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Etch-Tunnels in Lithium Fluoride Crystals  
and  
Concerning 'Anomalous' Solution and  
Etching Phenomena

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## ABSTRACTS

### I. Etch-Tunnels in Lithium Fluoride Crystals

The dissolution and growth behavior of lithium fluoride crystals in aqueous solutions containing long-chain fatty acids as step-poisons has been investigated. Both positive-crystals (whiskers and platelets) and negative-crystals (etch-tunnels) can be grown respectively from supersaturated and undersaturated solutions of lithium fluoride containing identical concentrations of stearic acid ( $\approx 2 \times 10^{-6} \text{N.}$ ). Dissolution behavior in stagnant environments is of particular interest for etch-tunnels some  $0.5 \mu$  in diameter and more than  $100 \mu$  in length (negative-whiskers) have been observed. Etch-tunnels grow preferentially in  $\langle 100 \rangle$  directions and are rectangular in section, their walls being low surface energy  $\{100\}$  planes.

Two types of etch-tunnel can be distinguished; those nucleated at a surface defect - such as a cleavage step or the point of emergence of a dislocation (D-type) and those nucleated at apparently random points on the crystal surface (R-type). Metallographic observations reveal that dislocations are not essential to negative-crystal growth and it is proposed that tunnels grow simply because dissolution is less efficiently inhibited at the end of a tunnel than at the external surface of the crystal. This is a consequence of the reduced number of poison molecules available to inhibit kink and step motion at the end of a tunnel because of their slow

rate of diffusion in a stagnant environment. Vigorous agitation of the environment suppresses etch-tunnel formation.

## II. Concerning 'Anomalous' Solution and Etching Phenomena

On the basis of observations on the etching and dissolution behavior of LiF crystals in aqueous solutions of fatty acids, it is suggested that certain solution phenomena previously considered anomalous are no longer so once the significant role of lattice defects and step-poisons in the dissolution process is appreciated.

## I. Etch Tunnels in Lithium Fluoride Crystals

### I.1 INTRODUCTION

There has been much discussion in the past as to the possible reciprocity of crystal growth and dissolution phenomena<sup>1</sup>. Debate has often centered upon whether or not the presence of small concentrations of a soluble impurity (poison) can affect both dissolution and growth behavior in an equivalent manner. To resolve some of the conflicting experimental evidence, Sears<sup>2</sup> has suggested that two types of poison be recognized. The first and more widely investigated type - of which large organic molecules such as the dyes are typical - are termed growth-poisons and are most effective at concentrations of  $10^{-3}$  -  $10^{-4}$  N. They are frequently grown into crystals in appreciable quantities and their poisoning action is not so effective in dissolution. The second type, described as step-poisons, are effective at concentrations of  $10^{-5}$  -  $10^{-6}$  N., their poisoning action appears to be reciprocal in growth and dissolution, and they are not grown into the crystal. Sears<sup>2</sup> has reported that certain complex inorganic ions can act as step-poisons, for example ferric fluoride for the dissolution<sup>3</sup> and growth<sup>4</sup> of LiF crystals in aqueous solutions.

The purpose of this paper is to report the results of an investigation in which certain large organic molecules, namely the  $C_{14}$  -  $C_{18}$  fatty acids, have been utilized as step-poisons, and to describe some observations on a particular form of crystal dissolution termed 'etch-tunneling'.

## 1.2 THE APPROACH

The rate and manner of dissolution of a LiF crystal into a corrosive environment depends on several factors including the degree of undersaturation of the environment and the possible presence of step-poisons. In unpoisoned, highly undersaturated environments, for example pure water, the rate of dissolution of a crystal parallel to its surface,  $V_p$ , is much greater than the rate normal to its surface,  $V_n$ , even at such energetic sites as the points of emergence of dislocations. To produce an observable pit,  $V_p$  must be  $\gg 5V_n$ , as in Fig. 1 at A. To achieve this,  $V_p$  can be decreased by the adsorption of inorganic ions<sup>3</sup> or organic molecules<sup>5</sup> at kink sites or by reducing the degree of undersaturation of the environment, and  $V_n$  can be increased locally in the presence of a lattice defect by virtue of the extra strain energy available for the nucleation of unit pits.

If, by suitable adjustment of environmental factors,  $V_p$  can be reduced below  $V_n$ , then the formation of 'etch-tunnels' might be expected, Fig. 1 at B. Indeed, such 'anomalous solution phenomena'<sup>6</sup> were observed as long ago as 1865 by Haushofer<sup>7</sup> in calcite and by other early mineralogists in other materials. More recently, Sears<sup>8</sup> has noted the formation of 'etch-channels' in LiF after immersing a freshly cleaved crystal face down in a beaker of distilled water for two weeks. In this instance, the formation of channels was attributed to preferential etching along dislocations in the presence of a poison (ferric ions) contributed by the

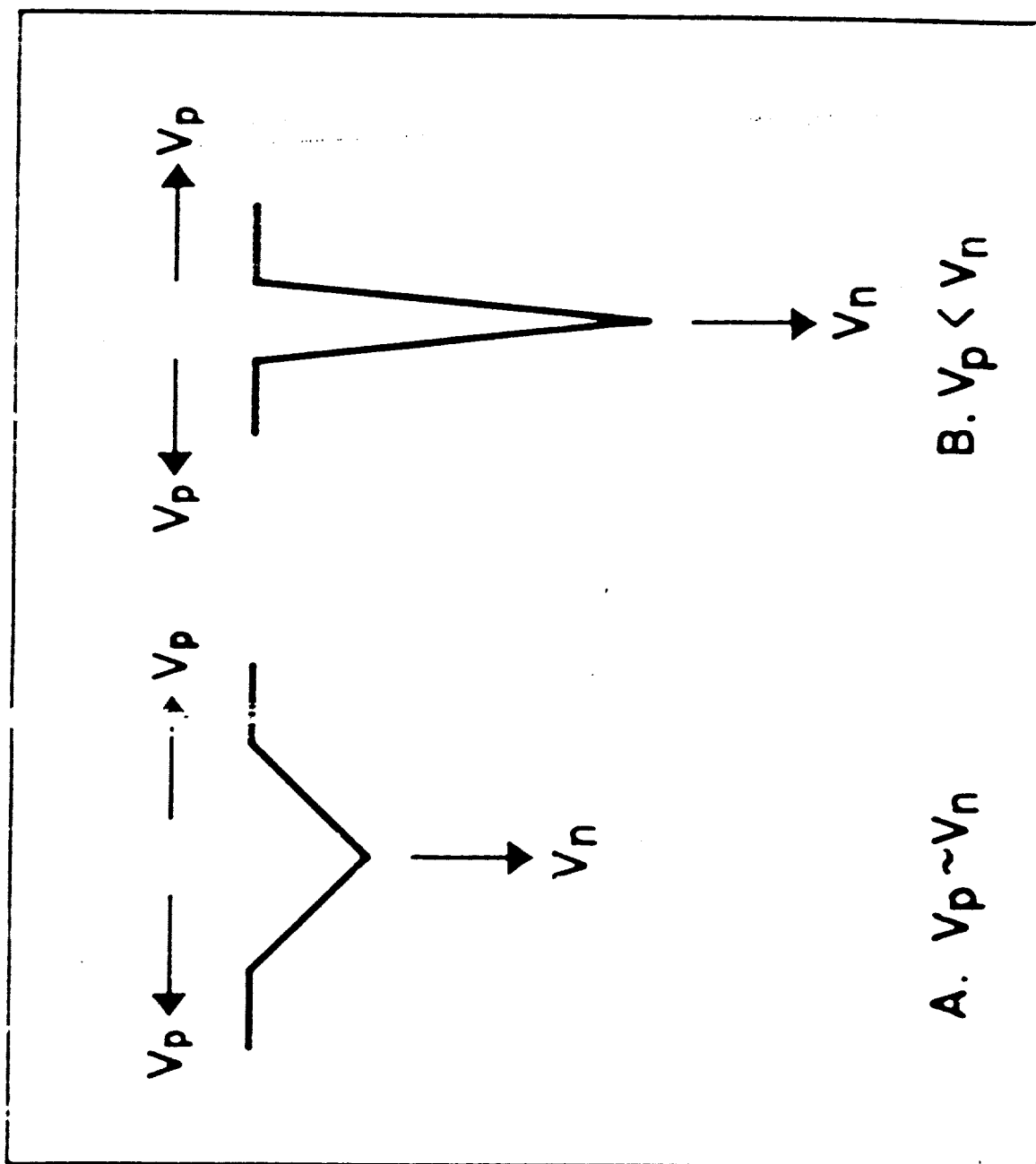


Figure 1 - Formation of an etch-tunnel.

dissolving crystal phase.

The present experiments are based on the observation that long chain fatty acid molecules are strongly adsorbed at certain sites on the surface of  $\text{LiF}^9$  and that aqueous solutions of the  $\text{C}_{14}$ - $\text{C}_{18}$  acids can serve as dislocation-revealing etchants for  $\text{LiF}^5$ . Utilizing these fatty acids as inhibitors, a study has been made of the effects of poison concentration, degree of saturation and agitation of the environment and time on etch-tunnel formation. Other experiments were performed in which whiskers and platelets of  $\text{LiF}$  were grown from similarly poisoned but supersaturated solutions. Similarities in appearance between etch-tunnels and 'positive' whiskers and platelets suggest that etch-tunnels may be conveniently described as negative-crystals<sup>10</sup>, or perhaps more precisely described as negative-whiskers<sup>8</sup> or negative-platelets, as appropriate to their form.

### 1.3 EXPERIMENTAL TECHNIQUES AND OBSERVATIONS

#### 1.3.1 - Etch Tunnels.

Aqueous solutions of myristic ( $\text{C}_{13}\text{H}_{27}\text{COOH}$ ) and stearic ( $\text{C}_{17}\text{H}_{35}\text{COOH}$ ) acid of  $10^{-5}$  -  $10^{-8}$  N. were prepared and freshly cleaved crystals of  $\text{LiF}$  were immersed in these solutions for various times up to 105 minutes<sup>a</sup>. The solutions were not agitated and, after an appropriate

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<sup>a</sup> The fatty acids were purchased from the California Corporation for Biochemical Research and the  $\text{LiF}$  crystals from the Harshaw Chemical Company. The  $\text{LiF}$  crystals contained  $< 10$  p.p.m.  $\text{Al} + \text{Fe}$ .

interval, the crystals were removed, cleaved into two pieces, and the freshly cleaved faces examined by transmitted light. Figure 2 illustrates a typical observation: A is a negative-whisker some  $0.5 \mu$  in diameter and  $40 \mu$  long and B is a negative-platelet; at C negative-platelets are becoming negative-whiskers. Etch-tunnels in LiF are rectangular in section their walls being low surface energy  $\{100\}$  planes. They grow preferentially in  $\langle 100 \rangle$  directions and increase in length at a decreasing rate with time. Tunnel length and form depend on many factors including the poison concentration, Fig. 3, the degree of saturation of the solution with LiF, and, in general, on those factors which govern the stability of an adsorbed polar molecule - LiF 'complex'<sup>9,b</sup>. With increasing complex stability, i.e., increasing poison and LiF concentration in the environment, tunnels change from short, wide, negative-platelets to long, narrow, negative-whiskers and finally dissolution is almost completely inhibited.

In distilled water, poison concentrations of some  $2 \times 10^{-6} N$ . stearic acid produce tunnels of maximum length and negative-whiskers of  $0.5 - 1.0 \mu$  in diameter and  $\sim 100 \mu$  in length are often observed. The addition of up to  $0.4 \text{ gm/liter}$  of LiF to the solution tends to induce the growth of negative-whiskers rather than negative-platelets and tunnels

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<sup>b</sup> Adsorption results from the electrostatic attraction of the dipole of a polar molecule towards the surface of the crystal. For brevity, the adsorbed polar molecule -  $\text{Li}^+$  ion -  $\text{F}^-$  ion aggregate is referred to as a 'complex'.



Figure 2 - Etch-tunnels in LiF. A is a negative-whisker and B is a negative-platelet; at C negative-platelets are becoming negative-whiskers. The etchant was  $3 \times 10^{-6}$  N. stearic acid in water.

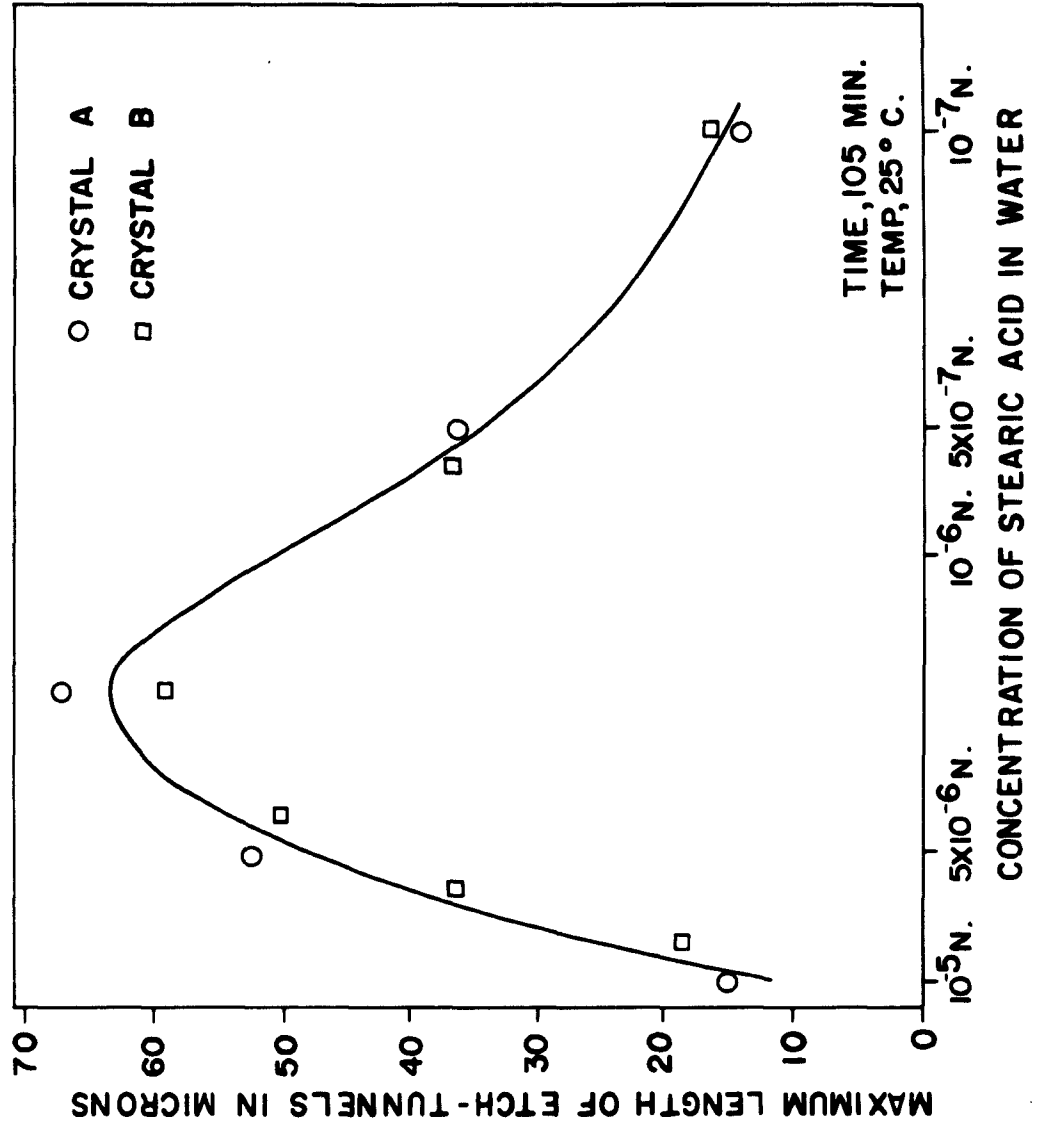


Figure 3 - Effect of poison concentration on etch-tunnel length.

up to  $200\mu$  in length were occasionally produced in such solutions.

However, tunnels were not formed in poisoned solutions containing

$> 0.7$  gm/liter of LiF. (The solubility of LiF in water at  $25^{\circ}\text{C}$ ,  $C_s$ , is  $\approx 1.33$  gm/liter<sup>11,12</sup>). A reduction in poison concentration induces the formation of negative-platelets and then large rectangular pits.

Figure 4 displays a cross-section of some gross pits formed at the surface of a crystal during immersion for 105 minutes in an unpoisoned, aqueous solution containing  $0.4$  gm/liter of LiF. Figure 5 is a micrograph of the edge of the top face of the same crystal and illustrates the crystallographic, yet somewhat haphazard nature of the dissolution process in 'unpoisoned' environments.

In addition to variations in form, two main types of etch-tunnel can be distinguished; those which are associated with a surface imperfection or 'defect' - such as the point of emergence of a dislocation or a cleavage step - 'D' type; and those which are formed only after an incubation period and which are nucleated at apparently 'random' points on the crystal surface - 'R' type. Figure 6 illustrates the development of both types of tunnel: Fig. 6.1 shows an area of a freshly cleaved LiF crystal after etching for two minutes in an aqueous ferric chloride etchant<sup>3</sup> - etch pits indicate the points of emergence of dislocations; fig. 6.2 illustrates the same area after re-etching for 5 minutes in aqueous  $2 \times 10^{-6}\text{N}$ . stearic acid. Flat-bottomed pits have formed at the dislocations (compare at A,B,...E in Figs. 6.1 and 6.2) and elsewhere (a,b,...e), possibly



Figure 4 - Section through gross pits formed during immersion in solution of 0.4 gm/liter of LiF in water.

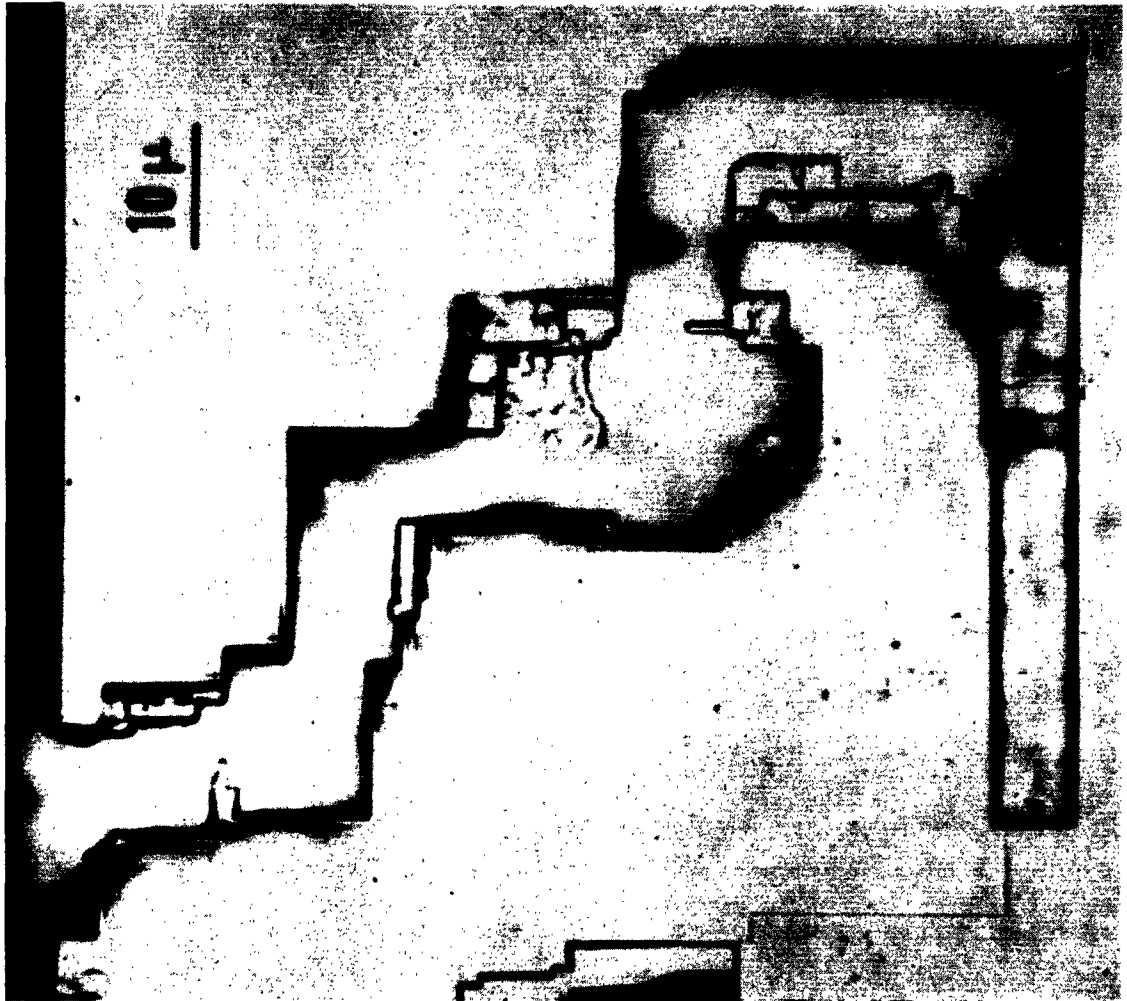
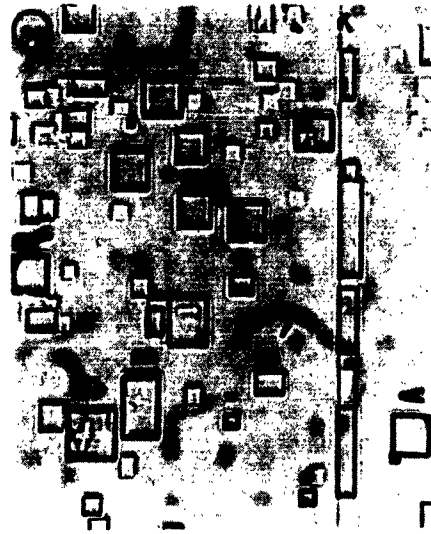


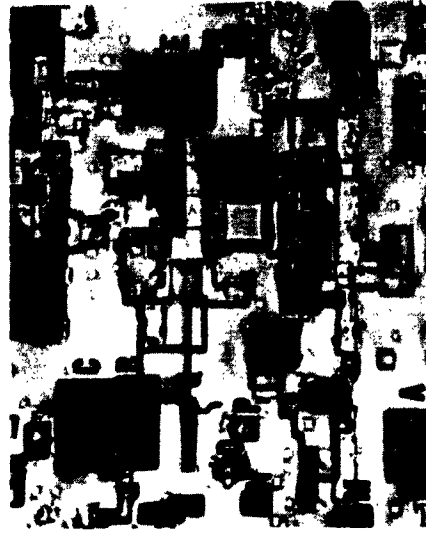
Figure 5 - Top face of crystal illustrated in Fig. 4 demonstrating the nature of dissolution in unpoisoned environments.



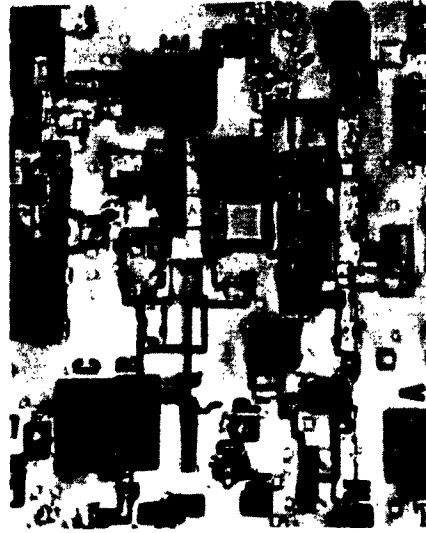
6.1 Freshly cleaved crystal after etching for 2 minutes in  $\text{FeCl}_3$  etchant.



6.2 Same area after 5 minutes in aqueous  $2 \times 10^{-6}$  N. stearic acid - flat-bottomed pits at dislocations A... E and elsewhere, a...e.



6.3 Area after 20 minutes in stearic acid etchant - D-type tunnels formed at dislocations A...E.



6.4 Area after 2 hours in stearic acid etchant - R-type tunnels have formed at positions M...V. These positions are also denoted by arrows in 6.1.

at sub-microscopic precipitate particles or vacancy clusters<sup>9</sup>. Figure 6.3 illustrates the area after a further 15 minutes in the stearic acid etchant. The pits at A, B, ...E have enlarged and are transforming into D-type tunnels, this being indicated by a darkening of the etch-pit. Finally, Fig. 6.4 displays the same area after a total of 2 hours in the stearic acid etchant. D-type tunnels now are readily apparent at A, B, ...E and, in addition, R-type tunnels have formed at M, N, ... V. The locations of the tunnels M, N...V are indicated by arrows in Fig. 6.1 demonstrating that R-type tunnels are not associated with the points of emergence of dislocations nor, apparently, with the 'random' etch-pits of Fig. 6.2.

D-type tunnels associated with dislocations sometimes grow along them, as in the sub-boundary illustrated in Fig. 7. In this example the tunnels appear to follow relatively straight screw dislocations into the crystal for some  $10\mu$  and then to branch off into a boundary network. However, growth along dislocations, especially in a  $\langle 110 \rangle$  direction as in Fig. 7, is a particular rather than a general phenomenon. Though a dislocation lying in a  $\langle 100 \rangle$  direction, say a  $(101) [10\bar{1}]$  edge dislocation, is likely to be tunneled, a dislocation lying in another direction may or may not be tunneled. As an example, Fig. 8 shows D-type tunnels associated with a cleavage step AB and C, D, E and F are dislocation sites previously revealed by a  $\text{FeCl}_3$  etchant. Note that tunnels have formed at C and E but not at D and F, even after 105 minutes in  $5 \times 10^{-6}\text{N}$ . stearic acid.



Figure 7 - D-type tunnels associated with a sub-boundary.

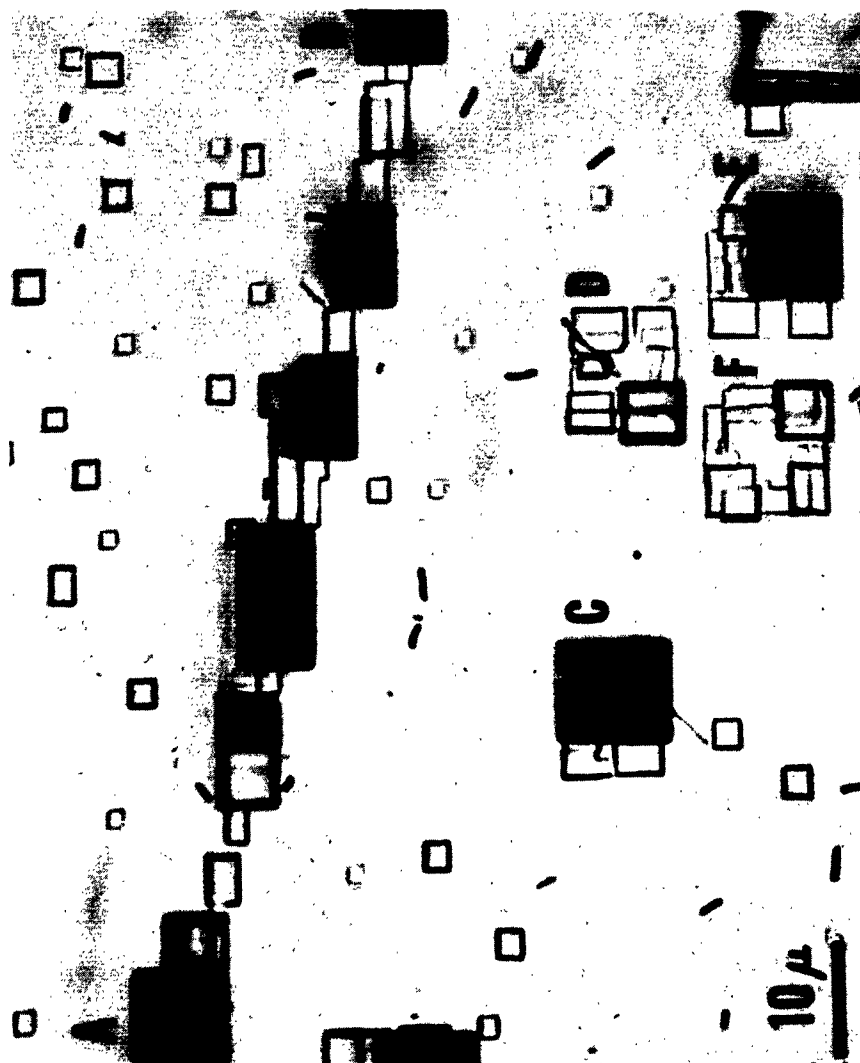


Figure 8 - D-type tunnels associated with a cleavage step, AB, and with dislocation sites at C and E, but not at D and F.

Other experiments demonstrated that gentle agitation of the environment increases the rate of tunneling but vigorous agitation, or heating to  $100^{\circ}\text{C}$ , inhibits tunnel formation. The incubation period for R-type tunnel formation also appears to depend on poison concentration. R-type tunnels usually form after some 30 - 50 minutes in a fresh solution of  $5 \times 10^{-6}\text{N}$ . stearic acid and then increase in number with time. However, if the solution has been used previously for a tunneling experiment, R-type tunnels may require 150 minutes to form in a freshly cleaved crystal.

Other crystals were tunneled for 105 minutes in  $5 \times 10^{-6}\text{N}$ . stearic acid and then immersed in distilled water for 60 minutes, dried, cleaved and examined by transmitted light. Figure 9 illustrates a typical observation. Between A and B the tunnels are typical negative-platelets but between B and C they increase in width. Other observations demonstrated that the widening occurred during the immersion in distilled water.

### 1.3.2 - Positive Whiskers and Platelets

To demonstrate the effectiveness of the fatty acids as growth poisons for LiF, aqueous solutions of 2.0 - 3.25 gm/liter of LiF (supersaturated) containing  $2.0 \times 10^{-6}\text{N}$ . stearic acid were prepared following the procedures outlined by Sears<sup>4</sup>. The morphology of the whiskers and platelets grown from these solutions on to the  $\{100\}$  surfaces of freshly cleaved LiF crystals was dependant on the degree of supersaturation.



Figure 9 - Tunnels formed during immersion first in  $5 \times 10^{-6}$  N. stearic acid (105 minutes) and then in distilled water (60 minutes).

Highly supersaturated solutions,  $> 2.5$  gm/liter of LiF, produced large, rectangular platelets; solutions containing 2.2- 2.5 gm/liter of LiF induced both platelet and whisker growth, Fig. 10, and solutions containing 2.0 - 2.2 gm/liter of LiF produced whiskers, sometimes up to 3 - 4 mm. in length. Positive-whiskers grew more rapidly from solutions containing  $2.0 \times 10^{-6}$  N. stearic acid and  $\approx 2.0$  gm/liter of LiF ( $\approx 20 \mu$ /min) than did negative-whiskers from solutions of identical poison concentration and 0.4 gm/liter of LiF ( $\approx 1 \mu$ /min).

#### I. 4 DISCUSSION

##### I. 4. 1 - Etch-Tunnels

Etch-tunnels form when a LiF crystal is immersed in a stagnant, corrosive environment containing a particularly strongly adsorbed step-poison, and it has been observed that whilst dislocations can, and sometimes do, assist the tunneling process, their presence is not essential to it. Dislocations and surface imperfections merely serve as sources of unit pits or kinks which may (Fig. 8 at C, E, and AB) or may not (Fig. 8 at D, F) be utilized in tunnel nucleation. The mechanism of tunnel growth also is independent of the presence of a line defect, though the strain energy<sup>13</sup> or core energy<sup>14</sup> of a propitiously sited line defect may assist tunnel growth or cause a tunnel to tend to grow in a particular direction, Fig. 7.

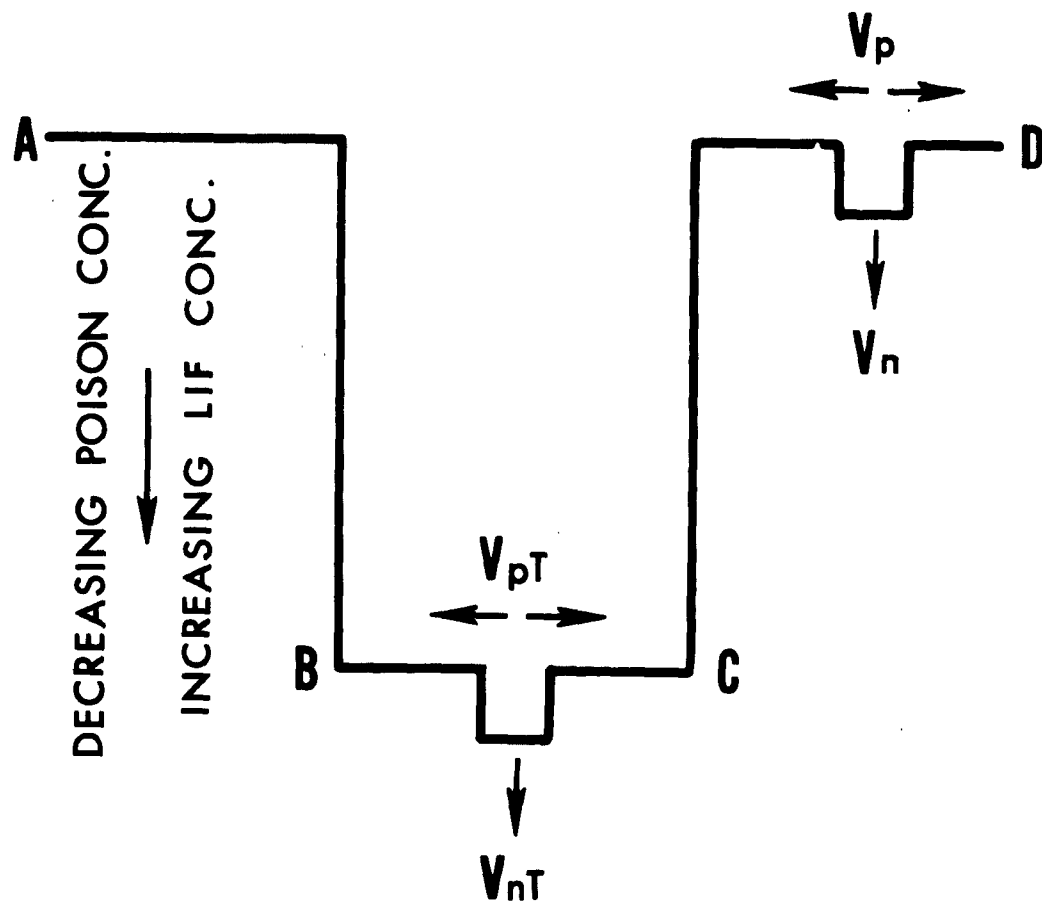
Tunnels continue to grow because the dissolution process at the end of a tunnel is favored over general dissolution of the external surface,



Figure 10 - Positive-whiskers and platelets of LiF.

that is, in Fig. 11,  $V_{pT} > V_p$ , and since  $V_n$  is related to  $V_p$ ,  $V_{nT}$  is also  $> V_n$ . In the present experiments, the differences in dissolution rate probably are caused by differential concentration effects, for at the growing end of a tunnel the poison concentration will be less and the degree of saturation of the aqueous environment with LiF will be greater than at the open end. In fact, it appears that the tunneling phenomenon can be largely explained in terms of these two factors, which tend to work in opposite directions. For example, the motion of kink sites away from a freshly nucleated pit on the external surface of a crystal (Fig. 11, AD) is promptly inhibited by the adsorption of readily available poison molecules. On the other hand, because of the reduced poison concentration at the end of a tunnel - a consequence of the relatively slow rate of diffusion of long-chain fatty acid molecules in a stagnant environment - a unit pit nucleated there (Fig. 11, BC) is able to expand over a considerable distance, before kink motion is inhibited.

Tunnel growth is opposed by the increasing LiF concentration at the end of a tunnel which tends to reduce both the rate of nucleation and rate of expansion of unit pits. This factor probably is responsible for the commonly observed reduction in width with increasing length of negative platelets, Fig. 2 at C. If, however, the effects of decreasing poison and increasing LiF concentration balance out along the length of a tunnel, a parallel sided tunnel results, Fig. 2 at A; but if the poison concentra-



$$V_{pT} > V_p$$

$$V_{nT} > V_n$$

Figure 11 - The mechanism of tunnel growth.

tion is severely reduced at the growing end of a tunnel and the LiF concentration there does not approach 0.7 gm/liter, then the tunnel increases in width with length, as demonstrated by the experiment in which a specimen was transferred from a stearic acid 'tunneling' solution to distilled water, Fig. 9. Tunnels of greater length than  $\approx 200 \mu$  were not observed however long the crystal remained in the corrosive environment. Since tunnels form extremely slowly, if at all, in solutions containing 0.7 gm/liter of LiF, it is possible that tunnel growth ceases when the LiF concentration at the growing end of the tunnel significantly exceeds this value. Gentle agitation of the environment aids tunnel growth probably by promoting transport of the  $\text{Li}^+$  and  $\text{F}^-$  ions out of the tunnel and thus reducing the concentration differential. However, vigorous agitation, or heating to  $100^\circ\text{C}$ , suppresses tunnel formation either by increasing the transport of poison molecules to the end of the tunnel via improved surface or through-the-liquid diffusion, or by mechanically or thermally disrupting the adsorption process at the external surface and thereby increasing the overall dissolution rate. In view of the stability of the LiF-polar molecule complex noted in previous studies<sup>9</sup>, the former possibility seems more likely.

R-type tunnels are not associated with the points of emergence of slip or grown-in dislocations nor with any visible surface imperfection and require an incubation period for formation. Once nucleated they grow at a similar rate to D-type tunnels - about  $1 \mu$ /minute initially, and probably by the same mechanism. However, their origin is uncertain.

One possibility is that they are associated either with vacancy clusters or with certain sites on an otherwise perfect crystal surface where a unit pit happens to be created, i. e., they are truly randomly distributed. On this model, the incubation period is the time required for a tunnel-nucleating pit to grow either to a critical depth or, and more likely, to a critical depth to width ratio such that a significant difference in poison concentration is produced between the top and bottom of the pit in a stagnant environment. The incubation period is relatively long because  $V_n$ , in the absence of a line defect, is small, but once a pit reaches this critical size it becomes self propagating, i. e., becomes a tunnel, and its growth ceases only when the LiF concentration at the end of the tunnel prohibits further unit pit nucleation. Only a small proportion of all the unit pits created at the external surface are likely to grow to the appropriate dimensions to nucleate a tunnel, but the continuing creation of unit pits at the external surface accounts for the increase in number of R-type tunnels with time.

It is also possible that some of the R-type tunnels are associated with prismatic dislocation loops, for such defects have been observed in  $MgO$ <sup>15</sup> (plus and minus pairs of dislocations) and suspected in  $LiF$ <sup>16</sup> (trails) on the basis of the high density of intermittently etching pits found in bands of edge dislocations. Moreover, dislocation loops of this type tend to be confined to a  $\langle 100 \rangle$  direction. However, on the basis of the

present observations, it is considered that the majority of R-type tunnels are not associated with any form of line defect.

#### 1.4.2 - Reciprocity of Growth and Dissolution

Figure 12 summarizes the effects of environmental LiF concentration on the dissolution and growth behavior of crystals in the presence of  $2.0 \times 10^{-6} N$ . stearic acid. Some measure of symmetry<sup>10</sup> or reciprocity of positive and negative crystal morphology about the solubility limit is apparent. However, Buckley<sup>1</sup> has commented that for complete reciprocity of growth and dissolution behavior, growth velocities (in a supersaturated environment) should be identical, but in the opposite sense, to dissolution velocities (in an undersaturated but presumably 'equivalent' environment). Whilst the practical problem of what constitutes an 'equivalent' environment remains, it is clear that on this definition the observations do not exhibit truly reciprocal behavior, for positive-whiskers grew more rapidly from a solution containing  $1.5 C_s$  LiF than did negative-whiskers in a solution of  $0.3 C_s$  LiF - both solutions having identical poison concentrations. However, such variations in the rate of growth of positive and negative crystals in the present experiments appear intuitively reasonable, for the continued growth of an etch-tunnel involves the diffusion of ions and long chain fatty acid molecules over relatively large distances ( $25 - 100 \mu$ ) through narrow ( $1 - 2 \mu$  diameter) pipes, and the extensive growth of tunnels ( $> 200 \mu$ ) is hindered by the increasing LiF concentration at the growing end of the tunnel. Such transport and concentration problems do not arise in the growth of positive crystals from solution.

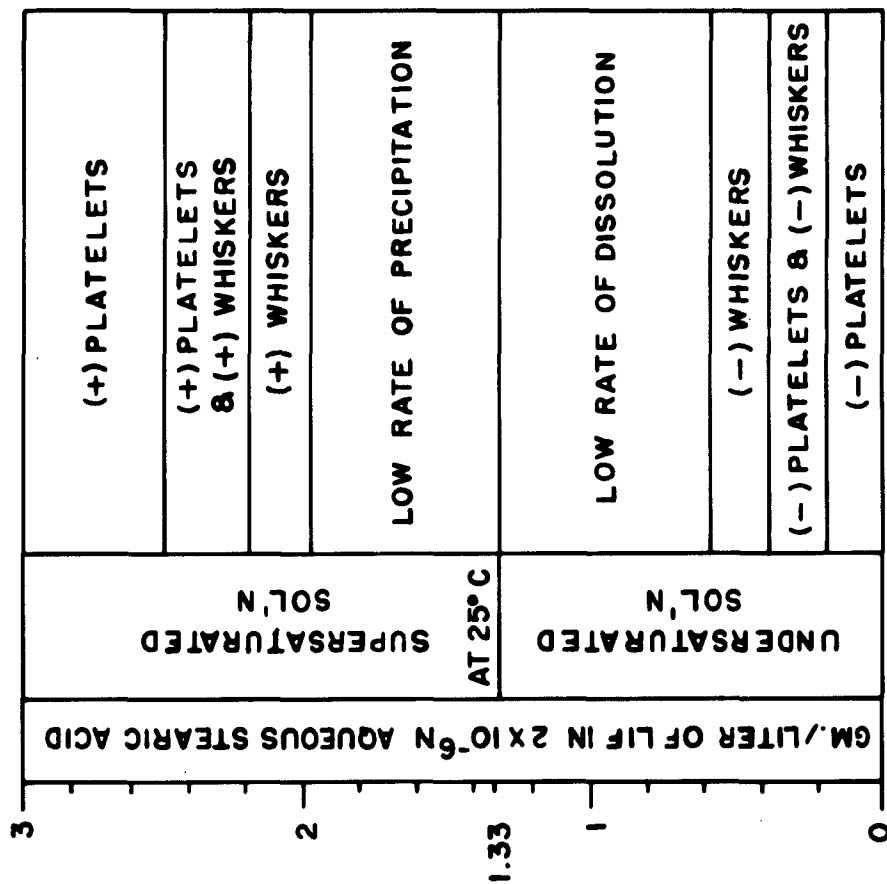


Figure 12 - Illustrating symmetry of positive- and negative-crystal morphology about the solubility limit in the presence of  $2 \times 10^{-6}$  N. stearic acid.

## 1.5 - SUMMARY

Within limits imposed by poison-molecule transport and differential concentration problems in dissolution, certain large organic molecules can act as step-poisons, as defined by Sears<sup>2</sup>, for LiF. In stagnant, corrosive environments containing such step-poisons, a specific form of dissolution termed etch-tunneling can occur: etch-tunnels form at the points of emergence of dislocations and other surface imperfections (D-type) and elsewhere, possibly nucleated at vacancy clusters or at sites where unit pits are created and which, by chance, grow to certain critical dimensions (R-type). Tunnel growth is a result of differences in poison concentration in the environment and at the end of a tunnel and this, in turn, is a consequence of the relatively low rate of diffusion of large organic molecules in stagnant environments.

## II. Concerning 'Anomalous' Solution and Etching Phenomena

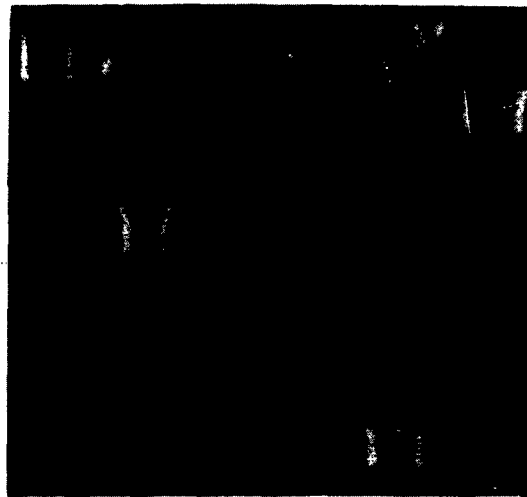
In his book published in 1927, the late A.P. Honess<sup>6</sup> summarised observations made by himself and by earlier mineralogists on certain etching phenomena that were not readily explicable in terms of crystal structure alone, for example the formation of various types of 'beaks'. Again, in 1951, Buckley<sup>1</sup> commented on anomalies in the development of etch figures which 'mask their true symmetry'. However, during the past ten years or so, it has become apparent that the presence of such lattice defects as dislocations and vacancy clusters at the surface is largely responsible for the nucleation of etch pits, and that the form of the nucleating defect (point or line) and such environmental factors as the presence, type and concentration of kink-motion inhibiting poisons, etc., also play a significant role in determining etching behavior. The purpose of this note is to report some observations on the dissolution behavior of lithium fluoride crystals in aqueous surface-active environments which suggest possible explanations for certain of Honess's 'anomalous' solution phenomena.

It has been observed that aqueous solutions of the long-chain fatty acids can serve as etchants for lithium fluoride revealing the points of emergence of dislocations and other surface features of interest<sup>5</sup>. Dilute solutions of stearic and myristic acids ( $\approx 10^{-5}$  N. -  $10^{-6}$  N.) are of particular interest for they can be used to control and reveal the motion of slowly-moving dislocations<sup>9,17</sup>. For example, the path of a cross-gliding

screw dislocation can be revealed as a stable etched-groove or 'track', Fig. 13. Other experiments have demonstrated that by suitably controlling those environmental factors which govern the dissolution of a crystal in the presence of step-poisons<sup>18</sup>, extensive etch-tunnels perhaps 0.5 - 1.0  $\mu$  wide and over 100  $\mu$  in length can be produced in lithium fluoride crystals. Following Friedel<sup>10</sup>, such tunnels may be conveniently considered as 'negative-crystals'. A comparison of these phenomena with the various types of solution 'beak' discussed by Honess reveals remarkable similarities some of which are illustrated in Figs. 14, 15 and 16.

Figure 14(a)<sup>19</sup> is a sketch of a 'solution-channel' observed on the (010) face of a colemanite crystal: Fig. 14(b) illustrates a similar etching formation on a  $\{100\}$  cleavage face of a lithium fluoride crystal. In the latter, what is in fact observed are the tracks of the gliding screw components of an unstable screw-edge-screw dislocation half-loop introduced into the surface of the crystal during the cleaving operation. Such half-loops are usually quite shallow ( $\sim 10 \mu$  deep) and, if they are smaller than a certain critical diameter (usually some 5 - 30  $\mu$ , this dimension being a function of the yield stress of the crystal<sup>20</sup>), are unstable and eventually anneal out of the crystal at room temperature. It seems likely, therefore, that the solution-channel of Fig. 14(a) similarly records the annealing-out of a dislocation half-loop.

Figure 15(a)<sup>19</sup> is a sketch of a 'beak' attached to the corner of a flat-bottomed etch pit again on the (010) face of a colemanite crystal.



**Figure 13 - Track of cross-gliding screw dislocation revealed after etching in  $5 \times 10^{-6}$  N. aqueous myristic acid.**

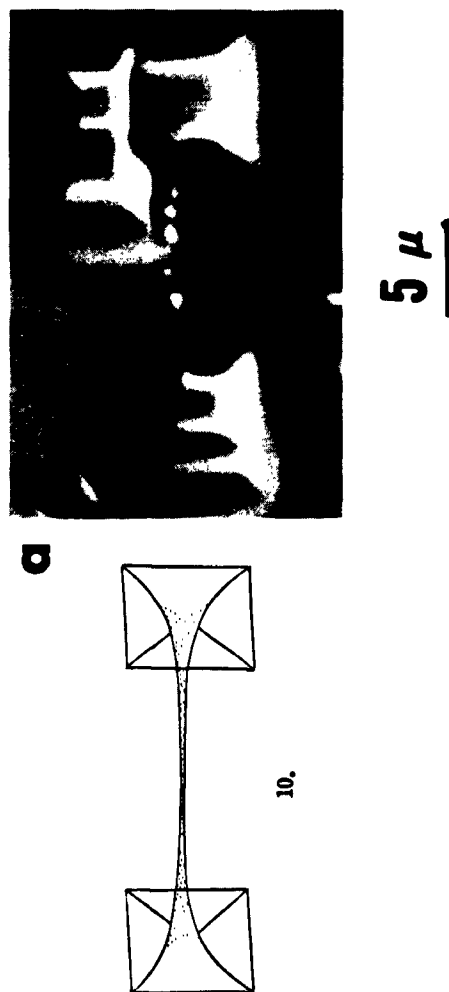


Figure 14 - (a) Sketch of 'solution-channel' on (010) colemanite (after Honess).

(b) Tracks resulting from the annealing-out of a dislocation half-loop on  $\{100\}$  lithium fluoride.

A similar formation in lithium fluoride is illustrated in Fig. 15(b): note that this etch pit is also flat-bottomed. This is considered to be significant, for other observations<sup>5,9,17</sup> lead us to suggest that such 'beaks' are the tracks of moving dislocations, usually cross-gliding screws. The etch-pit is flat-bottomed because the nucleating dislocation has moved away and its latest position is indicated by the end of the track or beak. Curvature of a beak results from alternate motion on glide and cross-glide planes.

Figure 16(a)<sup>19</sup> is a tubular or extended 'normal' beak in the (001) face of an apophyllite crystal and is of the type first reported by Haushofer<sup>7</sup> in 1865. For comparison, Fig. 16(b) illustrates the cross-section of an etch-tunnel formed at the bottom of an etch pit in lithium fluoride after immersion in  $2 \times 10^{-6}$  N. aqueous stearic acid for 105 minutes. Such tunnels are often, but not necessarily, associated with dislocations: Fig. 7, for example, displays etch-tunnels associated with dislocations arrayed in a sub-boundary. Etch-tunnels are formed during extended immersion in a slightly corrosive environment. A low rate of solution in the environment appears to be prerequisite for this specific form of dissolution. Experimentally this can be achieved in the presence of a suitable concentration of a strongly adsorbed step-poison, e.g., stearic acid for lithium fluoride<sup>18</sup>, or in a stagnant, near-saturated environment<sup>8</sup>. A more complete discussion of the factors which determine the form and rate of growth of etch tunnels will be published at a later date<sup>18</sup>.



**a**

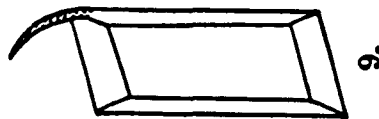
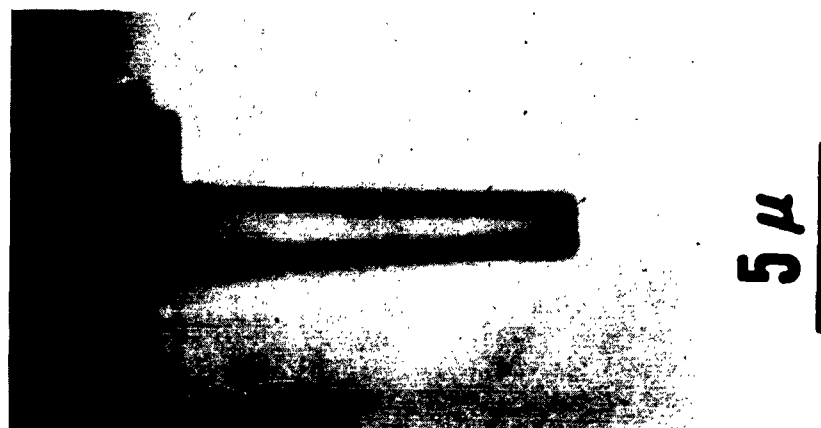


Figure 15 - (a) Sketch of 'beak' at corner of etch pit on (010) colemanite  
(after Honess).

(b) Track of slowly moving dislocation in lithium fluoride.



a

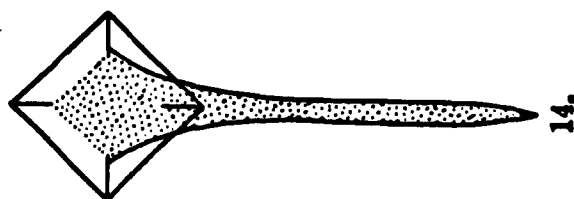


Figure 16 - (a) Sketch of tubular beak in (001) apophyllite (after Honess)  
(b) Cross-section of etch-tunnel in lithium fluoride.

Becke<sup>21</sup> has noted another example of apparently anomalous etching behavior. Etch pits on the top and bottom faces of thin cleavage plates of fluorite were sometimes oppositely directed (enantio-polar) and this could not be explained satisfactorily in terms of twinning or surface irregularity. However, the presence of dislocation lines traversing the thickness of the crystal and lying on planes meeting the surface at an angle could well be responsible for such an effect, as demonstrated schematically in Fig. 17.

In short, recent observations on the dissolution behavior of lithium fluoride crystals lead us to conclude that many of the 'anomalous' solution and etching phenomena recorded by Honess and earlier workers are no longer anomalous once the significant role of lattice defects and step-poisons in the dissolution process is appreciated. The formation of tubular beaks or solution channels is usually associated with preferred dissolution either along dislocations - by virtue of the extra strain energy available for the nucleation of unit pits - or in certain crystallographic directions as a result of anisotropic dissolution in the presence of poisons<sup>3</sup>. Other beaks result from dislocation motion at the surface.

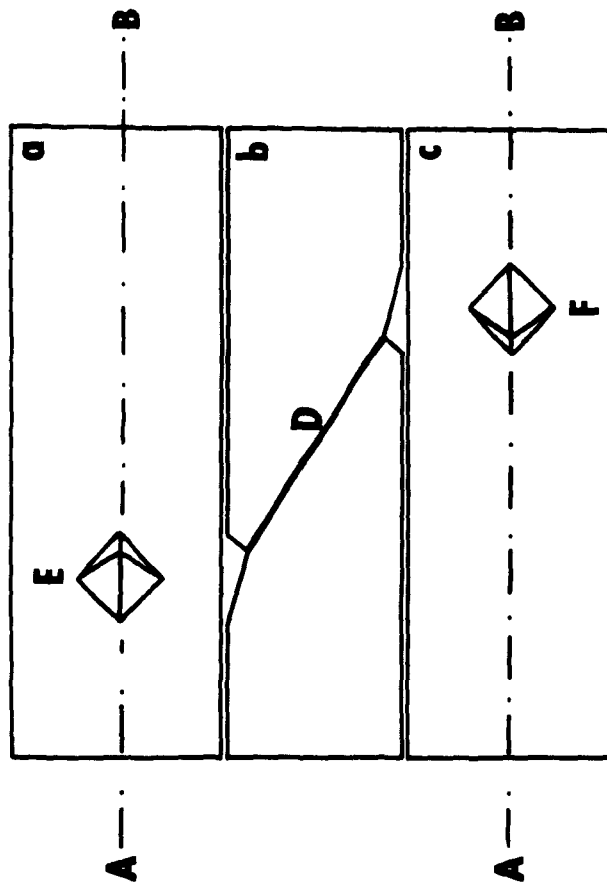


Figure 17 - Possible interpretation of Becke's etching phenomenon.

(a) and (c) represent the top and bottom faces of a thin crystal;  
(b) is a section through the crystal at A...B revealing the dislocation D which is responsible for the oppositely-directed etch pits at E and F.

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