Acta Cryst. (1965). **18**, 373

Etching of Calcium Fluoride Cleavages

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(*Received* 20 *March* 1964 *and in revised form* 30 *April* 1964)

The etch pattern obtained when the cleavage faces of calcium fluoride crystals are etched in hydrochloric and nitric acid consists of a random distribution of micropits and of individual isolated pits. The individual isolated pits are of different sizes and are either pointed or flat bottomed. The micropits involve general dissolution of the surface and hence expose new layers of the crystal to the etchant. The non-uniformity in the sizes of the pits produced has been tentatively explained.

By etching matched cleavage faces one-to-one correspondence has been established with regard to the number and positioning of the individual isolated pits of large size. This correspondence does not exist for the individual isolated pits of smaller size.

Stratigraphical etch patterns have been produced on some cleavage faces. The pattern is displaced when a large cleavage step is crossed. From measurements on the displacements and the corresponding step heights, it is conjectured that the stratigraphical pattern reveals the edges of the weak (111) planes deposited during growth of the crystal. Correspondence has been established for the stratigraphical etch patterns on the two sides of a 0·7 mm thick plate.

Introduction

Etch figures produced on crystal faces play an important part in gaining information regarding the history of growth of the crystal, the dislocations and their nature. Studies of etch patterns have been carried out by Patel (1961) on diamond, Patel & Ramanathan (1962) on mica, Patel & Goswami (1962) on calcite, Patel & Goswami (1964) on topaz, and Patel & Goswami (1963) on synthetic diamonds. Similar studies have also been made by Gilman & Johnson (1956) on lithium fluoride and Patel & Tolansky (1957) on diamond. Bontinck & Amelinckx (1957) have reported the existence of helical dislocations in calcium fluoride. Similar observations have also been made by Bontinck (1957) on the (111) cleavages of synthetic fluorite. The double rows of pits observed by him on the etched cleavage faces of annealed crystals of fluorite were identified with the emergence points of the parts of helical dislocations.

Experimental

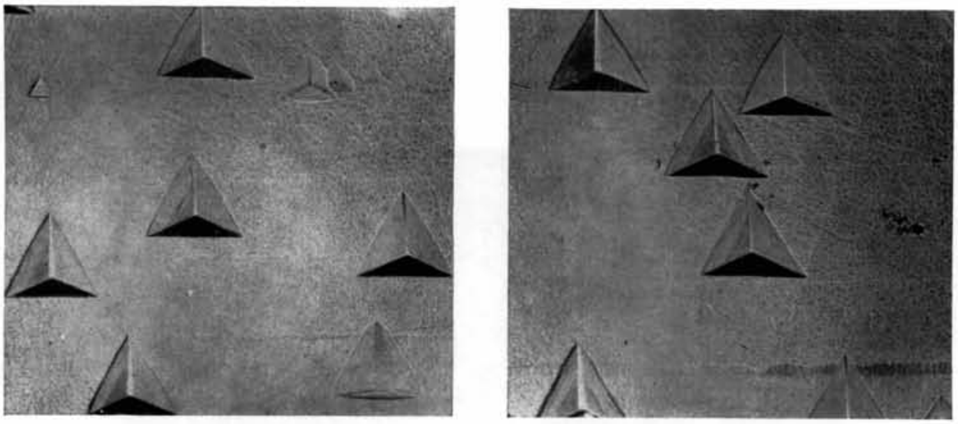
A number of transparent natural crystals of calcium fluoride from Amba-Dungar Mines of Chhota-Udepur in Gujarat State, India, were available. The crystals were of various colours, most being yellowish and greenish but some were colourless. The results obtained here are independent of the colour of the crystal. Very good transparent crystals were selected and cleaved along (111) planes. The freshly cleaved faces were treated with suitable etchants (nitric and hydrochloric acids of different concentrations) and examined under a metallurgical microscope after first depositing a thin silver film on the cleavage faces. They were then examined by multiple-beam interferometry (Tolansky, 1948); phase-contrast microscopy (Osterberg, 1951) and light-profile microscopy (Tolansky, 1952).

Observations

Figs. 1 and 2 illustrate etch patterns produced on (111) cleavage faces of a calcium fluoride crystal by etching with nitric acid of $0{\cdot}4N$ concentration for 45 minutes. The etch pattern consists of (*a*) a large number of small micro-pits randomly distributed and (*b*) individual large isolated pits. These are nearly but not quite the same size, and although most are point bottomed, some are flat bottomed. To decide the size differences in the individual isolated pits, a cleavage face was successively etched for two different periods. Thus Fig. 3(*a*) and (*b*) represent the etch patterns on the same region produced after 15 minutes and 30 minutes of etching respectively. These show the following features:

The individual isolated pits of Fig. 3(*b*) have grown larger because of increase in the time of etching and some additional smaller pits appear in Fig. 3(*b*), having clearly been nucleated during the second etching period.

The non-uniformity of the sizes of the individual isolated pits could be explained by postulating that the individual isolated pits nucleate at the sites of the intersection of a linear defect with the cleavage face. With the increase in the time of etching, the individual isolated pits grow in size while the micropits are linked with the general dissolution of the surface. As the surface is dissolved by the micropit mechanism, new layers of the crystals are exposed and hence new end points of defects, terminating in the layers just below the cleavage face, are now exposed to the etchant. Fresh pits will therefore nucleate at these newly exposed defects. These pits,



Figs. 1 and 2. Etch patterns on (111) cleavage faces of a calcium fluoride crystal (0·4N nitric acid, 45 min) (×245).

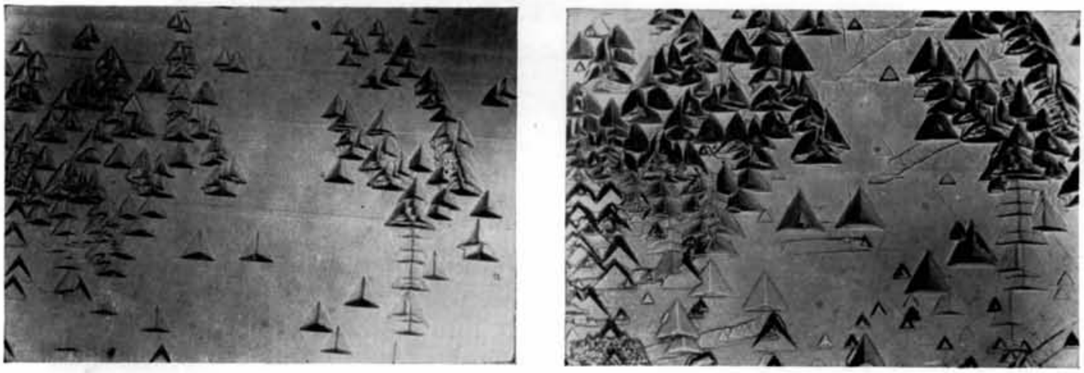


Fig. 3. Etch patterns on one region after (*a*) 15 min, (*b*) 30 min (×120).

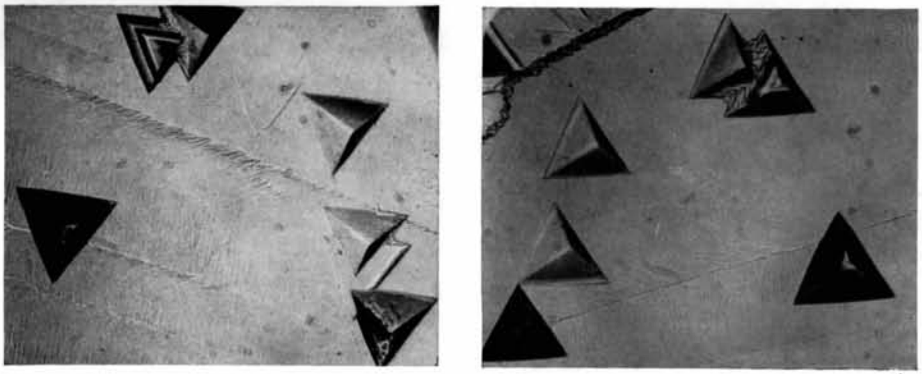


Fig. 4. Etch patterns on matched cleavages (×245).

Fig. 5. Linear etch patterns on a calcium fluoride cleavage face (× 245).

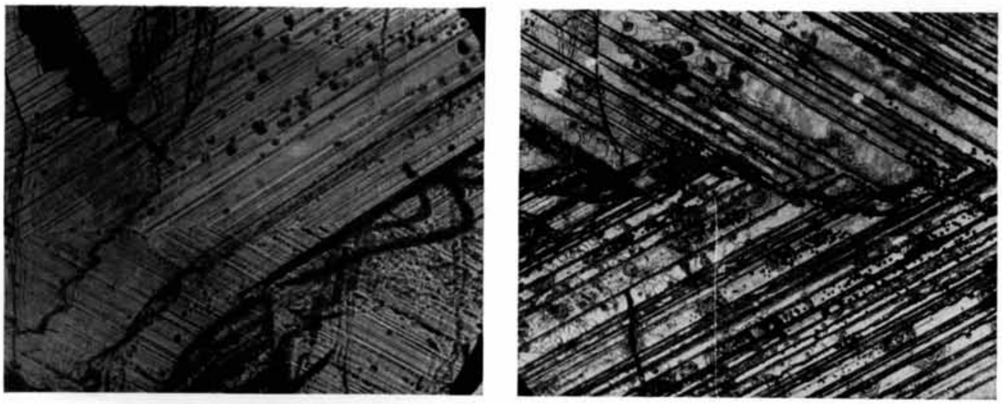


Fig. 6. Etch patterns on opposite sides of a single plate (× 120).

because they nucleated at a later period, will be smaller than the pits nucleated earlier, thus producing the observed non-uniformity in the sizes of the individual isolated pits. There is also no correspondence between the smaller pits produced on matched cleavage faces which confirm that they are nucleated at defects which initially were terminating below the cleavage face.

Etched patterns on matched cleavages, *e.g.* Fig. 4(*a*) and (*b*), reveal the following:

(1) The individual isolated pits have opposite orientation in the two pictures.

(2) There is one to one correspondence in the number and position of individual isolated point bottomed pits.

(3) Some are point bottomed, some are flat bottomed, and some terraced.

(4) The point bottoms of the point bottomed pits are not central but eccentric.

(5) The direction of the displacement of the point bottoms in matched pits is in opposite directions. The magnitude of the displacement is the same in both.

(6) The darker looking pits are the deeper.

(7) A darker pit on one face has a corresponding similar pit on the matched face.

(8) Some of the small and shallow pits observed in Fig. 4(*a*) have no corresponding pits on the matched face.

Etch-patterns on the opposite sides of a thick plate

In addition to etch patterns described above, on some crystal cleavages linear etch patterns are formed similar to those reported by Patel & Tolansky (1957) on diamond, Patel & Goswami (1962) on calcite, and Patel & Goswami (1964) on topaz cleavages. Thus Fig. 5 represents such patterns produced on calcium fluoride cleavages. The dark line running across the picture is a large cleavage step. The linear patterns are strictly crystallographically oriented in $\langle 110 \rangle$ directions. When such patterns cross cleavage steps, they are displaced from their original path, as can be seen in Fig. 5. The displacement of the linear patterns is different at different cleavage steps and some typical measurements are as shown in Table 1.

It is conjectured that, as in the case of diamond and calcite, the pattern might have been formed along the edges of the imperfect layers deposited during growth. From the displacement of the linear pattern across cleavage steps, the angle made by these planes with the cleavage face was calculated (Patel & Tolansky, 1957). This is given in the last column of Table 1. The weak planes whose edges are assumed to give rise to the rectilinear etch pattern clearly makes an angle of about 70° with the cleavage face. Since the crystal is of octahedral habit and, in the case of the octahedron, the angle made between the adjacent octahedral faces is 70° 31′, it may be conjectured that the linear patterns are the traces of some weak (111) planes deposited during growth.

Table 1. *Displacement of linear patterns at cleavage steps*

Step-height h (microns)	Displacement observed d (microns)	Angle calculated $\theta = \tan^{-1} (d/h).m$ where magnification $(m) = 18$
24	150	70° 48′
20	120	70° 30′
40	260	70° 6′
36	220	70° 17′
30	180	71° 36′
25	160	70° 24′
24	150	70° 47′

To investigate how far in the body of the crystal the pattern extends, a 0·7 mm thick plate of calcium fluoride was cleaved on both sides and lightly etched. The etch patterns on both sides were then examined. Fig. 6(*a*) and (*b*) represents the etch patterns on the two sides of one plate of calcium fluoride. There is close resemblance between the etch patterns on the opposite sides of the plate. It is thus clear that the stratigraphical pattern runs right through the body of the crystal.

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