Typical hillocks and spirals on flux-grown $DyFeO_3$ crystal surfaces

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Multi-sided and almost rectangular growth hillocks on {1 1 0} faces of flux-grown $DyFeO_3$ crystals are illustrated. Some such hillocks exhibit spiral growth layers originating from the summits of hillocks. Spiral growth layers originating from more than one initiation centre interact, giving rise to closed loop, interlocked and interlaced or other complex growth formations. The origin of the multi-sided hillocks is attributed to preferential growth at the sites of screw dislocations in $DyFeO_3$ crystals. Defects other than screw dislocations also stimulate growth on {1 1 0} faces of $DyFeO_3$ crystals. An example of this is offered. The mechanism of independent growth on {1 1 0} faces of these crystals is discussed.

1. Introduction
The formation and shaping of growth structures on crystal surfaces is significantly influenced by the presence of defects in crystals. Growth hillocks on crystal surfaces represent extraordinary regions of preferential growth. The preferential growth at certain exceptional regions has been attributed to different types of defects (namely, screw dislocations [1–4], microcrystals [5–11] or other defects [12–14]). Growth round screw dislocations, leading to the formation of hillocks in the form of a spiral staircase with a gradual slope perpendicular to the radius vector, was theoretically predicted [15, 16]. This prediction has been supported by the observation of growth spirals on SiC by Verma [17–19] and Amelinckx [20, 21], on CdI by Forty [22], on long-chain hydrocarbons by Anderson and Dawson [23], and on quartz by Joshi and Vagh [24–27], Joshi and Tolansky [28] and Joshi, *et al.* [29].

Kotru and co-workers [11, 14] have reported stimulation of growth by misfit boundaries, tilted portions, cracks and microcrystals on flux-grown $ErFeO_3$ crystals. To the best of the authors' knowledge, growth patterns due to screw dislocations or any other defect have not been put on record so far for flux-grown $DyFeO_3$ crystals. The present paper reports a study on hillocks of flux-grown $DyFeO_3$ crystal surfaces with the aim of understanding the growth mechanism of these crystals.

2. Experimental details
$DyFeO_3$ crystals were grown by the flux method using the composition 5.1 g Dy_2O_3, 3.8 g Fe_2O_3, 10.5 g PbO, 9.6 g PbF_2 and 1.2 g PbO_2. The whole composition, pressed into a 20 cm^3 platinum crucible, was soaked at 1260° C for 6 h and was then allowed to cool at 1 K h^{-1} down to 840° C. The material was separated from flux by inverting the crucible. Finally crystals were cleaned in 20% HNO_3. Typical features on the {1 1 0} faces were studied using the metallurgical microscope Neophot-2 (Carl Zeiss, Germany) and Cambridge stereoscan (SU-10) SEM.

3. Observations and discussion
Flux-grown $DyFeO_3$ crystals exhibit a wide variety of surface structures on their habit faces. These mainly include irregular elevated features, macro- and micro-discs. The irregular elevated features mainly owe their origin to the precipitation of secondary phases (namely platinum, $PbO \cdot 6Fe_2O_3$, DyOF and $DyBO_3$) as reported in our earlier communication [30]. In this paper we shall be dealing with some significant geometrically regular growth patterns.

Fig. 1 is an optical micrograph showing two polygonal growth structures having as many as ten sides. One of these structures is a point-topped one whereas the other seems to be flat-topped. These two structures seem to be the result of preferential growth nearly at the end of $DyFeO_3$ crystal growth. This is clear from the fact that these structures have not affected the growth fronts developed prior to their formation. In order to study the flat-topped structures of the type shown in Fig. 1 such features were studied under the electron microscope. Fig. 2 is an electron micrograph showing the seemingly flat-topped structure of Fig. 1 as seen under the SEM. The growth layers on the so-called flat portion are visible. Critical examination confirmed that the centre of initiation lies at the centre of the structure. Fig. 3 shows two more structures of this type. The structure at the top of Fig. 3 is shown at a higher magnification in Fig. 4. In this case also growth fronts initiate from the centre of the structure. In the case of such seemingly flat-topped growth structures (Figs 2 and 4), the growth layers in the beginning are of small step height and so the visibility in the microscope is very poor. However, the growth layers at a later stage get thicker and thus their visibility is

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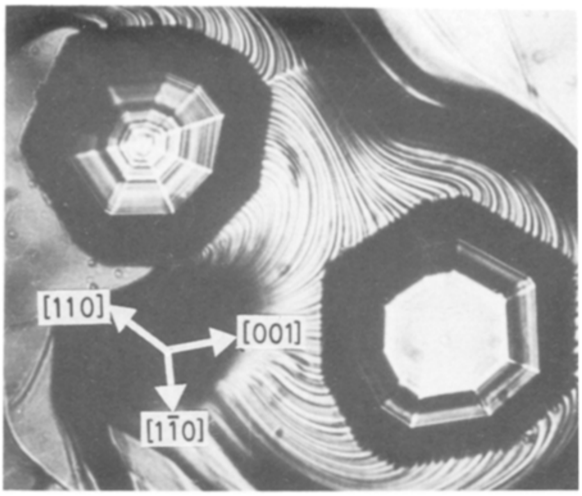

Figure 1 An optical micrograph showing point-topped and flat-topped hillocks on a {1 1 0} surface. Note growth layers in the background of the structures (× 44).

Figure 3 A scanning electron micrograph showing two multi-sided hillocks (× 88).

increased. There is in fact a virtual one-to-one correspondence between the height of a ledge and its visibility in the microscope. The terracing pattern of these structures is attributed to arhythmic fluctuation in the local conditions of crystal growth. Fig. 5 is an interesting example of growth layers emanating from the summit of a hillock. The growth structures exhibit terracing, the terracing exhibiting a periodic pattern of a pair of closely-spaced thick layers separated by a wider spacing. This is indicative of a local periodic fluctuation in the conditions of crystal growth.

In all the cases reported so far, one could see the growth fronts on the plane surface (the background surface) of the crystals. These growth fronts did not appear to have any interaction with the hillocks radiating from the summits of the point-topped as well as seemingly flat-topped surfaces.

Such cases were also observed where hillocks had developed on a $DyFeO_3$ surface devoid of any other growth layers. Fig. 6 shows two point-topped hillocks formed on the {1 1 0} face of a $DyFeO_3$ crystal. Unlike Figs 1 to 4, there are no other growth structures on the background surface. The hillock on the extreme right of Fig. 6 is shown at a higher magnification in Fig. 7. One can see the spiral turns at the summit of the hillock. The hillocks are twelve-sided. The initial turns are circular but gradually develop into a twelve-sided figure. Fig. 8 is a higher magnification photograph showing the topography of a hillock on the extreme left of Fig. 6. Here also the initial circular growth layers become twelve-sided, giving rise to a seemingly flat-topped hillock. The spacing of the growth layers changes at different intervals, giving the appearance of a terraced hillock.

Fig. 9 is an interesting example of a hillock, the summit of which exhibited growth layers originating from more than one initiating centre of growth. Spiral growth layers from very close sources have interacted to offer an example of interlocking spirals. In this case growth fronts cross each other, exhibiting interlacing spirals.

Most of the {1 1 0} faces of $DyFeO_3$ crystals studied here showed multi-sided growth hillocks comprised of spiral patterns. However, some, though very few, showed almost rectangular hillocks. The summits of

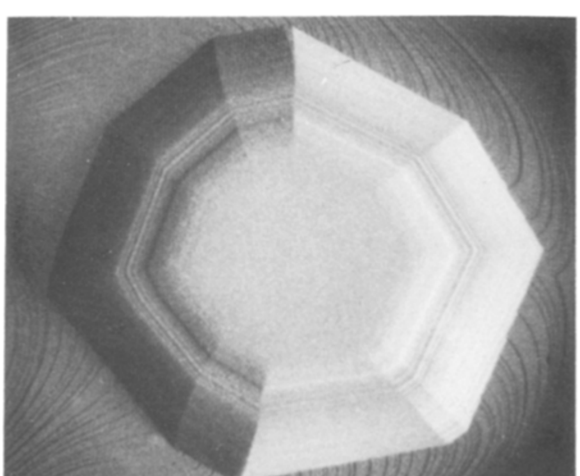

Figure 2 One of the flat-topped hillocks as seen under the SEM (× 176).

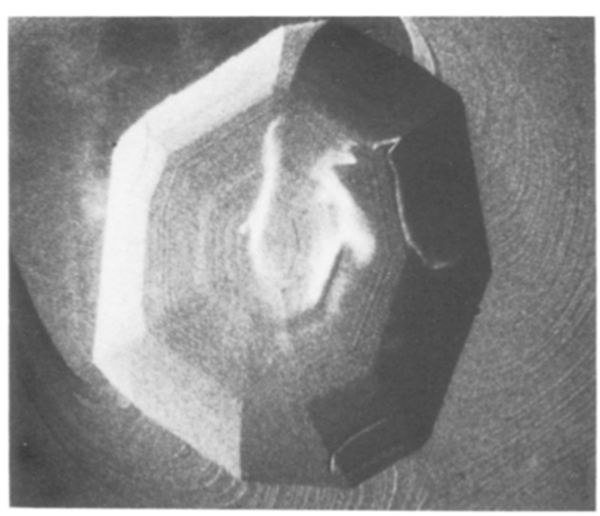

Figure 4 One of the flat-topped hillocks of Fig. 3 at a higher magnification under the SEM. Note the growth layers originating from the summit of the hillocks. Circular growth layers originating in the beginning get multi-sided at a later stage (× 176).

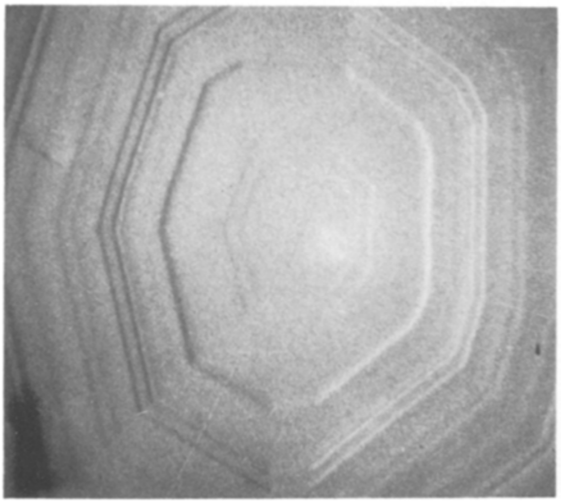

Figure 5 A multi-sided and periodically terraced hillock as viewed under the SEM (× 880).

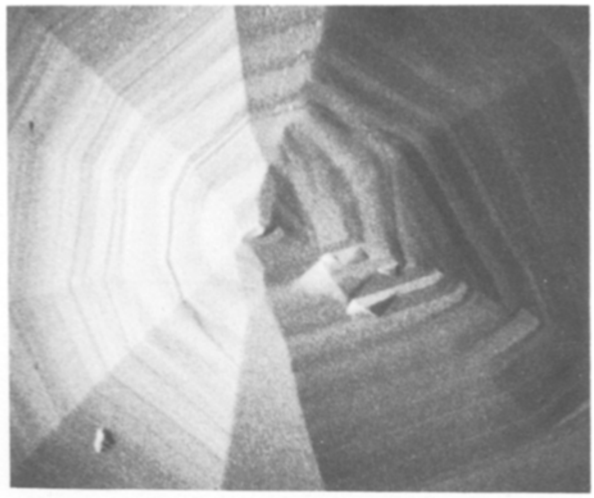

Figure 7 A hillock on the extreme right of Fig. 6 when viewed under the SEM. Note the spiral turns at the summit of the hillock (× 440).

these hillocks showed some kind of crystal fault. Fig. 10 shows a group of hillocks having their centres of initiation due to some crystal fault.

From the observations cited above, it is clearly indicated that extraordinary regions on {1 1 0} faces where preferential growth of $DyFeO_3$ occurs, giving rise to multi-sided hillocks (Figs 1 to 9), owe their origin to dislocations which result in spiral steps. These particular centres of preferential growth may be attributed to screw dislocations. Hillocks could originate from faults other than screw dislocations [9–11, 14]. The rectangular hillocks of Fig. 10 seem to originate from some kind of fault other than screw dislocations. The longer sides of such rectangular hillocks are found to be parallel to the edges of intersection between {1 1 0} and {1 $\bar{1}$ 0} surfaces, while the shorter sides are parallel to the edges of intersection between {0 0 1} and {1 1 0} faces.

Growth around a single screw dislocation should result in a growth pattern where spiral steps are seen to originate from the summit. Such a pattern is shown in Fig. 7. Growth fronts of more than one spiral of one sense may join with those of more than one spiral of the same or opposite sense, and finally result in cooperating spirals or closed loops, or at times complex growth forms or interlocked spirals or interlacing of spiral patterns [24, 28]. Fig. 9 offers an example of growth patterns where growth fronts from more than one centre at very close distances have resulted in a complex growth pattern. This appears to be the case for Fig. 8 also. Some of the seemingly flat-topped hillocks reported here offer possible examples of growth round closely-spaced screw dislocations of equal strength but of opposite senses, which have been annihilated leaving no visible sign at the centre.

The patterns observed here offer sufficient evidence of independent growth on {1 1 0} faces of $DyFeO_3$ crystals, at least in the later stage of growth. The fact that there is sufficient evidence to believe that the

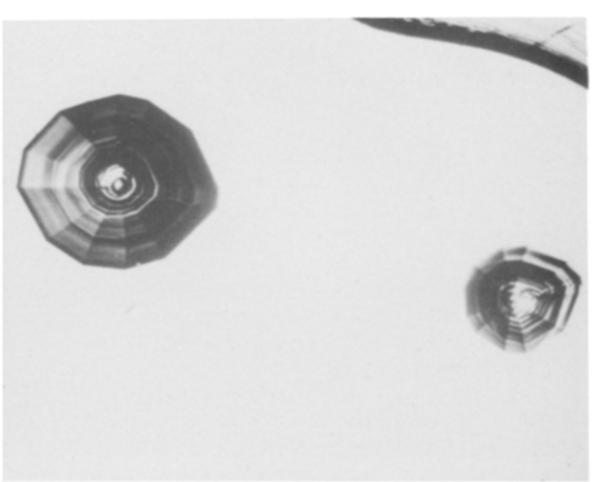

Figure 6 An optical micrograph showing two point-topped multi-sided hillocks on a {1 1 0} surface, practically devoid of any growth layers on the general surface (× 44).

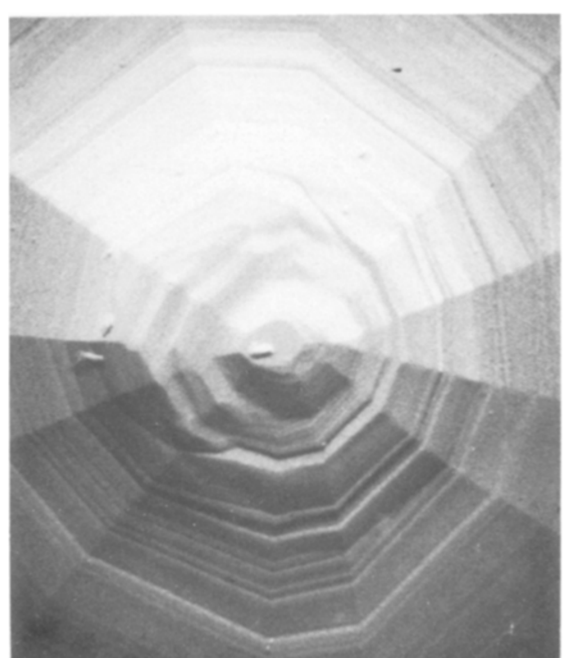

Figure 8 A scanning electron micrograph of the hillock on the extreme left of Fig. 6. Note closed loop formations due to more than one initiating centre of growth lying close by at the summit of the hillocks (× 200).

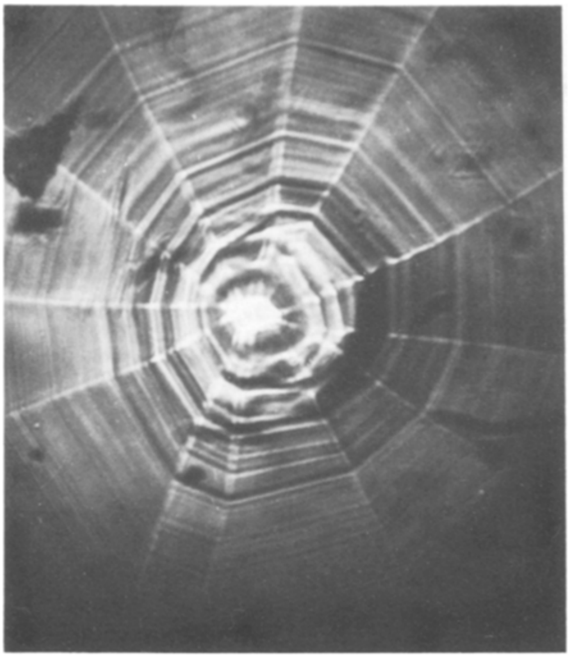

Figure 9 An optical micrograph showing interlocked spiral patterns, exhibiting interlacing of growth fronts originating from growth centres lying close by at the summit of the hillock (× 500).

growth of the hillocks takes place at the last stages of growth supports this viewpoint. In the initial stage, the growth of $DyFeO_3$ may be taking place by a two-dimensional nucleation process but after the development of a crystal with six habit faces of appreciable size, an independent growth on them may then be expected. The independent growth on these faces could be either by a two-dimensional nucleation process due to the spreading and piling up of growth layers parallel to the sides bordering the face, or by preferential growth at the sites of defects (namely, screw dislocations, impurities or lines of discontinuity). The independent growth on {1 1 0} faces at the later stage of growth, by the spiral growth mechanism on screw ledges or preferential growth at other faults, is amply supported by the observations reported above. We firmly believe that such was the case at least on the {1 1 0} faces studied during the present investigations. During the later stage of growth some internal stresses give rise to screw dislocations which appear as screw ledges on these faces. Such a process is likely to give rise to slip steps, thereby producing screw ledges on the {1 1 0} faces, and growth round such ledges will result in spiral patterns. The shape of the hillocks in all the cases except Fig. 10 is multi-sided, indicating thereby that at least at the last stages of growth the independent growth on these faces has the tendency to become directionally independent.

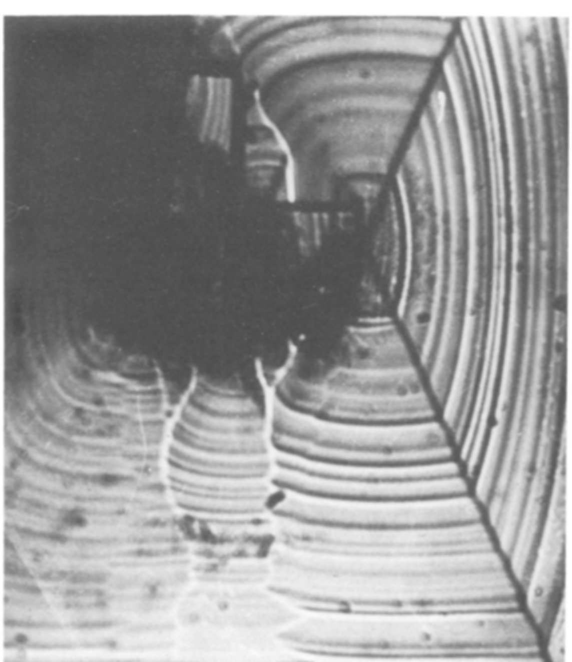

Figure 10 Almost rectangular hillocks originating from crystal faults (× 50).

4. Conclusions

Multi-sided hillocks on {1 1 0} faces of flux-grown $DyFeO_3$ are due to preferential growth around screw dislocations. A spiral growth mechanism operates at later stages of growth. Initial growth may have taken place by two-dimensional spreading and piling up of growth layers. Preferential growth on {1 1 0} faces takes place at other defect sites also. The presence of hillocks is indicative of independent growth on {1 1 0} faces of $DyFeO_3$, at least in the later stages of growth.

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