DIRECÇÃO GERAL DE MINAS E SERVIÇOS GEOLÓGICOS

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MEMÓRIA N.º 6 (NOVA SÉRIE)

GROWTH AND ETCH FEATURES OF HEMATITE CRYSTALS FROM THE AZORES ISLANDS, PORTUGAL

by

ICHIRO SUNAGAWA

Geological Survey of Japan

LISBOA

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CONTENTS

ABSTRACT

Detailed observation has been made on the surface structures of the basal plane of hematite crystals from Ponta da Serreta, Terceira (Azores Islands), Portugal, by means of a phase-contrast microscope and multiple-beam interferometry.

The results of these observations and measurements are described in terms of growth patterns and natural etch patterns.

Mechanism of growth and etching of these crystals is discussed and explained. It has been found that the growth of hematite mainly takes place by the spreading and piling up of two-dimensional layers, and that surface imperfections formed by internal and external stresses and screw dislocations play an important role in growth. It is also shown that the etching process is of the same type as growth process but in reverse.

From the observations of the surface structures, it is suggested that the hematite crystals from the Azores Islands are formed under fairly low supersaturation conditions, and that they crystallized in lava of submarine volcanoes.

Detailed observations are also made on the characteristics of twin boundaries of the crystals, and a new interpretation of the mechanism of contact twin formation is proposed.

Mineralogical description of the crystals is briefly given.

I — INTRODUCTION *

When a crystal face is examined under a reflection microscope, we observe various kinds of complex patterns which look like contour lines of a topographic map, even if the face is very flat and brilliant like a mirror. These patterns are considered to show the process of growth or of natural etching. Therefore, by observing surface structures of a crystal face, a good deal of information concerning the history of growth or etching of the crystal, as well as physical chemical conditions of crystal growth can be obtained.

Observations by BUNN and EMMETT [6] on the surface structures of cubic faces of sodium chloride crystals during growth gave a convincing proof of the layer growth theory put forward by STRANSKI [16] and KOSSEL [14]. At the time when FRANK proposed the screw dislocation theory of crystal growth in 1949 [11], it was thought that it would take long time before the theory could be proved experimentally. But the studies of surface microtopography of crystal faces, which were carried out under the guidance of TOLANSKY by means of phase-contrast microscopy, multiple-beam interferometry and fringes of equal chromatic order, gave the first and dramatic proof of the Frank's theory on the crystals of beryl [12] and SiC [19] only one year after the time the theory was published.

The writer has been engaged in the study of surface structures of the basal plane of natural hematite crystals from several different localities to clarify the mechanism and conditions of crystal growth of the mineral. Last year, he was presented with beautiful specimens of hematite crystals, which have recently been found at the Azores Islands, by the director of the Geological Survey of Portugal through Prof. N. Katayama of the Tokyo University. He has observed the surface structures of the basal plane of the crystals with a phase contrast microscope and multiple-beam interferometry, and found that they show extremely interesting features concerning mechanism of growth and especially that of etching.

In this paper, the writer intends to describe briefly his observations on the surface structures of these crystals and give an account of the mechanism of growth and natural etching. As the mineral has not been described so far, a mineralogical description is also given briefly. Some new observations on twin boundaries and the writer's proposed hypothesis on the mechanism of twin formation are presented as well.

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II — PRESENT STATE OF THE THEORY OF CRYSTAL GROWTH

As the topics in this paper are not popular in the field of geology and mineralogy, a brief review of the present state of the theory of crystal growth will be given here.

STRANSKI [16] and KOSSEL [14] calculated the possibility of adsorption of atoms or ions at various positions on the {100} face of NaCl type crystal, and found that the probability of adsorption is the highest at kinks, then along steps, and on the surface it is almost neglegible (Fig. 1). From these calculations, it is clear that growth mainly takes place in the form of two-dimensional spreading and piling up of the layers, and not by the three-dimensional precipitation around a nucleus. This theory is called the «layer growth theory», and was established by the observations by BUNN and EMMETT [6] on sodium chloride crystals during growth.

However, in 1948, BURTON, CABRERA and FRANK [7] calculated the supersaturation conditions required to form on the surface a new island of layer, which is the nucleus of a new layer, and found that 25 to 50 % of supersaturation is required for the formation

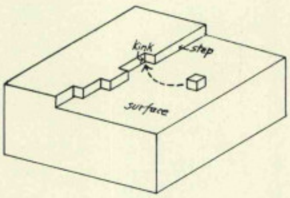

Fig. 1 — Model of the crystal surface at high temperature.

of a new island. But, as a matter of fact, crystals are found to grow from solutions at less than 1 % of supersaturation. Here is a discrepancy between the theory and the experimental fact. Therefore, we have to introduce some special structures into crystals so that growth can take place even under low supersaturation conditions.

It was revealed by BUNN [6] that a crystal can continue its growth only when imperfection parts such as kinks, steps or high index faces are exposed on the surface. In other words, growth will not take place if there is no imperfection part exposed on the crystal surface. Therefore, we can assume that growth may continue even under a very low supersaturation of less than 1 %, only when crystal has some kind of imperfection which will always remain exposed on the surface.

In 1949, F. C. FRANK introduced the idea of screw dislocation into the mechanism of crystal growth, and developed new theory [11]. A screw dislocation is a structural imperfection in which one part of the crystal material is pushed down by one molecular diameter, while the other part remains as it is. Fig. 2 shows a model of this dislocation. As a result of this slip, a step is created on the surface, which does not extend throughout the crystal surface but extends only from the dislocation point to the edge.

If atoms or molecules are precipitated on the surface, they will migrate towards this edge and preferentially get adsorbed to this, the edge will thus advance. As the edge of a screw dislocation terminates at a dislocation point which is fixed, the step can advance only by rotating round the dislocation point. As a result a spiral pattern will be formed on the surface as shown in Fig. 3. As clearly explained by this process, the step provided by a screw dislocation is self-perpetuating and always remains exposed on the surface. Therefore, if there is a screw dislocation exposed on the surface, the need of two-dimensional nucleation will never arise, and crystal can grow even under low supersaturation conditions.

This is the outline of the Frank's screw dislocation theory. Within less than one year the theory was published, GRIFFIN[12] found a razor-blade shape spiral pattern on the prism faces of natural beryl crystals; thereafter VERMA[19] observed triangular and circular spirals on SiC, FORTY on cadmium iodide[10], and AMELINCKX on mica[4], SiC[1], gold[2], and many other crystals[3]. They also measured step heights of the spirals with multiple-beam interferometry or shadow casting method of electron microscopy, and found that in most cases step heights of the spirals are either one unit cell height or a small rational multiple.

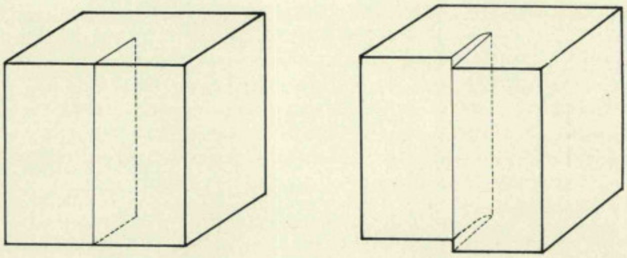

Fig. 2 — Model of a screw dislocation.

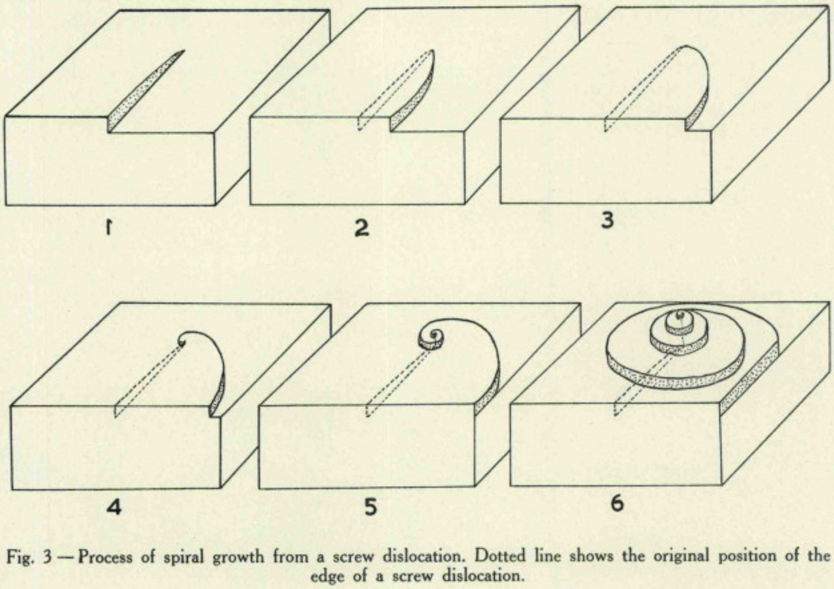

Fig. 3 — Process of spiral growth from a screw dislocation. Dotted line shows the original position of the edge of a screw dislocation.

III — METHODS OF OBSERVATION AND MEASUREMENT

1. METHODS OF OBSERVATION

We can easily observe thick layers more than 1000Å high with a usual reflection microscope. However, the most important features are the thin layers having step height of the unit cell order or even less, and unfortunately a usual reflection microscope is not sensitive enough to detect them. To observe such thin layers, the writer used a phase-contrast reflection microscope. By altering phase changes into amplitude changes, a phase-contrast microscope gives higher contrast than that given by a usual microscope, and thus makes it possible to detect very thin layers. If the surface under observation is reasonably flat, layers of up to 30Å high can easily be detected under the phase-contrast microscope used in the present study. Silvering the surface helps the visibility of thin layers. Furthermore, by using high contrast films and high contrast developer, it is possible to take photomicrographs of thin layers less than 15Å thick. In fact, the writer could take photomicrographs of triangular spirals whose step heights are only 2.3Å [17]. As the shortest distance, in the direction of c axis, between successive layers in the structures of hematite is 2.3Å, resolution of the phase-contrast microscope used in the present work is adequate enough to detect every kind of spiral existing on the crystal surface.

Another advantage of phase-contrast microscopy is that from the position of white fringes at the edge of the layers, one can easily tell which side is higher. In the case of positive phase contrast, white fringes always appear on the higher side and vice versa in the case of negative phase contrast.

The procedure of observations of thin layers taken in this study is as follow.

- *a*) Cleaning the surface with hydrogen peroxide and detergent solution.
- *b*) Silvering the surface in vacuum evaporation plant. Thickness of silvering is from 500 to 1500Å.
- *c*) Observation of coarse structures with a usual reflection microscope.
- *d*) Observation of thin layers with «Olympus PMF — Type Universal Metallurgical Microscope» (Phase contrast microscope).
- *e*) Photomicrography.
  Films used are Kodak Micro-File Panchromatic Film (35 mm) and Fuji Minicopy Panchromatic Film (35 mm). These are extremely fine grain and high contrast films for copying purposes.
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2. METHODS OF MEASURING OF STEP HEIGHT

Fizeau (multiple-beam interference) fringes and fringes of equal chromatic order were applied for precise measurement of step height of the layers. These methods have been developed by S. TOLANSKY [18] and have been applied for the study of the surface microtopography of various materials, and are capable of measureing, precisely, step height of up to 15Å, if the suitable conditions are available.

Since these methods are quite a well established technique, no attempt is made to give a general treatment of their theory, but only brief outline of practice of the methods is presented here.

If we silver the surface of a crystal face, match it against a silvered optical flat, and pass parallel monochromatic light through this optical flat, multiple-interference will take place between the flat and silvered surface. And hence the fringes will be very much sharper than in the case of two-beam interferometry. A fringe passing over a step on the surface shows a shift which is proportional to the step height, the latter being expressed by the relation,

$$h = \frac{s}{x} \cdot \frac{\lambda}{2}$$

h = step height, s = shift in the fringe, x = distance between successive fringes, λ = wave length of monochromatic light used (usually mercury green light $\lambda = 5461$ A is used).

It is assumed that dispersion is uniform.

Under suitable conditions, the fringes of a multiple-beam interferogram are very sharp, and hence step height up to 15A can be precisely measured. Furthermore, with the help of indirect methods such as measuring the total height of a spiral and dividing it by the number of turns of the spiral, less than 15A thickness of layers can be evaluated.

If we analyse the Fizeau fringes spectroscopically with white light, we can get the fringes of equal chromatic order. If there is elevation, the fringes of equal chromatic order, passing over the feature, will turn towards the violet end of the spectrum, and vice versa. Hence this is a precise way to determine whether the feature is an elevation or depression. Exact measurement of the step height will also be obtained with this method.

IV — MINERALOGICAL DESCRIPTION

The hematite crystals referred to in this paper come from Ponta da Serreta, Terceira Island, the Azores Islands, Portugal. They crystallize in a brownish red material *, formed by decomposition of trachyte lava due to post volcanic action.

Crystals are thin hexagonal plate or elongated hexagonal plate (Fig. 4), and range from 0.8 × 0.5 cm to 1.5 × 1.0 cm in size. Three faces of c(0001), r($10\bar{1}1$) and a($11\bar{2}0$)

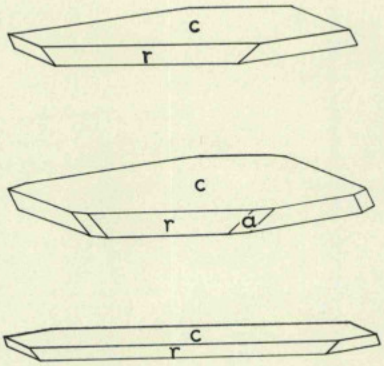

Fig. 4 — Crystal figures of hematite from the Azores Islands.

are observed. Among them c(0001) face is the most developed, next to it is r($10\bar{1}1$) face and a($11\bar{2}0$) face usually very small. Distinct growth and etch patterns are observed mainly on the basal plane. Rhombohedral and prismatic faces usually show hollow or skeletal appearence. The most common twinning is a contact twin with {$10\bar{1}0$} as composition plane, but repeat twin of this is also observed. Twinned crystals are rather difficult to distinguish from single crystals, especially in the case of repeat twin.

* This material mainly consists of the same minerals as the component of the trachyte lava. In the case of hematite crystals from Saganoshima, Japan, they also crystallize in a similar material, while those from Gihofuji and Ayumikotan, Japan, they crystallize in white clayey veins which consist of only tridymite and cristobalite.

V — COARSE STRUCTURES (THICK LAYERS)

Complicated surface patterns which look like contour lines of a topographic map of the mountaineous area are observed on the surface of the basal plane of the crystals under a reflection microscope. These patterns consist of the edges of layers which are parallel to the basal plane and have step heights ranging from a few hundreds to a few thousands Å. In the photographs, the edges of the layers appear as contour lines. These layers usually have circular or irregular form, and have smooth and continuous front. No regular triangular patterns which are rather common in the case of thin layers have been observed.

The surface patterns are broadly classified into two. The first one is a pattern, as shown in Pl. I-1, having one or a few elevated centres from which these layers spread out. The edges of the layers are smooth and have convex fronts. This is the pattern which is the most widely and universally observed on basal planes of hematite from many localities, and is definitely formed by the two-dimensional spreading of growth layers starting from the elevated centres. However, as compared with the second type, this type of pattern is rarely observed on the crystals from this locality, because the original growth patterns are strongly modified due to natural etching.

One of the typical patterns of the second type, which consists of many deformed triangular and circular centres, is shown in Pl. I-2. The triangular centres observed in this photomicrograph are all elevations, their edges being concave, but all circular centres observed are depressions. Pl. I-3 is another example of this type, having many circular centres, all of which are depressions. It is of interest to note that there is not a single elevation centre on this surface. Pl. II-1 is another extreme example in which no centre is observed and the edges of the layers show remarkable concave fronts. These patterns look similar to those of the first type commonly observed on hematite crystals from other localities. Although, at the first glance, it is very difficult to distinguish the first type from the second, patterns of the first type are definitely due to growth, while those of the second type are not. For the following reasons, it is concluded that the patterns of the second type are formed by natural etching and not by growth.

1. On the basis of growth mechanism, it is impossible to explain the fact that there are many depression centres on the surface and especially the fact that there is not a single elevation centre on some crystals. Certainly, on some crystals circular or triangular depressions will be formed at the places which are not filled up by growth fronts spreading from several different directions. But, this explanation cannot be applied to the depressions observed on the patterns of the second type.
2. Looking from the higher side of the layers, growth front should take convex form, concave front being theoretically impossible in the case of growth. On the other hand, if etching takes place two-dimensionally, the etch front will be always of the concave and not convex form as schematically shown in Fig. 5. Therefore, the concave fronts commonly observed on the patterns of the second type are certainly formed by etching, not by growth.

As regards to the formation of depression centres described above, the following two mechanisms are suggested.

1. If several concave etch fronts spreading in different directions join together, they will form a depression circle, as the process being schematically shown in Fig. 6. Pl. II-2a and b show an example of this kind. In Pl. II-2a, the area where depression circles appear densely is the lowest part of the surface. Pl. II-2b, a high magnification phase-contrast photomicrograph of the circular depressions, clearly shows that the depressions are formed by concave fronts.
2. Depression spirals are observed at the bottom of some depression circles. These depression spirals are formed by preferential etching along the edges of screw dislocations exposed on the surface. (Detailed explanation about mechanism of formation of depression spirals will be discussed later). Therefore, the depression circles of this type are considered to be formed by pronounced etch spirals.

From the observations described above, it is clear that growth and etching both take place two-dimensionally. If there is any impurity material or misoriented hematite crystal on the surface, it will play the role of an obstacle in the spreading of growth layers, and as a result, a pattern similar to the back current formed behind a rock in a stream will be formed. Pl. III-1 shows an example of this kind observed on the growth pattern of a crystal. In the case of etching, the process is just the reverse and those obstacles will play the role of resistance to etch fronts, which will consequently be concave with these obstacles on the top of wave. Pl. III-2 is an example, in which the impurity particles are situated at the top of concave fronts.

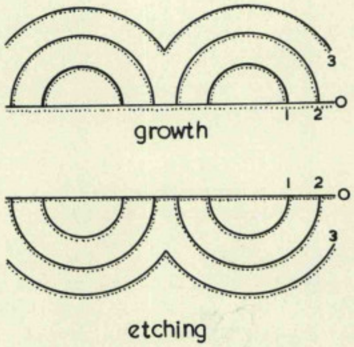

Fig. 5 — Process of formation of convex fronts (growth) and concave fronts (etching). Dotted lines show higher sides.

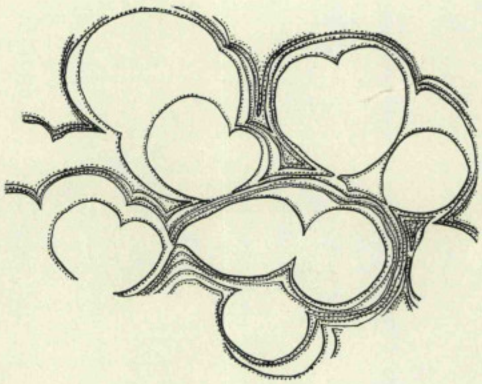

Fig. 6 — Process of formation of depression circles by joining many concave fronts. Dots show higher side.

VI — FINE STRUCTURES (THIN LAYERS)

Thin layers which are difficult to observe with a usual reflection microscope can be observed under a phase-contrast microscope.

The structures of these thin layers which the writer has observed so far on about 50 crystals are classified as below.

Growth features;

a) Typical spirals
b) Triangular cones
c) Spirals having big step height

Etch features;

a) Etch pits on the surface
b) Etching along growth front
c) Piled triangular layers
d) Depression spirals
e) Miscellaneous etch patterns

Overgrowth

1. GROWTH FEATURES

a) TYPICAL SPIRALS

Typical spiral means the spiral of which the spacing between successive arms is nearly uniform and the step height is of the order of a unit cell or less. Such spirals have been observed on four out of fifty crystals examined. Many types of spirals, from triangular to circular, are observed on the surface of the thick layers on these crystals.

Pl. IV-1 shows an example of typical circular spirals. Two right handed spirals start from a screw dislocation point, and after a few turns, two more spirals of the same sign join the main ones. As they all have the same sign and height, they completely co-operate together without any interference.

Pl. IV-2a and b show two examples of triangular spirals. The spirals shown in Pl. IV-2a start from two left handed screw dislocations, while those in Pl. IV-2b start from a row of left handed screw dislocations.

Pl. V-1 shows spirals which take triangular form at first but after a few turns become circular. Pl. V-2 shows an inactive spiral. Spiral fronts of this cannot rotate round the dislocation point after half a turn, because there is a predominant growth font near the dislocation.

When two screw dislocation of opposite sign emerge on the surface, spiral fronts originating from them join together forming a loop as shown schematically in Fig. 7. This is in according FRANK's explanation [11]. Pl. V-3 is an example of such loops observed on one crystal. In this case, since two spirals start from each dislocation point of the opposite sign, they show patterns similar to the third stage of Fig. 7.

Since visibility of the spirals described here is very high, it seems their step heights are very big. However, interferometric study shows that they are actually very small. Pl. VI-1 is a multiple-beam interferogram for the circular spiral of Pl. IV-1. It shows small bent at each spiral layer, but the fringe itself is almost a straight line, though it runs across the spiral centre. Fringes of equal chromatic order of this fringe prove that these bents observed at each spiral layer are not elevations but depressions (Pl. VI-2). These facts show that the step heights of the spiral layers are very small, probably a unit cell height or even less, and that etching has taken place on the spiral layers. This etching accounts for the high visibility of these spirals.

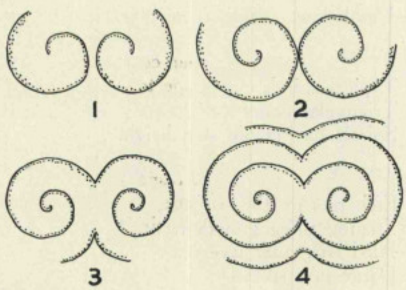

Fig. 7 — Formation of closed loops by co-operation of two spirals of opposite sign.

Density of this type of the spirals measured from several photomicrographs is of the order of $10^4/cm^2$. This value is in agreement with the largest density of dislocation points observed on SiC by VERMA [19], but is smaller than that given by DAWSON and VAND [9] for paraffin crystals.

b) TRIANGULAR CONES

Triangular cones are observed on many crystals. They are found to be scattered on the surface of thick layers, and in some cases they cover almost entire area of flat surfaces. They are very tiny and range from 10^{-4} to 2×10^{-3} cm in extension. A typical example of this is shown in Pl. VI-3.

When examined under lower magnification, these triangular cones do not show any fine structure on their side faces. However, high magnification phase-contrast photomicrographs taken with the help of highest contrast film show that these cones actually consist of narrow spaced triangular spirals. Pl. VII-1 is a high magnification photomicrograph of a triangular cone. This structure is exactly similar to that observed by the writer on a hematite crystal from Ayumikotan [17], which for the first time has shown that the step height of each layer is only 2.3 Å (the distance between successive oxygen layers or 1/6 of the unit cell of hematite in the direction of c axis).

Multiple-beam interference fringes running across triangular cones show triangular shifts, as shown by arrows in Pl. VII-2. These shifts of the fringes at triangular cones are extremely small as clearly seen in Pl. VII-2. This suggests that the heights of the triangular cones are very small, probably less than 30 Å. Therefore it is safe to say that the step height of each layer of triangular cones is possibly 2.3 Å as in the case of Ayumikotan.

It is noteworthy that on hematite from this locality the triangular cones are quite common, while the typical spirals are not. This shows that 2.3 A screw dislocations played an important role in the growth, at least in the latest stage.

Although triangular cones usually randomly distributed on the surface, sometimes they are aligned along particular lines of which several instances are shown in Pl. VIII-1. These lines are straight, curved or bent. As seen in these figures, neighbouring few lines usually have similar direction and bent. Another noteworthy point in the photographs is that triangular cones situated at one end of the line are usually larger than those at the other end, and that their sizes sometimes gradually increase from one end to the other. Since there are very few triangular cones which have not received etching and are large enough to make detail observation, it is rather difficult, with the present method, to determine whether the triangular spirals of the triangular cones on one line are all of the same sign or not. It is difficult, therefore, to give a conclusive explanation for the mechanism of the alignment of these triangular cones. However, from the above observations, it is supposed that this alignment is due to the movement of dislocations during growth. In other words, during the growth, dislocations moved due to internal or external stresses, and triangular spirals were formed at every points where they stoped. Triangular spirals thus developed will be along a definit line, and will be larger at the start than at the finish of this movement. Since the stress responsible for movement of dislocation is in the same direction within certain small area, neighbouring few lines of dislocations will show same bent or curve in the same direction.

Density of the triangular cones measured on photomicrographs is found to be $2 \sim 3 \times 10^5/cm^2$, which is higher than that of the typical spirals.

c) SPIRALS HAVING BIG STEP HEIGHT

Spirals described above have step heights equal to a unit cell or less. The spacing between successive arms of these spirals is usually regular, and so is their morphology. In addition to these, several different types of spiral patterns are observed on the surface. Usually they neither have a regular spacing between successive arms nor regular forms. Most of them have step heights larger than a unit cell. Spiral patterns of this type observed on the surface of hematite crystals from this locality are classified into three groups.

1. Spirals observed on the top of growth hill,
2. Spirals originating from the ends of misoriented portion,
3. Depression spirals formed by etching.

In the case of hematite crystals from other localities, it has been observed by the writer that the first and the second types are most common and the third type is rare. On the other hand, in the case of crystals from this locality, features of the third type are most common, while those of the first type are seldom observed. This can easily be accounted for by the fact that these crystals have received strong etching. The features of the third type will be described separately in the section of etch features.

As already mentioned above, there are a few steep hills on some crystals. They are certainly growth centres of the thick layers. When examined under a phase-contrast microscope, these hills show, on their top, irregular spiral patterns, which usually start from several dislocation points (Pl. VIII-2), or from a row of dislocations or from both the ends of a misoriented crystallite (Pl. VIII-3). From their visibility, it can be said that their step heights are definitely greater than the unit cell. Although this type of spiral is not commonly observed on the surface as stated above, the writer is pretty sure, from his observations on the crystals from other localities, that they must commonly be existing on the surface before the crystals received etching, and that they were then eaten away by etching. This is the reason why they are not commonly observed on the present surface.

The second type is fairly commonly observed on the crystals. If a part of the surface is inclined to the basal plane, or if there is a misoriented crystal on the surface, or if a part of the surface breaks up because of internal stress and forms several small portions which have small angle inclination to the original surface, then the boundary between these portions and the original surface will be a kind of twist boundary and has screw dislocation characteristics. This boundary is schematically shown in Fig. 8. Because of the characteristics of this boundary, growth will preferentially start from them forming spiral patterns. Two of the most outstanding examples of this kind of spirals, starting from the end of a misoriented portion, is shown in Pl. IX-1a, b. In these phase-contrast photomicrographs, the misoriented portions appear as white rods, because of their inclination to the axis of optical system. Spirals, having definitely very big step heights, spread out from the end positions of the misoriented portions. Pl. IX-2 is a multiple-beam interferogram of the area, in which misoriented portions can be seen as areas of low dispersion

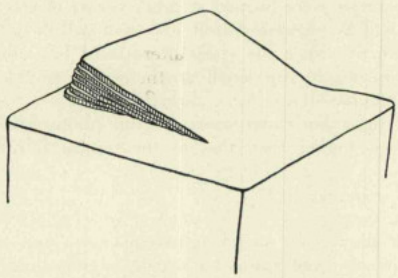

Fig. 8 — Schematic figure of misfit boundary.

fringes. Step height of the spiral measured from this interferogram is found to be about 200 Å.

Pl. X-1a and b show two examples of spirals originating from the end of inclined portions formed by breaking up, during growth, of the surface due to internal stress. Pl. X-1a is a phase-contrast photomicrograph, while Pl. X-1b is an oblique illumination photomicrograph. In both these photomicrographs, variation in intensity of the different portions indicates that the inclination is different for each portion. The boundaries between neighbouring portions are clearly seen as straight or curved lines in the photomicrographs. As seen in these photographs, spiral patterns start from the end of these boundary lines, especially from the points where two or more boundary lines meet. The step heights of these spirals are also clearly bigger than the unit cell height.

These high step spirals are considered to be one of the origins of the thick layers. They must have played an important role in the growth, especially in the earlier stage of crystallization.

2. ETCH FEATURES

As already described under the heading of coarse structures, hematite crystals from this locality have received strong etching. While it is hard to observe etch patterns on the crystals from other localities, most crystals from the Azores Islands show surface structures which are certainly formed by etching. Fine structures of the etch patterns are described below.

a) ETCH PITS ON THE SURFACE

Pl. X-2a and b show the surface covered with minute etch pits. Pl. X-2a represents an early stage, while Pl. X-2b a more pronounced stage of etch pits. In the former, etch pits look circular, but in the latter they take triangular form oppositely oriented with respect to growth triangles. Depth of these etch pits is very small and is estimated to be less than a few unit cell heights. Pl. XI-1, a phase-contrast photomicrograph, shows the surface which has received pronounced etching. Irregular or triangular flat bottom depressions seen in this photograph are formed by a combination of pronounced etch pits. These triangular depressions do not have any definite orientation. In this photomicrograph, special attention must be pointed to the following two points:

1. Depressions which are formed by a combination of many etch pits have flat bottoms (Pl. XI-2b). This fact shows that etch pits do not deepen three-dimensionally but extend two-dimensionally after they reach some depth. With the help of multiple-beam interference fringes, the depth of these depressions was found to be about $40 \sim 60$Å (Pl. XI-2a).
2. The surface A (Pl. XI-1), newly exposed by etching, is smoother than the top-most surface B which is pitted due to etching. This proves that the new fresh surfaces are exposed by etching.

b) ETCHING ALONG GROWTH FRONTS

Pl. XII-1 is a phase-contrast photomicrograph of a surface covered with a large number of minute etch pits. These etch pits are not evenly distributed on the surface, but they are arrayed along circular or triangular lines which certainly originally were growth fronts. Pl. XII-2 is also a phase-contrast photomicrograph of the surface on which a typical spiral is observed. Although the surface is evenly covered with minute

Fig. 9 — Schematic profile of a spiral received etching. Dotted line shows original surface.

etch pits, there is a dark and narrow zone along the edges of the spiral layers. The outer line of this zone is smooth, while the inner one is rugged. This clearly shows that as a result of preferential etching along the edges, growth fronts which originally were situated at the outer line have moved back to the present inner position leaving a dark and narrow zone behind. In this case again, the surface of the narrow, dark zone exposed by preferential etching is smoother than the original one. Pl. XII-3 shows strongly etched triangular spirals. Although, as seen clearly from its outer line, the original spiral has regular triangular shape, its present form is rather circular. This can be explained by the stronger etching at the corner than along the edge of the triangle. Pl. XII-4 shows fringes of equal chromatic order running across one of these spirals. Fig. 9 is a schematic profile of the spiral deducted from these fringes. These results show that etching preferentially starts from the edge of the spiral and deepen the surface of spiral layers, and that depth of etched portion is larger than the step heights of spirals. Depth measured from the fringes in Pl. XII-4 is about 30 A ~ 50 A, which is 2 or 3 times of a unit cell.

It has been said that etching will preferentially take place at dislocation points. However, so far as etching on the spiral patterns is concerned, there is no evidence in the favour of preferential etching at the dislocation points of spirals. No difference is observed between the grade of etching at dislocation points and that at growth fronts.

c) PILED TRIANGULAR LAYERS

As described earlier, triangular cones are widely observed on the surface. In addition, another triangular structure which looks like piling up of triangular layers is also widely observed on the surface of hematite crystals from this locality. The latter is considered to be formed from triangular cones by etching. With the help of photomicrographs of successive stages of etching, this can be explained as follows.

Pl. XIII-1a, b and c are phase-contrast photomicrographs of these triangular structures arranged according to the grade of etching. Pl. XIII-1a shows original triangular cones which are not etched, Pl. XIII-1b shows triangular cones, along the growth fronts of which minute etch pits are preferentially formed, and Pl. XIII-1c is a photograph of triangular structures which are considered to have been formed by etching from triangular cones. The similarity in size, form and orientation of these three is noteworthy.

Pl. XIII-2 is phase-contrast photomicrograph of a crystal surface, one part of which is covered with triangular cones which received weak etching along the growth fronts, while the other part is covered with triangular patterns of the latter type. In this case too, both the triangular cones and the latter triangular patterns have the same orientation and are of almost equal size. Pl. XIII-3 shows another example of coexistence of triangular structures of these two types on the surface of a thick layer. It is clear that the triangular cones are observed on the area where etching is not strong, while triangular patterns of the latter type are observed on that strongly etched. In this case too, both the patterns have the same orientation and similar size.

From these observations, it can be safely concluded that the triangular patterns of the latter type are formed by preferential etching along the edges of the triangular cones.

d) DEPRESSION SPIRALS

As already described under the heading of coarse structures, many circular depressions are observed on the surface of the crystals from this locality. Some of these circular depressions are formed by pronounced concave etch fronts as explained earlier, but most of them are formed by another mechanism.

When some of these depressions are examined with a phase-contrast microscope, depression spirals are observed at the bottom of the depressions. They have irregular or complex forms, the deepest point being the spiral centre. Usually they originate not from a single dislocation point but from few or many dislocation points close together or from a row of dislocations. However, although in their outer appearence they differ from elevation (growth) spirals, they principally have the same characteristics of the elevation spirals. Two spirals of opposite sign will join together and form a loop just as the elevation spirals do. They also rotate around the dislocation points. With the help of some photomicrographs, some of these characteristics of the depression spirals are given below.

Pl. XIV-1 is a photomicrograph of one of the simplest types of depression spirals. There are two spirals of the same sign. They are elliptical in shape and have big step heights. Near the centre, the spacing between successive arms is large, but it decreases for outer turns. Pl. XIV-2, a high magnification phase-contrast photomicrograph of one of these spirals, reveals that unlike the elevation spirals the edges of this depression spiral are not smooth but have a saw-tooth structure. This bears testimony to the fact that this depression spiral is formed by etching. Pl. XIV-3 is another example of a fairly simple depression spiral.

Pl. XIV-4 is an example of co-operation of depression spirals of opposite sign. As seen in the figure, one group of right handed and two groups of left handed spirals co-operate and form an elliptical depression loop. In this case, the process is somewhat

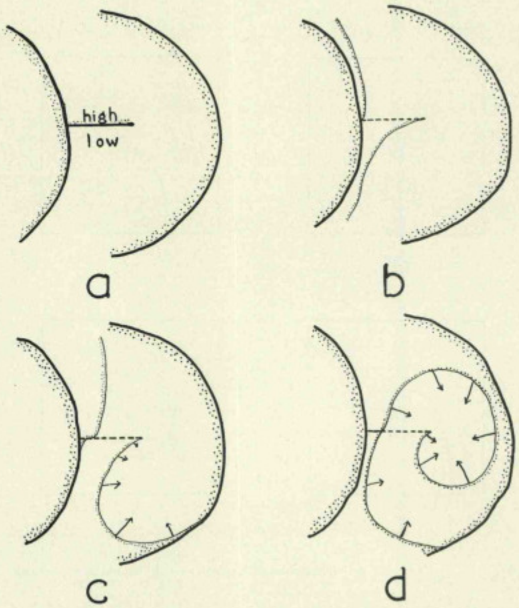

Fig. 10 — Process of formation of a depression spiral by growth.

complicated as compared with the formation of a growth loop, because there are three groups of dislocation points from which many spiral fronts start. However, they form closed loop by a process fundamentally similar to that for growth loops.

These examples, cited above, are rather simple cases, and the usual depression spirals are much more complicated. They usually start from many dislocation points and show quite irregular and complicated spiral patterns. Several examples of these are shown in Pl. XV-1, 2 and 3.

On the basis of growth mechanism, it is difficult to explain the mechanism of formation of these depression spirals, because they are depressions, they are situated at the bottom of depression circles, and their edges sometimes have a saw-tooth structure. Although the writer admits that there are cases in which depression spirals are formed by growth, as being shown schematically in Fig. 10, this is not true, at least, in the case of depression spirals observed on these hematite crystals. As the crystals have, without doubt, received strong etching, it is more reasonable to think that the depression spirals are formed by etching. The process of their formation can be explained in the following way.

If growth spirals (elevation spirals) receive etching, etching will mainly take place along the spiral fronts as stated earlier, and thus elevation spirals will remain as elevations. However, if a screw dislocation (not a spiral pattern) is exposed on the surface before etching starts, etching will preferentially take place along the edge of the dislocation, and in a similar but just the reverse process of growth, etch fronts will rotate around the dislocation points forming a depression spiral. This process is schematically shown in Fig. 11.

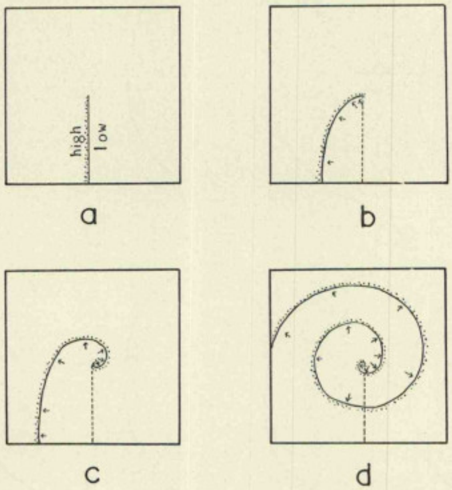

Fig. 11 — Process of formation of a depression spiral by etching.

From these observations and considerations it is safely concluded that etching preferentially takes place two-dimensionally along the edges of screw dislocations exposed on the surface, but will go deeper as a result of rotation round the dislocation point, and thus etching will be effective three-dimensionally.

e) MISCELLANEOUS ETCH PATTERNS

Miscellaneous etch patterns observed on these crystals are briefly described below.

1. *Tongue-like patterns*

On several crystals tongue-like patterns are observed. Thin tongue-like elevations are arranged along the edges of thick layers and sometimes they start radically from an etch centre on the surface. Each tongue has a rut along it. These ruts are in three different directions inclined at 120° to each other and perpendicular to m(1010) face. Pl. XVI-1 shows an example of such a pattern. These patterns are considered to have been formed by etching.

2. *Chrysanthemum patterns*

These patterns were observed only on one crystal, a typical one being shown in Pl. XVI-2. From the shape of fringes of equal chromatic order (Pl. XVI-3) running across the pattern, the profile of the pattern has been ascertained and is schematically shown

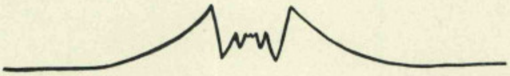

Fig. 12 — Schematic profile of crysanthemum pattern.

in Fig. 12. Although it is difficult to draw a definite conclusion about the origin of these patterns, it is suggested that they may have been formed by etching which starts from some kind of impurities or percussion marks on the surface.

3. OVERGROWTH

The surface of some crystals is observed to be covered with irregularlly oriented lines like a spider net. These lines generally have non-crystallographic orientations and show complicated bents and curves. Sometimes they occur along the edges of thin layers. Two examples of these are shown in Pl. XVII-1a and b.

From these phase-contrast photomicrographs, multiple-beam interference fringes (Pl. XVII-2) and fringes of equal chromatic order (Pl. XVIII-3), it is revealed that these lines are ridges and not ruts. Their step heights are about 140 Å.

The following two mechanisms are considered for the formation of these ridges.

1. After somewhat pronounced etching, a part of growth layer is left as ridges.
2. Overgrowth of foreign materials after the end of growth.

As these ridges have no crystallographic orientation and sometimes cross each other, the possibility of the first mechanism seems to be remote. It is difficult to determine the material forming these ridges, and hence a conclusive proof for the second mechanism can not be obtained. However, from their appearence it is reasonable to say that the second mechanism is more likely than the first.

VII. DISCUSSION ON THE MECHANISM OF GROWTH AND ETCHING

Growth features observed on the surface of hematite crystals from the Azores Islands are summarized as follows.

A. *Thick growth layers*

1. Growth patterns completely free from etching are seldom observed. However, some crystals which are not strongly etched do show the characteristics of the original growth form.
2. The surface patterns consist of many layers which are piled up parallel to the basal plane. These layers show circular or irregular form and do not show regular triangular form. Their step heights range from few hundreds to few thousands A.
3. If there are obstacles such as impurity materials or misoriented hematite crystals, spreading of the layers is intercepted and this would result in the formation of a pattern similar to back current behind a rock in a stream. This clearly shows that these layers spread out two-dimensionally.
4. There are a few centres of the layer spreading, though on many crystals they are completely eaten away by etching.

B. *Thin growth layers*

1. Spiral patterns of one kind or the other are always observed on almost every crystal examined with a phase-contrast microscope.
2. The spiral patterns observed are classified into four types; typical spirals, triangular cones, spirals having big step heights and depression spirals.
3. Typical spirals show triangular, circular or intermediate forms. Their step heights are one unit cell or half a unit cell. Spacing between successive arms is usually wide, which suggests that these spirals have grown under low supersaturation conditions. Interference and co-operation between spiral fronts from different dislocations form patterns similar to those which have been predicted and reported. Density of the spirals is in the order of $1 \sim 3 \times 10^4$ per cm^2. Such a type of spiral pattern is observed only on a few crystals.
4. On many crystals, triangular cones are observed, which sometimes cover all over the crystal surface. Each of these cones actually consists of a narrow spaced triangular spiral having step height of only 2.3 A. From its narrow spacing, it is suggested that the pattern is formed under supersaturation higher than that for the typical spirals. Their density is $10^5/cm^2$, which is higher than that of the typical spirals.
5. Spirals having irregular forms and big step heights are often observed at the end of misoriented crystals or inclined portions produced by breaking up of the surface by internal stress during growth. Density of these spirals is not high compared with that of the above two types, but these spirals do cover wide areas of the surface and certainly are one of the origins of thick growth layers.

6. On the top of steep growth hills or growth centres also, there are irregular spirals of big step heights. Although they are eaten away by etching, it is quite certain that these spirals do commonly exist on the surface before the onset of etching.

C. *Relation between thick and thin growth layers*

1. On a flat area of the surface, the process in which thinner layers bunch themselves together and form thicker layers is often observed. Therefore at least some of thick layers are formed by bunching of thinner layers.
2. However, the fact that there are spirals having big steps shows that the thick layers can be formed directly by these high step spirals.
3. In the case of many crystals, only a few spirals of small step heights are observed on the surface of a thick layer. In these cases, it is difficult to conclude that the thick layer is formed by bunching of such thin layers of the spirals.

From these observations, the following process can be suggested for the growth of hematite crystals from the Azores Islands.

Growth principally takes place by two-dimensional spreading of layers and their piling up, and not by three-dimensional precipitation of atoms or molecules around the nucleus. At the early stage of growth, under very high supersaturation conditions, two--dimensional nucleation will probably take place at first, and screw dislocations will not play any important role in crystal growth. When crystals reach some size and receive scratches or the surface is broken up into small portions inclined to the original surface by internal stresses, these portions are exposed on the surface as imperfections from which growth can preferentially start. As some of these imperfections have screw dislocation characteristics, new growth layers having high step heights will rapidely and continuously spread out from them. (The creation of high step spirals and the formation of most of the thick layers). During this period, although typical screw dislocations are exposed on the surface, they cannot play an important role in the growth because the growth from high step dislocations is overwhelming. However, if the supersaturation drops and the growth of thick layers becomes more difficult, then screw dislocations of one unit cell height or 2.3 Å height will begin to play an important role in the growth, and typical spirals or triangular cones are formed on the surface of the thick layers. Finally, after the cessation of growth, etching will commence.

From the comparision of the surface structures observed on the hematite crystals of this locality with those from other localities, it is considered that these crystals grow under lower supersaturation conditions than the other crystals. Detailed discussion about this will be presented elsewhere.

The following is a brief summary of the present observations on the etch features of hematite crystals from the Azores Islands.

1. Coarse etch patterns closely resemble the coarse growth patterns. However, on the coarse etch patterns, instead of elevation centres, many depression circles are observed. Fronts of layers are of the concave form. From these facts it is possible to distinguish etch patterns from growth patterns. If there are impurity materials or misoriented crystals, etch fronts will avoid these obstacles and form concave fronts and the obstacles will be situated at their top.
2. Many minute triangular etch pits are found all over the surface of etched crystals. These pits are very shallow and do not deepen themselves three-

-dimensionally. After reaching some depth, which is a few multiples of a unit cell height, they develope two-dimensionally and form flat bottom depressions. This mode of etching gives rise to a fresh new surface behind the etch fronts.

3. When etching takes place, it preferentially takes place along the edges of growth layers and progresses two-dimensionally. In this case also, a fresh new surface is exposed behind the etch front. In the case of triangular spirals, etching progresses much more rapidely at the corners than along the edges of the triangle with the result a circular spiral pattern is formed from a triangular one. No preferential etching takes place at a dislocation point as compared to that at the spiral fronts.
4. There are many depression spirals at the bottom of circular depressions on the surface. These depression spirals are formed by preferential etching along the edges of screw dislocations (not spiral patterns) which are exposed on the surface at or before the onset of etching. The process of formation of the depression spirals is just the same as that for the growth spirals but the reverse direction. In this case too, etching takes place principally two-dimensionally along the exposed edge of a screw dislocation, but as the etch front rotates round the dislocation point, it goes deeper and becomes effective three-dimensionally.

From these observations, the writer proposes the following mechanism for etching of the hematite crystals from the Azores Islands.

Etching principally takes place two-dimensionally, just as growth does. Etching starts preferentially along the growth fronts and developes two-dimensionally and exposes fresh new surface behind the etch fronts. At the same time, minute etch pits are formed all over the surface, but they do not deepen three-dimensionally. After they reach some depth they develope two-dimensionally, exposing fresh surface behind. These phenomena, namely (a) uniform distribution of minute etch pits on the surface, (b) the pits and triangular depressions have flat bottoms, (c) the depths of these pits are of the order of two or three unit cells depth and (d) that the newly exposed surface is fresh and smooth, can not be interpreted with the knowledge on etching mechanism commonly believed. The writer's interpretation is as follows. When a crystal is growing, the topmost surface of the crystal is always unsaturated. The term «unsaturated» means that bonding is not completed and the surface contains many vacancies or lattice imperfections. As growth proceeds and new growth layers are formed on the original surface, the vacancies and imperfections in the original surface, which is now a part inside the crystal, will be filled up and become saturated. Therefore, when crystal growth ends, inside of the crystal will be saturated, while the topmost surface will remain unsaturated and contains lots of vacancies and imperfections. Etching will preferentially start from these imperfections on the surface. Etch pits thus started will deepen themselves to some extent, but when they have reached the saturated zone, they can no more deepen, because there are very few imperfections. Hence, it is easier for etching to progress sideways rather than to deepen three-dimensionally. Therefore, flat-bottomed depressions are formed. The surface thus exposed will be fresh and smooth, since it is the surface of the saturated zone. The depth of the etch pits or flat-bottomed depressions is considered to correspond the depth of the unsaturated zone. If screw dislocations are exposed on the surface, etching will be effective three-dimensionally because the etch front rotates round the dislocation point. But in this case too, etching itself preferentially takes place along the edges of screw dislocations, thus it is principally two-dimensional.

If there are obstacles such as impurity materials or misoriented crystals, they will resist the progress of etching and this will result in the formation of concave fronts.

Therefore, it can safely be concluded that the etching process is exactly similar to that of growth, but in opposite direction.

Almost all crystals from the Azores Islands have received strong natural etching. The grade of etching is very much higher than that of crystals from other localities which the writer has examined so far.

Hematite crystals from lava are formed by the reaction between iron-chloride gases which migrated through lava from magma resorvoir as a post volcanic action and under ground water etc. which provide an oxidation condition. Therefore, after forming Fe_2O_3, separated Cl will combine with hydrogen easily forming HCl, which is a strong etching agent for hematite. Hence, if there is enough water, HCl will be formed strongly, and etching will also take place strongly on the crystals. It is supposed that hematite crystals from the Azores Islands received stronger etching than those from other localities, because they crystallized in a lava of submarine volcanoes.

VIII — TWINNING

The most common twin observed on the crystals from this locality is the type in which m{1010} is composition plane. In the case of a simple twin, twin crystals can be distinguished from single crystals from the positions of $r\{10\bar{1}1\}$ faces. But many crystals show repeat twinning, and in these cases, as their external forms are same as single crystals, it is difficult to distinguish them from a single crystal with naked eyes. By observing the surface structures under a microscope, one can detect twin crystals.

The twin boundaries which we can detect under a microscope are quite dissimilar to the boundaries which are as expected on the basis of the present theory of formation of contact twin. As detailed considerations will be presented elsewhere, it is intended to describe only briefly the writer's observations on twin boundaries and his proposed explanation for the mechanism of twin formation.

1. OBSERVATIONS UNDER LOW MAGNIFICATION

Thick growth layers and etch patterns show circular or irregular forms, but these fronts are usually smooth and continuous. However, on some crystals discontinuity in the growth and etch fronts is observed. A growth front bents suddenly at some points and forms a kink on the front. These kinks are aligned on one line which usually crosses the entire c(0001) face and appears on the face of the other side.

Generally this discontinuity line (or plane) is parallel to $m\{10\bar{1}0\}$ face. (From the fact that the discontinuity line which appears on the side face is perpendicular to the basal plane, it is clear that the line is not parallel to the rhombohedral face but to the prism face). However, the discontinuity lines often take quite complicated orientation. Three examples of them are shown in Pl. XVIII-1 to 3. It is not simply parallel to m(1010) face but shows very complicated turns and bents, and sometimes it is even a curved line. Quite often there are two or more discontinuity lines on one surface. They are boundaries of repeat twin and are usually parallel to each other but sometimes not. The orientations of these twin boundaries are schematically drawn in Fig. 13.

On the surface of twinned crystals, growth patterns do not develope independentally at the both sides of the discontinuity line, but develope in the same way as they do on a single crystal. No surface structures which show that some kind of interference patterns between growth fronts from two separate centres occured at the discontinuity line have been observed.

2. OBSERVATIONS UNDER A PHASE CONTRAST MICROSCOPE

Following features were observed under a phase-contrast microscope.

1. When growth fronts meet a discontinuity line, kinks are formed on the fronts and small amount of displacement results on the growth fronts at both sides

of the discontinuity line. Amount of this displacement is not definite. But the fronts of thick layers do not stop completely at the discontinuity line (Pl. XIX-1).

2. When growth fronts of thick layers meet a discontinuity line, they sometimes split into thinner layers (Pl. XIX-2). In the case of very thin layers, they usually cannot cross a discontinuity line and stop where they meet the line.
3. There is always a level difference on both sides of the discontinuity line. Pl. XIX-3 is a phase-contrast photomicrograph showing this level difference, in which white fringe appears on the higher side. Amount of the level difference , is not the same everywhere. Sometimes the difference is about 300A, and in some cases no detectable difference is observed by means of multiple-beam interferometry, though there is certainly a level difference. The higher side is not always on one side.

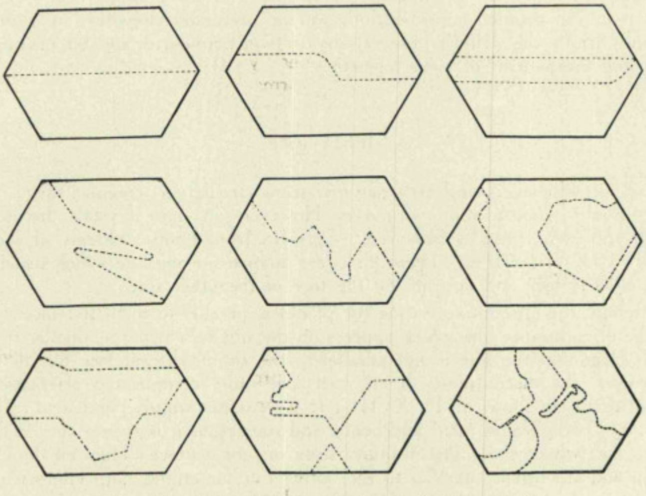

Fig. 13 — Orientations of twin boundaries (dotted line).

4. Sometimes new thin growth layers start from the step of a discontinuity line or from a corner which is formed by step of a discontinuity line and a growth front (Pl. XX-1). Edge nucleation is also observed in some cases at the edge of higher side of a discontinuity line (Pl. XX-2).
5. On some crystals, preferential etching along the step of a discontinuity line has been observed (Pl. XX-3). Usually, etching starts at the step and progresses towards one direction only, but rarely it developes on both sides of a discontinuity line.
6. The orientation of triangular spirals, triangular cones, piled triangular layers and triangular etch pits are usually oppositely oriented on opposite sides of

a discontinuity line, even if the line takes a complicated bents (Pl. XXI-1, 2). Their orientation is always the same on the entire area on one side of the line. This relation shows that the discontinuity line is definitely the twin boundary.

7. In a very exceptional case, it is observed that the orientations of triangular structures are the same on the both sides of a discontinuity line (Pl. XXI-3). But in this case, if the line is traced to the end of the crystal, it can be seen to split into two lines. Thus the line, though single in appearence, consists of two.

3. PROPOSED EXPLANATION FOR THE MECHANISM OF TWIN FORMATION

A great deal of study has been done on the mechanism of twin formation. Fairly satisfactory structural explanations have been put forward for the mechanism of formation of mechanical twins, annealing twins, repeat twin of feldspar or penetration twin such as dauphine twin of quartz [8,13]. However, as regards the contact twin which is most commonly observed on natural minerals, only a simple explanation that two single crystals joined together in twin position during the growth has been presented.

From the observations on the twin boundary described above, it seems that it is very difficult to explain the mechanism of the formation of this twin by such mechanism. According to this theory, the following surface structures can be expected.

1. The patterns of thick growth layers must be independent on either side of the twin boundary.
2. Twin boundary should be a straight line parallel to m($10\bar{1}0$) face and should not show irregular bent or curves.
3. Ridges or ruts rather than steps are expected at the twin boundary.

The facts observed are very much different from those expected.

Furthermore, if the contact plane of a twin is the same crystal face as the plane on which main growth takes place, there is certainly high probability that two single crystals join together in twin position. However, such probability is almost negligible, if two planes are different crystal faces. In the case of hematite, the contact plane is m$\{10\bar{1}0\}$, while main growth takes places on c$\{0001\}$ and not on *m* face.

Therefore, it is necessary to introduce a new mechanism of contact twin formation so that the observed facts on twin boundaries of hematite crystals can satisfactorily be explained. Among the features on twin boundaries observed in this study, the most characteristic and noteworthy points are,

1. that the twin boundary is not always a straight line parallel to m($10\bar{1}0$) face but often shows bents and curves,
2. that there is always a level difference at the twin boundary,
3. that there are evidences showing further growth after the formation of the twin boundary,
4. that the growth pattern of thick layers spread evenly all over the surface and that there is no instance which shows that they develop independently at the both sides of a twin boundary.

From 3 and 4, it can be said that the twin boundary was formed during the growth. From 4, it is considered that the twin boundary was formed during the growth on a crystal which was growing as a single crystal. The point 1 is a characteristic which we cannot expect if two single crystals join together in twin position during the growth. It can be accounted for if the twin boundary was formed by slip or fault of one part of a growing single crystal or by the movement of dislocations. The point 2 shows that a part of the crystal fault down and that the amount of this fault is such that the gap will not be filled completely by later growth and always remain as a small step even if a part of gap is filled up.

From these considerations, the writer would like to put forward the following mechanism of twin formation, with which the above observations can satisfactorily be accounted. When a crystal, growing as a single crystal, reaches some size, fault takes place in the crystal by external or internal stresses. If the amount of the displacement of this fault in the direction of c axis is rational multiple of a unit cell, the step will be formed

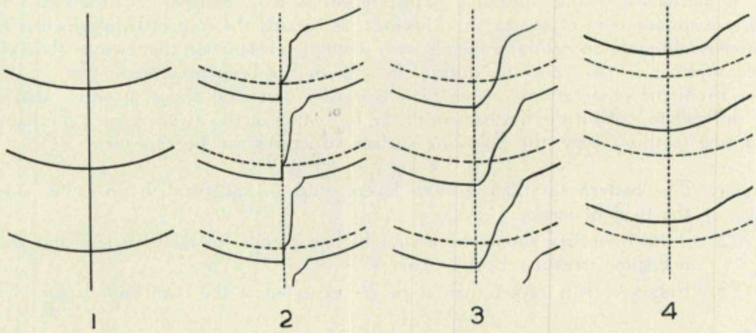

Fig. 14 — Process of further growth after the formation of a fault of rational multiple of a unit cell. (Both step heights of growth layers and amount of fault are one unit cell height in this figure). In this case, fault line will disappear by further growth. Dotted lines show the original position of fault line and growth fronts.

at first on the surface, but soon disappear by further growth (Fig. 14). In this case, twinning will not be formed.

If the amount of displacement is a fractional multiple, more exactely $6n + 1, 3, 5/6$ times of the unit cell, twinning relation will be formed by this displacement. The step formed by this fault will not be completely healed up by the further growth, and will remain as a step forever, because the usual growth step (except special cases) is a unit cell order. This process is schematically shown in Fig. 15.

The crystal structure of hematite has been analysed by BRAGG [5], and PAULING and HENDRICKS [15]. A unit which consists of three oxygen atoms and two iron is situated at a corner of a cell. Three oxygen atoms are situated in a plane parallel to (0001). Triangles which consist of these three oxygen atoms are oppositely oriented in successive layers. Six layers of these oxygen atoms as well as iron atoms form a repeat distance in the direction of c axis, which is 13.73 A. Fig. 16 shows this structure schematically.

Now, if a fault, the amount of which is $6n + 1, 3, 5/6$ in the direction of c axis, is formed parallel to m($10\bar{1}0$) or a($11\bar{2}0$), the resultant configuration will be as in Fig. 17. As clearly seen in this figure, the net plane created by the above fault will have opposite

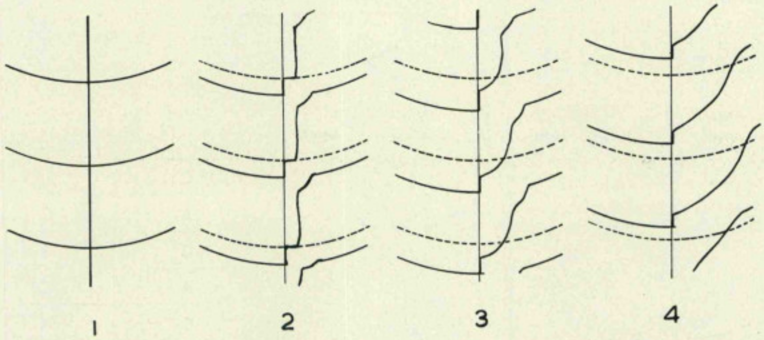

Fig. 15 — Process of further growth after the formation of a fault of a fractional multiple of a unit cell (Step height of growth layers is a unit cell height, while the amount of fault is $6n + 1, 3, 5/6$ times of a uni cell). Fault line will never disappear by the further growth.

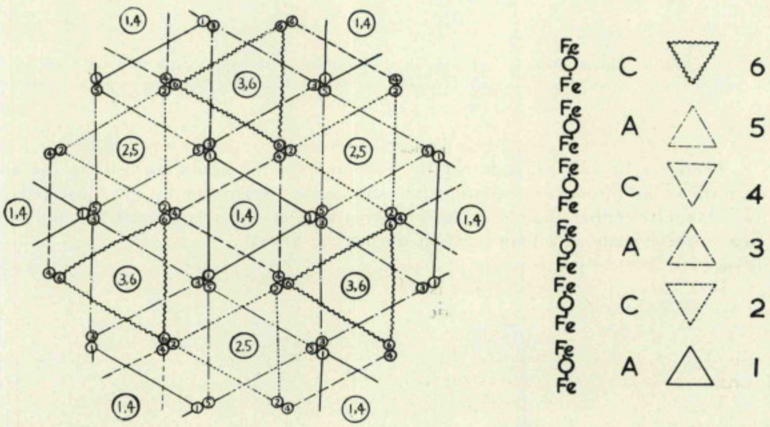

Fig. 16 — Schematic figures of the crystal structure of hematite. *Left;* plane projected on the basal plane. Large circles are positions of iron atoms, and small circles are that of oxygen atoms. *Right;* Section of the structure.

orientations of the triangles consisting of three oxygen atoms on opposite side of the fault line. If the amount of this fault is a rational multiple of the unit cell or 6n + 2, 4/6 times of the unit cell, twin relation will not be formed.

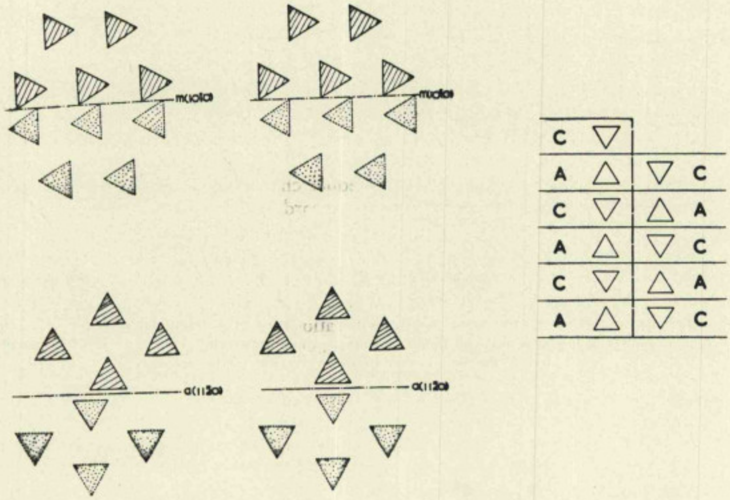

Fig. 17 — Schematic figures showing formation of the twin structure by the fault of a fractional multiple of the unit cell. *Left* ; plane. *Right* ; section. Triangles represent the triangles consisting of three oxygen atoms.

Therefore, it can be said that the twinning can be easily formed by the above mechanism. This mechanism seems better and easier to account for the observed facts on twin boundaries than the old explanation that twin crystal was formed by combination of two single crystals in a twin position during the growth.

IX — CONCLUSION

Hematite from the Azores Islands occurs in decomposed material of trachyte lava and shows beautiful hexagonal or elongated hexagonal crystals. Mineralogical descriptions of these crystals are presented briefly.

The surface structures of the basal plane of the hematite are observed with a phase-contrast microscope and the step heights of the layers are precisely measured with multiple-beam interferometry and fringes of equal chromatic order. The results of these observations and measurements are described according to growth patterns and natural etch patterns.

As a result of the observations on the surface structures, it is disclosed that the growth of hematite mainly takes place by spreading and piling up of two dimensional layer and that scratches, misfit boundaries etc., which were created on the surface by internal and external stresses, and screw dislocations play an important role in growth. The history and process of growth are explained. From detailed observations on the structure of spiral patterns, it is suggested that the crystals were formed under lower supersaturation conditions than those from other localities.

Hematite crystals from this locality have received stronger natural etching than those from other localities. From the observations of etch patterns, it is shown that the etching process is principally two-dimensional, just same as growth is. Etching mainly takes place along growth fronts, and developes two-dimensionally. Only in the case that screw dislocations are exposed on the surface, etching is effectively three-dimensionally, though actual process is two-dimensional along the edge of a screw dislocation. Although the etching process is just the same as growth process, its direction is completely opposite to the growth direction. The reason why the crystals received stronger etching than the crystals from the other localities is accounted for by the fact that these crystals crystallized in lava of submarine volcanoes in which enough formation of HCl is expected.

Detailed observations are also made on the characteristics of twin boundaries of the crystals. As a result it is disclosed that the observed characteristics of twin boundaries are difficult to be explained by the present theory on the mechanism of twin formation. New explanation is proposed for the mechanism of twin formation of hematite crystals. The twin, composition plane of which is m(1010), is formed by fault or slip, the amount of which is 6n + 1, 3, 5/6 times of the unit cell in the direction of c axis, during growth.

ACKNOWLEDGEMENT

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PLATES

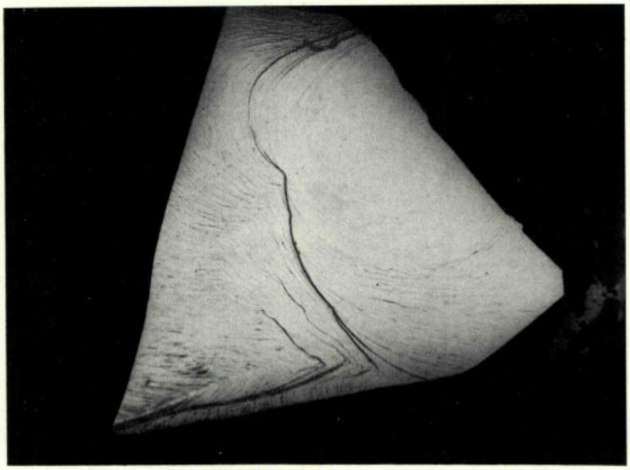
PLATE I

PLATE I

Fig. 1 — Coarse growth pattern on the basal plane. There is only one centre, which is an elevation. About × 7.

Fig. 2 — A low magnification photomicrograph of coarse etch pattern. Triangular patterns on the surface are elevations and are relics of etching, while circular patterns are depressions formed by etching. Concave fronts are observed. About × 7.

Fig. 3 — A low magnification photomicrograph of pronounced etch pattern. All circular patterns are depressions. There is no elevation centre on the surface. About × 6.



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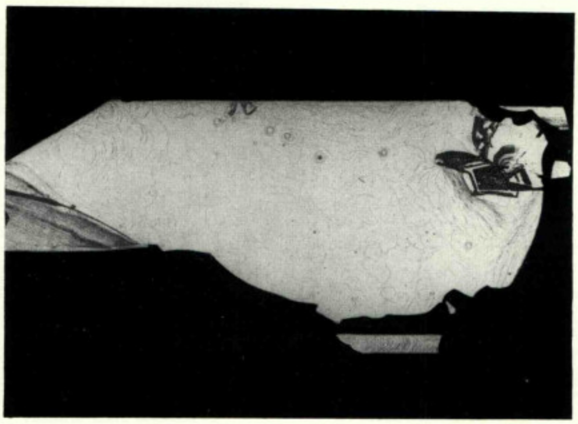

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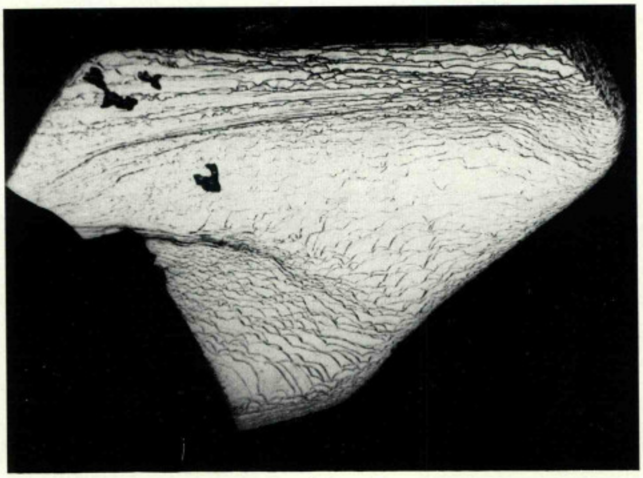
PLATE II

PLATE II

Fig. 1 — A low magnification photomicrograph of pronounced etch pattern. No centre is observed and the edges of layers show remarkable concave fronts. About $\times$ 7.

Fig. 2a — Another example of coarse etch patterns. There are large number of depression circles. About $\times$ 8.

Fig. 2b — A positive phase-contrast photomicrograph of the circular depressions of Fig. 2a, showing that these circles are formed by many concave fronts. $\times$ 180



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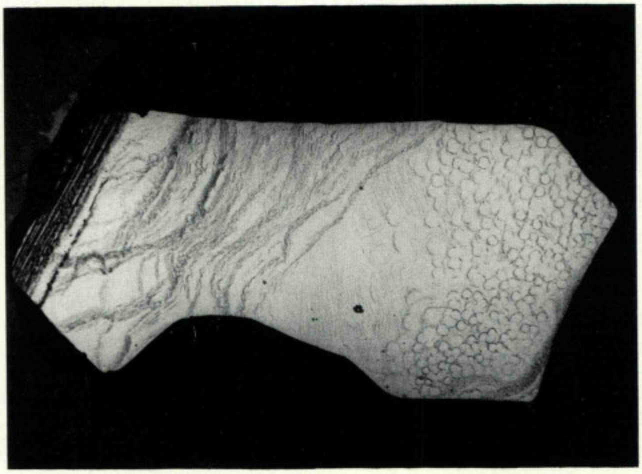

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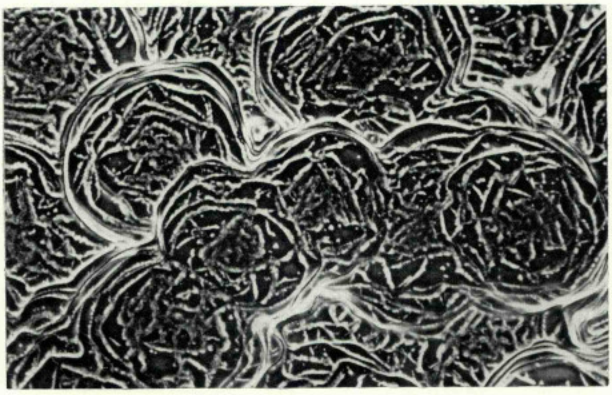

2b

PLATE III

PLATE III

Fig. 1 — A photomicrograph showing the influence of misoriented crystals upon the spreading of layers. About × 16.

Fig. 2 — A photomicrograph showing the effect of impurity materials upon etch patterns. Small black dotts are impurity materials, which are situated on the top of concave fronts. × 7.

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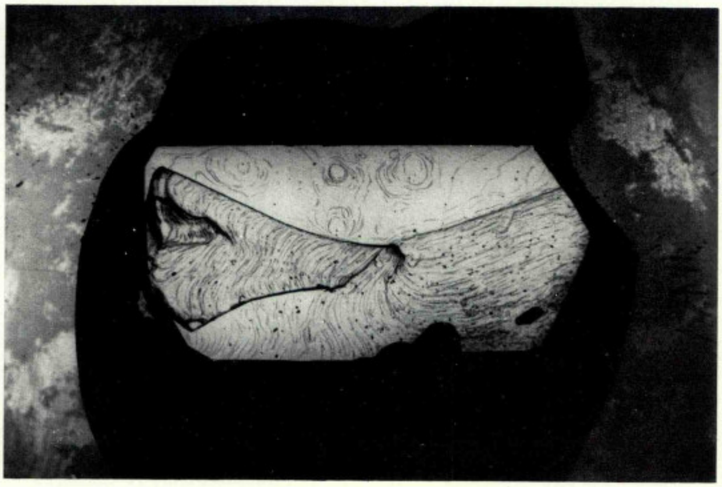

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PLATE IV

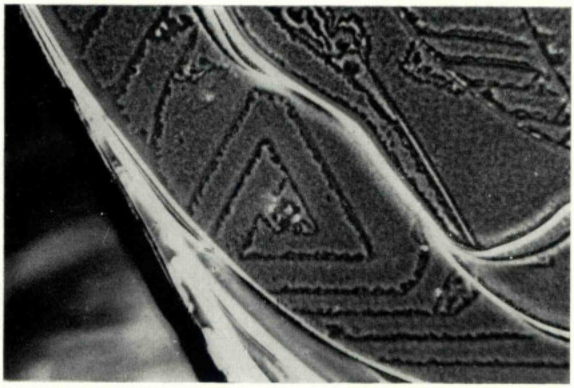
PLATE IV

Fig. 1 — A positive phase contrast photomicrograph of a typical circular spiral pattern. × 180.

Fig. 2a — Two typical triangular spirals starting from a screw dislocation point. × 180.

Fig. 2b — Many triangular spirals originating from a row of dislocations. × 180. Both are positive phase contrast photomicrographs.

1



2a

2b

PLATE V

PLATE V

Fig. 1 — A positive phase contrast photomicrograph of spirals of irregular form. × 180.

Fig. 2 — An example of inactive triangular spirals. Positive phase contrast photomicrograph. × 180.

Fig. 3 — An example of a loop formed by spiral growth starting from two dislocation points of opposite sign. Positive phase contrast. × 180.

1

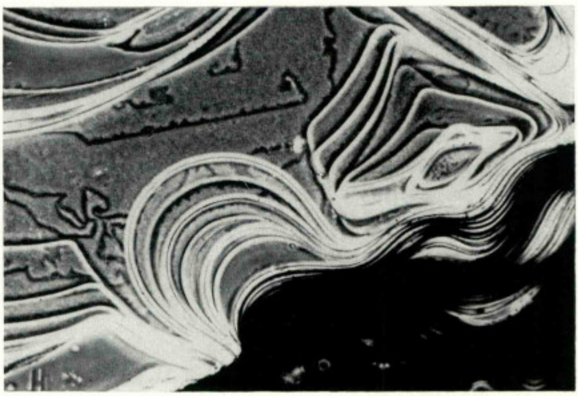


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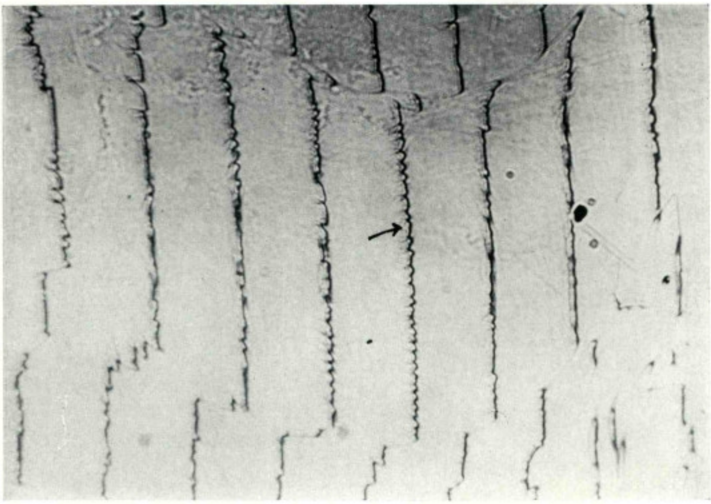
PLATE VI

PLATE VI

Fig. 1 — Multiple-beam interferogram of the circular spiral of Pl. IV-1. The arrow shows the positin of centre of the spiral. × 50.

Fig. 2 — Fringes of eqal chromatic order of a fringe in Fig. 1.

Fig. 3 — A positive phase contrast photomicrograph of triangular cones. Many triangular cones are observed on the surface of thick growth layers. × 180.



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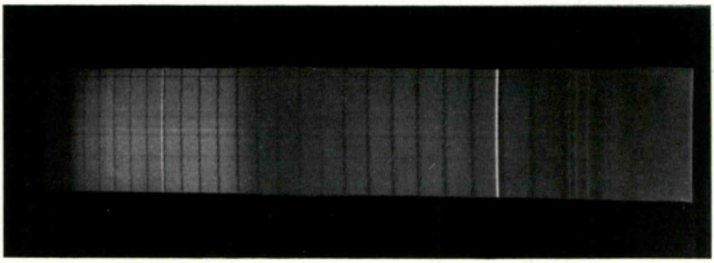

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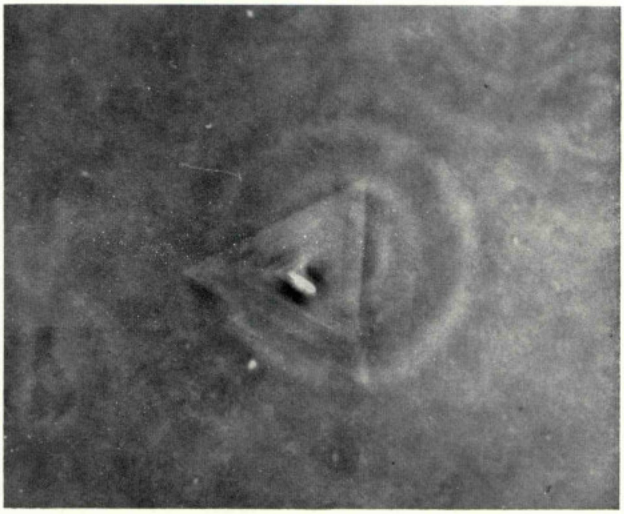
PLATE VII

PLATE VII

Fig. 1 — A high magnification positive phase contrast photomicrograph of a triangular cone. It shows that the triangular cone actually consists of narrow spaced triangular spiral. Circular pattern on the photograph is caused by a small scratch on the mirror in the optical system of the microscope used and not the original surface structure itself. × 2670.

Fig. 2 — A multiple-beam interferogram of a surface covered with many triangular cones. Arrows show triangular shifts of fringes at triangular cones. It must be noticed that these shifts are extremely small, which clearly suggests that the heights of the triangular cones are very small. × 50.



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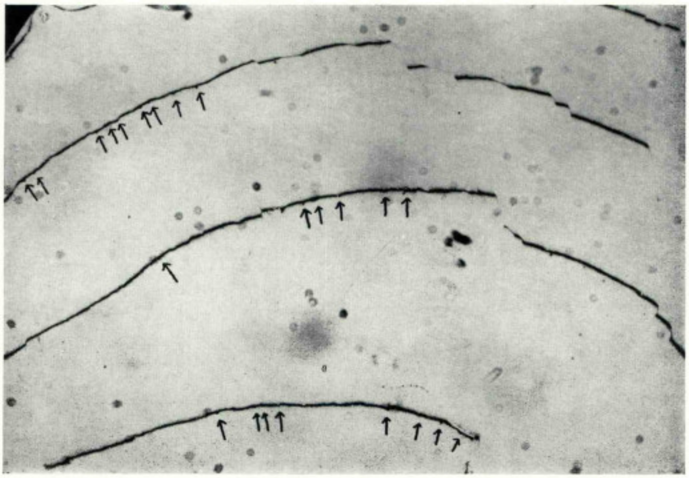

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PLATE VIII

PLATE VIII

Fig. la, b, c — Three examples of alignment of triangular cones. Positive phase contrast Photomicrographs. × 180.

Fig. 2 — Spiral patterns on the top of a growth hill. Irregular spiral patterns are observed. Positive phase contrast. × 135

Fig. 3 — Irregular spirals originating from both ends of a misoriented hematite crystal. Positive phase contrast. × 210.

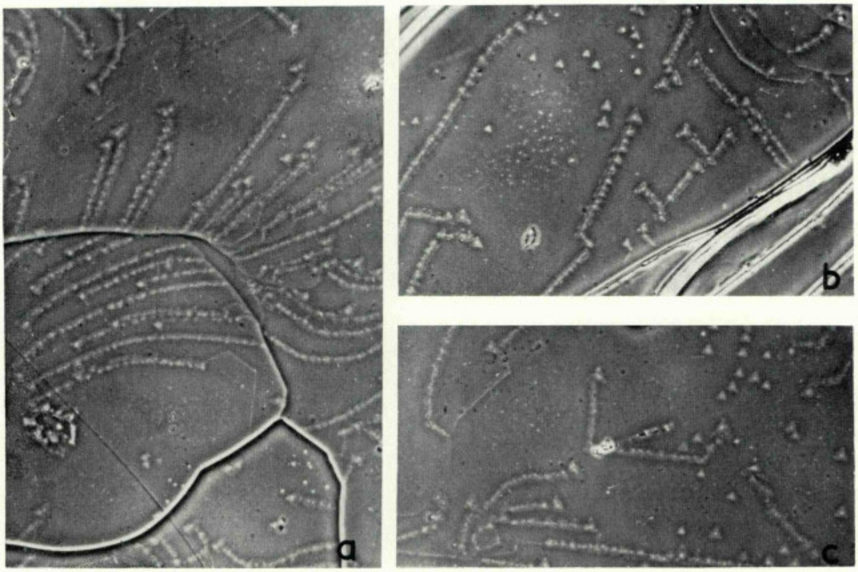

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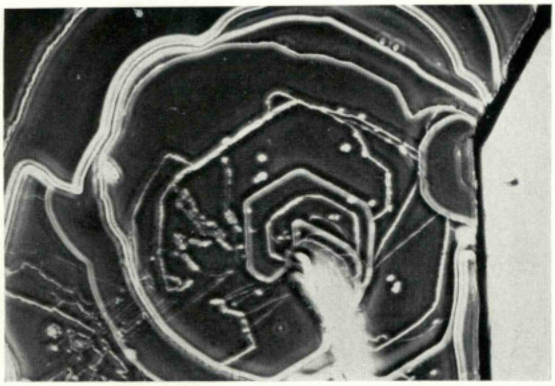
PLATE IX

PLATE IX

Fig. 1a, b — Spirals starting from the end of misoriented portions. White rods are misoriented portions. Positive phase contrast × 180.

Fig. 2 — A multiple-beam interferogram of the area where spiral start from misoriented portions. × 50.



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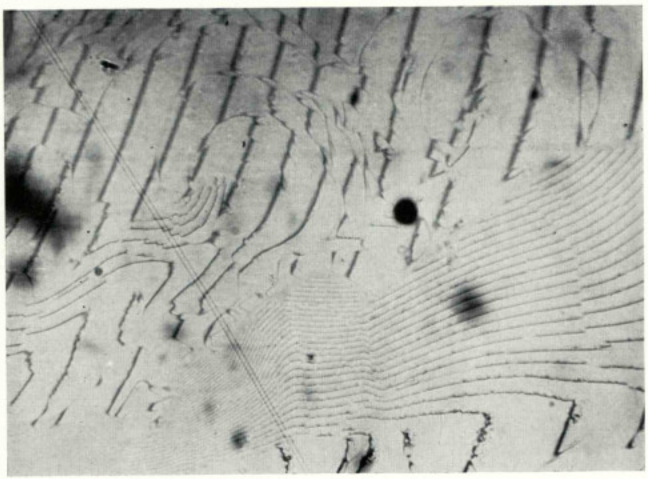

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PLATE X

PLATE X

Fig. 1a, b — Spirals originating from the ends of inclined portions formed by breaking up of the surface due to internal stress. Fig. a is a positive phase contrast photomicrograph and b is an oblique illumination photomicrograph. × 180.

Fig. 2a — Minute etch pits which cover all over the surface. × 180. b — Pronounced etch pits on the surface. Pits are triangular. × 300. Both are positive phase contrast photomicrographs.

1

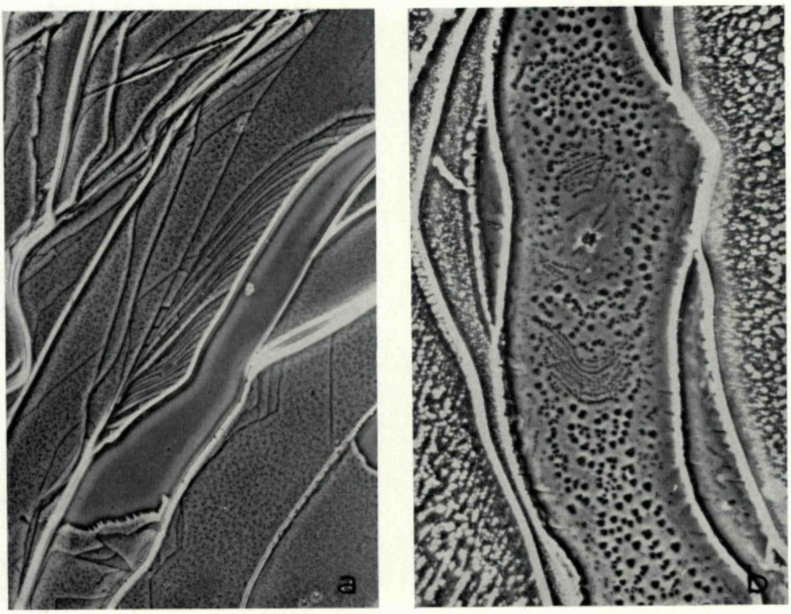

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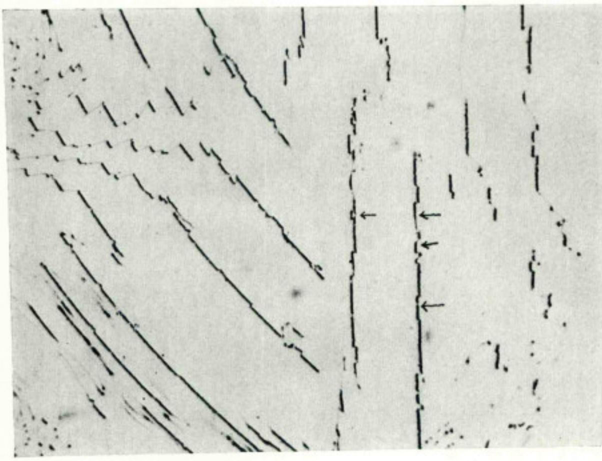
PLATE XI

PLATE XI

Fig. 1 — Irregular or triangular flat bottom depressions formed by pronounced etching. 'A' is a newly exposed area by etching, while 'B' is the original surface pitted with etch pits. Positive phase contrast. × 180.

Fig. 2a — A multiple-beam interferogram of the area of Fig. 1. × 100. b — Fringes of equal chromatic order of a fringe in Fig. 2a. Both fringes clearly show that the area 'A' is a flat bottom depression. Arrows show the positions of the area 'A'.

1



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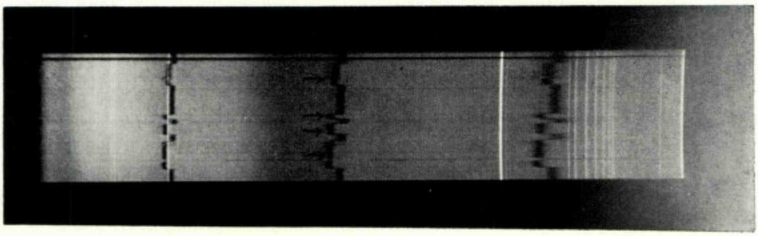

2b

PLATE XII

PLATE XII

Fig. 1 — Minute etch pits preferentially formed along spiral growth fronts. Positive phase contrast. × 180.

Fig. 2 — Preferential etching along growth fronts of spirals. Positive phase contrast. × 180.

Fig. 3 — A positive phase contrast photomicrograph showing stronger etching at the corner than along the edges of a triangular spiral. × 180.

Fig. 4 — Fringes of equal chromatic order running across one of the spirals in Fig. 2.

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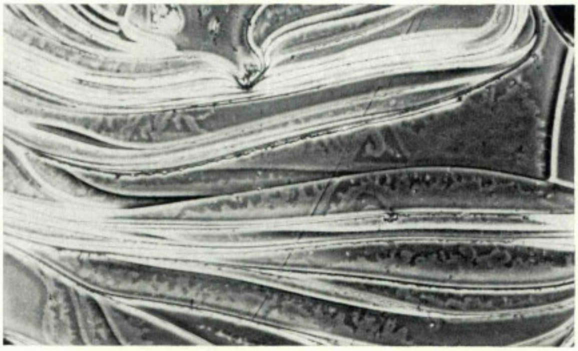

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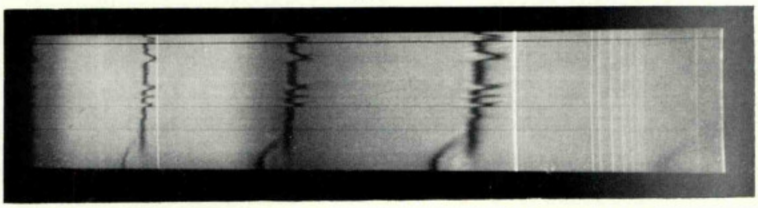

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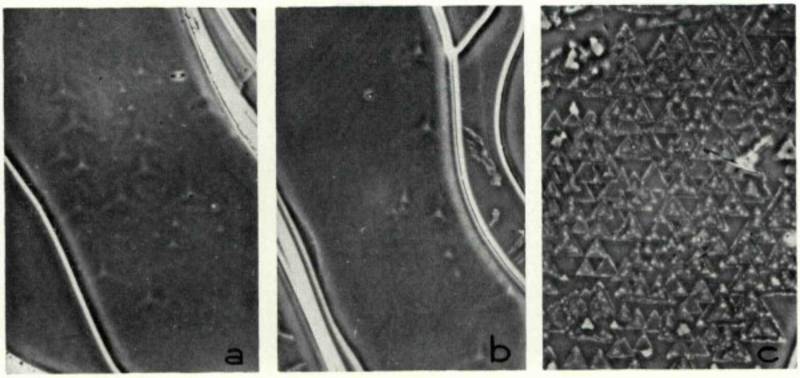
PLATE XIII

PLATE XIII

Fig. 1a — Triangular cones which received almost no etching. b — Triangular cones which received slight etching along their fronts. c — Piled triangular layers which are formed from triangular cones by pronounced etching. All are positive phase contrast photomicrographs. × 180.

Fig. 2 — A positive phase contrast photomicrograph showing the relation between triangular cones and piled triangular layers. Both structures have the same orientations and similar sizes, which suggests that the latter is formed by etching from the former. × 180.

Fig. 3 — Showing the same relation as Fig. 2 observed on the surface of a thick layer. Positive phase contrast. × 180.



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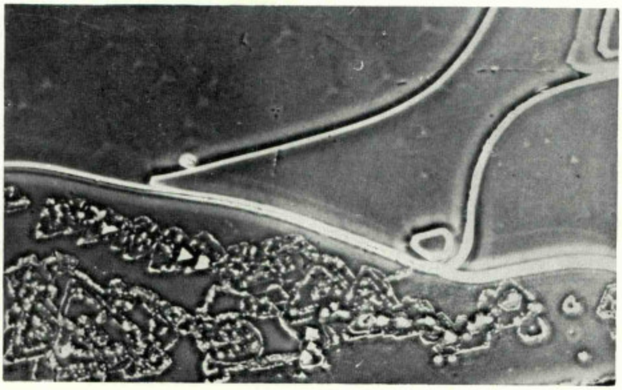

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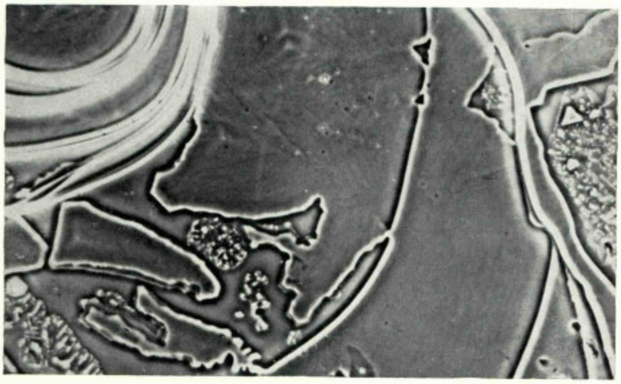

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PLATE XIV

PLATE XIV

Fig. 1 — An example of the simplest depression spirals formed by etching. Positive phase contrast. × 180.

Fig. 2 — High magnification positive phase contrast photomicrograph of the depression spirals shown in Fig. 1. From the position of white fringes it is quite clear that these spirals are depressions. Saw-tooth fronts are observed. × 710.

Fig. 3 — Another example of fairly simple depression spirals formed by etching. Positive phase contrast. × 180.

Fig. 4 — Depression loops formed by the co-operation of several spirals of opposite sign. Positive phase contrast. × 180.

1

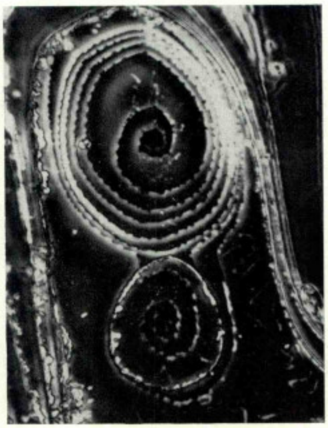

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PLATE XV

PLATE XV

Fig. 1, 2, 3 — Complicated depression spirals formed by etching. Positive phase contrast. × 180.

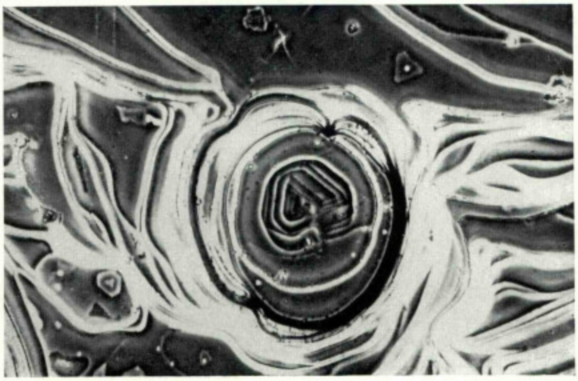

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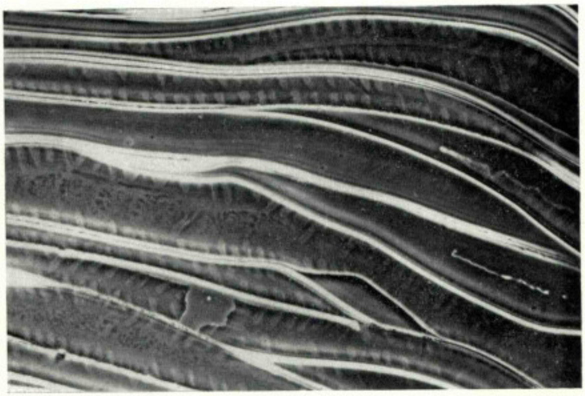
PLATE XVI

PLATE XVI

Fig. 1 — Tongue-like patterns. Positive phase contrast. $\times$ 180.

Fig. 2 — Chrysanthemum patterns. Positive phase contrast. $\times$ 180.

Fig. 3 — Fringes of equal chromatic order running across one of the chrysanthemum patterns. Positive phase contrast.



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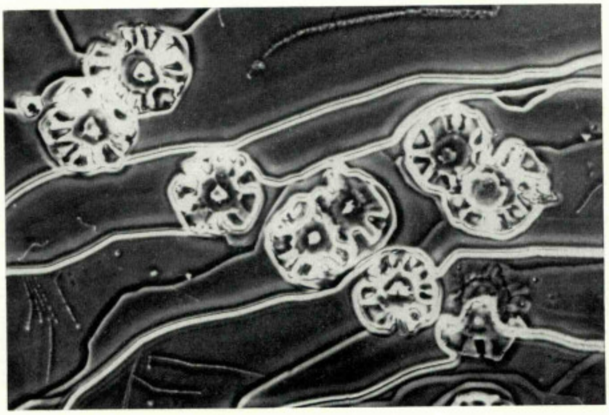

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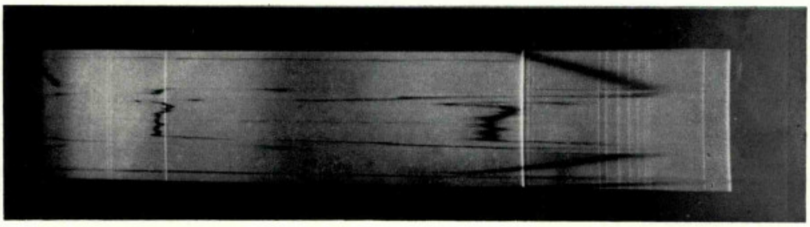

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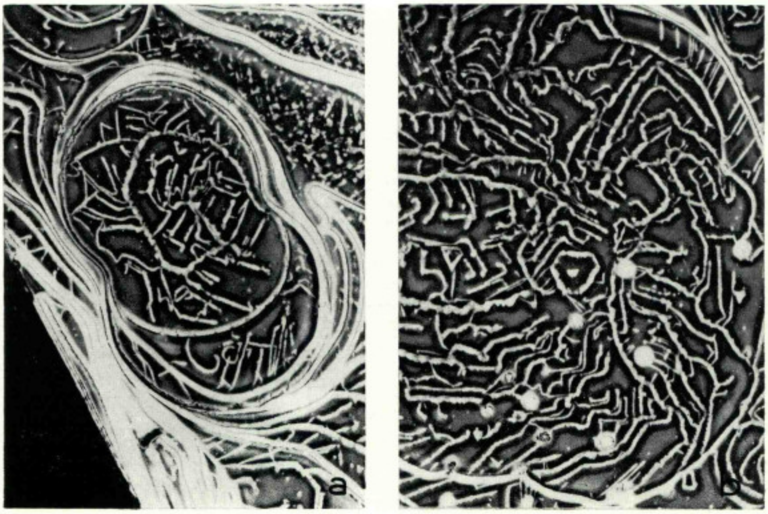
PLATE XVII

PLATE XVII

Fig. 1a, b — Two examples of irregular overgrowth. Positive phase contrast. × 180.

Fig. 2 — A multiple-beam interferogram of the surface covered with overgrown materials. × 75.

Fig. 3 — Fringes of equal chromatic order of Fig. 2. This clearly shows that the patterns are ridges and not ruts.



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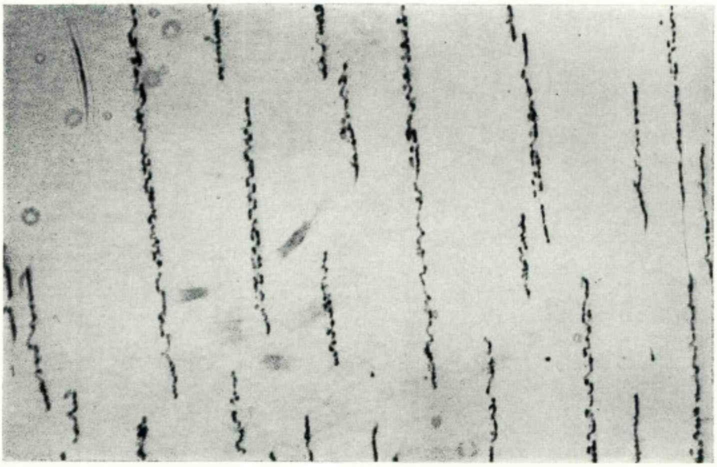

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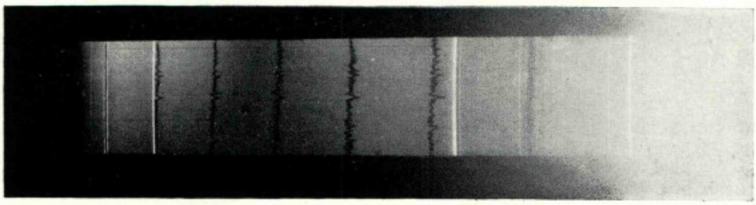

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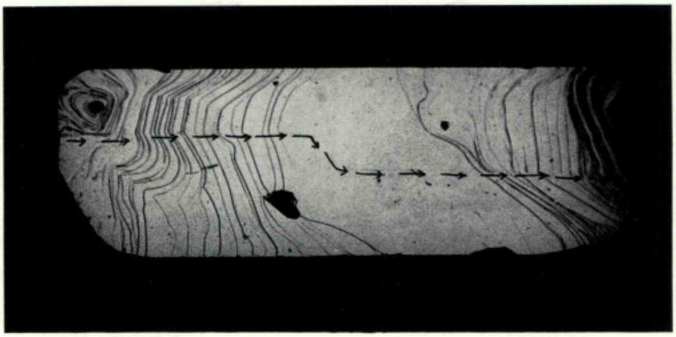
PLATE XVIII

PLATE XVIII

Fig. 1 — An example of simple discontinuity lines (twin boundaries). The line is shown by arrows. (Ditto in Fig. 2, 3). × 7.

Fig. 2 — An example of complicated discontinuity lines. × 7.

Fig. 3 — Another example of discontinuity lines. × 7.



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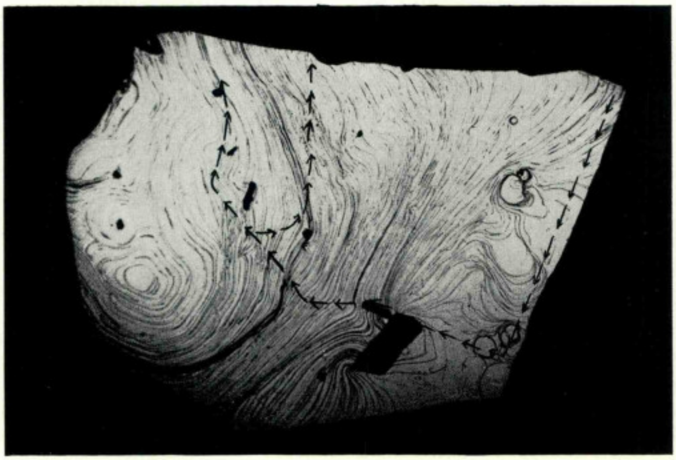

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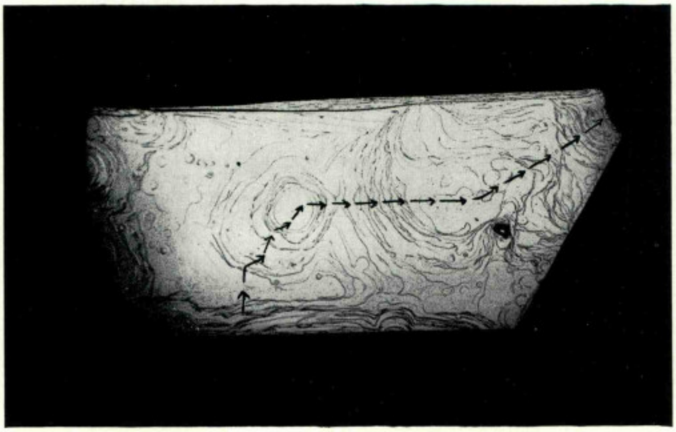

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PLATE XIX

PLATE XIX

Fig. 1 — A positive phase contrast photomicrograph showing kinks of layers at a discontinuity line. × 18.0

Fig. 2 — A positive phase contrast photomicrograph showing split of thick layers into thinner layers at a discontinuity line. × 180.

Fig. 3 — Showing the level difference on both sides of a discontinuity line. Positive phase contrast. × 180

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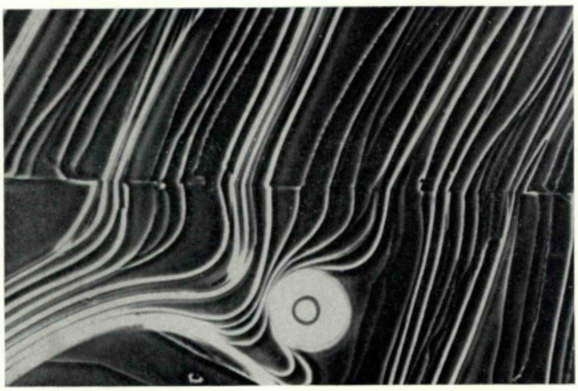

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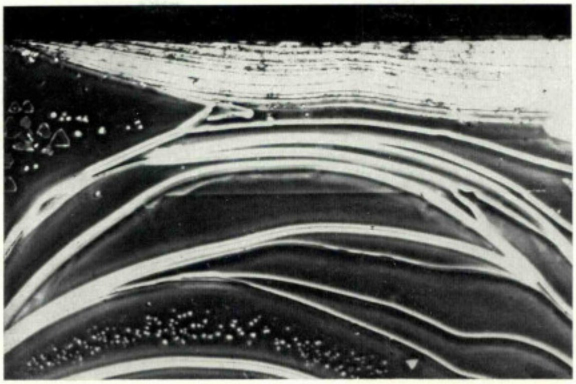
PLATE XX

PLATE XX

Fig. 1 — New growth layers starting at corners which are formed by the step of a discontinuity line and growth fronts. Arrows show new growth layers. Positive phase contrast. × 180.

Fig. 2 — New growth layers starting at the edge of higher side of a discontinuity line. Arrows show new growth layers. Positive phase contrast. × 180.

Fig. 3 — Preferential etching at a discontinuity line. Positive phase contrast. × 180.



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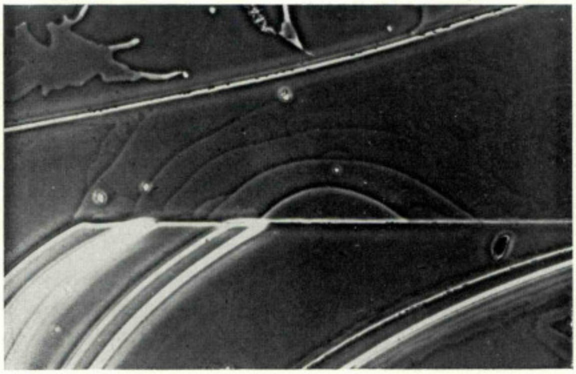

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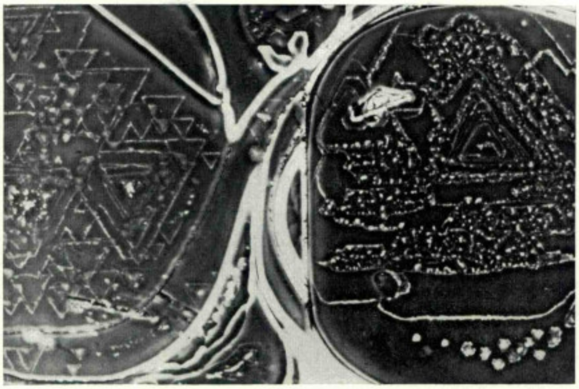
PLATE XXI

PLATE XXI

Fig. 1 — A positive phase contrast photomicrograph showing opposite orientation of triangular patterns on opposite side of a discontinuity line. × 180.

Fig. 2 — Same as Fig. 1, but the orientation of the discontinuity line is different. Positive phase contrast. × 180.

Fig. 3 — Exceptional instance that the orientation of triangular patterns are the same on both sides of the discontinuity line. In this case, if the line is traced to the end of the crystal, it splits into two lines, which suggests that the line actually consists of two lines, though it looks like a single line.



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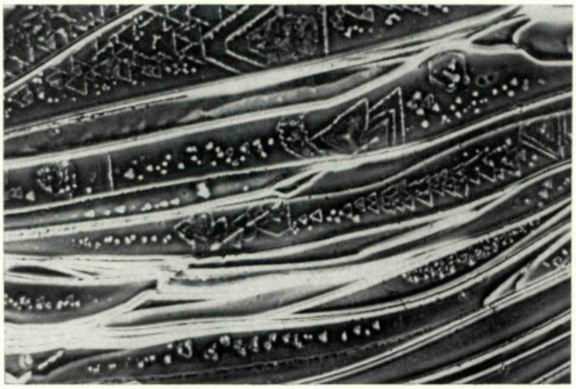

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