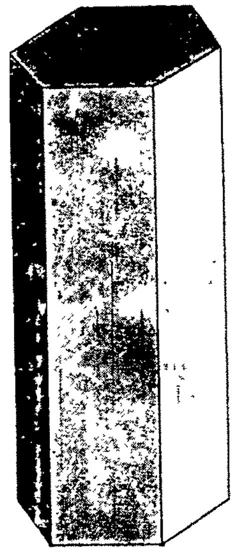


Chapter - 4

Surface Microtopographical Studies

4 - SURFACE MIRCROTOPOGRAPHICAL STUDIES

4.1 INTRODUCTION

Studies of surface features of crystals have been carried out by physicists, chemists, geologists and in particular by crystal growers. Unlike quartz and diamond which happen to be the most studied mineral in the entire mineral kingdom, not much investigations concerning surface markings on habit faces of natural beryl crystals have been done so far. Therefore, it was thought worthwhile to carryout investigations on surface features on faces of natural beryl crystals, and in the light of these observations make an attempt to work out the mechanism by which these crystals grew in nature. With a background of crystallography, mineralogy and petrology, the present author has attempted to interpret surface features of beryl crystals collected from Badmal mines of Orissa state with available instrumental facility.

4.2 IMPORTANCE OF SURFACE STUDIES ON CRYSTAL FACES

Examination of crystals reveal that the individual forms varies greatly from crystal to crystal, and even from face to face on the same crystal. While surfaces of some crystals apparently appear to be mirror smooth (surface irregularity can be observed mostly under high magnification), others show pitted or corroded faces in naked eye itself. This corrosion or etching is the result of dissolution or dissolving of previously formed crystal matter. Natural crystals, such as beryl, that grow from mineralising fluids are susceptible to etching or dissolution from residual fluids when the chemical environment changes sufficiently.

Although of a given minerals species has a definite chemical composition, it invariably possesses certain impurity contents in solid solution which modify their properties to certain extent.

Early investigations on crystals were carried using mainly an optical microscope. These early studies are very significant. Along with various growth features, studies on etch patterns on habit faces and cleavages of crystals are also helpful in the understanding of mechanism of growth of crystals. Surface features on habit faces reflect conditions of growth crystals in the concluding stage They are helpful in tracing history and mechanism of growth faces. Growth and subsequent etching mechanisms are regarded as phenomena depicting their reciprocity. Therefore, from the study of etch patterns useful informations could be derived about the growth of crystals.

With advance of technology more sophisticated tools are now available for studies of crystals. In spite of great progress in accuracy of measurements by use of sophisticated instruments, such as X - ray topography and tomography, light profile microscopy, phase contrast microscopy, and multiple beam interferometry. Optical microscopy, the primitive tool of characterisation of crystals, is still continue to have its own importance.

As early as 1878, Gibbs deduced a theory of crystal growth from his observations of growth patterns on habit prism faces of natural crystals Two of the renowned contemporary mineralogists who have made significant contribution in the field of surface study are : 1) Dr. Ichiro Sunagawa from Japan and 2) Dr. A. F. Seager from England. In 1954, Seager studied surface structures on habit faces of various minerals with the help of metallurgical microscope, and has interpreted growth mechanism and formation of growth hillocks. Sunagawa started his studies on hematite crystals (1962) from different localities. Most significant contribution of Sunagawa (1984) is the growth of crystals in nature - which includes (i) crystals from magma of various composition at different depths, (ii) in vapour with complex compositions, (iii) in hydrothermal solutions, in low temperature aqueous solutions, and (iv) in metamorphic and metasomatic environments. He has classified growth of crystals into (1) solid-solid crystallisation and (2) liquid-solid crystallisation He further classified the latter into (2a) melt growth, (2b) solution growth and (2c) vapour growth of minerals in the geological system. In India, Joshi (1961, 1967, 1976) has carried out extensive surface studies on minerals and his contribution to the above science is noteworthy.

A brief account of previous work on surface studies has already been described in chapter 2. It is interesting to note that the first experimental evidence of crystal growth by screw dislocation mechanism was reported by Griffin (1950) on natural beryl crystal

The present author has carefully examined over 100 prism faces of natural beryl crystals under an optical microscope and some under SEM (JEOL 300). The crystals were first thoroughly washed with soap solution, double distilled water and hydrogen peroxide They were then dried in air and then examined under an optical microscope. Most crystals studied lack basal pinacoid {0001} and pyramidal faces {1121}, {2241} as they are broken fragments of elongated prisms. In all 25 samples (100 prism faces) were investigated, of which only two crystals consisted of basal pinacoid and one crystals exhibited poorly developed pyramidal faces Therefore, the author's study is mainly restricted to prism faces with two observation of basal pinacoid.

4.3 STUDIES ON PRISM FACES

It is seen that among various prism faces examined, vertical striations parallel to *c*-axis were the most common features. These striations are disposed parallel to each other and most cases equally spaced (*Plate 4.1)*. A close examination revealed densely populated rectangular growth hillocks where found between striations (*Plate 4.2*). Some prism faces consisted of elliptical growth pyramids (*Plate 4.3*) Here, growth layers are clearly visible. On very close examination a very tiny, almost elliptical feature is observed at the growth centre of this pyramid. *Plate* (*4.4*) presents two half elliptical growth pyramids side by side with very distinct growth layers. Growth pyramids as seen in *Plates* (*4.3* & *4.4*) are oriented along the *c*-axis of the crystal. A few of the prism faces are seen densely populated with elliptical growth pyramids. Patterns formed by intergrowth of layers of these crowded growth pyramids are also seen in the form of 'V' shaped features.

Hexagonal (term is used to indicate six - sided features irrespective of interfacial angles) growth pyramids were commonly observed on prism faces. Hexagonal features with distinct growth layers composing it (*Plate 4.5 a & b)*. The outer layers are hexagonal, while a few inner ones are rhombus shaped. Only in one sample Hexagonal shallow growth hillocks with only one layer were also observed (*Plate 4.6*).

Growth layers form crowded hillocks and interact with one another and coalesce into a single growth hillocks (*Plate 4.7*) In rare cases, small hexagonal growth hillocks are so closely spaced that, the patterns resulting from intergrowth of layers are in the form of dark zigzag lines, which look like arcuate growth fronts (*Plate 4.8*)

An interesting case of hexagonal growth layers is depicted in an optical photomicrograph (*Plate 4.9*). These growth layers are distinctly hexagonal and are not equally spaced. Unequal spacing between these growth fronts is attributed to unequal rate of advance of growth layers on the prism face. *Plate 4.10* shows a region on a prism face which is densely populated with partially developed growth hillocks. When such features are fully developed, they resemble hexagonal growth steps as shown in *Plate 4.11*. On a few prism faces a large number of small and large elliptical or hexagonal elevations are observed. They are all mounds raised above the habit prism faces and oriented along *c*-axis of the beryl crystal.

On close examination of the corroded looking surface of a crystal reveal apparently haphazard irregular appearance giving rise to array of geometric patterns known as *etch figures* These etch figures on the surface reflect the internal symmetry of the crystal. But the three dimensional structural framework of beryl varies with direction in the crystal. Therefore, the crystal faces which are identical (e.g hexagonal prism $\{10\bar{1}0\}$) would display similar etch figures and would be visibly different from the etch figures found on dissimilar faces (e g $\{0001\}$ in comparison with $\{10\bar{1}0\}$) Each kind of facial plane (or crystal form) of beryl would thus have its own set of characteristic etch figures.

In the present investigation by the author, natural etch pits were clearly discernible on prism faces of some beryl crystal. *Plate (4.12)*, illustrates crowded rectangular natural pits oriented along the *c*-axis of the crystal. A few prism faces showed on them rhombus shaped natural etch pits with the initiation centres along the small m-m edge (*Plate 4.13*). This is the case of edge nucleation of etch pits (Sunagawa, 1962). Crowded rhombus shaped etch pits were also observed on a couple of prism faces (*Plate 4.14*). Here, etch fronts are distinctly seen, such growth is on account of their proximity. *Plate 4.15*, illustrates an isolated elliptical natural etch pit with distinct etch fronts. This pit is eccentric due to unequal rate of etching.

A large number of isolated small elliptical etch pits oriented along the *c*-axis of the crystal were also observed (*Plate 4.16*). On one of the prism faces a couple of oriented elliptical etch pits were observed, and are flanked on either side by growth curves (*Plate 4.17*). Close examination of these etch pits reveals presence of nuclei seen as dark spot (*Plate 4.18a*), signifying initiation centre at each pit. One of the hexagonal etch pit as shown in *Plate 4.18b*, discerns such spots near its centre. Occasionally very densely populated etch pits were observed on some prism faces (*Plate 4.19*).

Formation of etch pits on a habit face of a crystal during its growth is not uncommon. *Plate 4.20* shows a large number of densely populated rectangular etch pits oriented along the *c*-axis of the crystal. At few places these pits are seen with their longer axis perpendicular to the *c*-axis of the crystal.

Out of over twenty beryl crystals analysed, only on two crystals consisted of partially preserved basal pinacoid. Examination of this face on one of the crystal revealed couple of hexagonal solution cavities. The other beryl crystal discerned absence of such solution cavities, however, hexagonal spiral steps were observed.

Scanning electron photomicrograph of prism face has revealed spiral growth feature (*Plate 4.21*). SEM study also discerned presence of a guest microcrystal is seen attached at the growth centre of the growth pyramid. This guest microcrystal has no crystallographic orientation.

4.4 DISCUSSION

Striations are interpreted as edge of growth layers composing two adjacent faces. Unequal spacing between striations is attributed to unequal rate of advance of growth layers in a given direction. Rectangular growth hillocks are formed at growth nuclei (growth centres) between striations (Joshi, 1968). Dense population of such growth hillocks is due to heavy nucleation, which in turn, is due to high degree of supersaturation of the mother liquor. The rectangular/elliptical/rhombus shaped pits in *Plates 4.12, 4.13, 4.15, 4.16, 4.17* and *4.20* are all oriented along the *c*-axis of the crystal, and also the rectangular/hexagonal growth pyramids. These observations suggest reciprocity of growth and etching mechanism. Hillocks and the pits confirm symmetry of prism face on which they are observed.

In the present investigation presence of oriented rhombus and hexagonal shaped growth hillocks (*Plates 4.3, 4.4, 4.5 a & b and 4.6*) suggest that, in the early stages of growth begins with formation of elliptical features (containing only dipyramidal faces on either side). On further growth, basal pinacoidal face is added, resulting in type hexagonal growth layers (*Figure 4.1*) which spread out.

Examination of interfacial angles of the six sided growth features (*Plate 4.5 a & b and 4.6*) deduce that the initial rhombus shaped growth features make an angle of 54° and 126° (*Figure 4.1*). This elucidates that the face of a rhombus shaped hillocks belong to the dipyramid of second order $\{22\bar{4}1\}$. As growth proceeds, basal pinacoid {0001} begins to develop giving the appearance of six -sided growth hillocks. This observation is supported by the presence of six sided outer layers in almost all growth hillocks presented in this chapter. If at this stage, there is a fast rate of growth, the dipyramid face begins to develop at a faster

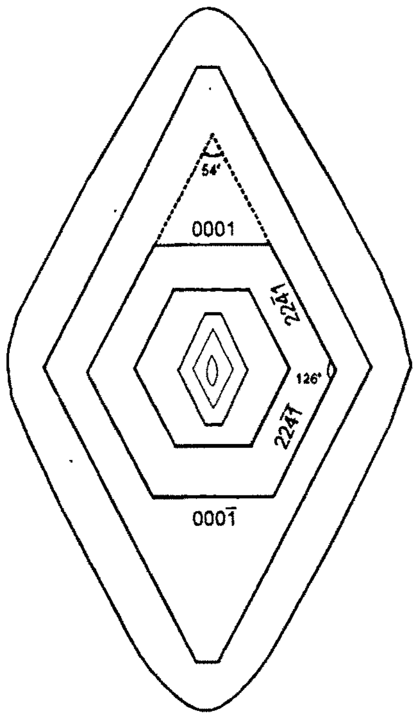


Figure 4.1 **: Illustrating formation of apparent hexagonal looking growth features on prism faces of beryl crystal, due to the development of 0001 (basal pincacoid) and $22\bar{4}1$ (dypyramid of 2nd order) faces.**

rate than the basal face, resulting again into rhombus shaped features (*Plate 4.4* and *4.8*). A fast rate of etching at this stage would result in rounding of the corners of dipyramidal face on either sides. Thus transforming rhombus shaped growth features into an elliptical one (*Plate 4.3*, *4.4* and *4.17*).

Presence of very tiny hexagonal etch pit at the centre of a growth hillock observed on one of the prism faces of the crystal suggests growth of rudimentary basal pinacoid {0001} and hexagonal dipyramid of second order {2241} Such patterns do not have any specified shape nor density (*Plates 4.7 & 4.8*). Such patterns throw light on shape of growth fronts, growth layers and growth pyramids/hillocks.

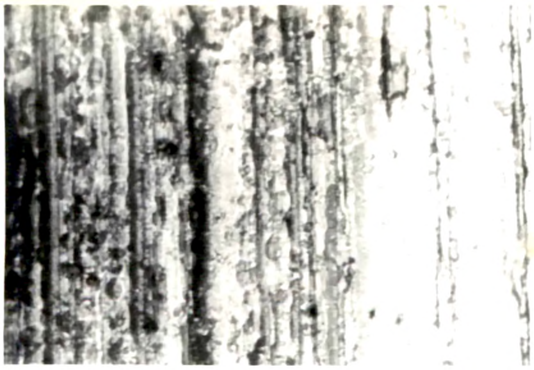
Observations presented above suggest that these crystals in general, and prism faces in particular have grown and developed by two-dimensional nucleation of growth, and spreading and piling of layers on prism faces. Presence of deep dark hexagonal pits indicate growth in form of hexagonal growth pyramids.

Presence of high density of rectangular etch pits indicates high density of imperfections on the crystal face, It is well known that imperfections (including surface impurities) are preferential sites for formation of etch pits. It is important to note here that the orientation of longer axis of the majority of rectangular etch pits (*Plate 4.20*) deduce that rapid growth of beryl crystal along the *c*-axis.

In the mother liquor, tiny microcrystals may be formed Such microcrystals are dragged or carried on the growing crystal face, on which they get attached. Such crystals are not expected to have any strict orientation of attachment, and uniformity in distribution. It is possible that the some of this microcrystal may drop out during the growth of a crystal and may have their foot print (impression) on the host face, which may be covered by layers in the later stage of growth (Joshi and Kotru, 1968; 1976). Another possibility is that guest microcrystals may remain attached onto the host habit face, and they may play the role of nuclei around which further growth may take place. It is also likely that the guest microcrystal may be grown over and covered by later growth of layers. In such cases the guest microcrystal get imbedded in the body of the main crystal as inclusion They may be observed if the crystal is transparent.

Presence of spiral steps (*Plate 4.21*) indicates the growth is also by screw dislocations. The presence of polygonal spiral discerns that the steps contain less kink site and therefore, growth by polygonal spirals were strongly crystallographically controlled (Sunagawa, 1984).

The wide step variation of polygonal spirals further elucidates that the beryl crystals have probably grown form vapour phase and the morphology followed the symmetry of the face on which they developed. Unequal spacing between growth layers observed in this case is on account of difference in rate of advancement of each layers.



(x 50)

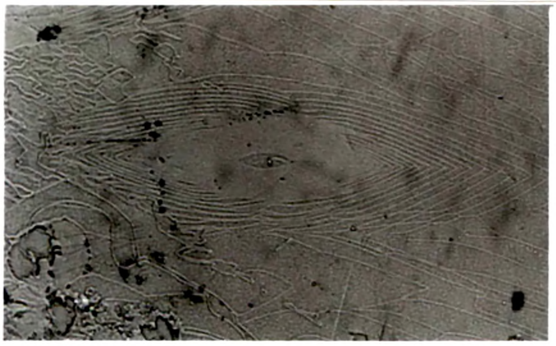
c-axis

Plate 4.1 : Striations on prism face of the beryl crystal oriented parallel to c-axis of the crystal

(x 50)

c-axis

Plate 4.2 : Rectangular growth hillocks in between striations



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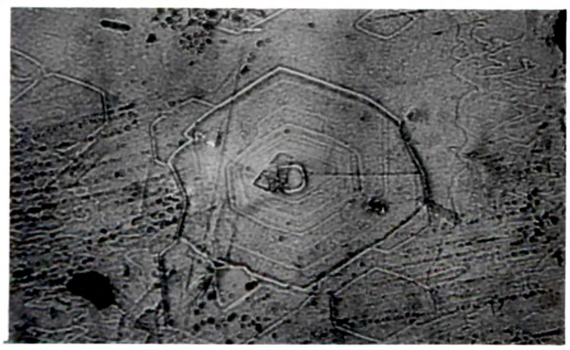
c-axis

Plate 4.3 : Elliptical growth pyramids with distinct growth layers

(x 50)

c-axis

Plate 4.4 : Two halves of elliptical growth features



(x 50)

c-axis

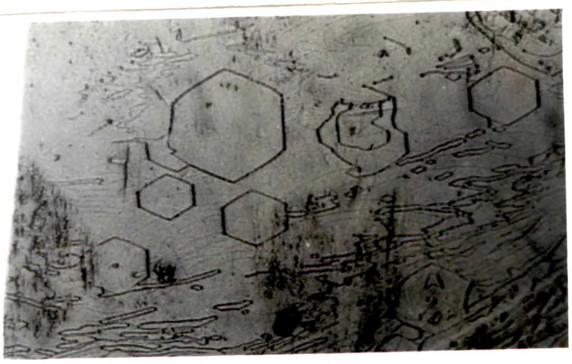
Plate 4.5a : Hexagonal growth features with distinct growth layers

(x 50)

c-axis

Plate 4.5b : Hexagonal growth features with distinct growth layers

(Inner layers elliptical, outer layers hexagonal)



(x 50) c-axis

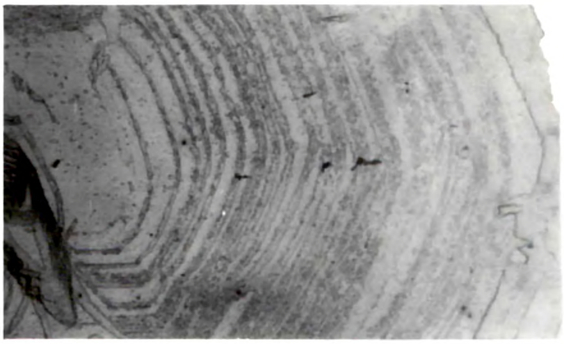
Plate 4.6 : Hexagonal growth hillock with single layer

(x 50) c-axis

Plate 4.7 : Numerous hexagonal growth features coalescing into one another

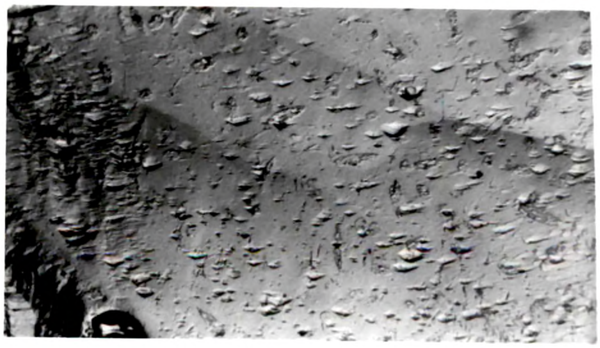
(x 50) c-axis

Plate 4.8 : Interaction of numerous hexagonal growth hillocks resulting in intergrowth of layers



(x 50) c-axis

Plate 4.9 : Unequally spaced hexagonal growth features



(x 50) c-axis

Plate 4.10 : Densely populated partially developed growth hillocks

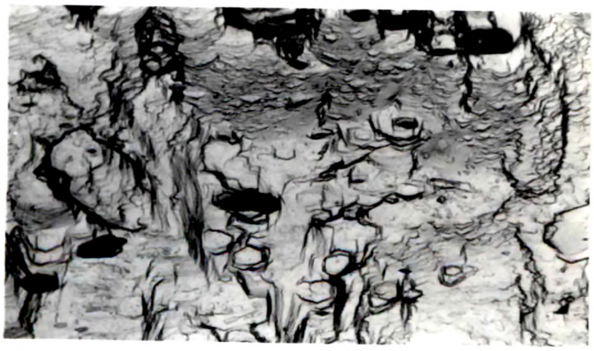


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Plate 4.11 : Fully developed growth hillocks

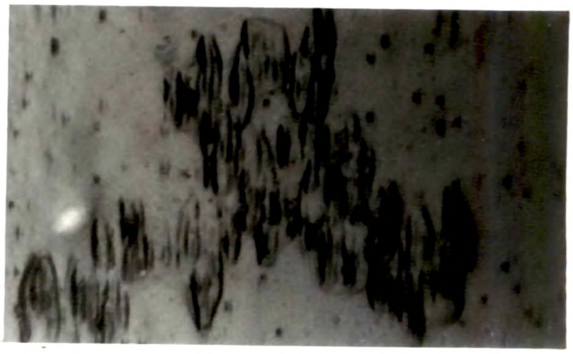

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Plate 4.12 : Natural etch pits on a prism face of beryl crystal

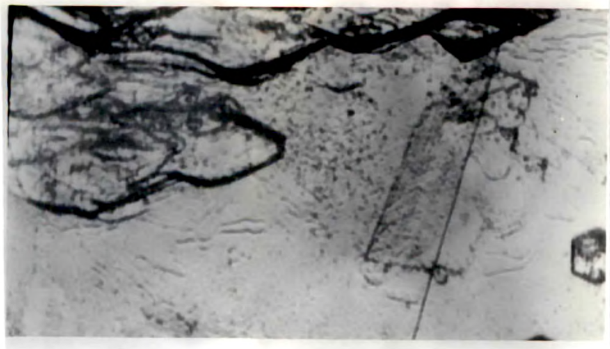

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Plate 4.13 : Rhombus shaped etch pit along m-m edge

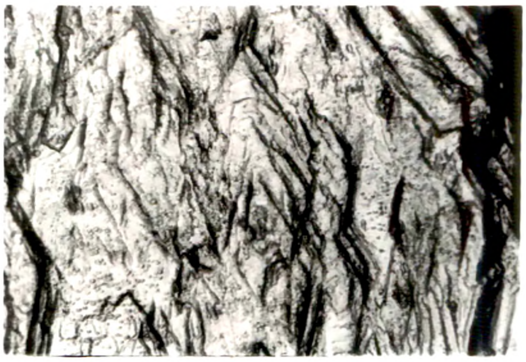

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Plate 4.14 :Crowded rhombus shaped etch pits

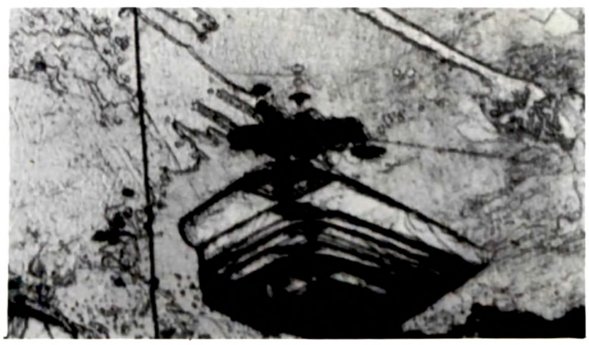

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Plate 4.15 : Isolated etch pits with distinct etch front

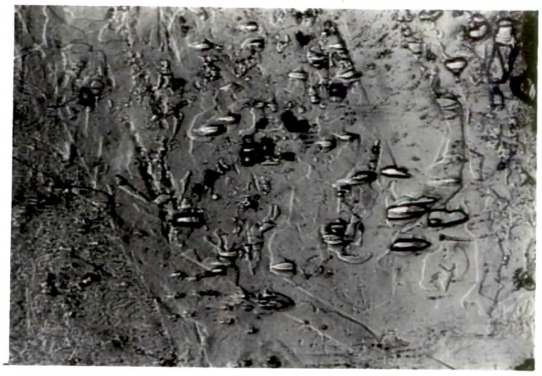

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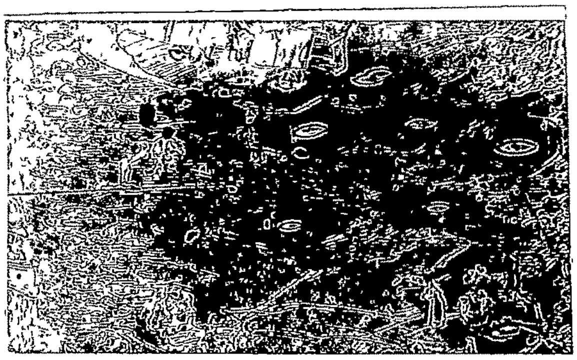
Plate 4.16 : Numerous isolated etch pits parallel to c-axis



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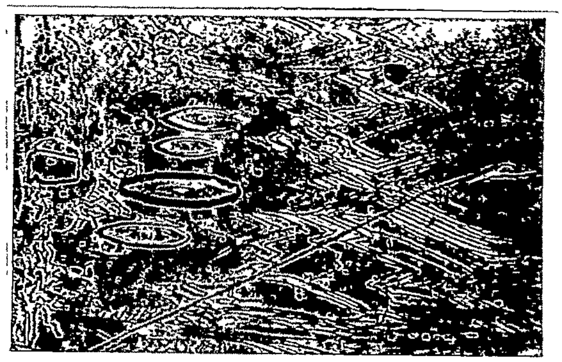
c-axis

Plate 4 17 Couple of oriented etch pits flanked on either side by growth curves



(x 50)

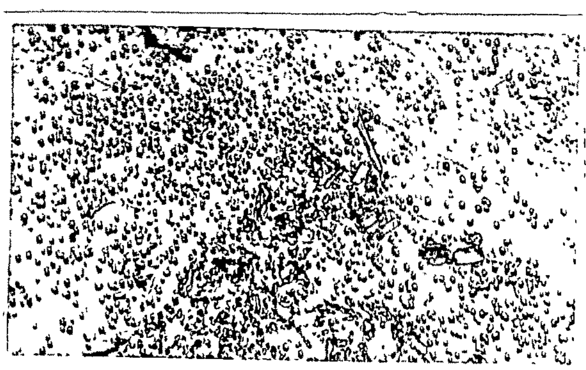
c-axis

Plate 4 18a Etch pits with growth nuclei at the centre of etch pit (Observed as dark spot)

(x 50)

c-axis

Plate 4 18b Etch pit with the presence of two growth nuclei in the centre of the pit (Observed as two dark spots)



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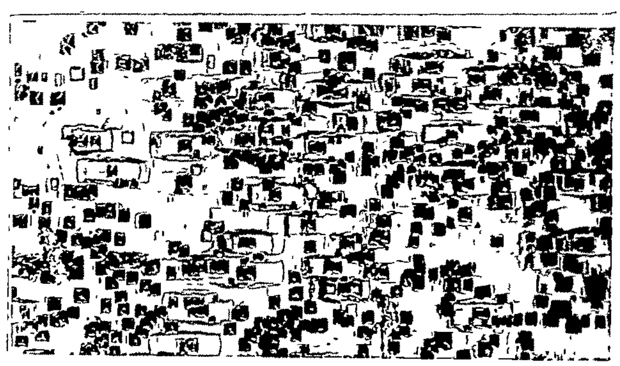
c-axis

Plate 4 19 Densely populated etch pits on a prism face



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c-axis

Plate 4 20 Rectangular etch pits with its longer axis parallel to c-axis of the crystal

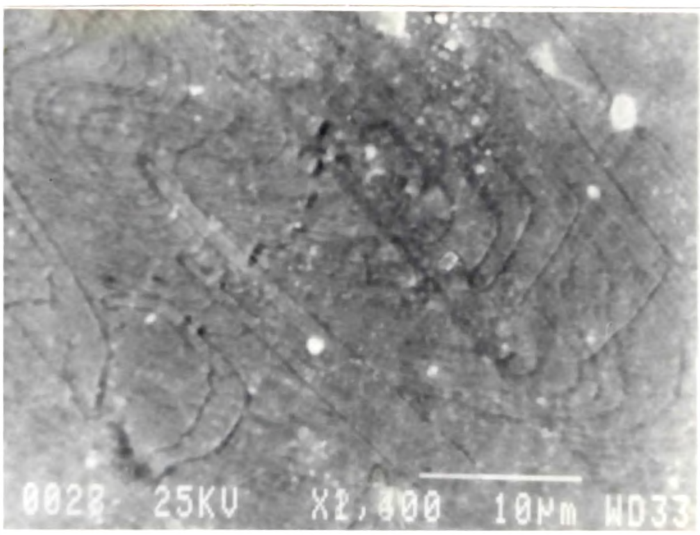

Plate 4.21 : SEM photograph of beryl on a prism face depicting screw dislocation on prism face

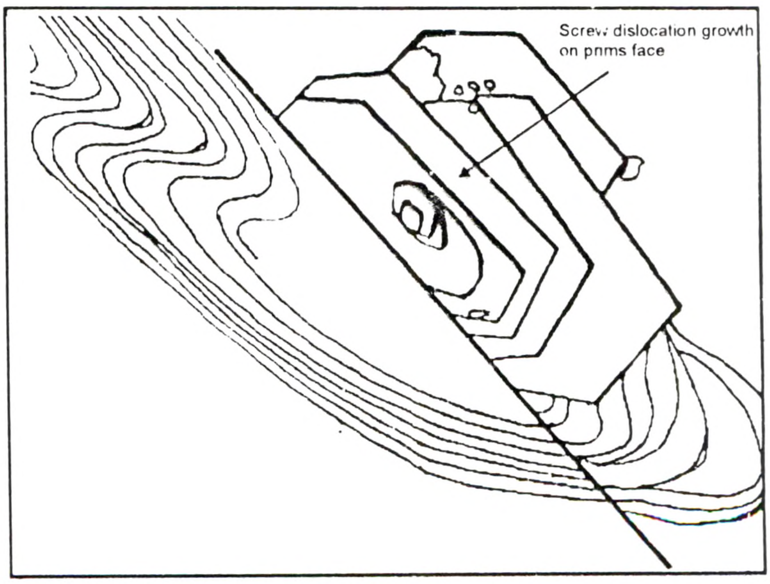

Figure 4.2 : Line drawing of above SEM photograph depicting screw dislocation on prism face