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STUDIES OF CRYSTAL SURFACES

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ABSTRACT

Four instances of imperfection or disorder in crystals are presented and interpreted in this paper. They are all obtained through the studies of crystal surfaces of silicon carbide and hematite. This paper consists of two parts; part 1 deals with observations on silicon carbide crystals and part 2 deals with the first direct observation of twinning due to stacking faults in hematite.

Part 1: It is clarified that the so-called single crystals are often not single but consist of several different polytypic domains having different c_0 values or even belonging to different crystal systems. They also sometimes consist of complicated twinned domains. Existence of stacking faults in silicon carbide crystals is also proved from the orientation of epitaxially grown impurity crystals on the surface of growth layers.

Part 2: The first direct evidence of twinning due to stacking fault is observed on the surface of the basal plane of natural hematite crystals. Three examples are shown. They consist of two sets of oppositely orientated triangular growth layers. In every case, it is noticed that one set of triangular laye has the height of a fractional multiple of that of the other set. The final level difference between the two sets of growth layers is measured to be less than 7Å and is considered to be one layer height in the unit cell. Structural consideration of hematite suggests that stacking faults with an odd number of layers missing from the normal stacking sequence can produce twinning structure parallel to the basal plane. The observed surface patterns can be explained in terms of twinning due to stacking fault.

INTRODUCTION

Since growth and dissolution of crystals take place through the surface of crystal faces, the crystal surfaces are the places where all phenomena concerning crystal growth and dissolution are most vividly reflected. Therefore, by studying surface structures of crystal faces, we are able to know the mechanism, process or history of crystal growth and dissolution. It is also possible to know the behavior of internal imperfections or disorders of crystals such as dislocations, stacking faults, etc., since their existence will affect greatly the surface patterns formed by growth or dissolution. Surface structures of crystal faces will also exhibit the differences in growth conditions, as well as the history that the crystals have experienced after their formation, since the difference in growth conditions will result in different growth patterns. Therefore, it can be said that the studies of surface structures of crystal faces are very important not only in studying genetical or dynamical nature of crystals, imperfections in crystals, but also to solve various geological or mineralogical problems.

Fortunately, remarkable developments in methods of observation and measurement have recently been achieved, and we are now able to study every minor detail of surface structures. Using a sensitive reflection phase contrast microscope, it is possible to observe growth layers as thin as a few Å. In fact, the writer has succeeded in observing spirals having a step height of only 2.3 Å, 4.6 Å or 7 Å on the basal plane of hematite crystals (Sunagawa, 1961). These values are in fact smaller than the height of one unit cell of hematite. The height or depth of such extraordinary thin growth layers or dissolution features can be precisely measured by the methods of multiple-beam interferometry and of fringes of equal chromatic order (Tolansky, 1948). With these methods, we can measure step height down to 10 Å, and if the indirect method is applied, it is possible to measure a height of less than this value. Therefore by using these sensitive methods of observation and measurement adequately, we can make a thorough survey of every minor detail of crystal surfaces, and so can discuss the mechanism of growth or dissolution and other problems relating to growth or dissolution in terms of a unit cell or on an atomic scale. We are also able to observe directly dislocations or stacking faults in crystals.

The writer has been engaged in studies of crystal surfaces of natural hematite from many localities, silicon carbide made at several different factories, natural and synthetic diamonds, pyrite and quartz. Many interesting results have been obtained through these studies, and some of them were reported previously (Sunagawa, 1958, 1960a, b, c, d, Seager & Sunagawa, 1962; Tolansky and Sunagawa 1959, 1960).

In this paper, four examples showing imperfection or disorder in crystals will be presented and interpreted. They contradict our general beliefs on the nature of crystals. The first three pieces of evidence to be presented in part 1 are observed on silicon carbide crystals, and the evidence presented in part 2 is observed on hematite. The interpretations to be discussed are all based on the following principles.

1. When growth spirals or growth layers—specifically those not having very big step height, namely less than several unit cell height—take on polygonal forms, the symmetry of the polygons is strictly in accordance with the symmetry of the face on which they appear. If a crystal face has a three-fold axis, polygonal spirals or growth layers will take on triangular forms, and if a face has a six-fold axis they will take on hexagonal form. This has invariably been observed on a large number of crystals which the writer has studied so far. Therefore, it is possible to conjecture the crystal system from the symmetry elements of growth spirals.

2. Growth spirals, growth layers or etch pits which have polygonal forms and have small step heights or depths are orientated in one direction on the whole surface of a crystal face, if the crystal is single, and oppositely orientated on the opposite sides of a twin boundary, if the crystal is a contact twinned (Sunagawa 1960b). If a surface pattern which is contradictory to this is observed, it shows that there must be some kind of disorder.

3. According to Frank's (Frank, 1951) and Mitchell's (Mitchell, 1956, 1957) theory, different polytypes of silicon carbide or cadmium iodide are formed from screw dislocations having different Bergers' vector. If this theory is correct, spirals having different step heights will belong to different polytypes, provided that they originate from single screw dislocation point and that the height of one spiral layer is a fractional multiple of that of the other.

Part 1. OBSERVATIONS ON SILICON CARBIDE CRYSTALS

Coexistence of Different Polytypes in Single Crystals

If a crystal possesses single external form and yields a single x-ray diffraction pattern, we consider it a single crystal. In practical procedure, we make x-ray analyses of a crystal having single external form, presuming that the crystal is single.

However, if detailed studies are made of the surface structures of such single crystals of silicon carbide, we are surprised to find that they often consist of several different polytypic domains. On the surface of basal planes, we often find that there are several spirals having different forms and step heights. In Figs. 1 and 2, two different spirals observed on one basal plane of a silicon carbide crystal are shown. The spiral in Fig. 1 has hexagonal form, which suggests that it belongs to a hexagonal polytype, whereas the spiral in Fig. 2 has regular triangular form, which shows that it belongs to a rhombohedral polytype. In Fig. 2, one can see on the lower left part of the photograph layers having regular hexagonal form, which clearly proves the coexistence of hexagonal and triangular spirals on the same surface. Step heights of the two spirals are quite different as can be seen from the width and brightness of white diffraction bands appearing along spiral steps in the phase contrast photomicrographs. Therefore, it can be said that this crystal, though having singular external form of hexagonal platy habit, is in fact not single but consists of two different polytpes.

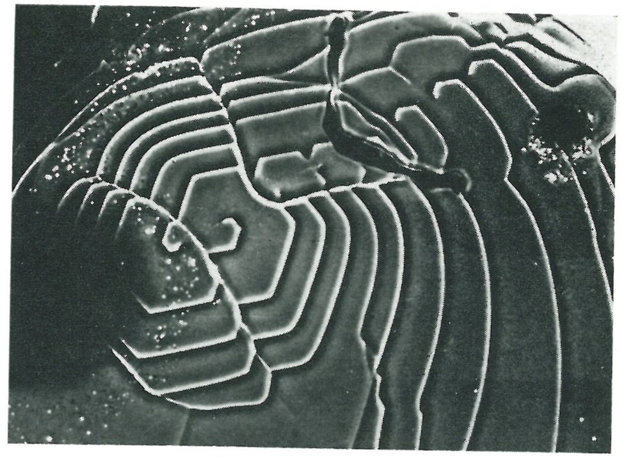

Fig. 1. Hexagonal spiral, positive phase contrast, ×250.

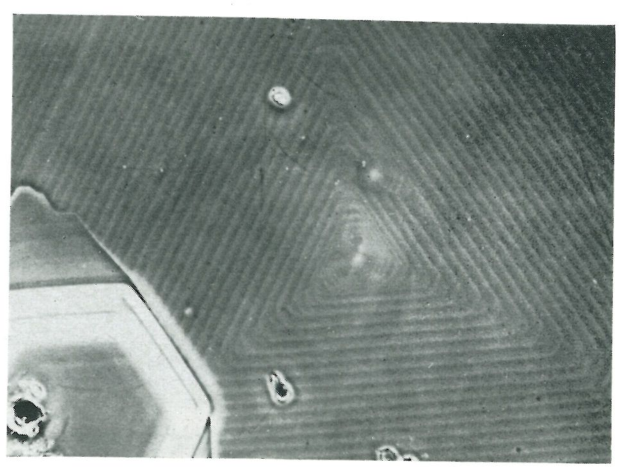

Fig. 2. Triangular spiral, positive phase contrast, ×1000.

FIG. 3. Hexagonal spiral belonging to 6H polytype, positive phase contrast, ×1000.

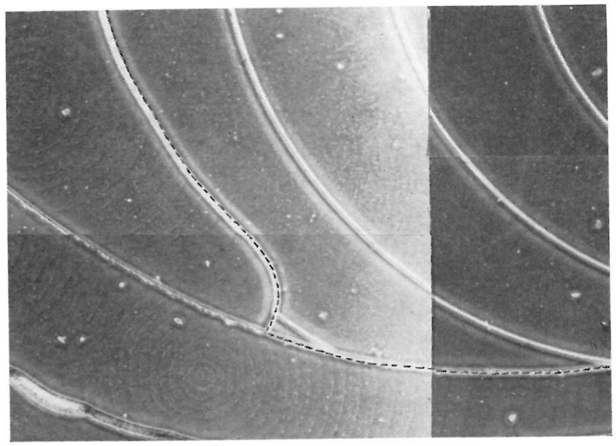

FIG. 5a. Built up positive phase contrast photomicrograph showing domain boundary, ×200.

Fig. 3 and 4 show two hexagonal spirals on the same surface of another silicon carbide crystal which has a regular hexagonal, thin, platy habit. Both spirals have hexagonal forms, but the former's hexagon is regular, while the latter spiral shows typical interlacing pattern. (The meaning of dots observed on both spirals will be reported elsewhere.) The step heights of the two spirals are measured with the method of multiple-beam interferometry. It is found that the former spiral has step height of 15 Å, while the latter has 10 Å. This shows that the former spiral belongs to 6H polytype, while the latter to 4H polytype. Here again, it is definitely proved that on one crystal face of a single crystal there are two different polytypes.

Figure 5 shows another example. In this photograph, we notice a typical circular spiral having very small step height in the lower and left part of the picture and very thick circular growth layers on the upper and right part. At the centre of the latter growth layers, there are typical circular spirals originating from three screw dislocation points, as shown in Fig. 5. The latter circular growth layers originate from these screw dislocations. The step height of the latter spiral layer is estimated to be very large, probably more than 1000 Å, whereas that of the former spiral will not exceed 50 Å. These two possibly belong to different polytypes, although it has not been proved up to the present time as their step heights are not precisely measured. However, the reason that the writer presents this photograph is to show the boundary between the two supposed-to-be polytypes. There is clear discontinuity between the two domains as shown by a dotted line. This sort of

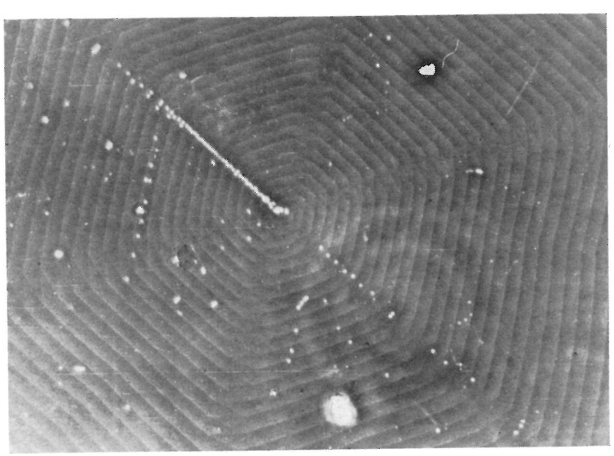

FIG. 4. Hexagonal spiral belonging to 4H polytype, positive phase contrast, ×1000.

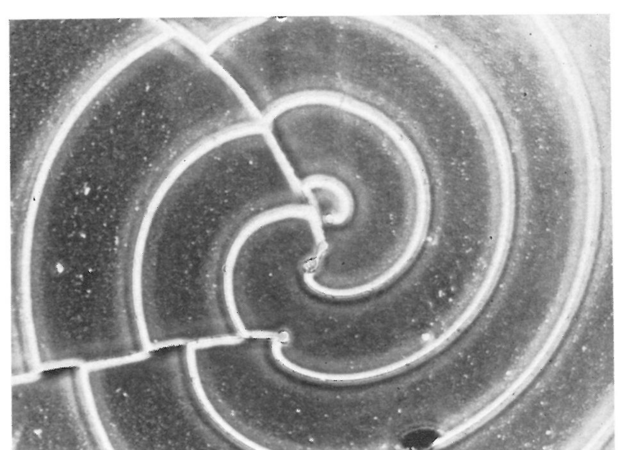

FIG. 5b. Positive phase contrast, ×350.

discontinuity is seen at the boundary between different polytypic domains in every case. Inside of one polytypic domain, no discontinuity of growth layers is seen.

The above described phenomena are not at all exceptional but are commonly observed on many silicon carbide crystals, as well as on some hematite crystals. These observations clearly show that the so-called single crystals are often not single but consist of different polytypes, which have different c and even belong to different crystal systems, and give an alarm to x-ray studies of polytypism. In an x-ray analysis of this sort of single crystal, we may get an x-ray pattern which is an integral of several different polytyes. Such a pattern is difficult to distinguish from the x-ray patterns of a real single crystal having a x-ray repeat distance which is equal to the integral of several different repeat distances. Therefore, x-ray analyses of such crystals may sometimes lead to a wrong conclusion and produce a new polytype which does not really exist. It is strongly suggested to make a thorough study of crystal surfaces before carrying out x-ray studies of polytypism.

Twinning Observed on the So-called Single Crystals of Silicon Carbide

As stated in principle 2, polygonal spirals or growth layers are orientated in one direction on the whole surface of one crystal face of a single crystal. However on some crystals of silicon carbide, evidences which show contradiction to this principle have been found, though the crystals have perfectly single external forms.

Figure 6 shows an example of such a case schematically. Two triangular spirals having rounded corners appear close together on the basal plane of one single crystal. There is a clear discontinuity between the two spirals. It is clearly noticed that the two triangles are oppositely oriented, which shows that the two are in a twin relation.

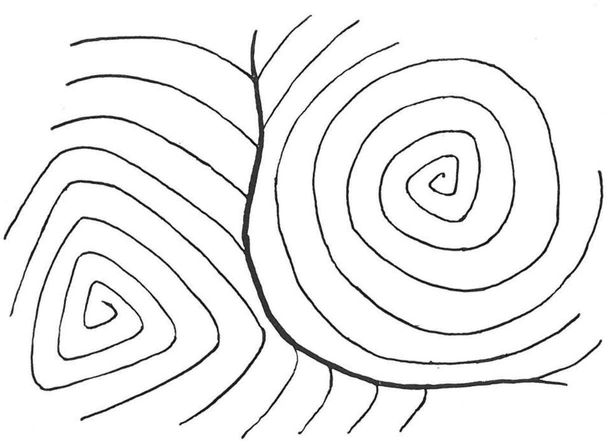

Fig. 6. Schematic figure showing two spirals in twin relation on one crystal face.

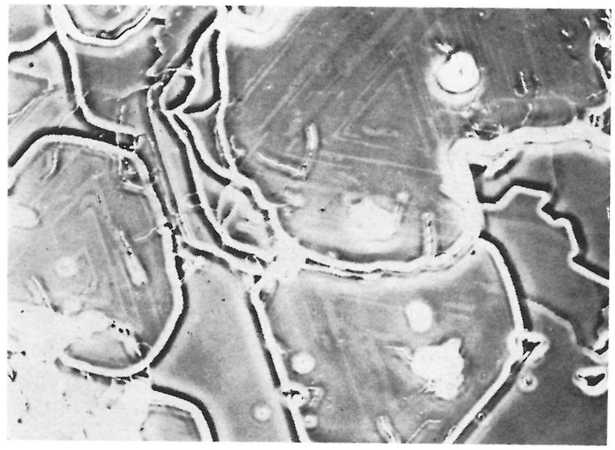

Fig. 7. Complicated twin domains observed on the basal plane of one silicon carbide single crystal. Positive phase contrast, ×250.

Figure 7 shows another example of much complicated twinning. This crystal came from the Norton Co. and has hexagonal habit with perfectly single appearance. The crystal received etching while it was still in furnace, as can be seen from the characteristics of surface structures. There are areas surrounded by broad white lines, which are considered to be domain boundaries. One triangular spiral occurs on one domain. It is noticed that some triangles of these spirals have opposite orientations in respect to the neighboring triangular spirals, but some are in the same orientation. This shows that some domains are in the twin position in respect to the other domains. In other words, this crystal, though having perfectly single appearance, consists of many domains which are in the twin relation with each other.

These observations again show that the crystal which we treat as a single crystal is in fact not single but consists of many twinned domains. It should be noted here that x-ray analyses of such crystals will not show the existence of twinning, especially in the case of the first example, since such spirals often occupy only a very thin part of the topmost surface of a crystal, as typical spirals are usually formed at the latest stage of growth. (Sunagawa 1960d, 1962). This again shows the necessity for studies of crystal surfaces before carrying out x-ray studies.

A Proof of Existence of Stacking Fault in Silicon Carbide Crystals

Figure 8 is a positive phase contrast photomicrograph of the surface of a single crystal of silicon carbide from the Norton Co. The crystal has thin hexagonal platy habit. Broad white lines running horizontally across the photograph are edges of very thick growth layers having step height of more than a few thousand Å. On the surface of these thick growth layers are many small star-like patterns. They sometimes aggregate together forming triangular pattern with a white circle at the centre. Since these patterns appear bright on the positive phase contrast photograph, they are all elevated. Since this type of growth feature has never been observed on any silicon carbide crystals and is quite different from ordinary growth features of silicon carbide, both the star-like and triangular elevations are considered to be impurity crystals which are epitaxially grown on the surface of the crystal. As it can be clearly seen on the photograph, these star-like patterns have the same orientation, without a single exception, on the whole surface of one growth layer but have entirely opposite orientation on the surfaces of the two neighboring layers. The stars on A layer are orientated oppositely in respect to those on B and C layers but are orientated in the same direction as those on D layer. If the surface of these thick growth layers have the same atomic arrangement, the epitaxially grown impurity crystals should also be arranged in one direction on the surfaces of every growth layer. However, if there is a stacking fault between the two successive layers, the surface of the two layers will have different (oppositely orientated) atomic arrangement, as silicon carbide has a polar structure. This will naturally result in the opposite orientation of epitaxially grown impurity crystals on the surface of the two layers. This is in fact the case. Therefore, it is quite safe to conclude that there are stacking faults in this crystal.

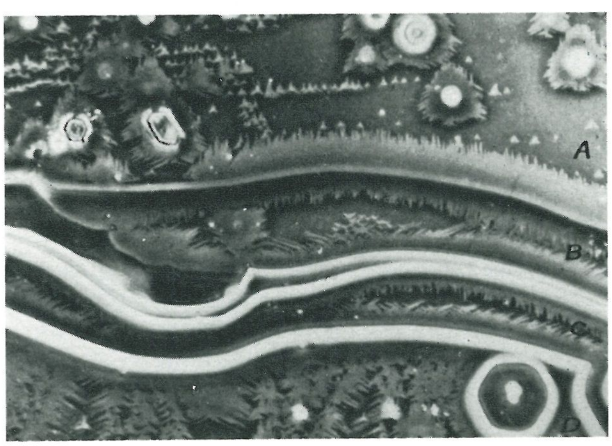

Fig. 8. Photomicrograph showing the existence of stacking fault in silicon carbide crystal. Positive phase contrast, ×1000.

Part 2. TWINNING OF HEMATITE DUE TO STACKING FAULT

Introduction

It has been theoretically conjectured that stacking fault can produce twinning. For instance an attempt has been made to interpret the origin of polysynthetic twinning, such as that of plagioclase feldspar in terms of stacking faults arising during growth. However, these are merely theoretical assumptions, and no clear experimental evidence of twinning due to stacking faults has yet been reported (Cahn, 1954).

Surfaces of the basal plane of hematite crystals usually exhibit thick growth layers of irregular or triangular shape. On the surface of these thick layers there are many thinner growth layers or growth spirals. These thinner growth layers at times have circular form, but in most cases they have a triangular form. These triangles are all orientated in the same direction over the whole surface, if a crystal is single. If the crystal is contact twinned, they have opposite orientations on opposite sides of the twin boundary, irrespective of the orientation of the twin boundaries. This was clearly demonstrated in the writer's previous study (Sunagawa 1960b).

It has been noticed from observations on large numbers of crystals from different localities that almost all crystals have the pattern of either a single or contact twinned crystal. In almost all cases, the triangular growth or etch patterns do not overlap each other, nor do two sets of oppositely orientated triangles coexist on the surface of a single crystal. However, on a very few crystals, it has been observed that on the surface of a single crystal there are two sets of triangular growth layers oppositely orientated. Such a pattern can only be explained in terms of twinning parallel to the basal plane. Considerations of the hematite structure in terms of a layer structure indicate that this twinning formed through a stacking fault during growth. The observations reported here are, as far as the writer knows, the first clear evidences of twinning due to stacking faults. Evidence from three examples showing twinning due to stacking fault will be described.

Observations

The first evidence is furnished from several crystals from Gihofuji, Japan. The surfaces of the basal planes of these crystals consist of thick triangular growth layers. On the surface of these thick growth layers, there are thinner triangular growth layers which originate from rows of screw dislocations and have very small step heights. They form complicated and combined spiral patterns. The orientation of these thin triangular growth layers is strictly crystallographic and has one direction over all the surface. However, it is noticed that many small tongues project along the fronts of these thin triangular layers (a typical example of which is shown by arrows in Fig. 9). These tongues have several different forms, but they are principally the same and a deviation from a simple triangle. The most noteworthy point is that these tongues have a completely opposite orientation to that of the main thin triangular growth layers. In fact, if they are in the same orientation, no projections will be formed along the fronts of main growth layers.

Under low magnification, the tongues appear to start from a part of a front of main growth triangles and do not cross or cover the other fronts. But, if they are observed under high magnification, it is found that they can cover several growth fronts, as schematically shown in Fig. 10. As it can be seen in this figure, the step height of the tongue is neither the same as that of a single layer of the main thin triangular growth layers nor rational multiples of them. Careful investigation of the boundaries between the tongue and the main growth fronts show

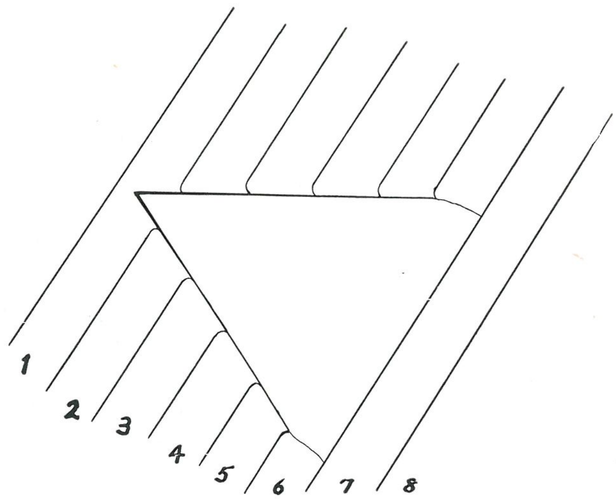

FIG. 10. Schematic figure showing the relation between triangular tongue and triangular thin growth layers.

that the surface of the tongue is higher than the surfaces of 1st, 2nd—6th main growth layers, but lower than the 7th, 8th, etc., layers in Fig. 10. Moreover, the surfaces of the tongue and the 6th layer are not on the same level but there is a very faint level difference between these two. Such relationships can be observed on every tongue.

Since the tongues are very small, it is virtually impossible to measure their step heights. It is also difficult to measure the step heights of the main thin growth layers, since they are irregularly spaced and very shallow. However, from the nature of white diffraction fringes appearing at the edges of these layers, the step heights can be roughly estimated. The heights of the tongues are estimated to be few tens of angstroms and that of the thinnest main growth layer is of the order of one unit cell height or even less than that. Therefore, the final displacement in height of the tongues and the main growth layers is considered to be less than a unit cell.

These observations clearly show that the tongues are not stacked on the substrate in the correct sequence. In other words, there must be stacking fault between the substrate and the tongues. Furthermore as the orientations of the tongues show, it is quite clear that the tongues are in the twin position to the main triangular layers (substrate), the twinning plane of which is c(0001). Therefore, it is safe to conclude that this twinning is formed by a stacking fault.

The second example appeared on a crystal from Saganoshima, Japan. More than half of the surface

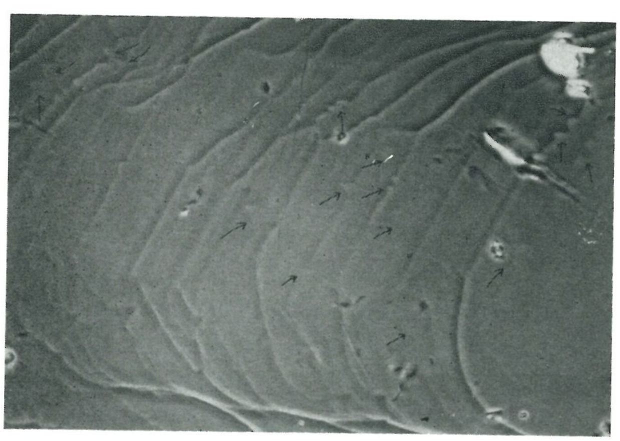

FIG. 9. Positive phase contrast photomicrograph showing triangular tongues projecting along the fronts of triangular thin growth layers. Arrows show the tongues, ×250.

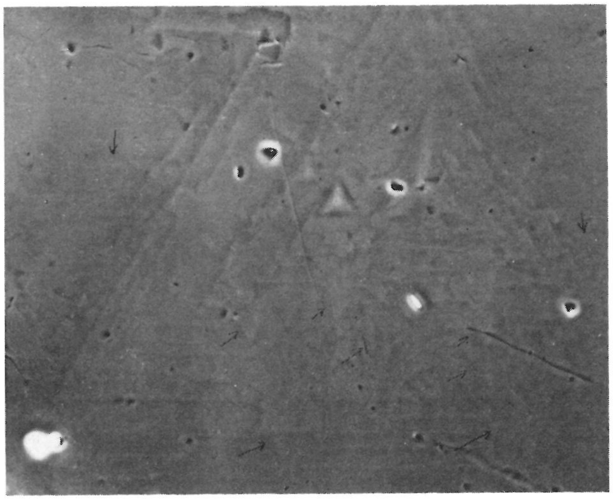

FIG. 11. Positive phase contrast photomicrograph showing the second evidence of twinning due to stacking fault. Arrows show projections, ×250.

of this crystal is flat and on it are more than ten triangular cones. The sides of these triangular cones are not straight but have many small triangular projections; Fig. 11 serves as an example. On the other parts of the surface, very thin straight growth fronts appear. Although the central parts of these growth fronts are not visible, the orientation of these fronts is certainly opposite to that of the triangular cones and nearly parallel to that of the triangular projections appearing along the sides of the cones. At several places on the surface, there are two sets of these oppositely orientated triangular layers. Noteworthy is the fact that the two sets of fronts do not cross each other, which clearly demonstrates that they are growth or etch fronts and not the lines formed by movement of dislocations (Seager and Sunagawa, 1962). For the following two reasons, these fronts are considered to be growth fronts and not etch fronts.

a) Triangular cones are commonly observed on other crystals in which they have been proved to be growth spirals.
b) Another set of triangular layers has very smooth fronts, which again can not be expected in the case of etching.

In the case of a contact twin, the triangular features have opposite orientations on opposite sides of a twin boundary, which appears like a discontinuity line of growth patterns. But on the surface of this crystal, no discontinuity line appears, and the two sets of triangular layers just overlap each other. This crystal therefore is not a contact twin but exhibits repeated twinning parallel to the basal plane. The thickness of the laminae of this polysynthetic twin is of the order of the height of one growth layer, which is estimated to be one unit cell or less.

Close investigation of the region where the two sets of layers coexist shows similar features as observed in the first example. It is reasonably safe to conclude that this polysynthetic twinning is also formed by successive stacking faults during growth.

The third example appears on one crystal from Saganoshima, Japan. Here, there is no projecting pattern on the surface which in fact reveals two different kinds of structure. There are triangular growth spirals with a step height of 7 Å and also triangular growth islands and tongue-like terraces with an average step height of about 40 Å. The tongue-like terraces are proved to be derived from the triangular growth islands. The mutual relationship between these two patterns shows that the spiral was formed after the formation of triangular islands (Sunagawa, 1960a).

These two growth patterns have opposite orientations, as schematically shown in Fig. 12. Close examination of the boundary between spiral fronts and the tongue-like terraces show that the heights of the tongue-like terraces and triangular islands are fractional multiple of the height of a single spiral layer; that is, 7 Å×n+0 to 7 Å. This level difference must be either 2.3 Å (one layer height in the unit cell) or 4.6 Å (two layers). The most probable level difference is 2.3 Å.

From these observations, therefore, it is quite clear that the spiral pattern is not stacked on the substrate in a correct sequence. In other words, there is a stacking fault between the spiral layers and the sub-

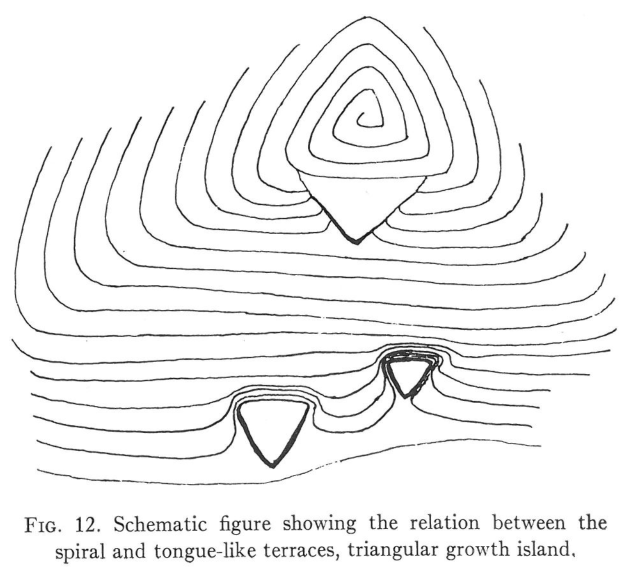

FIG. 12. Schematic figure showing the relation between the spiral and tongue-like terraces, triangular growth island.

strate which consists of triangular islands. Since these two triangular patterns have opposite orientations, it can be said that these two are in the relation of twinning, parallel to the basal plane, Thus, it is concluded that this twinning is formed by stacking faults.

Structural Considerations

We have observed in this study three different appearances of twinning, the twinning plane of which is (0001) and these are considered to be formed through stacking faults. Perhaps the first and the most primitive example may not be called twinning in the common sense of terminology, but it certainly has the nature of twinning. The second example is certainly polysynthetic twinning, but the laminae are thinner than formerly reported. The third example is again not twinning in the common sense, but its characteristic is without doubt that of twinned crystals. In any case, the appearance is not that of a twinned crystal in the ordinary sense, but the character is exactly that of a twinned crystal, at least in the fundamental meaning of the word twinning.

Two main characteristics commonly observed in the three examples are as follows:

1) there are two sets of triangular features oppositely orientated on the one surface, 2) the step height of the one triangular feature is a fractional multiple of the other.

The first characteristic clearly shows that these two sets of triangular features are stacked upon each other in twin orientation. The second characteristic shows that there is a stacking fault between the two sets of features. Since the final level difference between these two features is less than 7Å as in the case of the second example and from the nature of the stacking in hematite structure, it is considered that the most probable arrangement of stacking faults in these cases is that one layer is missing in the structure.

Now, if we consider the structure of hematite to be in terms of a layer structure, we notice that the unit cell consists of six layers in the sequence of (ABABAB). Triangles consisting of three oxygen atoms in A layer have opposite orientations to those in B layer. If the next growth unit settles on the substrate having one or an odd number of layers missing, the resultant sequence will be (ABABAB) (BABABA) which is exactly the sequence of twinning. If two or an even number of layers are missing, the resultant sequence will be of a single crystal. Therefore, as a result of an odd number of layers missing, twinning can be formed parallel to the basal plane. This mechanism seems to explain satisfactorily the facts reported here. So far as the writer knows, the observations presented here are the first showing the existence of twinning due to stacking fault during growth.

Conclusion

The evidence from the four examples presented in this paper definitely shows how real crystals are imperfect, far more imperfect than we had generally believed. Such imperfection in crystals is difficult to reveal by ordinary crystallographic methods. Detailed studies of crystal surfaces, using modern techniques can reveal such imperfections. The writer would like to stress the importance of studies of crystal surfaces, not only in studying imperfections of crystals, but also in studying many other crystallographic, mineralogical and geological problems.

Acknowledgments

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