CHAPTER V

SPIRAL CONFIGURATIONS IN SODIUM CHLORIDE

While discussing the formation of etch tunnels in chapter IV, I have briefly reviewed the theory of preferential etching at dislocations. Cabrera (1956) has shown theoretically that in the presence of a specific region of undersaturation the dissolution should proceed preferentially at dislocations as opposed to perfect surfaces. Much work has been carried to verify the validity of Cabrera's theory by utilizing the technique of chemical etching. Earlier, the correspondence of etch pits to emergent dislocations was suggested first of all by Shockley and Read (1950) to explain certain etch patterns observed by Lacombe et al. (1943 and 1944) on high purity aluminum. The comprehensive work of Gilman and Johnston on dislocations (1956, 1957, 1958, 1959, 1960, 1962) in Lithium fluoride indicates the mass of information that can be obtained by simple etching technique.

The present chapter reports some interesting patterns that have been obtained on single crystals of sodium chloride by selective etching. Etch patterns have been studied in as grown crystals, annealed crystals and elastically deformed crystals.
The presence of arrays of dislocation crosses and of dislocation configurations corresponding to Frank-Read mechanism have been observed. By the use of controlled etching dissolution spiral structures which were invisible in the unetched conditions have also been revealed. Thus further evidence has been presented to support the observation of Frank-Read mechanism in sodium chloride crystals by way of comparison with the dissolution spirals.

**Experimental**

The usual etchants for sodium chloride crystals are glacial acetic acid, methyl alcohol and ethyl alcohol containing some inhibitor. The etching time for glacial acetic acid and methyl alcohol is very short (\(\sim 1\) sec). Amelinckx (1958) has reported successful etching with methyl alcohol, the etching time, however, being very small due to the high solubility of sodium chloride in methyl alcohol. A good etchant should consist of a base which is a weak solvent for sodium chloride crystals. According to Moran (1958), when an etchant consisting of absolute ethyl alcohol with 3 grams of mercuric chloride per litre as inhibitor is used, the solubility of the crystals in the base is found to be between 0.07 and 0.08 gram per 100 ml. This gives an etching time of
up to 30 sec.

Methanol has been commonly used as the polishing agent for sodium chloride, but this gives a rather matt surface. For better polishing, Rozhanskii and Stepanov (1940) used methyl alcohol containing 10 percent of water and later the crystals were rinsed in butyl alcohol and dried well.

In the present case the etchant used consisted of glacial acetic acid diluted with methanol. Depending upon the dilution of glacial acetic acid, the etching time could be increased up to 40 sec. Distilled water and methyl alcohol were used as a polishing agent and were found to give a good polish. The crystals were polished by immersing first in distilled water; later these were rinsed in methyl alcohol and dried either by placing it on a filter paper or by blowing a stream of dry air on to these. This gave a good smooth surface.

The specimens used were cleaved from 99.99 percent pure single crystals of sodium chloride procured from the National Physical Laboratory, New Delhi. The plastic deformation of the crystals was carried by placing the crystal on two smooth glass strips and a normal stress of the order of $10^9$ dynes/cm$^2$ was applied with a semi-circular glass strip indenter. The radius of the area of contact between the
Fig. 1. Sub boundaries revealed by chemical etching in sodium chloride single crystal. (x400)

Fig. 2. Chemical etching of sodium chloride (matched cleavage). (x400)
indenter and the (100) surface of the crystal was 10^5 microns. Observations were made with Reicherts MeF universal camera microscope using bright field illumination.

Results and Discussion

Preliminary experiments on as grown crystals revealed a large number of etch pits corresponding to a high dislocation density. The crystals were, therefore, annealed to reduce the number of dislocations. Figure 1 shows the etch pits formed at the dislocation sites and along subgrain boundaries on (100) face of an annealed crystal. In agreement with the observation of Kostin and coworkers (1962), pits formed are shaped in relation to the crystal symmetry such that the diagonals of the square pits are along [100] and [010] directions. It was further seen that the etch patterns produced on both sides of a cleaved crystal are similar. This is shown in figure 2 in which one of the negative has been printed in reverse to show the matching patterns.

Indentation and Elastic Deformation

Gilman (1957), Vaughan and (1959), Aerts (1959), and Keh (1960) have shown that in case of alkali halide crystals with rock salt type structure, the
Fig. 3. Schematic drawing of (110) glide planes in sodium chloride.

Fig. 4. Arrows of dislocation crosses. (x300)
etch pits formed on an indentation arrange themselves in a rosette pattern; the shape and the orientation of the rosette being independent of the choice of the indenter. The eight rays of the rosette result from the interaction of \{110\} glide planes shown in figure 3 with the (100) indented surface. The diagonal rays of the rosette are always larger than the straight rays. This is attributed to the fact that the velocity of edge dislocations is higher than that of screw dislocations in the slip planes. In the present case indentation on (100) face resulted in the etch pattern shown in figure 4. It was observed that at comparatively lower stresses the pattern was not produced, whereas higher stresses resulted in the usual rosettee patterns. It shows that critical stress, similar to the macroscopic yield stress, exists for the nucleation of new dislocations. Figure 4 is interesting in so much as that only screw components of the rosette have been produced. This means that the glide planes corresponding to edge components of the rosette have not been activated. This can be accounted for due to the larger area of contact between the glass indenter and the crystal surface. Furthermore, the rough surface of the indenter made the contact between the indenter and (100) surface of the crystal quite non-uniform and this can be considered to be
equivalent to a large number of smaller indentations. On this basis it is fairly easy to understand the crosses observed in the pattern. These dislocation crosses are somewhat similar to those obtained on Lithium fluoride by Gillan and Johnston (1967) but are more in number. The much higher density of the crosses is believed to be due to the larger area of contact between the indenter and the indented surface of sodium chloride crystals. The radius of the area of contact was of the order of $10^2$ microns and therefore much larger as compared to the dislocation crosses. These crosses are along $\langle 100 \rangle$ directions. A plausible explanation for these dislocation crosses pattern can be the activation of Frank-Read sources on $\{110\}$ slip planes. The intersection of these $\{110\}$ slip planes, with $\langle 100 \rangle$ plane will give rise to these arrays of dislocation crosses. This view is in conformity with that of Mendelson (1962). Due to insufficient and uneven distribution of stresses in the present arrangement, the Frank-Read sources on all the six $\{110\}$ glide planes are not activated and this has resulted in dislocation crosses of figure 4 and not in the usual rosette patterns. This view is supported by the observation of etch configurations corresponding to Frank-Read sources on $\langle 110 \rangle$ plane.
Frank-Read Type Spirals

It was in 1950 that Frank and Read proposed a mechanism to account for the dislocations generated during plastic deformation. Direct confirmation of their ideas had to await the development of techniques for making dislocations visible within the interior of crystals. Dash (1956) was the first to reveal the internal dislocation sources, corresponding to the configuration predicted by Frank and Read (1950), by using his copper precipitation technique for rendering dislocations in silicon observable by infrared transmission microscopy. His photographs showed in spectacular fashion both the multi-turn spiral produced when the dislocation is anchored at only one point and the symmetrical source of closed loops formed when the dislocation has a pair of anchor points in its slip plane. In silicon Frank-Read sources have also been observed by Authier et al. (1964) and Neieran (1965) by X-ray topographic studies.

To look for the presence of sources in sodium chloride, the (110) face of the stressed crystal was subjected to repeated etching and polishing and each time the etch pattern obtained was studied under the microscope. In a very few of these observations interesting spiral configurations on (110) slip planes
Fig. 5. Etch pattern showing a single spiral on (110) face of sodium chloride. (x500)

Fig. 6. Etch pattern due to two spirals apparently resembling a Frank-Read source. (x250)
Fig. 7. Such pattern resulting from the combination of three spirals. (x300)

Fig. 8. A combined pattern consisting of a number of interesting spiral configurations. (x125)
were observed. The configurations disappear on removing a layer of a few microns thickness from the surface. Interferometric observations revealed the background to be levelled.

Figure 5 shows a single spiral. The central portion of the spiral is not developed and there is an indication of the presence of inclusion or precipitate. The spiral has a wavy structure. It is difficult to say whether this is due to inadequate stirring of the crystal in the etchant or it is due to some poison present in the etchant. In the background of the spiral are also seen the etch pits due to the emerging dislocations, the density of the pits being \( \sim 10^8 \text{ /cm}^2 \). The etch pattern shown in figure 6 represents a configuration which resembles the usual Frank-Read source. Analogous etch configurations have been observed by Tyler and Dash (1957) and by Demiano and Herman (1958), on Zinc-Strati (1958), and by Predvoditelev et al. on cadmium (1950). Figure 7, illustrates a pattern which seems to result from a combination of three spirals. The etch pattern reproduced in figure 8 is most interesting. In the upper portion are seen two spirals. These spirals are winding in the same direction and they do not combine to form a configuration similar to that illustrated in figure 6 as is also the case in the adjoining pattern in which the spirals are of opposite
type. In the lower half of this figure can be seen a more complicated pattern which has resulted from the combination of four spirals. It is interesting to consider the possibility whether the configurations corresponding to figures 5-8 are due to Frank-Read sources or are dissolution spirals.

The background of these configurations is seen to be levelled which is not the case for dissolution spirals. In the case of the dissolution spirals, especially of these dimensions, as pointed out by Dash (1960) and others (Johnston, 1961) the steps of the spirals are clear even from the photographs.

The pitch $d$ of the dissolution spiral due to unit Burgers vector screw dislocation is given by:

$$d = \frac{19 \gamma}{kT \log C/C_0}$$

(Cabrera and Levine, 1954, 1956)

where $\gamma$ is the crystal solution surface energy, $C_0$ is the equilibrium concentration of the crystal in the solvent and $C$ is the actual concentration. For sodium chloride crystals the value of $d$ comes out to be of the order of $10^{-6}$ cm. This value is much smaller than the value of pitch observed in case of figures 5-8. For dissolution spirals, presumably due to helical dislocations, a pitch of the order of $10^{-4}$ cm has been
observed (Deo and Sharma, 1963) but in that case the step height is also large and the background is not levelled.

Mendelson (1962) has suggested the operation of Frank-Read sources in (110) slip planes to explain the occurrence of glide bands in sodium chloride single crystals. For the operation of a Frank-Read Source a critical stress is needed which, according to Mott, is given by $Gb/L$, where $L$ is the length of the dislocation line fixed at two points in the (110) slip plane and $b$ is the Burgers vector. If the value of $L$ is substituted in the data obtained from figure 6, the critical shear stress comes out to be $\sim 10^5$ dynes/cm$^2$ which is quite probable as the maximum applied stress for deformation in the present case was $10^3$ dynes/cm$^2$ on (100) plane.

The projection of the spiral configurations resemble the geometry of Frank-Read sources and also have a reasonable spacing. For the activation of the Frank-Read mechanism, it is required that the dislocation must be anchored firmly to prevent the motion of anchored points under the applied stress. The anchoring may be due to a prismatic dislocation or by the intersection of dislocations which lie on planes that are not easy slip planes of sodium chloride lattice. Nodal points may also be provided
by the double cross slip mechanism recently utilized by Mendelson (1962) to explain the glide bands in sodium chloride single crystals. If a screw segment of a dislocation line in one plane cross-slips to a neighbouring plane, four nodal points will result and the dislocation lines may then operate by Frank-Read mechanism. The presence of segregated impurity atoms or precipitated particles may further stabilize these dislocations.

In all these possible mechanisms for anchoring the dislocations in the slip planes, it is evident that at least one dislocation line, which does not lie in the slip plane, emerges from each of the anchored points. It is, therefore, expected, that in case of Frank-Read spirals revealed by the selective etching of the crystals, etch pits should also be formed at the centres of these spirals. Predvoditelev et al. (1950) has actually observed the presence of such etch pits in the case of cadmium and these have been attributed to the emerging dislocations at the fixed points. They found that continued electrolytic etching revealed the etch pits which continued up to a certain depth well inside the crystal, even after the Frank-Read source had disappeared on removing a few microns thickness of the etched surface. However, if the emerging dislocation had been coming out of the
Fig. 9. A spiral configuration showing a finely developed annulus at the centre. (x750)
etched surface, it would disappear along with the spiral on subsequent etching. This has also been found true for some of the spirals observed in the present case.

In order to throw more light on etch pit formation at the centres of spiral configurations, these centres have been examined with high resolution objectives. Figure 9 shows the pattern obtained when the central portion of the spiral configuration has been sharply focussed and it reveals a finely developed etch pit. The geometry of the etch pit shows that the dislocation at this pit is normal to the surface. On the basis of Frank-Read mechanism, this is probable if the locking is due to an L-shaped dislocation which may be a segment of a prismatic dislocation or of a dislocation which has cross-slied. L-shaped dislocations may also be produced if stress applied on the crystal is sufficient to move dislocations far apart to intersect one another. Two dislocations lying on different slip planes will produce on intersection two L-shaped dislocations which separate and contract under their line tension. Amelinckx (1957) has in fact observed L-shaped dislocations in decorated sodium chloride crystals. Further, it has been observed that in some cases the etch pits are not well developed. The etch pit at the centre of
the spiral of figure 5 is not developed. This is possible if the emerging dislocation is not firmly anchored, thereby resulting in a slight dragging of the anchored point as the spiral rotates under the applied stress. Also, if the anchoring is due to the presence of nodes and/or the impurity atoms, the etch pits may not be well formed. Figure 5 shows that the oppositely winding spirals undergo a number of turns before giving a closed loop. A similar configuration has also been observed in the Frank-Read source obtained by Fedorovtsev et al. (1980) on electrolytic etching of cadmium. Such a Frank-Read configuration may result if the distance between the two anchored points of a dislocation line is large enough and if a supercritical stress be applied suddenly. Under these conditions, the dislocation segment between the two anchored points may make several turns around each point before giving off a closed loop. Two L-shaped dislocations can also give a off a similar configuration; each of the L-shaped dislocation will give a spiral and these later on combine to give the Frank-Read source. A similar reasoning can explain the geometry of figures 7 & 8. These configurations may correspond to complicated patterns in Frank-Read mechanism.
Dissolution Spirals

The evidence presented above strongly indicates that the observed spiral configurations correspond to Frank-Read mechanism in sodium chloride crystals. The probability of these being just dissolution spirals is indeed quite small. To set aside the controversy of these spiral configurations just being dissolution spirals, efforts were made to obtain dissolution spirals on sodium chloride single crystals. The results thus obtained on comparison with these spiral configurations show that dissolution spirals are of different nature than spirals of figures 5 - 8. Thus further evidence besides close resemblance of these spiral configurations to Frank-Read mechanism is presented in terms of dissolution spirals.

By controlled etching spiral structures which are invisible in the unetched conditions can also be revealed. The dissolution spirals which have been observed on (100) faces of sodium chloride crystals would be reported here. All the specimens used were again cleaved from the high purity single crystals procured from the National Physical Laboratory, New Delhi. The crystals were first polished by immersing in distilled water and afterwards rinsed in ethyl alcohol. The etching was done by methanol etchant.
Fig. 10. A single dissolution spiral on (100) surface of sodium single crystal. (x700)
Fig. 11. A pattern which has resulted from the combination of a number of dissolution spirals. (x700)

Fig. 12. A large number of spiral etch pits close together. (x700)
Gevers et al. (1952 & 1953) and Horn (1952) observed that on silicon carbide crystals, centres of growth spirals and surface steps are attacked preferentially. Jessensky (1958) earlier reported growth spirals on sodium chloride. In the present case, the etching of sodium chloride resulted in the development of a fine groove all along the steps which made the structure quite visible even in bright field illumination. Figures 10 - 12 were obtained on (100) face of sodium chloride crystal. Figure 10 shows a single dissolution spiral. Figure 11 consists of a pattern which has resulted from the combination of a number of spirals, at the centres of which can be seen fine etch pits due to the emerging dislocations. Figure 12 shows a large number of spiral etch pits close together.

The removal of atoms from the steps of a screw dislocation will result in the formation of a spiral etch pit, the process being just the opposite of a growth spiral. According to Burton et al. (1961), the pitch of the growing spiral is given by the relation

\[ d = 4 \pi \ell \]

where \( \ell \) is the critical radius of the two-dimensional nucleus. In the case of an evaporating crystal, taking into consideration the elastic strain energy of the
dislocation,

\[ d = 19 \ell \] (Cabrera and Levine, 1956)

The critical radius \( \ell \) is given by the expression

\[ \ell = \frac{\gamma \eta}{kT \log C/C_0} \]

so that

\[ d = \frac{19 \gamma \eta}{kT \log C/C_0} \]

where \( \gamma \) is the crystal solution surface energy, \( \eta \) is the molecular volume and \( C/C_0 \) is the ratio of actual concentration to that of equilibrium concentration of the crystal in the solvent. From this expression, the value of the pitch \( d \) can be estimated for sodium chloride crystals. Taking \( \gamma = 90 \) ergs/cm\(^2\) as the crystal-solution surface energy,

\[ \eta = 4.8 \times 10^{-23} \text{ cm}^3 \]

at 300° K, the value of the pitch will be

\[ d = \frac{19 \times 4.8 \times 10^{-23} \times 90}{300 \times 1.38 \times 10^{-16} \times \log C/C_0} \]

or \( d \sim 10^{-3} \) cm if \( C/C_0 = 0.1 \)

i.e. \( 10^{-3} \) cm is the value of the pitch of the dislocation spiral if it is to be formed at a unit Burgers vector screw dislocation.

In the case of figures 10-12, the value of pitch is of the order of \( 10^{-4} \) cm. It was suggested by Ellis (1955) in his observations of spiral pits on (111) surfaces of germanium that these spiral etch pits were
associated with screw type dislocations having large Burgers vectors. But there is no support for the notion that such large vectors are existing in inorganic crystals such as sodium chloride. Dash (1956) observed dissolution spirals on (110) surface of silicon and according to him these spirals were not related to screw dislocations. He concluded that pits associated both with edge and screw dislocations were of the same type. Vogel and Lovell (1956), however, felt that while they had no direct proof, the spiral pits they observed on (111) surfaces of silicon crystals were associated with screw dislocations. It was difficult to account for them on any other basis. Later on it was suggested by Amelinckx et al. (1957) and Ellis (1957) that these spirals may be formed at helical dislocations such that the pitch of the spiral corresponds to the pitch of the helical. It was, however, observed by Dash (1956) that sometimes the number of spiral etch pits observed is much larger than the number of possible helical dislocations. This contention is supported by the larger number of spiral pits, observed in case of figure 12. This density of spiral pits which is of the order of $10^5/cm^2$, is certainly much higher than the probable number of helical dislocations in sodium chloride crystals. Dash (1956) has suggested that these pits
may not be associated with dislocations. This is hardly plausible in view of the large evident support for the theory of preferential etching.

It is interesting to note that figures 10 - 12 which have been obtained on the same crystal using the same etchant are not exactly similar. The contrast between these figures suggests that the development of such etch pits by etching may depend not only on the Burgers vector or the strain energy of the dislocation, but also on the condition and nature of the film of reaction products which builds up in the solution adjacent to the surface of the crystals. For spiral etch pits, it is possible that the large value of the pitch of the pits depends more upon the influence of this film than upon the magnitude of the emerging dislocations. However, the question of the origin of the spiral etch pits can not be said to be fully established as yet.

In figures 10 - 12 have been reported the dissolution spirals and their origin has also been discussed. The comparison of these dissolution spirals with the spiral configurations of figures 5-8 shows that the two types of spirals are of different nature. In figures 10 - 12 the effect of depth is clear even from the photographs and these present further evidence to the fact that figures 5 - 8 cannot
be attributed to dissolution spirals.

Thus the presence of dislocation configurations corresponding to Frank-Read mechanism is confirmed in sodium chloride crystals. The increase in the number of dislocations in stressed sodium chloride crystals can be explained by the presence of these sources. However, before it can be concluded that dislocation multiplication results solely from the activation of these sources, more experiments under still better and specific conditions may be needed.

Authier et al (1964) have pointed out that the recent work using decoration, electron microscopy, and X-ray topograph techniques has shown that the ideal Frank-Read sources are something of a rarity. Under usual conditions of plastic deformation the lack of proper anchoring and interaction from other dislocations may prevent any single source from operating repeatedly more than a few times.

Moreover, surface sources generally predominate over internal sources in the initial stages of dislocation multiplication in nearly perfect crystals. The ideal Frank-Read source is, however, a feature worthy of study. It is of interest to examine the dislocation conditions that bring it into action and the circumstances that subsequently cause its operation to cease. Very delicate and precise apparatus and observations would perhaps be required to study these details.
Summary

99.99% single crystals of sodium chloride have been selectively etched and the etch patterns in as grown, annealed and plastically deformed crystals have been studied. Methanol acetic acid has been found suitable for the etching of dislocations in sodium chloride crystals as it gives a matched pattern on the opposite surfaces of the cleaved crystal. The etching of (100) surface on indented crystal reveals the presence of dislocation crosses which may result due to the activation of Frank-Read sources in some of the glide planes of the stressed crystal. The stressed crystal was subjected to repeated etching and polishing and each time the etch pattern was studied. In a few of these observations on (110) surface, spiral configurations corresponding to simple and complicated patterns of Frank-Read mechanism have been observed.

By the use of controlled etching, dissolution spiral structures, having large pitch, which were invisible in the unetched condition have also been revealed on (100) faces of crystals. The origin of such spiral structures is still unsettled and the possibility of these being due to screw or helical dislocations has been considered. The latter
possibility is excluded as in certain areas the density of these spirals has been observed to be more than the possible number of helical dislocations. It has been suggested that the spirals are formed at screw dislocations and that the film of reaction products, which builds up in solution adjacent to the surface of the crystal may partly be responsible for the observed large value of the pitch.

The comparison of the dissolution spirals to the spiral configurations observed on (110) surfaces of the stressed crystal provides further evidence to support the presence of Frank-Read mechanism in sodium chloride crystals. Apart from the close resemblance of the spiral configurations to the predicted Frank-Read mechanism spirals, the background, the pitch, and the value of stress required for the operation of the sources are all in agreement with the theory of Frank-Read mechanism.
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