CHAPTER 3
ETCHING AND DISSOLUTION

3.1 Etching:

Just as the regular geometry and external symmetry of a crystal are an expression of the orderly manner in which the units of construction are built up during the growth of the crystal, so when a crystal is attached by a suitable solvent, the initial dissolution often takes place in a manner which is related to the internal crystal structure. The dissolution is not uniform but begins at certain isolated points and proceeds more rapidly in some directions than in others. If the action is stopped at the right time, the uniform solid surface is found usually covered with little angular figures of definite geometrical shape and orientation. These figures are known as etch figures or etch pits. These are also known as solution figures or solution cavities since they are the result of the action of the solvent upon the crystal face. If the initial stages are not properly controlled, nothing other than the general retreat of the faces, edges and corners with rounding off and change of shape will be observed. The shape of the etch figures varies with the nature and the concentration of the solvent, the time and the temperature of etching. Whatever their shape they are practically always the same in symmetry,
and are strictly related to the molecular configuration of the crystal face.

3.2 Historical Review:

Etching, in general, dates back to 1808 when Widmann-Statten first produced the characteristic etch pattern on meteorites by the corrosion with acids. At that time it was treated merely as a curiosity rather than as a scientific investigation. The first publication in this connection is due to Wollaston (1816). Daniell (1816) was a pioneer, who tried to correlate the nature of the etch figures with the molecular structure of the crystalline solids. Increasing interest in the phenomenon of etching is attributed mainly to the efforts of German Scientists in the latter half of the nineteenth century. Notable contributions are due to Baumhauer, Becke, Traube, Tschermak, Wulff and Beckenkamp. Among these Baumhauer's work is very elaborate and comprehensive. These researches consist of theoretical studies dealing with the questions such as the conditions controlling the development of the etch pits, its relation to the crystalline molecules and to the symmetry of the crystal.

In the first two decades of the twentieth century, Goldschmidt, Weight, Kollar, Gaubert, McNarian and many others made goniometric study of etch figures,
A keen interest was developed in the methods of etch for gaining information in crystallography and mineralogy. An excellent account, covering every aspect of the subject, with detailed references and nicely illustrated by many practical examples, is given by Honess (1927). Miers (1904) made use of his special goniometer in studying etch pits while they were being developed in the solution. The discovery and the development of the X-ray analysis of the crystal structures created further interest in the method of etching. The uncertainties regarding the true molecular arrangement within a crystal and the crystal symmetry could sometimes be satisfactorily explained and decided by the nature of the etch patterns. The extensive and growing literature of the method of etching as applied to obtain a more exact knowledge of the various aspects of crystal symmetry is the evidence of the importance of this technique as one of the means of crystallographic research. Inspite of the vast literature, the origin of the etch patterns, their distribution and the subsequent growth have not yet been fully understood.

The first attempt to explain this aspect of the process of etching is due to Goldschmidt (1904). According to him, both etch pits and etch hillocks are the result of the movements developed in the solvent. The chemical action between the corrosive and the substance upon which it is acting gives rise to currents some of
which are directed towards and some away from the surface which is being etched, the interference of the ascending with the descending currents tends to form eddies, each of which is a starting point of a pit. The tendency of any solvent would then be to produce a regular and hemispherical hole, but this is offset by the force of crystallization, which constantly endeavours to keep the corroded surfaces bounded by crystal planes. The resultant of these opposing tendencies is a typical etch pit, the sides of which are neither wholly irregular nor plane crystal faces, but as a compromise, planes of similar nature to the vicinal faces appear.

Further he suggests that:

1. The etch pits are located at the places where the current starts in the corrosive.
2. Preferential etching takes place along fine scratches.
3. Small particles of dust on the substance provide the corrosive with the points of first attack.
4. The bunching of the etch pits takes place on the strained parts of the crystal and
5. The presence of inclusions or impurities are likely to be the starting point of etching.

Mc Nairan (1915) devised special methods of investigation to check the results of Goldschmidt and further to observe the origin and the subsequent stages of the
development of the pits. His observations are not in harmony with those of Goldschmidt. The observations on the etching of cleavage faces of calcium fluoride, obtained in the present investigation are in conformity with some of the results of Goldschmidt. Mc Nairan (1915) suggested that the lines of selective pitting are also the lines of weak cohesion as for example cleavage planes are corroded much more slowly than those of the lower degree. Desch (1934) performed etching experiments on alum and showed that the explanations offered by Goldschmidt and others, regarding the origin of etch pits, are inadequate.

The most obvious fact which even the simplest etching experiments reveal is that the etch pits are not evenly distributed or scattered over the crystal surface. Possible explanations for this irregularity in the density of etch pits have been given by a number of investigators. These have, however, proved inadequate. It may be realised that no satisfactory explanation of this difference in the density of etch pits can be given until the more fundamental problem of the origin of etch pits is solved.

A real advance in the understanding of the preferential etching at isolated points in an otherwise continuous lattice structure came with the recognition of a number of different structural defects. They are: (i) dislocations (ii) stacking faults (iii) vacancies
and
(iv) interstitial atoms/(v) impurity atoms. Seitz (1952) has given a detailed synthesis of the imperfections. It is conjectured that the structural defects may act as possible sites for the occurrence of pits.

Once the problem of the origin of the pits is tackled, it is then possible to determine the density and distribution of the etch pits which ultimately gives the density and distribution of the defects. It is therefore necessary to review briefly the views of several authors in this connection. Frank (1949) has given a satisfactory explanation for the spiral mechanism of crystal growth on the basis of dislocation theory. Dislocations, which provide steps for the growth of the crystal should also promote the developments of etch pits. By etching the crystal, the reverse process, i.e. the dissolution of the growth spirals may be observed.

Dislocation etch pits were first deliberately produced on crystals that exhibited growth spiral. Such crystals were used with the hope that the etch pits would form at the centre of the spiral which is a screw dislocation. Horn (1952) working with silicon carbide and Gevers and Co-workers (1952), working with silicon carbide and topaz, were the first to produce etch pits at the centres of growth spirals. These workers also observed formation of pits at locations other than the centres of
the growth spirals. They observed alignments of pits along lines and also solution channels. The straight lines looked as if they might have resulted from plastic deformation, and the solution channels were interpreted as small angle boundaries. It was thought that all the etch pits were formed at screw dislocations by the reverse of Frank's crystal growth mechanism.

The observations of solution channels in nonmetallic crystals, and the earlier observations of Lacombe and Beaujard (1948) of etch pits along boundaries in aluminium implied that pits were forming at the individual dislocations in the boundaries. The fine experiments of Vogeletal (1953) established a one to one relationship between etch pits and the dislocations. This experiment was perhaps the most important single piece of work towards establishing the correlation between the dislocations and the etch pits. They observed that the spacing of the etch pits on the small angle grain boundaries agreed with the spacing calculated from the measured difference in the orientation of grains determined by X-rays. They also observed that the densities of etch pits in bent germanium crystals correspond to densities calculated from the radius of curvature. It is reported (Amelinckx and Votav, 1954, Amelinckx, 1954) that etched crystals of sodium chloride show very deep pits at the edge dislocations, shallower pits
at the screw dislocations and very shallow pits at other surface steps. Study of the etch patterns on both the halves of a cleaved specimen of sodium chloride led Amelinckx (1954) to the conclusion that there is one to one correspondence between the etch pits and dislocations. He inferred from his experiments that cleavage is a slipless fracture.

The studies of the X-rays diffraction and the observed mechanical properties of certain crystals indicate that nearly $10^8$ dislocation lines thread through a square centimeter of the surface. However the studies of crystals indicate the value of $10^4$ to $10^6$. This order of magnitude very well agrees with the density of etch pits observed by Dey (1955). Omar, Pandya and Tolansky(1954) have reported that the number of etch pits per sq. cm. on the octahedral surface of diamond etched in hot potassium nitrate is of the order of $10^6$.

Gilman and Johnston (1956) from their studies on the etch patterns on the cleavage faces of lithium fluoride crystals have shown that dislocations do not move appreciably in the process of cleavage. They have shown that the etch pits corresponded to line singularities (dislocations) in the crystals. From the symmetric and asymmetric structure of the etch pits, they have very conveniently indexed the edge and the screw dislocations.
They made use of the double etching method, to observe for the first time the glide and climb of individual dislocations in lithium fluoride crystals.

Cabrera (1959) has considered the formation of dislocation etch pits by evaporation. Cabrera emphasised the role of dislocation energy in the nucleation of pits. He pointed out that effectiveness of a dislocation as a nucleation site depends on, among other factors, the character of the dislocation and the impurity content. The dislocation energy that contributes to the nucleation of a unit pit is that energy which is localised near the dislocation line. This 'localised energy' of a dislocation consists of two parts: (i) core energy and (ii) a small fraction of the total elastic energy.

The formation of visible dislocation etch pits depends on the nucleation rate for unit pit at a dislocation and the rate of motion of the steps across the crystal surface. These two quantities are reflected in the linear solution rates normal to the surface at a dislocation, and parallel to the surface. They are labelled $V_n$ and $V_s$ respectively in Fig. 23. If $V_n \ll V_s$, very shallow pits will be formed which could not be seen because they lack contrast when illuminated. It is found that readily visible pits can be obtained when $\frac{V_n}{V_s} \geq 0.1$ (however, if $V_n \gg V_s$ the deep pits which are formed will inhibit subsequent movement of the dislocation and in
experiments where the movement of dislocations is of interest, it is advisable to work with the least value of \( V_n/V_s \) that will give visible pits. The problem of developing a suitable etchant to reveal dislocations then can be solved by adjusting the ratio of pit nucleation rate at a dislocation to the dissolution velocity of steps. The ratio \( V_n/V_s \) can be increased by: (a) increasing \( V_n \), as in the case of most etchants for metals, which utilize a segregated impurity for this purpose, (b) decreasing \( V_s \) by addition of an inhibitor and (c) varying the temperature to take advantage of the difference in the activation energies of \( V_n \) and \( V_s \).

If a dislocation is moved during the etching process, the solution rate normal to the surface \( V_n \) at the original position of the dislocation becomes negligible. Since the velocity of steps, \( V_s \), remains the same, the pit will assume a flat-bottomed shape as depicted in Fig. 23(b). In the present investigation, Cabrera's theory has helped in selecting suitable etchants.

Loops and spiral etch patterns have been reported by Damiano and Herman (1959) on the basal plane of zinc. This they have tentatively interpreted as the dissolution of a step in the surface with the ends of the step pinned. Gilman (1960) has observed terraced pits on lithium fluoride crystals and has attributed them to the
Keith and Gilman (1960) have reported the etching of calcite using a number of different reagents. The pits were found to have unique shapes, characteristic of each chemical, its concentration and the nature of the diluent with it. The glide elements of calcite were confirmed by observing arrays of etch pits on glide planes. Mendelson (1961) has described dislocation etch pits on sodium chloride. He showed that the difference in shape of etch pits at edge and screw dislocations is consistent with that expected due to their different angles of inclination.

Levinstein et al (1963) have described an etch pitting technique for revealing the points of intersection of dislocations with the (100) and (001) surfaces of calcium tungstate single crystals. They showed that each etch pit represented one dislocation. Deo and Sharma (1964) have described dislocation motions in sodium chloride obtained by thermal etching. They have grown sodium chloride crystals containing the impurities of chlorides of magnesium, calcium and potassium from the melt. The surfaces of the grown crystals have platelet, cellular and triangular structures. They studied the density and distributions of dislocations in these structures. They further observed that thermal etching of the crystal revealed rows of dislocation pits along platelet
structure and cell boundaries.

Patel and Bahl (1965) established the correspondence in the etch patterns of the spiral etch pits on the opposite sides of a thin graphite flake and hence attributed their origin to the existence of screw dislocations in the body of the crystal. Patel and Agarwal (1965) from their studies on the microstructures of Panna Diamonds have concluded that trigons observed on the natural octahedral faces of diamonds are due to etch.

3.3 Etching Of Cleavage Faces:

As mentioned above, historically a very important part is played by etch figures for gaining information about crystal structure in crystallography and mineralogy. During the past few years it is becoming increasingly recognised that etch pits can nucleate on dislocations and other surface defects; Omar, Pandya and Tolansky (1954) have shown that etch pit formation, especially in the early stages of etch, can be a powerful technique for revealing subtle surface microtopography on crystals. In the early stages, etch pits form patterns intimately related to the growth conditions provided the etch is not carried too far such that general surface distortion sets in.

In the present investigation, a much more
comprehensive study is made on cleavages of natural and synthetic calcium fluoride crystals. These investigations are developed in three stages: Firstly studies are made on etched isolated cleavage faces, secondly on oppositely matched cleavages and thirdly on etched adjacent and opposite faces of small cleaved out blocks. These studies have given a valuable information not only as to the etching mechanism but also to the growth history of the crystal.

The cleavage surface to be studied both unetched and etched were coated with a silver film, some \(700\) \(\text{Å}\) thick by vacuum deposition. It has been established that such a film enhances contrast, perfectly contours microstructures and of itself introduces no falsification. These surfaces were then studied by (a) phase contrast microscopy (b) multiple beam interferometry and (c) light profile microscopy.