THE AMERICAN MINERALOGIST, VOL. 46, NOVEMBER–DECEMBER, 1961

STEP HEIGHT OF SPIRALS ON NATURAL HEMATITE CRYSTALS

ICHIRO SUNAGAWA,* *Physics Department, Royal Holloway College (University of London), Englefield Green, Surrey.*

ABSTRACT

The basal faces of hematite crystals from many localities have been observed with a phase contrast microscope. Different kinds of spirals are observed on the surface. The step heights are precisely measured by means of multiple-beam interferometry, and it is found that they are integral multiples of 2.3 Å, which is the height of a single layer in the structure, and not that of a unit cell height, which is 13.73 Å. Spirals having step heights close to 2.3 Å, 4.6 Å, 7 Å, 10 Å, 20 Å are observed.

Structural and theoretical consideration shows that the Burgers vector of screw dislocation or the unit of growth should be the height of the minimum component of the structure and not that of the unit cell. Therefore, both from theoretical consideration and the measurements, the widely accepted belief on the unit height of spirals is here contradicted.

INTRODUCTION

Ever since the importance of screw dislocations in crystal growth phenomena was predicted by Frank (1949), a wide variety of spiral patterns has been observed on many different crystals. Step heights of some of these spirals have been measured precisely by means of either multiple-beam interferometry or by the shadow-casting methods of electron microscopy. It has been widely believed that the step heights of the spirals are either one unit cell or a rational multiple thereof. However, it is not necessary to assume that the unit of growth is controlled only by the geometrical nature of the crystals.

Because of inadequate methods in some earlier studies, it is possible that the thinnest growth layers were missed. But there are cases in which the step heights of spirals less than the unit cell were found. Amelinckx (1951) observed spirals on SiC, type 6*H*, with a height of one half unit cell. He also reported (1955) spiral patterns on *n*-alcohol crystals having a height of one molecule, whereas the unit cell consists of two molecules. Verma and Reynolds (1953) detected spirals having half integral multiples of the unit cell on stearic acid. In this case, however, they did not find spirals having step heights less than one unit cell. Verma (1951) has also reported spirals on SiC having a smaller step height than the unit cell.

The most common spiral patterns found on hematite are deformed spirals revealing high step heights. They appear to have originated from scratches, misfit boundaries, etc., which have formed on the surface during growth, due to mechanical deformation, and external or

* Present address: Geological Survey of Japan, Hisamoto-cho 135, Kawasaki-shi, Japan.

internal stresses. Such high step spirals will not be discussed here. The spirals discussed in this paper are those having a regular form and spacing between successive layers. They might be called "typical spirals," and usually occur on the surface of thick growth layers, an indication that they are formed at the latest stage of growth. They sometimes cover nearly the whole crystal surface. They may be triangular, truncated triangular or circular. Precise measurements of the step heights of these spirals have been made with multiple-beam interferometry, and it is found that the step heights may be less than a unit cell, or greater. Successful phase contrast photomicrographs were obtained of steps, which measurements showed were 2.3 Å, 4.6 Å, 7 Å, 10 Å, 20 Å, etc.† Since c_0 for hematite is 13.73 Å, and as the unit cell consists of six layers of oxygen atoms sandwiching iron atoms, the height of the minimum component of the cell is indeed 2.3 Å. Therefore, it is concluded that the Burgers vector of screw dislocation of hematite, or the unit of growth, is not one unit cell in height, but is of the height of the minimum component of the unit cell. It is conjectured that this might be true not only for hematite but also, for other minerals having a layer structure, or having a structure which can be interpreted in terms of a layer structure. In the following section, the results of measurements of these very thin growth spirals are described and shown.

Methods of Observation and Measurement

With the usual metallurgical reflection microscope, growth layers of a thickness of less than a few hundred Å can hardly be observed. The very thin layers have been studied here with an "Olympus PMF type" phase contrast reflection microscope. Very absorbing phase disks give an exceptionally sensitive phase contrast effect, and permit observation of ultra-thin growth layers.

Multiple-beam interferometry has been applied to the measurement of step height of spirals, using the standard methods developed by Tolansky (1956). Since this method is well established, only a very brief account of the practice will be given here.

The surface is silvered to a thickness of about 1000 Å. It has been adequately established by Tolansky and Bhide (1956) that silvering with this thickness does not modify the surface structures. This silvered surface is matched against a silvered flat, and in accordance with familiar experimental arrangements, sharp, high precision multiple-beam Fizeau fringes are produced, using the green mercury line. Under normally good conditions, it is not difficult to measure step heights down to 15

† Photographs showing 2.3 Å, 4.6 Å and 7 Å spirals accompanied this paper, but lack of contrast made it impossible to reproduce them satisfactorily.

Å. However, in the case of layers thinner than 15 Å, it is necessary to apply indirect methods. For instance, when the spacing of the successive layers of a very shallow spiral is regular and narrow, it is easy to calculate the average step height of a single layer by dividing the easily measured total height of the spiral by the number of layers. The definite existence of spirals of layer height of only 2.3 Å has been confirmed this way. Quite often we observe that the thinner layers merge to form a thick layer. In such a case, we can derive the step heights of the thinner layers by dividing the measured step height of the thick layer by the number of thin layers present. Step heights of 4.6 Å, 7 Å, 10 Å, etc. have been obtained in this way. The 20 Å spiral was measured directly from the fringe displacement, using standard procedure.

Observations and Measurements

2.3 Å Spirals

On the basal planes of hematite crystals from many different localities, triangular structures have been commonly observed. When multiple-beam interference fringes are run across such structures, they show a very small shift, which clearly shows that the height of the structure is very small. Measurements of the total heights of these shallow hillocks have been made on one crystal of hematite from Ayumikotan in Japan. The smallest step height is about 20 Å, the maximum 110 Å, but the commoner step heights range from 30 Å to 50 Å (Sunagawa, 1958).

Under low magnification, no fine structure can be seen on the side faces of these triangular hills. However, when phase contrast photomicrographs of very high magnification and very high contrast sensitivity are taken, it is revealed that these actually consist of narrow spaced triangular spirals. Clearly the step height of each layer can be obtained by dividing total height by the number of clearly resolved spiral layers. The results measured and calculated for seven different cases show remarkably good agreement, ranging from 2.1 Å to 3.2 Å, with an average of 2.6 Å. Clearly this low value must be identified with the single layer of Fe_2O_3, which is 2.3 Å. This is quite a surprising result. This represents the smallest growth layer yet evaluated by multiple-beam interferometry. It clearly shows that there exists a screw dislocation with Burgers vector which is only one sixth of a unit cell. Many of our hematite crystals from different localities reveal that this type of unit spiral is quite common, and in some cases the whole surface is completely covered with this type.

The form of these spirals is always regular, consisting of straight-sided equilateral triangles. The spacings between successive layers are regular, and very narrow compared to most other spirals.

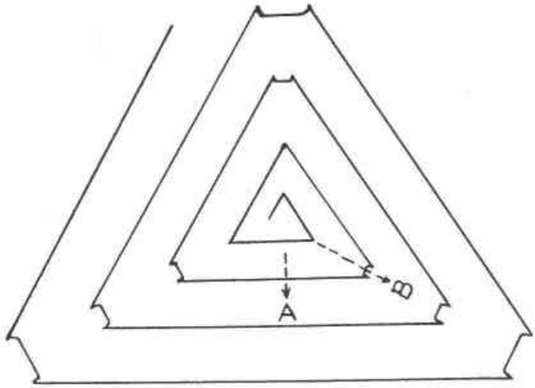

FIG. 1. Schematic drawing of horn-like projections at each corner of a 4.6 Å spiral.

4.6 Å Spiral

On one crystal from Saganoshima, Japan, nearly half the surface is covered with one triangular spiral originating form a single screw dislocation. At the center, the spiral has regular triangular form, but after several turns three of the corners truncate and a deformed hexagonal pattern appears. At each corner of this hexagon, a horn-like shape is observed as shown by the diagram in Fig. 1. This pattern is considered to be formed by the different rate of growth in the direction of A and B. A line crosses the whole crystal surface with a break at one portion. This line consists of two parallel twin boundaries (Sunagawa, 1959). Spiral fronts starting at a dislocation point on one side of the line spread out and cross this line at the break portion and cover nearly half the surface on the other side. This is schematically shown in Fig. 2. It is clear that the point A on the one side of the discontinuity line is higher

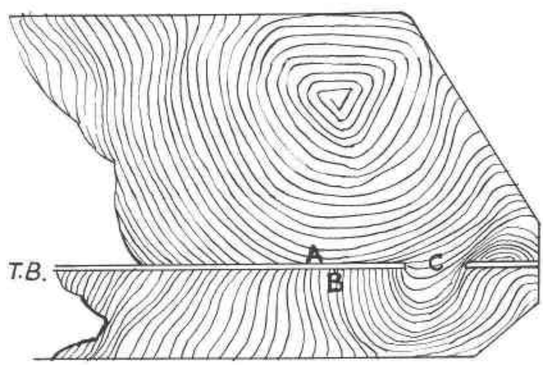

FIG. 2. Schematic drawing of crystal face covered with a 4.6 Å spiral.

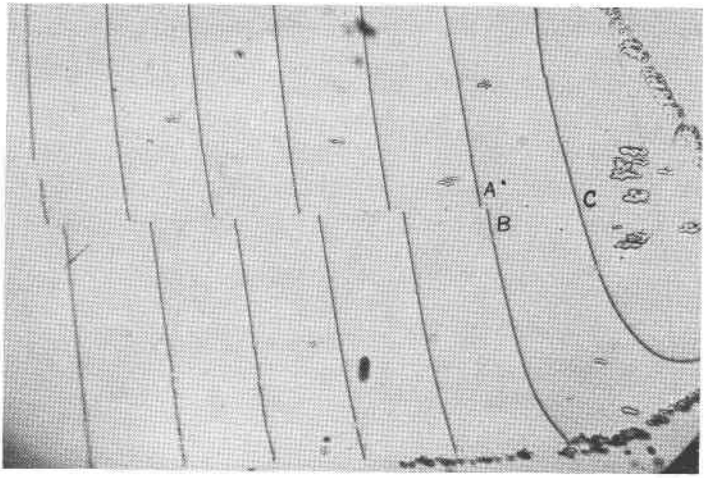

FIG. 3. Example of Fizeau fringes of a 4.6 Å spiral on a crystal from Saganoshima, Japan. ×27.

than point B on the other side, and that the level difference between A and B is equal to the multiple of the height of a single layer times the number of layers between two points. A multiple-beam interferogram for this area is shown in Fig. 3, which clearly shows the level difference between two sides of the discontinuity line. Measurements of the difference at several points have been made, and the number of layers counted on a phase contrast photomicrograph. The level differences, number of layers and the step heights of a single layer, calculated by dividing the level difference by the number of layers, are given in Table 1. The results at different points show remarkably good agreement, and the average step height is 4.5 Å, which effectively coincides with the predicted height of two layers in the structure.

TABLE 1. AVERAGE HEIGHT OF A SINGLE LAYER OF A 4.6 Å SPIRAL

Total level differences in Å	Number of layers	Height of a single layer in Å
116	29	4.0
186	37	5.0
266	60	4.4
422	95	4.4
450	97	4.6
601	132	4.6
655	139	4.7
	Average	4.5 Å

Another example of 4.6 Å spiral has been found on one crystal from the Ascension Islands. In this case, the spiral layers bunch together and form fairly thick layers, from which the total step heights can be measured, and so the individual spiral step is derived.

7 Å Spiral

On one crystal from Saganoshima, Japan, spirals with step height of about 7 Å have been observed. Two spirals start from either one screw dislocation point or alternatively two spirals of opposite sign are situated close together. On the spiral pattern, there are several tongue-like terraces at which the spiral growth fronts are intercepted. By dividing

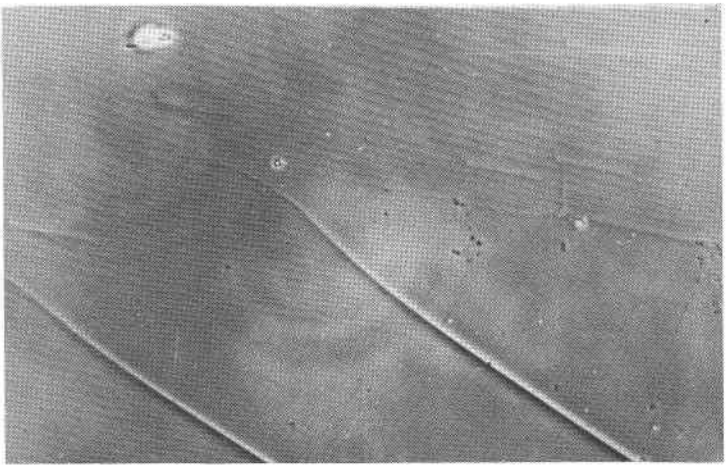

FIG. 4. Positive phase contrast photomicrograph showing bunching of 10 Å spiral layers. Ascension Island. ×160.

the total height of the tongue-like terrace by the number of intercepted spiral layers, the average step height is found to be 7 Å, which is clearly that of three layers in the structure, *i.e.*, $\frac{1}{2}$ unit cell height (Sunagawa, 1960). Similar spirals have been found on crystals from the Azores Islands, Portugal (Sunagawa, 1959).

10 Å Spiral

This spiral appears on a crystal from the Ascension Islands. At the marginal part of the spiral, growth layers bunch to form thick layers as shown in Fig. 4. No fringe shift is discernible at the edge of the spiral layer, but fortunately, very clear shifts can be obtained at the edges of the thick bunches. The number of spiral layers was easily counted with the phase contrast photomicrograph. Table 2 shows the results of measurements, number of layers and the average step height of a single layer. The step heights thus calculated range from 9.0 Å to 12.1 Å, and average is 10.3 Å. This range of 9 to 11 Å effectively coincides with about four or five layers.

TABLE 2. AVERAGE STEP HEIGHT OF A SINGLE LAYER OF A 10 Å SPIRAL

Step heights of bunched thick layers in Å	Number of layers	Step height of a single layer in Å
43	4	10.8
124	11	11.3
157	13	12.1
159	17	9.3
169	17	9.9
174	16	10.8
249	23	10.8
283	29	9.7
316	30	10.5
365	37	9.9
368	37	10.0
406	38	10.7
427	47	9.0
434	47	9.2
	Average	10.3 Å

20 Å Spiral

This spiral was found on one crystal from Saganoshima, Japan. Nearly half of the surface of the crystal is covered with a spiral pattern originating from one dislocation point. At the center, the spiral has a triangular form. The spacing between successive layers is very narrow. But after several turns, the spacing suddenly increases and the triangular form changes into a deformed circle. In one direction of the spreading of this spiral, all the layers of the spiral split up into two thinner layers and form a characteristic interlacing pattern, part of which is shown in Fig. 5. Multiple-beam interferograms of very different dispersion have been obtained. In the case of high dispersion fringes, a very small fringe shift is detectable at each edge of the spiral layers, from which a direct measurement of the step height has been made. As the shifts are very small, the value so obtained is not very precise. Measurements range from 18 Å to 25 Å, and average value is 20 Å. It is certainly not 14 Å, which is the height of one unit cell, but exceeds this. The fact that the spiral layers split into two in one direction of spreading fits in with this higher figure. (The interlacing pattern observed on this crystal is evidence which suggests the possibility of the existence of polytypism in hematite.) This spiral possibly originated from a screw dislocation with Burgers vector of value one and a half unit cell.

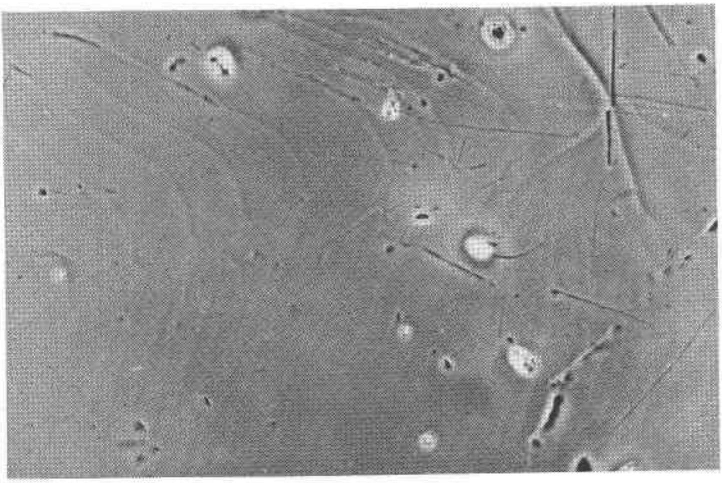

FIG. 5. Positive phase contrast photomicrograph showing interlacing pattern observed on portion of the 20 Å spiral. Saganoshima, Japan. ×180.

Spirals with Big Step Heights

On crystals from many localities, irregular formed spirals have been observed. These may owe their origin to scratches, distorted portions, misorientated portions, misfit boundaries, etc., formed by mechanical deformation and external or internal stresses taking place during growth. Judging from the visibility, width and the nature of white fringes appearing at the edges of layers on phase contrast photomicrographs, it is quite safe to say that the step heights of these spirals are large and variable.

SUMMARY AND DISCUSSION

As a result of detailed observations on the surface structures of hematite crystals from many localities, wide varieties of spiral patterns have been observed. Most spirals have relatively high step heights and are of irregular form. But some spirals appear having very small step height and are of regular triangular or circular form, often appearing on the surfaces of thick growth layers. At times they cover nearly the whole surface of a crystal. These shallow spirals originate from typical screw dislocations. The step heights of these typical spirals have been measured precisely by means of multiple-beam interferometry. Spirals having step heights of 2.3 Å, 4.6 Å, 7 Å, 10 Å, 20 Å have been found. It is also found that spirals with one unit cell in height are not at all common, while those having 2.3 Å, 4.6 Å are quite common features.

The characteristics of these spirals are as follows:

1) 2.3 Å spirals always occur as close-spaced triangular spirals. The form is always regular triangular, and no special pattern formed by the difference of growth rate in different orientations are observed at the corner of the triangles.
2) In the case of 4.6 Å spirals, the spiral pattern is a regular triangle at the center, but after a few turns three corners truncate, forming a slight displacement at each corner. This is due to the different velocity of spreading in different orientations.
3) In the case of 7 Å spirals, two spirals start at a single dislocation point, or two opposite-handed spirals start from two closely situated dislocation points.
4) In the 20 Å spiral, the pattern is triangular at the center, but after several turns it becomes first hexagonal and then circular. Furthermore, in one direction of spreading, the layers split in two, forming an interlacing pattern.

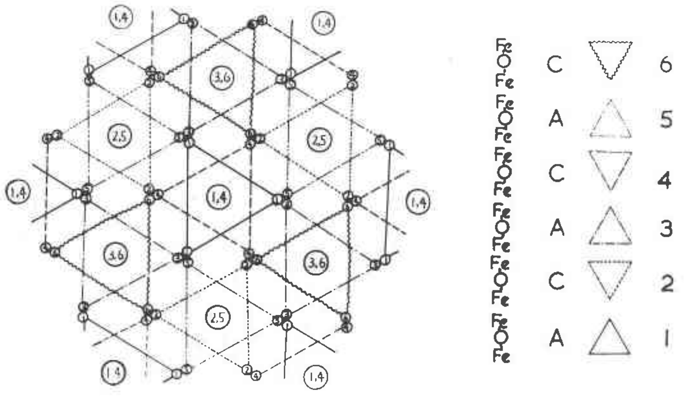

FIG. 6. Schematic drawing of the structure of hematite.

The unit cell of hematite consists of six layers of oxygen atoms parallel to 0001, alternating with Fe atoms. As shown in Fig. 6, triangles of three oxygen atoms are oppositely oriented in successive layers. Hence it is possible to subdivide the unit cell into six layers. It is quite reasonable to expect spirals of a step height of 2.3 Å, which is the height of one of these single layers, or step heights with rational multiples of 2.3 Å, but not multiples of a unit cell height. This conjecture is also supported from theoretical considerations on bond chains in the hematite structure, from the standpoint of the theory of Hartman.

If we consider the orientation of triangles consisting of three oxygen atoms, the characteristics of each spiral pattern can be explained clearly as follows. The 2.3 Å spiral should take on a simple and regular triangular pattern, as it consists of only one layer, on which triangles are arranged in the same direction. Since the 4.6 Å spiral consists of two layers, having triangles oppositely orientated, it will take on a hexagonal pattern, though in the center it will be of regular triangular form. In the case of the 7 Å spiral, it is considered that the screw dislocation of one unit cell height is split in two, thus forming a spiral having a half unit cell height. This is perhaps the reason why two 7 Å spirals usually are situated close together or start from a single dislocation point. In the case of the 10 Å spiral, no specific pattern has been observed. In the case of spirals having step height higher than the unit cell, the layer can split into two, or more than two. This is in fact observed in the case of 20 Å spiral.

Both from a theoretical and structural consideration and from precise measurements, it has been definitely clarified that the unit of screw dislocation or unit of growth is the minimum component of the unit cell and not one complete unit cell height. The step height of the spiral layer can be any rational multiple of the height of this minimum component. Since most measurements previously made on the step heights of spirals show that the heights of spiral layers are of unit cell height or rational multiples of this, it has been generally believed that the unit of screw dislocation is the *x*-ray repeat distance, but, as clearly seen here, this general idea is contradicted. It is conjectured that this may also be true in other crystal species, at least in the case of those crystals having a layer structure.

Acknowledgements

The writer expresses his heartfelt thanks to Professor S. Tolansky, in whose department the work was done, for his encouragement, helpful discussion and revising the first draft of this paper.

He also wishes to thank Professor F. C. Frank, S. Amelinckx and Drs. A. F. Seager, and P. Hartman for their constructive suggestions.

The specimens have been most generously supplied by the following people and organizations to whom the writer would like to express his gratitude.

Prof. Z. Harada, Dr. K. Sakurai, Messrs. N. Inai, K. Sawamura, H. Sato, K. Matsui.

British Museum (Natural History), Cambridge University (Department of Mineralogy and Petrology), Geological Survey of Portugal.

This work was undertaken while the writer was on leave from the Geological Survey of Japan, with the help of a Japanese Government grant.

References

AMELINCKX, S., Growth mechanism of carborundum crystals: *Nature*, **168,** 431 (1951).

———, Growth features on crystal of long-chain compounds, I, II, III: *Acta Cryst.*, **8,** 530 (1955); **9,** 16, 217 (1956).

FRANK, F. C., The influence of dislocations on crystal growth: *Disc. Farad. Soc.*, No. **5,** 48 (1949).

HARTMAN, P., Private communication.

SUNAGAWA, I., Crystal growth of hematite from Ayumikotan, Japan: *Jour. Miner. Soc. Japan*, **3,** 543 (1958).

———, Surface structures of twin boundary of hematite crystals: Symposium on twinning at IMA general meeting, Zurich (in press) (1959).

———, Growth and etch features of hematite crystals from the Azores Island, Portugal: *Serviços Geológicos de Portugal*, Memória No. 6 (Nova Série) (1960).

———, Growth history of hematite: Am. Mineral., **45,** 566–575 (1960).

TOLANSKY, S., Multiple-beam interferometry: Clarendon Press, Oxford (1948).

TOLANSKY, S. AND BHIDE, V. G., Sur la reproduction des reliefs par les couches minces utilisées en interférométrie a ondes multiples: *Jour. de Chim. Phys.*, 563 (1956).

VERMA, A. R., Growth spirals on carborundum crystals: *Nature*, **168,** 430 (1951).

VERMA, A. R. AND REYNOLDS, P. M., Interferometric studies of the growth of stearic acid crystals and their optical properties: *Proc. Phys. Soc.*, **B66,** 414 (1953).

Manuscript received January 16, 1960.