PART II

NATURAL CALCIUM FLUORIDE
CHAPTER 4

ETCHING OF CALCIUM FLUORIDE CLEAVAGES

4.1 Introduction:
Etch figures are the solution cavities, having some definite shape and orientation, produced by the momentary or prolonged action of some suitable etchant upon the faces of the crystals. It is believed that the shapes of the etch figures formed on crystal faces are strictly related to the nature of the etchant and the symmetry of the crystal face. In recent years, etching of crystal faces is taken up with a view to gain information regarding: (i) The history of growth of the crystal and (ii) The structural defects, such as the edge and the screw dislocations, twinning, lineage boundaries, etc..

4.2 Etching of Calcium fluoride Cleavages:
(Earlier Work):
Several investigators have carried out investigations on the etching of natural calcium fluoride crystals. Baumhauer (1894) has studied the etching of (111) faces of calcium fluoride produced by sulphuric acid and observed sharply defined triangular etch pits in bands. Tammann and Klings (1925) reported the study of etch figures on calcium fluoride and other crystals. Ernst and Goldschmidt (1928) studied the minute etch hills on a sphere of calcium fluoride by the solvent action of
nitric acid. Himmel (1930), Kleber (1932, 1934) and Himmel and Kleber (1934, 1935) studied the etch figures on calcium fluoride spheres by etching them with nitric acid, hydrochloric acid and sulphuric acid. Kleber (1932) has studied the effect of concentration of acid and temperature on etch figures of calcium fluoride crystals. Bontinck and Dekeyser (1956) were successful in decorating dislocation lines in natural and synthetic calcium fluoride. They have also observed regular six fold arrangements of dislocation walls. Amelinckx, Bontinck, Dekeyser and Seitz (1957) have discussed the factors favourable for the development of helical dislocations in calcium fluoride. According to them, negative ions are responsible for electrolytic current at or below 700°C. and positive ions at or above 1200°C. the latter producing a mild climb and hence the dislocations, having a screw component, assume helical forms. They have further pointed out that helical dislocations should be generated in many materials in which climb occurs. They have attributed the generation of whiskers to such dislocations, when they occur sufficiently near the surface. It has been proposed by them that a controlled climb in any material may be produced with the use of an approximate temperature gradient. Amelinckx, Bontinck and Dekeyser (1957) have suggested that the etching of a helical dislocation, under suitable conditions, may give rise to a spiral pit. Amelinckx, Bontinck and Maenhout Vander Vorst (1957) etched
calcium fluoride cleavages with sulphuric acid and observed the arrangement of etch pits corresponding to the intersection of the surface with helical dislocations. Near the surface of the crystals, the helices were noticeably "pulled out" towards straight lines, this indicates that vacancies have distilled from the dislocation to the surface during annealing. Pandya and Pandya (1958) established the correspondence in the patterns of large isolated triangular pits on the matched faces of calcium fluoride crystals. Schuller and Amelinckx (1960) carried out electron microscopic study of dislocations in calcium fluoride. Thin flakes of calcium fluoride were prepared by cleavage, mechanically polished and further thinned using concentrated sulphuric acid at 130°C, the latter process removing the material by about 7 microns/min. The flakes especially at their edges and near holes were then thin enough for electron microscopy. The contrast caused by strain near dislocations was high enough to reveal the presence of dislocations. Phillips (1961) has developed a successful etching technique for detecting the glide dislocations and he showed that in calcium fluoride, dislocations are mobile at elevated temperatures. Recently Steijn (1963) showed the movement of dislocation etch pits, produced by six percent solution of sulfamic acid on the cleavage face of calcium fluoride.
4.3 Etching Of Octahedral Cleavages Of Natural Calcium Fluoride:

Fig. 24 (x100) represents a portion of a (111) cleavage face of natural calcium fluoride crystal. The cleavage lines are clearly seen in the figure. The quality of the cleavage face is beautifully revealed by Fig. 25 (x100) which is a multiple beam interferogram, taken with the 5461 Å line of mercury, on the region shown in Fig. 24. Many of the cleavage steps appear quite sharp. Though the crystal has a perfect cleavage, the nature of the fringes reveal that the cleavage face is not quite plane but has a slight curvature which varies from place to place.

The defects in the surfaces of the crystals were revealed by etching the surfaces according to the procedure described in Part I.

In order to study the dislocation content of calcium fluoride crystals, a large number of cleavage faces of the crystal were etched under different conditions. Thus Figs. 26 (x350) and Fig. 27(x350) illustrate the etch patterns on the two cleavage faces produced by etching them in 0.4 N nitric acid for 45 minutes at room temperature.

It is interesting to note that as is the case with many other natural mineral crystals such as mica
and diamond as reported by Patel and Tolansky (1957), in the case of calcium fluoride also there are three kinds of distinctive distribution of etch pits namely (a) random distribution of micropits, (b) striking linear arrangements of etch pits and (c) individual isolated pits usually somewhat larger than others.

In addition to this, regions resistant to etch could also be marked. The linear arrangements of etch pits are but a simple elementary example of a wide-spread complex stratigraphical character observed on various cleavages of calcium fluoride. It is found that such patterns are more common on all the etched cleavages of calcium fluoride obtained from Amba Dungar mines of Chhotaudepur (Gujarat State, India). The linear stratigraphical character of the etch patterns will be discussed latter in chapter 5 in detail.

The individual isolated pits are nearly but not quite of the same size and although most of them are point-bottomed, some are flat-bottomed. In order to investigate the cause of non-uniformity in the sizes of the individual isolated pits, a cleavage face of calcium fluoride was successively etched for two different periods. Thus Figs. 28(a) and 28(b) (X 175) represent the etch patterns on the same region, produced after 30 minutes and 45 minutes of etching respectively. A careful examination and comparison of the etch patterns of Figs. 28(a)
and 28(b) reveals the following:

1. The individual isolated pits of Fig. 28(b) have grown larger because of the increase in the time of etching.

2. Additional micropits seen in Fig. 28(b), but absent in Fig. 28(a) are believed to be nucleated during the second etching period.

The topography of the etched cleavage faces were studied with the help of multiple beam interference fringes. Thus Fig. 29 (X 175) is a multiple beam interferogram taken on a highly etched cleavage face of the crystal. Comparison of interferograms of Figs. 25 and 29 reveals a striking contrast. The interferogram on the etched cleavage face (Fig. 29) reveals that the etch attack is twofold: (1) Attack producing general dissolution of the surface by the micropits formation and (2) Attack at isolated places indicating the sites of the dislocations. In order to investigate the nature of the individual isolated pits, a cleavage face was etched for a comparatively longer period so that the large pits may be developed which could be conveniently studied by interferometry. Thus Fig. 30 (X 100) represents the etch pattern on some region of a cleavage face. The topography of this region is revealed by the multiple beam interferogram in Fig. 31 (X 100) wherein fringes are seen
contouring large individual isolated pits. It is evident by the fringes that the depths of the etch pits vary from pit to pit. The depth of a pit can be estimated from the number of fringes contouring the pit. The depths of the pits in Fig. 31 are found to vary from $2\mu$ to $4\mu$. The fringes prove, beyond doubt, that the flat bottomed pits are shallower compared to the point bottomed pits.

4.4 Variation In The Density Of Pits:

It has been observed in the present investigation that the density of the etch pits on the cleavage faces of the crystal varies between wide limits. In some parts of the cleavage surface, there is a clustering of pits, while in other the pits are scattered over wide limits. Noteworthy is the fact that the density of etch pits on the cleavages of crystals obtained from different localities is also different. In some crystals, the density of etch pits is so large that the pits could not be resolved. Hence the study of such etch patterns contribute very little to the knowledge of the dislocation content of the crystal. The variation in the density of etch pits on different samples of calcium fluoride may be attributed to the variation in the factors controlling the growth of the crystal and the environment under which they are grown.

4.5 Etching Of Matched Cleavage Faces:

Studies regarding the etching of isolated
cleavage faces of calcium fluoride were extended to the matched cleavage faces of the crystal. This was done with a view that the etch patterns on the matched faces might probably throw some more light on the mechanism of etching, the nature of dislocation content and the history of growth of the crystal.

Matched cleavage faces were obtained in the laboratory by cleaving small crystals with a sharp razor blade. Figs. 32(a) and 32(b) (X 350) represent the etch patterns on the two exactly oppositely matched cleavage faces, etched in 0.25 N nitric acid for 55 minutes at room temperature. Figs. 33(a) and 33(b) (X 250) illustrate the etch patterns on other matched pairs, etched in 10 percent solution of sulfamic acid for 35 minutes.

The following points are worth considering from the etch patterns represented in these figures:

1. The etch patterns consist of individual isolated sharp triangular pits and randomly distributed micropits which are not resolved in the photographs.

2. The corresponding isolated pits on the two matched faces have exactly opposite orientation.

3. There is one to one correspondence in the number and position of the individual isolated point bottomed pits on the matched faces.
4. Pits have different structures; some are point-bottomed, some flat-bottomed and some terraced.

5. The point bottoms of the point-bottomed pits are not quite central but are eccentric.

6. The eccentricity is different in magnitude for different pits.

7. The displacement of the point bottoms is in different directions for different pits.

8. The direction of the displacement of the point bottoms in matched pits is in opposite directions. The magnitude of the displacement is the same in both.

9. A darker pit on one face has a corresponding similar pit on the matched face and such is also the case with other pits.

10. Some of the small and shallow pits observed in Fig. 32 (b) have no corresponding pits on the matched face.

11. A point of considerable significance is the existence of cleavage lines and their consequent movement produced by etching.

4.6 Discussion:

The non-uniformity in the sizes of the individual isolated pits can be explained with the help of Fig. 34. In this figure ABCD represents the crystal plate which is to be cleaved along EF. as, bb, cc, dd etc., illustrate
the dislocation lines, assumed to be existing in the crystal. As could be seen in the figure, some of these lines e.g. aa, cc, dd and ff are cut by the cleavage plane and hence they terminate on the freshly cleaved faces and as shown in the figure, one of their ends remain just below the cleavage face. Now when the freshly cleaved surface is etched, the etch patterns are produced as shown in Fig. 28 (a). It may be assumed that the individual isolated pits nucleate at the sites of the termination of the linear defects while the micropits develop at some superficial defects. With the increase in the time of etching, the individual isolated pits grow in size while the micropits are linked with the general dissolution of the surface. As the surface is dissolved by the micropit mechanism, new layers of the crystal are exposed and hence new end points of defects, such as bb, ee and gg which were terminating in the layers just below the cleavage face, are now exposed to the etchant. Fresh pits will therefore nucleate at these newly exposed defects. These pits, because they are nucleated at a latter period, will be smaller than the pits nucleated earlier, thus producing the observed non-uniformity in the sizes of the individual isolated pits. The individual isolated pits which persist for a long period of etching suggest that they are nucleated at surface defects of the type of dislocations.
To confirm the conjecture for the observed non-uniformity in the sizes of the individual isolated pits which are nucleated at dislocation sites, the following experiment was performed.

Matched cleavage faces of the crystal were etched successively for two different periods. Thus Figs. 35(a) and 35(b) (X 350) and Figs. 36(a) and 36(b) (X 350) illustrate the etch patterns on the same region of the matched faces produced after 20 minutes and 40 minutes of etching respectively in 0.3 N hydrochloric acid. One to one correspondence has been established in the number and positioning of individual isolated pits. Correspondence does not exist regarding small isolated pits on the matched faces. This confirms that smaller pits are nucleated at those defects which initially were terminating below the cleavage face.

The correspondence of etch pits on matched faces can thus be explained by postulating the existence of dislocation lines in the body of the crystal. Thus, when the crystal is cleaved, these dislocation lines will be cut into two and terminate on each of the matched cleavage faces. When the matched cleaved surfaces are etched, these termination points will be the sites of the nucleation of the etch pits and thus the correlation in the
etch pattern, as observed, will be produced.

The movement of cleavage lines can be explained by assuming that the raised ledges are eaten away without the visible recreation of etch pits as explained by Patel and Tolansky (1957) in the case of diamond and mica.