CHAPTER VII

SPIRAL PATTERNS ON THE RHOMBOHEDRAL PLANES OF CULTURED QUARTZ

7.1 Introduction

Surface study of over two hundred rhombohedral faces of cultured quartz crystals was carried out, as a result of which a wide variety of interesting features were observed. One of the more outstanding observations was the presence of spiral patterns on major and minor rhombohedral faces of cultured quartz. Perhaps it would not be out of place to record here that a great deal of experimental evidence in favour of the dislocation theory of crystal growth has been evidenced by Griffin (1950) who obtained the first evidence of spiral patterns on beryl, by Verma (1951, 1952) who showed a variety of patterns connected with spirals on silicon carbide and hematite. Sunagawa (1958) had been able to observe growth layers of spirals only 2.3 Å thick. Thus since the birth of the dislocation theory various workers in different laboratories have studied growth problems and surface features of various crystals, both metallic and non-metallic.

There was a notable absence of reports of spirals on quartz for a long time. Zimony (1957) published some photographs of large growth cones on a rhombohedral face which displayed spiralling lines after etching in a superheated
steam atmosphere. Despujols (1957) presented photographs of three synthetic quartz crystals having mound structures, probably spirals, on (011̅1) faces. Augustine and Hale (1960) reported some photographs of a (011̅1) face revealing many growth hillocks with spiral ramps. The present work was undertaken to find whether the spiral mechanism of crystal growth, which play a significant role in the development of faces of many crystals also plays a role in the development of the (011̅1) and (10̅1̅1) faces of synthetic quartz.

A very interesting and striking feature of the spirals observed on the rhombohedral planes of synthetic quartz crystals is that unlike spirals observed by Griffin, Verma, Amelinckx, Forty and others, these spirals have rippled convex profiles without abrupt steps. This is the first observation of its kind, in that the surface profile of these spiral growth pyramids is quite dissimilar to those previously observed, the surface between successive turns of a spiral being convex and not flat. This is established by the help of multiple beam interference fringes. A contribution is thus made in the present work in the form of observation of spirals and their interactions in the rhombohedral faces of cultured quartz.
7.2 Specimen and method of observation

One of the specimens examined weighs 2 lbs. The seed crystal was in the form of a slice cut perpendicular to the c-axis. It was 14 cms. long, 4.8 cm. wide and 0.2 cm. thick. Although the crystal was brilliantly transparent, its two basal planes (0001) were covered with a large number of mole-hills. It will be of interest to note the conditions of growth of this cultured quartz crystal which are as follows:

1.0 molar NaOH
0.82 density
742°F dissolving temperature
642°F growing temperature
23000 lbs. inch⁻² pressure in the autoclave
2 mm. day⁻¹ growth rate in the c-direction

The other synthetic quartz crystals examined were grown with different conditions.

A phase contrast microscope was unsuitable for the study of the rhombohedral planes, because, the faces were not sufficiently flat, and hence only a metallurgical optical microscope was used. Since these planes were invariably covered all over by a large number of hillocks of different
dimensions and slopes, it was difficult to get uniform illumination in the field of view. As a result, some photographs were taken with aperture wide open, while some were taken with oblique illumination. Some photographs were taken slightly off-focus because this increases the visibility of thin layers which otherwise could not have been traced. A large number of randomly distributed growth hills of various heights and slopes prevented the use of an ordinary optical flat for interferometric work, and hence micro-flat techniques (Tolansky 1960) were employed.

7.3 Spirals on rhombohedral faces

Six hundred rhombohedral faces of cultured quartz crystals were examined. Numerous novel surface features appeared. This chapter is exclusively devoted to give an account of the spirals observed on rhombohedral faces of cultured quartz. A typical (0111) face is shown in figure 73. It appears that all the hillocks are locked-up within certain boundaries. Such a situation is frequently occurred on such faces. Figure 74 is a photomicrograph showing a good example of a clockwise spiral at a higher magnification. The estimated step height of the spiral is to be 2500 Å. It should be noted that the step height in such a case, refers to the total vertical height between successive turns, although there may be a number of growth layers in between.
which are unresolved. Figure 75 shows an example of a spiral on a (1011) face of a cultured quartz. Figure 76 illustrates another example of a clockwise spiral where first few turns are clearly resolved. The region between first few inner turns and outermost ones appears to be composed of thin layers. It is indicated that the thin layers bunch into thick ones. Figure 77 is a similar case representing the bunching phenomenon.

Out of the several spirals examined on the rhombohedral planes of cultured quartz, a couple of cases of elliptical spirals were found. One of these is illustrated in figure 78. Here the outer turns are covered over by growth from another initiating centre. It seems that the rate of advance of the spiral steps is not dependent of the crystallographic direction, at least in this case. The steps are very nearly parallel to each other revealing that they all belong to one spiral only.

An interesting example was found in which one spiral was interlocked with others, as illustrated in figure 79. To increase the visibility of the thin layers, the picture was taken off-focus to some extent. Here, in addition to the main growth fronts of the spiral a few more clear lines are also visible which may be the growth fronts of other spirals.
In the present case growth fronts cross each other, exhibiting the interlacing phenomena. It may be said that the spirals in this case grew simultaneously with their respective Burgers vectors.

If two unlike screw dislocations having equal strength terminate on a crystal face growth will take place and closed loops of growth fronts will be formed if the distance between the points of emergence of the dislocations is greater than the size (diameter) of the critical nucleus (Frank and Read, 1950). If the distance of separation is less than this critical value no growth will take place. Figure 80 is a photomicrograph showing an example of the formation of closed loops due to Frank-Read mechanism. This was seen on a (01\overline{1}1) face of such a crystal. Figure 81 is another example of closed loops seen on a (10\overline{1}1) face of the same crystal on whose other rhombohedral faces spirals were observed. The formation of these features attributed to two-dimensional nucleation process would be absurd because several spirals are distributed in the vicinity of these features. No trace of dislocations were observed at the centres of closed loops shown in figures 80 and 81. It is conjectured that the two unlike dislocations might have annihilated leaving no sign at the centre. Such closed loops on different crystals have been reported by Forty (1952), Anderson and Dawson (1953) and
Figure 82(b) is a multiple beam interferogram corresponding to figure 82(a), which is a part of the spiral shown in figure 74. This interferogram reveals the unusual topography of the steps of the spiral. Such topographies were also observed for all directions of the spiral illustrated in figure 74. Similar profiles were found for all other spirals observed in the present investigation.

Figure 83 shows fringes of equal chromatic order for spiral steps corresponding to figure 82(b), which prove that the nature of the surface of the spiral steps is unlike the profile of surface of spirals reported by various workers. The fringes in figure 82 support the conclusion drawn, concerning the mechanism of the formation of such a profile of the spiral steps reported here.

7.4 Nature of the spiral step

In what way does the profile of the surface of spirals, observed in the present case, differ from the usual ones? They can readily be compared by considering the schematic diagrams shown in figures 84(a) and (b). The surfaces between successive turns of spirals observed by earlier workers were flat. Figure 84(a) illustrates a two dimensional outlook of the profile of such a spiral pyramid,
while figure 84(b) represents the nature of the surface of spiral pyramids observed on rhombohedral faces of cultured quartz. The latter diagram indicates that the surface between successive turns of the spiral pyramid is not flat but convex. Figure 82(b), a multiple beam interferogram in reflection, further suggests that the surface between successive turns of the spiral under discussion in convex. The fringes run continuously as they climb over the edges of the spiral layers. The V-shaped character of the spiral arms are clearly seen from the interferogram. The profile of the spiral-rut is smooth and curved and appears as sharp 'keel'. The continuous climbing of the fringes further establishes that there are no abrupt steps in the spiral. The convex nature of the area between neighbouring turns was very well established for all the spirals observed in the present study.

There is no report, so far, of spirals on rhombo-

hedral faces having such different nature, discussed above. Thus this is the first observation of a spiral on a rhombo-
hedral face with such a different nature since the birth of the dislocation theory sixteen years ago.

7.5 Interpretation

The patterns in the interferogram over the spirals are confusing. The nature of the spiral is completely
different from those of familiar growth spirals frequently recorded. The spirals are not restricted to very few turns as observed by Joshi and Tölansky (1961) on basal planes (0001) of synthetic quartz. The following characteristics about the spirals are noteworthy:

1. All the spirals are enclosed with a certain boundary.
2. They are not restricted to few turns but are composed of several turns.
3. The spiral arms are ruts but they are not cliff-edges.
4. The nature of the surface between consecutive ruts is highly convex and mottled. Such a convex profile of the spiral step could be a result of bunching of growth layers followed by their etching.

In the present investigation it was found that the outer turns of the spirals give the impression that they are singular, but close examination, near the centre, shows that there are more than one components starting from the centre, which can be traced only in the central region. Such an observation suggests that each step is composed of a group of growth fronts bunched together in such a way that each group forms a curved surface between successive turns, but the growth fronts are so closely spaced that it is difficult
to resolve them separately. Frank (1958) has derived the profile of spiral surfaces for both the processes of growth and dissolution. According to him, the assumed shape of a bunched step is schematically represented in figure 85(a). It is conjectured that the spirals reported here should have such a profile on the completion of the growth process.

Normal production procedure involves removal of the hydrothermal sludge, which brings the author to consider the possibility of etching. The practice at all manufacturing firms for sludge removal is to heat the crystal in a boiling concentrated solution of sodium hydroxide for one to two hours. The boiling lye appears to dissolve the sludge, which probably consists mainly of sodium silicate, and, while its attack on the crystalline quartz is slow, it appears probable that some etching would occur. Some manufacturers have changed to the use of hydrofluoric acid for the removal of the sludge, which probably etches the crystal more than the lye boiled. During such a process the etching might continue and thus dissolution would take place two-dimensionally. The assumed shape of a bunched step of figure 85(a) would be schematically represented as figure 85(b), as the bunch moves to the left during the dissolution in the absence of a step poison, leading thereby to the formation of a convex surface between successive turns.
Thus both the processes, first bunching and then etching, have played their respective roles in the formation of the convex profile of spiral steps in the present case.

7.6 Mechanism of growth

To discuss the mechanism of growth of rhombohedral faces of cultured quartz, it would be obvious to start with the seed crystal on which growth is initiated. It will be of interest to note that the surfaces of seeds are preferably etched or made rough prior to loading them in a rack of an autoclave for synthesizing the crystals. Bash (1959) has suggested several mechanisms by which dislocations can occur when growth of a crystal proceeds from a seed. The following are the four ways, by which dislocations can be introduced into a growing crystal:

(1) Propagation by growth of the dislocations which emerge from the seed.

(2) Generation of dislocations at damaged portions of the surface of the seed crystal.

(3) Multiplication of dislocations in the seed by a thermal shock.

(4) Imperfections formed by the poor epitaxy between the seed and the crystal.

By etching or making the surface of the seed
rough, the area on the seed crystal is damaged and dislocations are generated. The process of etching a seed plate may be for accelerating the growth process of crystal. Such a process provides a large number of growth nuclei, many of which may be in the form of exposed ledges. Such ledges may promote growth by spiral mechanism. It is further assumed that the growth takes place independently on a large number of centres of a seed plate in contrast to growth on a habit face where only a limited number of centres are active and growth takes place by sheet spreading across the growth surface. It may further be said that quartz material is deposited on the individual centres at different rates because the nuclei which grow faster overtake their more slowly growing neighbours and thus render them inactive. The crystals under investigations had two basal planes to each of them. Each basal plane was covered with, several, randomly distributed mole hills of different heights and slopes. Several such growth cones on (0001) faces displayed spiralling lines. Since Augustine and Hale (1960), and Joshi and Tolansky (1961) had reported such spirals on basal planes, it was felt reasonable not to duplicate it. Once the growth on basal planes has been initiated in this way (by spiral mechanism) will continue indefinitely, subject to supersaturation conditions.
In the early stage of growth the Z-cut seed (seed used to grow crystals under present study) is thin and possesses a large area. As growth proceeds the rhombohedral faces will develop and habit faces will be formed. The processed seed plates (Z-cut) with exposed screw ledges having great Burgers vector accelerate the rate of growth. Since no fresh nucleation is needed in the process of growth, the deposition of quartz material in the c-axis will be greater and rapid. As mentioned above, during the process of growth rhombohedral faces gradually develop while the area of basal planes is decreased and the axis of screw dislocations on basal planes will meet the rhombohedral faces and may become normal to them. If this be true then one should expect spirals on rhombohedral faces of such crystals, with screw axis either normal or inclined to the face. Mechanism of growth and development of rhombohedral faces has been proposed by Joshi (1959).

Thus the above described spiral patterns and circular growth or irregular growth fronts with several or occasionally no initiating centre support the proposed mechanism.