution in the 10.1 row of a polytype 126R, discovered by Verma (1957), shows that its structure is not based on any smaller type. The more intense spots do not lie around positions corresponding to any basic structure. All the same the crystal 126R shows a growth spiral with a step 42 layers high (Verma 1957) and is thus expected to have grown by the screw dislocation mechanism. The structure and spiral are thus at variance, and the former does not appear to have resulted from the latter. Similarly the polytypes 174R, with a structure \([33]_{6}(33)_{4}[33]_{6}\) (Tomita 1960), and 36H\(_6\), with a structure \([33]_{6}[34](33)_{6}[32]\) (Krishna & Verma 1962c), though based on the 6H phase, have stacking faults in the middle of a sequence of 33's. Such structures cannot result from a single screw dislocation created in the 6H structure. There are, at the same time, structures like 57R \([33]_{6}[34]_{6}\) and 111R \([33]_{6}[34]_{6}\) (Krishna & Verma 1962c, b), which are most readily understood as resulting from screw dislocations in the 6H structure, but an examination of their surfaces shows no spirals.

Generally a polytype based on a certain ideal structure (6H, 15R or 4H) has a repeat unit along c which is a non-integral multiple of the corresponding repeat
unit of the basic structure; but we have isolated a number of polytypes with contraindications including the three new types reported in this paper. Thus types $36H_a$, $36H_b$, and also the types $54$ and $66H$ reported by Verma (1957), give intense X-ray diffraction spots in $6H$ positions, showing that their structure is based on the $6H$ phase. The growth of these polytypes could not have taken place by the creation of a screw dislocation in the $6H$ structure since the Burgers vector of such a dislocation would be an integral multiple of the $c$ spacing of $6H$. A screw dislocation step of $36$, $54$ or $66$ layers, formed in a $6H$ structure, could result only in further growth of the $6H$ structure itself. All the same, crystals of $54H$ and $66H$ show spirals on their (0001) faces with a step height simply related to the height of the unit cell (Verma 1957). Similarly the polytype $90R$ with a structure $[(23)_{3322}]$, is definitely based on the $15R$ phase, but its growth is not possible from a screw dislocation in $15R$, since a ledge of $30$ layers exposed in the $15R$ structure would only cause further growth of $15R$ itself. It would, perhaps, be possible to explain the growth of these structures from two or more suitably ‘co-operating’ dislocations, but such explanations appear far-fetched in the absence of any surface-evidence to this effect. There is no evidence of co-operating dislocations on the surfaces of $36H$, $54H$, $66H$ or $90R$. On the other hand, there is definite evidence of single dislocations in $54H$ and $66H$ while $36H$ and $90R$ show no spiral markings. Moreover, it is difficult to understand how a system of dislocations generating the $36H_a$ structure could, at a later stage, generate a different structure $36H_a$.

While very large polytypes of silicon carbide have been observed with a high degree of order in their structure, e.g. $111R$, $90R$, $36H$, etc., it is also not uncommon to find polytypes with considerable one-dimensional disorder. Examples of two such crystals were shown in figures 10 and 11, plate 17. The growth of such structures, with a random disorder of layers, cannot be explained on the dislocation theory. The present position of observations regarding the growth of silicon carbide polytypes from screw dislocations is summarized in table 2, in the light of the above discussion.

It is evident from the above discussion that though the spiral step height on silicon carbide is simply related to the $c$ dimension of the lattice, the contents of the unit cell do not necessarily result from screw dislocations in one of the basic structures. It therefore appears that screw dislocations determine only the surface structure but not the structure of the unit cell. Jagodzinski (1954) has arrived at a similar conclusion from thermodynamic considerations. According to him, the high energy required for the creation of a screw dislocation can come from the lattice only after the crystal has acquired a considerable volume, by which time the structure of the crystal has already been determined. Therefore, screw dislocations could cause growth only in the later stages, thereby creating spirals on the surface. Once a polytype is formed the Burgers vector of a screw dislocation in it would be related to its lattice dimension so that there may be no misfit across the slip plane. This would explain the correlation observation between spiral step height and the height of the X-ray unit cell.

According to Jagodzinski & Arnold (1960) silicon carbide should normally have
<table>
<thead>
<tr>
<th>Polytype</th>
<th>Structure of Unit Cell</th>
<th>Surface Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H</td>
<td>33</td>
<td>Show spirals correlated with the unit cell</td>
<td>Growth completely explained in terms of screw dislocations</td>
</tr>
<tr>
<td>15R</td>
<td>(23)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21R</td>
<td>(34)₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33R</td>
<td>(3332)₃</td>
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<td></td>
</tr>
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</table>

**Polytypes Conforming with the Dislocation Theory**

**Structures Expected on Dislocations but Not Showing Growth Spirals**

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>57R</td>
<td>[(33)₃(34)₃]</td>
<td>Show no spirals</td>
</tr>
<tr>
<td>111R</td>
<td>[(33)₃(34)₃]</td>
<td>Show no spirals</td>
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</table>

**Structures Not Expected on Dislocations**

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>126R</td>
<td>Not based on any smaller type</td>
<td>Show spirals with correlation (Verma 1957)</td>
</tr>
<tr>
<td>36Hₐ</td>
<td>Based on 6H; unit cells</td>
<td>36H no spiral</td>
</tr>
<tr>
<td>54H</td>
<td>Integral multiples of the unit cell of 6H</td>
<td>54H, 66H show spirals with correlation (Verma 1957)</td>
</tr>
<tr>
<td>66H</td>
<td>Unit cell 6 times that of 15R</td>
<td>Shows no spiral</td>
</tr>
<tr>
<td>21R</td>
<td>[(33)₂(34)(33)₃]</td>
<td>Shows no spiral</td>
</tr>
<tr>
<td>36Hₐ</td>
<td>[(33)₂(34)(33)₃]</td>
<td>Shows no spiral</td>
</tr>
<tr>
<td>174R</td>
<td>[(33)₂(34)(33)₃]</td>
<td>No data</td>
</tr>
<tr>
<td>Disordered Polytypes</td>
<td>X-ray diffraction photographs show continuous streaks along 10.1 row (figures 10 and 11)</td>
<td>Not explained on dislocations</td>
</tr>
</tbody>
</table>

**Note**

1. The polytypes 51Rₐ (Thibault 1944; Zhdanov & Minervina 1945), 87R (Ramsdell 1947), 27R, and 51Rₐ (Ramsdell & Kohn 1952), 19H (Ramsdell & Mitchell 1953), 141R and 393R (Mitchell 1954), and 16H (Gasilova 1955) have structures that conform with the dislocation theory, but evidence of their growth from screw dislocations is incomplete since no data regarding their surface structure has been reported.

2. The polytypes 10H (Ramsdell & Kohn 1951), 75R and 84R (Ramsdell & Kohn 1952), and 18H (Gliky 1954) have structures that cannot originate from single screw dislocations in any of the basic structures, but may be thought of as resulting from two or more suitably 'co-operating' dislocations (Mitchell 1957). No surface evidence has, however, been put forth.

3. The polytypes 2H (Adamsky & Merz 1959) and 8H (Ramsdell & Kohn 1952) appear to be definite phases of silicon carbide, but no structures based on these are, as yet, known.

4. Though cubic or β-SiC (Hull 1919, 1920) can be easily derived from a screw dislocation in any of the basic structures, it does not form in this way since it is, unlike α-SiC, a low-temperature modification.
A n o m a l i e s  i n  s i l i c o n  c a r b i d e  p o l y t y p e s

501

a completely disordered structure since the different possible configurations have very nearly the same potential energy. It is the vibration entropy of the structure that is responsible for creating the observed order. Jagodzinski’s calculations have borne out the fact that $15R$ is the next commonest structure, after $6H$. The coexistence of order and disorder in the same crystal piece is expected on his theory, and therefore polytypes like $57R$ (Krishna & Verma 1962a) and the two disordered crystals discussed in this paper are very much in accordance with his ideas. However, completely ordered structures with a large periodicity are highly improbable according to Jagodzinski’s theory, and therefore the absence of any disorder, even in large polytypes like $90R$, $36H$, $111R$, and $126R$, is difficult to understand. Moreover, this theory has not, so far, accounted for the existence of structure series in silicon carbide. Schneer (1955) considers the phenomenon of polytypism to be analogous to that of order-disorder in alloys and has shown, along these lines, that the long period polytypes represent potential minima.

Lundqvist (1948) and Hayashi (1960) have established a correlation between the structure type and the content of aluminium (as impurity), for the types $6H$, $15R$ and $4H$. The role of the impurity in determining the structure type is not known and no such data is available for the other polytypes. It appears unlikely that the formation of the larger polytypes is also determined by the presence of impurities.

Ramsdell & Kohn (1952) have put forth a qualitative explanation for the creation of the different silicon carbide polytypes by the accretion of polymers. This has predicted the structure of several new polytypes and directly accounted for the existence of structure series; but polytypes like $174R$, $90R$ and $36H_b$, with three polymer units in their structure, are not in accordance with this theory. Moreover, the existence of such polymers as the theory assumes has yet to be experimentally demonstrated.

It would thus be seen that none of the existing theories of polytypism has been able to give a satisfactory explanation of all the observed facts. The cause of so many different modifications, some with unit cell heights much larger than the range of any known atomic forces has, therefore, to be reconsidered.

One of us (P. K) is grateful to the University Grants Commission of India for the grant of a research fellowship during the tenure of this work.

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Ramsdell, L. S. 1944 Amer. Min. 29, 431.
Ramsdell, L. S. 1947 Amer. Min. 32, 64.
Ramsdell, L. S. & Mitchell, R. S. 1953 Amer. Min. 38, 56.
Thibault, N. W. 1944 Amer. Min. 29, 327.
Vand, V. 1951 Phil. Mag. 42, 1384.
Verma, A. R. 1952 Phil. Mag. 43, 441.
This paper describes an unusual silicon carbide crystal of special crystallographic interest. During the growth of this crystal there has occurred a change in the structure, from one region of the crystal to another, without a change of space group (PSm) or of the dimensions of the unit cell. The crystal has been identified as type 36H (Ramsdell notation) and its two structures, designated as 36H_a and 36H_b, form respectively the upper and lower portions of a single crystal piece.

In addition to the usual extinctions inherent in all silicon carbide structures, the X-ray diffraction photographs of 36H_b show striking structural extinctions. In the 10.1 row the reflexions \( l = 6n \pm 2 \) (a any positive or negative integer) have zero intensity; this imposes on the structure, the conditions \[ \sum_{\alpha} \exp [2\pi i(6n \pm 2)\alpha] = \sum_{\beta} \exp [2\pi i(6n \pm 2)\beta] = \sum_{\gamma} \exp [2\pi i(6n \pm 2)\gamma] = 0. \]

From these, by working backwards in a novel way, the structure has been uniquely determined.

The polytype has an unexpected structure with the Zhdanov symbol (33334333332), which has been confirmed by the excellent agreement between the observed and calculated relative intensities of X-ray reflexions. The growth of this structure is discussed on the existing theories of polytypism, and it is concluded that none of them is able to provide a completely satisfactory explanation for the growth of the crystal.

**Introduction**

In a previous paper (Krishna & Verma, 1963) we reported on a group of silicon carbide structures which show anomalies that cannot be explained on Frank's screw dislocation theory of polytypism (Frank, 1951). One of the new polytypes discussed therein was 36H; it was apparent that the structure of this polytype would have considerable significance on account of the fact that its unit cell is an integral multiple of the unit cell of the 6H structure on which it is based. However, no structure based on the usual considerations employed in silicon carbide structure work could account for the intensity distribution observed on the X-ray diffraction photographs of this crystal. Unlike other known structures of silicon carbide, this polytype does not fit into any of the expected structure series.

In addition, the crystal showed several features of special crystallographic interest. It was discovered that in the same parent single-crystal piece there coexist two different structures having the same space group and unit cell dimensions. Further, one of these structures revealed numerous and striking structural extinctions on its X-ray diffraction photographs. It was therefore considered that a clue to this structure might lie in these extinctions. We have succeeded in determining the structure by a novel method employing the structural extinctions. This is perhaps a unique case where the structure of a crystal has been worked out almost entirely from a consideration of the structural extinctions observed on its X-ray diffraction photographs. The structure so determined has been confirmed by comparing calculated relative intensities of X-ray reflexions with those observed on Weissenberg photographs. The structure and growth of this polytype are discussed below.

**Experimental observations**

The polytype 36H was discovered in a mass of commercial silicon carbide, as a single-crystal piece with
a well-developed shining (0001) face about 1.0 × 0.5
mm² in size. The upper and lower parts of this crystal
piece were found to have different structures. The
10.1 row of spots as recorded on c-axis oscillation
photographs taken from (1) the composite 36H crystal,
(2) the upper part 36Hₐ, and (3) the lower part 36Hₗ
are reproduced in Figs. 1, 2 and 3 respectively and
reveal the existence of two different structures within
the same single-crystal piece without a change in
the periodicity of the lattice. The shape of the spots
obtained is discussed in a previous paper (Krishna
& Verma, 1963) where it was shown that the two
structures, designated 36Hₐ and 36Hₗ belong to the
trigonal system with a space group P3m1 and have the
same unit cell dimensions

\[ a = b = 3.078 \, \text{Å}, \quad c = 90.65 \, \text{Å}. \]

Figs. 4 and 5 show the complete 10.1, 20.1 and 30.1
rows of spots as recorded on the zero-layer, a axis,
Weissenberg photographs of 36Hₐ and 36Hₗ respectively.
The number of layers of structure in the unit
cell of each type can be confirmed by counting the
number of spacings after which the sequence of
relative intensities begins to repeat in the 10.1 row.
It is, of course, necessary to take into account the
absent reflections as well. Details of this method have
been described in the previous publication.

The oscillation and Weissenberg photographs of
36Hₗ show very unusual and interesting structural
extinctions. Thus from the Weissenberg photograph
of 36Hₗ (Fig. 5), considering the left side of the 10.1
festival to correspond to Z positive, we have the following
extinctions. Thus from the Weissenberg photograph
of 36Hₐ, the carbon atoms in all silicon
polytypes are displaced relative to the silicon
structure. The structure factor

\[ F = \sum \exp (2\pi i l z_{\text{Si}}/n), \quad Q = \sum \exp (2\pi i l z_{\text{C}}/n), \]

where \( z_{\text{Si}}, z_{\text{C}}, z_0/n \) are z coordinates of Si atoms
along A, B, and C respectively.

It can be readily seen that when

\[ h - k = 3r, \quad (r \text{ any integer}) \]

then

\[ F = [f_{\text{Si}} + f_{\text{C}} \exp (2\pi i p l)] [P + Q \exp (2\pi i/3)] + R \exp (-2\pi i/3). \]

It has been shown (Krishna & Verma, 1963) that
the sequence of relative intensities of 10.1 reflections
for a polytype \( nH \) or \( nR \) is similar after a change of
in the \( l \) value. For this reason, and on account of
the characteristic intensity variations in the 10.1 row
of a polytype, it suffices to compare the calculated and
observed relative intensities of spots from 10.0
to 10.\( n \) alone. However, some of the spots in the
larger \( l \) range may not be recorded on the photographs
owing to the small value of \( f_{\text{Si}} \) and \( f_{\text{C}} \); hence it is
advisable to compare the calculated and observed
intensities of spots from 10.1 to 10.\( n \) as well.

**Derivation of probable structures**

The polytype 36Hₐ above is one of the several
polytypes of silicon carbide. The structure factor

\[ F = \sum \exp (2\pi i l z_{\text{Si}}/n), \quad Q = \sum \exp (2\pi i l z_{\text{C}}/n), \]

where

\[ R = \sum \exp (2\pi i l z_{\text{C}}/n) \]

10.1 row of type 36Hₐ do not belong to this class
and are peculiar to this polytype alone. It would also
be noticed that the exponential part of \( P \) is the same
for the reflections 10.1, 20.1, 21.1 etc., for the same
value of \( l \) (positive as well as negative). The only
difference in the intensity of these spots would be
due to a variation in \( f_{\text{Si}} \) and \( f_{\text{C}} \). It follows that the
relative intensities along these rows would be very
similar. It would, therefore, suffice to compare the
calculated and observed intensities of 10.1 reflections
alone, to determine the validity of a proposed
structure. This was first pointed out for a rhombohedral
polytype, 21R, by Ramadell (1944).

The structure factor for the 10.1 row of spots is
given by

\[ F_{10.1} = (f_{\text{Si}} + f_{\text{C}} \exp (2\pi i p l)) [P + Q \exp (2\pi i/3)] + R \exp (-2\pi i/3). \]

The polytype 36Hₐ above is one of the several
polytypes of silicon carbide. The structure factor

\[ F = \sum \exp (2\pi i l z_{\text{Si}}/n), \quad Q = \sum \exp (2\pi i l z_{\text{C}}/n), \]

where

\[ R = \sum \exp (2\pi i l z_{\text{C}}/n) \]

and \( z_{\text{Si}}, z_{\text{C}}, z_0/n \) are z coordinates of Si atoms
along A, B, and C respectively.

It can be readily seen that when

\[ h - k = 3r, \quad (r \text{ any integer}) \]

then

\[ F = [f_{\text{Si}} + f_{\text{C}} \exp (2\pi i p l)] [P + Q \exp (2\pi i/3)] + R \exp (-2\pi i/3). \]

It has been shown (Krishna & Verma, 1963) that
the sequence of relative intensities of 10.1 reflections
for a polytype \( nH \) or \( nR \) is similar after a change of
in the \( l \) value. For this reason, and on account of
the characteristic intensity variations in the 10.1 row
of a polytype, it suffices to compare the calculated and
observed relative intensities of spots from 10.0
to 10.\( n \) alone. However, some of the spots in the
larger \( l \) range may not be recorded on the photographs
owing to the small value of \( f_{\text{Si}} \) and \( f_{\text{C}} \); hence it is
advisable to compare the calculated and observed
intensities of spots from 10.1 to 10.\( n \) as well.

**Derivation of probable structures**

The polytype 36Hₐ above is one of the several
polytypes of silicon carbide. The structure factor

\[ F = \sum \exp (2\pi i l z_{\text{Si}}/n), \quad Q = \sum \exp (2\pi i l z_{\text{C}}/n), \]

where

\[ R = \sum \exp (2\pi i l z_{\text{C}}/n) \]

and \( z_{\text{Si}}, z_{\text{C}}, z_0/n \) are z coordinates of Si atoms
along A, B, and C respectively.

It can be readily seen that when

\[ h - k = 3r, \quad (r \text{ any integer}) \]

then

\[ F = [f_{\text{Si}} + f_{\text{C}} \exp (2\pi i p l)] [P + Q \exp (2\pi i/3)] + R \exp (-2\pi i/3). \]

It has been shown (Krishna & Verma, 1963) that
the sequence of relative intensities of 10.1 reflections
for a polytype \( nH \) or \( nR \) is similar after a change of
in the \( l \) value. For this reason, and on account of
the characteristic intensity variations in the 10.1 row
of a polytype, it suffices to compare the calculated and
observed relative intensities of spots from 10.0
to 10.\( n \) alone. However, some of the spots in the
larger \( l \) range may not be recorded on the photographs
owing to the small value of \( f_{\text{Si}} \) and \( f_{\text{C}} \); hence it is
advisable to compare the calculated and observed
intensities of spots from 10.1 to 10.\( n \) as well.
Fig. 1. 
The parent 36H crystal.

Fig. 2. 
Type 36Hₐ.

Fig. 3. 
Type 36Hₙ.

Figs. 1, 2, and 3. The 10.l row of spots recorded on 15° c-axis oscillation photographs with Cu K radiation (filtered for Figs. 1 and 2) and a camera of radius 3 cm (all × 2).

Fig. 4. Zero-layer α-axis Weissenberg photograph of 36Hₐ taken with Cu Kα radiation on a camera of diameter 5.73 cm. The lowest 'festoone' records the 10.l row of spots, the missing spot near the minima of the festoon being 10.0 (×1).
Fig. 5. Zero-layer $a$-axis Weissenberg photograph of $\text{ZnBr}_2$ taken with Cu $K\alpha$ radiation on a camera of diameter 5-73 cm. The lowest festoon records the 10.1 row of spots, the four faint spots near the minima of the festoon being, from left to right, 10-3, 10-1, 10-1 and 10-3 ($\times 1$).

Fig. 6. First-layer $a$-axis equi-inclination Weissenberg photograph taken with Cu $K\alpha$ radiation on a camera of diameter 5-73 cm. The lowest ‘festoon’ records the 01.1 row of spots, the four spots near the minima of the festoon being, from left to right, 01-3, 01-1, 01-1 and 01-3 ($\times 1$).
the polytype \(36H_6\) is a pure structure free from any \(36H_n\). The absence of the reflexions \(36n+6\) eliminates any possibility of a coalescence with \(6H\) which would otherwise have been difficult to detect. The absence of any diffuse streak along the 10.1 row of spots indicates the high degree of order present in this crystal.

The structure of this polytype was first attempted by the usual methods employed in silicon carbide structure work (Ramsdell, 1947; Zhdanov & Minervina, 1945; Krishna & Verma, 1962a). Almost all the known SiC structures have a Zhdanov symbol (Zhdanov, 1945) consisting of a number 33, 22 or 23 units with faults at the end. Considering that the X-ray diffraction photographs obtained from \(36H_6\) (Figs. 3, 5 and 6) reveal intense reflexions in most \(6H\) positions, a large number of structures based on the \(6H\) phase, like (33)\(3432\), (33)\(2412\) [33]323244, etc., were tried. None of these could account for the intensity-distribution observed along the 10.1 row of type \(36H_6\). It thus became evident that the structure does not belong to any of the usual structure series. Attempts were therefore made to find a clue to the structure from the observed extinctions.

It is evident from (3) that for a 10.1 reflexion to be absent

\[
P + Q \exp \left( \frac{2\pi i q_x}{3} \right) + R \exp \left( -\frac{2\pi i q_y}{3} \right) = 0
\]

whence, equating real and imaginary parts to zero,

\[
P = Q = R.
\]

The extinction of 10.1 reflexions, when \(l = 36m\) requires

\[
ge = n_B = n_C
\]

where \(n_A, n_B\) and \(n_C\) denote the number of atoms on \(A, B\) and \(C\) respectively. Hence the structure has 12 silicon and 12 carbon atoms on each of the symmetry axes.

Now since the reflexions 10.\(6m\pm2\) are absent, we have from (4) by writing \(6m \pm 2 = q\):

\[
(P)_{l=q} = (Q)_{l=q} = (R)_{l=q} = \frac{1}{2} (P + Q + R)_{l=q}.
\]

But

\[
(P + Q + R)_{l=q} = 3 \sum_{r=0}^{35} \exp \left( \frac{2\pi i q_A}{36} \right) = 0 \text{ since } q + 36n.
\]

Hence

\[
\sum_{r=0}^{35} \exp \left( \frac{2\pi i q_A}{36} \right) = 0
\]

The problem of determining the structure, therefore, reduces to that of selecting three sets, \(z_A, z_B\) and \(z_C\) of 12 numbers each, from the 36 numbers 0, 1, 2, \ldots, 35 such that condition (6) is satisfied. For this, \(z_A, z_B\) and \(z_C\) must be arranged in a partial periodic way; thus each must be given by a series of the kind

\[
z_A, z_A + m, z_A + 2m, \ldots, z_A + 6m.
\]

Then the term \((P)_{l=q}\) may be represented as follows:

\[
(P)_{l=q} = \sum_{r=0}^{35} \exp \left( \frac{2\pi i q_A}{36} \right) \sum_{r=0}^{7} \exp \left[ 2\pi i r (\frac{n}{12} + \frac{k}{6}) \right] = 0.
\]

This will be true for all values of \(n\) only if it is independent of \(n\). For this we must have

\[
m = 6t (t = \text{integer})
\]

whence

\[
\sum_{r=0}^{7} \exp \left( \pm 2\pi i r |t/3| \right) = 0.
\]

This has two solutions*

\[(1) t = 1, \quad n_0 = 2; \quad (2) t = 2, \quad n_0 = 2.\]

The second one would require every layer to repeat after 12 layer spacings and, since \(12 \times 3 = 36\), this would reduce the \(z\) period of the lattice by a factor of \(\frac{1}{3}\). It, therefore, affords no solution. The first one requires three layers at \(z_A, z_A + 6, \) and \(z_A + 12\). This is quite possible and means that each set \(z_A, z_B\) and \(z_C\) consists of 12 numbers of the kind \(x, \beta, \gamma, \delta, x + 6, \quad \beta + 6, \quad \gamma + 6, \quad \delta + 6, \quad x + 12, \quad \beta + 12, \quad \gamma + 12\) and \(\delta + 12;\) where \(x, \beta, \gamma\) and \(\delta\) are different for the three sets.

We shall now assume the following limitations commonly used in silicon carbide structure work:

(i) That the interval between successive Si (or C) atoms along any of the three symmetry axes \(A, B\) or \(C\) is limited to 2, 3 or 4 layer spacings only (Ramsdell, 1945). This would mean that if the numbers in each set \(z_A, z_B\) or \(z_C\) are arranged in increasing order, no two consecutive numbers will differ by anything other than 2, 3 or 4. No structures of SiC so far known contradict this condition though no theoretical reason has yet been assigned for this limitation.

(ii) That the zigzag sequence, or Zhdanov symbol, does not contain the number 1. All structures so far known agree with this except type \(2H\) with a sequence (11). But type \(2H\) is not found in commercial silicon carbide and has been synthesized only by the method of gaseous cracking (Adamsky & Merz, 1959). Since the present crystal under investigation was found in a commercial sample it is reasonable to apply the above limitation.

Now the unit cell of type \(36H_6\) is made up of 36 unit layers of structure, each layer occupying one of the three possible positions \(A, B\) or \(C\), analogous to close-packed layers of spheres (Zhdanov & Minervina, 1945). Let the origin be chosen on a silicon atom at

\[
\theta_n = 2\pi (6m \pm 2)r_{n/36}.
\]

\[
\sum_{n=1}^{3} \cos \theta_n = \sum_{n=1}^{3} \sin \theta_n = 0,
\]

if

\[
r_0 - r_1 = r_1 - r_2 = 0,
\]

which suggested the proof given here. Dr Sharan's proof is given in the Appendix.

---

* We are grateful to Dr Behari Sharan who showed that with \(\theta_n = 2\pi (6m \pm 2)r_{n/36}\)

\[
\sum_{n=1}^{3} \cos \theta_n = \sum_{n=1}^{3} \sin \theta_n = 0,
\]

if

\[
r_0 - r_2 = r_1 - r_2 = 0,
\]

which suggested the proof given here. Dr Sharan's proof is given in the Appendix.
which there is a ‘stacking reversal’, so that the sequence of layers $A$, $B$ and $C$ changes from anticyclic to cyclic. Then since the smallest number in the Zhdanov sequence is 2, the 34th, 35th, 0th, 1st and 2nd layers in the unit cell may be written down as $C$, $B$, $A$, $B$, and $C$ respectively. It is evident that the condition on the sets $z_A$, $z_B$ and $z_C$, as derived from (6), would require the first 18 layers in the unit cell to be represented by a thrice repeated sequence of 6 letters starting with $ABC$. Similarly the next 18 layers would be represented by another sequence of 6 letters repeated three times.

To derive the possible $ABC$ sequences for the first 18 layers, consider Table 1, which tabulates the numbers 0, 1, 2, ..., 17 along 3 rows and 6 columns. Each column is to be assigned one of the three letters $A$, $B$ or $C$, subject to the conditions (i) and (ii) stated above. As discussed earlier the choice of origin assigns to the first three columns the letters $A$, $B$ and $C$ respectively. Since a letter cannot follow itself column VI cannot be $A$ and column IV must be either $A$ or $B$.

If it is $A$ then two possibilities result: (a) and (b). If column IV is $B$ then column V must be $A$ since two $A$'s cannot be separated by more than 4 layer spacings. Column VI then cannot be $B$ as this would involve a number 1 in the zigzag sequence. Of the three possibilities (a), (b) and (c), the first one would cause the Zhdanov symbol to have a number 17 or more, and is, therefore, highly improbable. Thus only two possible arrangements for the first 18 layers need to be considered:

1. $(ABCACB)_3$ and 2. $(ABCBA)$_3.

Now consider the next 18 layers in the unit cell. To derive the possible $ABC$ sequences for these the numbers 18, 19, 20, ..., 35 are tabulated in Table 2, in a manner similar to Table 1. In the first 18 layers there are 6 $A$'s, 6 $B$'s and 6 $C$'s and, therefore, from equation (5) we have that the next 18 layers must also consist of 6 $A$'s, 6 $B$'s and 6 $C$'s. It follows that the six columns in Table 2 have to be filled with 2 $A$'s, 2 $B$'s and 2 $C$'s. As discussed earlier, with the present choice of origin the 34th and 35th layers in the unit cell are $C$ and $B$. Columns V and VI are filled accordingly. Proceeding in a manner similar to that in Table 1, only four different possibilities are obtained, (a), (b), (c) and (d), subject to the conditions (i) and (ii) cited earlier (see Table 2). Of these, (e) is highly improbable since it would involve a number 18 in the Zhdanov symbol. We are therefore left with the following probable sequences for the last 18 layers in the unit cell:

1. $(ACABCB)_3$. 2. $(CABACB)_3$. 3. $(ABCACB)_3$.

To obtain the probable sequences for the whole unit cell, each of these has to be coupled with the two sequences derived for the first 18 layers. One obtains five possible combinations:

1. $(ABCACB)_3 (ACABCB)_3$. 2. $(ACABCB)_3 (CABACB)_3$. 3. $(ABCACB)_3 (ABCACB)_3$. 4. $(ACBCAB)_3 (ACABCB)_3$. 5. $(ACBCAB)_3 (ABCACB)_3$. Of these, (3) represents merely the $6I$ structure and (4) involves a number 1 in the zigzag sequence. Both these are therefore ruled out. The other three sequences have the Zhdanov symbols:

(1) $33334333332$, (2) $33333233334$ and (3) $23333433333$.

It will be seen that all the three represent the same structure and differ only because of a shift of origin. There is thus only one probable structure for $36I_b$, namely, $33334333332$.

**Calculation of intensities**

The $ABC$ sequence of the postulated structure is $ABCAAABCACBACBABCACBACB$ and it shows a centre of symmetry for the silicon atoms, at the atom marked by an arrow. Shifting the origin to this atom one obtains the sequence of layers in the new unit cell as $ABCBACBACABCACBACB$, for which
The intensity formula for a 10.1 reflexion then simplifies to
\[ I_{10.1} = \frac{f_{2}^{2} + f_{2}^{2} + 2f_{2}f_{2} \cos 2\pi \theta}{\left[ 1 + \cos \phi + 2 \sum_{n=1}^{14} \cos \frac{2\pi n a_{0.1}}{36} + 2 \sum_{n=1}^{2} \cos \frac{2\pi n a_{0.1}}{36} (l_{2} a_{0.1} + 12) \right]^{2}}. \]

The intensity values obtained from this were multiplied by the Lorenz-polarization factor \((1 + \cos^{2} \theta / \sin \theta)\) where \(\theta\) is the Bragg angle.

The relative intensities so obtained are tabulated in Table 3 together with the visually estimated values.

### Table 3. Calculated and observed relative intensities \((I)\) of 10.1 reflexions

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<th>(I_{o})</th>
<th>(I_{c})</th>
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The quantitative estimation of observed intensities was done from Weissenberg photographs, by the method described in an earlier publication (Krishna & Verma, 1962b). The excellent agreement between the calculated and observed relative intensities establishes the postulated structure.

### Atomic coordinates

The coordinates of atoms in the unit cell of the polytype \(36 H_{0}\) are as follows:

- 12 Si at \(0,0,0\) where \(t=0, 4, 6, 10, 12, 15, 18, 24, 26, 30, 32\)
- 12 Si at \(1,3,5,7,9,13,15,19,22,25,28,31,34\)
- 12 Si at \(1,3,5,7,9,13,15,19,22,25,28,31,34\)
- 36 C at \(0,0,1/4\) plus the coordinates of the 36 Si atoms.

### Discussion

The polytype \(36 H\) is a unique crystal within which there has occurred a transition in the structure without affecting the periodicity of the lattice. This is similar to the observations of Edwards & Lipson (1942) and Wilson (1942) in cobalt, where 'the structure possesses a lattice in which the unit cells are all of the same size and shape but the distribution of atoms within the unit cell varies throughout the crystal,' with the difference that the distribution of atoms in this case appears to have changed more or less abruptly, across a certain \((0001)\) plane. Any theory of growth must not only account separately for the growth of the two structures \(36 H_{0}\) and \(36 H_{b}\) but also for the transition from the one to the other.

The structure of type \(36 H_{b}\) differs from the other known structures of silicon carbide in many important respects and this is perhaps the first instance where a structure could be determined almost entirely from a consideration of the structural extinctions noticed in its X-ray diffraction photographs. The structure \((33334333332)\) does not fit into any of the silicon carbide structure series formulated by Ramsdell (1947), Mitchell (1957) and others. Almost all the silicon carbide structures known so far have a zigzag sequence consisting of a series of \(33, 23\) or \(22\) units with faults at the end of the sequence. The discovery of this structure with a sequence \((333334333332)\) shows that faults may occur in the middle of a sequence as well, resulting in a series of structures of the type \([33]_1{34}[33]_2{32}\). Tomita (1960) has reported a polytype \(174R\) with a structure \([33]_3[36][33]_4[43]\) which also has faults in the middle of a 33 sequence. This increases considerably the configurations possible in silicon carbide and structure work in future should take these into consideration.

According to the polymer theory of the growth of silicon carbide polytypes (Ramsdell & Kohn, 1952) only two polymers can coexist at a time in a certain temperature range. The structure \([33]_1{34}[33]_2{32}\) includes three different polymers \(33, 34\) and \(32\) and is thus at variance with the above theory. None of the silicon carbide structures determined so far has all the three numbers \(2, 3\) and \(4\) in its zigzag sequence; the discovery of the structure \(36 H_{0}\) shows that such
structures, though rare, are actually possible. The zigzag sequence of the structure is, however, limited to 2, 3 and 4, like most other polytypes.

The X-ray diffraction photographs of $36H_b$ do not reveal any diffuse streak connecting the 10.1 row of spots, indicating a high degree of order in the crystal. According to the disorder theory of polytypism (Jagodzinski, 1954) it is increasingly improbable for polytypes of larger periodicity to have a completely ordered structure. The larger the periodicity, the smaller is the contribution of the vibration entropy to the total entropy of the structure and the greater is the probability of random faults. Indeed as we have discussed in an earlier paper (Krishna & Verma, 1963), the creation of large polytypes like $36H, 54H, 66H, 128R, 111R, 90R$, etc., with a completely ordered structure, is thereby contrary to the expectations of the disorder theory of polytypism.

Since the polytypes $36H_b$ give intense X-ray diffraction spots at the 6H positions they were believed to be based on the 6H phase. This has been confirmed by the predominance of the 33 group in the structure of $36H_b$. For the growth of a 36H structure from a single screw dislocation, according to the ideas of Frank (1951), the exposed ledge should consist of 36 layers; but a ledge of 36 layers, exposed in a 6H structure, would necessarily cause further growth of type 6H itself, the Burgers vector being an integral multiple of the basic unit. However, the structure (33334333332) can be considered to result from the cooperation of two sufficiently close screw dislocations, one with a Burgers vector 19 layers high and the other with a Burgers vector 17 layers high. The exposed ledges of the two dislocations should have the sequences 333334 and 333332 which by themselves would have created the already discovered types $57R$ (Krishna & Verma, 1962a) and $51R$ (Zhdanov & Minervina, 1945) respectively. But it is difficult to understand how such a system of cooperating dislocations could in the later stages generate a different structure, $36H_a$. Moreover, the (0001) face of $36H$ would be expected to show a growth spiral with a step height of the order of 90 Å, which ought to be easily observable; but a careful examination of the smooth, shining, plane (0001) face of this crystal under the Vicker's projection phase-contrast microscope failed to reveal any spiral markings on the surface. We are thus led to conclude that this crystal has not grown by the screw dislocation mechanism. None of the existing theories of polytypism is thus able to provide a completely satisfactory explanation for the growth of this crystal.

**APPENDIX**

**By Behari Sharan**

Let the conditions

\[ \sum_{n=1}^{3} \cos \left( \frac{2\pi}{36} \right) q^a \sin \left( \frac{2\pi}{36} \right) q^a = 0 \]  

(A2)

be simultaneously true for a set of 3 integers, $r_1$, $r_2$, and $r_3$. It is required to find a relation between $r_1$, $r_2$ and $r_3$. Let

\[ r_1 = x, \quad r_2 = x + \beta_1 \]  

and \[ r_3 = x + \beta_2 . \]  

Then writing $2\pi/36 = 10^\circ$, we get from (A1)

\[ \cos 10\theta x \cos 10\theta (x + \beta_1) + \cos 10\theta (x + \beta_2) = 0 \]  

(A3)

or

\[ 2 \cos 10\theta (x + \beta_2/2) \cos 10\theta \beta_2/2 + \cos 10\theta (x + \beta_1) = 0 . \]  

(A4)

Similarly from the equation (A2)

\[ 2 \sin 10\theta (x + \beta_2/2) \cos 10\theta \beta_2/2 + \sin 10\theta (x + \beta_1) = 0 . \]  

(A5)

If the expressions on the left hand sides of (A4) and (A5) have a common factor which is zero, they would both vanish. They would have a common factor if, say,

\[ 2\beta_1 = \beta_2 = 2\beta . \]

For then (A4) and (A5) may be written respectively as

\[ \cos 10\theta (x + \beta) \{1 + 2 \cos 10\theta \beta\} = 0 \]  

(A6)

and

\[ \sin 10\theta (x + \beta) \{1 + 2 \cos 10\theta \beta\} = 0 \]  

(A7)

whence

\[ 1 + 2 \cos 10\theta \beta = 0 \]  

or

\[ q \times \beta = 2 \times 6, 4 \times 6, 8 \times 6, \ldots \text{ etc.} \]

\[ = (6n \pm 2) \times 6 . \]

If $q = 6n \pm 2$ then $\beta = 6$ and relations (A1) and (A2) would be satisfied by a set of three numbers

\[ r_1 = x, \quad r_2 = x + 6, \quad \text{and} \quad r_3 = x + 12 \]

where $x$ may be any integer.

Our thanks are due to Dr Behari Sharan for the above proof and to Prof. Jagodzinski for valuable comments on the paper. One of us (P.K.) is grateful to the University Grants Commission for the award of a Senior Research Fellowship.

**References**


Structure and growth of a new polytype of cadmium iodide 22H

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With 4 figures

(Received May 14, 1962)
Auszug

Es wurde ein neuer Polytyp von Cadmiumjodid, 22H₆, aus 22 Cd-J-Schichten, gefunden; die Gitterkonstanten sind \( a = 4.24 \, \text{Å}, c = 75.18 \, \text{Å} \). Eine eingehende Untersuchung ergab, daß der neue Polytyp sich auf einer idealen 2H-Struktur aufbaut. Er ist der größte Cadmiumjodid-Polytyp, dessen Struktur bisher ermittelt wurde. Sein Wachstum wird auf der Grundlage der Theorie der Schraubenversetzung diskutiert; es wird auf dabei auftretende Schwierigkeiten hingewiesen.

Abstract

A 22-layered new polytype of cadmium iodide, designated as 22H₆, with unit cell dimensions \( a = 4.24 \, \text{Å}, c = 75.18 \, \text{Å} \) has been discovered. The detailed structure of the polytype has been worked out. It is shown that this polytype is based on a 2H ideal structure. The polytype 22H₆ is so far the largest of the cadmium iodide polytypes whose detailed structure is known. The growth of the polytype has been discussed in terms of screw-dislocation theory and the difficulties which arise in this are pointed out.

Introduction

Several crystals including silicon carbide\(^1\), cadmium iodide\(^2\), cadmium bromide\(^3\), zinc sulphide\(^4,5\) etc. are now known to exhibit

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\(^1\) C.S.I.R. Research Fellow.
A new polytype of cadmium iodide 22 $H$

polytypism. Various theories have been put forward to explain the formation of such a large variety of polytypes, including some with very large unit cells. In silicon carbide the phenomenon of polytypism has been mainly explained on the screw dislocation theory$^6$. Other theories such as polymer theory$^7$, vibration entropy — layer transposition theory$^8$—$^{10}$, impurity-content theory$^{11}$$^{14}$$^{15}$ have also been advanced to account for polytypism in silicon carbide. However for cadmium iodide the only prominent theory is the dislocation theory which was a direct outcome of the observation of growth spirals on cadmium iodide crystals$^{16}$$^{18}$. In fact Forty$^{16}$$^{18}$ predicted the exist-

$^{12}$ G. S. ZHADANOV and Z. V. MINERVINA, On the superperiodicity in carborundum crystals. J. Physics USSR 9 (1945) 244—245.
ence of polytypism in cadmium iodide. Mitchell\textsuperscript{19--20} has verified Forty's prediction by reporting more than thirty polytypes of cadmium iodide. All the polytypes discovered by him in his x-ray diffraction study of the compound are of hexagonal type. However, for an unequivocal verification of Frank's screw-dislocation theory in case of cadmium iodide Trigunayat and Verma\textsuperscript{21} performed x-ray diffraction and interferometric study upon the same crystals. Surprisingly they found that a correlation between spiral step height and x-ray unit cell does not exist. Since the growth-spiral step height is directly related with the Burgers vector of screw dislocation, a non-correlation would mean that the unit cell and Burgers's vector are different. Thus it is not understood as to how screw dislocation could create various polytypes in cadmium iodide.

The present work was undertaken to work out the detailed structure of different cadmium-iodide polytypes, with a view to see if the detailed structure could be explained as having originated by screw-dislocation mechanism. A large number of different cadmium-iodide polytypes were isolated, but the type with a 22-layered unit cell was found to be of particular interest. The detailed structure of this polytype is reported below and its growth is discussed. It is now the largest cadmium-iodide polytype with a known structure.

**Experimental details**

Crystals were grown from aqueous solution by a method similar to that used by Mitchell\textsuperscript{19--20}. The perfection of crystals was verified by observing them under the polarising microscope. It was found that $a$-axis oscillation photographs give discrete sharp spots whereas in $c$-axis photographs the spots show arcing and streaking effect.

Hence, for purposes of identification and also for detailed structure analysis, $a$-axis oscillation and Weissenberg photographs were taken. The identification of the crystal type by an $a$-axis oscillation photograph has been discussed by Trigunayat\textsuperscript{22}.

\begin{itemize}
\item\textsuperscript{19} R. S. Mitchell, Screw dislocations and polytypism of cadmium iodide. Philos. Mag. 46 (1955) 1141--1146.
\end{itemize}
A new polytype of cadmium iodide $22H$

Structure of polytype $22H_c$

Figure 1 shows an $a$-axis oscillation photograph of the crystal taken with CuK$_\alpha$ radiation. Measurements made with the Bernal chart on this revealed that the $c$ dimension of present type is 75.2 Å. Since the $c$ dimension of type $2H$ is 6.835 Å, the present type is $22H$. On the Weissenberg photograph (Fig. 2) there are eleven reflections of equal spacings between two consecutive spots of polytype $2H$. This confirms the present type as $(2 \times 11) = 22H$. Two polytypes with this number of layers have been reported by Trigunayat and Verma$^{21}$. However, they did not determine the structure of these polytypes. A comparison of intensity distribution on x-ray photographs of the present polytype and the other two polytypes$^{23}$ revealed that the present polytype has a completely different intensity distribution. Thus the present polytype has a different arrangement of layers and may be designated as $22H_c$.

The structure determination of the present polytype appeared to be difficult since there are a large number of possible arrangements for the ions in the unit cell that will give a 22-layered polytype. However, nearly all structures reported by Mitchell$^{19-20}$ have only numbers 1 and 2 in zig-zag sequence representing the sequence of

iodine ions in the (1120) cross section. Thus it may be assumed that in the case of polytype $22H_e$ also only these numbers occur in the iodine zig-zag sequence. Even when such is the case, there are a large number of ways in which these numbers may be combined and permuted to give a 22-layered unit cell. Further simplification is thus needed. Close inspection of intensity distribution on Weissenberg film revealed the following striking features:

(a) The most intense reflections fell at positions occupied by $2H$ reflections. This indicated the presence of many (11) units in the iodine zig-zag sequence of the unit cell of the $22H_e$ polytype.

(b) The reflections which were of next considerable intensity fell around points at distances of 1/3 and 2/3 the way between the two most intense $2H$ reflections. These positions are representative of a $6H$ polytype. The only $6H$ polytype as reported by Mitchell\textsuperscript{19–20} has a structure represented by iodine zig-zag sequence (2211). Thus


\textsuperscript{25} L. S. Ramsdell, Studies on silicon carbide. Amer. Mineralog. 32 (1947) 64–82.
A new polytype of cadmium iodide $22H$

(2211) units must be present in the iodine zig-zag sequence of the present polytype. However, Pinsker\textsuperscript{26--27}, in his electron diffraction study of cadmium iodide, has reported another $6H$ polytype having structure (33). Since such a polytype has neither been observed by Mitchell\textsuperscript{19--20} and other workers, nor in the present investigation, we have ruled out the possibility of presence of any (33) units in the iodine zig-zag sequence of present polytype.

Led by these characteristics of intensity distribution, structures with the following iodine zig-zag sequences were thought of as probable structures

(i) 11111111111111112211 (with one group of 2211)

(ii) 11111111122112211 (with two groups of 2211)

(iii) 1111221122112211 (with three groups of 2211)

These can be easily transformed into classical $ABC$ notation. For example the $ABC$ sequence for the iodine zig-zag sequence represented by (ii) is

$$ABABABABABCBABABCABAB$$

Bozorth\textsuperscript{28} was the first to determine the structure of the basic layer of cadmium iodide. The same has been described by Wells\textsuperscript{29} and Mitchell\textsuperscript{19--20}. As determined by Bozorth the basic polyatomic layer of cadmium iodide consists of two layers of hexagonal close-packed iodine ions with small cadmium ions nested between them. The vertical I—I distance is 3.41 Å and the vertical Cd—I distance is nearly half of this distance. The thickness of the basic layer is 6.83 Å. Thus if we represent the iodine ions by Roman letters and cadmium


\textsuperscript{27} Z. G. Pinsker, Structure of simple layer lattices. Uspekhi Khim. 12 (1943) 396—405 (in Russian).

\textsuperscript{28} R. M. Bozorth, The crystal structure of cadmium iodide. J. Amer. Chem. Soc. 44 (1922) 2232—2236.

ions by Greek letters, as has been done by Hagg\textsuperscript{30}, Pinsker\textsuperscript{31} and Mitchell\textsuperscript{18–20}, the structure of $22H_c$ polytype corresponding to an iodine zig-zag sequence

\begin{align*}
1111111122112211
\end{align*}

may be represented in the $ABC$ notation as following:

$$(A \gamma B) (A \gamma B) (A \gamma B) (A \gamma B) (A \gamma B) (A \gamma B) (C \alpha B) (A \gamma B) (A \gamma B) (A \gamma B) (A \gamma B) (A \gamma B) (C \alpha B) (A \gamma B)$$

For structure determination, as is now well known, it suffices to compare the calculated and observed intensities of $10\bar{1}l$ row of spots alone. The space group of polytype $22H_c$ is $P3m1$. The intensities of the $10\bar{1}l$ row of spots for the above space group in the case of cadmium iodide is written as

$$I \propto \left[ \sum f_{l,cd} \cos 2\pi l z + \sum f_{l,cd} \cos 2\pi \left( lz - \frac{1}{3} \right) + \sum f_{l,cd} \cos 2\pi \left( lz + \frac{1}{3} \right) \right]^2$$

$$+ \left[ \sum f_{l,cd} \sin 2\pi l z + \sum f_{l,cd} \sin 2\pi \left( lz - \frac{1}{3} \right) + \sum f_{l,cd} \sin 2\pi \left( lz + \frac{1}{3} \right) \right]^2$$

where $z_{A,\alpha}$ denotes the $z$ coordinates of I atoms at $A$ sites and Cd atoms at $\alpha$ sites; similarly for $z_{B,\beta}$ and $z_{C,\gamma}$.

Intensities for 10 important reflections were calculated for each of the structures proposed by the above iodine zig-zag sequences. The intensity values calculated from the above formula were multiplied by Lorentz-polarisation factor $(1 + \cos^2 \theta)/\sin 2\theta$. Table 1 compares the calculated and observed intensities for the arrangement (ii). In Fig. 3 the calculated relative intensities are plotted against $l$ values for arrangements (i) and (iii). Fig. 4 represents such a plot for arrangement (ii). A comparison of graph with the Weissenberg photograph shows that arrangement (i) and (iii) show marked discrepancies between observed and calculated intensities, while arrangement (ii) shows excellent agreement. Arrangement (ii) is thus accepted as correct one. For this arrangement intensities for complete 44 reflections have been calculated. In Fig. 4, intensity values have not been plotted for intense reflections corresponding to $l = 11, 22$ and 33 because the heights would be beyond the limits of the graph; instead arrows indicating large intensity values have been shown for the

Table 1

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<th>(l)</th>
<th>Calculated intensity</th>
<th>Relative intensity</th>
<th>Observed intensity</th>
<th>(l)</th>
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Fig. 3. Calculated relative intensity against \(l\) values for arrangements (i) (above) and (iii) (below)
above three reflections. However, as can be seen from Table 1, these three reflections show agreement between their observed and calculated intensities. No corrections for absorption were made since suitable absorption factors for a thin crystal are not available. However, it is the change in absorption as one goes from one reflection to the other which is of importance. In present case it is thought that the change in absorption is not of considerable magnitude and hence observed intensities may be accepted as correct for a relative comparison. The observed intensities are actually taken from the series 1 0 • 44 through 1 0 • 88. This series has the same intensity sequence as 10 • 0 through 1 0 • 44 which is not clearly visible on the Weissenberg photograph because of absorption caused by the non-equidimensional crystal plate.

The coordinates of the iodine and cadmium ions are not listed since these can easily be derived from the above ABC sequence.

Fig. 4. Calculated relative intensity against l values for arrangement (ii)
Discussion of results — mode of growth

Eighty crystals were analysed in the present investigation. All were found to have a hexagonal lattice. This is in agreement with MITCHELL's observation that cadmium iodide does not display any rhombohedral polytypes. This should be expected theoretically since, as suggested by KRISHNA and VERMA, the rhombohedral polytypes would grow when the ledge exposed by the dislocation has the first and the last layer in the same orientation, i.e. either $A$ or $B$ or $C$. Any ledge exposed in the $2H$, $4H$ or $6H$ cadmium iodide structures, and consisting of an integral number of minimal sandwiches, necessarily has the first and last layer in a different orientation and would not lead to the generation of a rhombohedral polytype. This conclusion is borne out by observation.

Of the 80 crystals examined so far by x-ray diffraction techniques twenty were found to belong to type $2H$ while thirty were of type $4H$. This is at variance with the observation by MITCHELL who reported nearly $50\%$ crystals of type $4H$ but only $4\%$ of type $2H$. In fact, in the present work, in some batches of crystals, type $2H$ was found to be the most abundant type. TRIGUNAYAT, in his combined interferometric and x-ray diffraction study of cadmium iodide, has drawn a similar conclusion. The polytype $22H_c$ was isolated from a group of crystals having an abundance of type $2H$.

Thus if in addition to $4H$, type $2H$ is also regarded as an ideal structure, then polytypic series based on the $2H$ structure would also be expected to exist. Polytypes belonging to this series would have an intensity-maxima distribution resembling that of $2H$. In the present investigation such crystals have been encountered; type $22H_c$ is an example. Many of the photographs obtained by TRIGUNAYAT exhibit this feature. Thus, contrary to MITCHELL's suggestion, structures based on type $2H$ should not be regarded as improbable. However, as described below, screw-dislocation theory is unable to provide a satisfactory explanation for the formation of polytypes based on type $2H$.

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32 The only exception being $24R$, about the existence of which MITCHELL has expressed doubt.


According to Frank a higher polytype results from the creation of a screw dislocation in a basic structure of non-integral Burgers's vector. Since the step exposed in cadmium iodide invariably consists of an integral number of minimal sandwiches, it follows that a screw dislocation in a 2H structure would generate the 2H structure itself. Such a difficulty is not unique to cadmium iodide. In the case of lead iodide, which has 2H as the only ideal structure, other polytypes, according to screw-dislocation theory, should not exist. However, Pinsker, Tatarinova and Novikova have showed the existence of other polytypes. Thus the present polytype $22H_c$, which appears to be based on 2H structure because of presence of many (11) units in its iodine zig-zag sequence, does not appear to have grown from a dislocation mechanism.

However, one may assume that, in an initial 4H structure, first a 2H step with iodine zig-zag sequence (11) was formed having a Burgers's vector equal to half of the c value of 4H, and then a 6H step, (2211), was formed in the same initial 4H structure with a Burgers's vector equal to 1.5 the c value of 4H. Further, if both steps were close enough to cooperate in such a manner as to form a final step having structure 11111111122112211, the growth of polytype $22H_c$ can perhaps be explained in terms of dislocation theory. The above explanation of the growth of polytype $22H_c$ by screw-dislocation mechanism is far fetched and it appears more reasonable to believe that polytype $22H_c$ does not grow by a dislocation mechanism but from some other mechanism. In fact Trigunayat and Verma have concluded from their observation of non-correlation between spiral step height and the c dimension of the unit cell that the dislocation mechanism does not explain the phenomenon of polytypism in cadmium iodide.

Acknowledgement

The present work has been conducted under a scheme of the Council of Scientific and Industrial Research of India.

Fig. 1. The 10.1 row of spots as recorded on a 15° c-axis oscillation photograph of the 105R crystal, on a camera of radius 11.48 cm. (×1).

Fig. 2. Zero-layer a-axis Weissenberg photograph taken with unfiltered Cu Kα radiation on a camera of diameter 5.73 cm. (×1.5).
The Structure of a New Silicon Carbide Polytype 105R

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(Received 26 June 1962 and in revised form 19 March 1963)

A 105-layered rhombohedral polytype of silicon carbide has been discovered with unit-cell dimensions \(a = b = 3.078\) and \(c = 264.39\) Å as referred to hexagonal axes. By comparing the calculated relative intensities of 10.\(L\) reflections with those observed on Weissenberg photographs, its structure has been confirmed to be \((333333333332)_g\) in Zhdanov’s notation. This polytype thus belongs to the \([(33)_s 32]_g\) series of structures whose existence is expected on the dislocation theory.

Introduction

Over 40 different polytypes of silicon carbide have been discovered, and their number is continually increasing. To understand how such a large number of modifications of the same substance occur the theories advanced are (a) the impurity theory (Zhdanov & Minervina, 1945a, Lundqvist, 1948), (b) screw dislocation theory (Frank, 1951), (c) polymer theory (Ramsdell & Kohn, 1952) and (d) thermodynamical theory (Jagodzinski, 1954). But because of the complicated nature of growth none of these attempts has been completely successful. Attempts are being made here to study the nature of growth of these polytypes and for this purpose we are searching for new polytypes and studying their detailed structure by X-ray diffraction to ascertain whether the data collected in relation to them can be explained on the basis of the above theories. During the course of above study a new 105-layered polytype was discovered, and we describe below its detailed structure.

Structure of the unit cell

The crystal under investigation was a small dark crystal of dimensions \(1 \times 0.5 \times 0.5\) mm\(^3\). From a 15° oscillation photograph about the \(c\) axis taken on a camera of radius 11.48 cm, the rhombohedral symmetry of the crystal was confirmed since the nearest spots (of the 10.\(L\) row) on either side of the zero-layer Laue streak were in the ratio of 1:2. The number of layers in the unit cell was approximately determined from the measured \(\xi\) value from Fig. 1. The number of layers was accurately determined on a zero-layer Weissenberg photograph taken about the \(a\) axis by the method of Krishna & Verma (1962a) where the exact number of layers is obtained by counting the number of spacings after which the intensity sequence begins to repeat in the 10.\(L\) row. Fig. 2 shows this Weissenberg photograph in which the above number of spacings was 35. Because of the rhombohedral symmetry the unit cell contains \(35 \times 3 = 105\) layers.

The number of layers in the unit cell of the polytype 105R fits in the series of silicon carbide polytypes in the Ramsdell zigzag sequence \([(33)_s 32]_g\). Indeed 105R was an undiscovered member of this series, the known members being 15R, 33R, 51R, 87R, 141R and 393R. It was therefore suspected that the structure of 105R was \([(33)_s 32]_g\) (Zhdanov notation). This was further confirmed by comparing the characteristics of intensity in the 10.\(L\) row with an intensity plot given by Mitchell (1954) for five other members of this series. The structure \([(33)_s 32]_g\) in the \(ABC\) notation is

\[
\text{ABACBABCABABCACBABCACBABCACB}\n\]

\[
\text{ABACBABCABABCACBABCACBABCACB}\n\]

\[
\text{ABACBABCABABCACBABCACBABCACB}\n\]

\[
\text{ABACBABCABABCACBABCACBABCACB}\n\]

which has a centre of symmetry for the silicon atoms at the atom marked by an arrow. Choosing the origin on this atom the interval sequence (Ott, 1925a, b) is

\[
2424242424333333333333424242424242.
\]

because of the centre of symmetry the intensity calculations are very much simplified. As is generally done in silicon carbide to establish the structure, it is sufficient to show an agreement between the calculated and observed relative intensities in the 10.\(L\) row up to \(l=105\) on the positive as well as the negative side (Ramsdell, 1944). The intensities of these 10.\(L\) reflections were calculated in the usual manner (Ramsdell, 1944) and multiplied by the Lorenz polarization factor.

For the estimation of observed intensities following Krishna & Verma (1962a, b), zero-layer Weissenberg photographs were taken for 10, 25, 50, and 100 oscillations of the crystal. A standard intensity scale was prepared by exposing a particular intense spot for 1, 2, \ldots, 100 oscillations of the crystal. All these films were processed under identical circumstances. Hence the intensity estimations were done with enough


**The Structure of a New Silicon Carbide Polytype 10572**

Calculated values and observed values for the 10.1 reflexions are listed in Table 1. The close agreement between these establishes the postulated structure. The reliability factor is found to be 0.14.

**Unit-cell dimensions and atomic positions**

The space group of 10572 is $P6_3m$ with its cell dimensions based on hexagonal axes:

$$a = 3.078, \quad c = 264.39 \text{ Å}.$$  

The zigzag sequence given above results in the following atomic positions in the hexagonal unit cell:

- 35 silicon atoms at $0 \ 0 \ z$, where $z = 0, 2z, 6z, 10z, 14z, 18z, 20z, 24z, 26z, 30z, 32z, 36z, 39z, 42z, 45z, 48z, 51z, 54z, 57z, 60z, 63z, 66z, 69z, 73z, 75z, 79z, 81z, 85z, 87z, 91z, 93z, 97z, 99z, 103z,

where $z = 1/105$.

- 35 silicon atoms at $\frac{5}{2}, \frac{5}{2}, \frac{1}{2}$ plus the above coordinates

- 35 silicon atoms at $f, f$ plus the above coordinates;

- 105 carbon atoms one above each silicon atom at $0 \ 0 \ p$, where $p = 1/140$.

**Discussion**

The growth of 10572 is expected on dislocation theory. As suggested by Krishna & Verma (1962a, b), rhombohedral polytypes grow only when the first and last layer of the exposed ledge is in the same orientation ($A$, $B$ or $C$). Consider a screw dislocation ledge of 35 layers exposed in the basic $6H$ structure, $A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B$, as growth proceeds, this would wind up spirally, creating a structure

$$B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A\ G\ B\ A\ B\ G\ A.$$

Confirmation of the structure of 105R as [(33)$_n$32)$_3$ (Zhdanov notation) shows the utility of Mitchell's method (1954) for detecting directly the structure of unknown polytypes of silicon carbide belonging to [(33)$_n$32)$_3$ series. A similar intensity plot was made by Krishna & Verma (1962a, b) for the direct determination of structures of the unknown members of the series [(33)$_n$34)$_3$. These suggestions have simplified the structure work in silicon carbide to a large extent. Similar attempts can be made for other series also.

The above work was conducted under a scheme sanctioned by the Council of Scientific and Industrial Research of India.

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**Table 1. Intensities of 10.1 reflexions**

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The determination of the structure of a silicon carbide polytype becomes difficult when it has a very large periodicity. Since silicon carbide crystallizes into innumerable modified types with unit cell heights ranging from 5.048 Å in type 2H to nearly 1500 Å in type 594R (and to more in many of the unidentified types), it is necessary to suitably modify the X-ray diffraction methods for their investigation. By these methods, a detailed analysis of the structure of some of the large polytypes has been carried out. The growth of these structures, with a periodicity much larger than the range of any known atomic forces, is discussed on the dislocation theory.

1. Introduction

Silicon carbide is known to crystallize into several modified types, all of which have the same a and b dimensions of the unit cell (a = b = 3.078 Å) but differ along c. The unit cell consists of layers of structure stacked along c at constant intervals of 2.518 Å, in a close-packed manner. The repeat period along c varies from 5.048 Å in type 2H (Adamsky and Merz, 1959) to nearly 1500 Å in type 594R (Honjo et al., 1950), and to more in many of the unidentified types. A simple explanation of the origin and growth of so many different modified types can be found in terms of the screw dislocation theory of crystal growth (Frank, 1951). The direct correlation observed between the step-height of growth spirals and the height of the X-ray unit cell, in different polytypes (Verma, 1952, 1957) left little doubt about the validity of this theory. Using the theory it was possible to explain the origin of the structure series in silicon carbide and it was, therefore, felt that the phenomenon of polytypism had been satisfactorily explained.

However, doubts have been expressed by Jagodzinski (1954) according to whom the structure of a polytype is determined by thermodynamic considerations and screw dislocations play a role only in the later stages of growth. Recently Trigunayat and Verma (1962) have reported a non-correlation between the step-height of growth spirals on cadmium...
iodide polytypes and the height of their X-ray unit cells. This has further enhanced the doubts expressed by Jagodzinski regarding the origin of polytypes from screw dislocations.

We, therefore, undertook to isolate a number of silicon carbide polytypes and determine their detailed atomic structure with a view to examine whether the structure conforms with the dislocation theory. This paper describes the experimental methods used for this investigation. The results obtained are discussed on the dislocation theory.

2. Experimental Methods

A. Determination of the unit cell

Since successive unit layers of structure, in silicon carbide, are spaced at intervals of 2.518 Å along the c-axis, it is possible to calculate the number of layers in the unit cell by determining the c-parameter from the oscillation and Weissenberg photographs. The method works quite well with small polytypes like 4H, 6H and 15R, but for larger polytypes the results obtained become ambiguous on account of the limited experimental accuracy of determining c. Honjo et al. (1950), as well as Mitchell (1954), identified large polytypes by counting the number of spacings between two known 6H spots. However, this was possible because these polytypes had type 6H in syntactic coalescence.

A simple method of counting the exact number of layers in the unit cell has been used by us in our investigations. It requires only an approximate idea of the number of layers in the unit cell, which can often be had by a comparison of the c-axis oscillation photograph with that of type 6H. The number of layers in the unit cell is obtained from the number of spacings after which the sequence of relative intensities begins to repeat in the 10.l row. The intensity of a 10.l reflection from a silicon carbide polytype nH or nR is given by

\[ I_{10.l} \propto (f_{Si}^2 + f_{C}^2 + 2f_{Si}f_{C}\cos 2\pi lp)(A_{Si}^2 + B_{Si}^2) \]

with

\[ A_{Si} = \sum_{z_A} \cos 2\pi lz + \sum_{z_B} \cos 2\pi (lz + \frac{1}{3}) + \sum_{z_C} \cos 2\pi (lz - \frac{1}{3}) \]

and

\[ B_{Si} = \sum_{z_A} \sin 2\pi lz + \sum_{z_B} \sin 2\pi (lz + \frac{1}{3}) + \sum_{z_C} \sin 2\pi (lz - \frac{1}{3}) \]

where \( z_A, z_B \) and \( z_C \) denote the z-coordinates of silicon atoms on the A: 00z, B: \( \frac{1}{3}z \) and C: \( \frac{2}{3}z \) axes respectively, and \( p = \frac{3}{4\pi} \) is the displacement of the carbon atoms above the silicon, along c. Now, since \( z = r/n \), \( r \) being an integer, the values of \( A_{Si} \) and \( B_{Si} \) are the same for the reflections 10.l and 10.(l+n). The difference in intensity of these spots is due to the
change in the factor \( f_{\text{Si}}^2 + f_{\text{C}}^2 + 2f_{\text{Si}}f_{\text{C}}\cos 2\pi lp \). But, since \( f_{\text{Si}} \) and \( f_{\text{C}} \) change monotonously with \( \theta \) and \( f_{\text{Si}} \approx 3f_{\text{C}} \), the variation in \( \cos 2\pi lp \) does not affect the intensity much and the sequence of relative intensities of 10. \( l \) spots is similar after a change of \( n \) in the \( l \)-value. Thus the sequence of the intensity of spots 10. \((l+n)\), 10. \((l+n+1)\), ... etc., would be similar to that of the spots 10.\( l \), 10. \((l+1)\), ... etc. This repetition of relative intensities was first noticed by Ramsdell (1944) in type 21R and applied by us to identify the polytype 90R (Krishna and Verma, 1962c). Thus if the sequence of relative intensities of 10.\( l \) spots, recorded on a Weissenberg or oscillation photograph repeats after \( q \) spacings (counting the absent reflections also), the polytype has \( q \) layers in its smallest hexagonal unit cell.

Figure 1 shows the \( c \)-axis oscillation photograph of a large polytype of silicon carbide, as recorded on a 3 cm camera. The non-symmetrical arrangement of spots about the zero layer line indicates rhombohedral symmetry. It can be noticed that the sequence of relative intensities along the 10. \( l \) row is similar after every 37 spacings. Since each spacing corresponds to a change of 3 in the \( l \)-value, the polytype is \( 37 \times 3 = 111R \). The number of layers can also be determined, with advantage, from the \( a \)-axis Weissenberg photographs (Figs. 3 and 4) by observing the above repetition of intensities in the lowest “festoon” of spots. Figure 3 shows the \( a \)-axis first layer equi-inclination Weissenberg photograph of type 111R, while Fig. 4 is the \( a \)-axis zero layer Weissenberg photograph of a polytype 90R. The relative intensities of 10.\( l \) spots in Fig. 4 repeat after every 30 spacings.

This method of identifying a polytype, however, requires that the 10. \( l \) row of spots be both present and well-resolved in the entire range of counting. It can be seen in Figs. 1, 3 and 4 that the first layer equi-inclination Weissenberg photograph provides a much greater resolution than the oscillation or zero-layer Weissenberg. We have obtained still greater resolution by using an oscillation camera of 11.46 cm radius and collimating the X-ray beam further. It is, however, imperative to choose extremely small crystal pieces for taking the X-ray diffraction photographs, so that the width of successive 10. \( l \) spots may be less than the distance between their centres. Thus a somewhat bigger crystal piece would have produced continuous streaks along the Bernal row lines in Fig. 1, which could be incorrectly taken to have resulted from a random disorder in the structure. The choice of a small crystal piece also reduces errors in the intensity work, due to variable absorption and secondary extinction, the corrections for which are difficult to evaluate. We therefore employed crystal pieces with dimensions of the order of 0.1 mm. Such minute crystal pieces often exhibit no natural faces and, therefore, present some difficulty in setting in a crystallographic direction. In such
cases one can adopt the procedure described by Jeffrey (1949); but the peculiarities of the structure of silicon carbide affords a much simpler method. The reciprocal lattice rows parallel to \( c \) are densely crowded with reciprocal lattice points. These rows therefore record as a line of closely spaced spots, which are easily recognized even when the crystal is oscillating about a random direction. For adjusting the rotated crystal about [001], these rows were made parallel to the rotation axis, and for adjusting about [100] or [210] they were made perpendicular to the latter.

Having determined the number of layers in the unit cell of a polytype, their probable stacking sequences can be worked out by the methods employed by Ramsdell (1944, 1947), Zhdanov and Minervina (1945) and Krishna and Verma (1962a, b, c). To determine the correct structure from the probable ones so worked out, it suffices to calculate the relative intensity of 10.\( \ell \) reflections and compare these with those observed on Weissenberg photographs (Ramsdell, 1944). It is usually not necessary to perform a quantitative estimation of the observed intensities since the large number of 10.\( \ell \) reflections recorded, themselves, form a scale of relative intensities, whose self-consistency is enough evidence of the correctness of a proposed structure. However, when there are two or more probable structures giving a fairly good qualitative fit with observed intensities it is essential to perform a quantitative estimation. This presents some difficulty on account of the proximity of successive 10.\( \ell \) reflections on the Weissenberg photograph of large polytypes. It is not possible to use Weissenberg photographs of the integrating type since the spots would overlap. It is also difficult to isolate each spot for photometric estimation of relative intensities. We, therefore, employed the following method:

A standard scale of relative intensities was prepared by selecting a single 10.\( \ell \) reflection and then recording it on different portions of the same Weissenberg film. The exposure time for successive recordings was measured in terms of complete oscillations of the crystal. For estimating the spots in different intensity ranges, Weissenberg films of different known exposures were used. For these films also the exposure time was reckoned by counting the number of complete oscillations of the crystal. The different Weissenberg films, as well as the one recording the standard scale were processed under identical conditions. We found that for estimating intensities over such a large range, as that obtained on the Weissenberg photographs of these polytypes, the above method yielded more consistent results than the usual multiple-film method. The excellent agreement obtained between calculated and observed intensities for various structures has confirmed the suitability of the above method (Krishna and Verma, 1962b).
3. Results of the Investigation

Of the many large polytypes discovered during the course of the present investigation special attention was given to the following polytypes of interest:

(i) Type 57R: This crystal is based on the 6H phase with a structure $[(33)_{5}34]_{3}$ (Krishna and Verma, 1962a).

(ii) Type 111R: The oscillation and Weissenberg photographs obtained from this polytype are shown in Figs. 1 and 3. The polytype has been shown to have a structure $[(33)_{5}34]_{3}$ and has enabled a detailed study of the $[(33)_{n}34]_{3}$ series of structures (Krishna and Verma, 1962b).

(iii) Type 90R: A Weissenberg photograph obtained from this crystal is shown in Fig. 4. This polytype was found to have a structure based on the 15R phase with a Zhdanov symbol $[(23)_{3}3322]_{3}$ (Krishna and Verma, 1963a).

(iv) Type 36H: This is a unique polytype within which there has occurred a change in the structure without a change of space group or of the periodicity of the lattice. The two structures have been designated as $36H_{a}$ and $36H_{b}$ and were found in a single crystal piece. Figure 2 (a), (b) and (c) show the 10. $l$ row of spots recorded on $c$-axis oscillation photographs taken from (a) the composite parent 36H crystal, (b) the upper portion, 36H$_{a}$, and (c) the lower part, 36H$_{b}$, respectively.

The lower part 36H$_{b}$ reveals striking structural extinctions on its X-ray diffraction photographs. Thus the 10. $l$ reflections are absent when $l = 36n$, 36$n + 6$ and $6n + 2$, where $n = 0, 1, 2, ...$. This polytype has an unusual structure which could not be determined by the usual methods employed for other polytypes. The structure has been determined in a novel manner from the conditions

$$\sum_{z_{A}} \cos 2\pi lz = \sum_{z_{B}} \cos 2\pi lz = \sum_{z_{C}} \cos 2\pi lz = 0$$

$$\sum_{z_{A}} \sin 2\pi lz = \sum_{z_{B}} \sin 2\pi lz = \sum_{z_{C}} \sin 2\pi lz = 0 \quad (l = 6n + 2)$$

imposed on the structure by the extinctions. The structure so worked out has a Zhdanov symbol $[(33)_{5}34(33)_{5}32]_{3}$ (Krishna and Verma, 1963b).

(v) Disordered Polytypes: In addition to the ordered structures like 90R, 111R and 126R, silicon carbide also forms polytypes with considerable one-dimensional disorder. Fig. 2 (d) shows the 10. $l$ row of spots recorded on a $c$-axis oscillation photograph of one such crystal. The continuous streak along the row line indicates a random disorder superimposed over the order in the crystal. A tendency towards long-range order can, however, be seen. Figure 2 (e) is the enlargement of a part of Fig. 2 (d) and reveals very closely spaced spots corresponding to
a periodicity of about \((33 \times 5)H\) or \((33 \times 15)R\). The “continuous” streak along the row lines therefore appears to be partly due to a lack of resolution of spots corresponding to a very high periodicity and partly due to a random disorder in the structure.

4. Discussion of Results—Growth of Polytypes

According to Frank’s dislocation theory, the different polytypes of silicon carbide grow from basic structures like 6H, 15R and 4H, by the creation of a screw dislocation with a Burgers vector which is a non-integral multiple of the height of the parent unit cell. When the Burgers vector is an integral multiple of the height of the parent unit cell the resulting structure is the same as the basic structure. It has been experimentally demonstrated that the Burgers vector, which is the step-height of the growth spiral, is equal to \(c\) for hexagonal polytypes and \(c/3\) for the rhombohedral ones (Verma, 1957). It follows, therefore, that the value of \(c\) for hexagonal polytypes and \(c/3\) for rhombohedral ones should be a non-integral multiple of the \(c\)-spacing of the basic structure. However, we have isolated a number of polytypes with contra-indications, including the types 36H\(_a\) and 90R described in this paper.

The polytypes 36H\(_a\) and 36H\(_b\), as also the types 54H and 66H reported by Verma (1957), give intense X-ray diffraction spots in the 6H positions showing that their structure is based on the 6H phase. The growth of these polytypes could not have taken place by the creation of a screw dislocation in the 6H structure since the Burgers vector of such a dislocation would be an integral multiple of the \(c\)-spacing of 6H. A screw dislocation step of 36, 54 or 66 layers, formed in the 6H structure could result only in further growth of the 6H structure itself. All the same the crystals of 54H and 66H shows spirals on their \((0001)\) faces, with a step-height simply related to the height of the unit cell (Verma, 1957).

Similarly, the polytype 90R with a structure \([(23),3322]_b\) is definitely based on the 15R phase but its growth is not possible from a single screw dislocation in 15R, since a ledge of 30 layers exposed in the 15R structure would result in further growth of the 15R itself. It would perhaps be possible to explain the growth of these structures from two or more suitably “co-operating” dislocations, but such explanations appear far-fetched in the absence of any surface evidence to this effect. There is no evidence of co-operating dislocations on the surfaces of 36H, 54H, 66H or 90R. On the other hand there is definite evidence of single dislocations in 54H and 66H, while 36H and 90R show no spiral markings. A growth spiral on the surface of 36H would be expected to have a step-height of over 90 Å, which ought to be easily visible under a phase-contrast microscope. Moreover, it is difficult to understand how a system of co-operating
Fig. 1. A $15^\circ$ c-axis oscillation photograph of SiC type 111R ($r = 3$ cm, $\lambda = 1.54 \text{ Å}$).

Fig. 2. The 10-φ row of different SiC polytypes, as recorded on $15^\circ$ c-axis oscillation photographs: (a) 36H parent crystal ($r = 3$ cm, $\lambda = 1.54 \text{ Å}$, mag. x 3). (b) Type 36H$_a$ ($r = 3$ cm, $\lambda = 1.54 \text{ Å}$, mag. x 3). (c) Type 36H$_b$ ($r = 3$ cm, Cu K radiation, mag. x 3). (d) Disordered polytype ($r = 11.46$ cm, Cu K radiation, mag. x 1). (e) Enlargement of a part of Fig. 2 (d).
Fig. 3. First layer, $\alpha$-axis, equi-inclination Weissenberg photograph of SiC type 111 (r = 2.86 cm, $\lambda = 1.54 \AA$). The eleven consecutive faint spots near the minimum of the lowest festoon are, from left to right, 01-16, 01-13, ..., 01-1, 01-2, ... 01-11 and 01-14. The $l$-values of successive spots differ by 3 (mag. $\times$ 1).

Fig. 4. Zero-layer, $\alpha$-axis Weissenberg photograph of SiC type 90 (r = 2.86 cm, Cu K radiation). The lowest festoon records the 10, 1 row of spots. The ten faint spots near the minimum of the festoon are, from left to right, 10-19, 10-16 ..., 10-8, 10-11. The $l$-values of successive spots differ by 3 (mag. $\times$ 1).
dislocations, creating the structure $36H_b$, could at a later stage generate a different structure $36H_a$.

Polytypic structures originating from a single screw dislocation ought to have a number of 33, 23 or 22 units in their zigzag sequence, with faults at the end. However, the X-ray diffraction photographs of type $126R$ show an intensity maxima distribution unlike that of any smaller polytype. This polytype is therefore not based on any smaller structure and could not have grown from a single screw dislocation. All the same it shows a growth spiral with a step 42 layers high (Verma, 1957). The structure, therefore, does not appear to have resulted from the growth of the spiral. Similarly the polytypes $174R$ with a structure $[(33)_{6}(33)_{5}4]_3$ (Tomita, 1960), and $36H_b$, with a structure $[(33)_{3}4(33)_{2}32]$ (Krishna and Verma, 1963a) have stacking faults in the middle of a sequence of 33's. They cannot, therefore, result from single screw dislocations in the basic structures. There are, at the same time, structures like $57R$ and $11R$ (Krishna, and Verma, 1962a, b), which are most readily understood as originating from single screw dislocations in the $6H$ structure, but an examination of their surfaces shows no spirals. The existence of random disorder in some SiC crystals (see Fig. 2 (d) and (e)) also cannot be explained on the screw dislocation theory. Table I summarizes the present position of observations regarding the growth of silicon carbide polytypes from screw dislocations, in the light of the above discussion.

### Table I. Summary of observations on silicon carbide polytypes

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<td>Growth completely explained in terms of screw dislocations</td>
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<tr>
<td>$57R$</td>
<td>$[(33)_{6}34]_3$</td>
<td>Show no spirals</td>
<td>Structure readily explained on dislocation theory, but no surface evidence of dislocation</td>
</tr>
<tr>
<td>$11R$</td>
<td>$[(33)_{6}34]_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$126R$</td>
<td>Not based on any smaller type</td>
<td>Shows spirals with correlation (Verma, 1957)</td>
<td>Surface evidence of dislocation. Structure at variance</td>
</tr>
</tbody>
</table>
Table I—continued

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Structure of unit cell</th>
<th>Surface structure</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>36H, 54H, 66H</td>
<td>Based on 6H. Unit cells integral multiples of the unit cell of 6H</td>
<td>36H No spiral. 54H, 66H show spirals with correlation (Verma, 1957)</td>
<td>Structure not accounted on dislocation theory. Evidence of single screw dislocations in 54H and 66H</td>
</tr>
<tr>
<td>90R</td>
<td>[(23)_4(322)_6]. Unit cell 6 times that of 15R</td>
<td>Shows no spiral</td>
<td>Structure based on 15R, but growth not possible from screw dislocation in 15R</td>
</tr>
<tr>
<td>36H, [(33)<em>{34}(33)</em>{32}]. c-dimension six times that of 6H</td>
<td>Shows no spiral</td>
<td>Structures have stacking faults in the middle of a sequence of 33’s.</td>
<td></td>
</tr>
<tr>
<td>174R</td>
<td>[(33)<em>{6}(33)</em>{4}]_3 (Tomita, 1960)</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>Disordered X-ray diffraction polytypes photographs show continuous streaks along 10.7 row</td>
<td>No data</td>
<td>Not explained on dislocations</td>
<td></td>
</tr>
</tbody>
</table>

1. The polytypes 51R (Thibault 1944; Zhdanov and Minervina, 1945), 87R (Ramsdell, 1947), 27R, and 51R (Ramsdell and Kohn, 1952), 19H (Ramsdell and Mitchell, 1953), 141R and 393R (Mitchell, 1954), and 16H (Gaslova, 1955) have structures that conform with the dislocation theory, but evidence of their growth from screw dislocations is incomplete since no data regarding their surface structure has been reported.

2. The polytypes 10H (Ramsdell and Kohn, 1951), 75R and 84R (Ramsdell and Kohn, 1952), and 18H (Glinsky, 1954) have structures that cannot originate from single screw dislocations in any of the basic structures, but may be thought of as resulting from two or more suitably “co-operating” dislocations (Mitchell, 1957). No surface evidence has however, been put forth.

3. The polytypes 2H (Adamsky and Merz, 1950) and 8H (Ramsdell and Kohn, 1952) appear to be definite phases of silicon carbide, but no structures based on these are, as yet, known.

4. Though β-SiC (Hull, 1919, 1920), which is cubic, can be easily derived from a screw dislocation in any of the basic structures, it does not form in this way since it is, unlike α-SiC, a low-temperature modification.

5. **CONCLUSION**

It is evident from the above discussion that though the spiral step-height on silicon carbide is simply related to the c-dimension of the lattice, the contents of the unit cell do not necessarily result from a screw dislocation in one of the basic structures. It appears, therefore, that screw dislocations determine the surface structure but not the structure.
of the unit cell. Jagodzinski (1954) has arrived at a similar conclusion from thermodynamic considerations. According to him the energy required for the creation of a screw dislocation can come from the lattice only after the crystal has acquired a considerable volume, by which time the structure of the crystal has already been determined. Therefore, screw dislocations could cause growth only in the later stages, thereby creating spirals on the surface. Once a polytype is formed the Burgers vector of a screw dislocation in it would be related to its lattice dimension so that there may be no misfit across the slip plane. This would explain the correlation observed between the spiral step-height and the height of the X-ray unit cell; but the structure of different polytypes cannot be understood on the dislocation theory and the cause of so many different modifications of silicon carbide, especially those with unit cell heights much larger than the range of any known atomic forces, has to be reconsidered.

Acknowledgement

One of us (P. Krishna) is grateful to the University Grants Commission of India for the grant of a research fellowship during the tenure of this work.

REFERENCES

SILICON carbide is known to crystallize into several polytypic modifications, all of which have the same \( a \) and \( b \) dimensions of the unit cell \((a = b = 3.078 \text{ Å})\), but differ along the \( c \) dimension. The unit cell consists of layers of structure, stacked along the \( c \) dimension at constant intervals of 2-5 \( \pm 0.48 \text{ Å} \) in a close-packed manner. Already over 30 different modifications have been reported, with unit cell heights ranging from \( c = 5.048 \text{ Å} \) in type 2H to \( c = 1500 \text{ Å} \) in type 594R and there appears to be no upper limit to the number of modifications that exist. Ott\(^9\), Ramsdell\(^{10}\), and Zhdanov and Minervina\(^{11,12}\) were among the first to investigate the detailed atomic structure of some of these modifications. Ott showed that all these structures had the same basic tetrahedral arrangement of silicon and carbon atoms, while Zhdanov and Minervina were the first to describe the structures in terms of the sequence of close-packed silicon-carbon layers in the unit cell. Ramsdell\(^{10}\) classified these structures into structure series which are conveniently described in the intervals of \( 2 - 5 \text{ Å} \) in a close-packed manner. The unit cell consists of layers of structure, stacked along the \( c \) dimension at constant intervals of 2-5 \( \pm 0.48 \text{ Å} \) in a close-packed manner.

**Formation and Growth of Polytypes**

Attempts to explain the formation and growth of so many different modifications of silicon carbide have been made on the basis of : (1) the impurities present during the process of growth\(^{13}\); (2) spiral growth from screw dislocations\(^7\); (3) the accretion of polymers of silicon carbide with a stacking reversal inherent in their structure and stability governed by temperature\(^8\); and (4) layer transpositions based on the vibration entropy of the structure\(^9\).

Of these, it is the screw dislocation mechanism that has received considerable attention, since it provides a very simple and direct explanation of the phenomenon of polytypism in support of which considerable experimental evidence has been put forth. According to this theory, the different polytypes of silicon carbide grow from basic structures like 6H, 15R and 4H by the creation of screw dislocations of different Burgers vectors. A new polytype would result when the Burgers vector of the screw dislocation is a non-integral multiple of the \( c \) dimension of the basic structure. The observation of growth spirals\(^{20,21}\) on the (0001) face of silicon carbide crystals and of a direct correlation between the step-height of these spirals and the height of the X-ray unit cell\(^{20,22}\) left little doubt about the validity of the theory. The theory was able to explain the origin of all the different structure series discovered in silicon carbide and it was, therefore, felt that the phenomenon of polytypism had been satisfactorily explained.

However, doubts have been expressed by different workers regarding some aspects of the dislocation theory\(^{19,23}\). According to Jagodzinski, the structure of a polytype is determined by thermodynamic considerations. He has, accordingly, suggested a layer transposition mechanism based on the vibration entropy of the structure. Recently, Triginavat and Verma\(^{24}\), from their interferometric and X-ray diffraction study of cadmium iodide polytypes, have reported a non-correlation between the step-height of the observed growth spiral and the height of the X-ray unit cell. It has thus become increasingly evident that the screw dislocation mechanism does not fully explain the formation of all the different polytypes. Other mechanisms suggested for silicon carbide have also not been able to explain all the observed facts.

We have, therefore, extended the investigation further, by working out the detailed atomic structure of different silicon carbide polytypes with a view to studying their growth in the light of the existing theories of polytypism. In particular, it was proposed to examine whether the structure of different polytypes conforms with the dislocation theory. The results are summarized in Table 1.

**Interpretation of Polytypes on the Dislocation Theory**

According to Frank's dislocation theory, the different polytypes of silicon carbide grow from basic structures like 6H, 15R and 4H, by the creation of a screw dislocation with a Burgers vector which is a non-integral multiple of the height of the parent unit cell. When the Burgers vector is an integral multiple of the height of the parent unit cell, the resulting structure is the same as the basic structure. It follows from these considerations that:

1. Crystal faces should exhibit growth spirals whose step-height is directly related to the height of the unit cell of the structure.

2. The large polytypes should have a structure based on one or other of the basic structures, i.e. a major portion of the unit cell of large polytypes should have the same structure.
The end. They, therefore, have an intensity maxima of a number of 33, 23 or 22 units with faults at the basic structures, and have a zigzag sequence consisting of one of the basic structures, so that the Zhdanov symbol is made up of a number of 33, 23 or 22 units with faults at the end of the sequence.

3. The Burgers vector of the screw dislocation (= c for hexagonal polytypes and c/3 for rhombohedral ones) should be a non-integral multiple of the repeat unit of the basic structure, along the c dimension.

4. The resulting polytype should have a completely ordered structure.

**Experimental evidence for and against the dislocation theory** — The experimental evidence both against and in favour of each of these is discussed below. Most of the crystals examined during the present investigation were flat plates with well-developed faces. As pointed out by Vand, such crystals would require for their growth three non-coplanar screw dislocations. However, growth spirals are observed only on the (0001) face of some silicon carbide crystals, while most of the crystals show no spiral markings at all. Moreover, a single-screw dislocation would form needle-shaped crystals. The step-height of growth spirals observed on the (0001) face is found to be directly related to the height of the X-ray unit cell, being equal to it for hexagonal types and one-third of it for rhombohedral ones; a similar study on cadmium iodide, by Trigunayat and Verma, has revealed the absence of such a correlation in this substance.

Most of the large polytypes of silicon carbide, so far discovered, are found to be based on one of the basic structures, and have a zigzag sequence consisting of a number of 33, 23 or 22 units with faults at the end. They, therefore, have an intensity maxima distribution similar to that of the basic structure. However, the intensity distribution in the 10. row of a polytype 126R, discovered by Verma, shows that its structure is not based on any smaller type. The more intense spots do not lie around positions corresponding to any basic structure. Nevertheless, the crystal 126R shows a growth spiral with a step 42 layers high, and is thus expected to have grown by the screw dislocation mechanism. The structure and spiral are thus at variance, and the former does not appear to have resulted from the latter. Similarly the polytypes 174R, with a structure [(33)6(33)4]3, and 36Hb, with a structure [(33)34(33)23]6, though based on the 6H phase, have stacking faults in the middle of a sequence of 33's. Such structures cannot result from a single-screw dislocation created in the 6H structure. There are, at the same time, structures, like 57R [(33)34]6 and 111R [(33)34], which are most readily understood as resulting from screw dislocations in the 6H structure, but an examination of their surfaces shows no spirals.

Generally, a polytype based on a certain ideal structure (6H, 15R or 4H) has a repeat unit along the c dimension which is a non-integral multiple of the corresponding repeat unit of the basic structure; but we have isolated a number of polytypes with contra-indications. Thus types 36Hc, 36Hb, and also the types 54H and 66H reported by Verma, give intense X-ray diffraction spots in 6H positions, showing that their structure is based on the 6H phase. The growth of these polytypes could not have taken place by the creation of a screw dislocation in the 6H structure, since the Burgers vector of such a dislocation would be an integral
multiple of the c spacing of 6H. A screw dislocation step of 36, 54 or 66 layers, formed in a 6H structure, could result only in further growth of the 6H structure itself. At the same time, crystals of 54H and 66H show spirals on their (0001) faces with a step-height related in a simple way to the height of the unit cell. Similarly, the polytype 90R with a structure \( (23)_{3723} \) is definitely based on the 15R structure, but its growth is not possible from a screw dislocation in 15R, since a ledge of 30 layers exposed in the 15R structure would only cause further growth of 15R itself. It would, perhaps, be possible to explain the growth of these structures from two or more suitably "cooperating" dislocations, but such explanations appear unconvincing in the absence of any surfece-evidence to this effect. There is no evidence of cooperating dislocations on the surfaces of 36H, 54H, 66H or 90R. On the other hand, there is definite evidence of single dislocations in 54H and 90R, while 36H and 90R show no spiral markings.

While very large polytypes of silicon carbide have been observed with a high degree of order in their structure, e.g. 11IR, 90R, 36H, etc., it is also not uncommon to find polytypes with considerable one-dimensional disorder. The growth of such structures, with a random disorder of layers, cannot be explained on the dislocation theory.

It is evident from the above discussion that though the spiral step-height on silicon carbide bears a simple relation to the c dimension of the lattice, the contents of the unit cell do not necessarily result from screw dislocations in one of the basic structures. It, therefore, appears that screw dislocations determine only the surface structure but not the structure of the unit cell. Jagodzinski arrived at a similar conclusion from thermodynamic considerations. According to him, the high energy required for the creation of a screw dislocation can come from the lattice only after the crystal has acquired a considerable volume, by which time the structure of the crystal has already been determined. Therefore, screw dislocations could cause growth only in the later stages, thereby creating spirals on the surface. Once a polytype is formed, the Burgers vector of a screw dislocation in it would be related to its lattice dimension so that there may be no misfit across the slip plane. This would explain the correlation observation between spiral step-height and the height of the X-ray unit cell.

Other Proposed Theories

According to Jagodzinski and Arnold, silicon carbide should normally have a completely disordered structure since the different possible configurations have very nearly the same potential energy. It is the vibration entropy of the structure that is responsible for creating the observed order. Jagodzinski's calculations have borne out the fact that 15R is the next commonest structure after 6H. The coexistence of order and disorder sometimes observed in the same crystal piece is expected according to his theory. However, completely ordered structures with a large periodicity are highly improbable according to Jagodzinski's theory, and, therefore, the absence of any disorder, even in large polytypes like 90R, 36H, 11IR and 126R, is difficult to understand. Moreover, this theory has not so far accounted for the existence of structure series in silicon carbide. Schnee\(^2\) considers the phenomenon of polytypism to be analogous to that of order-disorder in alloys and has shown, along these lines, that the long-period polytypes represent potential minima.

Lundqvist\(^3\) and Hayashi\(^3\) established a correlation between the structure type and the content of aluminium (as impurity) for the types 6H, 15R and 4H. The role of the impurity in determining the structure type is not known and no such data are available for the other polytypes. It appears unlikely that the formation of the larger polytypes is also determined by the presence of impurities.

Ramsdell and Kohl\(^8\) put forth a qualitative theory which explains the creation of the different silicon carbide polytypes by the accretion of polymers. This theory has predicted the structure of several new polytypes and directly accounted for the existence of structure series; but polytypes like 174R, 90R and 36H, with three polymer units in their structure, are not in accordance with this theory. Moreover, the existence of such polymers as the theory assumes has yet to be experimentally demonstrated.

Conclusion

It would thus be seen that none of the existing theories of polytypism has been able to give a satisfactory explanation of all the observed facts. The cause of so many different modifications, some with unit cell heights much larger than the range of any known atomic forces, has, therefore, to be reconsidered.

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VERMA & KRISHNA: DISLOCATIONS & POLYTypism IN SILICON CARBIDE

**Fig. 1.** 15° oscillation photograph about the $a$ axis, with Cu Kα radiation, on a camera of radius 3 cm ($\times 1.2$).

**Fig. 2.** 15° oscillation photograph about the $a$ axis, of the other face of the crystal taken with Cu Kα radiation, on a camera of radius 3 cm.

**Fig. 3.** First layer $a$-axis Weissenberg photograph taken with Cu Kα radiation on a camera of diameter 5.73 cm. The lowest festoon shows the 01.1 row of spots. The spots on the festoon were indexed with the help of a Weissenberg photograph of a 4H polytype as well as with the help of a Weissenberg chart. The first visible intense spot corresponds to $l=63$; the visible series of spots have $l$ values ranging from $l=56$ to $l=112$.

**Fig. 4.** First layer $a$-axis Weissenberg photograph of the other face of the crystal taken with Cu Kα radiation on a camera of diameter 5.73 cm.
Fig. 5. Surface micrograph of the crystal obtained with narrow pencil of white light \((\times 25)\).

Fig. 6. Magnified view of the central portion of Fig. 5 \((\times 100)\).

Fig. 7. Interferogram of crystal obtained with mercury light of wavelength 5461 Å \((\times 29)\).

Fig. 8. Magnified view of the central portion of Fig. 7 \((\times 100)\).
A twenty-eight layered new polytype of cadmium iodide, designated $28H_c$, with unit-cell dimensions $a = 4.24$, $c = 95.69\ \text{Å}$, is described. The detailed atomic structure has been worked out and its zigzag sequence is found to be 2222222222221111. The growth of the polytype is examined in the light of the screw dislocation theory of polytypism. The screw dislocation theory is not able to explain fully the growth of this polytype. The polytype $28H_c$ is so far the largest cadmium iodide polytype with a known atomic structure.

**Introduction**

Polytypism, first observed in silicon carbide, found a simple explanation in terms of the screw dislocation theory of crystal growth (Frank, 1951). The theory gives a pictorial representation of the formation of various polytypes — and direct experimental evidence in support of it came from the observation of a correlation between the step-heights of growth spirals on silicon carbide polytypes and the heights of their X-ray unit cells (Verma, 1957). No such extensive and conclusive experimental support has yet been given for other existing theories of the origin of polytypism such as the polymer theory (Ramsdell & Kohn, 1952), vibration entropy — layer transposition theory (Jagodzinski, 1949; Jagodzinski & Arnold, 1960), and the impurity content theory (Lundqvist, 1948; Hayashi, 1960).

The main aim of the present work has been to carry the investigation further by testing the validity of the dislocation theory among other known polytypic substances. The substance chosen for the present work was cadmium iodide. From an interferometric and microscopic study of cadmium iodide crystals Forty (1952) predicted polytypism in this compound. Mitchell (1956) carried out an extensive X-ray diffraction study of cadmium iodide crystals and correlated the unit-cell dimensions with the step-heights measured by Forty (1952). However, for an unequivocal verification of Frank’s dislocation theory of polytypism in the case of cadmium iodide, Trigunayat & Verma (1962) tried to find a correlation between the spiral step-height and the height of the unit cells by performing both the X-ray diffraction and the interferometric studies upon the same crystals. They found that no such correlation exists. Thus it is not completely understood why, even when a crystal shows a growth spiral and thus appears to have grown by the dislocation mechanism, there should not be a direct correlation between the spiral step-height and the X-ray unit cell.

We have examined numerous cadmium iodide crystals by X-ray methods and have isolated several long-period polytypes. Since only little work has been done on the structural analysis of cadmium iodide polytypes, we have directed our attention towards the structure determination of these long-period polytypes, to see whether these can be explained in terms of screw dislocation theory.

Generally, a cadmium iodide polytype is based on a certain ideal structure ($2H$ or $4H$) and has a repeat unit along $c$ which is a non-integral multiple of the corresponding repeat unit of the basic structure. The formation of such polytypes is easily understood on the screw dislocation theory. However, we have isolated three polytypes, namely $22H$, $26H$ and $2SH$, which are in contradiction to the above. The first two polytypes have $c$ spacings respectively eleven times and thirteen times the $c$ spacing of their basic $2H$ structure; and the third has a $c$ spacing seven times the $c$ spacing of its basic $4H$ structure. These polytypes are unusual since their creation requires a screw dislocation whose Burgers vector is an integral multiple of the $c$ spacing of the basic structure. Their growth is not directly understood on the dislocation theory since such a screw dislocation could only cause further growth of the basic structure itself. Hence it was aimed to work out the detailed atomic structures of these polytypes, to see whether the structure could be explained on screw dislocation theory.

The results obtained on the $22H$ polytype have already been reported (Srivastava & Verma, 1963). This paper describes the detailed atomic structure of the polytype $28H$. This polytype is of special interest since, as shown later, the observations obtained on it furnish evidence both for and against the screw dislocation theory. Moreover, this is the first among the...
known polytypes which gives evidence as to what happens in the initial and final stages of growth of any polytype. This is now the longest cadmium iodide polytype with a known atomic structure.

Experimental
Crystals of cadmium iodide used in the present investigation were grown from aqueous solution at room temperature. The method is similar to that used by Mitchell (1957). The crystals were observed under a polarizing microscope and only those which showed uniform extinction were subjected to X-ray examination. The c-axis oscillation photographs generally showed smearing and streaking of diffraction spots and were found unsuitable either for identification of the polytype or for structure determination, while a-axis oscillation photographs showed discrete sharp spots. Therefore, a-axis oscillation photographs were taken for an oscillation range starting from the position when the c-axis (perpendicular to the crystal platelet) made an angle 25° with the incident X-ray beam, and was carried on to the position (25+15)=40°. This range was found most convenient for the identification of a polytype since it records a large number of 10.l spots. For the structure determination a-axis Weissenberg photographs recording either the 01.l or 10.l row were taken.

Fig. 1 reproduces a 15° a-axis oscillation photograph of the crystal, recorded on a 3 cm camera with Cu Kx radiation. Fig. 2 shows the a-axis oscillation photograph of the crystal taken after it was rotated through 180° from the position for Fig. 1. Similarly Figs. 3 and 4 show the first layer a-axis equi-inclination Weissenberg photographs taken from the two sides of the crystal platelet, on a camera of diameter 5-73 cm with Cu Kx radiation.

As is evident from Figs. 1 and 3, the present polytype is 28H since there are seven equal spacings between two consecutive 4H reflexions. However, Figs. 2 and 4, which represent photographs taken from the other side of the crystal, show it to be the ideal 4H structure. Thus there is a surprising situation in which one side of the crystal piece is the 4H ideal structure while the other side of the same piece is the polytypic 28H structure. By taking Laue photographs of different regions of the same face of the crystal it has been concluded that a single face contains a single polytype only. It has been possible to detect the presence of the two polytypes within the single crystal piece, because of the high absorbing property of both cadmium and iodine ions. The high absorption does not allow the weak diffracted beams from the polytypic structure 28H to be recorded on the film when this is facing the incident beam. When the crystal side containing polytypic structure 28H is away from the incident beam, evidently the polytypic spots of 28H are recorded since they have not to travel the whole thickness of the crystal.

Structure of 28H
The new modification exists in the form of a hexagonal platelet with a well developed and shining (0001) face. The c dimension evaluated from Fig. 1 is 95.7 Å. The known c dimension of the type 4H is 13.67 Å. The present polytype is thus 28H. This is confirmed because of the presence of six diffraction spots between two consecutive intense 4H spots. Mitchell (1956) has reported two other 28-layered polytypes 28Ha and 28Hb. In the absence of any structural data published by him and in view of the fact that in cadmium iodide almost all the polytypes with the same number of layers have different stacking sequence, the present polytype is designated 28H.

For a large polytype such as this it is not possible to decide the correct structure by following the usual method of working out all possible structures involving Zhdanov (1946) numbers 1, 2, 3, 4, etc., in their Ramsdell's (1944) zigzag sequence. Since almost all the polytypes of cadmium iodide have only the numbers 1 and 2 in their zigzag sequence, we shall also restrict ourselves to these numbers alone. Thus the problem of determining the probable structures reduces to arranging the numbers 1 and 2 in different ways so as to give a 28-layered unit cell and trying each structure separately. The number of such arrangements would be enormous because of the presence of number 1 and structure determination would become formidable. The correct structure was therefore anticipated as follows:

The diffraction spots which coincide in position with the spots of the 4H polytype are distinctively more intense than the rest of the spots. The unit cell of the polytype then must contain many (22) units. The following possible structures are thus formulated with decreasing number of (22) units:

(i) 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 1 1
    which for brevity can be written as (22)24 1 1
(ii) (22)24 2
(iii) (22)6 1 1 1 1
(iv) (22)4 2 2
(v) (22)3 1 1 2 2 1 1
(vi) (22)5 1 2 1 1 2 1
(vii) (22)5 1 1 1 1 1 1
(viii) (22)4 1 2 1 1 1 1 2
(ix) (22)4 1 2 1 1 2 1
(x) (22)4 1 2 2 1
(xi) (22)4 1 2 2 2 1

We cannot further decrease the number of (22) units since then the structure would not be based on a 4H ideal structure. As shown previously (Srivastava & Verma, 1963) all the polytypes of cadmium iodide necessarily have the hexagonal lattice. The above arrangements involving (22)24 and (22)14 do not repre-
sent a hexagonal lattice as for example the ABC sequence corresponding to first structure is

\[ \text{AB CB AB CB AB CB AB CB AB CB AB CB C} \]

In the above the number of \( \Delta \)'s (reversal in one direction) is 15 and number of \( \nabla \)'s (reversal in other direction) is 13. For an arrangement representing a hexagonal lattice the number of \( \Delta \)'s and \( \nabla \)'s should either be equal or should differ by a multiple of 3. Thus the arrangements (i), (viii), (ix), (x) and (xi) do not represent hexagonal structure and are, therefore, discarded. Structures (ii) and (iv), which are equivalent, are also disregarded since they represent the 4H structure itself. To decide the correct structure, intensities for six important O l.Z reflexions were calculated for each of the remaining structures.

The intensity formula for O l.Z reflexions for the structure itself. To decide the correct structure, in-

\[ I = \left( \sum_{\Delta, \gamma} f_{\Delta, \gamma} \cos 2\pi Iz + \sum_{\nabla, \delta} f_{\nabla, \delta} \cos 2\pi (lz - \frac{1}{3}) \right)^2 + \left( \sum_{\Delta, \gamma} f_{\Delta, \gamma} \sin 2\pi Iz + \sum_{\nabla, \delta} f_{\nabla, \delta} \sin 2\pi (lz - \frac{1}{3}) \right)^2 \]

Table 1. Comparison of calculated and observed intensities

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*The observed intensities were taken from the series 10-56 through 10-112. This series has the same intensity sequence as 10-0 through 10-66 which is not visible on the film because of absorption caused by the non-equidimensional crystal plate.

where \( \Sigma \) denotes the summation over the \( z \) coordinates of I atoms at \( A \) sites and Cd atoms at \( x \) sites; similarly for \( \Sigma \) and \( \Sigma \).

Here \( z \) represents the \( z \) coordinates of ions on the three vertical symmetry axes \( A, B \) and \( C \) passing through \( 00z, \frac{2}{3} z \) and \( \frac{1}{3} z \) respectively. Roman letters represent the iodine ions and Greek letters the cadmium ions. In cadmium iodide the basic polyatomic layer consists of two layers of hexagonal close-packed iodine ions with the small cadmium ions nested between them. The vertical I-I distance is 3.4175 \( \AA \) and the vertical Cd-I distance is nearly half of this distance. The cadmium layer is thus midway between two iodine layers.

The intensity values obtained from the above formula were multiplied by the Lorenz polarization factor \((1 + \cos^2 2\theta)/\sin 2\theta\). Fig. 9 shows plots of the calculated relative intensities for the 6 possible structures. A comparison of the calculated intensities with those observed on a Weissenberg photograph makes it evident that only the structure (iii) gives the right fit. For an unequivocal verification of the structure of an
According to Frank's (1951) screw dislocation theory, this structure itself grows in the initial stages. Through supersaturation at the beginning is highest. Thus in the crystals initially grow into thin plates of uniform slips of various magnitudes in the crystal platelet, non-uniform distribution of impurities the platelet thickness by a surface nucleation mechanism, as the growth of polytype and is, therefore, buckled. This buckling is relieved by cadmium iodide, regarding 4\textit{P} as the ideal structure, is not thought to be so abrupt as to cause appreciable difference in observed relative intensities within a small range.

The detailed structure of 28\textit{H}c is, therefore, as follows:

Space group \textit{I}\textit{3m}1

Zhdanov symbol 2222222222221111

\textit{A}B \textit{C} sequence

(\textit{A}\textit{y}\textit{B}) (\textit{C}\textit{x}\textit{B}) (\textit{A}\textit{y}\textit{B}) (\textit{C}\textit{x}\textit{B}) (\textit{A}\textit{y}\textit{B}) (\textit{C}\textit{x}\textit{B}) (\textit{A}\textit{y}\textit{B}) (\textit{C}\textit{x}\textit{B})

\textit{a} = 4.24 \text{ Å} \quad \textit{c} = 95.69 \text{ Å}

Atomic coordinates:

8 iodine at (0 0 1)_{t_1}

\textit{t}_1 = 0, 8z, 16z, 24z, 32z, 40z, 48z, 52z,

14 iodine at \frac{1}{3} \text{ } \textit{t}_1

\textit{t}_2 = 2z, 6z, 10z, 14z, 18z, 22z, 26z, 30z, 34z, 38z, 42z, 46z, 50z, 54z

6 iodine at \frac{1}{2} \text{ } \textit{t}_1

\textit{t}_3 = 4z, 12z, 20z, 28z, 36z, 44z

6 cadmium at 0 0 1\textit{t}_1

\textit{t}_4 = 5z, 13z, 21z, 29z, 37z, 45z

8 cadmium at \frac{1}{3} \text{ } \textit{t}_1

\textit{t}_5 = z, 9z, 17z, 25z, 33z, 41z, 49z, 53z where \textit{z} = 1/56

\section{Discussion}

According to Frank's (1951) screw dislocation theory, the crystals initially grow into thin plates of uniform thickness by a surface nucleation mechanism, as the supersaturation at the beginning is highest. Thus in cadmium iodide, regarding 4\textit{H} as the ideal structure, this structure itself grows in the initial stages. Through non-uniform distribution of impurities the platelet containing the 4\textit{H} ideal structure becomes self stressed and is, therefore, buckled. This buckling is relieved by slips of various magnitudes in the crystal platelet, resulting in the creation of one or more dislocations of various strengths. These very dislocations are responsible for the final creation of the polytype. The growth of polytype 28\textit{H}c is examined below in the light of these considerations.

The crystal platelet of the present polytype as shown previously has a 4\textit{H} structure on one face and a 28\textit{H} structure on the opposite face. This may be taken to furnish evidence that an initial 4\textit{H} platelet has finally grown into a 28\textit{H} polytype. Similarly the presence of the basic and polytypic structure within the same single-crystal piece has been detected in other cadmium iodide crystals also.

The polytype 28\textit{H}c is based on an ideal 4\textit{H} structure. According to the screw dislocation theory the growth of a polytype from a single screw dislocation in an ideal 4\textit{H} structure may result only if the Burgers vector of such a dislocation is a non-integral multiple of the \textit{c} spacing of 4\textit{H}. In the present case, since the Burgers vector of screw dislocation which will create a polytype 28\textit{H}c will have to be a seven times integral multiple of the \textit{c} spacing of 4\textit{H}, the growth cannot result by a single dislocation. A step of 24 layers formed in a 4\textit{H} structure could only result in the further growth of 4\textit{H}.

To explain the growth of polytypes which cannot result from a single screw dislocation one may postulate two or more cooperating dislocations as was done by Mitchell (1956). Below it is shown how the growth of 28\textit{H}c can be visualized in terms of such an idea.

A single screw dislocation in a 4\textit{H} ideal structure can easily create a step corresponding to the structure (22\textit{a}) 11. Let there be another step corresponding to the structure 11 (obtained from 2\textit{H}) in the vicinity of the above. If the above two steps are close enough to cooperate in such a manner as to form a final step having the structure (22\textit{a}) 1111, the growth of 28\textit{H}c can then take place. But if such is the case the surface observations must conform with the above.

At this stage, therefore, it was thought desirable to examine the crystal surface for growth features. However, there were difficulties. The crystal had been mounted on a glass fibre for X-ray diffraction studies, and had also been exposed to atmospheric moisture. Such exposure is known (Trigunayat, 1962) to be likely to blur the surface features. Secondly (Trigunayat, 1962), cadmium iodide crystals, because of their chemical reactivity with silver and other substances, cannot easily be coated to increase the reflectivity. Thus we were able only to get two-beam internal interference fringes and not multiple beam fringes which are much sharper. No attempt was made to dismount the crystal from the glass fibre because of the possibility of deformation. A micrograph of the (0001) face (mag X 30) using bright field illumination is shown in Fig. 5. The phase contrast illumination did not show any improvement. The central part, shown enlarged in Fig. 6 (mag. X 120), illustrates the growth spiral observed on that face of the crystal which exhibited 28\textit{H} polytypic structure. No spiral was observed on the opposite face of the crystal. This is a broken spiral, of symmetry intermediate between hexagonal and circular symmetries, with no clear evidence of cooperation of two dislocations. According to the screw dislocation theory of polytypism as shown above, the crystal should have exhibited two cooperating spirals of heights 80 Å and
7 Å respectively with a resultant spiral step-height of 96 Å for a direct correlation to exist between spiral step-height and c dimension of the unit cell. Fig. 7 shows the two-beam internal interferogram of the crystal obtained with green monochromatic light of mercury (\( \lambda = 5461 \, \text{Å} \)) (mag. X 30). An enlargement of the corresponding central part of Fig. 7 is shown in Fig. 8 (mag. X 120). The mean value of the spiral step-height \( \langle h \rangle \), measured by counting the number of steps \( (n) \) and the member of fringes \( (m) \) between two points, by superimposing Figs. 6 and 8, is nearly 2580 ± 70 Å taking \( \mu = 1.3 \) for cadmium iodide from \( \delta = (\lambda m) / (2 \mu n) \). Thus it is evident that there is no direct correlation between the spiral step-height and the c dimension of the unit cell. However, it can be argued that the above large step-height results from multiple dislocation in the polytype 28H itself. This will require that at first the polytype 28H grows by the postulated cooperation of two dislocations; then that a further dislocation occurs in 28H, which now acts as a basic structure to give a spiral step-height of 26 times the size of the unit cell of 28H. Here we have assumed that the observed spiral step-height is an integral multiple of the c dimension of 28H, but on account of the limitations of experimental techniques it has not been possible to determine the step-height very accurately. The matter will be still more complicated if the spiral step-height is a non-integral multiple of the c dimension of 28Hc, the above explanation is far fetched. The surface spiral step-height does not seem to be in accordance with the screw dislocation theory of the growth of the polytype. Jagodzinski & Arnold (1960) after examining fault-order phenomena in crystals of silicon carbide have postulated another theory of polytypism based on the vibration entropy of crystals. The essential features of Jagodzinski's theory are the 'diffuse' background and 'smearing' of diffraction spots. Trigunayat & Verma (1962) have observed high disorder and smearing phenomena on some crystals of cadmium iodide. They have indeed given evidence in favour of Jagodzinski's theory. However, as is evident from Figs. 1 to 4, the polytype 28Hc shows absence of any disorder. Thus it appears difficult to understand the growth of polytype 28Hc by Jagodzinski's theory.

It may be concluded that the growth of polytype 28Hc shows some evidence in favour of the screw dislocation theory, only as far as the initial growth, the dependence on 4H structure and the resulting order are concerned. However, the large spiral step-height, the kind of spiral observed on the surface, the integral multiplicity of the Burgers vector, and the repeat unit of the basic structure along c, are at variance with the screw dislocation theory of polytypism. In fact Trigunayat & Verma (1962) have concluded that the screw dislocation theory does not provide a satisfactory explanation for the growth of different polytypes of the compound. More recently Krishna & Verma (1962) have shown that the screw dislocation theory is also not able to explain fully the creation of all the polytypes in silicon carbide. Indeed no single theory is able to explain all the observed facts for any of the known polytypic substances.

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References

On the deduction of silicon-carbide polytypes from screw dislocations

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With 1 figure

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Auszug

MITCHELL hat die SiC-Polytypen, die aus den Phasen 6H, 4H und 15R durch Schraubungsversetzungen entstehen können, auf Grund des Spiralwachstums-Mechanismus von FRANK abgeleitet. Er nahm dabei an, daß zur Zeit der Entstehung einer Schraubungsversetzung der wachsende Kristall durch vollständige Elementarzellen begrenzt wird und daß die Versetzungsstufe während des folgenden Spiralwachstums sich ohne Rücksicht auf ihre eigene Struktur als dichteste Kugelpackung um die Versetzungsrichtung weiterwendet. Es wird gezeigt, daß die beiden einschränkenden Annahmen nicht berechtigt sind und daß die Anwendung von Zdanow-Symbolen zu fehlerhaften Ergebnissen führt.

Die möglichen Polytypen werden unter Berücksichtigung der Struktur der Stufe und der Schichtenfolge beim Spiralwachstum neu abgeleitet. Das Ergebnis unterscheidet sich von dem MITCHELLS vor allem dadurch deutlich, als eine viel größere Anzahl von Polytypen möglich wird.

Abstract

MITCHELL has deduced the polytypic structures that would arise from theoretical screw dislocations in the 6H, 4H and 15R phases of silicon carbide, by the spiral-growth mechanism of FRANK, and compared these with the structures actually observed. In doing so, he assumed that at the instant of the creation of a screw dislocation, the initial platelet consists of a completed number of unit cells and that the exposed ledge, irrespective of its own structure, can wind over itself in a close-packed manner, thereby repeating its own zig-zag sequence indefinitely during the subsequent spiral growth. It is shown that both these assumptions are not justified and that the use of Zhdanov symbols alone leads to incorrect results. The possible polytypic structures that can be derived from theoretical screw dislocations of different Burgers vectors are rededuced with corrected assumptions, by considering the different possible structures of the exposed ledge in terms of ABC layers and investigating the
On the deduction of silicon-carbide polytypes

stacking of these layers during the subsequent spiral growth of the ledge. The results so obtained differ markedly from those of Mitchell. In particular a much larger number of structure series are shown to be actually possible. The results are compared with the polytypic structures reported so far.

Introduction

Several different explanations have been put forth to account for the phenomenon of polytypism in silicon carbide. Besides the early attempts at trying to correlate the structure type with the colour or the content of impurities, the following theories have so far been advanced:

i) The screw-dislocation theory of polytypism.

ii) The 'polymer' theory.

iii) The theory of layer displacements based on the vibration entropy of the structure.

iv) Polytypism as second-order transformation.

v) Polytypism due to the influence of lattice vibrations on the growth front, during crystallization.

None of the above theories is able to account for all the observed facts, but the screw-dislocation theory of polytypism has, so far, proved to be the most successful. In spite of the anomalies discussed in earlier papers, it remains the only theory that explains the existence of structure series in polytypic crystals as well as the

formation of ordered long-period polytypes—both of which are prominent facts among polytypic substances.

The screw-dislocation theory of polytypism was first put forward by Frank to explain the formation of silicon-carbide polytypes in terms of the regular spiral growth of the (0001) face of the crystals. He was able to account for the \([(33)_n 32]_3 R\) series of structures as originating from screw dislocations in the basic \(6H(33)\) structure, with a Burgers vector which is a non-integral multiple of the c dimension of type \(6H\). Direct experimental evidence in support of the theory came from the observation of growth spirals on silicon-carbide polytypes and the measurement of their step heights. It was found that the spiral step height and therefore, the Burgers vector of the screw dislocation is equal to the height of the x-ray unit cell for hexagonal polytypes and one-third of it for the rhombohedral ones.

The application of Frank’s idea was extended by Mitchell, who considered all theoretically possible screw dislocations in three basic phases of silicon carbide, namely, \(6H\), \(15R\) and \(4H\), and attempted to explain from them not only the formation of all known silicon-carbide polytypes but also the absence of certain series of structures, which was an anomaly to Frank. These deductions met with considerable success in that a fairly complete correlation was found between the theoretically possible structures and those actually observed. A similar study of cadmium-iodide and lead-iodide polytypes was also reported and it was concluded from these that polytypism in all these compounds results from screw dislocations.

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11 Ajit Ram Verma, Further observations of growth patterns on silicon carbide (SiC) crystals. Phil. Mag. 43 (1952) 441–446.
14 It should be noted that these are not thermodynamic phases of the compound. The word phase is used here only in the sense that these are the more common modifications on which the others appear to be based.
In this paper it is attempted to show that Mitchell's deduction of SiC polytypes is based on certain assumptions which are not wholly justified but which considerably influence the results. The results obtained by starting with corrected assumptions are tabulated. These differ considerably from the results of Mitchell and are compared with the observed data.

**Mitchell's deduction and its assumptions**

Since all the atoms of a silicon-carbide structure lie on the (11\(\overline{2}0\)) planes, Mitchell considered the atomic configurations resulting from possible screw dislocations, on these planes. It is well known that the silicon and carbon atoms in this plane lie on zig-zag chains, by describing the sequence of which, Ramsdell\(^{17}\) represented the structure. The numerical symbol describing the zig-zag sequence of a structure is the same as the Zhdanov symbol\(^{18}\). Figure 1 shows the atomic configurations on the (11\(\overline{2}0\)) plane resulting from possible screw dislocations of different Burgers vector strengths created in the 6\(H\) phase (as plotted by Mitchell\(^{19}\)). These figures contain, in addition to the vertical shift parallel to [0001], a small horizontal displacement of the atoms in the substrate, assumed in order to ensure lattice continuity between the generated structure and the horizontal and vertical portions of the exposed dislocation step. Thus in Fig. 1A, which shows a dislocation with unit (or one-layer) Burgers vector, the portion of the structure under the line CD has been dislocated relative to that under AB so that CD lies one layer of atoms below AB and, in addition, the atoms under CD have a horizontal displacement of one spacing to the right (equal to one third the spacing between A and B). Although there is no direct evidence of such a horizontal displacement, this assumption is justified since an absence of such a displacement would cause a discontinuity at the surface and would imply a closer approach of the atoms than appears possible. It would be noted that this horizontal displacement does not in any way alter the structure of the exposed step or that of the resulting polytype.

The atomic configurations resulting from screw dislocations of 1,2,3,4,5,6 and 11-layered Burgers vectors in the 6\(H\) phase are shown

\(^{17}\) Lewis S. Ramsdell, Studies on silicon carbide. Amer. Mineralogist 32 (1947) 64–82.

in Fig. 1 A, B, C, D, E, F, and G respectively and include suitable horizontal displacements of atoms whenever required for continuity at the step. The dislocations cause gaps in the substratum labelled in.
the Figure as $R_1$, $S_1$, $T$, $S_2$, $R_2$, $N$ and $R_2$ respectively. These are the only six different kinds of gaps that can result from screw dislocations in the $6H$ structure. MITCHELL postulated that the gaps $S_1$, $T$ and $S_2$ are unstable and therefore structures resulting from corresponding dislocations are not to be expected. The atomic configurations resulting from similar dislocations of different Burgers vectors in the $4H$ and $15R$ phase were also investigated by MITCHELL. The different kinds of gaps that result in the $4H$ and $15R$ phases respectively, from screw dislocations of various Burgers-vector strengths were studied by him. The gaps $V$ in $4H$ and $X$, $Y$ in $15R$ (see Figs. 2 and 3 of MITCHELL$^{13}$) were postulated to be too large to be stable.

On the basis of the above considerations MITCHELL deduced all the theoretically possible structures and established an excellent correlation with the observed types. However, these deductions suffer from three assumptions which do not appear to be justified.

(i) The basic phases in which the screw dislocations are generated are considered to consist of a completed number of unit cells. Thus the zig-zag sequence of the last 6 layers in $6H$ is assumed to be 33, of the last 5 layers in $15R$ to be 23, and of the last 4 layers in $4H$ to be 22, which is not necessarily true.

(ii) All the deductions of MITCHELL were based on Zhdanov symbols and it was assumed that the spiral growth of a screw-dislocation ledge would cause its own zig-zag sequence to repeat indefinitely. He did not take into account the $ABC$ sequence of the exposed ledge and this sometimes leads to incorrect deductions. For example, in Fig. 1E the exposed ledge has a layer sequence $CACBA$, and it is logical to suppose that during spiral growth each of these layers would extend horizontally in the same orientation ($A$ as $A$, $B$ as $B$, and $C$ as $C$). The resulting structure would be $CACBA$, $CACBA$, ... etc., which is a polytype $5H$ with a Zhdanov sequence (14). MITCHELL however arrives at a structure (23), corresponding to the zig-zag sequence of the layers in the ledge. One must, therefore, deduce the structure in terms of the actual $ABC$ sequence of layers in the ledge rather than of their inter-relationships as expressed by the Zhdanov symbol.

(iii) It was assumed in MITCHELL's deductions that whatever the structure of the screw-dislocation ledge, it would be able to wind itself during the subsequent growth, so as to repeat its own zig-zag sequence. As shown later this may not be permitted in some cases because of the requirements of close-packing.
Corrected assumptions for the deduction of possible polytypes

(i) Though not much is known about the creation of the basic initial platelet and its surface layers, there is no reason to think that, at the instant when a screw dislocation arises, the initial platelet is composed of a completed number of unit cells. When a screw dislocation arises in the $6H$ phase the zig-zag sequence of the last 6 layers may well be 132 or 231. Similarly in the $15R$ phase it may be 122 or 221 and in the $4H$ phase, 121.

While this would in no way affect the stability of the dislocation gaps (and therefore that of the dislocation system) in the basic structure, it would affect the structure of the exposed screw-dislocation step, which in turn determines the structure of the polytype to be generated. In general, therefore one must consider that, during crystallization, the basic structure might consist of an uncompleted number of unit cells at the time of the origin of a screw dislocation.

(ii) The growth of any polytype by screw-dislocation mechanism may also be considered in terms of the $ABC$ layers. This is because the exposed ledge winds itself into a very flat spiral whose pitch is the same as the height of the ledge, thus producing a close-packed structure. Any one layer is not really in one plane but is winding upwards, very gradually, so that over fairly large areas (of several unit-cell dimensions) any layer might be taken to be in one plane. Hence the structure can be also be described by the closepacking of plane $A,B,C$ layers, a model repeatedly employed in structure determinations. When the first and last layers of an exposed screw-dislocation ledge are in different orientations it is easy to picture its winding over itself in a close-packed manner. The structure so resulting would in this case have a periodicity along $c$ equal to the height of the exposed ledge and the lattice would be hexagonal. But, this will not be possible if the first and last layers of the exposed ledge are in the same orientation ($A$, $B$ or $C$) for then the laws of close packing would not permit the first layer to grow over the last one without slipping the whole stack of layers.

It was suggested by Krishna and Verma\textsuperscript{19} that rhombohedral polytypes result when the first and last layers of an exposed ledge are in the same orientation. Thus every time the stack of layers moves through one pitch there would be a horizontal displacement or slip.

On the deduction of silicon-carbide polytypes

shifting the layers of the stack in a cyclic or anticyclic manner (A → B, B → C, C → A or vice versa). It is of little consequence whether the slip occurs in the cyclic or anticyclic direction, though this might affect the structure of the resulting polytype. What is of greater importance is that whatever forces cause it to occur in any particular direction, would cause it to occur in the same direction every time the stack moves through one pitch, since it comes back to an identical situation. Three such shifts in the same direction would bring back the stack into its original position completing one repeat period. It is easy to see that the resulting structure would have a rhombohedral lattice.

Presumably, therefore, it is this factor which decides whether an n-layered screw-dislocation ledge would generate a polytype nH or (3n)R. This was overlooked by Mitchell because he used Zhdanov symbols in his deductions.

The deduction of possible polytypic structures

In the light of the above considerations, we shall now deduce the polytypic structures that would result from the theoretical screw dislocations in the 6H, 4H and 15R phases of silicon carbide. The study can be extended to other polytypic substances such as CdI₂, PbI₂, ZnS, etc., with advantage.

a) Polytypes based on the 6H phase. There are six different ways in which a screw-dislocation ledge may be exposed in the 6H structure depending upon the six possibilities that exist for the end surface of the initial crystal platelet. Thus the crystal platelet may have any one of the following structures:

i) ABCACB (ABCACB . . .
ii) BCACB (ABCACB . . .
iii) CACB (ABCACB . . .
iv) ACB (ABCACB . . .
v) CB (ABCACB . . .
vi) B (ABCACB . . .

The first letters in these sequences represent the top layer and the group of letters outside the brackets represent the incomplete unit cell. The sequence of layers of the exposed ledge when a dislocation of 1, 2, 3, 4, 5 . . . n layers is created in (i) will be respectively A, AB, ABC, ABCA, ABCAC, ABCACBABC . . . n terms. All these dislocations will be referred to a step structure (i). Similarly for the
other crystal platelets in the above serial order the step structure for
dislocations are:

(ii) $BCACB \ldots$ (iii) $CACBA \ldots$ (iv) $ACBAB \ldots$

(v) $CBABC \ldots$ (vi) $BABCA \ldots$

where the number of terms in each will be equal to the strength of
the dislocation.

In any one of the above structures when a ledge consisting of $6m$
layers ($m$ being an integer) is created, the same structure repeats
itself in growth and the structure of the added crystal continues to
be $6H$. There is no fault across the slip plane, the layers being identical
on both sides of it. However, if ledges of 1, 2, 3, 4, 5, 7, 8, $\ldots$ number
of layers are created, the resulting structure is not $6H$. We now
consider dislocations of different heights in the above six cases.

First consider a ledge of one layer. In all the six cases this would
produce a situation in which the top and the bottom of the ledges are
in the same orientation so that an $A$ ($B$ or $C$) layer will have to spread
on an $A(B$ or $C)$ layer itself, which will violate the close packing. As
explained earlier, by a cyclic slipping of the layer this will lead to
$ABGABG \ldots$ which is the cubic arrangement.

A ledge of two layers would produce a structure (i) $AB \ldots$
(ii) $BC \ldots$ (iii) $CA \ldots$ (iv) $AC \ldots$ (v) $CB \ldots$ (vi) $BA \ldots$
in the above six cases. All these are type $2H$ with Zhdanov symbol (11).
The corresponding dislocation gap is $S_1$ which is unstable and hence
such a step is not expected to form.

The sequence of layers in the above cases when a ledge of three
layers is created will be (i) $ABC \ldots$ (ii) $BCA \ldots$ (iii) $CAB \ldots$
(iv) $ACB \ldots$ (v) $CBA \ldots$ (vi) $BAC$. Cases (i) and (iv), (ii) and (v),
and (iii) and (vi) can be made to coincide with one another by a
rotation of $60^\circ$ about $[0001]$ at $A$ sites and, therefore, only (i), (ii)
and (iii) need be considered. Now (i) and (ii) would give rise to cubic
structure $ABC ABC \ldots$ but arrangement (iii) has the first and last
layers in the same orientation $C$ and will, therefore, give rise to a
structure

$$|C^+ A^- C^+ A^+ B^- A^+ B^+ C^- B^-| C \ldots = 11 21 21 1 = (21)_3 = 9R$$
or

$$|C^+ A^- C^- B^+ C^- B^- A^+ B^- A^-| C \ldots = (12)_3 = 9R$$

according as the stack slips in the cyclic or anticyclic direction.
In the Zhdanov symbol the first number represents the number of
layers in the positive sequence and successive numbers give alternately the number of positive and negative layers. It may be noted that the two structures \((21)_3\) and \((12)_3\) are identical, the one being related to the other by a rotation of \(60^\circ\) about \([0001]\) and a shift of origin. These are, however, not expected to form because the dislocation gap \(T\) is unstable (Fig. 1C).

A ledge of 4 layers will have the structure (i) \(ABCA\) . . . .
(ii) \(BCAC\) . . . .
(iii) \(CACB\) . . . .
(iv) \(ACBA\) . . . .
(v) \(CBAB\) . . . .
(vi) \(BABC\) . . . . As explained earlier only the first three need be considered. The resulting structures in the three cases may be deduced as follows:

i) First and last layers in the same orientation:
   a) Cyclic slip
      \[
      |A^+B^+C^+|A^+B^+C^+A^+B^+C^+A^+B^+C^+ = \infty = 3C
      \]
   b) Anticyclic slip
      \[
      |A^+B^+C^+A^+B^+C^+A^+B^+C^+B^-| = (31)_3 = 12R
      \]

ii) First and last layers in different orientations:
   No horizontal slip
      \[
      |B^+C^+A^-C^-|B^+C^+A^-C^- = 22 = 4H
      \]

iii) First and last layers in different orientations:
   No horizontal slip
      \[
      |C^+A^-C^-B^+|C^+A^-C^-B^+ = 121 = 22 = 4H.
      \]

These structures again are, however, not expected to form because the associated dislocation gap \(S_2\) is unstable (Fig. 1D).

Now consider a ledge of five layers. It may have the structure

(i) \(ABCA\)
(ii) \(BCAC\)
(iii) \(CACB\)
(iv) \(ACBA\)
(v) \(CBAB\)
(vi) \(BABC\).

Again only the first three need be considered since ledges (iv), (v), and (vi) are the same as (i), (ii) and (iii) respectively except for a rotation through \(60^\circ\) about \([0001]\). It may easily be shown that (i) and (iii) will lead to the formation of \(5H\) structure with a Zhdanov symbol \((41)\) and the associated dislocation gap will be \(R_2\).

Thus this structure is not expected to form. The ledge (ii) \(BCAC\) will lead to a rhombohedral arrangement since the first and last layers are in the same orientation. Depending upon whether the slip is cyclic or anticyclic, it will form the polytype \(15R\) with the Zhdanov symbol 32 or 23 respectively.
Table 1. *Structures resulting from dislocations of 6H (33)*

<table>
<thead>
<tr>
<th>Burgers-vector strength</th>
<th>Dislocation gap</th>
<th>Structure of step</th>
<th>Horizontal slip, if any</th>
<th>Resulting structure</th>
<th>Polytype</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$R_1$</td>
<td>(i), (ii), (iii)</td>
<td>Cyclic or anticyclic</td>
<td>$\infty$</td>
<td>$3C$</td>
</tr>
<tr>
<td>(2)</td>
<td>$(S_1)$</td>
<td>(i), (ii), (iii)</td>
<td>No</td>
<td>(11)</td>
<td>$(2H)$</td>
</tr>
<tr>
<td>(3)</td>
<td>$(T)$</td>
<td>(i), (ii)</td>
<td>No</td>
<td>(11)</td>
<td>$(3C)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Cyclic</td>
<td>(21)</td>
<td>$(9R)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>(12)</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>$(S_2)$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>$\infty$</td>
<td>$(3C)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii), (iii)</td>
<td>No</td>
<td>(22)</td>
<td>$(4H)$</td>
</tr>
<tr>
<td></td>
<td>$R_2$</td>
<td>(i)</td>
<td>No</td>
<td>41</td>
<td>$5H$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Cyclic</td>
<td>32</td>
<td>$15R$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Anticyclic</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>(i), (ii), (iii)</td>
<td>No</td>
<td>14</td>
<td>$5H$</td>
</tr>
<tr>
<td></td>
<td>$R_1$</td>
<td>(i)</td>
<td>No</td>
<td>33</td>
<td>$6H$</td>
</tr>
<tr>
<td>(8)</td>
<td>$(S_1)$</td>
<td>(i)</td>
<td>No</td>
<td>(3311)</td>
<td>$(8H_a)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>No</td>
<td>(2321)</td>
<td>$(8H_a)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>No</td>
<td>(1331)</td>
<td>$(8H_a)$</td>
</tr>
<tr>
<td>(9)</td>
<td>$(T)$</td>
<td>(i), (ii)</td>
<td>No</td>
<td>(63)</td>
<td>$(9H)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Cyclic</td>
<td>(2331)</td>
<td>$(27R)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>(1332)</td>
<td></td>
</tr>
<tr>
<td>(10)</td>
<td>$(S_2)$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>(73)</td>
<td>$(30R_a)$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii), (iii)</td>
<td>No</td>
<td>(333)</td>
<td>$(30R_a)$</td>
</tr>
<tr>
<td></td>
<td>$R_4$</td>
<td>(i)</td>
<td>No</td>
<td>(4331)</td>
<td>$11H$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Cyclic</td>
<td>3332</td>
<td>$33R$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Anticyclic</td>
<td>2333</td>
<td>$33R$</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>(i), (ii), (iii)</td>
<td>No</td>
<td>1334</td>
<td>$11H$</td>
</tr>
<tr>
<td>(12)</td>
<td>$R_1$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>4333</td>
<td>$39R_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>3334</td>
<td>$39R_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Cyclic</td>
<td>4333</td>
<td>$39R_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>233311</td>
<td></td>
</tr>
<tr>
<td>(13)</td>
<td>$R_1$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>4333</td>
<td>$39R_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>3334</td>
<td>$39R_a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(iii)</td>
<td>Cyclic</td>
<td>133321</td>
<td>$39R_a$</td>
</tr>
</tbody>
</table>
On the deduction of silicon-carbide polytypes

Table 1. (Continued)

<table>
<thead>
<tr>
<th>Burgers-vector strength gap</th>
<th>Structure of step</th>
<th>Horizontal slip, if any</th>
<th>Resulting structure</th>
<th>Polytype</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (14)</td>
<td>(S₁)</td>
<td>No</td>
<td>(333311)</td>
<td>(14H₄)</td>
</tr>
<tr>
<td>(ii)</td>
<td></td>
<td></td>
<td>(233321)</td>
<td>(14H₆)</td>
</tr>
<tr>
<td>(iii)</td>
<td></td>
<td></td>
<td>(133331)</td>
<td>(14H₈)</td>
</tr>
<tr>
<td>(15)</td>
<td>(T)</td>
<td>No</td>
<td>(6333)</td>
<td>(15H)</td>
</tr>
<tr>
<td>(i), (ii)</td>
<td></td>
<td></td>
<td>(233331)</td>
<td>(45R)</td>
</tr>
<tr>
<td>(iii)</td>
<td>Cyclic</td>
<td></td>
<td>(133332)</td>
<td>(45R)</td>
</tr>
<tr>
<td>(16)</td>
<td>(S₂)</td>
<td>No</td>
<td>(7333)</td>
<td>(48R)</td>
</tr>
<tr>
<td>(i)</td>
<td></td>
<td></td>
<td>(333331)</td>
<td>(48R)</td>
</tr>
<tr>
<td>(ii), (iii)</td>
<td></td>
<td></td>
<td>(233332)</td>
<td>(16H)</td>
</tr>
<tr>
<td>(17)</td>
<td>R₃</td>
<td>No</td>
<td>433331</td>
<td>17H</td>
</tr>
<tr>
<td>(i)</td>
<td></td>
<td></td>
<td>333332</td>
<td>51R</td>
</tr>
<tr>
<td>(ii)</td>
<td>Cyclic</td>
<td></td>
<td>233333</td>
<td></td>
</tr>
<tr>
<td>(iii)</td>
<td>Anticyclic</td>
<td></td>
<td>233334</td>
<td>17H</td>
</tr>
<tr>
<td>(18)</td>
<td>N</td>
<td>No</td>
<td>33</td>
<td>6H</td>
</tr>
</tbody>
</table>

etc.

In the same way the possible structures resulting from screw-dislocation ledges of different Burgers-vector strengths must be worked out. Table 1 lists the results obtained from such an analysis for Burgers-vector strengths of 1 to 18 layers. The structures corresponding to unstable dislocation gaps are put in parenthesis. It may be remarked here that a structure (abcd) is identically the same as (bcda) or (cdab) but it is not identically same as (dcba). The silicon atoms in (abcd) can be made to coincide with the silicon atoms in (dcba) but the carbon atoms in one would lie above the silicon and in the other below it. However, two such structures are indistinguishable by x-ray methods due to FRIEDEL’s law and are, therefore, regarded as the same for the present discussion.

A study of Table 1 reveals that the dislocation gaps have various structural series associated with them, as follows:

<table>
<thead>
<tr>
<th>Gap</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>(33)ₙ  = 6H</td>
</tr>
<tr>
<td>R₁</td>
<td>(33)ₙ34, (33)ₙ3211</td>
</tr>
<tr>
<td>S₁</td>
<td>(33)ₙ11, (33)ₙ2123</td>
</tr>
<tr>
<td>T</td>
<td>(33)ₙ36, (33)ₙ21</td>
</tr>
<tr>
<td>S₂</td>
<td>(33)ₙ37, (33)ₙ31, (33)ₙ22</td>
</tr>
<tr>
<td>R₂</td>
<td>(33)ₙ32, (33)ₙ41</td>
</tr>
</tbody>
</table>
If one assumes, with Mitchell, that the gaps $S_1$, $S_2$ and $T$ are unstable then structures belonging to the $(33)_n$, $(33)_{34}$, $(33)_{3211}$, $(33)_{32}$ and $(33)_{41}$ series alone are theoretically expected to exist.

**Polytypes based on the 4H phase**

There are four different ways in which a screw-dislocation ledge can be exposed in the 4H structure, one beginning with each layer in the unit cell:

(i) $ABCBA$ . . . 
(ii) $BCBAB$ . . .
(iii) $CBABC$ . . .
(iv) $BABCBA$ . . .

Of these (iii) and (iv) are identical with (i) and (ii) respectively, except for a rotation through $60^\circ$ about an axis parallel to [00.1] and passing through $\frac{3}{4}$ 0. Hence only two possibilities (i) and (ii) need be considered.

The structures that can result from screw dislocations of different Burgers-vector strengths can be deduced as for the case of type 6H. For example consider a screw-dislocation step of 9 layers. It can have two different structures

(i) $ABCBAABCBA$  
(ii) $BCBABCBAB$

In both cases the first and last layers are in the same orientations, so that the resulting polytypes would be 27R. Their structures can be worked out as follows:

(i) (a) Slip clockwise

$$\begin{align*}
|A^+ B^+ C^- B^- A^+ B^+ C^- B^- A^+ B^+ C^- A^- C^- B^- A^+ C^+ B^- A^- C^- | = 2222322232221 = (3222)_3 = 27R_a
\end{align*}$$

(b) Slip anticlockwise

$$\begin{align*}
A^+ B^+ A^- C^- | = (2223)_3 = 27 R_a
\end{align*}$$

(ii) (a) Slip clockwise:

$$\begin{align*}
B^- A^- C^+ A^- | = (3222)_3 = 27 R_a
\end{align*}$$

(b) Slip anticlockwise:

$$\begin{align*}
A^- C^- B^- | = (122211)_3 = 27 R_a.
\end{align*}$$
On the deduction of silicon-carbide polytypes

The results of a similar analysis for screw dislocations with Burgers-vector strengths from 1 to 12 layers are listed in Table 2. Structures corresponding to unstable dislocation gaps are put in parenthesis.

A study of Table 2 reveals that the various dislocation groups are associated with the following structure series:

<table>
<thead>
<tr>
<th>Gap</th>
<th>Structure series</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>$(22)_n = 4H$</td>
</tr>
<tr>
<td>$U_1$</td>
<td>$(22)<em>{123}, (22)</em>{2111}$</td>
</tr>
<tr>
<td>$V$</td>
<td>$(22)_{11}$</td>
</tr>
<tr>
<td>$U_2$</td>
<td>$(22)<em>{n21}, (22)</em>{n25}$</td>
</tr>
</tbody>
</table>

Table 2. *Structures resulting from dislocations of $4H(22)$*

<table>
<thead>
<tr>
<th>Burgers-vector strength</th>
<th>Dislocation gap</th>
<th>Structure of step</th>
<th>Horizontal slip, if any</th>
<th>Resulting structure</th>
<th>Polytype</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$U_1$</td>
<td>(i), (ii)</td>
<td>Cyclic or anticyclic</td>
<td>$\infty$</td>
<td>$3C$</td>
</tr>
<tr>
<td>(2)</td>
<td>(V)</td>
<td>(i), (ii)</td>
<td>No</td>
<td>(11)</td>
<td>(2H)</td>
</tr>
<tr>
<td>3</td>
<td>$U_2$</td>
<td>(i)</td>
<td>No</td>
<td>$\infty$</td>
<td>$3C$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Cyclic</td>
<td>21</td>
<td>9R</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$N$</td>
<td>(i), (ii)</td>
<td>No</td>
<td>22</td>
<td>$4H$</td>
</tr>
<tr>
<td>5</td>
<td>$U_1$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>32</td>
<td>$15R_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>23</td>
<td>$15R_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>1211</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>(V)</td>
<td>(i)</td>
<td>No</td>
<td>$(2211)$</td>
<td>(6H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>No</td>
<td>$(1221)$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$U_2$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>2221</td>
<td>21R</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>1222</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$N$</td>
<td>(i), (ii)</td>
<td>No</td>
<td>22</td>
<td>$4H$</td>
</tr>
<tr>
<td>9</td>
<td>$U_1$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>3222</td>
<td>$27R_5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>2223</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cyclic</td>
<td>3222</td>
<td>$27R_5$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Anticyclic</td>
<td>122211</td>
<td>$27R_5$</td>
</tr>
<tr>
<td>(10)</td>
<td>(V)</td>
<td>(i)</td>
<td>No</td>
<td>$(222211)$</td>
<td>(10H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>No</td>
<td>$(122221)$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$U_2$</td>
<td>(i)</td>
<td>Cyclic</td>
<td>5222</td>
<td>11H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii)</td>
<td>Anticyclic</td>
<td>222221</td>
<td>33R</td>
</tr>
<tr>
<td>12 etc.</td>
<td>$N$</td>
<td>(i), (ii)</td>
<td>No</td>
<td>22</td>
<td>$4H$</td>
</tr>
</tbody>
</table>

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If it is assumed that the gap \( V \) is unstable then structures belonging to the \((22)_{n}\), \((22)_{23}\), \((22)_{2111}\), \((22)_{21}\) and \((22)_{25}\) series alone are theoretically expected to exist.

**Polytypes based on the 15\(R\) phase**

Type 15\(R\) (23) has a structure \(|ABCBACABACBCACB|A \ldots\) and though there would be 15 possible types of ledges, one starting from each layer in the unit cell, only the first five need be considered since the other ten are related to these by a cyclic shift in \(A\), \(B\) and \(C\). The structure 15\(R\) (32) is the same as the structure 15\(R\) (23), the two being related by a rotation of the entire structure through 60° about [00.1] and a shift of origin. Thus a 60° rotation of the (23) structure about [00.1] would transfer \(A\) to \(A\), \(B\) to \(C\), and \(C\) to \(B\) giving a sequence \(|ACBCABACABCB(A)BC|A \ldots\) in which if the origin is chosen on the atom marked by parenthesis the unit cell would have a structure \(ABCACBCABACABCB = (32)_b\). Therefore, dislocation ledges in the (32) structure would yield no new results and only the following five types of ledges need to be considered:

(i) \(ABCBA \ldots\)  
(ii) \(BCBAC \ldots\)  
(iii) \(CBACA \ldots\)  
(iv) \(BACAB \ldots\)  
(v) \(ACABA \ldots\)

The polytypic structures that would result from screw dislocations of different Burgers-vector strengths may be deduced from these as for the 6\(H\) and 4\(H\) phases. For example a four-layered ledge would create a 4\(H\) (22) polytype except when it is exposed in manner (iii) when it will generate either a 12\(R\) or a 3\(C\) polytype. The structures that would result from dislocations with Burgers-vector strengths from 1 to 15 layers are listed in Table 3. Structures corresponding to unstable dislocation gaps are put in parenthesis.

A study of Table 3 reveals that the various dislocation gaps are associated with the following structure series:

<table>
<thead>
<tr>
<th>Gap</th>
<th>Structure series</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>((23)<em>{n}), ((23)</em>{32}), ((23)<em>{14}), ((23)</em>{2111})</td>
</tr>
<tr>
<td>(W)</td>
<td>((23)<em>{33}), ((23)</em>{24}), ((23)<em>{1111}), ((23)</em>{2211})</td>
</tr>
<tr>
<td>(X)</td>
<td>((23)<em>{34}), ((23)</em>{11}), ((23)<em>{25}), ((23)</em>{2212})</td>
</tr>
<tr>
<td>(Y)</td>
<td>((23)<em>{35}), ((23)</em>{21}), ((23)<em>{12}), ((23)</em>{26})</td>
</tr>
<tr>
<td>(Z)</td>
<td>((23)<em>{22}), ((23)</em>{13}), ((23)<em>{27}), ((23)</em>{2133})</td>
</tr>
</tbody>
</table>
### Table 3. Structures resulting from dislocations of 15R phase

<table>
<thead>
<tr>
<th>Burgers-vector strength</th>
<th>Dislocation gap</th>
<th>Structure of step</th>
<th>Horizontal slip, if any</th>
<th>Resulting structure</th>
<th>Polytype</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( W )</td>
<td>(i) to (v)</td>
<td>Either ( \infty )</td>
<td>( 3C )</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>( (X) )</td>
<td>(i) to (v)</td>
<td>No ( (11) )</td>
<td>( 2H )</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>( (Y) )</td>
<td>(i), (iii), (iv)</td>
<td>No ( (\infty) )</td>
<td>( 3C )</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>( 36R_{ab} )</td>
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Table 3. (Continued)

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<th>Structure of step</th>
<th>Horizontal slip, if any</th>
<th>Resulting structure</th>
<th>Polytype</th>
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<td>42R$_5$</td>
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<td></td>
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<td>7232</td>
<td>14H$_5$</td>
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<tr>
<td>15</td>
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<tr>
<td>etc.</td>
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</tr>
</tbody>
</table>

If the gaps $X$ and $Y$ are assumed to be unstable then the structural series associated with them are not expected to exist but structures belonging to all the others listed above, are theoretically possible.

Discussion

The results obtained above differ considerably from those of Mitchell. A much larger number of structure series are found to be theoretically possible. However, for some unknown reason silicon-carbide polytypes (unlike those of cadmium iodide) never involve a number 1 in their zig-zag sequence. The only exception to this is the polytype $2H$ with a sequence (11), synthesized by Adamsky and Merz by the gaseous cracking of SiCl$_4$ and C$_6$H$_5$CH$_3$ mixture in the presence of hydrogen, at a temperature between 1400—1600°C. It is, however, never found to occur in the commercial material or among the other polytypes and is presumably a separate phase of the compound altogether. While it can result from screw dislocations of Burgers vector strength 2 in any of the basic structures, such dislocations are always associated with unstable dislocation gaps. Similarly the cubic modification ($3C$) which has been recently shown to be metastable at all temperatures (Knippenberg), also perhaps

On the deduction of silicon-carbide polytypes

does not result from screw dislocations though it can be easily generated.

It was for long believed that the zig-zag sequence of silicon-carbide polytypes is restricted to the numbers 2, 3 and 4. This has been disproved by the observation of a polytype $174R$ with a structure $[(33)_46(33)_54]_3$ (Tomita $^{22}$) and a polytype $24R$ with a structure $(35)$ (Mesquita $^{23}$). However, the Ott interval sequence of all silicon-carbide polytypes known so far is confined to the numbers 2, 3 and 4 and this fact, first stated by Ramsdell $^{24}$, appears to constitute a more definite law governing the formation of silicon-carbide structures. Even if one arbitrarily leaves out the structure series containing the numeral 1, there are nine series of structures that should exist, besides the basic structures themselves. These are $(33)_n32$, $(33)_n34$, $(22)_n23$, $(22)_n25$, $(23)_n32$, $(23)_n33$, $(23)_n24$, $(23)_n22$ and $(23)_n27$.

The known polytypes belonging to each of these series are listed in Table 4. The $(33)_n32$ series has the largest number of members, then come in order $(33)_n34$, $(22)_n23$, $(23)_n32$, $(23)_n23$ and $(23)_n22$ series. All the other series represent polytypes that have not so far been observed.

In addition to the above polytypes silicon carbide is known to display the structures $[(33)_46(33)_54]_3 = 174R$ (Tomita $^{22}$), $[(33)_234(33)_232]_3 = 36H$ (Krishna and Verma $^8$), $[(23)_33232]_3 = 75R$ (Ramsdell and Kohn $^3$), $[(23)_3322]_3 = 90R$ (Krishna and Verma $^8$), $(23)_33333 = 27H$

<table>
<thead>
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<th>Serial No.</th>
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<th>Known polytypes</th>
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<tr>
<td>2</td>
<td>$(33)_n34$</td>
<td>$21R$, $39R$, $57R$, $111R$</td>
</tr>
<tr>
<td>3</td>
<td>$(22)_n23$</td>
<td>$15R$, $27R$, $51R_8$</td>
</tr>
<tr>
<td>4</td>
<td>$(22)_n25$</td>
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</tr>
<tr>
<td>5</td>
<td>$(23)_n32$</td>
<td>$15R$, $10H$</td>
</tr>
<tr>
<td>6</td>
<td>$(23)_n33$</td>
<td>$6H$, $33R$</td>
</tr>
<tr>
<td>7</td>
<td>$(23)_n24$</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>$(23)_n22$</td>
<td>$4H$, $19H$</td>
</tr>
<tr>
<td>9</td>
<td>$(23)_n27$</td>
<td>None</td>
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</tbody>
</table>


$^{24}$ Lewis S. Ramsdell, The crystal structure of α-SiC type VI. Amer. Mineralogist 30 (1945) 519—525.
The suggestion that rhombohedral polytypes originate when the first and last layers of the exposed ledge are in the same orientation not only resolves the difficulty of explaining the formation of rhombohedral polytypes but also predicts certain limitations on the structure of polytypes. Thus according to this, a structure \((pn + 1)H\) cannot be based on a \(p\)-layered polytype since a ledge of \((pn + 1)\) layers exposed in a structure \(pH\) or \(pR\) will invariably have the first and last layers in the same orientation, resulting in a polytype \(3(pn + 1)R\). No structures known so far contradict this. Indeed conversely it should be possible to assume both end-layers of rhombohedral units in any rhombohedral structure of SiC to be at the same sites \(A\), \(B\) or \(C\). It is easy to see that this can be done by a suitable choice of origin. Thus, consider a pair of layers \(AB\) (or \(BC\) or \(CA\)) in the structure of any polytype \(nR\). Then due to rhombohedral symmetry there would be, after \(\frac{n}{3}\) layer spacings, a corresponding pair of layers \(BC\) (or \(CA\) or \(AB\)) respectively. If the origin is chosen on the second layer of the pair \(AB\) (or \(BC\) or \(CA\)), the rhombohedral unit would have the first and last layers in the same orientation \(B\) (or \(C\) or \(A\) respectively).

On the basis of this criterion, it is possible to predict whether a screw-dislocation ledge of \(n\) layers will generate a polytype \(nH\) or \(3nR\). This is in complete accordance with the experimentally observed fact that the step height of growth spirals on hexagonal polytypes is equal to the height of the x-ray unit cell while that on rhombohedral polytypes is one-third this height (Verma\(^{12}\)). The suggestion also accounts for the non-existence of rhombohedral polytypes in CdI\(_2\), where the exposed ledge cannot have the first and last layers in the same orientation whatever the manner of exposing it (Srivastava and Verma\(^{27}\)).

Review Article

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Crystal-Polymorphism in One Dimension

By

P. Krishna and Ajit Ram Verma

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References

1) Now at the National Physical Laboratory, New Delhi.
1. Introduction

Some of the simple inorganic substances, like SiC, CdI₂, and ZnS, exhibit a complex one-dimensional polymorphism, called polytypism. Despite the simple proportions of atoms in these compounds they occasionally crystallize into fairly complicated structures known as polytypes. Initially this was believed to be a peculiar structural feature displayed by a few odd compounds; but it is now known to be a more general phenomenon affecting a large number of substances with close-packed as well as layer structures. In these structures the first coordination of some atom can be satisfied in more than one way, usually equivalent to cubic versus hexagonal close-packing. The different polytypic modifications called polytypes can be considered to result from different manners of stacking identical layers of structure over each other at a constant interval. They therefore have identical unit-cell dimensions in two directions lying in a plane parallel to the stacked layers and differ only in the direction perpendicular to the layers. The unit-cell dimension perpendicular to the layers is an integral multiple of the separation between successive layers of structure. It varies from polytype to polytype and may range from 5 Å in the small-period modifications to over 1000 Å in some of the long-period polytypes. Structurally, polytypism may be included within the definition of polymorphism but physically it is quite distinct from the latter since it does not appear to be governed by the same thermodynamic factors.

Polytypism was first discovered in SiC, which has a close-packed tetrahedral structure. It exhibits a large number of beautifully crystalline polytypic modifications. Partly due to this and partly because of its increasing industrial importance as a high-temperature semiconductor, SiC is the most widely investigated of all the polytypic substances. Nearly all the theories of polytypism have been put forth to explain the polytypism in this compound, in the first instance. We shall therefore regard SiC as a good representative example of all polytypic substances and dwell on the polytypism of this compound in greater detail. Similar considerations can, however, be extended to other polytypic substances. Like SiC, most of the other polytypic substances also have a close-packed structure with one kind of atoms occupying positions corresponding to those of equal spheres in a close-packing and the other atoms distributed among the voids. The special notations evolved for describing polytypic structures of a compound are therefore based on the geometry of close-packing equal spheres.

The first comprehensive explanation of polytypism came as an offshoot of the dislocation theory of the spiral growth of crystals, some fifteen years ago. It was only then that the phenomenon of polytypism came into limelight in physics. It has since been a subject of an increasingly large number of investigations. While the dislocation theory of polytypism was very successful in explaining certain aspects of the problem, there were others in which it failed. Consequently several alternative explanations have been advanced during the last one decade. It has been suggested that polytypism is not a growth feature, as suggested by the dislocation theory, but is governed by thermodynamic factors. That it could result from second-order phase-transformations or from the influence of lattice vibrations on the growth front has also been considered. However, none of the explanations has so far succeeded in satisfactorily answering all aspects of the problem.
In recent years a large number of experimental investigations have been conducted to determine which of the various theories best explains the observed facts. These investigations include studies of the actual growth process, the surface structure of crystals as determined by phase-contrast microscopy and multiple-beam interferometry, the internal structure of crystals as determined by X-ray diffraction methods, the electronic band structure as determined by optical absorption or electrical measurements, and the dislocation structure as observed by transmission electron microscopy as well as X-ray microscopy.

This paper describes the above developments after enunciating the problem of polytypism and the factors influencing it. The results of the recent experimental investigations are discussed in the light of the existing theories of polytypism and the present position summed up.

2. Polymorphism

Polymorphism has long been recognized as the ability of a chemical compound to exist with more than one crystal structure. The different modifications or polymorphs are known to be definite thermodynamic phases of the substance, whose relative stabilities are governed by their free energies. From a purely theoretical point of view any crystalline arrangement of the atoms of a solid represents a possible polymorphic modification. There is an indefinite number of possibilities, ranging from a simple periodic arrangement of the atoms in one dimension, to complicated three-dimensional packings. Each one of these is characterized by an internal energy $E$ that depends on the forces bonding the atoms together, a volume $V$ that depends on the density of packing and an entropy $S$ which depends on the state of order in the crystal lattice. At a temperature $T$ and pressure $P$, each modification therefore has a Gibbs' free energy $G$, given by

$$G = E - T S + P V$$

and the particular structure for which this is minimum is thermodynamically the most stable (state) at that temperature and pressure. If the conditions of temperature and pressure are changed, the free energies of the different modifications change, and it may happen that some other structure has the least free energy under a different set of external conditions. The substance will therefore tend to undergo a structural transformation which is a phase-transition of the first order, with a discontinuous change in the internal energy, entropy, and volume of the substance, accompanied by an abrupt change of almost all the physical properties. Such phase-transitions between polymorphs are quite common and have been widely investigated. A great majority of substances are now known to undergo structural transformations when subjected to extreme temperatures and pressures. Two recent instances of this are:

1. the polymorphic transition in NaCl from its f.c.c. structure to CsCl-type structure, with a simple cubic lattice [1] (this occurs at a pressure of about 18000 atm)
2. the conversion of graphite into diamond at pressures of the order of 75000 atm, and a temperature around 1800 °C in the presence of “catalysts” like Cr, Mn, Co, Ni, Pd, Pt, and Fe$_3$O$_5$.

The polymorphic transitions are in many respects completely analogous to the changes of state from solid to liquid or liquid to vapour. Both are first-order phase-transformations accompanied by a discontinuous change in volume and the evolution or absorption of latent heat. They obey the Gibbs' phase rule
as well as the Clausius-Clapeyron equation. There is, however, one essential difference between the two. While changes of state are almost instantaneous, the velocity of polymorphic transitions varies nearly from zero to infinity. Unlike changes of state the structural transformations face an energy-barrier which depends on the structural bonds that have to be disrupted during the transition from one structure to another. The transition therefore requires an activation energy, which when not available causes the substance to exist in a metastable state. This common occurrence of metastable states leads to the simultaneous existence of two or more modifications of a substance under the same conditions of temperature and pressure. Indeed it is not uncommon to find two modifications of a substance both occurring as minerals in nature.

It has not been possible to calculate theoretically the relative stability of different crystalline phases from the properties of isolated atoms and molecules, because the changes of internal energy and entropy between phases is ordinarily quite small and the errors in calculating these are much larger than the magnitude of the differences being sought. It has therefore not been possible to predict theoretically, which of two phases should be stable under given conditions or where the equilibrium line between them should lie. Nor is it possible to predict which substances should be polymorphic and which should not be. However, the phenomenon of polymorphism is at least qualitatively fairly well understood on thermodynamic grounds and though it is not possible to make quantitative predictions, it has been possible to correlate general thermodynamic features with specific structural characteristics. For a detailed account of this the reader is referred elsewhere [2, 3].

3. Polytypism

3.1 Polytypism and silicon carbide

The phenomenon of polytypism falls, structurally, within the definition of polymorphism, since the latter, according to Barth [4] "includes every possible difference encountered in the crystal structure of a substance, excepting homogeneous deformations". The assignment of a separate name to it has often been criticized; but a little consideration reveals that polytypism is physically quite distinct from ordinary polymorphism since it does not appear to be governed by the thermodynamic factors discussed above.

Consider the polytypism in SiC. This substance is known to crystallize into more than 45 different modifications, all of which have the same tetrahedral arrangement of Si and C atoms, with each Si surrounded by 4 C and each C by 4 Si. The structure is close-packed with one kind of atoms in positions corresponding to those of equal spheres in a close-packing and the other distributed among half the tetrahedral voids. That is, the structure consists of two identical interpenetrating close-packings, one of Si atoms and the other of C, with the one displaced relative to the other along the c-axis through one-fourth of the layer spacing. The different polytypic modifications correspond to different manners of close-packing equal spheres and their structure is therefore appropriately described by the ABC notation for the close-packing of spheres. All modifications can be regarded as built of identical atomic layers of structure stacked on top of each other at equal intervals of 2.518 Å. They differ only in the stacking-sequence of these layers.
The most common modification is a 6-layered hexagonal polytype, called 6H with a stacking sequence ABCACB of layers in its hexagonal unit cell. The second commonest polytype has a rhombohedral lattice with 15 layers in its hexagonal unit cell, and a stacking sequence ABCBACABACBCACB. It is denoted as 15R. The third common modification is type 4H with a stacking sequence ABCB of layers in its hexagonal unit cell. The structure of these modifications was first worked out by Ott [5 to 7] and is shown in Fig. 1. All modifications have the same hexagonal unit-cell dimensions along two directions, \( a = b = 3.078 \, \text{Å} \), while the third \( c = 2.518 \times n \, \text{Å} \) where \( n \) is the number of layers in the hexagonal unit cell. The silicon-carbon bond is 1.889 Å long and is known to be strongly covalent.

Modifications corresponding to the cubic close-packing ABC, ABC . . . and the hexagonal close-packing AB, AB . . . are also known but do not normally occur along with the other polytypes. The cubic modification, 3C, which has a structure analogous to diamond (with half the carbon atoms replaced by silicon), normally forms at a comparatively lower temperature, around 1800 \( ^\circ \text{C} \), and transforms irreversibly into the 6H modification on heating above 2000 \( ^\circ \text{C} \). It is therefore believed to be a separate thermodynamic phase of the compound and is denoted as \( \beta \)-SiC. All the other modifications are denoted as \( \alpha \)-SiC. \( \beta \)-SiC was for a long time believed to be the low-temperature modification of SiC, but recent observations of Knippenberg [8] suggest that it is probably metastable at all temperatures. The 2H modification, AB, AB . . . , has a structure analogous to the wurtzite form of ZnS, and has been synthesised by a special
process of gaseous cracking [9] at temperatures of 1400 to 1600 °C. Neither of these two modifications occur normally in the commercial SiC manufactured by the Acheson process at temperatures around 2500 °C by passing an electric arc through a mixture of sand (SiO₂) and coke (C).

In addition to the above comparatively small-period modifications, silicon carbide also crystallizes in a large number of less common long-period polytypes with c-spacings ranging from 50 up to 1500 Å or more. Some of these are beautifully crystalline structures while others are accompanied by a certain measure of random disorder. Fig. 2 shows the 10./ reciprocal lattice rows of some long-period polytypes of SiC as recorded on c-axis oscillation photographs. The polytype 90R gives discrete and sharp X-ray reflections indicating a perfectly crystalline structure with a periodicity c = 226.6 Å (Fig. 2a). The 10./ row of spots recorded from the 57R polytype (Fig. 2b) shows a faint streak connecting sharp reflections indicating a small amount of superposed random disorder of layers. Fig. 2c shows the 10./ row of a polytype with a much greater amount of random one-dimensional disorder, but even in this a tendency towards the formation of long-range periodicities is evident on closer inspection (see Fig. 2d). It is these long-period polytypes that constitute the major problem of polytypism.

3.2 The problem of polytypism

The different polytypic modifications of α-SiC present little evidence of being definite thermodynamic phases of the compound. They appear to form together under nearly the same conditions of temperature and pressure. Thus a single lump of commercial SiC often contains a number of different modifications, two or more of which are frequently coalesced. Within the same single-crystal piece, two different structures have even been reported [10, 11]. Even if there is some vaguely defined temperature-structure relationship it is only for the more-common small-period polytypes. Unlike the ordinary polymorphic phases, SiC polytypes have almost identical physical properties. Thus the density of all modifications is 3.217 g/cm³ and the indices of refraction are nearly constant [12].

No polymorphic transformations between polytypes (other than the β-α-transformation) have ever been observed. Polytypes do not transform into one another on heating [13], nor are they expected to do so under pressure since they all have the same density.
The Si and C atoms in all modifications have the same first and second nearest neighbours, and since homopolar forces are known to fall off rapidly with distance, the different polytypes must have very nearly the same internal energy $E$. In fact two or more long-period polytypes often have structures in which most of the atoms have identical environments up to very distant coordinations. They also have the same density and hence occupy the same volume for a given mass. At any temperature and pressure the thermodynamically stable state of minimum free energy $E - TS + PV$ must therefore correspond to maximum of entropy $S$. This probably means the structure should be completely disordered in one dimension. It should be noted, however, that entropy differences due to one-dimensional disorder are also small compared to the total entropy of the crystal, but they might still influence the free energy sensitively because of the high temperature ($\approx 2500 \, ^{\circ}C$) at which SiC is normally formed.

However, SiC never forms completely disordered crystals. The structures observed are either completely ordered or partially disordered. The periodicities in a number of long-period polytypes are very much larger than the range of any known atomic forces, and this poses two vital questions:

1. Do the different SiC polytypes have any thermodynamic stability?
2. What is the nature of the forces that occasionally cause a strict ordering of the layers over several hundreds of Angstroms?

Several different explanations have been put forth during the last decade or so. Polytypism has been regarded as a growth feature, originating from the screw dislocation mechanism of crystal growth. It has also been considered to arise from an orderly distribution of stacking faults caused by a layer-transposition mechanism governed by the vibration entropy of the structure. The vanishingly small differences in the internal energy of polytypes has led Schneer to regard them as related by phase-transformations of the second order. The influence of lattice vibrations of the growth front during crystallization has also been suggested as a possible cause of polytypism. The explanations are discussed later but we wish to emphasize here that though polytypism is structurally a form of polymorphism, it is physically quite distinct from it.

4. Description of Polytypic Structures

4.1 Common notations of polytypic structures

Since polytypic structures of a compound are both numerous and closely related to each other, special notations have been evolved to describe and differentiate between them. A brief summary of the notations employed in this paper follows.

4.1.1 The Ramsdell notation [14]

This is by far the commonest notation used to denote a polytype whose unit cell and lattice type have been determined. It consists of a number denoting the number of layers in the unit cell of the polytype, followed by a capital letter denoting the lattice type. Thus a polytype $nH$ denotes a hexagonal polytype with a stacking sequence that repeats after $n$ layers. By a “hexagonal polytype” is meant a polytype with a hexagonal lattice; it may belong to either the hexagonal or the trigonal systems. A symbol $nR$ denotes a polytype with a rhombohedral lattice having $n$ layers in its hexagonal unit cell.

The symbol does not tell the actual arrangement of layers in the unit cell. Indeed two polytypes may have the same Ramsdell symbol but different struc-
natural arrangement of the layers. In such cases it is customary to distinguish them by using subscripts $a$, $b$, $c$, etc., after the symbol. For example, two known polytypes of SiC with identical lattice dimensions but different structures are designated as $51R_a$ and $51R_b$. The notation is applicable to all polytypic substances, including those that are not close-packed, and is the only suitable notation to designate polytypes with an undetermined structure but known lattice.

### 4.1.2 The classical ABC notation

Most of the polytypic substances have a close-packed structure, which can therefore be described in terms of the classical ABC notation for close-packings of spheres. Thus the SiC type 6H has six Si and six C layers in its hexagonal unit cell stacked as $\text{AxB}\gamma\text{C}\gamma\text{AxC}\gamma\text{B}$, where the Roman letters denote positions of layers of Si atoms and the Greek letters those of C atoms. Since the positions of C atoms are fixed relative to the Si atoms, it is customary to omit the Greek letters and write the structure as $\text{ABCACB}$. The SiC polytype 15R has a stacking sequence $\text{ABCABCACABACBCACB}$, for the 15 layers in its hexagonal unit cell.

In case of CdI$_2$ polytypes, where the Cd atoms lie in octahedral voids between successive close-packed iodine layers, it is customary to retain the Greek letters as well to denote the positions of Cd layers. Thus CdI$_2$ type 4H has a structure $(\text{A}\gamma\text{B})(\text{CzB})$ and type 10H a structure $(\text{A}\gamma\text{B})(\text{CzB})(\text{A}\gamma\text{B})(\text{CzB})(\text{A}\gamma\text{B})$.

### 4.1.3 Hågg’s notation [15]

The structure of a polytype can also be described in terms of the relationship between successive layers of structure. Thus a passage from A to B, B to C, or C to A involves a translation $\frac{1}{3}, \frac{2}{3}$ in the basal plane, while a passage from B to A, C to B, or A to C involves a translation of $\frac{2}{3}, \frac{1}{3} = -\frac{1}{3}, -\frac{2}{3}$. Hågg denoted the former by a plus (+) sign and the latter by a minus (−) sign. A structure $\text{ABAB...}$ is thus represented as $++−+−−...$, while the structure $\text{ABCACB}$ is denoted as $+++−−−...$. If $n_+$ and $n_−$ denote the number of (+)- and (−)-signs required to complete the hexagonal unit cell then $n_+−n_−=3r$ for hexagonal polytypes and $n_+−n_−=3r+1$ for rhombohedral polytypes where $r$ is any positive or negative integer including zero.

### 4.1.4 The Zhdanov symbol [16, 17]

Zhdanov proposed [16] a numerical symbol for describing the close-packings of equal spheres and later [17] used it to describe the polytypic structures of SiC. The symbol consists of a series of numbers which denote alternately the number of (+)- and (−)-signs in the Hågg symbol. Thus the structure $\text{ABAB...}$ which in Hågg’s notation is $++−+−−...$ is denoted as $(11)$. Similarly the structure $\text{ABCACB}$ with Hågg’s notation $+++−−−...$ is denoted as $(33)$. In the case of rhombohedral polytypes the symbol needs to be repeated thrice before completing a hexagonal unit cell. Thus SiC type 15R is denoted as $23\ 23\ 23$ and is written as $(23)$. Ramsdell [14] interpreted the symbol in terms of the zig-zag sequence of Si and C atoms in the $(1120)$ plane of a SiC polytype. This is by far the most convenient and concise notation to describe the structure of polytypes.

### 4.1.5 Notation used by Pauling [18], Wyckoff [19], and Jagodzinski [20]

These authors have found it more useful to specify each layer in terms of the orientation of layers above and below it. A layer surrounded on either side by
layers in the same orientation (A, B, or C) is denoted as h, because it has the same surroundings as a layer in the hexagonal close-packing ABAB……. A layer surrounded on the two sides by layers in dissimilar orientations is denoted as c since it is like a layer in the cubic close-packing ABCABC……. Thus the SiC type 6H structure (ABC ACB) is denoted as hcc and SiC type 15R as hcchec. The notation is useful in describing the configuration-statistics of one-dimensionally disordered structures and for calculating the interaction energy between layers.

It is quite easy to transform one notation to another. It is probably most convenient to write first the full ABC sequence of the structure and then express this in the desired notation.

4.2 The known polytypes of SiC

Polytypism was first discovered by Baumhauer [21] (1912) from his optical studies of the morphology of SiC crystals. He found evidence of the existence of three different modifications later identified as 6H, 15R, and 4H, the three commonest polytypes. The complete structure of these was first determined by Ott [5 to 7] (1925). The structure of the cubic modification (p-SiC) had earlier been reported by Hull [22] (1919).

Since then over 45 different polytypes of SiC have been discovered by different workers from X-ray investigations and the structure of over 25 of these is known. Table 1 lists all the known modifications along with the Zhidanov symbols of known structures. The known structures have been classified according to the “basic phase” 6H, 15R, or 4H, which they resemble most. It should be noted, however, that there is no evidence at all to indicate that these are definite thermodynamic phases of the compound. This classification is merely for the convenience of discussing their growth in terms of the dislocation theory of polytypism. The lattice constants of the different polytypes are not stated since the hexagonal unit cell in all of them has very nearly the dimensions

\[ a = b = 3.078 \text{ Å} , \quad c = 2.518 \text{ Å} \times n , \]

where \( n \) is the number of layers in the hexagonal unit cell. Small variations from these values have been reported but these are perhaps not very significant and may possibly be attributed to variable impurity contents.

The crystals in which the different SiC polytypes have been discovered are mostly flat platelets parallel to (0001). This is the most prominent face of the crystals and often exhibits growth spirals. A number of structures listed in Table 1 have been found intergrown with each other in parallel growth along the \( c \)-axis. This “syntactic coalescence” of different types is of common occurrence in SiC and so is twinning. The latter occurs with the line of contact parallel to an edge [11.0] of the hexagonal basal faces and with an angle between these faces approximately equal to the octahedral angle of the cubic system, 70°31’44”.

The syntactic coalescence of two or more structures can cause a seemingly single-crystal piece to have different polytypic structures in different regions. Perhaps the only instance of a change in structure occurring within the same single-crystal piece is that noticed in SiC type 36H. The upper and lower parts of this single-crystal piece were found to have two different structures designated [11] as 36Hₐ and 36Hₐ. Both have identical unit cell dimensions and space groups, but differ in the arrangement of layers within the unit cell. This differs
### Table 1

#### Known polytypes of SiC

<table>
<thead>
<tr>
<th>No.</th>
<th>Polytype (Ramsdell notation)</th>
<th>Structure (Zhdanov notation)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Structures based on the 33 phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6H</td>
<td>33 (3332)₃</td>
<td>Most common polytype</td>
</tr>
<tr>
<td>2</td>
<td>33R</td>
<td>[(33),32]₃</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>51R₃</td>
<td>[(33),32]₃</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>87R</td>
<td>[(33),32]₃</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>105R</td>
<td>[(33),32]₃</td>
<td>Ordered structure</td>
</tr>
<tr>
<td>6</td>
<td>141R</td>
<td>[(33),32]₃</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>393R</td>
<td>[(33)₅32fi]₃</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>21R₃</td>
<td>(34)₃</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>39R₃</td>
<td>(3334)₃</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>67R₃</td>
<td>[(33),34]₃</td>
<td>Structure has superposed random disorder</td>
</tr>
<tr>
<td>11</td>
<td>111R₃</td>
<td>[(33),34]₃</td>
<td>Beautifully ordered structure</td>
</tr>
<tr>
<td>12</td>
<td>16H₃</td>
<td>[(33),22]</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>84R₃</td>
<td>[(33),3232]₃</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>99R₃</td>
<td>[(33),3222]₃</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>174R₃</td>
<td>[(33),6(33),4]₃</td>
<td>Only known polytype with a 6 in the Zhdanov symbol</td>
</tr>
<tr>
<td>16</td>
<td>36H₃₂₃</td>
<td>[(33),32(33),34]</td>
<td>Shows unusual extinctions on X-ray photos</td>
</tr>
<tr>
<td>17</td>
<td>39H₃₂₃₃₃₃₀₂₂₃</td>
<td>[(33),32(33),3232]</td>
<td></td>
</tr>
<tr>
<td>B. Structures based on the 23 phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>15R₃</td>
<td>(23)₃</td>
<td>Second commonest polytype</td>
</tr>
<tr>
<td>19</td>
<td>19H₂₃</td>
<td>[(23),22]</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>10H₂₃</td>
<td>2332</td>
<td>Simulated hexagonal symmetry on X-ray photo</td>
</tr>
<tr>
<td>21</td>
<td>75R₃</td>
<td>[(23),3232]₃</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>27H₃₂₃₃₃₃₃₃₃₃</td>
<td>(23),3333</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>90R₃₂₃₃₃₃₃₃₃₃</td>
<td>(23),3322]₃</td>
<td>Beautifully ordered structure</td>
</tr>
<tr>
<td>24</td>
<td>108R₃₂₃₃₃₃₃₃₃₃</td>
<td>[(23),33]₃</td>
<td>Structure not certain</td>
</tr>
<tr>
<td>C. Structures based on the 22 phase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>4H₂₃₃₃₃₃₃₃₃₃₃</td>
<td>(22)</td>
<td>Third commonest polytype</td>
</tr>
<tr>
<td>26</td>
<td>27R₃₂₃₃₃₃₃₃₃₃</td>
<td>(22),23]₃</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>51R₃₂₃₃₃₃₃₃₃₃</td>
<td>[(22),23]₃</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>18H₂₃₃₃₃₃₃₃₃₃</td>
<td>(22),33]₃</td>
<td></td>
</tr>
<tr>
<td>D. Miscellaneous structures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>β-SiC₂₃₃₃₃₃₃₃₃₃</td>
<td>(∞)</td>
<td>Usually forms at lower temperatures (∼1800 °C)</td>
</tr>
<tr>
<td>30</td>
<td>2H₂₃₃₃₃₃₃₃₃₃</td>
<td>(11)</td>
<td>Not found in commercial SiC; grown by special method of gaseous cracking; a = 3.076 Å, c = 5.048 Å</td>
</tr>
<tr>
<td>31</td>
<td>8H₂₃₃₃₃₃₃₃₃₃</td>
<td>(44)</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>24R₂₃₃₃₃₃₃₃₃₃</td>
<td>(53)₃</td>
<td></td>
</tr>
</tbody>
</table>
from the observations of Edwards and Lipson [25] and Wilson [26] in cobalt, where "the structure possesses a lattice in which the unit cells are all of the same size and shape but the distribution of atoms within the unit cell varies throughout the crystal", in that the distribution of atoms has changed more or less abruptly across a (0001) plane. A situation like that in cobalt has never been encountered in SiC.

A number of polytypes show tendency towards the formation of structure series with a sequence of 33, 23, or 22 units associated with faults at the end. This was first discovered by Ramsdell [14] who predicted the existence of many series. The \([(33)_b32_{b\bar{h}}\) series of structures has the largest number of known members. The X-ray diffraction from this series of structures has been studied in detail by Mitchell [23]. A similar study of the \([(33)_b34_{b\bar{h}}\) series of structures has been done by Krishna and Verma [24]. Empirical rules have been laid down for the identification of other members of the series without intensity calculations.

The Zhdanov symbol for most of the structures is restricted to the numbers 2, 3, and 4. The only known exceptions to this are \(\beta\)-SiC, 2H, 174R, and 24R. Even for these the interval between successive atoms along any of the three symmetry axes, parallel to \([00.1]\) and passing through \(000\), \(2/3\ 1/3\ 0\), and \(1/\bar{3}\ 2/\bar{3}\ 0\), is limited to 2, 3, or 4 layer spacings. No theoretical reason has so far been assigned for this fact.

---

Table 1 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Polytype (Ramsdell notation)</th>
<th>Structure (Zhdanov notation)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>24H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>33H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>36H(_b)</td>
<td>Based on 33 phase</td>
<td>Found in the same single crystal piece with 36H(_b)</td>
</tr>
<tr>
<td>36</td>
<td>48H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>54H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>66H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>72R</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>78H</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>120R</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>124R</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>126R</td>
<td>-</td>
<td>Completely ordered structure</td>
</tr>
<tr>
<td>44</td>
<td>192R</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>(\approx270)R</td>
<td>([23]<em>{1,22}) or ([23]</em>{1,33})</td>
<td>Structure not certain</td>
</tr>
<tr>
<td>46</td>
<td>(\approx400)H or (\approx1200)R</td>
<td>-</td>
<td>Known polytype with largest unit cell; (c \approx 1500) A</td>
</tr>
<tr>
<td>47</td>
<td>594R</td>
<td>-</td>
<td>X-ray photos show continuous streaks along reciprocal lattice rows parallel to (c^*)</td>
</tr>
</tbody>
</table>

48 Disordered polytypes (several)
All the hexagonal polytypes belong to the space group P3m1 except the types 2H, 4H, 6H, and 8H which belong to P6₃mc. The rhombohedral polytypes have space group R3m. Some structures have a random disorder of layers superposed over the existing order, while others are beautifully ordered. No structure with a completely disordered arrangement of layers has been reported.

4.3 Other polytypic substances

For a long time polytypism was believed to be a special structural feature of SiC crystals. It is now known to be a more general phenomenon exhibited by several close-packed and layer structures. Thus polytypism has been reported in zinc sulphide, cadmium iodide, cadmium bromide, lead iodide, molybdenum disulphide, niobium and tantalum selenides, graphite, potassium cobalticyanide, coquimbites, chlorites, china-clay minerals, micas, manganpyrosmalite, hexagonal ferrites, crenstedtite, and other layer silicates as well as certain long-chain organic compounds. This is possibly not an exhaustive list since more and more substances are being discovered to be polytypic. For a detailed description of the various polytypic structures of all these compounds the reader is referred to a separate publication [3]. No polytypic substance, however, appears to crystallize into such a large number of beautifully ordered long-period structures as SiC.

Zinc sulphide, which has a structural similarity to SiC has at least ten different polytypes. The structures are both rhombohedral as well as hexagonal. Some of the known polytypes are 2H, 4H, 6H, and 15R, all of them isotypic with SiC. Others such as 8H, 10H, 9R, 12R, and 21R have been more recently reported [27, 28] to occur as minerals.

Cadmium iodide probably exhibits the largest number of polytypic modifications with over 64 different types already identified. All modifications of this compound have a hexagonal lattice and the absence of rhombohedral structures can be understood in terms of the dislocation theory. A random one-dimensional disorder of layers is much more common than in SiC, but there is evidence of the formation of at least two structure series, (22)₉₁, 11 and (22)₆₁,1111. In contrast lead iodide and cadmium bromide, which are structurally similar, display polytypism on a very limited scale, while cadmium chloride is not polytypic at all.

Polytypism in all these compounds is known to be strongly dependent on the mode of growth of the crystals. Thus crystals grown from solution and those grown from vapour show polytypism to different extents. The most common modification is also different for each compound, but no polymorphic transformations between polytypes have been observed.

5. Factors Influencing Polytypism

Several different factors have been found to affect the formation of polytypic structures. As early as 1912 Baumhauer [21] attempted to correlate the first few polytypes of SiC with their colours. He stated that the green crystals were type 6H, the yellow crystals type 15R while the dark blue or black crystals represented all three types. But an extensive optical and X-ray study of SiC crystals by Thibault [12] failed to establish any well-defined correlation. He suggested that the differences in colour might be due to different impurity contents. It was suggested by Zhdanov and Minervina [17] that the accumulation of impurities on the face of a growing crystal might cause a periodic disturbance resulting in the formation of different polytypes.
The correlation of structure-type with impurity-content was first established for SiC by Lundqvist [29] from a spectrochemical analysis of the first three types of crystals. Type 6H was found to be characteristic of pure SiC, type 15R of SiC with moderate amounts of Al, and type 4H of SiC saturated with Al. Other impurities, such as Mg, Mn, and Fe, showed no such correlation with structure type.

Recently Hayashi [13] has confirmed the correlation between structure type and the content of Al as impurity. From a chemical and X-ray powder analysis he has concluded that 6H crystals lie in two ranges of Al impurity, one from 0.00 to 0.05% and the other from 0.10% to 0.30%; the 15R crystals lie in the Al range of 0.05% to 0.1% while the 4H crystals have an Al content of more than 0.3%.

The role of impurities in the stabilization of polytype is not known and no such correlation has been attempted for the longer-period polytypes. Knippenberg [8] examined SiC crystals grown at a fixed temperature with different amounts of Al impurity and found no correlation between the structure type and impurity content. He concluded that the impurity–structure relationship observed by other workers might really have been a temperature–structure relationship. However, the fact that the very high purity SiC crystals display little or no polytypism indicates that impurities play a role in the formation of polytypes.

In cadmium iodide the formation of the more common modifications like 4H and 2H is reported [30, 31] to be related to some extent to the rate of crystallization from solution. It has been found that at a constant temperature of formation the 4H structure is obtained at low speeds of crystallization, the highly disordered structures at very fast speeds of crystallization, while intermediate speeds give rise to type 2H.

The control of temperature on the formation of polytypic structures has been considered both for ZnS [32, 33] as well as for SiC [34 to 36]. It was concluded by Müller [32] from his X-ray investigations of one-dimensional disorder in ZnS that the various polytypes represent transition states intermediate between the zinc blende (3C) structure and the wurtzite (2H) structure. He believed these states to be formed in a temperature range intermediate between the stability ranges of 3C and 2H structures, a range in which the free energies of the hexagonal and cubic close-packings are equal. This view was supported by Smith [33] who stated that below the 3C to 2H transition temperature of 1024 °C, but close to it, there is a range of the existence of various polytypes with mixtures of cubic and hexagonal close-packings. He believed that it is, in principle, possible to predict theoretically the polytype most likely to crystallize under a set of given conditions. Thus the polytypes were believed to be definite thermodynamic states of the compound.

A completely analogous view is held by Jagodzinski [34, 35] for SiC polytypes. He regards the 3C modification to be stable between 1600 to 2000 °C and the 6H modification to be stable around 2500 °C. All the other polytypic structures (except 2H) are believed to form in a temperature range around 2000 °C. It is suggested that in this range it is the vibration entropy of the structure that determines the polytype. This explanation will be discussed later. Experimental investigations of SiC structures obtained in various zones of a graphite furnace confirm the temperature-structure relationship suggested by Jagodzinski [35].

While there appear to be fairly definite ranges of temperature for the formation of polytypic structures, it is not known if each structure is characterized by
a definite temperature of formation. No solid-state transitions between polytypes have been found to occur with changes of temperature [13]. More recent observations of Knippenberg [8] indicate the temperature-structure relationship plotted graphically in Fig. 3. According to him the 3C modification is metastable at all temperatures and forms first in accordance with the Ostwald rule. The 2H modification is a low-temperature modification forming between 1300 and 1600 °C, while all the other polytypes are formed in the temperature range from 2000 to 2750 °C with the probability distribution shown in Fig. 3.

6. The Dislocation Theory of Polytypism

The first satisfactory explanation of polytypism came as an offshoot of the dislocation theory of crystal growth put forth by Burton, Cabrera, and Frank [37] (1951). The mechanism of spiral growth required that crystal surfaces should exhibit growth spirals whose shape should be in accordance with the symmetries of the crystal. There followed an intensive search for growth spirals on the crystal surfaces of various substances. Some of the first few substances on which growth spirals were observed included two polytypic substances, SiC and CdI₂. A large number of beautiful growth spirals were observed and photographed on SiC crystals by Verma [38 to 40] and Amelinckx [41, 42] by the technique of phase-contrast microscopy. Verma measured the step-height of growth spirals and showed them to be equal to the height of the X-ray unit cell. These results led Frank [43] to suggest that polytypism in SiC might be brought about by the spiral growth of crystals round screw dislocations of different Burgers vectors.

That the regular spiral growth of the (0001) face of SiC crystals could bring about the formation of the many-layered “superstructures” had been inferred much earlier by Lemmelin [44, 45] in Russia from a study of the appearance of growth spirals on these faces. Knowing of Lemmelin’s work, Zhdanov and Minervina [46] had also suggested tentatively that polytypism might be connected with the formation of spirals on SiC basal faces. However, no details concerning this mechanism were given and neither Lemmelin nor Zhdanov and Minervina correlated the occurrence of these spirals with screw dislocations in the structure. In fact spiral markings had also been observed on SiC by Tone [47] (1908), Menzies and Sloat [48] (1929), Padurow [49] (1949), and Kalb and Wittbog [50] (1951), but not much significance was attached to these observations. Their correct interpretation came from the dislocation theory put forth by Frank.
6.1 Frank's theory [43, 51]

According to Frank, SiC crystals grow initially, at high supersaturations, into thin plates by the surface-nucleation mechanism in accordance with the theory of growth of perfect crystals. These plates then become self-stressed through a non-uniform distribution of impurities or thermal stresses due to partially screened intense radiation, till the theoretical yield stress is exceeded and the plate shears, raising terminated steps on the crystal face. If the shear is by a uniform amount terminating abruptly, a screw dislocation will be created, exposing a ledge on the surface. The crystal growing subsequently will necessarily have a structure corresponding to that of the ledge and will repeat with a period equal to the pitch of the screw. Screw dislocations of different Burgers vectors may thus create different polytypes.

When the Burgers vector of the screw dislocation is an integral multiple of the height of the parent unit cell, then the resulting structure will evidently be the same as the basic structure. On the other hand, a screw dislocation with a Burgers vector which is a non-integral multiple of the height of the parent unit cell would give rise to a new polytype whose periodicity along c is determined by the height of the exposed screw-dislocation ledge. Vand [52, 53] who also gave an explanation of polytypism on similar lines, pointed out that accidental stacking faults in the exposed screw-dislocation ledge would afford an alternative explanation of polytypism since the spiral growth mechanism will cause these to repeat periodically in the structure. He further stated that a single screw dislocation would give rise to needle-shaped crystals with the dislocation line as an axis and, therefore, for the growth of a three-dimensional crystal, at least three non-coplanar screw dislocations would be required.

6.2 The origin of structure series

The formation of structure series in polytypic crystals is readily understood in terms of the above mechanism. Consider the formation of SiC polytypes. If we assume that the initial platelet, forming presumably at high supersaturations by the nucleation mechanism, has the structure of the commonest modification, then it has a layer sequence

\[ |ABC\ ACB|\ ABC\ ACB \ldots \]

with the vertical bars indicating a unit cell. A screw dislocation arising in this would expose a step whose layer sequence will necessarily consist of a number of complete \(|ABC\ ACB|\) units with incomplete portions at either end, like for example

\[ CB(ABCACB)_n\ AB \]

The incomplete parts at the beginning and the end will join in subsequent growth and if the total number of layers exposed is not a multiple of six, a new unit cell with a structure

\[ [(ABCACB)_n\ ABCB] \]

will result. In terms of the Zhdanov notation this is \((33)_n\ 22\), and represents a series of possible structures with different values for \(n\). The mechanism therefore required a number of series of polytypes to form with a Zhdanov symbol consisting of a sequence of \((33)\) units with faults at the end.
Frank [43] was thus able to account for the observed \((33)_3^32\) and \((33)_3^34\) series of structures in SiC, but the absence of other structure series, like \((33)_3^31\) and \((33)_3^35\), was problematical to him. Mitchell [54] suggested that these structure series were absent because they were associated with unstable dislocation gaps in the basic structure. He accordingly undertook a detailed study of the resulting atomic configuration in the basic structure, due to screw dislocations of different Burgers vector strengths, and attempted to explain all the observed SiC polytypes as resulting from theoretical screw dislocations in three basic structures 6H, 15R, and 4H. Since all the atoms in a SiC structure lie in the \((1120)\) planes he plotted the atomic configuration of the dislocated structures in this plane. Fig. 4 shows the atomic configurations resulting from screw dislocations of 1-, 2-, 3-, 4-, 5-, 6-, and 11-layer Burgers vectors in the 6H basic

![Fig. 4](image-url)

Fig. 4. \((11.0)\) cross sections of screw dislocations of different Burgers vector strengths in SiC type 6H. ○ Si atoms, ● C atoms. (After Mitchell [54])
structure. A small horizontal displacement of the atoms in the substrate was assumed in order to ensure lattice continuity between the generated structure and the horizontal and vertical portions of the exposed dislocation step. Thus in Fig. 4a, which shows a dislocation with unit (or one-layer) Burgers vector, the portion of the structure under the line CD has been dislocated relative to that under AB so that CD lies one layer of atoms below AB and, in addition, the atoms under CD have a horizontal displacement of one spacing to the right (equal to one-third the spacing between A and B). Though there is no direct evidence of such a horizontal displacement, this assumption is justified since the absence of such a displacement would cause a discontinuity at the surface and would imply a closer approach of the atoms than appears possible. This horizontal displacement does not in any way alter the structure of the exposed step or that of the resulting polytype.

It is evident from Fig. 4 that only six different kinds of gaps, labelled as $R_1$, $S_2$, $T$, $S_2$, $R_2$, and $N$, can result from screw dislocations in the 6H structure. Mitchell postulated that the gaps $S_1$, $T$, and $S_2$ are too large to be stable and consequently structures resulting from corresponding dislocations are not to be expected. The atomic configurations resulting from dislocations of different Burgers vectors in the 4H and 15R phases were also similarly investigated. Mitchell deduced from the above considerations all theoretically possible structures and established an excellent correlation with the polytypes observed till then.

### 6.3 The origin of rhombohedral polytypes

Both Frank and Mitchell employed Zhdanov symbols in their deductions and assumed that the Zhdanov sequence of layers in the exposed step would repeat indefinitely in the resulting structure. They did not attempt to explain how rhombohedral structures could arise or why they were absent in 6H. It was pointed out by Krishna and Verma [55] that the screw-dislocation ledge can wind over itself during the subsequent growth only if its first and last layers are in different orientations (A, B, or C). The resulting polytype then necessarily has a hexagonal lattice. But if the first and last layers of the exposed screw-dislocation ledge happen to be in the same orientation then the laws of close-packing would require the whole stack of layers in the ledge to slip horizontally into a neighbouring orientation, every time the ledge moves through one pitch. The slip shifting the layers horizontally may occur in a cyclic or anticyclic manner, i.e. $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow A$, or vice versa. It is of little consequence whether the slip occurs in the cyclic or anticyclic direction, though this might affect the structure of the resulting polytype. What is of greater importance is that whatever forces cause the slip to occur in any particular direction will cause it to occur in the same direction every time the stack moves through one pitch, since it comes back to an identical situation. Three such shifts in the same direction would bring back the stack into its original position completing one repeat period. It is easy to see that the resulting structure will have a rhombohedral lattice.

The periodic horizontal slip would contribute an edge component to the dislocation, causing it to be inclined. Evidence of inclined dislocations in rhombohedral polytypes of SiC has been reported by Bhide and Verma [56] from observations of growth spirals. Verma [57] measured step-heights of growth spirals on hexagonal and rhombohedral SiC polytypes and found that while the
step height on hexagonal polytypes was equal to the height of the hexagonal
unit cells, on rhombohedral polytypes it was only one-third of it. This fact
follows as a natural consequence of the mechanism proposed above. The mecha­
nism implies that rhombohedral polytypes grow only when the first and
last layers of the exposed ledge are in the same orientation. Thus a polytype
\((6n + 1)\) \(H\) cannot result from the 6\(H\) structure. This is in agreement with
the fact that the SiC polytype 19\(H\) has a structure 23 23 23 22, which is based
on the 15\(R\) phase. In Cd\(I_2\) the exposed ledge cannot have the first and last
layers in the same orientation, whatever the manner of exposing it. Consequently
Cd\(I_2\) displays no rhombohedral polytypes. The fact that it is always possible
to assume both end-layers of rhombohedral units in any rhombohedral structure
is also in agreement with the proposition. Presumably, it is this factor which
decides whether an \(n\)-layered screw-dislocation ledge would generate a polytype
\(nH\) or \((3n)R\); and therefore the actual ABC sequence of layers in the exposed
ledge must be taken into account while trying to deduce possible polytypic
structures.

The polytypic structures resulting from theoretical screw dislocations in the
6\(H\), 15\(R\), and 4\(H\) phases have been reëxamined [55] in the light of the above con­
siderations. Each dislocation gap in Fig. 4 is found to be associated with a number
of structure series, as follows:

<table>
<thead>
<tr>
<th>Gap</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>((33)_n = 6H)</td>
</tr>
<tr>
<td>R</td>
<td>((33)_n34, (33)_n3211)</td>
</tr>
<tr>
<td>S</td>
<td>((33)_n11, (33)_n2123)</td>
</tr>
<tr>
<td>T</td>
<td>((33)_n36, (33)_n21)</td>
</tr>
<tr>
<td>S</td>
<td>((33)_n37, (33)_n31, (33)_n22)</td>
</tr>
<tr>
<td>R</td>
<td>((33)_n32, (33)_n41)</td>
</tr>
</tbody>
</table>

If one assumes, with Mitchell, that the gaps \(S_1\), \(S_2\), and \(T\) are unstable then struc­
tures belonging to the \((33)_n34\), \((33)_n3211\), \((33)_n32\), and \((33)_n41\) series alone are
theoretically expected to result from the 6\(H\) phase. The absence of SiC struc­
tures with the number 1 in their Zhdanov symbol (with the exception of SiC
type 2\(H\)) is not yet understood.

From an analogous investigation of Cd\(I_2\) polytypes Mitchell [58,59] has shown
that these can also be understood to result from screw dislocations in the basic
4\(H\) phase, \((A\gamma B) (Cz B)\). The \([(22)_n11]\) \(H\) series of Cd\(I_2\) structures can be very
readily pictured to arise from single screw dislocations in the most common 4\(H\)
phase, but the creation of other polytypes requires a system of two or more
cooperating dislocations. The cooperation of two or more dislocations is an
experimentally observed fact and will be discussed in the next section along
with other observations of growth spirals. A number of SiC polytypes like
10\(H\), 75\(R\), and 84\(R\), which do not belong to any series of structures, would also
require the assumption of two or more cooperating dislocations of a suitable
type. All polytypes of SiC and Cd\(I_2\) can thus be regarded as forming either from
a single dislocation or from a system of cooperating dislocations in the basic struc­
tures.

The absence of polytypism in many other compounds that grow by the dis­
location mechanism and exhibit growth spirals is attributed to the fact that
a screw dislocation of non-integral Burgers vector is either not possible or extremely unstable in the basic structure of these compounds. Thus PbI$_2$, which is isostructural with CdI$_2$, displays polytypism on a much smaller scale because the most common PbI$_2$ polytype is type 2H. Screw dislocations in the 2H phase cannot give rise to any new polytypes since the Burgers vector will always be an integral multiple of the height of the 2H unit cell. The few structures observed in this compound must therefore be attributed to the accidental creation of stacking faults in an exposed screw-dislocation step.

6.4 Experimental evidence supporting the dislocation theory of polytypism

There is a considerable amount of experimental evidence to support the dislocation theory of polytypism. The dislocation theory requires that the faces of polytypic crystals should exhibit growth spirals whose step-height is directly related to the corresponding dimension of the unit cell. As mentioned earlier growth spirals had been observed on SiC crystals [47 to 50] even prior to the dislocation theory of crystal growth. Lemmlein [44, 45] who had observed these spiral markings in detail, also made an estimate of their step-heights, using the two-beam interference technique. Fig. 5 shows one of the early interferograms obtained by Lemmlein from the (0001) face of a SiC crystal. From these he calculated the step-height to be in the neighbourhood of one-tenth the wavelength of light. The presence of even smaller step-heights was indicated by his "dew" method. From this work Lemmlein inferred that the step-heights might be

Fig. 5. One of the early two-beam interferograms obtained by Lemmlein [44] from the (0001) face of a SiC crystal (110).
(By courtesy of A. A. Chernov, Institute of Crystallography, Moscow)
equal to or a multiple of the unit cell c-dimension. Being aware of the polytypism in this compound he postulated that the regular spiral growth of this face could bring about the formation of the many-layered superstructures. However, no details concerning this mechanism were given and the occurrence of growth spirals was not attributed to the screw dislocations in the structure.

After Burton, Cabrera, and Frank [37] had put forth the dislocation theory of crystal growth there followed a systematic quest for growth spirals on several different substances. It was in this context that Amelinckx [41, 42] and Verma [38 to 40] observed a profusion of beautiful growth spirals on SiC crystals by phase-contrast microscopy. Around the same time Forty [60, 61] photographed growth spirals on CdI₂ and PbI₂ crystals and took a series of time-lapse photographs of a growing crystal face, confirming that these crystals grow in accordance with the dislocation theory of crystal growth. The shapes of different growth spirals were completely explained in terms of the symmetry of the crystals.

The first definite correlation between the step-height of growth spirals on SiC and the c-dimension of the unit cell was established by Verma [38, 39], who measured the step-height of growth spirals on two 6H crystals by Tolansky's method [62] of multiple-beam interferometry and showed these to be 15.2 and 15.1 Å. Amelinckx [14, 15] independently observed the same correlation from his measurements of the step-heights of growth spirals on SiC. Soon afterwards Verma [63, 64] reported step-heights on SiC differing from 15 Å and corresponding to 15R (12 ± 2 Å) and 33R (28 ± 2 Å). Later [57] he performed the interferometric and X-ray studies on the same single crystals of different polytypic modifications of SiC and conclusively established the correlation between the step-heights and c-dimension of the unit cell for different polytypes. The results obtained by him are listed in Table 2. It will be noticed that for hexagonal polytypes the step-height \( h \) is equal to the c-dimension of the hexagonal unit cell, but for rhombohedral polytypes \( h = c/3 \).

On CdI₂ crystals Forty [61, 65] observed spiral patterns similar to those on SiC and measured their step-heights. Finding step-heights of different magnitudes, all of which were a multiple of a common unit, he predicted polytypism in this compound. The prediction was verified by Mitchell [58, 59] by the X-ray investigation of CdI₂ crystals. He found a large number of polytypic modifications with unit-cell heights corresponding to the step-heights reported by Forty. The X-ray and interferometric observations were not performed on the same crystals but the excellent correlation obtained confirmed that the polytypism in this compound also resulted from the screw-dislocation mechanism proposed by Frank.

In addition to the above experimental evidence obtained from the observation and measurement of growth spirals on polytypic crystals, the fact that a number of polytypes had structures belonging to the \((33)_{32}\) and \((33)_{34}\) series in SiC and the \((22)_{11}\) series in CdI₂ lent decisive support to the dislocation theory of polytypism. The dislocation theory completely did away with the thermodynamic anomaly regarding the formation of polytypic modifications. According to this theory polytypism is a growth feature and polytypes are not thermodynamic phases at all.

It was therefore felt that the phenomenon of polytypism had been satisfactorily explained and only a few details probably remained to be worked out.
Crystal-Polymorphism in One Dimension

Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Polytype</th>
<th>Interferometric data $h$ (Å)</th>
<th>X-ray data $c$ (Å)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Polytypes showing unit Burgers vectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6H</td>
<td>$15 \pm 2$</td>
<td>15.08</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>15R</td>
<td>$12 \pm 2$</td>
<td>$12.5 \times 3 = 37.5$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>33R</td>
<td>$27 \pm 3$</td>
<td>$27.5 \times 3 = 82.5$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>126R</td>
<td>$102.8, 109 \pm 5$</td>
<td>$105.8 \times 3 = 317.4$</td>
<td>Both positive and negative rhombohedra are present simultaneously in the crystal piece</td>
</tr>
<tr>
<td>5</td>
<td>66H</td>
<td>$168 \pm 3$</td>
<td>165.88</td>
<td></td>
</tr>
<tr>
<td>B. Crystal showing multiple Burgers vectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6H</td>
<td>88.8</td>
<td>15.08</td>
<td>Fixed $h$ and fixed $c$</td>
</tr>
<tr>
<td>7</td>
<td>6H</td>
<td>624, 264</td>
<td>15.08</td>
<td>$h$ varies in different parts of the growth spiral but the polytype is fixed</td>
</tr>
<tr>
<td>C. Submultiple Burgers vectors</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>168R, 84R</td>
<td>68</td>
<td>140.8</td>
<td>The crystal contains two polytypes, one twice as big as the other</td>
</tr>
<tr>
<td>9</td>
<td>54H</td>
<td>63</td>
<td>135.7</td>
<td>Only one part of the crystal showed this $c$-spacing</td>
</tr>
<tr>
<td>D. Mixture of polytypes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>6H, 15R, 72R</td>
<td>Shows an interlaced spiral</td>
<td></td>
<td>Both the rhombohedral crystals 15R and 72R are of the same sign (i.e. both in obverse or reverse position)</td>
</tr>
<tr>
<td>11</td>
<td>$h_1 = 404$</td>
<td>$h_2 = 270$</td>
<td>Shows two growth spirals, $h$ varies</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>18, 40, 100, 177, 298, 434</td>
<td></td>
<td>$h$ varies; it may be regarded as a mixture of polytypes, one or two types being dominant</td>
<td></td>
</tr>
<tr>
<td>E. Unresolved structure or disordered types</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>–</td>
<td>414</td>
<td>–</td>
<td>Diffraction spots not well resolved and unevenly spaced</td>
</tr>
<tr>
<td>14</td>
<td>–</td>
<td>185</td>
<td>–</td>
<td>Not well-resolved diffraction spots connected by streaks</td>
</tr>
<tr>
<td>15</td>
<td>–</td>
<td>267, 305</td>
<td>–</td>
<td>Sharp 6H spots with a gradually fading but continuous streak joining them</td>
</tr>
</tbody>
</table>
6.5 Criticism of the dislocation theory

While on the one hand, evidence in favour of dislocation theory of polytypism was mounting continuously, there were on the other hand workers who expressed doubts about several aspects of it. As early as 1951 Vand [53] had pointed out that a single screw dislocation would give rise to needle-shaped crystals and the growth of flat platelets of SiC would require screw dislocations in other directions as well. No growth spirals have, however, been observed on any face of a SiC crystal other than (0001). The formation of flat platelets, both in SiC and CdI₂, therefore contradicts their growth by the dislocation mechanism. Buckley [66, 67] regarded the formation of spirals and the growth of a crystal as two unconnected phenomena, each demanding a separate explanation. According to him the growth of SiC is essentially dendritic with the (0001) face appearing later on as an "after thought to the growth proper". The step-heights of growth spirals are often too large to be understood in terms of screw dislocations and Buckley suggests that the formation of spirals is connected with macroscopic events occurring in the vapour adjacent to the surface, at the moment of solidification. If so, the polytypic structure is not determined by screw dislocations at all.

Jagodzinski [34, 68] has reached a similar conclusion from energy considerations. According to him the high energy required for the creation of a screw dislocation cannot come from the crystal structure until the crystal has grown to a considerable volume, by which time it has already settled down to a certain structure. This is particularly true for screw dislocations of large Burgers vectors required for the formation of the long-period polytypes. The screw dislocation will therefore play a role only in the later stages of the growth of a crystal thereby determining its surface structure, but not its crystal structure. The correlation between the Burgers vector of the dislocation and the unit-cell dimension can be accounted for by the fact that the displaced crystal parts have a greater probability of locking up in a position of mutual fit. No new structure would thus result and the formation of different polytypic structures cannot be due to screw dislocations. Moreover, the energy required for the creation of an edge dislocation with a Burgers vector \( \frac{1}{3}a + \frac{2}{3}b \) or \( \frac{2}{3}a + \frac{1}{3}b \) or a multiple of these is much less than that required for the creation of a screw dislocation of large Burgers vector. Edge dislocations would therefore destroy any order created by a screw dislocation.

The screw-dislocation mechanism explains only the formation of completely ordered types, but it is quite common to find SiC and CdI₂ polytypes with a superposed partial disorder of layers. This one-dimensional disordering is distinct from polytypism where there is a perfect periodicity. The dislocation mechanism does not also account for the observed temperature-structure relationship between the small-period modifications of SiC. To explain this and the disorder effects, Jagodzinski introduces the concept of layer displacements governed by the vibration entropy of the crystal and regards the different SiC polytypes as definite intermediate states in the transition from the 3C to the 6H polytype. Smith [69] has similarly regarded the ZnS polytypes as intermediate states in the transition from 3C-ZnS to 2H-ZnS.

7. Other Theories of Polytypism

On account of the above drawbacks of the dislocation theory of polytypism, alternative explanations have been put forth by different workers from time to time. A brief resume of these follows.
7.1 The polymer theory of polytypism in SiC

Since many SiC polytypes have structures consisting of different proportions of 33, 23, and 22 units, Ramsdell and Kohn [36] postulated the existence of such "polymer units" in the SiC vapor and assumed growth to occur by the accretion of these units. Seven different polymer units were postulated with the following stacking sequences: 33, 32, 23, 22, 34, 43, and 44. Structures with numbers other than 2, 3, or 4 in their Zhdanov symbol were then not known. Ramsdell considered these polymer units to have a stability governed by the temperature in the furnace. While the stability ranges of two polymers could overlap it was not considered possible for three different polymers to coexist at any temperature. The polymers 32 and 23 would have the same temperature range and so also the polymers 34 and 43.

According to this theory the formation of polytypes is temperature-dependent. The polymers were listed in order of increasing stability temperature as: 22, 23, 33, 34, 44. The growth of SiC by the accretion of each of these "crystallization units" alone would result in the formation of "pure" types, like 6H(33), 15R(23 or 32), 4H(22), and 8H(44). The long period polytypes result when two such polymers coexist in the furnace in an overlapping temperature range. No structure could involve three or more polymer units in its zig-zag sequence, since it is not possible for three polymers to exist simultaneously at the same temperature.

If the two polymers present were in equal proportions structures such as 33 32 and 33 34 result, while unequal proportions give rise to various different structures. For example, if the polymers 33 and 32 are present in the proportion 3:1 type 69R with a structure (33)32 is expected to result. Thus it was suggested that the polymers provide the mechanism for the change in the stacking sequence while the periodicity is a function of the relative proportions of the polymers present.

This explanation was able to account for almost all the polytypes known till then and served the useful purpose of predicting the structure of many other polytypes not known at that time. It is, however, far from convincing, firstly because there is no experimental evidence of the existence of such polymers as the theory assumes, and secondly, because it is not clear why the polymers should be added in any specific order. While the relative proportion of the two polymers might be determined by the temperature, the periodicity can hardly be understood. The main problem thus remains untouched.

7.2 Jagodzinski's disorder-theory of polytypism

Jagodzinski [34, 68], whose criticism of the dislocation theory of polytypism has been mentioned earlier has put forth an alternative theory. According to him the one-dimensional "disorder" in SiC is governed by the vibration entropy of the structure. We have already discussed that since the internal energy and density of the different polytypes are almost identical, the stable thermodynamic state should correspond to one of maximum entropy. According to Jagodzinski it is not possible to neglect the vibrational entropy of the crystal in comparison with the configurational entropy for cases of one-dimensional disorder since there are altogether $2 \cdot 3 \cdot N_1 \cdot N_2 \cdot N_3$ eigenvibrations but only $N_3$ double-layers subjected to configuration statistics in SiC. The total
the total entropy would occur at $\alpha = 0.12$, where $\alpha$ is the degree of disorder defined by

$$\alpha = \frac{n_h}{n_h + n_c}.$$  

Here $n_h$ is the number of layers in the hexagonal orientation and $n_c$ the number of layers in the cubic orientation. If the cubic structure is assumed to be the completely ordered states then the degree of disorder is directly proportional to the number of layers in the hexagonal orientation.

The assumed variation of the vibration entropy with increasing disorder was qualitatively justified by assuming that every fault in the stacking sequence will give rise to a series of low-frequency terms in the vibration spectrum of the crystal, thus producing a smaller number of frequency distributions within a given energy interval, i.e. a smaller vibration entropy. This assumption has however been questioned recently by Knippenberg [8]. The effect of perturbation is a splitting-up of the energy-levels of vibration modes of the structure but it is a priori not clear whether this leads to higher-energy modes or not.

7.2.1 The layer-transposition mechanism

In order to visualize the role of the vibration entropy in the formation of polytypes Jagodzinski [34] suggested a layer-transposition mechanism for their generation from the parent cubic modification in SiC. It was argued that the ordering forces that guide the structure of a two-dimensional critical nucleus must be provided by the structure already attained by the crystal. A number of stacking faults will cooperate to lower the energy required for forming such a nucleus, and the vibration entropy will effect an orderly distribution of these stacking faults. A polytype will therefore result whenever the “superstructure of faults” markedly succeeds in forming.

The most probable structural arrangements may be derived easily from the
ordered cubic structure as shown below. The transposed layers are underlined.

(i) [ABCABCABCABCABC], e (cubic),
[ABCBACABACBCACB], hecc (15R),

(ii) [ABCABCABCABCABC], e (cubic),
[ABCABCAABACBCABAC], hecc (6H).

Similarly all other polytypic structures can be derived.

7.2.2 Experimental evidence

Jagodzinski [68] examined 150 SiC crystals, picked at random, by X-ray diffraction, and found 62 of these displaying one-dimensional disorder. On the X-ray diffraction photographs this meant the occurrence of continuous streaks connecting spots corresponding to a certain periodicity, as in Fig. 2d. About 70% of the ordered as well as “fault-ordered” crystals were 6H and nearly 12% were 15R. The 4H polytypes were found to be rare but well ordered. All long-period polytypes were found to be partially disordered. This is to be expected from the theory since the contribution of the vibration entropy to the total entropy of the crystal decreases with increasing periodicity. Hence completely ordered long-period polytypes are improbable and should be associated with a certain measure of random disorder.

Jagodzinski determined the degree of fault-order for the partially ordered polytypes from their X-ray diffraction photographs. From a mathematical formulation of the X-ray scattering from one-dimensionally disordered structures [20] he obtained the following relation:

\[
\frac{\alpha}{1 - \alpha} = \frac{\int_0^1 \frac{I_d}{F^2} \, dA}{\int_0^1 \frac{I_s}{F^2} \, dA},
\]

where \( I_d \) and \( I_s \) denote the intensities of the diffuse background and the sharp reflections, respectively, \( F \) is the structure factor for a double layer, and the integrations are over the range of the reciprocal-lattice interplanar distance in Fourier space. From this he deduced the value of \( \alpha \) for the 150 SiC crystals studied by him. The experimental results [35] are plotted in Fig. 7, which

![Fig. 7. The distribution of the amount of disorder, \( \alpha \), in SiC crystals, as observed by Jagodzinski [68].](image)
shows that the probability distribution of fault-order degree has two maxima, one at \( \alpha = 0 \) corresponding to completely ordered crystals, and the other at \( \alpha = 0.12 \) corresponding to a partial disorder of about 1 stacking fault in every 10 layers. This is in agreement with the theoretical predictions made earlier.

7.2.3 Discussion

Jagodzinski's explanation is able to account for the partially disordered structures observed in polytypic substances, on a thermodynamic basis. The fact that there is a definite temperature-structure relationship for the small-period polytypes suggests a thermodynamic basis. Growth by nucleation is also in agreement with the plate-like shape of most crystals. However, the theory is unable to explain the formation of ordered long-period polytypes, nor does it explain the formation of structure series.

The explanation is essentially qualitative and based on assumptions that can be questioned, such as the dependence of vibration entropy on disorder. The theory predicts that a particular value of \( \alpha \) is thermodynamically favourable but does not explain why faults should occur in a particular periodic way over macroscopic distances. Lastly, if the growth of the structures occurs by the nucleation mechanism and the structure of the nucleus is determined statistically by the vibration entropy then the resulting crystal ought to be an aggregate of several polycrystallites, each with a different structure, but SiC is known to form large crystals with a single polytypic structure.

7.3 Schneer's theory of polytypism

Since the internal energy of the different SiC polytypes is very nearly the same Schneer [70] considers them to be related by second-order phase transformations. He has accordingly developed a theory of polytypism analogous to that of Bragg and Williams [71] and Bethe [72] for order-disorder in binary alloys. It is assumed that the phase transformation occurs over a temperature range by infinitesimal steps so that the density and probability distribution vary continuously with temperature, while their derivatives are discontinuous.

Any layer in a close-packed structure is either in a hexagonal (h) or in a cubic (c) environment. If we assume that at a temperature \( T \) there is a dynamic equilibrium between the number of h and c layers then the structure is characterized by a distribution function

\[
D = \frac{n_c}{n_h + n_c},
\]

where \( n_h \) and \( n_c \) stand for the number of layers in h and c states, respectively. Let the difference in structure energy of layers in the two states be denoted by \( V \). Then

\[
V = V_h - V_c. \quad (1)
\]

Evidently,

\[
D = D(V, T) \quad (2)
\]

since the partition of layers into h and c states would depend on \( V \). Similarly,

\[
V = V(D, T) \quad (3)
\]

if we assume that the structure energy of a layer is influenced by long-range
interactions whose value would depend on $D$. The explicit dependence of $V$ on $T$ must however be slight since it can occur only through a change in the elasticity of the crystal.

The equilibrium values of $D$ and $V$ at any temperature would be given by the intersection of $D$-$V$ curves plotting (2) and (3) for that temperature. To arrive at explicit forms of equations (2) and (3) we make the following assumptions:

(i) $V_h > V_c$.  

This means the cubic arrangement has a lower potential energy than the hexagonal arrangement.

(ii) $V = V_0 (2D - 1)$.  

This means $V$ varies linearly with $D$ and rises to a maximum value $V_0$ at $D = 1$. This is probable since the excess of $c$ over $h$ neighbours influencing a $c$ to $h$ displacement is on the average proportional to $(2D - 1)$.

(iii) \[
\frac{n_h}{n_c} = \frac{1 - D}{D} = e^{-V/kT} = e^{-X},
\]

where $X = V/kT$. This means the layers have a Boltzmann distribution between $h$ and $c$ states.

The $V(D)$ and $D(V)$ curves representing (5) and (6) are plotted in Fig. 8 for different temperatures. The intersections marked $E_n$ represent stable equilibrium states at the temperatures $T_1 < T_2 < T_3 \ldots$. The cubic modification ($D = 1$) is thus the low-temperature modification and more and more layers go over to the hexagonal state as the temperature rises till, at a temperature $T_a$, there are as many layers in the hexagonal as in cubic orientation. The distribution $D$ is an example of a cooperative phenomenon in physics because it is measured by the proportions of layers in the two states and these layers in turn cooperate to alter the energy difference $V$.

7.3.1 Interaction energy

Several different arrangements of the $h$ and $c$ layers are possible for the same value of $D$. Of these the observed polytypic structures form a limited set. To explain this we assume a difference $e$ between the interaction energy $e_{ij}$ of two adjacent layers when they are in the same environment and when
they are in different environments. Let

\[ e_{ij} = e_{cc} \text{ when } i, j \text{ are adjacent and both } c, \]

\[ e_{ij} = e_{hh} \text{ when } i, j \text{ are adjacent and both } h, \]

\[ e_{ij} = e_{eh} \text{ when } i, j \text{ are adjacent but different,} \]

and \( e_{ij} = 0 \) when \( i, j \) are not adjacent.

Then

\[ e = \frac{1}{2} (e_{cc} + e_{hh}) - e_{eh}. \]  \hspace{1cm} (7)

Let the function \( q \) represent the distribution of interaction contacts. Then

\[ q = \frac{n_{eh} - (n_{cc} + n_{hh})}{n_{eh} + (n_{cc} + n_{hh})}, \]  \hspace{1cm} (8)

where \( n_{eh} \) is the number of contacts between layers in unlike states and \((n_{cc} + n_{hh})\) between layers in like states. Evidently

\[ n_{eh} + (n_{cc} + n_{hh}) = N, \]  \hspace{1cm} (9)

the total number of layers in the crystal, and the number of like contacts is

\[ n_{cc} + n_{hh} = \frac{N}{2} (1 - q). \]  \hspace{1cm} (10)

This causes the assembly to have an interaction energy

\[ E = \frac{1}{2} \left(1 - q\right) N e \]  \hspace{1cm} (11)

in excess over the interaction energy for an arrangement \( hc \) \( hc \) \ldots with all contacts unlike. If the latter is regarded as zero, \( E \) represents the total interaction energy of the assembly. It is the potential energy supplemental to that required to maintain a given distribution \( D \). Consequently, for a given \( D \), the arrangement of \( h \) and \( c \) layers that minimizes \( E \) will be the most stable. It follows that \( q \) must be a maximum for all observed polytypes.

We have assumed \( e > 0 \), because \( e < 0 \) would mean that every layer will try to have like contacts and the crystal would divide into two pure phases — one hexagonal and the other cubic. This does not happen with polytypic substances, but may explain the cases where only the 2H and 3C modifications exist. If \( e \approx 0 \), \( h \) and \( c \) layers will arrange themselves at random in the proportion fixed by \( D \). This has been observed by Edwards and Lipson [25] and Wilson [26] to occur in cobalt.

For polytypic substances, therefore, we must assume \( e > 0 \) and polytypes must represent states of maximum \( q \). A completely disordered arrangement would correspond to \( D = \frac{1}{2} \), \( q = 0 \) and is not expected to occur. The structure will tend to have a maximum number of unlike contacts. For \( D > \frac{1}{2} \), \( n_c > n_h \) and the maximum number of unlike contacts possible is \( 2 n_h \) while the number of like contacts is \( n_c - n_h \). Hence

\[ \Phi_{\text{max}} = \frac{2 n_h - (n_c - n_h)}{N} \]

or

\[ \Phi_{\text{max}} = 3 - 4 D. \]  \hspace{1cm} (12)
Fig. 9. The plot of $\Phi_{\text{max}}$ vs. $D$ in Schneer's theory. The different SiC polytypes all lie on the line. (After Schneer [70])

Fig. 9 shows a plot of this equation on the ($\Phi$, $D$) plane. The ($\Phi$, $D$) values for 14 different SiC polytypes are also plotted and they all lie on the straight line representing the above equation. There is thus an excellent agreement between theory and observation.

It will be noticed that there are three polytypes, 15R, 10H, and 75R, which have the same value of $(D, \Phi) = (3, \frac{5}{6})$. Thus even the parameters $D$ and $\Phi$ do not completely specify a single polytype. To account for these structures it is therefore necessary to take higher-order interactions into consideration and this has been done by Schneer [70] with the aid of certain added assumptions; but this is a matter of detail and the major success of the theory lies in the exact fit of the $(D, \Phi)$ values for observed polytypes with equation (12).

### 7.3.2 Conclusions and discussion

According to Schneer's theory, polytypism is a cooperational phenomenon analogous to order–disorder in alloys and ferromagnetism. The different polytypes represent intermediate states in a second-order transition between the cubic and hexagonal (2H) structures. The observed polytypes are characterized by maximum numbers of interaction contacts between layers in unlike states and correspond to potential minima. Minute differences in temperature or in the degree of approach to equilibrium can bring about major differences in periodicity.

Apart from the fit of the $(D, \Phi)$ values of observed polytypes there is little experimental evidence in favour of the theory. There is some evidence [35] to indicate that polytypic structures form in a temperature range intermediate between that for 3C and 6H polytypes and may therefore be regarded as intermediate states. However, it has not been possible to associate definite polytypes with specific temperatures and no phase transformation other than that from 3C to 6H has ever been found to occur between polytypes, and this too is irreversible. One polytypic modification does not go over to another on heating [13]. According to the theory the high-temperature form should be characterized by $D = \frac{3}{2}$, but the high-temperature form of SiC is known to be 6H with $D = \frac{5}{2}$. Moreover, the theory does not explain either the formation of structure series or the origin of long-range periodicities, both of which are prominent facts among polytypic substances. The absence of polytypism in other compounds with parallel structures is also difficult to understand.

### 7.4 Peibst's theory of polytypism

Recently Peibst [73] has made an attempt to explain the origin of polytypes from the influence of thermal vibrations of the structure on the growth front
during crystallization. To consider this influence we must start with the idea that there is no strong discontinuity between the crystal and the surrounding phase, so that the thermal vibrations are acting into the melt. It is argued that when there exist, during the formation of a two-dimensional nucleus on a closed plane, two energetically equivalent possibilities for further growth (i.e. hexagonal and cubic in the case of polytypic structures), it is to be expected that the structure-vibration amplitudes will effect an orderly fitting in of the nucleus, according to the base. If this does not succeed, there will occur an increase in the kinetic energy of the crystal causing a statistical insertion of stacking faults in order to lower the Helmholtz free energy.

The explanation is essentially qualitative and there is no experimental evidence to justify the assumptions. The idea has been put forth as a new approach to the problem of polytypism and evidently needs to be developed further. Since crystal growth is a surface phenomenon it is doubtful whether the lattice modes of vibration in the bulk of the crystal can be considered to affect the crystallization front. The more complicated surface modes of vibration may have a far greater influence. We shall therefore not elaborate on this explanation here and those interested are referred to the original paper [73] or to reference [3].

8. Recent Experimental Observations — Discussion

It is evident from the above discussion of the different theories of polytypism that the only theory, other than the dislocation theory, to receive any experimental support, is the disorder theory put forth by Jagodzinski. The other theories are largely speculative since the assumptions on which they are based are not experimentally verified. Despite all criticisms, the screw-dislocation theory appears to explain the largest number of important facts associated with polytypism. In recent years several experimental investigations have been undertaken to determine which of the above theories is best applicable and in particular whether the origin of polytypes is governed by growth mechanisms starting with screw dislocations or whether thermodynamics considerations are more important. These will now be discussed briefly.

8.1 X-ray, microscopic, and interferometric studies of polytypic substances

Verma and his coworkers have conducted extensive studies of single crystals of CdI₂ and SiC by the X-ray diffraction, optical microscopic, and interferometric methods. X-ray diffraction was employed to obtain atomic structure of certain long-period polytypes of special interest. For details of the interpretation of the X-ray diffraction photographs as well as the special methods employed for structure analysis the reader is referred to reference [3]. We shall quote here only the results of the investigations. Microscopy (both ordinary as well as phase-contrast) was used to photograph the surfaces of the same single crystals as those examined by X-rays, and interferometry (usually multiple-beam) was employed to measure accurately the step-heights of any spiral features present on the surface. For details of these techniques see Verma [40].

Trigunayat and Verma [74] examined 88 different crystals of CdI₂. Of these 18 were found to be 4H, 5 to be 2H, 19 were other rare polytypes, 20 had a structure "resembling 4H", 8 resembling 2H, 1 resembling 8H, 8 with coales-
ence, and 1 unidentified. The step-height was found to be an integral multiple of the c-dimension on all 2H types. Such a correlation could, however, be found only on two 4H types and was definitely absent for most of the long-period polytypes. The results obtained for the long-period polytypes are tabulated in Table 3.

In a surprisingly large number of cases there is no correlation between the spiral step-height and the height of the X-ray unit cell. Thus Mitchell's conclusion of a correlation was erroneous and arose because the interferometric and X-ray investigations were not carried out on the same crystals. The correlation observed on 2H crystals results from the fact that the step-height in CdI₂ must always be an integral multiple of the c-dimension of the 2H unit cell which corresponds to a minimal sandwich of CdI₂. The correlation observed on a few 4H crystals is probably accidental since it does not occur for any of the longer-period polytypes. This would indicate that the formation of a growth spiral on the crystal surface is not linked with the formation of the polytype but occurs in the later stages of growth, as suggested by Jagodzinski. The incidence of a random fault-order was also found to be quite common in these crystals, favouring their growth by the mechanism suggested by Jagodzinski.

It was therefore proposed to carry the investigation a stage further by working out the detailed atomic arrangements in different SiC and CdI₂ polytypes to examine if their structures conform with the dislocation theory. A large number of SiC and CdI₂ crystals were studied and this led to the discovery of several anomalous structures in both compounds.

### Table 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Polytype</th>
<th>Interferometric data</th>
<th>X-ray data</th>
<th>Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6Hc</td>
<td>369.3 ± 7.7</td>
<td>20.05</td>
<td>Error in h too large to tell</td>
</tr>
<tr>
<td>2</td>
<td>10Ha</td>
<td>247.9 ± 20.7</td>
<td>34.2</td>
<td>No</td>
</tr>
<tr>
<td>3</td>
<td>10Hb</td>
<td>184.8 ± 5.8</td>
<td>34.2</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>12Hd</td>
<td>260.9 ± 7.8</td>
<td>41.0</td>
<td>No</td>
</tr>
<tr>
<td>5</td>
<td>16H</td>
<td>70.4 ± 1.7</td>
<td>54.7</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>18H</td>
<td>82.3 ± 4.6</td>
<td>61.5</td>
<td>No</td>
</tr>
<tr>
<td>7</td>
<td>18Ha</td>
<td>≥500</td>
<td>61.5</td>
<td>Error in h too large to tell</td>
</tr>
<tr>
<td>8</td>
<td>20H</td>
<td>[h₁ = 369.8 ± 15.4, h₂ = 87.2 ± 5.1]</td>
<td>68.4</td>
<td>No</td>
</tr>
<tr>
<td>9</td>
<td>22Ha</td>
<td>175.8 ± 1.6</td>
<td>75.2</td>
<td>No</td>
</tr>
<tr>
<td>10</td>
<td>22Hb</td>
<td>107.1 ± 1.6</td>
<td>75.2</td>
<td>No</td>
</tr>
<tr>
<td>11</td>
<td>32H</td>
<td>246.9 ± 13.8</td>
<td>109.4</td>
<td>No</td>
</tr>
<tr>
<td>12</td>
<td>34Ha</td>
<td>170.2 ± 3.0</td>
<td>116.3</td>
<td>No</td>
</tr>
<tr>
<td>13</td>
<td>34Hb</td>
<td>160.0 ± 1.3</td>
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</tr>
<tr>
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<td>38Hb</td>
<td>245.6 ± 3.1</td>
<td>129.9</td>
<td>No</td>
</tr>
<tr>
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<td>38Hc</td>
<td>371.1 ± 2.0</td>
<td>129.9</td>
<td>No</td>
</tr>
<tr>
<td>17</td>
<td>50H</td>
<td>231.8 ± 1.3</td>
<td>171.0</td>
<td>No</td>
</tr>
<tr>
<td>18</td>
<td>52H</td>
<td>288.9 ± 0.8</td>
<td>177.8</td>
<td>No</td>
</tr>
<tr>
<td>19</td>
<td>4H</td>
<td>189.7 ± 1.0</td>
<td>13.7</td>
<td>Correlation exists</td>
</tr>
<tr>
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<td>4H</td>
<td>358.7 ± 1.7</td>
<td>13.7</td>
<td>Correlation exists</td>
</tr>
<tr>
<td>21</td>
<td>4H</td>
<td>182.2 ± 1.8</td>
<td>13.7</td>
<td>No</td>
</tr>
</tbody>
</table>
8.1.1 Anomalous polytypic structures

A number of polytypic structures were found to have a structure that conforms with the dislocation theory but their (0001) faces displayed no growth spirals. Two SiC polytypes 57R and 111R were found [75, 24] to have structures \((33)_3\)34 and \((33)_5\)34, respectively. They are thus very much expected on the dislocation theory. However, a careful examination of their smooth shining (0001) faces under the phase-contrast, Vicker's projection microscope revealed them to be plane surfaces devoid of any spiral markings. According to the dislocation theory the crystals ought to display growth spirals with step-heights of 47.84 and 93.17 Å respectively, both of which are large enough to be easily observable under the microscope. Similarly a CdI₂ polytype 26H₄ was found [76] to have a structure \((22)_6\)11 but it displayed no growth spiral. The absence of any growth spirals indicates that these structures have not resulted by the dislocation mechanism. Moreover, the 10.₁ reflections of the 57R SiC polytype are connected by a faint streak (see Fig. 2a), indicating a superposed random disorder of layers. This too cannot be understood in the dislocation theory and would favour the formation of the polytype by the mechanism proposed by Jagodzinski. The polytype 111R was however beautifully crystalline and gave sharp reflections (Fig. 2b). The absence of any random disorder of layers in such a long-period polytype is not in accordance with Jagodzinski's theory.

Some of the polytypes were found to have a unit cell whose height is an integral multiple of the height of the unit cell of their basic structure. The growth of such polytypes cannot occur from single screw dislocations created in the basic structure since the Burgers vector of the screw dislocation will be an integral multiple of the c-parameter of the basic phase. Examples of such crystals are the SiC polytypes 36H, 54H, 66H, and 90R, and the CdI₂ polytypes 22H₅, 26H₆, and 28H₇. The SiC polytype 36H was found to contain two different structures 36H_a and 36H_b. The X-ray diffraction photographs obtained from the two structures are shown in Fig. 10a and 10b. The positions of the X-ray reflections are the same on both photographs but the intensity distribution along the 10.₁ row is completely different in the two cases. The structure 36H_a gives intense reflections in 6H positions showing that its structure is based on the 6H phase. 36H_b on the other hand is an unusual structure dis-

Fig. 10. The 10.₁ row of X-ray reflections recorded on c-axis oscillation photographs from SiC type. a) 36H_a, b) 36H_b, c) 66H, d) 126R
Fig. 11. The first-layer $a$-axis equi-inclination Weissenberg photograph recorded for SiC type 36Hb. The lowest festoon records the 101 reflections and the four faint reflections near the minimum are 103, 101, 101, and 103 from left to right.

playing very characteristic structural extinctions. These extinctions can be seen more clearly in Fig. 11 which reproduces the first-layer $a$-axis equi-inclination Weissenberg photograph obtained from the crystal. The reflections 101 are absent when $l = 36n$, $6n \pm 2$, and $36n + 6$ ($n$ any integer or zero). By equating the intensities for these reflections to zero and solving the equations so obtained it has been possible to determine uniquely [11] the structure of this polytype to be (33)$_4$34 (33)$_3$32. But for the extinctions observed on the X-ray diffraction photographs such a complex structure with faults both at the end and the middle of a sequence of (33) units could not have been worked out.

The growth of a 36H polytype by the screw-dislocation mechanism would require the dislocation to have a Burgers vector of $36 = 6\times6$ layers. Such a dislocation created in the 6H phase would generate only the 6H structure. The growth of such a polytype is therefore not possible by the dislocation mechanism, nor is it possible to explain the existence of two different structures with the same periodicity within a single crystal piece. That this crystal has not grown by the screw-dislocation mechanism is further confirmed by the fact that its shining (0001) face (on the 36H$_a$ polytype) shows no spiral features whatsoever when examined under the phase-contrast microscope.

The SiC polytypes 54H and 66H are, like the type 36H, based on the 6H phase for they too give intense reflections in 6H positions on the X-ray photographs. Their unit cell height is also an integral multiple of the unit cell height of the 6H polytype and hence they cannot result from single screw dislocations in the 6H phase. However, the (0001) surfaces of these crystals show beautiful growth-spiral patterns originating from a single screw dislocation. The step-height of the growth spiral is equal to the $c$-dimension of the unit cell for 66H but a sub-multiple of it for 54H. The spiral observed on the (0001) face of 66H is shown in Fig. 12 and the corresponding 101 row of X-ray reflections in Fig. 10c. It is apparent that in these crystals the spiral has not generated the structure but has arisen in the later stages of growth.

The polytype 90R, unlike the others, has a structure based on the 15R phase. It gives intense X-ray reflections near 15R positions on the X-ray diffraction photographs (see Fig. 2a) and its structure as determined by usual methods [10] is (23)$_4$33 22. Being a rhombohedral polytype it would require for its growth
a screw-dislocation ledge of 30 layers with the first and last layers in the same orientation. It is impossible to obtain such a ledge from a single screw dislocation in the 15R phase. Any ledge of 30 layers, exposed in the 15R phase, would necessarily generate only the 15R structure. We may consider the structure to result from the cooperation of two or more suitable screw dislocations but the surface of the crystal presents no evidence to this effect since the (0001) face of the polytype shows no spiral features. We are forced to conclude that this crystal too has not resulted by the dislocation mechanism.

Another SiC polytype 126R shows growth spirals on the (0001) face originating from screw dislocations of opposite hand and of equal strength, reproduced in Fig. 13. The step-height of both growth spirals is equal to one-third the height of the hexagonal unit cell. The polytype is therefore expected to have grown by the dislocation mechanism. However, the intensity distribution in the 10.1 row of X-ray reflections (Fig. 10d) shows that its structure is not based on any smaller type. The more intense reflections do not lie around positions corresponding to any basic structure. The structure therefore does not appear to have resulted from the spiral.

Similar anomalies are exhibited by the CdI₂ polytypes 22H₆, 28H₆, and 26H₆ discovered by Srivastava and Verma [76 to 78]. The X-ray diffraction photographs obtained from these polytypes are shown in Fig. 14. These are a-axis oscillation photographs because CdI₂ crystals grow into flakes parallel to (0001) and it is not possible to obtain good c-axis oscillation photographs except by cutting the crystals. But the crystals are soft and get distorted if an attempt is
made to cut them. Hence the crystal flakes were used as such and the range of oscillation was adjusted so as to record a number of \(10\) reflections along the layer lines. The polytype \(22H\) was found [76] to be based on the \(2H\) phase (Fig. 14a) with a structure \((11)\)\(22\) \(11\) \(22\). However, Cdlg structures based on the \(2H\) phase are not expected on the dislocation theory of polytypism since any dislocation in the \(2H\) structure would necessarily have an integral Burgers vector. This is confirmed by the fact that step-heights of growth spirals on Cdlg are always an integral multiple of the \(c\)-dimension of the \(2H\) polytype.

Similarly the Cdlg polytype \(28H\) is based on the \(4H\) phase (Fig. 14b) but has a unit cell height exactly seven times the \(c\)-dimension of \(4H\). The structure has been shown [77] to be \((22)\)\(1111\). It cannot result from a single dislocation in the \(4H\) phase, but the \((0001)\) face of the crystal displays a single growth spiral with a symmetry intermediate between circular and hexagonal. The spiral is reproduced in Fig. 15.

The Cdlg polytype \(26H\) is, like \(22H\), based on the \(2H\) phase (Fig. 14c). It has a very unusual structure with a Zhdanov symbol \(2(11)2(11)2(11)2(11)\), which has been determined by a special method [78] making use of the more
intense reflections to deduce the probable positions of layers. Such a structure with faults at several places in the Zhdanov sequence is impossible to obtain by the dislocation mechanism. Moreover, the surfaces of the crystal displayed no spiral markings, confirming that the polytype has not resulted by the dislocation mechanism.

![Fig. 14. a-axis oscillation photographs from different CdI₂ polytypes. The 10./ row of spots is recorded on the first layer line. a) 22H₀, b) 28H₀ (1.5 ×), c) 36H₀, d) 26H₀, e) 50H₁, f) partially disordered. (After Srivastava and Verma [76 to 78])](image)

![Fig. 15. Surface micrograph of the (0001) face of CdI₂ crystal type 28H₀, showing a single growth spiral (100 ×). (After Srivastava and Verma [77])]
Srivastava and Verma [78] have reported another interesting crystal of CdI₂. A seemingly single-crystal flake exhibited two different structures on the two sides of the flake. On the one side was a polytype 26H₄ (Fig. 14d) with a structure (22)₁₁ which is very much expected from the dislocation theory. The face containing the 26H polytype, however, showed no spiral markings. The other face was found to contain a polytype 50H (Fig. 14e), whose structure is not based on either the 2H or 4H phases and could not therefore be determined. The face containing the 50H polytype, however, displayed the complicated growth pattern reproduced in Fig. 16.

From the above observations it appears that the formation of the spiral on the surface and the formation of polytypic structures are two unconnected phenomena. The observations give credence to Jagodzinski’s suggestion that the screw dislocation and therefore the growth spiral appear only in the later stages of growth. When the screw dislocation follows the structure of the polytype there is a correlation between the step-height of the growth spiral and the height of the unit cell. In other cases there is not. In addition, there are the partially disordered structures, both in SiC (Fig. 2d) and in CdI₂ (Fig. 14f) which the dislocation theory is unable to explain even in principle. The existence of these disordered structures favours Jagodzinski’s theory of polytypism but this theory is unable to account for the beautifully ordered long-period polytypes like SiC types 126R, 111R, 90R and CdI₂ types 22H, 26H, 28H, and 50H. None of the existing theories of polytypism is therefore able to account for all the observed facts.

8.2 Observations of the growth process

It is interesting to note that Knippenberg [8] has arrived at the same conclusion from his recent observation on the growth of SiC by the Acheson process, the Lely process, and by crystallization from solution at different temperatures and with different impurity-contents. For details of the investigation the reader
is referred to the original paper [8]. The main conclusions relevant to the problem of polytypism are as follows.

The growth of SiC largely occurs not on the well-developed (0001) face of the crystal which shows growth spirals but on the opposite face which is usually stepped and undeveloped. This was found by growing SiC crystals first in an inert argon atmosphere and then adding a small pressure of 10 Torr of nitrogen during the second half of the growth. The incorporation of nitrogen produces colour in SiC and consequently the thickness of the coloured layer in the product obtained finally indicates the relative velocity of growth in different directions. The lateral growth of the initial crystal platelet was found to be a constant while almost all the growth in thickness of the platelet occurred on the side of the badly developed basal face.

By growing crystals at a constant temperature, with different amounts of Al as impurity, it was found that there is no correlation between structure type and the content of impurities. There was, however, a temperature-structure relationship for the small-period polytypes as depicted in Fig. 3. The cubic modification was regarded as metastable at all temperatures, forming first in accordance with the Ostwald step-rule. This was concluded because its formation was not found to be limited only to low temperatures as believed earlier but took place at all temperatures; it transformed irreversibly into type 6H on heating above 2000 °C, but without a definite transition temperature, and it had a higher chemical reactivity than the other structures.

It was found by examining the SiC crystals at different stages of growth that the SiC crystals formed first into exceedingly thin microscopic whiskers and not into platelets as visualised by Frank. The whisker formation was found to be independent of the chemical reaction producing SiC and the temperature of formation. In an electron microscopic examination of these SiC whiskers obtained in the early stages of growth Knippenberg et al. [79] did not find any axial dislocation of the kind reported earlier by Hamilton [80] in the whiskers grown by him. Parts of the whiskers were found to be cubic and other parts hexagonal. At temperatures above 1700 °C the whiskers quickly grew to macroscopic size and above 1900 °C even crystal platelets were obtained.

The transformation from cubic SiC to type 6H does not occur by solid state transitions. It occurs by way of the vapour phase by a process of surface diffusion which is appreciable above 2000 °C. Above 2000 °C recrystallization begins to take place.

These observations contradict all the existing theories of polytypism. It was suggested by Knippenberg that the top lamella containing the growth spiral was perhaps formed during cooling, since it was on the non-growing side.

Kleber and Fricke [81] have investigated CdI₂ crystals grown from aqueous solution, from melt, and from vapour. They found that the crystals grown from the vapour displayed circular growth spirals on the (0001) face while those grown from solution showed polygonal spirals. It was also found that the phenomenon of polytypism was limited by the manner of growth. From the vapour phase and from melt only the 4H type was obtained. It is only among crystals grown from aqueous solution that other polytypes were found. Mitchell [82] has also found that in CdBr₂ crystals grown from the vapour phase are always type 6R only. The fact that CdI₂ crystals grown from vapour have no polytypism but display circular growth spirals indicates that the two phenomena are not necessarily connected.
9. Conclusion

It is evident from the foregoing that no satisfactory explanation of polytypism exists. As an alternative to all the existing theories of polytypism Knippenberg [8] has suggested that the energy of the electrons might constitute the decisive factor in determining the structure. This possibility was suggested by the fact that acceptors and donors have a preference for the hexagonal and cubic structures respectively and seem to stabilize them. The electron-energy band gap is different for different polytypes and since the other free-energy differences are negligibly small it is possible that this might influence the formation of a polytype. From his measurements of the band gap for different polytypes Knippenberg found the following systematic correlation:

<table>
<thead>
<tr>
<th>Polytype</th>
<th>2H</th>
<th>4H</th>
<th>15R</th>
<th>6H</th>
<th>21R</th>
<th>24R</th>
<th>8H</th>
<th>3C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>11</td>
<td>22</td>
<td>25</td>
<td>33</td>
<td>34</td>
<td>35</td>
<td>44</td>
<td>oo</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>&gt;3</td>
<td>3.1</td>
<td>2.9</td>
<td>2.86</td>
<td>2.77</td>
<td>2.72</td>
<td>2.56</td>
<td>2.2</td>
</tr>
</tbody>
</table>

It is known (Welker [83]) that in a series of analogous structures the band gap increases with structure energy, but the idea needs to be developed further before it can be applied theoretically to the case of polytypism.

It is evident that the phenomenon of polytypism is influenced by a large number of factors. Thus the temperature and rate of crystallization, the correlation of impurities, the dislocations created during growth, the thermal vibrations of the structure, and the electron energy may all have a role to play and the polytypic structure may depend upon the factor that is dominant at any one time. The theories so far advanced take only one factor at a time into account. The final explanation must perhaps take all the factors into consideration, if it is to account for every aspect of the problem.

References

Crystal-Polymorphism in One Dimension


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SOLID STATE COMMUNICATIONS
INTERFEROMETRIC AND X-RAY DIFFRACTION STUDY OF "BUILT-UP"
MOLECULAR FILMS OF SOME LONG CHAIN COMPOUNDS

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By using the Blodgett and Langmuir technique, monomolecular
films of barium palmitate, barium margarate, barium stearate
and barium behenate have been built-up to films of 2, 4 and 7
mono-molecular layer thicknesses, on a silver substrate. The
metrical thickness has been determined by multiple-beam inter­
ferometry. The c-spacings measured by X-rays are found to be
twice the molecular chain length. A correlation between the
interferometric measurement of the thickness and the lattice
spacings normal to the film, is established. The correlation be­
tween the unimolecular film thickness and the chain length of
the corresponding fatty acid leads to the conclusion that the fatty
acids spread on a water surface mono-molecularly, oriented with
their hydrocarbon chains almost at right angles to the substrate.

THE Blodgett-Langmuir molecular film techni­
que has only been studied in detail on barium
stearate. It has been shown that the films consist of superposed sheets of oriented molecules
and form positive uniaxial birefringent crystals
with the optic axis perpendicular to the plane of
the film. Electron diffraction investigations show
that the films form hexagonal crystals with the
symmetry axis i.e. the optic axis, perpendicular
to the plane of the film. X-ray diffraction studies
have also been reported. The optical birefrin­
gence and the electron and X-ray diffraction effects
show that the films are crystalline and can be regarded
as almost "two-dimensional" crystals. The
building up of mono-molecular layers may thus be
regarded as a special case of a layer by layer
growth of a crystal.

Determination of thickness of barium stearate
films, optical studies of built-up films

The thickness of built-up barium stearate
films has been measured from interference of
monochromatic polarized light reflected by the
film. Jenkins and Norris varied the wave­
length until the reflected intensity recorded by
a spectrophotometer fell to a minimum. In an­
other method a Michelson interferometer was
utilized. In the polarimetric method, reference
films having a known number of layers of
stearic acid or barium stearate are used as an
optical gauge for comparison. In a more recent
work an interference reflector of barium stearate
itself was used to determine the thickness by
Hartman's polarimetric method.

The optical methods used in the past determine only the optical thickness. Since the built-up
films are obtained only with condensed mono­
layers which are maintained at surface pressures
generally much below their collapse pressures,
the density and therefore the refractive index of
the films cannot be taken to be equal to that of the
substance in bulk. The refractive index depends
on the density since it depends on the extent of
polarization of the atoms which in turn is deter­
mined not only by the electric field of the incident
electromagnetic wave but also by that of the
electric dipoles produced in other atoms in the

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neighbourhood and their interaction. Further, the refractive index of the built-up film depends in an unknown manner on the proportion of free stearic acid molecules present in it. There is no complete conversion of fatty acid molecules into soap (e.g. barium stearate) under the film deposition conditions.

Determination of the refractive index of a thin optically anisotropic film is difficult, because the built-up barium stearate film is birefringent and also lacks homogeneity in preparation. Thus, neither can the refractive index of the built-up film be assumed equal to that of the substance in bulk nor can an accurate determination of the refractive index of the film be easily carried out. For determining the metrical thickness of the film the method employed should be independent of its refractive index and should not be subject to differential phase change influences.

The application of the multiple-beam interferometric technique for determining the thickness of a molecular film was first made by Courtney-Pratt. He studied the monomolecular layers of fatty acids spread by the droplet retention technique on mica cleavage surface. His method of measurement with doubly silvered mica forming the interference system, also requires a knowledge of the refractive index of the film. Moreover, the differential phase changes consequent on reflections at mica-silver and monolayer-silver interfaces are involved, and these are not unambiguously known.

In a preliminary report, we applied the multiple-beam interferometric method for measuring the metrical thickness of a built-up 4-layer barium stearate film. In the present work a combined multiple-beam interferometric and X-ray diffraction study of the built-up films of different thicknesses of barium palmitate, barium margarate, barium stearate and barium behenate, is reported.

Experimental

On a clean glass slide selected for its planeness, a thin layer of silver is deposited in vacuum by thermal evaporation. This provides a clean hydrophobic surface for the deposition of molecular films. Over a large area of this silvered glass slide a suitable number of layers (say 20) of the barium soap under study (e.g. barium palmitate, margarate, stearate or behenate) are deposited to form a base film. This deposition is done by the standard Blodgett-Landmuir technique. The successive monolayers are transferred from the water surface to the slide such that the molecules in the adjacent layers in the crystal lattice are oppositely oriented. Now over a part of this area is deposited a second film of the required number of layers; this produces a step on the surface. The base film provides the same material on both sides of the step and thus avoids any differential phase changes in reflection from the two sides of the step. For multiple-beam interferometry an almost opaque coating of pure silver is then deposited over a region including the step. The silvered film is matched at a small angle, against a reference optical flat which is silvered with a low absorption coating having about 80% reflectivity. The system is illuminated with normally incident, parallel, white light to obtain fringes of equal chromatic order in the reflected system. This method evaluating film thickness is independent of the refractive index of the film. And since differential phase changes have also been eliminated, it leads to an accurate determination of the metrical thickness of the molecular film. As an example multiple-beam interferogram over a 7-layer Ba-margarate step is shown in Fig. 1.

For the determination of the lattice spacing perpendicular to the plane of the film (c-spacing), conventional sealed off X-ray sources have been employed. However since the built up films have a limited number of scattering centres, this requires long exposure times and the resolution is also low. To overcome this we have employed a microfocus X-ray source of the kind described by Ehrenberg and Spear and the diffracted spectra were recorded on a Bragg-Muller spectrograph. For X-ray diffraction studies the molecular films were also built up on silvered

![Fringes of equal chromatic order from a 7-layer barium-margarate step. (x 1.8).](image)
microscopic slides. The supporting base for
the built-up films i.e. the glass slide coated
with silver, does not produce any diffraction ef­
facts which would confuse or interfere with the interpretation of the pattern from the film.

Results
For each of the long-chain compounds the
thickness was measured with a two-layer, a
four-layer and a seven-layer film. For the X­
ray diffraction study the number of layers de­
posited on the glass slide was 100. An example
of the X-ray photograph taken with a micro­
focus X-ray source (100 μ line source and CuKα
radiation λ = 1.54 Å) is given in Fig. 2 for
barium stearate.

The interferometric and X-ray diffraction
observations on the built-up films are given in
Table 1.

Discussion
The agreement between the measured thickness
of the unimolecular film and the chain length
implies that the fatty acids spread on a water
surface monomolecularly. Indeed, in accordance
with Langmuir’s hypothesis, short range forces
being responsible for nearly all types of adsorp­
tion, the aqueous substrate does not seem to
produce any long range surface effects bringing
about the attachment and orientation of poly­
molecular chains.

The nature of monomolecular spreading
of fatty acids on water surface is by now well
established by many, though indirect, methods.
Most of the evidence is based on the determina­
tion of the thickness of the monolayer on the
water surface by the area-density method, in
which the density of the monolayer is assumed
to be equal to that of the bulk. This assumption

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Substance & No. layers & \begin{tabular}{c} Mean thickness Å \end{tabular} & \begin{tabular}{c} Unimolecular film thickness Å \end{tabular} & \begin{tabular}{c} X-ray value of the spacing from 100 layer film Å \end{tabular} & \begin{tabular}{c} Unimolecular chain length Å \end{tabular} \\
\hline
Barium Palmitate & 2 & 46.0 ± 5 & 23.0 ± 2.5 & c=46.5 ± 1 & 23.3 ± 0.5 Å \hline
(C₁₅H₃₁COO)₂Ba & 4 & 94.6 ± 0.1 & 23.7 ± 0.1 & 24.5 ± 1.5 & 24.4 ± 0.8 Å \hline
 & 7 & 159.5 ± 5 & 22.8 ± 0.7 & 23.4 ± 1 & 23.4 ± 0.4 Å \hline
 mean = & & 23.2 ± 1.1 Å & & & 24.1 ± 1.1 Å \hline
Barium Margarate & 2 & 48.9 ± 3 & 24.5 ± 1.5 & c=48.0 ± 1 & 24.0 ± 0.5 Å \hline
(C₁₆H₃₃COO)₂Ba & 4 & 97.6 ± 3 & 24.4 ± 0.8 & & & 25.7 ± 0.3 Å \hline
 & 7 & 163.8 ± 7 & 23.4 ± 1 & & & 26.1 ± 0.2 Å \hline
 mean = & & 24.1 ± 1.1 & & & 26.2 ± 0.3 Å \hline
Barium Stearate & 2 & 53.6 ± 1 & 26.8 ± 0.5 & c=50.6 ± 0.8 & 25.3 ± 0.4 Å \hline
(C₁₇H₃₅COO)₂Ba & 4 & 102.9 ± 1 & 25.7 ± 0.3 & & & 29.9 ± 1 Å \hline
 & 7 & 182.7 ± 1 & 26.1 ± 0.2 & & & 30.4 ± 1.3 Å \hline
 mean = & & 26.2 ± 0.3 & & & 30.4 ± 1.3 Å \hline
Barium Behenate & 2 & 60.8 ± 4 & 30.4 ± 2 & c=59.4 ± 1 & 29.7 ± 0.5 Å \hline
(C₂₁H₄₅COO)₂Ba & 4 & 123.0 ± 4 & 30.8 ± 1 & & & 28.9 ± 1 Å \hline
 & 7 & 209.9 ± 6 & 29.9 ± 1 & & & 30.4 ± 1.3 Å \hline
 mean = & & 30.4 ± 1.3 & & & 30.4 ± 1.3 Å \hline
\end{tabular}
\end{table}
is however open to objection because it can be true only if the substance in bulk has a close-packed layer structure similar to that of the monolayer.

According to the process of building up of the films, the c spacing should be twice the molecular chain length $^{3+4}$ i.e. it should be twice the thickness of the unimolecular film. This is verified here within experimental error. Further, since the interferometric values of the unimolecular thickness and the X-ray values of the molecular chain lengths of the substances studied are equal within experimental error, it may be concluded that the molecules in the transferred layers are oriented with their hydrocarbon chains almost at right angles to the silver substrate. For, if the molecules were obliquely oriented to the substrate, the interferometric value of the unimolecular thickness would be less than the molecular chain length. This interferometric and X-ray diffraction evidence regarding the perpendicular orientation of the long chain molecules in the built-up films studied is in accord with that deduced from electron diffraction studies for the case of barium stearate. $^5$ The long chain molecules are expected to be oriented perpendicularly on the slide. $^4$ It is interesting to compare the molecular chain lengths of barium soaps with the chain lengths of corresponding fatty acids. The chain lengths of palmitic, margaric, stearic and behenic acids are 21.6, 23.0, 24.42, and 30.2 Å, respectively. Our molecular chain length for the barium soaps appears to be about 1 Å greater than those of the acids. This amount is on the very limit of our accuracy, yet it possibly does indicate the influence of the barium atom.

The built-up films are almost neutral soaps at the pH value (7.0 to 7.2) used. But some free fatty acid molecules are also present in the interstices of the crystal lattice of the soap $^{17+2}$ the amount depending on the pH. These free fatty acid molecules in the soap film do not appear to cause any change in the metrical thickness but they can alter the refractive index and therefore the optical thickness.

Gregg and Widdowson $^{27}$ have studied the evaporation of free fatty acid from built-up soap films kept in a vacuum. According to their observation, the built-up films are slowly "skeletonized" in a high vacuum. This phenomenon must be considered in connection with the present study because the built-up films are here silvered in vacuum for interferometry. Such "skeletonization" of the film does not seem to change the metrical thickness as is suggested by the close correlation between our interferometric and X-ray data.

### References


En se servant de la technique de Blogett et Langmuir, on a construit à partir des films mono-moléculaires du palmitate de barium, du margarate de barium, du stérate de barium et du béhénate de barium des films à épaisseur de 2, 4 et 7 couches monomoléculaires sur le substrat d'argent. On a déterminé l'épaisseur métrique par l'interférométrie à faiseaux multiples. Les espacements c mesurés par les rayons X par paraissent être deux fois plus grands que la longueur de la chaîne moléculaire. On a établi une corrélation entre la mesure interférométrique de l'épaisseur et la constante du réseau normal au film. La corrélation entre l'épaisseur du film unimoléculaire et la longueur de la chaîne de l'acide gras correspondant conduit à la conclusion que les acides gras se repandent d'une façon mono-moléculaire sur une surface d'eau, ses chaînes d'hydrocarbures étant orientées presqu'à l'angle droit au substrat.
Anomalous Polytypic Structures: Investigation on Cadmium Iodide Crystals

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A direct correlation between the step heights of growth spirals and the heights of the X-ray unit cells, previously observed in silicon carbide crystals, furnished strong experimental support for Frank's dislocation mechanism for the genesis of various polytypes of this substance, but some recently reported anomalous polytypic structures cannot be directly understood in terms of screw dislocation theory. An X-ray diffraction and microscopic study of cadmium iodide has now revealed that these anomalies exist also for other polytypic substances. It is concluded that polytypism is influenced also by factors other than the spiral growth round screw dislocations.

X-ray diffraction studies of three new cadmium-iodide polytypes 26Hc, 26Hd and 50Hc show that 26Hc and 26Hd have different structures but identical lattices with \( a = b = 4.24 \), \( c = 88.8 \) Å. Both belong to space group \( P 3m 1 \). 50Hc has the same \( a, b \) dimensions and space group as 26Hc and 26Hd but has \( c = 171 \) Å; it has been identified from a diffraction photograph taken on a microfocus X-ray generator, and was found on the opposite face of the single-crystal piece which exhibited 26Hd. The detailed structures of 26Hc and 26Hd have been worked out. While the determined structure of the polytype 26Hc has the Zhdanov sequence 211112 11 11 11 11 11, that for 26Hd is 22 22 22 11 22 22 22. The former structure was solved by a graphical method which is a special case of Lipson & Taylor's Fourier Transform method. The method outlined may be helpful in determining structure of polytypes which are not highly based on a basic phase but show characteristic intense X-ray reflexions. Structures 26Hc and 26Hd come respectively from the parent structures 2H and 4H, but it is shown that 50Hc has not originated from any of these basic phases.

The combined microscopic and X-ray studies of these structures reveal certain anomalies. In the case of 26Hc these are concerned with, firstly, the integral multiplicity of the Burgers vector and \( c \) spacing of the parent structure, secondly the absence of any spiral growth feature on its surface, and thirdly the inexplicable character of its atomic zigzag sequence. In 26Hd and 50Hc the anomalies are that there is no spiral growth feature on the surface of polytypic crystal 26Hd though its structure appears to have resulted from dislocation mechanism, that spiral growth feature is present on the surface of 50Hc whose structure does not appear to have originated by dislocation mechanism, and that both these unrelated structures exist in the same single-crystal piece.

Introduction

In a recent publication Krishna & Verma (1963) have reported a detailed X-ray diffraction and microscopic study of a large number of SiC polytypes, in which attention was mainly directed towards the analysis of the results in terms of the screw dislocation theory of polytypism. This theory, which was put forth by Frank (1951), and experimentally verified in the case of SiC crystals (Verma, 1952, 1957), gives a vivid and pictorial representation of the formation of different polytypes. However, the results obtained by Krishna & Verma (1963) revealed certain anomalous polytypic structures which could not be explained as having resulted directly by the dislocation mechanism. In particular the observation of polytypic structures which would require the Burgers vector of the generating screw dislocation to be an integral multiple of the lattice parameter of...
the parent structure was anomalous. It was concluded that the cause of polytypism in SiC needs to be re-
considered.
In the present work we were interested to investigate whether these anomalies were peculiar to silicon car-
bide crystals or whether they existed for other poly-
typic substances also. We therefore decided to investiga-
te cadmium iodide, which is also known to exhibit a
large number of polytypic modifications. An extensive
investigation was carried out with the main emphasis
on the identification and structure determination of
long-period polytypic crystals; the determination of
the structure of long period polytypes has not pre-
viously been done and it is mainly these polytypes that
display anomalous features. However, such a study
presents both experimental and theoretical difficulty.
The experimental difficulties arise from the fact that
X-ray diffraction photographs obtained with a conven-
tional sealed off X-ray tube lack the high resolution
which is necessary for the identification of the long
period polytypes of cadmium iodide. Minute pieces of
cadmium iodide, which would result in higher resolu-
tion of X-ray reflexions, could not be obtained. This
was so since, unlike silicon carbide, cadmium iodide
is soft and flexible and any attempt to cut the flake
invariably leads to the distortion of the lattice. To over-
come this difficulty we have used a microfocus X-ray
tube in cases where higher resolution of X-ray re-
flexions was required. The theoretical difficulty arises
since the usual trial-and-error methods of structure
determination do not always lead to a successful sol-
tion of the long-period polytypic structures. In fact
to work out the detailed structure merely by trial-and-
error methods is practically impossible for these long
period polytypes. We have, therefore, made use of a
novel method to determine the structures by critically
examining the intensity distribution in the 10-/ re-
ciprocal lattice row.
Over 20 new polytypic modifications of cadmium
iodide have been identified by us. These show a wide
variety of growth features and structures. Among new-
ly isolated polytypes, types 22Hc, 28Hc, 26Hc, 26Hd and
50Hc are of special interest. The polytypes 22Hc and
28Hc have been described elsewhere (Srivastava & Ver-
ma, 1962, 1964). This paper reports the investigations
on polytypes 26Hc, 26Hd and 50Hc which show anom-
 Alaniz. Thus the polytype under consideration is designated
as 26Hc.

X-ray methods
The a-axis oscillation and Weissenberg photographs
of cadmium iodide crystals have invariably been found
to show streaking between X-ray diffraction spots. This
rendered their use practically impossible either for the
identification of the polytype or for structure deter-
mination. However, a-axis oscillation photographs
showed discrete sharp spots. Therefore, a-axis oscil-
lation and Weissenberg photographs recording either
10/- or 01/- rows were taken. As had been shown by
Ramsdell (1944) and Mitchell (1955) for SiC, for struc-
ture determination it is sufficient to compare the obser-
vanced and calculated intensities for 10/- or 01/- reflex-
ions alone.
For simple and moderately long-period polytypes
diffraction patterns were obtained by employing con-
ventional sealed off X-ray tubes. We have used a micro-
focus X-ray tube when higher resolution of X-ray re-
flexions and greater brilliance of the source are re-
quired. A commercial microfocus X-ray generator
based on the design of Ehrenberg & Spear (1951) and
manufactured by Hilger and Watts has been employed
in the present investigation. This microfocus X-ray
tube differs chiefly from the conventional tube in its
small focus size so that the intensity per unit area in
this is considerably larger, and also because of
small focus size the resolution of X-ray reflexions is
much higher. A line focus of 100/x and copper target
were used for recording diffraction pattern shown in
this paper.

Results
Figs. 1 and 2 refer to a hexagonal shaped crystal with
a well developed and shining (0001) face of dimensions
about 1 mm x 1 mm. This will be referred to as crystal
No. 1. Fig. 1 shows a 15° a-axis oscillation photograph
of this crystal recorded on a 3 cm camera with Cu Kα
radiation. Fig. 2 shows the corresponding zero-layer
a-axis Weissenberg photograph of the same crystal
taken on a camera of diameter 5-73 cm, using Cu Kα
radiation. Measurements on these photographs reveal
that the a spacing of this crystal is 8.88 Å. The a spac-
ing of the basic 2H structure is 6.835 Å. Therefore the
present crystal is a 26 layered polytype. This is con-
Alaniz. Thus the polytype under consideration is designated
as 26Hc.

Experimental
Crystal growth
The crystals used in the present study were all grown
by slow evaporation of an aqueous solution of the com-
ound at room temperature. The hexagonal shaped
crystals were gently removed from the dish with the
help of a sharp needle after complete evaporation. This
method is similar to that of Mitchell (1955) but differs
in that the crystals were not taken out of the mother
liquor but were removed only when they had grown
fully and the water completely evaporated. As will be
shown later, the crystals grown by this method are of
added interest as their X-ray diffraction study throws
light on what happens both in the initial and final
stages of growth of the crystal.

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Fig. 7. A magnified view of the X-ray reflexions in Fig. 6. (x 2)

Fig. 8. Further magnification of X-ray reflexions in Fig. 6. (x 3)
Fig. 1. A 15° α-axis oscillation photograph of the polytype 26Hc, recorded on 3 cm camera with Cu Kα radiation employing a conventional X-ray tube. (×$	ext{3/4}$)

Fig. 2. Zero-layer α-axis Weissenberg photograph of polytype 26Hc taken with Cu Kα radiation on a camera of diameter 5-73 cm, employing a conventional X-ray tube. The festoon corresponding to the 10./ row of spots is recorded on the right side of the straight row of 00./ spots. The first intense reflexion towards the minimum correspond to l = 58 and 59. (×$	ext{3/4}$)

Fig. 3. A 15° α-axis oscillation photograph of the polytype 26Hc, recorded on a 3 cm camera with Cu Kα radiation employing a conventional X-ray tube. (×$	ext{3/4}$)

Fig. 4. Zero-layer α-axis Weissenberg photograph of polytype 26Hc taken with Cu Kα radiation on a camera of diameter 5-73 cm, employing a conventional X-ray tube. The festoon corresponding to the 10./ row of spots is recorded on the right side of the straight row of 00./ spots. The first two visible reflexions towards the minimum correspond to l = 58 and 59. (×$	ext{3/4}$)

Fig. 5. A 15° α-axis oscillation photograph of the polytype 50H, recorded on a 3 cm camera with Cu Kα radiation employing a conventional X-ray tube. (×$	ext{3/4}$)

Fig. 6. A 15° α-axis oscillation photograph of the polytype 50H, recorded on a 3 cm camera with Cu Kα radiation employing a microfocus X-ray tube. (×$	ext{3/4}$)

[To face p. 58]
dimensions about 2 mm x 1 mm. This crystal will be referred to as crystal No. 2. Fig. 3 shows a 15° a-axis oscillation photograph of this crystal recorded on a 3 cm camera with Cu Kα radiation. Fig. 4 shows the zero-layer a-axis Weissenberg photograph of the same crystal taken on a camera of diameter 5-73 cm with conventional sealed off X-ray tube. This crystal is also of the polytype 26H. However, since the intensity distributions of these two 26H crystals are different, their crystal structure must also be different. Mitchell (1956) has already reported two other 26 layered polytypes but no structural data were given. We have, therefore, referred to the polytypic structure of crystal No. 1 as 26H₁ and to that of No. 2 as 26H₆.

Fig. 5 represents a 15° a-axis oscillation photograph obtained with conventional sealed-off tube by reversing the crystal so that the opposite face of crystal No. 2 faces the X-ray beam. This shows it to be a high polytype. Thus two different polytypic structures are present in the same single crystal of the compound. As will be shown later it has been possible to detect the presence of these two polytypes in the same crystal because of the high absorbing property of both the cadmium and iodine atoms. However, the X-ray reflexions on this photograph do not show good resolution and it was therefore decided to use the micro-focus X-ray tube.

Fig. 6 shows the same X-ray photograph as Fig. 5, employing the microfocus generator. For Fig. 5 the exposure time was 10 hours while for Fig. 6 it was 6 hours. Even with less exposure time, the diffraction spots obtained with the microfocus generator are brighter. The background is also considerably less than on Fig. 5. Each reflexion in Fig. 6 can be distinguished separately and accurate measurement revealed the crystal to be type 50H. Since two such polytypes have already been reported (Mitchell, 1956; Trigunayat, 1960) the present polytype is designated 50H₆.

Structure of polytypes

Structure of polytype 26H₁

The usual method of structure determination consists in calculating all possible structures involving Zhdanov numbers 1,2,3,4 etc. (Zhdanov, 1945), in their Ramsdell zigzag sequence (Ramsdell, 1944, 1947) and deciding the correct structure by comparing the calculated intensities with the observed ones; this becomes practically impossible for a large polytype. The following simplifications are then made. Since almost all the cadmium iodide structures have only the Zhdanov numbers 1 and 2 in their zigzag sequence we shall restrict the structures to contain these numbers only. Even then there will be a large number of ways which will be geometrically possible for a 26-layered unit cell because of the presence of No. 1 in the zigzag sequence. However, the following are the important features observed on the X-ray diffraction patterns of the structure 26H₁.

(i) All the reflexions which coincide in position with those from a basic 2H phase are intense and outstanding.

(ii) The 10/ reflexions corresponding to l = 13n ± 1 (n = 1,2,3) are either absent or are very weak. The reflexions 10/13n ± 1 and 10/13n ± 1 are also weak or absent.

(iii) The 10/ reflexions corresponding to l = 13n ± 2 (n = 1,2,3) are the second most intense reflexions. At some places they are almost as intense as the reflexions described in (i). Reflexions 10/13n ± 2 and 10/13n ± 2 are also strong.

The above observations suggest the presence of a large number of 11 units in the zigzag sequence of 26H₁, i.e. the basic phase of this structure is 2H. Mitchell (1956) has suggested that a polytypic series based on the basic 2H phase should not exist. However, this does not appear to be quite correct since in the present investigation as well as previously (Srivastava & Verma, 1962), polytypes showing X-ray reflexions having intensity distribution corresponding to the 2H phase have been observed. We expect therefore the structure 26H₁ to be composed of many (11) units with some faults at the end of the sequence. The sequences derived in this manner will be of the type (11)₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁₁�

\[
I \propto A'^2 + B'^2
\]

where

\[
A' = \sum_{Z_{A,\alpha}} f_{1,\alpha} \cos 2\pi(lZ+\Sigma f_{1,\alpha} \cos 2\pi(lZ-\frac{1}{2})) + \sum_{Z_{B,\beta}} f_{1,\beta} \cos 2\pi(lZ+\frac{1}{2})
\]

\[
B' = \sum_{Z_{A,\alpha}} f_{1,\alpha} \sin 2\pi(lZ+\Sigma f_{1,\alpha} \sin 2\pi(lZ-\frac{1}{2})) + \sum_{Z_{C,\gamma}} f_{1,\gamma} \cos 2\pi(lZ+\frac{1}{2})
\]

where \(Z_{A,\alpha}\); \(Z_{B,\beta}\) and \(Z_{C,\gamma}\) denote the Z coordinate of iodine and cadmium atoms respectively on the A vertical axis passing through (000), the B vertical axis passing through (0 0 0) and the C vertical axis passing through (1 0 0), which can be written in short as \(A: 00z; B: \frac{1}{2} \frac{1}{2} z\), and \(C: \frac{1}{2} \frac{1}{2} z\). \(\Sigma\) means summation over \(Z_{A,\alpha}\) iodine atoms at A sites and cadmium atoms at \(z\) sites. Similarly for \(\Sigma\) and \(\Sigma\). In cadmium iodide, as has been shown by Bozorth (1922), the basic polyatomic layer consists of two layers of hexagonal close packed iodine
ions with the small cadmium ions nested between them. The vertical I-I distance is 3.41 Å and the vertical Cd-I distance is nearly half of this distance. The cadmium layer is thus midway between two iodine layers.

The calculated intensities for none of the 21 structures matched with the observed intensity distribution on the X-ray diffraction photograph. It became then imperative to find other clues to the structure. Tomita (1960a, b) has theoretically shown in the case of silicon carbide structures that if there is a minimum intensity observed between two successive reflexions corresponding to the basic phase then the structure should consist of two separate multiple units of the basic phase separated by a few layers in between. Taking this into account we tried nine possible structures of the type \( (11)_n (22)_p (11)_q (22)_r \), where \( m, p, q \) and \( r \) are integers.

However, these attempts also did not lead to success. It was then thought that the minimum corresponding to \( l=13n \pm 1 \) may be structural extinctions. Since only few combination of atomic positions could produce these extinctions, it was tried to see if these extinctions could suggest some clue to the structure. Following Krishna & Verma (1962) it can be shown that if reflexions \( 10 \cdot \ell (q=13n \pm 1) \) are absent the following relations must hold good for iodine atoms.

\[
\Sigma \cos 2\pi qZ_A = \Sigma \cos 2\pi qZ_B = \Sigma \cos 2\pi qZ_C = 0 \quad (4)
\]

\[
\Sigma \sin 2\pi qZ_A = \Sigma \sin 2\pi qZ_B = \Sigma \sin 2\pi qZ_C = 0 \quad (5)
\]

Similar relations should hold for cadmium atoms also. By trial and error in an Argand diagram it was found that only the sequence 1111114111111 satisfied the above relations. This sequence satisfied relations (4) and (5) only for even values of \( n \) and not for odd values. The sequence, however, contained Zhdanov number 4 which has never been found to exist in the cadmium iodide structural series. Calculation of intensities showed large intensity for odd values of \( n \) in \( 13n \pm 1 \), whereas the opposite has been experimentally observed. This solution was therefore rejected.

Having exhausted the above possibilities we thought it opportune to see whether the above described feature (iii), viz. the reflexions \( 10 \cdot 13n \pm 2 \) being very intense, could be of any help in finding a possible solution of the structure. The outstanding intense reflexions corresponding in position to \( 2H \) reflexions have already indicated the presence of many (11) units in the atomic sequence of \( 26H_e \). The next most intense reflexions corresponding to \( l=13n \pm 2 \) should therefore be informative regarding the atomic position in the structure. This is so since there are comparatively few ways in which atoms can be placed to scatter in phase for a given reflexion, whereas there are many ways in which approximately zero scattering can be produced. Lonsdale (1929), Robertson & White (1945) and Abrahams & Robertson (1948) have made use of the criterion in determining certain organic structures. This consideration has helped us to solve the structure as shown below. The method used to deduce the atomic positions is in fact a special case of Fourier transform methods (Lipson & Taylor, 1958).

All the cadmium iodide polytypes which are based on some ideal phase are formed by sandwiches of the type \( A_yB \) or \( C_zB \) in which \( A, B, C \) refer to iodine positions and \( y \) and \( z \) to the cadmium positions. Therefore, it can well be concluded that atoms along the \( B \) axis are always fixed along odd sites only, the layer passing through the origin being taken as the zero layer. In the present case \( B \) atoms occupy positions \( 1, 3, 5 \ldots 25 \). Any sequence of \( A_yB \) and \( C_zB \) sandwiches to form the \( 26H \) structure will always give the above \( B \) position. Therefore, \( B \) atoms contribute significantly to the intensities corresponding to \( 2H \) positions only and give almost negligible contribution to other reflexions. Thus it remains to decide about the atomic positions along \( A \) and \( C \) axes only. Now keeping the atoms along the \( B \) axis fixed and interchanging the positions of atoms along \( A \) with those along \( C \) does not alter the structure. It merely means changing the origin and inverting the whole atomic sequence. Thus it remains to decide the positions of atoms along either of the two vertical axes \( A \) or \( C \) only. The positions of cadmium atoms are automatically fixed when the positions of iodine atoms are decided.

Since in cadmium iodide structures the plane \( (1120) \) contains all the atoms along the three vertical axes \( A, B \) and \( C \), it would be profitable to consider the \( (1120) \) projection. As is obvious from Fig. 9 the matrix effecting the required transformation is:

\[
\begin{pmatrix}
1 & 1 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\]

In the special case of \( 10l \) planes the new indices will be

\[
h' = h - k = h \\
k' = k = 0 \\
l' = l
\]

Thus the transformation does not lead to a change in the indices of planes of the type \( 10l \). Accordingly in the deduction below the same indices of the \( 10l \) planes have been used when the \( (1120) \) projection is considered.

As has already been mentioned the reflexions which correspond in position to the basic \( 2H \) phase are most
intense. Fig. 10 shows the traces of planes in the (1120) projection so that the atoms lying on them would scatter in phase for each of the 10-13n (n = 1, 2, 3) reflexions. The atoms must lie on the intersection of these planes if all of the above reflexions are to be outstanding. As is evident from Fig. 10 the intersections are at heights 0, 2, 4, ..., 26 along either of the A or C axes. Since the A or C atoms are present at even sites only the intersections in Fig. 10 represent the actual atomic sites. The presence of A or C atoms at heights 0, 2, 4, ..., 26 means that the atomic sequence must contain many (11) units, i.e., many (\(AyB\)) or (\(CxB\)) sandwiches, which is in agreement with the previous deduction. Figs. 11 and 12 show the traces of planes in which the atoms should lie if they were to scatter in phase to make the reflexions 10-13n ± 2 (n = 1, 2, 3) intense. These are the next most intense reflexions. Fig. 11 shows the case for 10-13n+2 (n = 1, 2, 3) reflexions and Fig. 12 for 10-13n-2 (n = 1, 2, 3). The atoms should lie at the intersection of the planes if all the reflexions in either of Figs. 11 or 12 are to be prominent. The places where atoms could be fitted on to the closest possible intersections of the traces of planes, and which lie either exactly or are near enough to atomic sites, are shown in Figs. 11 and 12. Now if all the reflexions corresponding to 10-13n, 10-13n+2, and 10-13n-2 are to be intense the atoms should lie at sites which are common to Figs. 10, 11 and 12. From Figs. 10, 11 and 12 it could be seen that in the first instance these sites are at heights 0, 2, 12, 14, 24 along either of the A or C axes. Among the thirty atomic sequences mentioned on pages 58 and 59 for the structure of \(26\text{H}_c\), only those gave a rough fit for the calculated and observed intensities in which pairs of atoms along either of the A or C axes having a difference of either 12 or 14 units were present. Since 12 and 14 add to 26 in the case of polytype 26\(\text{H}_c\) the two atomic arrangements which have either 12 or 14 as the common difference among atomic positions along any axis give identical structures and any of them could be derived from the other by a shift of the origin. Keeping this in view the positions 0, 2, 12, 14, 24 were considered in two ways, firstly taking the positions 0, 2, 12, 14 which represent two pairs of atoms with a common difference of 12 units and secondly taking position 24 also. Since the atomic positions along the B axis have already been fixed to have odd atomic positions only, the atomic positions on both A and C axes are automatically decided when positions on any of them are fitted at the heights mentioned above. These considerations gave the following two sequences:

(i) 2112 11 11 11 2112 11 11 11
(C atoms at heights 0, 2, 12, 14)

(ii) 211112 11 11 11 2112 11 11
(C atoms at heights 0, 2, 12, 14, 24)

Intensities were calculated with the use of expression (1) for some important reflexions for the above sequences. It was found that though the above sequen-

---

Fig. 10. Traces of 10-13, 10-26 and 10-39 planes in the (1120) projection. To distinguish between these planes the traces of 10-13 have been shown extended towards the left and those of 10-26 towards the right, while the traces of 10-39 are confined to the rectangular area itself.

Fig. 11. Traces of 10-15, 10-28 and 10-41 planes in the (1120) projection. To distinguish between these planes the traces of 10-15 have been shown extended towards the left and those of 10-28 towards the right, while the traces of 10-41 are confined to the rectangular area itself.

Fig. 12. Traces of 10-11, 10-24 and 10-37 planes in the (1120) projection. To distinguish between these planes the traces of 10-11 have been shown extended towards the left and those of 10-24 towards the right, while the traces of 10-37 are confined to the rectangular area itself.
positions 10 and 22 together and thirdly taking all the positions 4, 10, 16, 22. Above considerations led to the following sequences:

(i) $21112$ 11 11 21112 11 11 2121
(C atoms at heights 0,2,4,12,14,16)

(ii) $2112$ 11 11 21112 11 11 22
(C atoms at heights 0,2,10,12,14,22)

(iii) $21111112$ 11 11 21112 11 11
(C atoms at heights 0,2,4,12,14,16,24 or 0,2,10,12,14,22,24)

(iv) $21112$ 11 2111112 11 11 22
(C atoms at heights 0,2,4,10,12,14,16,22)

(v) $21111112$ 11 11 21112 11 11
(C atoms at heights 0,2,4,10,12,14,16,22,24)

Calculation of intensities showed that all of the above sequences gave large intensities for reflections $10-13/\theta$ ± 2. To decide the correct structure, the intensities for other reflections were calculated and compared with the observed intensities. The first sequence, viz. $21112$ 11 11 21112 11 11 11, showed an excellent agreement as shown in Table 1. Other sequences gave discrepancies for reflections other than $10-13/\theta$ and $1013/\theta$ ± 2. The detailed structure of polytype $26H_c$ is therefore as follows:

Space group: $P 3 m 1$
Zhdanov symbol: $21112$ 11 11 211112 11 11 11

ABC sequence for iodine atoms:

$\text{ABCCBCBCBABABABABABABABAB}$

ABC sequence for both cadmium and iodine atoms:

$(\text{AB})_2(\text{CaB})(\text{CaB})(\text{CzB})(\text{AB})_2(\text{CaB})(\text{CaB})(\text{CzB})(\text{AB})_2(\text{CaB})(\text{CaB})$

<table>
<thead>
<tr>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 iodine at $0 0 0$</td>
</tr>
<tr>
<td>$t=0, 8r, 10r, 12r, 20r, 22r, 24r$.</td>
</tr>
<tr>
<td>13 iodine at $\frac{1}{2} \frac{1}{2} t''$</td>
</tr>
<tr>
<td>$t''=z, 3z, 5z, 7z, 9z, 11z, 13z, 15z, 17z, 19z, 21z, 23z, 25z$.</td>
</tr>
<tr>
<td>6 iodine at $\frac{1}{2} \frac{1}{2} t''$</td>
</tr>
<tr>
<td>$t'=z', 2z', 3z', 4z', 5z', 6z', 7z', 8z'$.</td>
</tr>
<tr>
<td>7 cadmium at $0 0 0 t_1$</td>
</tr>
<tr>
<td>$t_1=5z', 9z', 13z', 29z', 33z', 37z'$.</td>
</tr>
<tr>
<td>7 cadmium at $\frac{1}{2} \frac{1}{2} t_1$</td>
</tr>
<tr>
<td>$t_1'=z', 17z', 21z', 25z', 41z', 45z', 49z'$.</td>
</tr>
</tbody>
</table>
| where $z'=\frac{3z}{4}$ and $z'=\frac{z}{2}$.

Structure of polytype $26H_a$

Here again the structure determination by mere trial and error would be an arduous task. This can be made easy if some information can be gathered from the intensity distribution on the X-ray diffraction pattern. The following significant features are observed:

(1) All the reflections which coincide in position with the reflections of the basic $4H$ phase are distinctly more intense than the others and have intensity distribution similar to that from a $4H$ structure.

| Table 1. Calculated and observed relative intensities for the structure $26H_c$ |
|-----------------|-----------------|-----------------|
| $l$  | Calculated intensities | Observed* intensities | $l$  | Calculated intensities | Observed* intensities |
| 0  | 0.13                  | a                | 27 | 1.43                  | a                |
| 1  | 0.17                  | a                | 28 | 2.43                  | s                |
| 2  | 0.43                  | a                | 29 | 1.49                  | vvw              |
| 3  | 1.44                  | a                | 30 | 2.68                  | vvw              |
| 4  | 0.39                  | a                | 31 | 4.69                  | vvw              |
| 5  | 1.53                  | a                | 32 | 18.75                 | w                |
| 6  | 6.43                  | a                | 33 | 19.92                 | w                |
| 7  | 0.79                  | a                | 34 | 2.57                  | vvw              |
| 8  | 2.05                  | a                | 35 | 2.59                  | vvw              |
| 9  | 2.84                  | a                | 36 | 2.94                  | a                |
| 10 | 4.53                  | vvw              | 37 | 117.92                | ms               |
| 11 | 170.96                | ms               | 38 | 1.12                  | a                |
| 12 | 1.36                  | a                | 39 | 399.96                | s                |
| 13 | 1000.00               | vvw              | 40 | 1.21                  | a                |
| 14 | 1.81                  | a                | 41 | 56.27                 | vvw              |
| 15 | 256.07                | s                | 42 | 2.97                  | a                |
| 16 | 19.97                 | vw               | 43 | 0.30                  | a                |
| 17 | 2.51                  | vvw              | 44 | 0.89                  | a                |
| 18 | 8.16                  | vvw              | 45 | 2.09                  | a                |
| 19 | 34.35                 | w                | 46 | 1.80                  | a                |
| 20 | 46.02                 | w                | 47 | 0.24                  | a                |
| 21 | 3.90                  | vvw              | 48 | 0.96                  | a                |
| 22 | 7.02                  | vvw              | 49 | 0.12                  | a                |
| 23 | 7.27                  | vvw              | 50 | 1.81                  | a                |
| 24 | 276.57                | s                | 51 | 0.45                  | a                |
| 25 | 1.86                  | a                | 52 | 0.01                  | a                |

* The observed intensities were actually taken from the series 10-52 through 10-104. This series has the same intensity sequence as 10-0 through 10-52 which is not clearly visible on the Weissenberg photograph because of absorption caused by the non-equidimensional crystal plate.
(2) The reflexions which do not coincide with the corresponding 4H reflexions, but are nearest to them, are intense but not so much as their corresponding 4H reflexions.

The above features suggest the presence of a large number of 22 units in the zigzag sequence of the structure 26H. Below are listed the possible structures with decreasing probability:

(i) 22 22 22 22 22 22
(ii) 22 22 21121112 22 22
(iii) 22 22 11122111 22 22
(iv) 22 22 1111111111 22 22
(v) 22 22 11211211 22 22
(vi) 22 22 12111121 22 22

It will be seen that each of the above arrangements has a mirror plane. This is because any number of (22) units have in themselves a mirror plane and after taking any number of (22) units the remaining layers could only be arranged taking the Zhdanov numbers 1 and 2 in sequences having a mirror plane. As for example, keeping 4 units of (22) the remaining 10 layers could be arranged in sequences 21111112, 112 11 11, 212212, 122221, and 11 11 11 11, each of which has a mirror plane. When two sequences each of which has a mirror plane are placed together as such, the resulting sequence also exhibits a mirror symmetry about either of the mirror planes of the two sequences. In fact all the determined sequences of cadmium iodide consisting of Zhdanov members 1 and 2 have mirror planes (Mitchell, 1956; Srivastava & Verma 1962, 1963). Intensities for a few important reflexions were calculated for each of the above structures. The intensity formula for 10q reflexions corresponding to space group P3m1 to which the polytype belongs has already been given in (1). A comparison of the calculated intensities with those observed on the X-ray diffraction photograph showed that the first sequence in the above list gives a close agreement with the observed intensities. The calculated intensities for other sequences showed marked differences with the observed ones. Table 2 shows the good agreement between the two intensities. The detailed structure of the polytype 26H is, therefore, as below:

Space group: P3m1
Zhdanov symbol:

22 22 22 22 22 22 11

ABC sequence for iodine atoms:

ABCB ABCB ABCB ABCB ABCB ABCB AB

ABC sequence for cadmium and iodine atoms:

(AYB)(CaB)(AYB)(CaB)(AYB)(CaB)(AYB)(CaB)
(AYB)(CaB)(AYB)(CaB)(AYB)(CaB)(AYB)

Atomic coordinates:

7 Iodine at 0 0 t

I = 0, 4z, 8z, 12z, 16z, 20z, 24z,
13 Iodine at 3 1 0 t

I = z, 3z, 5z, 7z, 9z, 11z, 13z, 15z, 17z, 19z, 21z, 23z, 25z

6 Iodine at 3 1 0 t

t" = 2z, 6z, 10z, 14z, 18z, 22z

6 Cadmium at 0 0 t

t = 5z, 13z, 21z, 29z, 37z, 45z

7 Cadmium at 3 1 0 t

t = z, 9z, 17z, 25z, 33z, 41z, 49z

where z = ±1/6 and z = ±5/6

The intensities of 10q reflexions obtained by expression (1) were multiplied by the Lorentz-polarization factor (1 + cos θ)/(sin θ) where θ is the Bragg angle and is calculated from the relation

\[
\sin \theta_{10q} = 1/2a^* + 1/2c^*\]

where a and c represent unit-cell vectors of the reciprocal lattice given by aa^* = λ, cc^* = λ. To verify the proposed structure, intensities for a complete range of 52 reflexions in the 10q row were calculated in both cases. It is not necessary to check the agreement beyond this range since in a cadmium iodide structure 4H intensities repeat themselves after l = 2n. In cadmium iodide crystals high absorption occurs owing to the presence of both the heavy atoms cadmium and iodine. Moreover, since cadmium iodide crystals grow in the form of a thin hexagonal platelet, the absorption varies because of the shape effect. The absorption correction which would have improved the results could not be applied since suitable absorption factors for a thin platelet like the present crystal were not available. However, it is believed that this will not cause any abrupt change in the observed intensities, since the recorded reflexions correspond to the crystal face (0001) nearly perpendicular to the X-ray beam.

Discussion

It will now be examined how far the experimental results agree with those expected on Frank's (1951) screw-dislocation theory of polytypism originally proposed for silicon carbide. Forty (1952) has applied Frank's theory to explain the generation of cadmium iodide polytypes in the following manner. Regarding type 4H as the parent structure, slips of various magnitudes in this structure in the initial stages of growth create both even and odd dislocations, raising terminated steps of various heights. These steps will ultimately wind up into spirals so that the structure and height of the unit cell are controlled by the structure and height of this step. An even dislocation, i.e., a dislocation whose Burgers vector is an integral multiple of the c parameter of parent 4H structure, will leave the layers in perfect fit with each other, so that the parent structure itself continues during further growth. But odd dislocations of different strength leave a misfit in the structure at the initial step, so that the subsequent growth leads to the generation of various polytypic structures. Therefore, a polytype which has resulted by the screw-dislocation mechanism should exhibit spiral feature on its surface, should be based on a parent structure, should have
the Burgers vector of the generating screw dislocation as a non-integral multiple of the c parameter of the parent structure, and also should be completely ordered.

The polytype 26Hc has been shown to be based on 2H phase; therefore the Burgers vector of the generating screw dislocation will be exactly 13 times the c parameter of 2H. A step of 26 layers formed in a basic 2H structure could result in nothing else except in the further growth of type 2H itself. A single screw dislocation in basic 2H phase cannot, by itself, create any other polytype. Other polytypes from basic 2H phase could then only result when a basic (11) step combines with another (22) step from a basic 4H phase. Though the Zhdanov sequence 211112 11 11 211112 11 11 of 26Hc contains a large number of (11) units the faults are not of the type 22 and are also at several places within the sequence. The atomic zigzag sequence of polytype 26Hc 2(11)2 (11), 2(11)2 (11) has stacking changes at intervals of 3, 4, 3, 3, in the sequence of basic polytype 2H, (11)₄. If one wanted to explain the origin of this structure in terms of cooperation of dislocations, one would have to postulate at first the creation of step 8H, (211112) by cooperation of basic 4H, (22) and 2H, (11) steps and then further two 8H, (211112) steps would have to cooperate with a postulated presence of nearly (11) steps in the manner 211112 (11), 211112 (11). This is inconceivable and thus cooperation of dislocations cannot give rise to the polytype 26Hc. The surface of this crystal (No. 1) was examined under a narrow pencil of white light in bright field illumination for any growth feature. It was also examined by incident phase contrast illumination but this did not show any improvement. The surface of the polytypic crystal 26Hc did not reveal any growth features at all. The above observations indicate that the structure 26Hc has not grown as visualized by dislocation mechanism.

X-ray diffraction photographs from crystal No. 2 show that it consists of a 26-layered polytype on one face called 26Hd and a 50-layered polytype on the other. The diffraction from the two opposite faces could be separately recorded because of the high absorbing property of both the cadmium and iodine atoms, owing to which at one time only that diffraction pattern is recorded which corresponds to the polytypic structure of the crystal face which is away from the incident radiation (Srivastava & Verma, 1962). We thus have a peculiar instance when a single-crystal piece possesses two modifications both of which have the same a, b dimensions and space group but differ in the c dimensions of the unit cell, one being 88.8 Å and the other 171 Å.

The polytype 26Hd with the Zhdanov sequence 222222222222 11 is one of the polytypes of the series which will be formed by dislocation mechanism from the 4H structure. However, surprisingly, no spiral was observed on this face of crystal No. 2. From this it may be concluded that though the structure of polytype 26Hd conforms to that expected on dislocation theory, there is no evidence from the surface features

Table 2. Calculated and observed relative intensities for the structure 26Hd

<table>
<thead>
<tr>
<th>l</th>
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<td>a</td>
<td>52</td>
<td>0·25</td>
<td>a</td>
</tr>
</tbody>
</table>

* The observed intensities were actually taken from the series 10-52 through 10-104. This series has the same intensity sequence as 10-0 through 10-52 which is not clearly visible on the Weissenberg photograph because of absorption caused by the non-equidimensional crystal plate.
Fig. 13. Surface micrograph of crystal No. 2 corresponding to type 50Hc employing a narrow pencil of white light. (x 130).

Fig. 14. Interferogram of crystal No. 2 corresponding to 50Hc structure employing green mercury light of $\lambda = 5461$ Å. (x 130).
to support this. The other face of crystal No. 2 which consists of polytype 50H shows a complicated growth pattern illustrated in Fig. 13. But the intensity distributions in X-ray patterns of 50H reveals that this is not based on either of the basic 2H or 4H phases, nor does it appear to have originated from 26H. But the observation of a spiral feature corresponding to 50H polytype would indicate growth by dislocation mechanism. Thus we have the curious situation that in the same crystal piece on one side we have the polytypic structure 26H whose parameters can be explained by dislocation mechanism but not does not exhibit any spiral feature, whereas on the other side there is the polytype 50H, which does not seem to have resulted by dislocation mechanism but still shows a complicated spiral feature.

Figs. 13 and 14 respectively show the surface micrograph and interferogram of that face of crystal No. 2 which exhibits the polytype 50H. The interferogram in Fig. 14 shows the two-beam internal interference fringes. For step height estimation, only the method of two-beam internal interference (Forty, 1952) could be used. The method of multiple-beam interference similar to that used for stearic acid crystals by Verma & Reynolds (1953) could not be applied here since cadmium iodide reacts with silver. As is evident from Fig. 14 the fringes observed do not contour the growth steps. Owing to this an estimation of spiral step height and thus a verification of the correlation between this and the c dimensions of the unit cell was not possible.

However, it is known (Trigunayat & Verma, 1962) that such a correlation is not observed on any of the cadmium iodide polytypes except for the basic 2H and 4H structures. This suggests that the formation of a polytype is not necessarily governed by dislocation mechanism. Jagodzinski (1949a, b, c, 1954) who has also arrived at a similar conclusion from thermodynamic considerations, has suggested that the formation of a polytypic structure is governed by its vibration entropy. Accordingly highly ordered long period polytypes like 26H, 26Ha and 50H would become increasingly improbable.

To sum up the polytypes 26H, and 26Ha show some evidence in favour of the screw-dislocation theory inasmuch as the dependence on the basic 2H and 4H structures and the resulting orders of the structure are concerned. The absence of any spiral features on the surfaces of the structures 26H, and 26Ha, the unexpected atomic zigzag sequence of the structure 26H, and the fact that the Burgers vector for 26H is an integral multiple of the c dimension of the basic 2H structure, do not support the origin of these structures by the screw dislocation mechanism. However, the absence of spiral growth features on the crystal 26H, and 26Ha can be explained if the growth conditions of the end surface were different from those ruling during the growth of underlying layers and were not based on dislocation mechanism. The polytype 50H, furnishes a peculiar case where surface evidence indicates growth by the screw dislocation mechanism but the unit cell of

the structure does not appear to have resulted by this mechanism.

In conclusion we find that anomalous polytypic structures first observed in silicon carbide, in which the Burgers vector of the generating screw dislocation is an integral multiple of the c parameter of the basic structure, exist for cadmium iodide crystals also. In addition, cadmium iodide polytypes exhibit the anomaly regarding the existence of two polytypic structures in the same single-crystal piece unrelated to each other and not being based on the same basic structure. All these facts put together indicate that the real cause of polytypism in cadmium iodide lies somewhere else and not just in the screw dislocation theory. In fact, no single theory is able to explain all the observed facts in any of the known polytypic substances.

The present work was done under a scheme of the Council of Scientific and Industrial Research of India.

References


Crystal Growth & Polymorphism

The application of X-ray diffraction methods to the study of the internal atomic structure of solids has revealed that almost all solids are crystalline. They consist of a regular periodic arrangement of atoms, or a group of atoms, in three dimensions. This is true even of such solids as plastic, hair and wool. The exact arrangement of atoms inside a solid material is called its crystal structure, and most chemical compounds normally crystallize into definite crystal structures, each with a definite symmetry, unit cell, and number of formulae units per cell. Thus, sodium chloride, whether obtained from the sea or prepared in the laboratory or found as a mineral, has always shown the same arrangement of sodium and chlorine atoms at the same distance from each other. But there are some substances which crystallize into more than one structure and this property is called polymorphism. A classical example is that of calcium carbonate, which as the mineral Iceland spar was the subject of much study because of its striking property of double refraction. The formation of two images of an object when viewed at an angle to the trigonal axis of the rhombohedral cell could not be satisfactorily explained on the basis of Newton's corpuscular theory of light, whereas on the basis of Huygen's wave theory of light, the phenomenon could be well understood. Aragonite, another mineral with the same chemical formula, did not show this property because of the different spatial relationship of the carbonate groups in the orthorhombic unit cell. To the chemist the two modifications are one and the same substance, CaCO₃; but to the crystallographer they are two different crystals with different structures and different physical properties.

Polymorphism

This phenomenon of polymorphism is now fairly well understood, and the different structural modifications are known to be definite thermodynamic phases whose relative stability depends on the conditions of temperature and pressure. In fact, a majority of substances has been found to undergo structural transformations when subjected to extremes of temperature and pressure, and the phenomenon is known to be quite general. Thus, sodium chloride undergoes a polymorphic transition to a cesium chloride type structure when subjected to a pressure of about 18,000 atm., and the graphite form of carbon has been converted to diamond under a pressure of 55,000-100,000 atm. at a temperature of 1200-2400°C. However, the synthetic diamonds made so far are small and the process uneconomical.

Polytypism

There is a special kind of one-dimensional polymorphism, called polytypism, which is quite different from the ordinary polymorphism in that it appears to lack the thermodynamic or phase aspect. This is exhibited by certain close-packed and layer structures like silicon carbide, zinc sulphide and cadmium iodide. The structure of these substances is built up of identical layers of atoms stacked on top of each other at regular intervals. Each such
substance displays a large number of structural modifications, called polytypes, which differ only in the manner of stacking these layers on top of each other. The layers themselves in any polytype are identical and so are the forces holding the atoms together. There is no effect of temperature or pressure on these modifications and they have nearly the same physical properties. There is an unlimited number of modifications for each substance and these do not transform into one another. Thermodynamically they have very nearly the same free energies and cannot be regarded as different phases of the compound. The most striking feature is the continued repetition and the stacking sequence of the layers, often with perfect crystalline regularity, after more than a hundred, or sometimes even a thousand, layers. Such enormous repeat distances, of the order of 250-2500 Å, are rare in the inanimate world but common in the crystaline viruses and other biological specimens. Well-known examples are turnip yellow mosaic virus (i.e., \( a \approx 700 \AA \), diamond structure) and some of the fibrous proteins (\( a \approx 100-1400 \AA \)). What could be the nature of the forces and the mechanism that can cause such a long-range periodicity in the polytypes? No atomic forces known to physicists till now have such a long-range influence, and it is this question that has held our attention for the last many years and which has yet to be answered satisfactorily.

It may appear to the layman that this is a purely academic question of limited significance. But it is these oddities of nature which must be investigated and explained if we are to know the true nature of interatomic forces in solids. It is in these that nature has left warnings for the scientist that he is yet far from his goal of a complete understanding. The progress of science has always hinged itself on the study of such exceptions.

### Dislocation Mechanism

Several different theories have been put forward to explain the phenomenon of polytypism. Most prominent among these is the one suggested by Frank and is based on the dislocation mechanism of crystal growth. It is now well known that crystals grow from solution or vapour, at low supersaturations, by spiral growth around screw dislocations. It is believed that crystallization begins with the formation of a thin platelet of microscopic dimensions, which gets self-stressed due to a non-uniform distribution of impurities or due to one of the several other causes. This stress is relieved by one portion of the platelet slipping past another, over a slip plane, thus creating a screw dislocation in the crystal platelet. This raises a terminated step on the surface of the crystal, the step being anchored at one point but free to rotate round this point as crystallization proceeds. The step height has molecular dimensions. The step is self-perpetuating during the growth and thus growth at low supersaturations continues. There are two consequences of this mechanism: (1) after growth is complete the crystal surface should be left with or spiral marking whose shape should be in accordance with the symmetries of the crystal face exhibiting it; and (2) the step height of these growth spirals should be simply related to the size of unit cells as determined by X-ray diffraction methods.

When these ideas were put forward around 1950, it was at first thought that these molecular growth spirals would not be observable. However, on the (0001) faces of silicon carbide crystals, by using phase contrast microscopy, I was able to observe a wide variety of growth spirals. For a precise determination of the spiral step heights which were of the order of 10 Å, I employed Tolansky's technique of multiple-beam interferometry. The step heights were found to be equal to or simply related to the X-ray unit cell size. The screw dislocation theory of crystal growth was thus verified.

An extension of this study was done on some polytypes of silicon carbide and a correlation between their step heights and the X-ray unit cell size was discovered. This led Frank to put forward the screw dislocation theory of the formation of polytypes. Accordingly, the height and the structure of the initial step formed on the crystal surface determined the polytype that would be formed. Polytypism thus can be explained as resulting from crystal growth; the pitch of the screw becomes the length of the unit cell and the need for ordering forces over long distances does not arise. Thus, as an example, an initial step of 100 layers would give rise to polytype in which the structure repeats after 100 layers. The explanation is both simple and convincing. A detailed study of growth spirals observed on different polytypes was made. A direct correlation between the step heights of growth spirals observed and the size of X-ray unit cells for a large number of polytypes was observed and we felt in 1957 that the phenomenon of polytypism had been satisfactorily explained.

### Anomalies in Silicon Carbide and Cadmium Iodide

However, several workers, in particular Prof. Jagodziński, had expressed doubts regarding certain aspects of dislocation theory of polytypism. We, therefore, undertook a detailed experimental investigation of the phenomenon of polytypism in silicon carbide and cadmium iodide in the first instance. The investigation consisted of the following aspects:

1. To grow well-developed single crystals of polytypic substances;
2. To observe, by phase contrast microscopy, the surfaces of these crystals for growth spirals;
3. To measure accurately the spiral step heights by Tolansky's multiple-beam interferometric methods;
4. To record X-ray diffraction spectra from the same crystal which had been examined optically; and
5. To determine the unit cell size and the detailed atomic structure of different polytypes.

Having obtained all the above experimental data about a crystal we set ourselves to interpreting it in two ways. First, to correlate the step height of the growth spiral with the height of the X-ray unit cell. Secondly, to examine whether the actual crystal structure could result from theoretical dislocations in any of the basic phases of the compound. Such an analysis, performed for a large number of silicon carbide and cadmium iodide crystals, has revealed several anomalies that cannot be accounted for by the screw dislocation theory of polytypism.
CRYSTAL GROWTH & POLYTYPIISM

Other theories advanced so far also do not explain the observations of the phenomenon of polytypism. A collected account of these recent observations on polytypism and the present position is given in the book *Polymorphism and polytypism in crystals* written by myself and Dr P. Krishna, published by John Wiley & Sons Inc., New York.

In conclusion, it should be pointed out that none of the existing theories of polytypism gives a completely satisfactory explanation of observed facts and the formation of such a large number of long period ordered polytypes, some with unit cell heights much larger than the range of any known atomic forces, needs to be theoretically reconsidered.

References

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THE GROWTH OF POLYTYPIC CRYSTAL STRUCTURES

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INTRODUCTION

A large number of compounds, with widely different physical and chemical properties, are now known to exhibit the special one-dimensional polymorphism called polytypism. Thus silicon carbide with a strongly homopolar tetrahedral bonding of atoms and cadmium iodide with strong ionic and weak van der Waals' bonds between atoms both crystallize into a large number of polytypic modifications. The different polytypes consist of identical layers of structure stacked on top of each other at constant intervals along the c-axis, perpendicular to the layers. The polytypes differ only in the stacking sequence. Consequently the \(a\) and \(b\) dimensions of the unit cell are the same for all modifications while the \(c\) dimension is an integral multiple of a common unit equal to the separation between layers.

THE PROBLEM OF POLYTYPISM

All atoms in the polytypic structures of a compound have identical nearest-neighbour relationships and hence the polytypes have very nearly the same binding energy. They also have identical packing density. At any temperature and pressure the free-energy, \(E = TS + PV\), of different polytypic modifications is nearly the same. To minimize the free-energy, the entropy would tend to be maximum and this should lead to the insertion of stacking faults disordering the crystal in one dimension. The different polytypic modifications can therefore be regarded as resulting from a regular distribution of stacking faults in certain basic ordered structures.

To explain the formation and growth of polytypic structures FRANK\(^{11}\) suggested that they result from spiral growth round screw dislocations of the non-integral Burgers vector created in certain basic structures. Initial observations of growth-spirals on SiC crystals by Verma,\(^{22}\) AMELINCKX\(^{33}\) and others lent support to the theory but subsequent observations of step-heights on CdI\(_2\) crystals by Trigunayat and Verma\(^{41}\) did not agree with the theory. Observations of the latter indicated that the spirals form during the later stages of growth and do not determine the structure of the polytype. This was first suggested by JAGODZINSKI\(^{[6]}\) who proposed an alternative mechanism for the formation of polytypes based on the vibration entropy of the structure.

To determine whether the formation of polytypes is governed by the spiral-growth mechanism or whether thermodynamic considerations are more important we undertook a combined optical and X-ray investigation of SiC and CdI\(_2\) crystals. The surfaces of the crystals were examined by phase-contrast microscopy, step-heights of growth spirals were measured by multiple-beam interferometry while the unit-cell dimensions and the atomic structure of the same crystals were determined by X-ray diffraction methods. For an account of the techniques, the earlier investigations and the notations employed, the reader is referred to other publications.\(^{[6,7]}\)

EXPERIMENTAL RESULTS AND DISCUSSION

According to the dislocation theory of polytypism the step-height of the growth spiral must be simply related to the \(c\) dimension of the unit cell of the polytype. Moreover, the Burgers vector of the screw-dislocation and therefore the step-height of the resultant growth spirals should be a non-integral multiple of the \(c\) dimension of the basic structure. The structure of the polytype must consist of a number of basic structure units with faults in the end. The structure should be
Fig. 1. The 10-1 reciprocal lattice rows of three SiC polytypes as recorded on 15° c-axis oscillation photographs: (a) completely ordered polytype, 36H, \( c = 90.65 \) Å, (b) partially disordered polytype, 57R, \( c = 143.5 \) Å, (c) strongly disordered polytype based on 6H.

![Fig. 1](image1)

Fig. 2. The \( a \)-axis oscillation photographs from two CdI\(_2\) polytypes. (a) An ordered polytype, 20H, (b) a disordered polytype, completely ordered with no random disorder of layers (e.g., Figs. 1a, 2a).

The experimental evidence both against and in favour of the theory is given below. Earlier observations were done on silicon-carbide crystals. We have now extended these observations to CdI\(_2\) crystals. Comparison of the results obtained on SiC and CdI\(_2\) crystals is given below:

(1) Polytypes conforming with the dislocation theory

<table>
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<tr>
<th>Polytype</th>
<th>Zhdanov symbol</th>
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<tbody>
<tr>
<td>SiC:</td>
<td></td>
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</tbody>
</table>
| 6H       | (33)           | These crystals exhibit growth spirals with step-height simply correlated to the unit cell size both for hexagonal and rhombohedral polytypes.\(^{(10)}\)  
| 15R      | (23)\(_3\)     |
| 21R      | (34)\(_3\)     |
| 33R      | (33 32)\(_3\)  |

<table>
<thead>
<tr>
<th>CdI(_2):</th>
<th>(11)</th>
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<td>2H</td>
<td>The spiral step-height was an integral multiple of the ( c ) dimension of the 2H-type only.</td>
</tr>
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</table>

Conclusion. Growth of the above SiC polytypes is completely explained by dislocation mechanism. But in CdI\(_2\) no correlation was observed for polytypes other than 2H.
(2) Polytypes expected on dislocation mechanism but not showing growth spirals

**Polytype** | Zhdanov symbol | Formation of these polytypes is readily explained on dislocation mechanism but there is no evidence of a dislocation since they do not exhibit growth spirals.
---|---|---
**SiC:** | | 
57R | \([(33)_{6}^{54}4]_{5}\) | 
111R | \([(33)_{6}^{54}4]_{5}\) |
**CdI₂:** | | 
26H | \((22)_{6}^{11}\) |

**Conclusion.** Either these polytypes have not resulted by spiral growth or the growth spiral was wiped off in the later stages of growth.

(3) Polytypes not expected on dislocation mechanism but exhibiting growth spirals

**SiC:** | | 
54H | Both are based on 6H phase but the detailed structures have not been worked out. Since the unit cells are integral multiples of the \(c\) dimension of the basic structure, these cannot result from dislocations yet these show growth spirals with step-height correlated with the unit cell size.
66H | | 
126R | The correlated spiral step-height gives evidence of growth by dislocation mechanism but its structure \([(33)_{6}(43)_{6}^{54}32 23]_{5}\) is at variance.
**CdI₂:** | | 
28H | Its Zhdanov symbol is \((22)_{6}^{11}\). It is based on 4H phase but its unit cell is exactly 7 times the \(c\) dimension of the 4H. The (0001) face shows a single spiral.

**Conclusion.** These polytypes do not appear to have resulted from the spiral growth which they exhibit.

(4) Polytypes not expected on dislocation and also not showing growth spiral

**SiC:** | | 
36H | Based on 6H with structure \((33)_{6}^{54}(33)_{6}^{54}32\) (see Fig. 1a).
90R | Based on 15R with structure \([(23)_{6}^{54}3322]_{3}\).
**CdI₂:** | | 
22H | Based on 2H with structure \((11)_{6}^{2211 2211}\).
26H | Based on 2H with structure \([2(11)_{6}]_{3} 2(11)_{6}\).

**Conclusion.** These polytypes could not have resulted from the respective basic phases since the Burgers vector of the resultant polytypes is an integral multiple of the \(c\) dimension of the basic phase. These also do not show growth spirals.

(5) Disordered structures

Partially disordered polytypes with a random distribution of stacking faults have been observed with a tendency towards long-range order (see Figs. 1b, 1c, and 2b).

**Conclusion.** Such structures cannot be understood in terms of dislocations. These structures are expected on Jagodzinski’s theory based on thermodynamic considerations.\(^{[5]}\)
SUMMARY

The dislocation theory is unable to account for all the observed polytypic structures. The polytypes resulting by the dislocation mechanism form a very limited set. In the others the growth spiral and the structure appear to be independent of each other and demand a separate explanation. The origin of these polytypes, some of which have periodicities as large as 1000 Å, is not yet fully understood.

REFERENCES

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DISCUSSION

This paper was discussed with the next paper, C18, "Optical and X-ray Study of Polytypism in Vapour-grown Crystals", which was also presented by Dr. Verma.

J.S.