Preferential crystal growth along tilt and twist boundaries in hematite

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Summary. Evidence of preferential crystal growth along tilt and twist boundaries was observed on a hematite crystal from St. Gothard, Switzerland. Irregular lines that cut across the triangular growth layers on the (0001) face develop around a misoriented hematite crystal. There is a slight inclination of the surface on both sides of the lines, suggesting that they are small-angle grain boundaries (tilt and twist boundaries), consisting of screw and edge dislocations. Both spirals and triangular terraces occur along these lines, in addition to the original triangular growth layers. Growth spirals are also present on the $(10\bar{1}1)$ faces, distributed along certain lines. From these observations it is concluded that preferential crystal growth took place, during the final stage of growth of the host crystal, at both screw and edge dislocations in the tilt and twist boundaries. The latter were formed by the impinging of another hematite crystal on the growing surface of the host crystal.

In previous papers dealing with the mechanism of crystal growth of hematite, the writer (Sunagawa, 1960 *a*, *b*, 1962) emphasized that the imperfections formed by internal or external stresses on the growing surfaces play an important role in the growth of hematite. These imperfections are formed by several different causes such as: randomly distributed screw dislocations that move and concentrate into a small area, due to internal or external stresses, forming clusters, which give rise to composite spirals; the impinging of other crystals on the growing surface, which creates surface imperfections from which new growth layers originate; coalescence of two or more crystals with misfit at their contact, which also provides a new growth centre; and break-up of the growing surface, due to strong or prolonged internal or external stresses, which provides big twist boundaries from which thick spiral layers originate. Growth layers initiated by these four mechanisms are either monomolecular layers or thick layers, depending on the nature of the imperfections. Even if they start as monomolecular layers, they soon bunch together to form thicker layers. While supersaturation is still high, thick growth layers can advance freely and the main part of the crystal is formed at this stage by piling up of these layers. However, when the supersaturation falls at the final stage of crystal growth, such thick growth layers can no longer advance, but thin spiral layers, originating from individual screw dislocations, will develop freely on the surface of the thick growth layers. Typical spirals with monomolecular step heights and wide spacings are formed only at this stage and will not contribute much to the formation of the crystal. It should be stressed again that the major part of a crystal is formed by the growth of layers originating from the imperfections described above.

The observations to be presented here will offer new evidence to illustrate the importance of imperfections in crystal growth, differing from those previously reported. These observations were made in the basal plane of a hematite crystal from St. Gothard, Switzerland, which was borrowed from the Mineralogical Museum of Harvard University (H.U.M. no. 93312). Observations on growth spirals on the rhombohedral faces of the same crystals will be described as well.

Observations

{0001} faces. Fig. 1 is a low-magnification photograph of the (0001) face, taken with ordinary incident light, and shows the following four characteristics: Triangular growth layers cover the whole surface, and a few growth centres, i.e. triangular hillocks, are seen; the triangular growth layers emanate from these centres. A large hematite crystal is attached to the surface of the host crystal; it is misoriented relative to the host crystal, and appears as a black area at the right-hand edge of the photograph. A large number of irregular lines develop all over the surface; they appear to radiate from the misoriented hematite crystal, and cut across the straight triangular growth steps, causing no visible deformation of their triangular morphology; this suggests that the irregular lines formed during or after the latest stage of growth of the main triangle layers since no marked modification of the latter was observed. A small portion of the surface of the host crystal is broken up, forming a slightly inclined area of darker grey colour at the centre of the photomicrograph; it is interesting to note that even in this area the triangular growth layers are continuous with the surrounding region.

When the surface of this crystal is observed with a phase-contrast microscope in reflected light, several striking features can be seen (figs. 2, 3, 4, and 5). The features commonly noticed on these photomicrographs are: Triangular growth layers, generated by clusters of screw dislocations; this is shown by the fact that the growth centres, i.e. the triangular hillocks seen in fig. 1, consist of composite spirals (fig. 2). Along

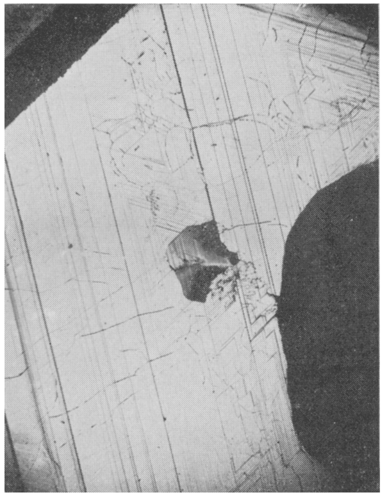
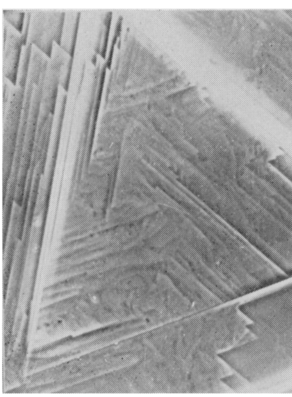
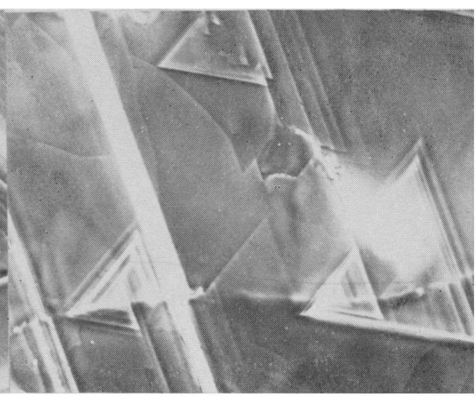


FIG. 1. Photomicrograph of (0001) face in ordinary light. ×20.

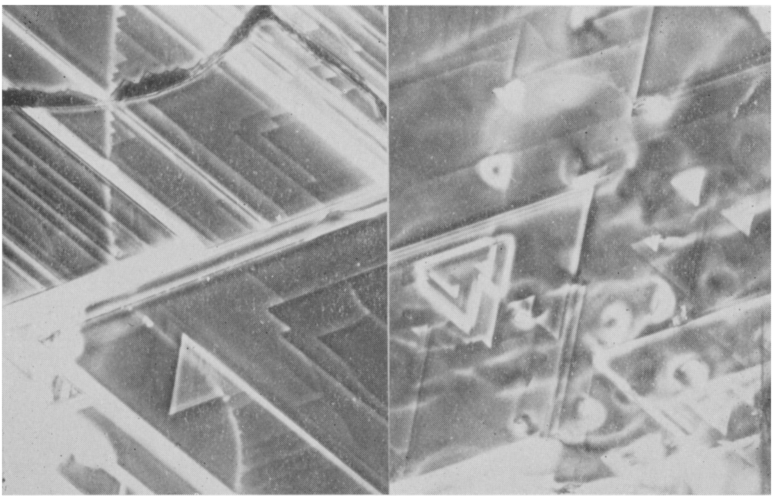




FIGS. 2 and 3: Positive phase-contrast photomicrographs: FIG. 2 (left). A growth centre, showing composite spirals ×200. FIG. 3 (right). Irregular lines and triangular spirals originating from points along the lines. ×250.

irregular lines, brightness or darkness of the surface changes considerably from place to place. Straight triangular growth layers show minute shifts where they meet the irregular lines; the shift is greater for thinner layers than for thicker ones. Small triangular spirals, as well as minute triangular tongue-like terraces, occur along the irregular lines, but they do not extend over a wide area.

Under a sensitive phase-contrast microscope the molecularly flat surface of a growth layer has a uniform colour, and steps have a white diffraction band, the width of which varies according to the height of the step. On the contrary, if the surface is wavy or has a slightly inclined area, this can be seen as a change of colour or brightness. Thus the changes of brightness along the irregular lines suggest that the



FIGS. 4 and 5: Positive phase-contrast photomicrographs: FIG. 4 (left). Triangular tongue-like terraces and a spiral occurring along an irregular line. ×250. FIG. 5 (right). Complexly deformed surface, spirals and triangular terraces from tilt and twist boundaries. ×250.

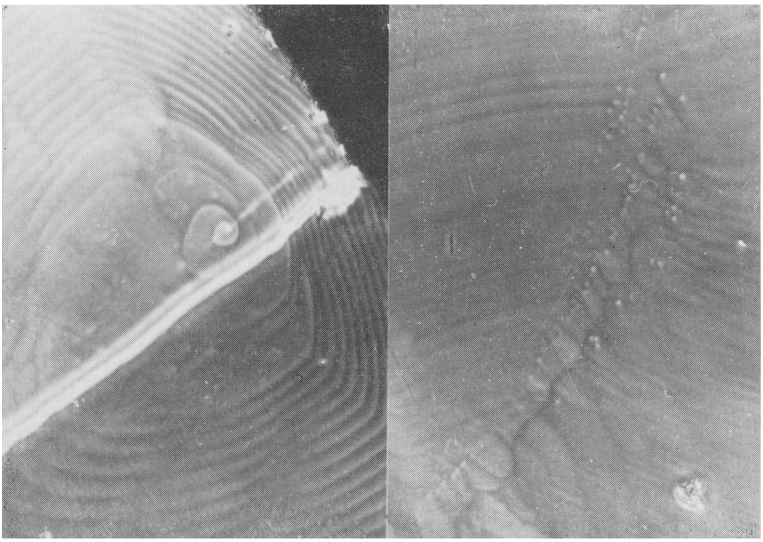
surfaces on both sides of the lines are inclined to each other. This means that the irregular lines are either tilt or twist boundaries or have the characteristics of both types of boundary. A tilt boundary consists of edge dislocations, whereas a twist boundary consists of screw dislocations. Actual grain boundaries have both tilt and twist components.

Since growth layers are slightly displaced at the intersection of triangular growth layers and the irregular lines, the latter must have been formed before the cessation of growth. However, they must have been formed during the last stage of crystal growth, as the morphology of the triangular growth layers is not strongly modified (see fig. 1). Since the irregular lines develop around the misoriented hematite crystal, it is conjectured that their formation is closely connected with the impinging of the misoriented crystal on the growing surface of the host crystal, or with the coalescence of the two hematite crystals.

The most striking feature observed along the irregular lines is the occurrence of small triangular growth spirals and many minute tongue-like terraces. These triangular and composite spirals, emanating from points on the lines, have only a few turns. The triangular tongue-like terraces are much smaller than the above spirals, they always occur along one side of the line, and never on both sides at the same place. Therefore it is naturally conjectured that these spirals and terraces have a close connexion with the structure of the irregular lines. Since these lines consist of both screw and edge dislocations, it is to be expected that spirals will form at screw dislocations and terrace-like growth layers at edge dislocations if further growth takes place after the formation of the irregular lines. The formation of terraces needs further explanation. If an edge dislocation is situated in the plane of a tilt boundary, it will produce on the surface a step that has no screw component; therefore, no spiral layer will be formed from the step, but only small simple growth layers, which will not develop far because they have no self-perpetuating source.

$\{10\bar{1}1\}$ faces. Large numbers of growth spirals are observed on these faces (figs. 6 and 7). Fig. 6 shows a typical example of well-developed spirals, which have a peculiar morphology but are in accordance with the symmetry of the face. The faint line that runs through the centre of the spiral, and is geometrically related to it, is nearly parallel to a thick white line, which is considered to have been formed after the spiral. Furthermore, along this line several minute hills occur; they are also present in large numbers on the surface of the spiral and elsewhere, as shown in fig. 7. Here, too, some of the minute hills occur along lines, a type of development that is universal on $\{10\bar{1}1\}$. These linear arrays are always closely connected with either well-developed spirals or minute hills. Some minute hills occur independently of the linear arrays, but they are rather exceptional. At higher magnification these minute hills are seen to consist of spirals having a similar morphology to the large well-developed spirals. Therefore it can be concluded that these lines are twist boundaries, which were presumably formed simultaneously with those on $\{0001\}$.

Well-developed growth spirals are not commonly observed on rhombohedral faces of hematite, which usually exhibit either a skeletal surface or growth patterns that are greatly elongated parallel to $\{0001\}$. Freely developed growth spirals like those observed on this crystal are rather exceptional. This again suggests that the development of these spirals must be closely related to the formation of twist boundaries.



FIGS. 6 and 7: Positive phase-contrast photomicrographs: FIG. 6 (left). Typical growth spirals and twist boundaries on the $(10\bar{1}1)$ face. $\times 200$. FIG. 7 (right). Minute hills, which also consist of spirals, on the $(10\bar{1}1)$ face. They are in linear arrays. $\times 200$.

Conclusions

The observations presented in this paper provide new evidence of the importance of imperfection in crystal growth and suggest that the following process took place during the formation of this hematite crystal.

The major part of the crystal formed by the spreading of spiral growth layers emanating from clusters of screw dislocations; these spiral layers have monomolecular step heights at first, but they soon bunch together to form thicker layers and make the triangular growth layers observed under low magnification. During the last stage of crystal growth, when no rapid growth was taking place, another hematite crystal became attached to or impinged on the crystal, causing severe damage, which created tilt or twist boundaries on the growing surface. The screw dislocations and edge dislocations in these boundaries gave rise respectively to spiral growth layers and simple growth layers (or tongue-like terraces); however, from the nature of the dislocations, spirals develop further, whereas simple growth layers do not. Growth spirals were also formed on the $\{10\bar{1}1\}$ faces from twist boundaries created by the same cause; such well-developed growth spirals would not be formed on this face in the absence of twist boundaries.

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References

SUNAGAWA (I.), 1960*a*. Min. Journ. (Japan), vol. 3, pp. 59–69.
—— 1960*b*. Serv. Geol. Portigal, Mem. 6.
—— 1962. Amer. Min., vol. 47, pp. 1139–1155.

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