CHAPTER I
INTRODUCTION

The concept of dislocation - a linear imperfection in crystal lattice - was introduced in physics independently by Taylor, Crow and Polanyi in 1934 mainly to account for the great disparity in the values of observed and theoretical strengths of crystals. Subsequent researches in this field during the last few years have increased the confidence in the validity of the dislocation theory and in its power to provide fundamental understanding of various physical phenomena such as crystal growth, crystal plasticity and structure of grain boundaries (Shockley et al., 1952; Read, 1953; Cottrall, 1953; Van Bueren, 1961; Friedel, 1964 and Rhodes, 1964). Recently, a number of methods (Amelinckx, 1964) for the direct observation of dislocations have been developed and these have given further impetus to the studies of dislocations in crystalline solids.

Origin of Dislocations in Crystals

In the crystals grown from the melt, dislocations are invariably present and their number depends upon the conditions of growth. Dislocations are not thermodynamically stable lattice defects (Cottrall 1953) as they do not appreciably lower the configurational entropy of a crystal through their presence, and their
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energy of formation is very large. Several mechanisms have been proposed to explain the origin of dislocations. For crystals drawn from melt by the conventional techniques, the hypothesis of Tejtegtonian and Chalmers (1961), elaborated by Frank (1956), might be applicable. In the cooling crystal, behind the solid-liquid interface, the concentration of vacancies would become more than the thermal equilibrium content, and as it may not be possible for these to diffuse out of the solid in the time available, the excess vacancies must condense in the solid itself. The appearance and subsequent collapse of these vacancy discs behind the interface can give rise to dislocation loops. Shockey and Tiller (1960), Elbaum (1963) and others have suggested that the formation of the vacancy condensation-dislocation loops is an important source of dislocations in crystals grown from melt. Jackson (1962) has concluded that the excess vacancy concentration available during growth from the melt is insufficient to nucleate sufficient number of dislocation loops to account for the observed dislocation densities. Young and Savage (1964) have attempted to grow copper crystals of low dislocation density and from their experimental observation they have concluded that the vacancy
condensation-loop formation was not the most significant mechanism in the dislocation production. Gilman and Johnston (1967) have concluded that in lithium fluoride loops are not created by vacancy condensation mechanism. At the same time Kuhlmann-Wilsdorf et al. (1958) have proposed a theory in which it is assumed that dislocation formation by vacancy condensation takes place not only during growth but also during the plastic deformation of metals. There is conclusive electron microscopy evidence available to show that collapse of a vacancy disc can result in the formation of a dislocation loop. On the other hand it is quite likely that the mechanism may be more pronounced in particular crystals and that it is insufficient to account for the dislocation density observed in solids. Billig (1959) and Penning (1959) have shown that the plastic deformation caused by the non-uniform heat flow during the cooling of the crystal can also lead to the formation of considerable number of dislocations. Billig has shown that thermal stresses of the order of $10^8$ dynes per cm$^2$ are quite likely and this is of the order of yield point of many solids. An inhomogeneous temperature gradient is always accompanied by stresses and if these become quite large, plastic flow can take place and a number of
dislocations will be formed in the material. When the crystal is cooling, a gradient normal to the growth direction is also set up. The idea of the stress can be had from the relation \( \sigma = \alpha E \Delta T \) where \( \alpha \) is linear coefficient of expansion and \( E \) is the Young's modulus; \( \alpha = 4 \times 10^{-5} \) and \( E = 4.4 \times 10^{11} \) dynes/cm\(^2\) for sodium chloride and for a lateral temperature gradient of 1° per cm, the stress comes out to be of the order of 10 dynes per cm\(^2\). From the existing evidence it can be said that the sources of dislocations in the purer crystals are not clear. It is believed that one and more than one mechanism may be operative in individual cases and generalization is not possible.

In case of impure crystals constitutional stresses can also be set up due to the segregation of the impurity atoms. According to Tiller (1968) the number of dislocations that should result from the impurity segregation in the growth process can be calculated.

\[
N \sim (\frac{E}{b^2})(\Delta c(\Delta \lambda/\lambda) - \xi_e)
\]

where \( b \) is Burgers vector, \( d \) is the wave length of the fluctuation, \( \xi_e \) is the elastic strain, \( \Delta \lambda/\lambda \) is the change in lattice parameter per atom per cent solute concentration fluctuations. Till recently (Deo and Sharma 1964) experimental evidence was not available
to support the Tiller's model. In case of dilute alloys where homogenization has taken place, Elbaum (1963) has suggested that the Kirkendall effect at the impurity substructure can increase the concentration of vacancies which on collapsing would produce dislocations. Davis and Fryzek (1964) have studied the substructures in melt grown zinc 0.1 percent thallium alloys by chemical etch pit method. Their observation does not favour the Tiller's model and they have concluded that most of the dislocations are created by thermal stresses set up on cooling.

**Detection of Dislocations**

Dislocation theory was coming up in 1947, when the conference on 'Strength of Solids' was held at H.H.Wills Physical Laboratory of University of Bristol. Its essentials had been well developed by April 1949 when the discussion on crystal growth, organized by Faraday society, was held at Bristol University but it did not have any experimental support except the speculations of Shockley and Read (1949 & 1950) that the etch pits on the surfaces of aluminium crystals observed by Lacombe and Beaujard (1944 & 1948) might be associated with dislocations. At this conference Frank pointed out that as the crystal growth could not take place by
two dimensional nucleation at low supersaturations, the imperfections present in the crystal might help the growth at low supersaturations. Frank concluded that the presence of a screw dislocation would eliminate the need of a two dimensional nucleus and that spiral terraces should appear on a crystal that has grown by this mechanism. The first observation of the spiral terraces was of Griffin in September 1949 on the surface of beryl crystals and this provided the confirmation of the validity of Frank's mechanism. Spiral terraces were then reported by Verma (1951, 1953) and Amelinkx (1962) on the surfaces of carborundum crystals. The observations of Griffin (1951 & 1952), Dawson and Vand (1951) and Forty and Frank (1963) indicated that the screw dislocations responsible for the crystal growth could move during growth or subsequently. In this way the surface topography provided the first evidence for the presence and motion of dislocations in crystals. The scope of this method was limited only to the observations of dislocations with a component of the Burgers vector normal to the observed surface and this was a serious drawback to the study of other dislocations. The fact that the dissolution of a crystal occurs preferentially at the site of
emergence of a screw dislocation was first established by Horn (1962) and Horn et al (1962). This combined with the observation of Vogel et al (1963), which introduced a new phase of the etch pit technique, indicated that selective etching techniques could be used for the study of dislocations in crystals. Since then this technique has been widely used and most of the data on dislocations have been obtained by selective etching of the sites of emergence of dislocations on the crystal surfaces. Gilman and Johnston (1966-57) have carried the selective etching of lithium fluorride crystals and have investigated the kinetics of the movement of individual dislocations and the dependence of the rate of dislocation motion on stress. On a few occasions the method has also been used to observe dislocation etch grooves (Low and Guard 1959, Dash 1958, Tyler and Dash 1957), etch tunnels (Sears 1960, Westwood and Rubin 1962) and Frank-Read mechanism configurations (Deo and Sharma, 1964).

Etch pit method has a number of advantages over other methods for the preliminary investigation of plastic deformation in single crystals. The main limitation of the method is that it has not been established positively if there exists a one to one correspondence between emergent dislocations and etch
pits. The strongest evidence in support of such a correspondence has been provided by Vogel et al. (1953), who have observed the dislocation etch pits at the tilt boundary in germanium, by Dunn and Hibbard (1955) and Vogel (1955), who compared etch pit counts of bent crystals of Fe-3% Si and Ge with dislocation densities calculated from the radius of curvature, and by Gilman and Johnston (1956) who have compared etch pits on matched cleavage surfaces in lithium fluoride. Very recently (1965) Pickering has studied the morphology of etch pits at aged dislocations by transmission electron microscopy and has shown that a one to one correspondence between etch pits and termini of dislocations does not always occur in Fe-3% Si alloys. The correspondence is favoured if the dislocation density is below a certain as yet undetermined critical density. Thus the etch pit methods should give satisfactory results on single crystals with moderately low dislocation contents.

In the year 1953 Hedges and Mitchell made the first observation of dislocations inside silver halide crystals by decoration of dislocation lines by photolytic silver when they exposed the crystals to light. The more conventional way of making the dislocations visible is by impurity decoration.
Amelinckx, Dekeyser and co-workers (1956, 1966, 1967 & 1968) have used the technique extensively to study dislocation configurations in ionic crystals. Dash (1956, 1957, 1958 & 1959) has made spectacular observation of copper decorated dislocations in silicon by using infra-red light. He has observed for the first time Frank-Read sources and has established one to one correspondence between etch pits and dislocation lines. Decoration technique has also been used to study dislocation net works and sources in zinc crystals containing cadmium (Servi, 1958). The decoration technique can be effectively used in case of crystals which are transparent in some part of the spectrum and a single experiment can provide a great deal of information, because all the dislocations in the crystal can be studied in three dimensions. During decoration, however, the dislocations are made immobile by impurity pinning and this impedes the study of dynamics of shearing. Furthermore, the configurations of dislocations are modified by the processes that cause decoration and frequently the crystal is spoiled for further physical investigation.

Maximus resolution of the dislocation structures can be achieved by means of transmission electron microscopy introduced by Hirsch et al (1956) and
Bollmann (1956) for direct observation of dislocations in metal foils. Since then the method has been extensively used for detailed studies of arrangement, movement, and interaction of dislocations as well as for getting information concerning the development of dislocation structures at very high degree of deformation. Electron microscopy has been mainly used for metals though the recent observations show that the technique is applicable to non-metals as well (Grenall 1958, Amelinckx and Delavignette 1960 and Washburn et al 1960). Initial difficulties in manipulating the thin specimens for controlled experiments are being overcome (Wilsdorf 1955, Fisher 1959, Berghesan and Fourdeaux 1958, Pashley 1969). The major drawback of the technique is that it is applicable only to the films that are transparent to electron beam and the specific influence of surface is certain to affect the dynamic behaviour of dislocations.

The drawback encountered in decoration technique is absent in diffraction microradiography which renders the dislocations visible without the aid of decoration. The X-ray method has been developed by Lang (1957, 1968 & 1969) and Newkirk (1958). At present a number of X-ray diffraction methods exist for the observation of dislocations and all these allow the Burgers
vector of dislocation to be determined from the observation of the contrast in the images formed by reflection from different systems of lattice planes intersected by the dislocation. The distribution of the dislocations in thin crystals can be examined without spoiling the specimens for further physical investigation. However, the method is limited to crystals with low dislocation densities as records are usually made at near unit magnifications and have subsequently to be enlarged photographically through the new X-ray diffraction topography methods have attained a resolution of the order of 5 microns which is available for surface etch pit techniques. Recently (Heieran, 1965) Frank-Read sources have also been revealed by this method.

Besides the above mentioned five methods, there exist a number of other techniques as well which have either limited capability or have not been much developed. These include etching by ionic bombardment (Wehner 1958, Meekel and Svalin 1959, Dillon and Oman 1960); direct resolution of lattice planes developed by Menter (1958) and Espagne (1960); observation of Moire patterns used by Hashinotu and Uyeda (1967) using transmission electron microscope; observation of dislocations in metal specimens by field ion microscope by Muller (1957, 1958 & 1959); stress
birefringence and the technique of thermal etching.

Bond and Andrus (1956) were the first to show that the polarized light method can be used for observing individual dislocations and birefringence at an edge dislocation was obtained. Indenbom et al. (1962) have further shown that in crystals with low dislocation density the polarized light method enables observation of the strain field surrounding each dislocation parallel to the illumination axis and in principle completely characterizes the dislocation structure of the specimens. This polarized light method of stress investigation which is usually applied to the analysis of macroscopic stress, gives data concerning the macroscopic density of the dislocations due to these stresses. It has been reported that cross-slip is quite significant in affecting dislocation multiplication in alkali halide single crystals (Mendelson 1962). Sources are formed and activated in the central regions of the specimen which emit dislocations of opposite signs which move towards the opposite edges of the crystal. That this is so has been verified by the birefringence technique (Mendelson 1961, 1962 & 1963). This method permits direct observation of glide bands as they form while the stress strain behaviour is simultaneously recorded. Mendelson (1962) has studied dislocation multiplication
and glide bands formation in NaCl single crystals by using birefringence technique and has discussed the plastic behaviour and slip on various systems and has recorded simultaneously the stress strain behaviour at various stages of plastic flow. Dislocation etch pit observations have supplemented these results. Using birefringence technique, Mendelson has recently (1963) also made numerical calculations in the flow behaviour of Sodium chloride single crystals for which much data have previously been gathered. Sun Jui-fang and Shaskol'skaya (1960) have also observed that the number of etch pits along the birefringence bands in plastically deformed rock salt related to the difference between the amounts by which these bands are displaced when they emerge at the side of the crystal.

Thermal etch pits are expected to be formed at the sites of emergence of dislocations on the surface of the crystals when the crystals are heated to high temperatures due to the establishment of equilibrium between the line tension of the dislocation and the surface tension of the crystal (Frank 1951). The formation of etch pits by evaporation is also expected on theoretical grounds (Cabrera 1956, Hirth and Pound 1957). Thermal etching of dislocations has been reported on silver by Mashlin (1957), Hirth et al (1958), Winterbottom et al (1962).
on antimony by Lavrent'ev et al. (1960); on copper by Young and Swathmey (1960); on cuprous oxide by Andrivskii et al. (1964); on NaCl by Grinberg (1963) and Deo and Sharma (1964 & 1965). However, some discrepancies between thermal etch pits and the dislocation densities inferred from other data have also been reported (Semmel and Machlin 1957, Hirth and Vassamillet 1958) and the correlation between thermal etch pits and dislocations has not been sufficiently well established (Hirth and Vassamillet 1958).

Resume of the Investigations

The work reported in this thesis is concerned with the studies of dislocations in sodium chloride crystals, with a special reference to their nucleation, observation, motion, multiplication and role in fracture. Sodium chloride was chosen for these studies as this material possesses a favourable combination of properties; single crystals of NaCl can be grown and obtained in fairly good perfection and purity, these have a simple crystal structure, and being transparent can be studied with a number of newly developed techniques.

The experimental techniques that have been employed for these studies are well established and are
discussed only briefly in chapter II. Chapter III deals with the study of impurity substructures, in crystals grown from the melt, and the dislocations nucleated at these structures. Evidence has been presented in support of platelet structure as a general phenomenon of growth, and for the cellular structure, need of an incubation distance has been confirmed. Microphotographs of transition stages from platelet to cellular structure, from cellular structure containing platelets to cellular structure alone and from cellular structure to cellular dendrites have been obtained. Concrete experimental evidence has been presented which supports the Tiller's model of nucleation of dislocations at the impurity substructures and it has been concluded that the dislocations are produced due to the varying lattice parameters at the segregated impurity regions. The origin of dislocations in impure crystals has been made more clear.

Chemical etching of dislocations in as grown, annealed and stressed crystals has been reported in Chapters IV and V. Chapter IV describes rather rare observations of etch tunnels and etch grooves and the role of poison in their formation has been discussed. Growth of whiskers, which are thought to be a
phenomenon opposite to etch tunnels, from the solution and vapour phase has also been described. Chapter V relates the results of etch study of dislocations in indented crystals. Besides the observation of dislocation crosses, interesting spiral configurations corresponding to Frank-Read Mechanism have been observed. Dissolution spirals, whose origin is still unsettled, have also been reported and their origin discussed.

Chapter VI deals with the study of fracture in NaCl single crystals. A study of cleavage surface in relation to crack velocity has been made and the presence of glide at the crack tips has been observed. Apart from the normal fracture, unusual fracture in non-cleavage planes has also been reported. Evidence obtained indicates that the non-cleavage plane fracture may indeed consist of stepped cleavage plane surfaces.

The process of thermal etching has been exploited for the study of dislocations in Chapter VII. It has been clearly demonstrated that the pits produced by thermal etching, a technique yet to be firmly established relate to the sites of dislocations at the crystal surface. This has been achieved by observing symmetrical and asymmetrical thermal etch pits,
individual dislocation motion as revealed by paired pits and grooves, motion of individual dislocations of a tilt boundary, and the differential motion of dislocations in pure and impure regions of the grown crystals.
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