Pramāṇa, Vol. 17, No. 1, July 1981, pp. 39–53. © Printed in India.

An optical topographic technique to study the dissolution kinetics at dislocation sites in sodium chloride crystals

A K SHRIVASTAVA and K G BANSIGIR
School of Studies in Physics, Jiwaji University, Gwalior 474 002, India

MS received 1 January 1981; revised 8 May 1981

Abstract. A technique has been developed to study the dissolution kinetics at dislocation sites in sodium chloride single crystals. A parallel beam of light is allowed to fall upon the silvered etched surface of the crystals and the reflected beam is received back on a photographic film. The pattern thus obtained on the photographic film gives information about (i) the structure of the etched surface (ii) the nature of the surface forming the pit and (iii) the slope of the pit at the source of dissolution.

Keywords. Dissolution; multiple reflection; topograph; etching.

1. Introduction

Attempts have been made to understand the dissolution kinetics at dislocation sites in single crystals, but very little progress has been made so far. Ives and Hirth (1960) studied the theories of dissolution put forward by Frank (1958) and Burton *et al* (1951) and found that the results obtained by the latter workers agreed with many of the theoretical conclusions. In verifying the theoretical predictions, an interference technique was used, which did not however give correct information about the slope of the pit at the source of dissolution (Ives and Hirth 1960), the nature of the sides which form the pit; or the general features of the dissolved crystal face. A technique was therefore developed which is more sensitive than the interference technique. Although reflectograms have been used by Brewster (1840) to study the symmetry and structure of the dissolved crystal faces, they have neither been used for the study of the dissolution kinetics nor has the technique been perfected. The present paper reports the technique, the effects of poison concentration and the effect of time on the etch pit formation.

2. Experimental

2.1 *Description*

In figure 1 light from a source A is focussed by a lens L on the slit of a collimator C. Parallel beams emerging from the collimator fall on a circular hole S_1 of 0·8 mm diameter. The narrow beam passes through a photographic film having a circular hole of 2 mm diameter, fixed to a film holder which acts as a second circular slit S_2, and finally falls on a silvered specimen under investigation fixed to a specimen holder *SH*. S_1 is part of a light tight box which encloses the film and specimen. A vernier scale is attached to the holder *SH* and its position with respect to the photographic film can be accurately determined using a scale fixed to the base of the box. Two more circular slits S_3 and S_4 are also provided for adjustment.

2.2 *Principle*

When a parallel beam of light falls upon an etched silvered face at right angles to the surface, it is reflected back and the rays retrace their path in the opposite direction. But if the reflecting surface contains tiny faces with different inclinations, then the light falling on these tiny faces, gets reflected towards the film as shown in figure 2, which also shows how the position of the reflected ray alters with the variation of the inclination of the pit face. It is found that one can expect multiple reflection from the pit faces provided the angle of inclination with the etched surface is equal to or more than 70°. This can also be easily proved with the help of figure 3.

The inclination of the pit sides with respect to the etched surface can be determined as follows. Let us assume that a ray represented by bO_1 as shown in figure 3 is inci-

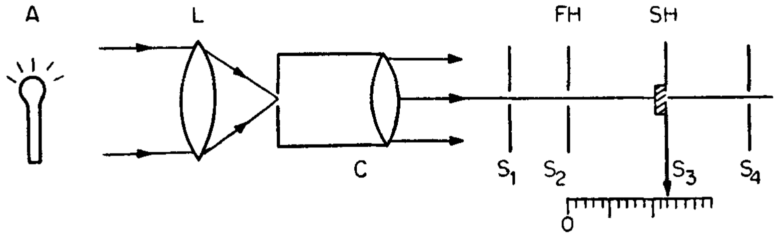


Figure 1. Experimental arrangement. A. light source. L. the lens. C. collimator. S_1 circular slit. PH photographic film holder. SH sample holder.

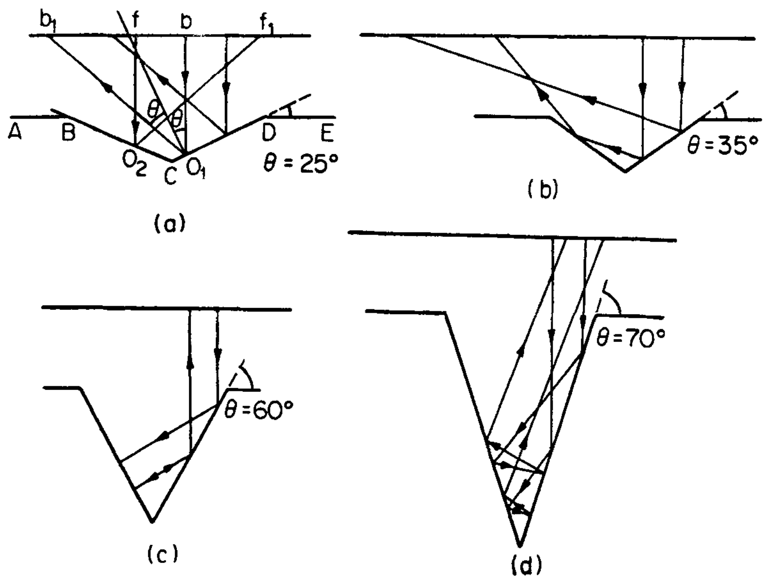


Figure 2. a-d. A vertical section of an etched surface showing pits of different inclinations and the reflected beams.

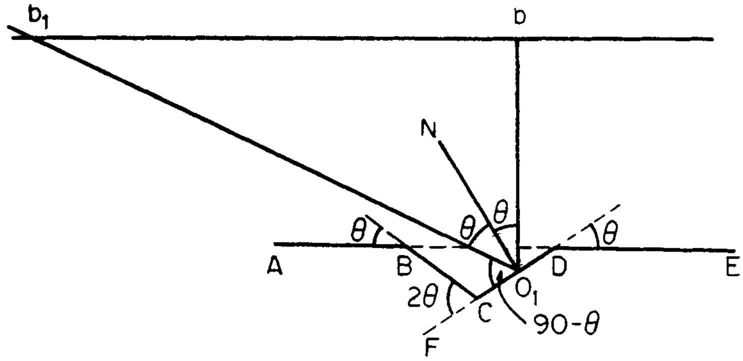


Figure 3. Vertical section of an etch pit.

dent on the silvered side CD of the pit. The pit side CD is inclined to the general surface DE by an angle θ. Since bO_1 is perpendicular to DE, one can show that the angle of incidence of the ray bO_1 is also equal to θ. The reflected ray O_1b_1 meets the film at b_1 making an angle θ with the normal NO_1. If the distance between the incident and reflected rays on the film is equal to X and the separation of the film from the etched surface is equal to d then from the triangle $bO_1\,b_1$

$$\tan 2\theta = X/d.$$

Therefore $$\theta = 1/2 \tan^{-1} X/d \tag{1}$$

Using this relation, the inclination of the pit side with respect to the general etched surface can be determined.

2.3 *Experimental results and discussion*

2.3a *Effect of poison concentration.* Freshly cleaved NaCl crystals are etched in an etchant (Hari Babu and Bansigir 1968) consisting of ethyl alcohol, water and $CdCl_2$ as a poison. The amount of water is adjusted such that by varying the concentration of $CdCl_2$ only the positive cycle of the pits is obtained *i.e.* pit from $\langle 100\rangle$ orientato $\langle 110\rangle$ orientation. An etching time of 15 min is kept constant throughout the experiment. Etched faces are then silvered and fixed in the specimen holder at the slit position S_3. The film-to-specimen distance is kept at 4 cm and the light is allowed to fall on the specimen. The film is exposed for 3 hr if an ordinary source of light is used, and for 2 min if a laser source is used. About 50 pits take part in reflecting the incident beam. The optical topographs obtained are shown in figures 4a, 5a, 6a and 7a and the photographs of etched and silvered faces taken by a Zeiss NU-2 research microscope are shown in figures 4b, 5b, 6b and 7b.

From the optical topographs, the pit slope at the source θ_s and the mean pit slope θ_m are calculated and given in table 1 together with the concentration of the poison. The slope of the pit at the source of dissolution has not been determined earlier due to the insensitive techniques used in the past and ours is the first effort in this direction. If the pits formed due to etching are bounded by plane single faces, then an optical topograph should show four spots situated symmetrically in the case of edge dislocation pits and asymmetrically situated in the case of screw dislocation

Table 1. Etch pit slopes for different poison concentration (time of etching 15 minutes).

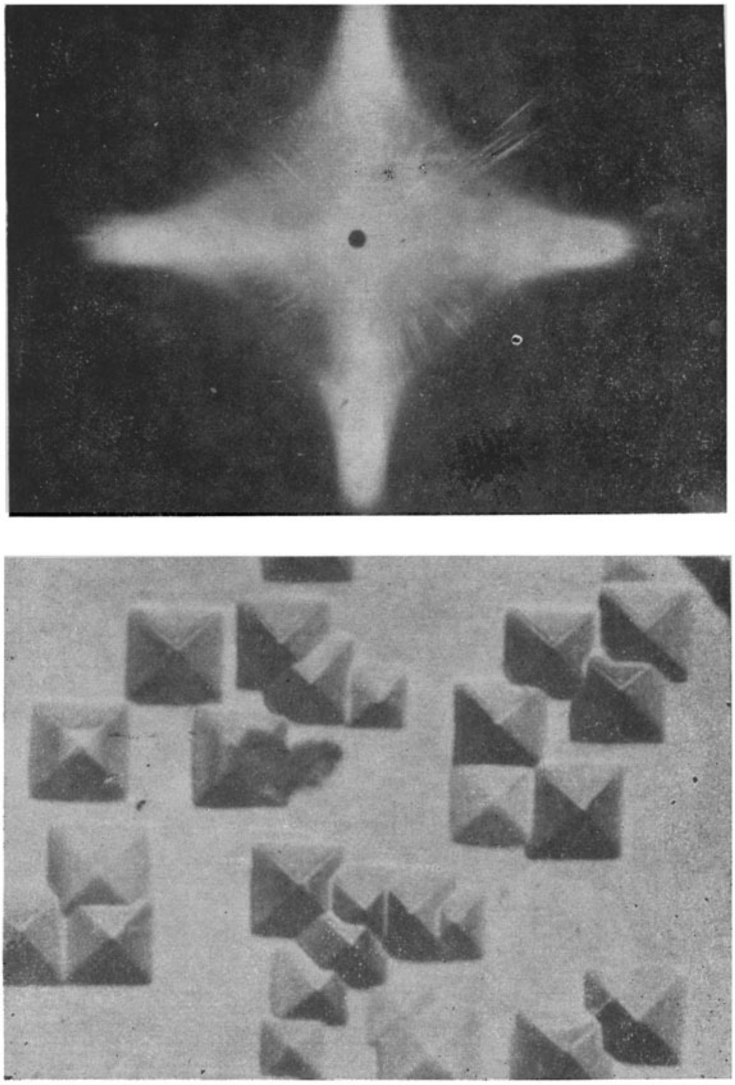
Concentration of the poison (mg/cc)	Slope at the source		Mean slope	
	Orientation		Orientation	
	⟨100⟩ $(\theta_s)_{100}$	⟨110⟩ $(\theta_s)_{110}$	⟨110⟩ $(\theta_m)_{100}$	⟨100⟩ $(\theta_m)_{110}$
4×10^{-4}	19°35′	No pits	11°	No pits
$2{\cdot}1 \times 10^{-3}$	19°20′	17°30′	10°54′	9°39′
4×10^{-2}	19°20′	21°45′	10°27′	12°40′
*1×10^{-1}	No pits	21°45′	No pits	12°40′
		19°23′		10°36′

*Since the dislocations are screw type, therefore the pits are asymmetrical and one gets two inclinations of the sides of the pit.

pits. Instead of single spots, we get extended spots (figures 4a, 5a, 6a and 7a). Therefore the pit sides are not formed by single faces but consist of tiny faces differently oriented with respect to the etched surface (figure 8) The slope of these tiny planes increases as one moves from the crystal surface to the source of dissolution *i.e.* at the site, where the dislocation exists. Ives and Hirth (1960) also obtained a similar result, but concluded that the pit sides are convex and not planar. From the values of θ_s and θ_m it appears that the slope of the ⟨100⟩ orientation pits remains constant as the concentration of $CdCl_2$ increases. The main effect of the increase in the poison concentration is the appearance of pits with ⟨110⟩ orientation. In the initial stages θ_s and θ_m of ⟨110⟩ orientation pits are smaller than the ⟨100⟩ orientation pits, but with increase in $CdCl_2$ concentration their slope increases and attains a value greater than that of a pit of ⟨100⟩ orientation. It is because of this that one sees pits of ⟨110⟩ orientation only. In this case also, an increase in the poison concentration does not change the pit slope, once it attains a critical value, provided the time of etching is not altered.

2.3b *Effect of time.* In order to find out the effect of time on etching, while keeping the concentration of the poison constant, freshly cleaved sodium chloride crystals were etched in an etchant containing 4×10^{-4} mg/cc $CdCl_2$ as poison. The effect of etching for 2, 6, 10, 15, 20 min is shown in figures 9b, 10b, 11b, 12b, 13b respectively and their corresponding optical topographs in figures 9a, 10a, 11a, 12a, 13a. The mean slope θ_m and the slope at the source θ_s calculated from these topographs are given in table 2. From the optical topographs it is evident that there are two source of reflection, *viz* the general etched surface and the etch pits formed at the dislocation sites.

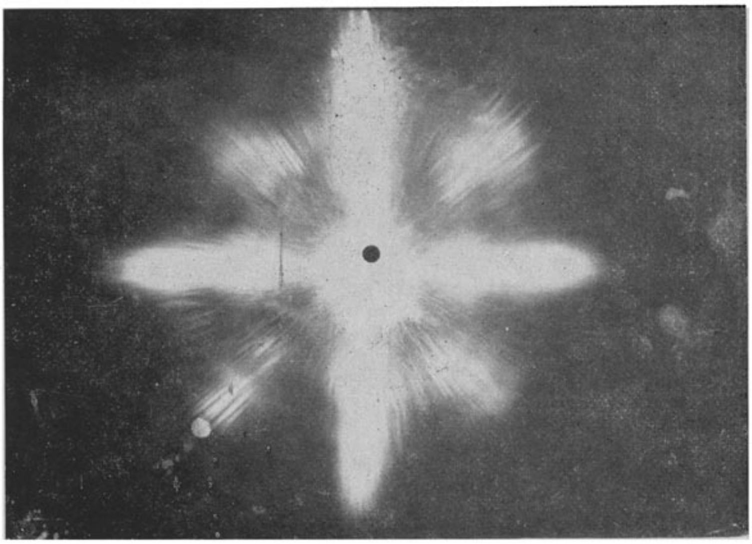
(i) From the optical topographs it is quite clear that the general etched surface does reflect the light falling on it. There is no definite pattern but only a uniform illumination at the centre which is due to such reflections. The origin of such a reflection must be the tiny planes formed due to the etching action of the etchant at all sites, where the point and line defects meet the surface. These planes must have been formed by ⟨100⟩ and ⟨110⟩ ledges and the general etched surface can be assumed to have a pit-like structure. The slope of these planes, calculated and



(a)

(b)

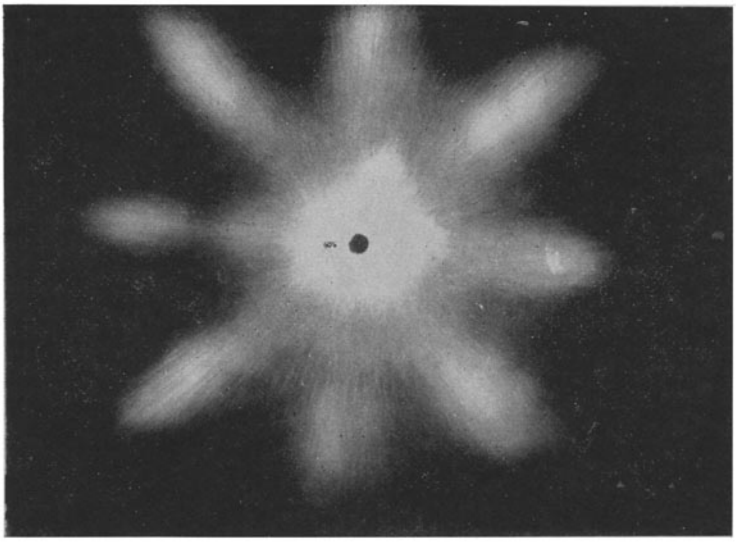
Figure 4. Square pits with edges parallel to ⟨100⟩ direction. Poison concentration: 4×10^{-4} mg/cc. Etching time: 15 min. **a.** Optical topograph. **b.** etched and silvered faces ($\times$ 1200)



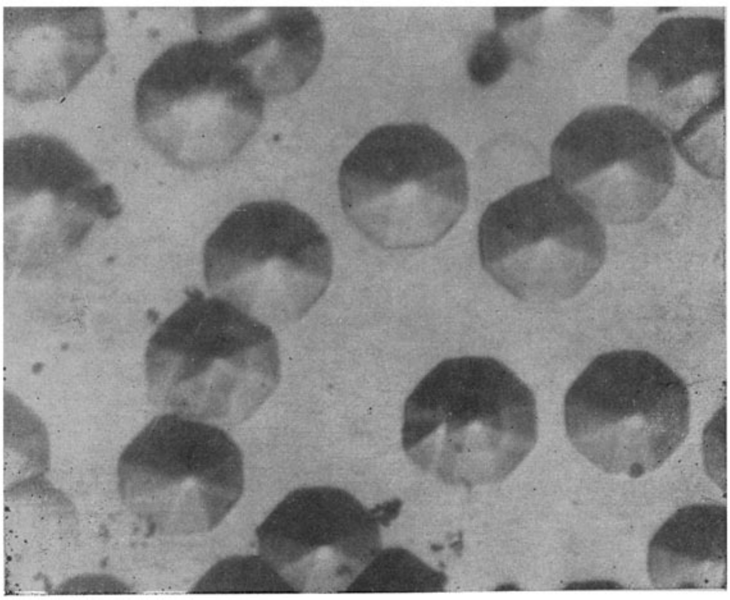
(a)

(b)

Figure 5. Octagonal pits with edges parallel to ⟨100⟩ direction greater than that of ⟨110⟩ direction. Poison concentration: $2{\cdot}1 \times 10^{-3}$ mg/cc of $CdCl_2$. Etching time: 15 min. **a.** Optical topograph. **b.** etched and silvered faces (× 1200).

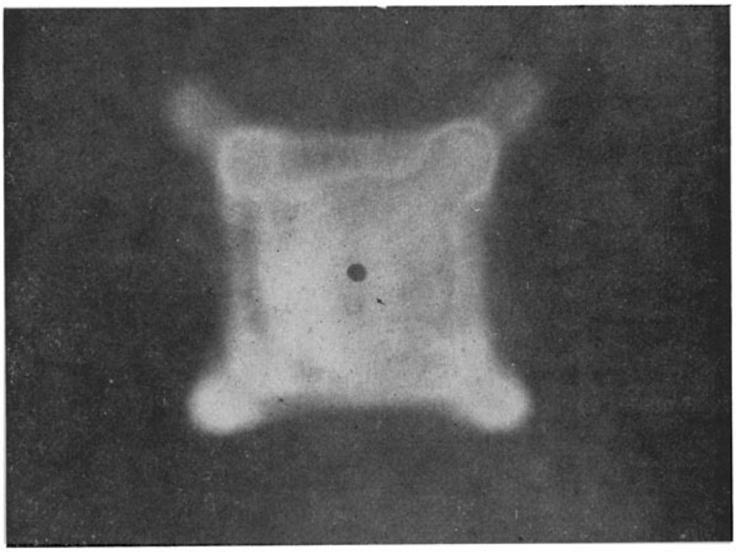


(a)

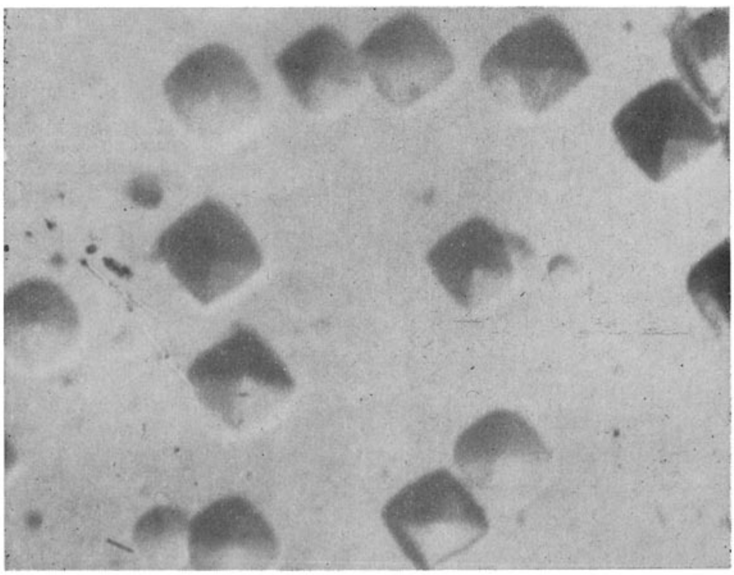


(b)

Figure 6. Octagonal pits with edges parallel to ⟨110⟩ direction greater than that of ⟨100⟩ direction. Poison concentration: 4×10^{-2} mg/cc. Etching time: **15 min.** **a.** Optical topograph. **b.** etched and silvered faces (× 1200).



(a)



(b)

Figure 7. Square pits with edges parallel to ⟨110⟩ direction. Poison concentration 1×10^{-1} mg/cc. Etching time: 15 min. **a.** Optical topograph. **b.** etched and silvered faces (× 1200).

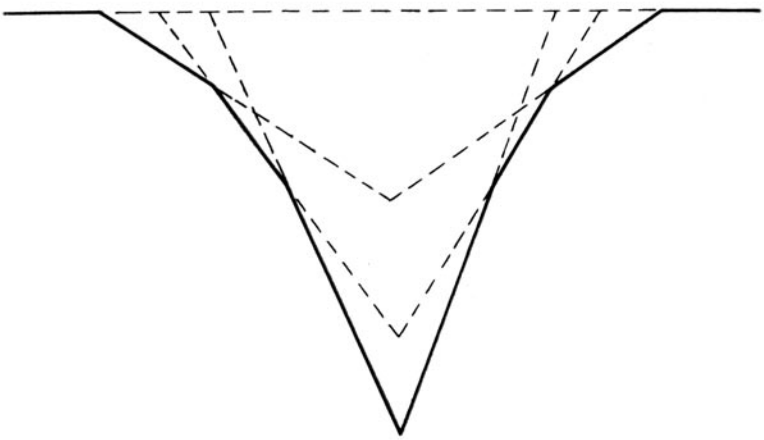
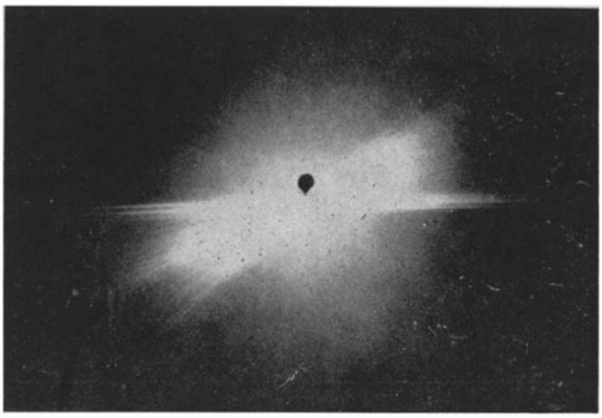
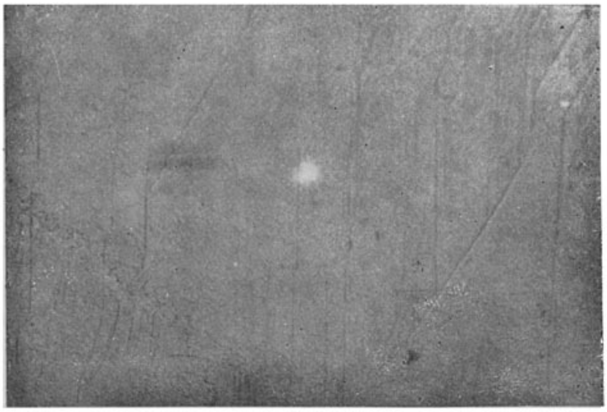


Figure 8. A vertical section of an etch pit illustrating the nature of the surface forming the pit sides.

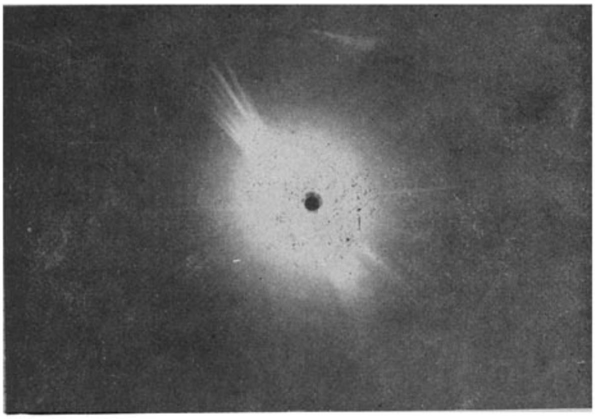


(a)

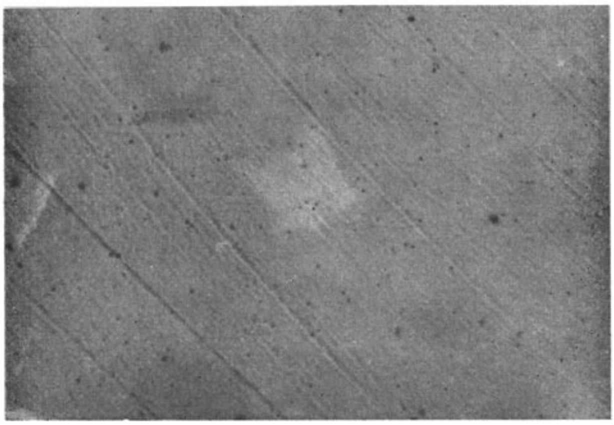


(b)

Figure 9. General etched surface. No pits visible. Poison concentration: 4 × 10^{-4} mg/cc. Etching time: 2 min. **a.** Optical topograph. **b.** etched and silvered faces (× 300).

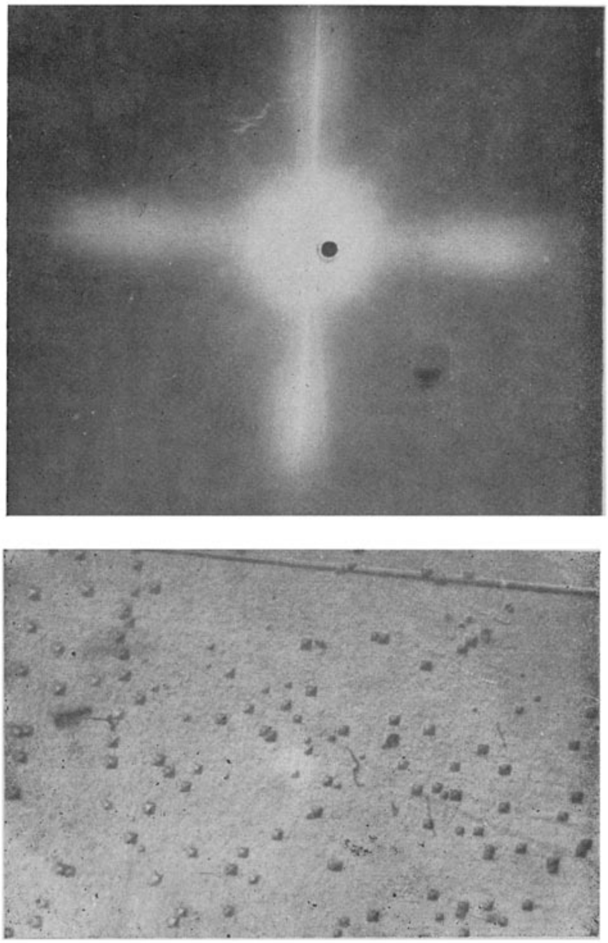


(a)



(b)

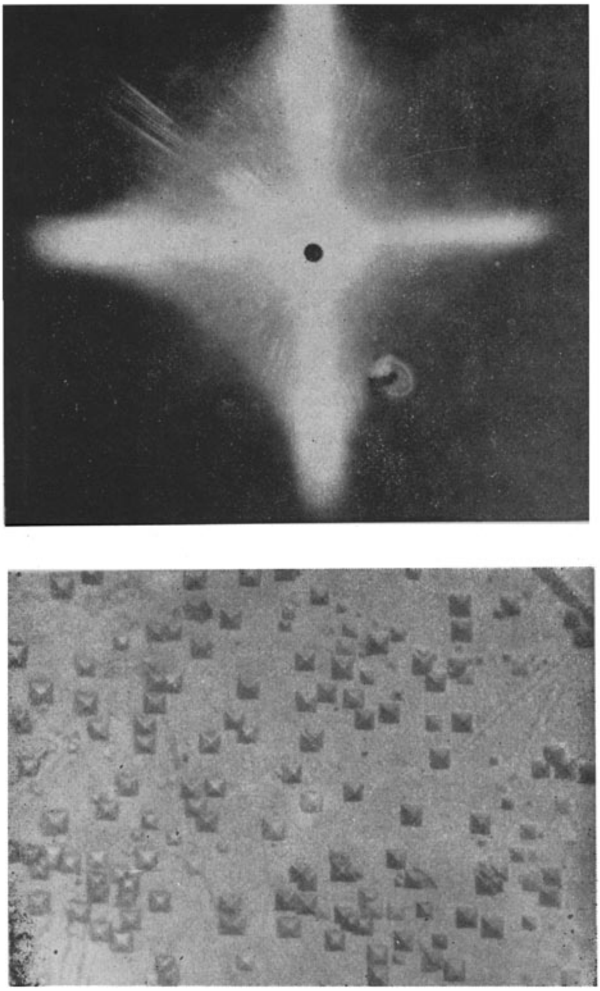
Figure 10. Etched surface. Poison concentration 4×10^{-4} mg/cc. Etching time: 6 min. **a.** Optical topograph. **b.** etched and silvered faces ($\times$ 300).



(a)

(b)

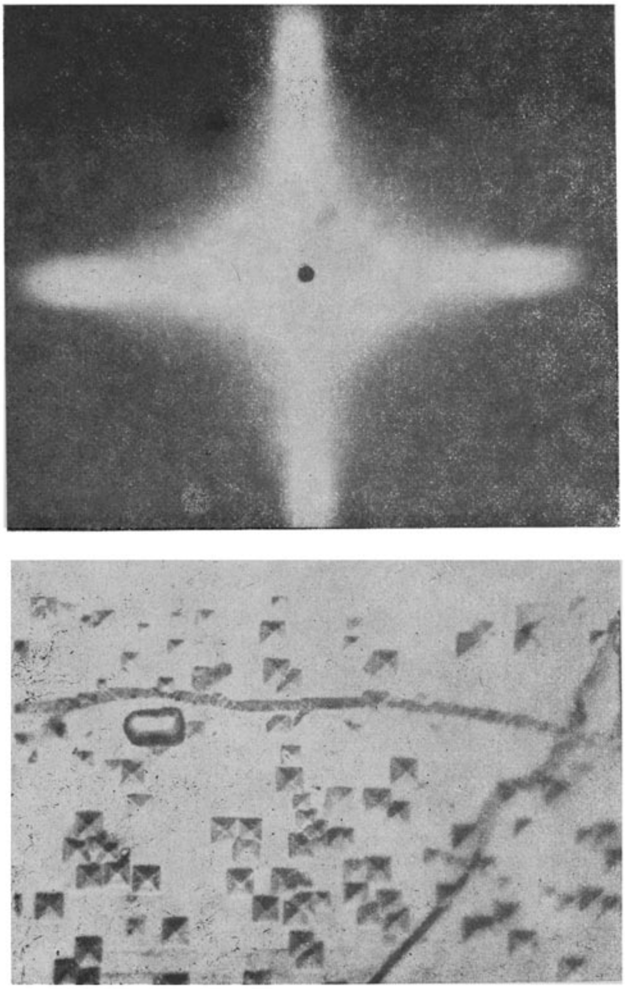
Figure 11. Pits with edges parallel to ⟨100⟩ direction. Poison concentration: 4×10^{-4} mg/cc. Etching time: 10 min. **a.** Optical topograph. **b.** Etched and silvered faces ($\times$ 300).



(a)

(b)

Figure 12. Square pits with edges parallel to ⟨100⟩ direction. Poison concentration: 4×10^{-4} mg/cc. Etching time: 15 min. **a.** Optical topograph. **b.** Etched and silvered faces (× 300).



(a)

(b)

Figure 13. Square pits with edges parallel to ⟨100⟩ direction. Poison concentration: 4×10^{-4} mg/cc. Etching time: 20 min. **a.** Optical topograph. **b.** Etched and silvered faces ($\times$ 300).

Table 2. Etch pit slope with time (poison concentration: 4×10^{-4} mg/cc)

Time of etching (min.)	Pit slope		Inclination of the general etched surface
	θ_s	θ_m	
2	No pits visible	No pits visible	8°21′
6		Tiny pits are visible	8°21′
10	18°27′	10°18′	8°21′
15	19°35′	11°	8°21′
20	21°	12°	8°21′

given in table 2, reveal that the inclination of these planes remains constant and does not vary with time.

(ii) As the time of etching increases, pits start appearing as shown in figures 9b, 10b, 11b, 12b and 13b. Reflection from the pit sides gives a well-defined, symmetrical pattern, reflecting the symmetry of the face on which the pit has formed. In the initial stages of etching, one can see the absence of the symmetrical spots, but as the time of etching increases the pits appear and grow, and because of this, the extended spots appear and the length of these spots increase as is evident from the optical topograph (figures 9a, 10a, 11a, 12a and 13a). The mean pit slope θ_m and the slope at the source of dissolution θ_s calculated from these topographs are given in table 2. These values show that the pit slope whether mean θ_m or at the dissolution source θ_s does vary with time, a result significantly different from that of Ives and Hirth (1960). The etch pit profiles obtained by Ives and Hirth (1960) by increasing the time of etching show that there is no change in the slope of the pit and the pits grow only in size. However, our studies show that not only the size of the pit increases, but the slope also increases with time.

The effect of temperature and undersaturation is now being studied and will be reported separately.

3. Conclusions

(i) A technique has been developed to study the dissolution kinetics at dislocation sites in sodium chloride single crystals. (ii) From the optical topographs, it is concluded that the pit sides are not curved faces but consist of tiny plane faces. Tiny planes close to the source of dissolution have maximum inclination with respect to the cleaved surface. (iii) It is observed that the general etched surface consists of tiny planes of all orientations formed due to ⟨100⟩ and ⟨110⟩ ledges and the inclination of these planes is independent of the time of etching. (iv) The effect of time on the etch pit slope is that it increases with the increase of time, a result which is different from that of Ives and Hirth (1960).

Acknowledgement

The authors are thankful to B. Subramaniam for the fruitful discussions we had with her.

References

Brewster D 1840 *Philos. Trans. R. Soc. Edinburgh* **14** 164
Burton W K, Cabrera N and Frank F C 1951 *Philos. Trans. R. Soc. (London)* **A243** 299
Frank F C 1958 *Growth and perfection of crystals* (ed.) R H Doremus (New York: John Wiley)
Hari Babu V and Bansigir K G 1968 *J. Cryst. Growth* **2** 9
Ives M B and Hirth J P 1960 *J. Chem. Phys.* **33** 517