PART I

A GENERAL SURVEY OF GROWTH, CLEAVAGE AND ETCH PHENOMENA ON CRYSTALS.

CHAPTER 1

A GENERAL SURVEY OF GROWTH, CLEAVAGE AND ETCH PHENOMENA ON CRYSTALS

Introduction:-

Information regarding the conditions of growth and growth mechanism of certain crystals which cannot be observed while they are in the process of growing can be obtained to a certain extent from the study of their finished surfaces after growth has ceased. In recent years the optical and interferometric techniques developed by Tolansky have been extensively in use for the studies of the surfaces of crystals (natural and synthetic). Further information can be gained from the etch marks produced on the natural and synthetic surfaces by some suitable solvents under proper conditions.

The micro-topographical studies of natural surfaces and their etch patterns provide information with regard to the last stage of the history of growth of the crystal. The history of the crystal during growth can probably be obtained from the study of the cleavage surfaces. It is considered that more information in this connection can be gained from the optical and interferometric study of the matched cleavage faces of crystals and their etch patterns.

In this laboratory, a systematic micro-topographical studies on various natural and synthetic crystal surfaces are being undertaken in detail and as a part of the programme, the present work is taken up.

The purpose of the work to be described in this thesis was to study the growth, cleavage and etch phenomena on natural and synthetic crystals and these studies are made, in the present case, on mica, fluorite, calcite and sodium nitrate crystals.

This chapter will be devoted to a brief general survey of the existing information on the growth, cleavage and etch phenomena and the details of the crystals studied are reported in their relevant chapters.

1.2 Growth:

A birds-eye-view of the information on growth phenomena upto the present time is described in this section.

The regular geometrical forms of the crystals were the chief attraction of earlier workers on -

crystallography and as a result of the detailed study of the external form of crystals they were led to the following important laws of crystallography:- Law of constancy of the interfacial angles and the law of rational indices. It was soon realized from a more accurate goniometric studies of crystals, which made the measurements more precise than before, that the crystal surfaces obey the law of rational indices only approximately. Small variations of interfacial angles were found to occur from one crystal to another of the same substance, and these variations were discovered even between the faces giving sharp and single signals in the goniometer. The observations of Pfaff (1878) and Brauns (1887) point out that the difference between the observed interfacial angle and the theoretical value calculated on the basis of the law of rational indices, varies by a factor of about one minute to thirty minutes of arc. This shows that the main habit faces of crystals make a very small and variable angle with the low index plane and cannot be referred to simple indices. Since these planes are very near to the faces of the simple form, they possess high indices. Such faces are called vicinal faces.

Miers (1903, 1904) constructed a special goniometer with the help of which he could measure the interfacial angles of a crystal while it was growing in aqueous solution. On potassium alum crystals he found that the octahedral faces gave three closely spaced images whose positions were a few minutes of arc from the [111] direction. During growth multiple images were repeatedly replaced by other images lying in definite zones. It was found that the transition which often occurred after an interim period of confused signals, was not gradual but in steps. However, Hedges (1926) on repeating the observations has found this process to be continuous. The discontinuous replacement of vicinal forces during growth was believed to indicate that the indices of the vicinal faces were rational, however, large they may be. Another important observation by Miers was that vicinal faces corresponding to any single habit face frequently produce low pyramids or "growth pyramids". The angles between the individual vicinal faces of any growth pyramid and the underlying low index plane were constant to within a few minutes of arc. Miers suggested the explanation that compared to the low index planes, the deposition oh vicinal faces, which have low reticular density, will have a less abrupt change in density of the crystal growing from solution. Kalb (1930, 1933, 1934) extended the goniometric study of the vicinal faces to non-cubic minerals including quartz, and showed that the vicinal faces can occur along certain well-defined zones. Schubinikow and Brunowsky (1931) applied X-ray and goniometric methods to the study of vicinal faces and concluded that the vicinal faces are truly plane surfaces within the accuracy of their experiments.

In a posthumous publication by A.Marcelin (1918) the first indication of growth by layer deposition was given. He observed the growth of thin plates of p-toluidine from alcoholic solution. The plates being very thin, the increase in thickness could be observed from the interference colours in reflection simultaneously with the growth in extension. He concluded that crystals grow by deposition and spreading of successive layers whose thicknesses approached molecular dimensions. Similar layer formation was also observed on napthalene and several other organic crystals (Marcelin and Boudin 1930). Volmer (1922) observed similar thin layers on thin crystals of

PbI_2 formed by mixing $Pb(NO_3)_2$ and KI solution.

Kowarski (1935) extended observation of layer formation in the growth of p-toluidine from vapour. He found that layers were usually initiated at the edges of the faces, and particularly at the point of intersection of the edge with a neighbouring crystal. The layer edges were initially circular but as they spread across the face they become more irregular. The thinner layers were observed to advance faster than the thick ones.

Bunn and Emmett (1949) studied a number of crystals using dark ground illumination under high resolution and found that on fairly thick crystals of some substances, layers several hundred angstrom units high could be seen spreading across the face. On some crystals the layers were so thick that they could be seen by ordinary transmitted light or in birefringent crystals by using crossed nicols. Non polar crystals were not observed to show layer formation and hence the studies were confined to ionic or polar crystals. As a result of their observations they found that layers often start from the centre of the faces spreading outwards, the thickness of the layers increasing as they approached the edges. At rapid growth rates the boundaries of these layers are irregular, but at slow growth rates these take regular shapes conforming to the symmetry of the crystal face. Dissolved impurities were observed to influence strongly the thickness and shape of the layers.

In the growth of a perfect crystal from vapour or solution this concept of successive deposition of layers during growth is applicable. Indeed Gibbs (1906) remarked that "we cannot imagine a body of the internal structure and external form of a crystal to grow or dissolve by an entirely continuous process" but rather by "successive layers of molecules". The first quantitative theory of crystal growth was given by Gibbs (1878) on thermodynamical grounds. Curie (1885), Wulff (1901) and others followed it. An atomic theory of crystal, growth has been developed by Volmer (1939), Kossel (1927~~)~~, 1928), Stranski and co-workers (1928, 1949), Becker and Doring (1935), Becker (1949) and Frenkel (1945, 1946). This theory considers the growth of an ideally perfect crystal. No mathematical details of these theories will be given here but only briefly, the theory is qualitatively outlined below. A review of the historical development of crystal growth theories has been given by Wells (1946) and Buckley (1951), and a discussion of the various aspects of the theory of crystal growth is given in a series of papers in the Disc. Faraday soc., 5, 1949.

Any ideal crystal face with a step will continue to grow because of the presence of a large number of kinks due to thermal fluctuations. During the process of growth, this step will travel to the edge of the crystal, and thus disappear leaving a complete crystal surface. When all the steps have been eliminated by advancing and forming complete layers, further growth will continue only if new steps can be formed. Now on a low-index face steps cannot be created by thermodynamic fluctuations (as suggested by Frenkel 1945, 1946) in the same way as the creation of kinks in a step below a certain critical temperature which is close to the melting point (Burton et al 1949, 1951). Therefore, for further growth on low index faces, steps must be formed gradually at ordinary temperatures by some mechanism. This can happen by the formation of a two dimensional nucleus or island of molecules, the edges of which will provide the necessary steps. The crystal will then continue to grow by two dimensional nucleation of new molecular layers on the surfaces of low indices. The theory explains why regular forms in the plane habit faces are assumed by the crystal when growth takes place under non-uniform conditions. For a long time it was believed to be satisfactory in explaining the growth of real crystals. But the observations have shown that growth fronts are slower than predicted by theory. The interpretation of vicinal faces as a succession of uniformly spaced growth edges is also not in tune according to the nucleation theory. The initiation of layers in ionic crystals almost invariably took place at the centre of the faces as mentioned before. Similarly, diffusion experiments carried out by Berg (1938), Bunn (1949) and Humphreys-owen (1949) for the study of the growth of crystals from aqueous solution showed that the concentration along the growing surface is not constant, but is lowest at its centre, rising one each side to the corners. Two dimensional nucleation theory could not account for these observations.

Detailed calculations regarding the probability of the formation of nuclei show that it is a very sensitive function of super-saturation and is quite negligible below a certain critical value which for typical values of the constants involved is of the order of 25-50 per cent. Volmer and Schultze (1931), trying to verify this result, studied the growth rate of individual iodine crystals in slightly super-saturated vapour at 0°C. They found the growth rate proportional to the super-saturation down to a value of only one per cent whereas the theoretical predication of the rate at which a crystal should grow at this saturation turned out to be too small by a factor of 10^{1000}. showing a record discrepancy between theory and experiment. Only below this degree of super-saturation did it fall below proportionality and then not abruptly. These observations are in total disagreement with the theoretical conclusions.

However, the observations of Haward (1939) are in agreement with the theory of surface nucleation. He studied the deposition of several sublimable solids such as HgI_2, on a metal surface coated with a previous deposit of the same substance. This coated metal target was subjected to a vapour "beam" of controlled intensity at a fixed temperature. Using a weighing technique to measure the mean overall rate of deposition, the theory of surface nucleation was verified.

There are however, no other known experiments of this kind. In general for those crystals which grow, the growth rate is proportional to super-saturation down to values much lower than the critical super-saturation as calculated from the surface nucleation theory; in fact the most regular and well developed crystals are obtained at low super-saturations at which the probability of the formation of nuclei is negligible.

The theory, therefore, implies that when the habit is polyhedral and the super-saturation small-in most systems a super-saturation of a few per cent still counts small perfect crystals cannot grow, and the fact that the crystals do grow at low super-saturation, therefore, leads to the inevitable conclusion that the real crystals are not perfect. There is also a strong evidence for the existence of imperfections in the lattice structure of real crystals. The intensities of X-ray reflections indicate mosaic structure (consisting of minute blocks of perfect crystals in imperfect alignment) and strength of real crystals is only a small fraction of the strength expected by theory.

In order to explain the growth of real crystals at a much lower super-saturations than was permitted by the surface nucleation theory, Burton et al (1949, 1951) developed a theory of crystal growth which takes into account the presence of a particular type of lattice imperfection called a screw dislocation. A detailed synthesis of different imperfections in crystals has been given by Seitz (1952). A good account of the crystal growth and dislocations is given by Frank (1952, 1955), Burton (1951), Verma (1953) and Fullman (1955). In the books of Cottrell (1953), Read (1953) and more briefly in Cottrell's earlier review article (1944) are given excellent accounts of the theories of dislocations. It was shown that a crystal containing a screw dislocation emerging on the surface is fundamentally different from one having the topology of a perfect lattice, in that it does not consist of many layers, but of a single self-over lapping layer so that ~~on~~ when one, two or any number of layers of atoms have been laid down on the crystal surface, the step remains. Hence the steps needed for the growth of a crystal are provided by the screw dislocations and the need of two dimensional nucleation never arises. So long as the dislocation is there, the step can never disappear. New molecules are deposited at the step, so that the step moves normal to itself across the face of the crystal and the crystal can continue to grow indefinitely. It is apparent that the step will not remain straight in this process, for that would require its speed of motion to be proportional to its distance from the dislocation whereas it will in fact be more nearly uniform. As a result it trails behind at the outside and winds itself into a spiral. In the final steady state attained under uniform super-saturation, the spacing between spiral turns is inversely proportional to super-saturation. The rate of growth is inversely proportional to this spacing and directly proportional to their rate of advance. The latter is proportional to super-saturation when the steps are far apart, but becomes independent of super-saturation when they are close enough together to compete for material from the environment. Hence the rate of growth is proportional to the square of the super-saturation when this is small, the relationship becoming linear at higher super-saturation.

Although experimental evidence in support of this theory of crystal growth by spiral mechanism was first given by Griffin (1950) on Beryl crystals, rigorous optical and interferometric study on Sic crystals (Verma 1952) provided a very effective and decisive support in its major and in very many minor features. Since then the volume of experimental observations supporting this mode of crystal growth has increased considerably (for literature, see for example, Verma (1952), Joshi (1959)). Most of the workers have, in general, obtained spirals only on one form of a particular crystal under study, and in all cases the profile of a spiral has always been flat with abrupt steps, as opposed to the spiral observed by Joshi (1959) on quartz crystals - natural and synthetic. He observed spirals on two different forms-basal and rhombo-hedral. It is further reported that some spirals have ripple shaped convex profile, unobserved before and have no abrupt steps. Features having some similarity with those reported by Joshi (1959) have been observed (Augustine and Hale 1960) on rhombo-hedral surfaces and on the irregular surfaces of growing basal pinacoids (0001) of synthetic quartz crystals.

Tolansky and Sunagawa (1960) reported growth spirals on the cube faces of G.E.C. synthetic diamonds. A co-ordinated, microscopic, interferometric and X-ray diffraction study of the phenomenon of polytypism in cadmium iodide crystals (Verma 1959) has resulted in a discovery of 13 definitely new polytypes of CdI_2 (possibly 18) in addition to those found by Mitchell earlier. Further study has revealed that it is not possible to connect the shape and form of the growth spirals on crystal surfaces to their internal structure and that the step heights of the growth spirals may not have a direct correlation with the unit cell size. Verma (1953) in his earlier observations had shown that the step heights of spiral steps were either the same or integral multiples or submultiples of X-ray unit size.

Theoretically only one screw dislocation is required by the crystal to support growth at low super-saturations. The only examples of crystals known to contain only one dislocation are the crystal Whiskers (filamentary single crystals). Here a single screw dislocation is believed to extend axially along the whisker. They are crystals whose diameter may be a few microns and length upto several centimeters. It is recently discovered at the Bell Telephone Laboratories that these crystals show strength comparable to the theoretical value predicted from the bond energy and 10^4 times the value usually observed in practice. The importance of this result was immediately realized and it followed major developments which vindicated the dislocation theories for various aspects of crystal behaviour. According to Sears (1956) if a crystal bears a screw dislocation in a single direction, it grows at low super-saturations as a whisker. If a crystal bears a screw dislocation in two directions, it grows as a platelet at low super-saturations. An excellent account on the growth and properties of whiskers and other problems related to crystal growth is given in "Growth and Perfection of Crystals" (edited by

Doremus et al, 1958).

Although, Frank gave a plausible solution for the known fact that crystals bounded by molecularly densely packed faces usually grow at sensible rates in dilute fluids at low super-saturations, many important problems have not yet been fully explained, for example the mechanism of growth of crystals into concentrated solutions and melts; the role of impurities in crystal growth; the mechanism of crystallization of very complex molecules such as polymers, and the mechanism of branching in dendrites.

In this thesis, the study of growth of calcite and sodium nitrate crystals is reported in their respective chapters.

1.3 Cleavage:

It is necessary to know the 'plane' on which growth and etch features are studied and as there was no reliable means available in the laboratoryfor ascertaining the crystal planes, it was decided to carry out, particularly the etching, work on cleavage planes of natural crystals and due care was therefore taken in selecting crystals having perfect cleavages.

Many crystals have the property of breaking with smooth surfaces in certain directions which are parallel to either actual or possible crystal faces. This important property is known as cleavage, which is one of the characteristics that distinguishes a crystalline body from an amorphous one. Cleavage is defined (Dana & Ford, 1952) according to the direction as cubic, rhombohedron, prismatic, etc., and according to the character of the surface, such terms as imperfect, good, perfect, very perfect or eminent are being used. Thus the micas have a very perfect cleavage parallel to (001) while the feldspars have a perfect cleavage parallel to (001) and a good cleavage parallel to (010).

A crystal can be broken in any direction and the result is a fracture. It is important to distinguish between a fracture and a cleavage (Read, H.H. 1952), as the former is irregular and not concerned with the crystalline structure of the substance. Depending upon the type of surface obtained, fracture may be conchoidal, even, uneven hackly or earthy.

According to Tutton (1922) cleavage is not a mere tendency to fracture with production of two more or less plane fracture surfaces, one on each side of the two separated fragments, and along an approximately definite direction. Cleavage is much more than this, namely the facility for splitting along an absolutely true plane, having an orientation within the crystal definitely fixed to one or two minutes of arc and with definite direction that is identical with that of an important face of low indices; and the plane surfaces of the fracture are endowed with the same high degree of natural polish, as the best formed faces.

The cleavage planes which are always planes of the crystal structure and are therefore par~~r~~allel to possible crystal faces, have simple relations to the crystallographic ax~~a~~s and are usually commonly occuring forms on the crystal in question. That this is not always true is shown in the cases of calcite and fluorite where the cleavage forms, though simple in their crystallographic relations, seldom occur as natural forms upon their crystals. Further, cleavage is the same in all directions in a crystal which are crystallographically identical, e.g., if a cleavage exists parallel to one octahedral plane in an isometric substance it must occur also and with equal ease parallel to the three other octahedral planes. Cleavage planes have commonly been assumed to be those planes of the atomic structure in which the atoms are most closely packed together while the distance between the successive planes is relatively large. Conditions of this sort are undoubtedly important in determining the existence of cleavage but they cannot be the only controlling factors. For instance, it is known that sphalerite and the diamond have the same atomic structure, but in one case the cleavage is dodecahedral and in the other octahedral. Cleavage apparently depends not only upon the geometrical position of the constituent atoms, but also upon their electrical charges. The electrical forces existing between the different layers in the atomic structure are of great importance and cleavage takes place when the attractive forces are at a minimum. Stark (1915) supposed that the thrust preceding the fractures of an ionic crystal brings ions of the same charge opposite to one another and the electric repulsive force between these brings about separation of the crystal plane. This is proved by Winkler (1950) who also made a detailed study of heterodesmic and homodesmic crystals.

Wulff (1920) who studied cleavages of fluorspar, zinc blende, diamond etc., in their relations to the crystallographic investigations, contends that it is possible to determine the direction of cleavage from the crystalline structure and conversely from the cleavage to determine the crystal structure.

Graz Rudolf Schraizer (1920) considered the cleavages of a number of crystals (diamond, fluorite, pyrite etc.), in the light of the space lattices determined by Bragg & Bragg. His findings show that: (a) the cleavage is parallel to the groups of lattice planes, if these contain like atoms, (b) when the lattice planes are equally distant, they must be similarly constituted in order to have cleavage parallel to them; and (c) when there are several possibilities, the cleavage is parallel to that plane showing greatest reticular density.

From a close study of cleavage, illustrated by two dimensional unit-cube and other diagrams of diamond, sphalerite etc., Huggins (1923) arrived at the following rules which are believed to govern crystal cleavages:-

(1) Cleavage tends to occur so as to leave the new surfaces electrically neutral;

(2) Where some of the bonds in a crystal are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones;

(3) All bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area of the cleavage plane.

Wooster N. (1932) from the known cleavages has given empirical laws correlating cleavage with structure, for (1) homopolar crystals with equal and unequal bonds (2) ionic compounds (a) with simple, formula of the A X type (b) compounds with more complex formulae but having (i) radicals and (ii) no radicals.

If Z is the total stress per unit area along a rod of material and θ the inclination of the cleavage plane to the axis, the stress per unit area of cleavage plane in the direction of the axis of the rod is Z $\sin\theta$ The component at right angles to the cleavage plane is thus $Z \sin^2 \theta$. The critical normal stress is $P_c = Z \sin^2 \theta$ and according to a law proposed by Sohncke (1869) Pc is constant for a particular substance. This holds only for crystallographic cleavage.

The theoretical strength of an ideally perfect crystal has been calculated from the energy required to form two new surfaces at the break, with results much higher than the cleavage strengths normally observed - usually by a factor of hundred to thousand. (See for example, Polanyi 1921; Zwicky 1923; Kuznestov 1927). Attempts have been made by a number of authors at various times to explain this discrepancy (Griffith 1920; 1924; Orowan 1934, 1946, 1955). Orowan and others argued that to account for the cleavage of crystalline solids the application of the classical Griffith energy principle for the propagation of cleavage cracks in brittle solids cannot be made immediately. For, in a crystal, in addition to the increase in surface energy accompanying the spreading of a crack, there is the possibility of some plastic work also releasing the elastic energy which is stored up when a stress is applied. Thus it is reasonable to expect to find some evidence for plastic deformation as a crack passes through a crystal, occuring either in the form of activation of dislocation sources of the Frank-Read type (Frank & Read, 1950) or by a process of spontaneous nucleation of dislocation loops.

The theoretical calculations of the cleavage energies along different planes of diamond have been made by Ramasheshan (1946) who holds the view that the perfection of the (111) octahedral cleavage plane is not merely because the plane has a minimum cleavage energy, but also due to the fact that on either side of the plane of easy cleavage, lie layers of atoms having three times the cleavage energy.

The relation between cleavage and rift in crystals and lattice structure was reviewed by Belov and Klassen-Keklyndova (1948). According to Stepanov (1949) the pre-requistic conditions for the occurence of cleavage phenomena in crystals are to be found in an anisotropy of the elastic properties which are investigated in detail and brought out by the fundamental dissimilarity of the stress diagrams along the principal axis of the crystal. The observations are discussed with special reference to cubic and rhombic crystal systems, in particular with Mg, Zn, Cd and Be crystals.

Custers (1952) examined a (111) cleavage face of type II diamond and from the direction of the cleavage lines which corresponded with the cleavage directions suggested the laminated structure for that diamond.

Optical interference methods were used for the examination of cleavage faces of mica, calcite, selenite and diamond by Tolansky and his collaborators (Tolansky 1945; Tolansky and Khamsavi 1946, 1948;) and are thoroughly described by Tolansky (1948) in his well-known and standard book "Multiple-Beam-Interferometry of Surfaces and Thin Films". Some of the important conclusions are.:-

(1) The cleavage steps are multiples of X-ray unit cell of the crystal examined and that step height is constant along a cleavage line of the crystal.

(2) The existence of mosaic block structure (in calcite and selenite) is predicted.

Interferometric examination of cleavages of metal crystals (magnesium, antimony, etc.) grown by the travelling furnace method, is made by Holden (1952) whose observations reveal sub-boundaries, with a typical tilt of

$\sim 1^{o}$.

Koehlar and Eberstein (1953) who used fringes of equal chromatic order, claiming an accuracy of ± 1.2A found, on cleavages of topaz, the step heights to be integral multiples of the X-ray unit cell, 8.78A.

Zapffe and his collaborators (1949 a,b,c) carried out extensive studies of the surfaces of cleaved metals, alloys and other crystals as fractography. They have defined (1949a) two fundamental types of patterns on the cleavage faces (i) patterns determined by factors within the crystal and (ii) patterns determined by the nature of the stress. The latter are the so-called hackle structures and they reveal the existence of the fracturing force as the cleavage traversed the matrix. The former are affected by the structural factors within the crystal and therefore they are of paramount importance in studying the crystal imperfections. Hence information regarding the texture-quality of the crystal can be gained from the studies of the type I patterns.

In most of this work no evidence was produced as to the true nature of the sub-structure and in particular as to cleavage steps and other features of the cleavage structure. Amelinckx (1951) from a study on rock salt cleavages, accounted for the occurence of cleavage steps. He suggests that cleavage begins in a plane where dislocation concentration is largest and proceeds until it reaches some other plane containing higher concentrations of dislocations. Cleavage then jumps into the new plane and proceeds along this plane. The process is repeated and steps are produced. This accounts for smaller steps. The bigger steps are due to the existence of inner cracks or boundaries of separate blocks which build up a coarse mosaic structure of the crystal. Wilks (1952) also arrived at similar conclusions and suggested the dependence of the quality of cleavage upon the concentration of dislocations and defects within the lattice. In this way good quality of cleavage in the diamond of type II, assuming a lower density of dislocations or defects within the lattice of the crystal is accounted for. From the cleavage studies on ionic crystals, the occurence of cleavage steps has been explained on the basis of tilt -, twist and mixed tilt and twist boundaries by Pratt (1956). He also obtained good agreement between calculated and measured angles of twist on a cleaved NaCl crystal (Pratt 1953). Pratt's observations of cleavage patterns are important in two respects:- (i) It might prove to be a powerful method of determining dislocation distributions in crystals. (ii) complicated cleavage step patterns may not necessarily imply the existence of a fine lamellar structure, but simply that of a twist boundary.

Pandya's observations (1954) indicate that the cleavages, if perfect, should show a perfect agreement in all features and the step heights should also agree at the corresponding places (with negative reversal).

The markings on zinc single crystals are not reflected on the opposite cleavage faces obtained by cleaving single crystals of various orientations at different temperatures (Derceyttere & Greenough, 1954). The majority of the observations on twin are entirely in accord with the theory of Bilby and Bullough (1954). However, in the case of kink bands, there is little agreement between the observations and the theoretical results.

Recently Gilman (1955) applied cleavage method to study polygonization in zinc. The ideas of Orowan, Mott were developed specifically for the study of cleavage cracks by Gilman (1956) who was of the opinion that, since the actual initiation of a crack can occur by any of several possible processes associated with the initial deformation of the crystal by a cleavage chisel or by extension in a machine, the factor which really determines whether a crystal will cleave is the ability of the crack to propagate more easily. More specifically it is the velocity of propagation of the crack relative to the rate at which the surrounding structure can deform plastically which is of principal importance. For it is evident that if the stresses concentrated around the tip of the crack contain a shear component and if these shear stresses can be relieved by plastic flow in the crystal, the crack will fail to propagate. However, if the crack velocity is such that little or no plastic flow can develop (that is, high rate of loading in a crystal in which glide is difficult or quasi-viscous) the crack should propagate easily. In this way Gilman explains the failure to cleave metals like copper and silver which flow readily . and the contrasting "brittleness" or cleavability of materials such as steels, rocksalt, LiF, which show only a viscous form of glide. Alternatively, if the glide planes in the crystal are unfavourably oriented relative to the stress field around the crack, plastic flow will again be difficult to develop and the crystal will cleave easily. This, for example, explains the excellent cleavage of zinc.

An investigation of crack development in crystals of the alkali halides, LiF (Forty, 1957) provides some confirmation of the idea that a cleavage crack can nucleate dislocations if it can be arrested for a time sufficient to allow deformation to develop. The study of interference patterns produced by light reflected from the two surfaces of the crack makes it possible to detect and at the same time estimate the magnitude of this deformation. The interference technique is also valuable for displaying the presence of the slowly moving crack so that its mode of propagation can be studied.

An independent investigation of the plastic deformation introduced into crystals of LiF by cleavage has also been carried out recently by Gilman (1957). Gilman et al (1958) have shown that dislocations are nucleated ahead of the tips of cracks that move slower than $\sim$ $6X10^3$ cm/sec. in LiF crystals. The motion of cracks that move slower than $\sim$ $3X10^3$ cm/sec is unstable, i.e., the velocity oscillates. About $2X10^3$ cm/sec is the terminal velocity for (100) cleavage cracks in LiF. For constant driving force, cracks move more slowly in crystals with high dislocation densities than in relatively perfect crystals.

Dislocations which are nucleated by the propagation of a cleavage crack of appropriate speed are decorated by a method (Amelinckx 1958) which leaves the dislocation pattern after deformation practically undisturbed and therefore makes it possible to observe dislocation loops in a more direct way.

The markings and step structures observed on cleavages of ionic crystals are decorated and made visible in the electron microscope by a technique (Bassett 1958) which is able to display unit lattice steps on cleavage surfaces of NaCl and LiF and has the lateral resolution of the electron-microscope. The mechanism by which the decoration phenomenon occurs is not quite clear.

Using microscopy and multiple beam interferometry Wilks (1958) examined type I and type II diamond cleavages and confirmed the earlier qualitative observations (1952) regarding the more regular cleavage patterns on the cleavage surfaces of type II diamonds. She also showed that birefringence and counting properties are not appreciably reflected in the cleavage patterns and that a very few type II diamonds show evidence of a laminated structure.

Electron microscopic studies are reported on the matching of cleaved counterparts of sodium chloride crystals (FUJIWARA Nakagawa and Izni 1959). Feltynowski and Gorski (1959) also made electron microscopical investigation of (111) and (100) cleavage faces of indium antimonide. Their observations show the main structural elements to be the cleavage steps and the slip lines, the former being originated from screw dislocations. Two sets of slip systems at a mutual angle of 45° on a (100) cleavage plane are also observed, arising from the two different slip planes (111) and (110). Cleavage whiskers of silicon, and indium antimonide were studied. (Venables 1960) with the help of optical and electron microscopes. The size of the whiskers ranges from 5000 to 500 A or even less and the study indicated their origin to be in cleavage steps.

In the present case, cleavage work is taken up for studying the oppositely matched cleavage faces of mica, fluorspar and calcite by the techniques described in chapter II. All the selected crystals have perfect cleavages.

In case of calcite, the cleavages are produced in different ways and the resulting patterns are studied, and are reported in the relevant chapter.

1.4 Etching:

Just as the regular geometry and external symmetry of a crystal are an expression of the orderly manners in which the units of constructions are built up during the growth of the crystal, so also when a crystal is attacked by an appropriate solvent which chemically or physically dissolves it, the initial dissolution often takes place in a manner which is visibly related to the underlying crystal structure. It is found that the dissolution, in general, is not uniform, but begins at certain points and proceeds more rapidly in some directions than in others. If the action is stopped at the right time, the seemingly uniform solid surface is usually found to be covered with little angular figures of definite geometrical shape and orientation, variously referred to as etch figures, etch marks or etch pits. These definitely shaped figures are also called solution figures or solution cavities because they are results of the action of the solvent upon the solute (the crystal face). If the initial stages are not carefully controlled, nothing other than the general retreat of the faces, edges and corners with rounding off and change of shape (due to unequal solution velocities at corners, edges and faces) will be noted.

The shape of the etch figures varies with the nature and concentration of the solvent, time and temperature, but whatever their shape they are practically always the same in symmetry, and are strictly related to the molecular configuration of the crystal face. The formation of ~~th~~ etch figures represents the very early stage of crystal dissolution and consequently information, concerning their origin, their distribution and other allied points can be secured by studying the etching of crystals at a very slow rate of etch. This point has been kept in mind while studying the etch patterns, in the present case, on mica, fluorite and calcite.

Historical:

Etching, in general, dates back to 1808 when Widmann-Statten first produced the characteristic etch pattern on meteorites by the corrosion with acids. It was treated as merely a curiosity rather then as a scientific investigation. The first publication in this connection is due to Wallaston (1916) and the earliest detailed study is due to Leydolt (1855). Daniell (1816) who was a pioneer, 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 later half of the nineteenth century. The notable contributions on theory and application of etch method were made by Baumhauer, Becke, Traube, Tschermark, Wulff, Beckenkamp and others. Among these Baumhauer's work is very elaborate and comprehensive. The 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 20th century, Goldschmidt, Wright, Kollar, Gaubert, McNairan and many others made goniometric and projection studies. A keen interest was evinced 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 was given by Honess (1927). The discovery and the development of the X-ray analysis of the crystal structures created further interest in the methods of etch since, with an appropriate solvent etch method is known to be the simplest and powerful tool for revealing the symmetry of the crystal. Buckley (1951) has also given a nice account on etch figures.

Hirsch (1956) has also given account of etching as a means of revealing mosaic structure. As a result of the studies by etch method, the following results have been arrived at:-

(1) Generally etch does not take place uniformly over the whole surface but begins at different points proceeding more easily in some directions than in others, thereby giving rise to regular and often geometric figures of microscopic size upon the crystal face.

(2) The figures produced are in the majority of cases angular depressions, such as low triangular or quadrilateral pyramids, whose outlines may run parallel to the crystalline edges. Occasionally minute elevations or hillocks are also observed. The etch hillocks can be interpreted as the intervening spaces between etch pits, the rest of the crystal face having been eaten away. Examples of both kinds, depressions and elevations, are known and sometimes it becomes difficult to decide whether a feature is a growth or etch figure. The well-known case is that of diamond.

(3) The form of the etch figures, in general, corresponds to the symmetry of the group to which the given

crystal belongs.

(4) In some cases the planes produced can be referred to occuring crystallographic faces; more often they are of the nature of the vicinal faces with complicated indices or are in fact curved surfaces.

(5) Etch pits commonly lie, however, in definite and simple crystal zones.

(6) They appear alike on similar faces of crystal and hence serve to distinguish different forms, perhaps in appearance identical, as the two sets of faces in the ordinary double pyramid of quartz.

(7) They also reveal the compound twinning structure common on some crystals, e.g. quartz and aragonite.

(8) With the same crystal face, the shape of the etch figures may vary with the nature and concentration of the solvent employed, though their symmetry remains constant.

(9) If the etching process is continued, the result may be to destroy the original crystalline surface

and to substitute for it perhaps a multitude of minute elevations, more or less distinct; or further new faces may be developed, the crystallographic position of which can often be determined, though the symbols may be complex. It should be noted that according to the present ideas of crystal growth, so-called vicinal faces are of great importance in displaying the crystal symmetry ~~as~~ and growth mechanism. The similarity between etch figures and vicinal faces, (see (4) above) suggests the importance of etch figures in a similar capacity since a number of etch facets of a corroded crystal taken together correspond to a negative crystal of the substance, there must be a direct relation between the faces bounding a figure and the molecular face upon which it occurs and doubtless, the same causes that are instrumental in the development of natural crystal faces are operative in the growth of etch pits.

Inspite of the extensive and ever growing literature of the etch methods the origin of the etch patterns, their distribution and the subsequent growth have not yet been fully explained.

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 actimg 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 be then 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, whose sides 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 the dust on the substances 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 inclusion or impurities are likely to be the starting point of etching.

McNairan (1915) devised special methods of investigation to check the results of Goldschmidt and further to observe the origin and subsequent stages in the growth of a pit. His observations are not in harmony with those of Goldschmidt. According to him 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.

The explanations offered by Goldschmidt and others, regarding the origin of etch pits, were shown to be inadequate by Destch (1934) who performed etching experiments on alum. A closely related problem, not yet satisfactorily explained, is the distribution of etch pits on the crystal surface.

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 (iv) interstitial atoms and (v) impurity atoms. A detailed synthesis of the imperfections, primary and secondary, is beautifully given by Seitz (1952). It is, therefore, possible that the structural defect may act as the probable sites for the occurence of pits. Once the problem of origin of pits is tackled, it is then possible to determine the density and distribution of etch pits and hence the density and distribution of the defects. It is, therefore, necessary to review briefly the views of several authors in this connection. According to Frank (1949), who gave 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, with the difference that whereas the "line tension" of a dislocation draws it away from a salient corner, so that one dislocation will provide growth for one face only, it holds it at a re-entrant corner so that a single dislocation should be able to promote the development of three or four faces in an etch pit. By etching the crystal the reverse process i.e., the dissolution of the growth spiral may be observed. In order to attack the region of screw dislocation preferentially, the chemical etching should be rapid since dissolutions at the equilibrium conditions would cause a general disintegration of the crystal. Horn (1952) was the first to show that etch pits are formed preferentially at screw dislocations in SiC crystals, when etched in fused alkali carbonates at 1006°C. The growth spiral is obliterated in a few minutes and a pit is formed which widens and deepens, takes on a hexagonal shape and eventually produces a hole through the crystal. Gevers, Amelinckx and Dekeyser (1952) observed the same phenomenon for topaz and CdI_2; in the latter case they were able to follow closely the process of formation of the pits, which consists in an unwinding of the growth spirals. Hexagonal etch pits have been observed not only at centres of visible growth spirals but also elsewhere on the crystal face. These latter etch pits are often arranged regularly in lines parallel to characteristic crystallographic directions. A detailed investigation of etch pits on SiC (Gevers 1953a, b) treated with borax at 800°C showed that deep pits are always formed at screw dislocations, and that these are often arranged in twist boundaries, but that shallower pits were formed at the edges of the growth fronts (Gevers 1953a). On crystals of topaz (Gevers 1953b), it was observed that certain low angle boundaries were not attacked and it has been suggested that these low angle boundaries might consist of edge dislocations.

Etch pits on growth steps have also been observed on crystals of beryl (Kay & Applebe ~~& Kay~~ 1953) and this fact has been used to ~~to~~ explain the apparent visibility of growth steps of unit Burgers vector on these crystals. On haematite (Fe_2O_3) crystals (Verma 1952a) observed etch figures of molecular thicknesses and consisting of a very large number ($\sim 10^7/cm^2$ of the crystal surface) of similarly oriented small triangular figures and some more complex shapes.

Lacombe and his colleagues studied the etching of aluminium crystals. According to Lacombe and

Yannaquis (1947) who found large angle grain boundaries in aluminium etched referentially and which appear as grooves in the surface, the small angle grain boundary which is indeed due to a row of edge dislocations should appear on etching as a row of discreate etch pits. Further it is shown (Lacombe 1948; Lacombe & Beaugard 1945,1948) that annealed crystals of aluminium contain substructure of diameters 0.1 mm. or larger. X-ray work showed that these boundaries separate regions of crystals slightly misorientated relative to one another. Each boundary was shown up by virtue of the concentration of etch pits along it. Cahn (1949) showed that similar but more regular boundaries could be observed on bent and annealed crystals of aluminium and zinc. Observations on the Germanium crystals grown from the melt (Vogel et al 1953, Vogel 1955) show a very striking evidence of preferantial etching of dislocations. They (Vogel et al 1953) confirmed the identity of the disorientation measured at a sub-boundary by X-ray diffraction and inferred from the spacing of dislocations revealed by etch pits. They also observed that the density of etch pits in bent Germanium crystals corresponds to the density calculated from the radius of curvature.

Kleber and Koch (1952) investigated the effect of various electric fields (alternating, constant, pulsating) on the appearance of etch figures obtained on quartz and zinc sulphide crystals etched by 40 per cent solution of hydrofluoric acid. Etching of diamond (Tolansky and Omar 1952) in Hot KnO_3 and Na_2CO_3 at 525°C gave rise to etch spiral in the form of a row of triangular pits making the shape of one turn of a spiral whose arms were found, by the application of thin oil film interference fringes, to be some 700 A deep. This pseudo spiral is not one corresponding to the growth spiral which is the consequence of crystal growth by spiral mechanism observed by Verma (1951) on SiC. It was subsequently established (Pandya 1954) as being due to the result of preferential etching in the first stage along the surface flaws. Custers (1954), by etching octahedral cleavage face of diamond in air at 1400°C for two minutes, reported the formation of bridges starting from the centres of the sides of the etched triangular pit and meeting at the centre. Omar et al (1954) and Pandya and Tolansky (1954) from their studies of the etch patterns on the natural (111) polished (110) and (100) faces of diamond have reported, the formation of crystallographically oriented straight line patterns, which have revealed for the first time the sectional history of the growth of diamond. Ferroelectric $BaTiO_3$ single crystals (Hootan and Merz 1954) were etched by HCl. Observations of etched surface revealed that the positive end of the electric polarization etches much faster than the negative one. This differential etching rate, thus, provides an excellent method for the investigation of ferroelectric domains. Besides using HCl as an etchant, Campbell (1955) also used phosphoric acid to etch $BaTiO_3$ crystals grown from the melt. His observations also indicated the differential etching rate enabling the separate identification of positive and negative limits to the domains. Furthermore almost perfect head to tail ordering of domains upto 0.07 mm was found. Study of etch patterns on cleavage surface of ferroelectric trigycerin sulphate (Toyoda 1959) showed a correlation between the etch pits and the polygonization of the ferroelectric domains.

It is reported (Amelinckx, Votava 1954; Amelinckx 1954) that etched crystals of NaCl show very deep pits at screws, shallower pits at edge dislocations and very shallow pits at surface steps. Further study of the etch patterns on both the halves of a cleaved specimen 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. Electron microscope observations (Hocart et al 1955) of the cleavage faces of natural and artificial crystals of sodium chloride etched in water for short periods suggest the removal of material in layers composed of packets of planes.

The influence of impurities on the etching characteristics of dislocations have been the subject of recent investigation, (Forty 1954; Wyon and Marchin 1954; Wyon and Lacombe 1955); Wyon and Lacombe (1955) from their studies on etched super purity aluminium crystals show that the presence of impurities exert an appreciable influence on the distribution and size of etch figures and their observations stressed the importance of purity as well as dislocation density in determining the etched structure. Forty and Frank (1955), from an examination of etch patterns produced by Lacombe's etchant on polycrystals of super purity aluminium, suggest that an etch pit is produced only where there is a precipitate of impurity present in the surface and that these are located on dislocations which can, therefore, be regarded as an indirect cause of etching. Their observations further indicate that only about 60 or 70 per cent of the dislocations in super purity aluminium produce etch pits in comparison with those of Vogel et al (1953) on Germanium crystals where about 90 per cent of dislocations produce etch pits. Wyon and Marchin (1954), who studied the formation of etch pits on slip lines in aluminium found preferential occurence of etch pits on slip systems with a [100] direction normal to the surface.

Study of etch patterns produced on (100) faces of Germanium crystals by CP_4- led Okada (1955) to the conclusion that there is a one-to-one correspondence between etch pits and edge dislocation so far as grain boundaries are concerned and that the etch pits, distributed randomly, are in edge orientation. An electrolytic etching technique is used to differentiate p-type regions from n-type regions on a Germanium crystal surface containing both the regions (Jackson 1956), and n-p-n and p-n-p junctions transistor structures of Ge and Si (Lesk and Gonzalez, 1958).

Etching technique has been used in revealing the sub-boundaries in the crystals of AgCl and AgBr . deformed at room temperature (Kanzaki 1956) whose origin is attributed to polygonization during the deformation. Spiral etch pits of opposite hand have been observed (Bardsley and Straughan 1956) on silicon crystals.

Gilman & Johnston (1956) from their studies on the etch patterns on the cleaved faces of LiF crystals have shown that dislocations do not move appreciably in the process of cleavage. They have shown beautifully that the etch pits correspond to the 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 LiF crystals.

Dislocation etch pits are observed on silicon crystals (Spray 1960; Vogel and Lovell 1957; Matukura and Suzuki 1957). By the use of etching techniques, Vogal and Lovell were able to observe dislocations in various arrays low angle boundaries, slip lines, polygonization walls and bent crystal distributions; whereas using acid mixture containing potassium nitrate as an etchant, Matükura and Suzuki found on (111) plane, etch pits of various sizes some containing spiral terraces. Etch spirals on silicon iron (Kroupa 1958) were also observed with step heights (measured by multiple beam interferometry), varying from about 100 to 1000 A°. Kikuchi and Denda (1956, 1957) studied etching of Germanium crystal surfaces. Using an etchant containing a mixture of HCl and HNO_3 acids, etch pits with terrace structure were observed, whereas with the use of an etching solution consisting of HNO_3, HCl, HF and H_2O_2, they observed left and right hand spiral etch pits, having density 100 - 1000 times smaller than those of normal pits on Germanium crystals.

Jones and Mitchell (1957) made use of etching and decoration techniques to reveal dislocations associated with both annealing and deformation structures in crystals of silver halides. Etch method was also used to reveal the distribution of edge dislocations on the

(111) faces of indium antimonide (Bardsley and Bill 1957). Selective etching of single crystals of indium antimonide, enabling the identification of positive and negative dislocations led Venables & Broudy (1958,1959) to believe that in InSb the stress required to generate dislocations in a dislocation source is greater than the stress required to move them in the slip plane.

Omar and Kenavi (1957) reported etching of diamond cleavages by heating them on molybednum filament in a low pressure (about 2.5 uHg) of oxygen. The etch figures obtained by this method have the same orientation as those obtained by etching in oxidizing melts, but differ in outline by being sharply rectilinear, being oppositely oriented to the growth trigons. From these observations they conclude that the growth trigons are also etch figures produced by an unknown natural etching process. That their triangular pits were very sharp in outline, primarily because the etching used by them was slow is shown by Tolansky and Patel (1957) who proved that the rectilinearity or curvelinearity of an etch pit depends in a sensitive way upon the temperature and the rate of etch. The rate of etching increases with increase in temperature. They showed that pits strictly rectilinear in outline were obtained by etching in potassium nitrate at 475°C whereas at 525°C the etching was much faster and the rounding of the pits was found. The present author observed the same phenomenon in case of mica etched by fused alkalies at their melting points. At low temperatures the pits were very sharp in outline whereas at higher temperatures (from the melting point y temperatures of alkalis and upwards), the triangular pits were curvelinear in outline. Emara and Tolansky (1957) have shown that dodecahedron surfaces of diamond are much more subject to solution in nature than the octahedral faces.

According to Ellis (1957), the origin of spiral etch pits arises from dislocations in the form of hebies by supposing that the lateral rate of etching is constant and that the point of nucleation moves in a circle. Rhodes et al (1957) from their studies on (111) and (110) crystal surfaces of Germanium single crystals grown from the melt and etched by iodine, found left and right hand spiral etch pits, with a few double spirals and having step heights of the order of 2000 A°. They measured electrical resistivity as a function of the density of pits. Their observations suggest that the pits are related to the presence of impurities in the crystals. Elliot (1958) also observed the spiral etch pits on Germanium single crystals of {100}orientation. From the observations of polygonized structure, he inferred a connection between etch pits and structural imperfections, in the crystals. Tylor and Dash (1959) arrived at the conclusion that internal Frank-Read sources and surface dislocations are of importance in the deformation of Germanium crystals in which dislocation arrays were disclosed by selective etching. Ellis (1957) had studied etching of Germanium crystals in the form of spheres. Batterman (1957) has shown on single crystal Germanium surfaces crystallographic etch hillocks which are surface nucleated and do not represent interior perfection nor do they correlate with dislocations intersecting the crystal surface. The bounding faces of hillocks are concluded to be the limiting etch planes. His findings justified the reciprocity between limiting plane and curvature, viz.,upon dissolution convex surfaces will limit on fast etching planes while slow etching planes will bound on concave surfaces. Irving (1960) extended Batterman's work to account for all the crystallographic etch hillocks produced by a dil H_2O_2-HF acid etchant on Germanium surfaces. Johnston et al (1957) studied spiral etch pits on (111) and (110) surfaces of n type silicon. From their observations they attributed larger pits to edge dislocations and smaller pits containing spiral terraces with screw dislocations. Spiral pits have also been observed on SiC crystals (Bhide 1958), having step heights 27 ± 2 and 1050 A.

Gilman (1956b) and Malika (1956) etched single crystals of zinc and etch pits have been produced at the sites of dislocations. Servi (1958) observed spiral etch patterns on single crystals of high purity zinc and Frank and Vreeland (1958) explained the patterns in terms of Frank-Read sources. Pandya and Shah (1958) also observed etch spirals on the cleavage planes of pure zinc single crystals grown from the melt by Bridgmann's method. Star shaped terraced etch pits at the sites of dislocations were obtained on the basal plane of crystals of vapour grown zinc (George 1959), Damiano and Herman (1959) also observed on the surfaces parallel or nearly parallel to the basal plane of zinc, the motion and growth of loops and spiral etch patterns. These observations (George 1959, Damiano & Herman 1959) are explained in terms of Frank-Read sources.

Etch pits which are shown to be at dislocation sites were observed on cleavage faces of monocrystals of antimony (Shigeta and Hiramalton, 1958; Wernick et al 1959), on cleavage planes of bismuth single crystals and on (111) plane of high purity copper single crystals (Lovell and Wernick 1959a, 1959b), on tungsten crystals (Wulff 1958) on cleavage planes of tellurium crystals (Lovell et al 1959). The etching of cleaved surfaces of monocrystals of bismuth grown from the melt was also studied by Pandya and Bhatt (1960), who observed beautiful block patterns similar to those observed on diamond (Pandya and Tolansky 1954), on fluorite (Pandya and Pandya 1958) and on calcite described in the present work.

Potassium chloride crystals were etched by dehydrated acetic acid and one-to-one correspondence between etch pits and dislocations was observed (Sakamoto and Kobayshi 1958). Etching of NaCl crystals by NaCl solution was employed to reveal slip sources in the crystals (Merlin 1959).

Gilman (1959) studied the nucleation of dislocations in LiF crystals. He concluded that small foreign homogeneuties cause most of the dislocation nucleation in real crystals, whereas homogeneous nucleation occurs only at high stresses. Ultrasonic etch figures (produced by exposing crystals in water to an ultrasonic field of frequency 25 kcs/s and of intensity 0.5 w/cm^2) on LiF and other crystals have a correspondence with those obtained by Standard etching techniques and therefore, indicate the presence of dislocations (Kapustein 1959).

Etch pit technique is used to study quantitatively dislocations introduced into single crystals of silicon (Patel 1958) by plastic bending at high temperatures. The density of etch pits in the annealed and polygonized specimen closely correspond with the predicted dislocation densities whereas the average etch pit density after deformation is approximately two or three times higher than the calculated dislocation density. Similarly, there was no close agreement between the value of yield stress obtained from the geometrical distribution of dislocation arrays and the reported experimental value. Copper decoration technique was also used to study, in the crystals deformed at 1000°C, the dislocations which were found by the use of infra-red-transmission microscopy to lie in the [211] direction.

In the etching of recrystallized aluminium, Broun et al (1958) from their observations on the resistance of fresh grain boundaries and susceptibility of aged grain boundaries to etch attack at room temperature, interpreted this behaviour of grain boundaries as being due to diffusion of impurities along the grain boundaries into the oxide film.

An interesting and important application of etch and decoration methods in given by Dash (1959) who grew silicon crystals free from dislocation. He observed that for certain crystallographic directions it was possible to eliminate residual dislocations and thenceforth grow a dislocation free crystal. When the dislocations are eliminated, the growing crystal can withstand large temperature fluctuations without further generation of dislocations. Germanium crystals free from dislocations were grown by this method, which might also prove to be useful for growing dislocation free crystals of other substances.

The above general review which is made somewhat more exhaustive indicates that under suitable conditions, etch methods are reliable, simple in operation and powerful in revealing the lattice defects when substantiated by other experiments. But one should be very cautious in interpreting the etch pattern observed on crystal surfaces. That this fact is of vital importance is shown by observations of several workers. Because once the problem of origin of pits is resolved, the density and distribution of etch pits should correspond with the density and distribution of lattice defects. The latter can be found by other means and these observations should, therefore, perfectly agree with those obtained by etch methods. That this is not always so is shown by the observations of various workers, some of which are given below. The spacing of etch pits observed by Lacombe on etched aluminium crystals (Lacombe 1948) points that the angle of tilt is only a few seconds of arc, while the observed angle is of the order of few minutes of arc. Similarly, observations for plastically bent and subsequently annealed Germanium rods (Pearson et al 1954) indicate the density introduced by bending $\sim 3 \times 10^{7}$ cm^{-2} and the density of etch pits $\sim 3 \times 10^{6}$ cm^{-2}. Similar discrepancies are apparent from Cahn's observations on bent and polygonized aluminium and zinc (1949) and Gever's (1953b) observations on topaz.

Vogel et al (1953) observed dislocation density on Germanium crystals to be $\sim 2 \times 10^5$ cm^{-2} while Ream and Pearson (1954) found density in Germanium to be of $10^3 - 10^5$ cm^{-2} whereas etch pits counts on other crystals of Germanium give densities of $10^{+6} - 10^8$ cm^{-2} (Kulin and Kurtz 1954).

According to Ellis (1955) the density of dislocations in Germanium to be $10^6 - 10^7$ cm^{-2}. Patel's observations on silicon crystals (1959) also show the variation between the observed and calculated densities of dislocations.

All these observation show that adequate care must be exercised in interpreting the etch patterns on crystal surfaces. The factors influencing the preferential attack of dislocation should be thoroughly investigated. In such experiments, the type of etchant used and the etching conditions must be important variables. It is known that sub-boundaries are attacked particularly strongly by certain etchants and the smaller the angle across the boundaries the more difficult it becomes to reveal them by etching. Metzner and Intrator - (1954) have, however, shown that the addition of very small amounts of copper (0.5 part of copper to million parts of HCl) to a solution of 7 per cent HCl enabled this etchant to show up sub.boundaries in aluminium with angles of tilt of only 5" of arc or possibly less.

The studies of the X-ray diffraction and the observed mechanical properties of certain crystals indicate that nearly 10^8 dislocation lines thread through a square centimeter of the surface. The studies of crystal growth and dissolution, however, indicate the value of about 10^4 to 10^7. This order of magnitude agrees well with the density of etch pits observed on certain crystal surfaces by several workers (see for example, Dekeyser, 1955, Omar et al 1954 etc.).

The present author had studied etch patterns on a few crystals but in the present investigation is reported a detailed systematic and comprehensive study of etch patterns produced by a variety of etchants on the cleavage faces of mica, fluorspar and calcite by the techniques which will now be briefly reviewed in the next chapter. The detailed discussions of the crystals studied in this work will be taken up in their respective chapters.