OPTICAL STUDIES OF GROWTH FEATURES

ON

THE SURFACES OF SOME DIAMONDS

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B Y

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ABSTRACT

Part I of this thesis deals with a brief historical review on diamond together with the studies made on crystal growth with the existing information on diamond.

Part II deals with the experimental techniques employed for the present investigation including an interference technique whereby, it has been shown for the first time, that very sharp multiple-beam interference fringes can be produced with a high power 3 mm. lens of numerical aperture 0·95. The optical conditions necessary to secure high definition in the fringes are discussed together with the arrangement used which can resolve a lateral extension about 0.7μ and a depth of 50 A^{o}. Volume elements as small as 5 x 10^{-15} cc. can be resolved.

Part III deals with the optical studies of growth features on the octahedron faces of some diamonds. Some features of particular interest are described namely :-

1 - A number of anomalies in trigons.
These are discussed in detail.

2 - An occasional mode of growth sheets is shown to operate on the octahedral faces of diamond which leads to the formation of six-sided growth features containing alternate angles of approximately 90^{o} and 150^{o}. It is shown that the edges of these are effectively parallel to the directions $\langle 431 \rangle$.

These may possibly arise through intersections of (221) with (111)

3 - A remarkable case of multiple linear processes has been observed on five faces of a well formed good octahedron. This has been well interpreted as due to crystallographic slip in diamond.

Part IV deals with the microstructure on the dodecahedral faces of some diamonds. Some new surface structures are described. A mosaic structure exists. At least three main different structures for the (110) faces can possibly arise during the growth of diamond namely :-

1 - Striated surfaces either smooth or coarse.

2 - A network structure.

3 - A parallelogram structure related to 2.

These structures are described and discussed in detail.

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P A R T I

CHAPTER I.

INTRODUCTION

From the earliest times diamond has fascinated mankind. It has been prized as a precious stone on account of its rarity and pre-eminence. As a gemstone, it is altogether unique, for it is distinguished from all precious stones by remarkable qualities, and justly so, since it combines in itself extreme hardness, high refraction, large colour dispersion, and brilliant lustre. Some Hindu proverbs relate to the hardness of the diamond - "Diamond cuts diamond", "The heart of a magnate is harder than the diamond" etc.

Besides its pre-eminence as a gemstone diamond finds a demand in industry for cutting and abrasive purposes. Boring through solid rock has been greatly facilitated by the use of the diamond drill. The tenacity of diamond renders it most suitable for wire-drawing. Diamond powder is used for cutting and turning the hardened steel employed in modern industry. There are also many specialised scientific uses, for example, for cutting fine line-gratings, for hardness indentation test-tools, for the fine stylus used in some instruments, and even as a detector of atomic radiations.

Not all diamonds are of gem quality; some 60 per cent of the raw stones are unsuitable for gems; industry absorbs about 80 per cent of the diamonds by weight, the remaining 20 per cent being used for jewellery etc.

Diamonds as they occur in their natural state are often more or less rounded, rough-looking pebbles. The natural diamond must be cut and polished to bring out its lustre and sparkle. The shape of the so called crystal as it leaves the diamond-cutter has little relation to the natural crystalline shape. About half the mass of the diamond is lost in the cutting. The object of the lapidarist is to get the maximum reflection of light from the interior of the stone for the high reflecting and refracting power of the diamond are the particular qualities which make it supreme above other gems.

Of all gem stones diamond is the simplest in chemical composition, being composed entirely of carbon. In every diamond the arrangement of carbon atoms remains the same but the structure of the individual stone may have been subject to imperfect crystallization, which may appear as internal fractures, known to the trade as "feathers" or "cloudy texture". Imperfect crystallization also sometimes results in surface fissures or separations along cleavage planes, which may be located within the body of the diamond and may or may not extend inward from the surface. In their growth, certain diamonds may have enveloped crystals or fragments of other minerals which appear as inclusions. Graphite, perhaps is the most common inclusion. It occurs in small thin flakes, single, few, or many, scattered at random through the interior of the crystal giving the various qualities of "spotted" stones. In general these flakes are irregular in outline and give no indication of their crystal form. Other black inclusions less common than graphite, occur in small rounded grains or fragments which are mostly ilmenite, chromite and magnetite. They occur singly or scattered at random throughout the diamonds or embedded in its surface. Garnet, in small rounded grains hardly ever with crystal faces, is a frequent inclusion. One of the rarest inclusions is iron pyrites. Diamond itself forms a very important inclusion. There are many cases of one diamond crystallizing around another, the inner diamond often differing in crystal form and colour from the outer crystal with the more tinted stone inside. By far the most common form is the octahedroid and with less occurrence dodecahedroid, flat or sharpless grains and very occasionally a perfect octahedron. In many cases when one diamond is found as an inclusion in another, crystallization of the diamond has stopped and then restarted. The building up of the second diamond does not in any case, unless it is accidental, follow the crystallographic lines of the first. Sometimes for example the first diamond takes the form of the octahedron, while the second stage of crystallization on the octahedron takes the form of a rhombic dodecahedron. In many cases the first diamond may be covered with some foreign matter and this, together with the original diamond is completely enclosed in the second diamond. Diamonds containing solid inclusions of foreign matter, and especially diamonds containing diamonds as inclusions, are most easily broken. Diamonds containing solid, liquid or gas inclus-

-ions generally reveal under the microscope the presence of internal strain. In many such diamonds minute cracks are perceptible, radiating from the area of foreign inclusion. Sutton (1928) pointed out that diamonds do cleave freely across foreign inclusions. These defects in crystallization are recognized by diamond merchants as flaws or imperfections.

Diamonds when absolutely limpid and free from flaws, are said to be of the "first water"; they are most prized when devoid of any tinge of colour except perhaps a bluish shade. Stones with a slight tinge of yellow are termed off-coloured. Stones of a canary-yellow colour, however belong to a different category, and have a decided attractiveness. Greenish stones are also common, though it is rare to come across one with a really good shade of that colour. Brown stones, especially in South Africa, are not uncommon. Pink stones are less common, and ruby-red, mauve, and blue stones are rare. Those of the last-named colour usually have what is known as a "steely" shade, that is, they are tinged with green. Stones of a sapphire blue are very seldom met with. Doelter attributed the colouration of diamonds to the presence of oxides of iron, chromium, manganese and titanium. Hydrocarbons may also give rise to a yellowish colouration. Some diamonds are dark grey and even black. They exhibit an imperfect crystalline structure, and are known as black diamonds, bort, or boart, or carbonado. Boart is an imperfectly crystallized, translucent, dark coloured diamond which has various colours, but no clear portions. Its hardness is fully equal to that of crystalline diamond and is used in drilling rocks, and in cutting and polishing other stones. Carbonado is the Brazilian term for a still less perfectly crystallized black diamond. It is as hard as boart, and has similar uses. Boart and carbonado are usually regarded as forms intermediate between diamond and graphite.

The crystal shapes of the diamond all belong to the "isometric" or "cubic" system, but for many years there has been much controversy among crystallographers as to the particular class to which it should be assigned. The most common form is the octahedron. There are rhombic dodecahedral, and hexakis - octahedral forms; the cube with rounded edges is also represented, but a few crystals are found which are tetrahedra and these lead to the view that the symmetry is tetrahedral as in class 31. The octahedral crystals are thus on this view regarded as two interpenetrating tetrahedra twinned about a cube face, an interpretation which is supported by the grooves often present along octahedron edges. The opposing view is that diamond should be assigned to class 32, having the highest possible crystal symmetry, with the octahedron as the characteristic form. This opinion is supported by the absence of detectable piezo-electric and pyro-electric effects. The tetrahedra are then explained as octahedra distorted by the suppression of alternate faces.

Haüy in an early investigation (1743-1822) made a very careful study of diamond, and came to the conclusion that the symmetry of the diamond was that of the regular tetrahedron. He was supported in his view by others including Mohr, Haidinger, Miller, Rose and Des Cloizeau. Fersmann and Goldschmidt (1911) in their treatise on diamond make a very strong plea for the hemihedral structure basing their arguments on morphological and etch characters and stated that their experiments proved unequivocally the hemihedrism of diamond.

On the other hand Van der Veen (1913) vigorously opposed the theories advanced by Fersmann and Goldschmidt and proposed holohedral symmetry.

In their early application of the X-ray technique to diamond W.H. Bragg and W.L. Bragg favoured the holohedral class and demonstrated in a striking way the tetrahedral arrangement of bonds around a carbon atom. They pictured the structure by starting with a face centred cubic lattice of the points marked A in figure (1). A similar lattice is then so placed so that every B point lies between four A points at the corners of a tetrahedron. It follows that every A point lies between four B points. Carbon atoms are placed at A and B and if they are joined by heavy lines as shown in figure (1), it will be seen that every carbon atom is linked tetrahedrally to four neighbours. The length of the C.C bond is 1·54A^{o}, but the edge of the cubic lattice cell is 3·650A^{o} in length. Figure (1) shows such a cell; the planes designated by AAA - are the (111) planes.

Figure (2) shows the structure of the diamond with the (111) plane horizontal. The single vertical bonds are broken to secure the (111) planes.

The extreme hardness of diamond can be considered to be a direct result of such a structure. On the basis of this view Rinne (1924) calculated the number of carbon atoms in one C.C. of diamond to be 1.8×10^{23} which when compared with 1.3×10^{8} at $5500^{\circ}C$ in carbon vapour suggest the existence of a strong cohesive force between the atoms. The energy to break the C-C. bond has been calculated by Harkins (1942) from theoretical considerations to be 6.22×10^{-12} ergs.

The rigidity of the diamond and the open character of its structure, imply that great force is required to alter the orientation of coupling. Were it otherwise, all atoms would seek to be surrounded by as many neighbours as possible; the substance would then be close-packed, and its density would be more than double what it is. The structure of diamond may also be looked on as constituting a series of puckered layers parallel to a given tetrahedral plane. A sharp blow may cleave the diamond along one of these layers although diamond is the hardest substance known. It occupies position 10 on Moh's scale, but the difference in hardness between it and carborundum, which ranks as 9 on the scale is enormous. No precise measurements have been made of the hardness of diamond but it is estimated that it is at least eighty-five times as hard as

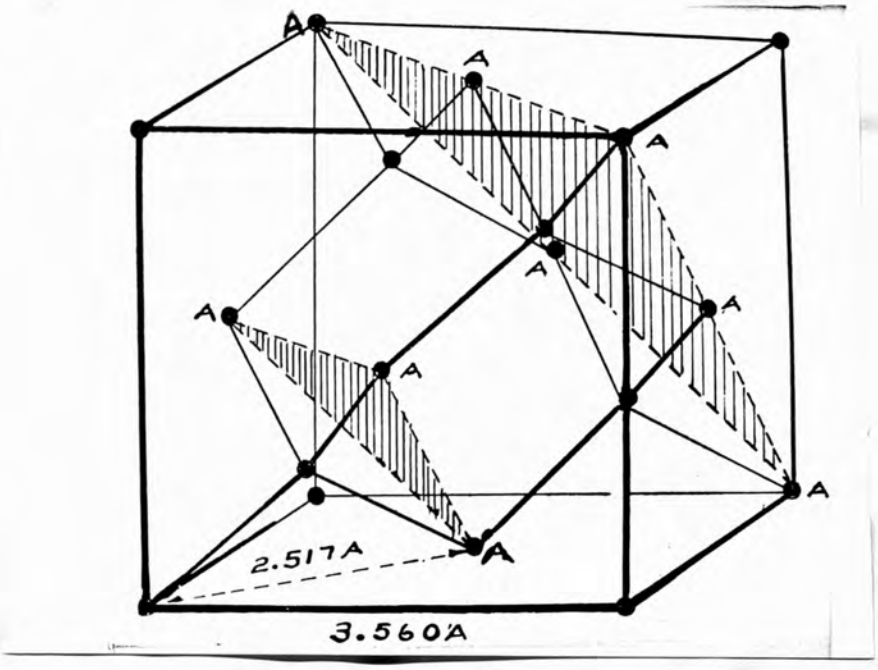


Fig. 1.

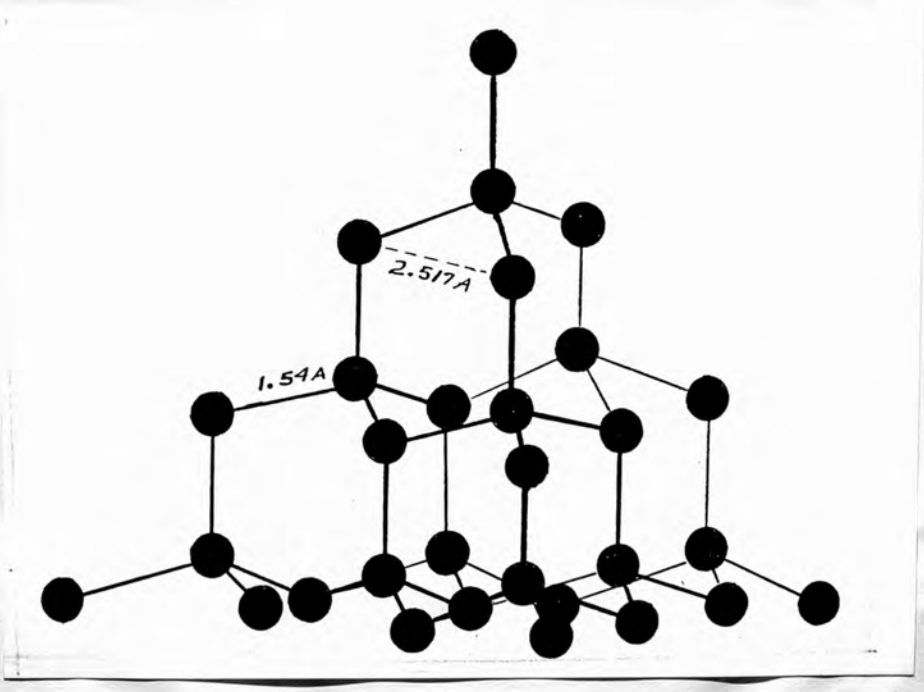


Fig. 2.

carborundum.

Lonsdale (1928) using X-ray analysis has shown that the crystal structure of many of the carbon compounds, and also of carbon in the free state, can be explained by supposing that the carbon atom has two different types of valency. If this is true it is probable, though not certain, that diamond would show piezo-electric effects.

Elings and Terpstra (1928) sought for a piezo-electric effect in diamond but failed to find it.

Robertson, Fox and Martin (1934) showed that the great majority of diamonds exhibited optical birefringence and also infra-red activity in the region of 8μ of the spectrum. They were opaque to ultra-violet light below 3000A^o. These they called type I. On the other hand a few diamonds have no absorption bond at 8μ and are transparent to ultra violet light up to some 2250A^o. These were designated as type II.

Lonsdale (1944) has established that type II diamonds have the same dielectric constant and lattice constants as ordinary diamonds the differences not being due to impurities.

Raman (1944), (1945) has pointed out that, because of both sense and direction in the tetrahedral axis, carbon atoms in the diamond may be oriented in four ways in space and that four possible diamond structures might exist. Two of these will be tetrahedral (TdI and TdII) and identical in characteristics (referred to as positive and negative). These structures are common ones. The other two will have full octahedral symmetry (Oh I and Oh II) and are physically different from each other. They will be comparatively rare but, where they do occur, interpenetration of the two octahedral forms imparts laminar characteristics to the diamonds.

Krishnan (1944) using X-ray and spectroscopic techniques indeed confirmed the existence of all the four types suggested by Raman.

Raman and Jay Raman (1949) found that diamonds exist which show infra-red activity but do not show any visible bire-fringence and that those which show birefringence also exhibit lamellar structure. They also found that both the infra-red activity and the ultra-violet transparency vary in a continuous manner.

Grenville-Wells (1952) using X-ray diffraction found that whereas type I could still be regarded perfect, type II could be either perfect or mosaic. (In the present work the usual nomeclature of type I and type II means those opaque to ultra-violet and transparent to ultra-violet respectively).

Champion (1952), (1953) carried out a series of experiments on many diamonds to examine their ability to give large conduction pulses when subjected to an electric field and irradiated with A-particles or B-particles. He conjectured that diamonds which show good electrical conduction pulse properties are composed of layers of highly crystalline material separated by relatively few, and much thinner, partial barriers of imperfect material. He further pointed out that a nearly perfect specimen is one which belongs to the rare type II and contains but few vacant sites and interstitial atoms. Slightly more common specimens are those in which the crystal is almost perfect but which under electrical test, shown to contain traps for electrical charges, the trap density being particularly high close to the surface. Custers (1952), (1954) reported that type II diamond did not form a homogenous group in themselves, and suggested that they should be sub-divided into two further groups type II(a) and type II(b). The differences between the new groups being that, unlike the former, the latter group shows a strong phosphorescence when irradiated by short wave ultra-violet light in the region 2500A^{0}.U. He also added that type II(a) diamonds are fairly rare and are only found in certain mines in South Africa, while type II(b) diamonds are still more rare, however they conduct electricity relatively well.

This diversity in the results of the various workers using different optical and electrical techniques lends support to the view that the mechanism of growth of diamond is very complex. In fact, numerous studies have been made by several workers and many guesses and theories have appeared in attempt to explain how diamonds have been formed in nature. In one set of hypotheses, the diamond is considered to be of organic origin and formed at relatively low temperatures. In another set of hypothesis the mineral is supposed to have been formed at relatively a high temperature and high pressure.

The earliest research of any importance on the synethesis of diamond was carried out by Hannay (1880) who described a long series of experiments aimed at achieving the artificial formation of diamonds. These were based on the fact that, when a gas containing carbon and hydrogen was heated under pressure in the presence of lithium, potassium, sodium, or magnesium, the hydrogen combined with the metal and the carbon, being thus set free, was deposited in a very hard scaly form. He believed that carbon under such conditions might crystallize out as diamond. Bannister and Lonsdale (1943) using X-ray diffraction technique justified the work of Hannay in that the crystals he obtained were shown to be diamonds of the rare type.

Moissan (1893), (1896) claimed to have obtained tiny diamonds by suddenly quenching in cold water molten iron containing dissolved carbon, dissolving away the iron in acid, but no really confirmatory evidence was presented.

Sir William Crookes (1909) repeated successfully Moissan's experiments. He found minute diamonds in the residues formed in closed steel tubes in which cordite was exploded.

Ruff (1917) also claimed success with Moissan's method, and offered experimental evidence supporting his statements. Parsons (1919), (1920) carried out numerous experiments and claimed to have produced synthetic diamonds by using methods tried by previous workers with improved apparatus which achieved still higher temperatures and pressures.

Rossini and Jessup (1938) discussed the relations existing between diamond and graphite and showed by calculations that at Ca. 13,000 atmospheres there is no temperature at which diamond is stable with respect to graphite. At Ca. 16,000 atmospheres equilibrium should result at 300°K, and at Ca. 20,000 atmospheres it should be established at 470°K.

Günther, Geselle and Rebentish (1943) have shown that diamond is the unstable allotrope, under ordinary pressures from low temperatures up to at least 2300°C, but it is 1.6 times as dense as graphite; hence the conditions that favour its formation are a high pressure (to make it stable) and a high temperature (to overcome its inertness). Prosen, Jessup and Rossini (1944) showed that the heats of combustion at 25°C and one atmosphere for diamond and graphite are 94.49K cals. per gm. atom and 94.04K cals. per gm atom respectively, i.e. a difference of +0.45K cals per gm. atom. They concluded therefore, that at ordinary temperature graphite is the stable form. This has already shown experimentally (Günther *et al.*) to be so up to at least 2,300°C at ordinary pressures.

Bridgman (1947) exposed graphite either alone or seeded with diamonds to pressures from 15,000 to 30,000 $K.g/cm^2$ at 2000°C. When the graphite was alone, no diamonds were formed;

when it was seeded, the diamonds went over completely to graphite under 15,000 K.g/cm^2, but less readily as the pressure rose, until at 30,000 K.g/cm^2 there was no change. Hence above this pressure we should expect the graphite to go over to diamond, but this could not be tested experimentally. In as much as diamond does not form under conditions much more drastic than those calculated theoretically (Rossini and Jessup) it is possible that the controlling factor is the speed of conversion. Recently the General Electrical Co. Laboratories in U.S.A. have reported the artificial production of diamond, though reaching higher pressures than were formerly available.

In fact, the mechanism by which diamonds were formed in nature remains a mystery, although it seems obvious from the thermodynamic evidence cited that extremely high pressures are essential. The matter is, therefore, still occupying considerable attention in several laboratories.

CHAPTER II.

CRYSTAL GROWTH AND VICINAL FACES.

The study of crystal growth has assumed increasing importance in recent years in both theoretical and experimental physics and chemistry.

A review of the historical development of crystal growth theories has been given by Wells (1946) and Buckley (1951). Only a brief review of the previous studies of growth mechanism of crystals together with the available information about diamond will be given.

The first quantitative theory for the study of crystal growth was given by Gibbs (1878) on thermodynamical grounds. Pfaff (1878) made a study of several cubic crystals, and later Brauns (1887) on octahedra of lead nitrate, came to the conclusion that many habit faces make a very small and variable angle with the low index plane, and cannot be referred to the simple indices. Such faces are called "vicinal faces".

Miers (1903), (1904) constructed a telescope-goniometer, arranged so that the crystal was suspended in the acqueous solution; with the zone which was being measured had all its faces vertical, so that the possible distorting action of gravity was eliminated. Miers began his studies with cubic crystals whose theoretical angles were calculable, and found that for potassium alum the goniometer reflection from the octahedral faces gave three closely spaced images, whose positions were between one minute and twenty minutes of arc from the (111) direction. During growth the multiple images were repeatedly replaced by other images lying in definite zones. The most important conclusion which Miers has drawn from his studies is that the vicinal faces corresponding to any single habit face frequently produce low pyramids, or growth pyramids and that the indices of the vicinal faces, however high were rational. He believed that vicinal faces are produced by the deposition of molecular planes of solute parallel to high index planes of the lattice.

Hedges (1926) using the same kind of goniometer for his studies on Epsom and Rochelle salts supported Miers' main views. Kalb (1930), (1933), (1934) extended the goniometric study of vicinal faces to non-cubic crystals including quartz and topaz. He showed that the vicinal faces can occur along certain well defined zones and that to determine the exact positions of the low-index planes it is essential to determine the points of intersection of these zones.

Schubnikow and Brunowsky (1931) applied X-ray and goniometric methods to the study of the relationship of vicinal faces to the true lattice planes and came to the conclusion that vicinal faces are truly plane surfaces. More recently Tolansky (1945) using multiple-beam interferometry showed that the vicinal faces on a major rhombohedral face of quartz possess a slight cylindrical curvature.

In recent years, experiments have been carried out by several workers, as a result of which the comment has gained ground that a crystal grows by successive deposition of layers on the main faces of the crystal.

Marcelin (1918) in a posthumous publication reported growth by layer deposition. He studied the growth of thin plates of p. toluidine from alcoholic solutions and concluded that crystals grow by deposition and spreading of successive layers whose thicknesses approach molecular dimensions.

Volmer (1922) observed similar thin layers in studies on thin crystals of lead iodide (PbI_2) formed by mixing lead nitrate $Pb(NO_3)_2$ and potassium iodide KI.

Marcelin and Boudin (1930) also observed similar layer formation on naphtalene and on several other organic crystals.

Kowarski (1935) extended the studies of the growth of p.toluidine crystals from the vapour. He found that the layers were usually initiated at the intersection of an edge with a neighbouring crystal. Also thin layers propagated faster than the thicker ones.

Tolansky and Wilcock (1946) using the crossed-fringe technique for the study of diamond surfaces have given evidence for the growth of diamond by layer deposition. They explained the well known triangular depressions (trigons) as possibly formed by the intersection of growth sheets advancing across the crystal surface in three directions inclined at 60^o to each other.

Bunn and Emmet (1949) have described the growth of a number of crystals, both ionic and non-polarbylayer deposition. Their study consisted in placing a drop of warm saturated solution on a warm microscopic slide. This was then covered with a thin cover-slip, and observed under the microscope using dark-ground illumination under high resolution. Their main conclusions can be summarized as follows:-

1. Growth sheets spread very often not from the edges or corners, but from the centres of the faces.
2. The thickness of sheets increased as they spread away from their points of initiation.
3. The growth fronts were often irregular if the growth was rapid but tended to be more regular and conform to the crystal symmetry as the growth rate decreased.
4. The shape of a crystal could be modified, or even completely changed by the presence of certain impurities in the solution. The reason is that the impurities are strongly absorbed only on certain faces of the crystal, thereby retarding the growth of these faces. The impurity may be absorbed on faces which normally grow rapidly (that is, planes which are not the simplest and do not normally appear), and in these circumstances the rate of growth of the faces may be so much reduced that they become the predominant faces on the crystal. The presence of modifying impurities may often by unsuspected; hence we sometimes find crystal exhibiting for no

—— apparent reason faces not of the simplest type.

Gibbs (1878) gave the first quantitative theory for the study of growth of a perfect crystal. Curie (1885), Wulf (1901) and others followed. During the last thirty years an atomic theory of crystal growth has been developed by Volmer (1939), Kossel (1927, 1928), stranski and his co-workers (1928, 1949), Becker and Döring (1935), Frenkel (1945, 1946) and Doring (1949).

The theory considers the growth of an ideally perfect crystal. Although it explains why regular forms in the plane habit faces are assumed by the crystal when growth fronts which is smaller than the theory predicts.

Moreover the interpretation of vicinal faces as a succession of uniformly spaced growth fronts is not possible according to the nucleation theory.

More recently Burton, Cabrera and Frank (1949) have pointed out that the observations of Volmer and Schuttz which were published in (1931) on the growth of iodine crystals from the vapour at supersaturations as low as $1^{o}/_{o}$ could not be interpreted by the nucleation theory; they found that the calculated rate of nucleation was smaller than the observed rate by the enormous factor of e^{3600}.

In fact, any visible crystal needing fresh two-dimensional nucleation in order to grow would not be expected to exhibit a complete face.

Owing to the serious discrepancies between theory and experiment Burton and Cabrera (1949) re-examined the basis of the nucleation theory. They modified it to incorporate the concept of Frenkel (1945, 1946) that the boundary of the nucleus is not exactly rectilinear at finite temperatures owing to the presence of thermal ('Frenkel') kinks; they considered the effects of the surface diffusion of adsorbed molecules, and the change in shape of the nucleus in various stages of its growth. They concluded that apart from the omission of relatively unimportant numerical factors, the formulae developed by Becker and Doring (1935) were essentially correct and the discrepancy between theory and the experimental results of Volmer and Schultz was still enormous. However, Frank (1949) suggested as a possible explanation that the results were in much closer accord with the theoretical rate of growth of iodine crystals containing a particular type of lattice imperfection (screw dislocation). He has pointed out that dislocations catalyze crystal growth so that an otherwise perfect crystal containing dislocations should grow far more quickly than one which does not. In fact, Frank's analysis has shown that the presence of dislocations is almost a necessity in growth of crystals by vapour deposition or from solution in periods of time of everyday or even of geological interest. Hence crystals may grow until at least one dislocation is generated "accidentally" if equilibrium means are not available. It may thus be concluded that at least a fraction of the dislocations in a crystal is generated during growth and plays an important role in such growth.

According to Frank 1949a, if dislocations are present, there will in general be exposed molecular terraces associated with their terminations on a crystal face, and growth can continue on these terrace edges; there is then no need for repeated nucleation. On this basis Frank (1949b) predicted that the front attached to a single dislocation grows outwards in a spiral fashion while a pair of dislocations emit growth fronts as closed rings; formations such as these have in fact been observed by various workers. The first direct visual evidence of the existence of dislocations was reported by Griffin in (1950) as the result of his microscopic observations on beryl crystals. Since then the volume of experimental observations carried out by various workers in support of the theory of spiral mechanism has grown considerably. Dawson and Vand (1951) using electron-microscopic techniques observed growth spirals on certain paraffin crystals of relatively high molecular weight. Amelinckx (1951a), Verma (1951a) and others also observed spirals on silicon carbide crystals. Further Forty (1952a) has shown that cadmium iodide crystals occasionally develop spiral polymolecular growth fronts.

Although the two-dimensional nucleation theory fails to explain the universal presence of vicinal faces, Frank's theory gives a natural interpretation for each growth spiral gives rise to a low growth pyramid centred on any 'active' dislocation group. The successive branches of the spiral are uniformly spaced and if the spiral is polygonal, rather than circular, each side of the polygon will give rise to a vicinal face. But there is little experimental evidence in favour of this interpretation, as the growth spirals are polygonal only on the paraffin crystals studied by Dawson and Vand.

However, doubts about the theory have been expressed by some workers, notably Buckley (1952 a,b), (1953) who has had experience of hundreds of individual crystals in all, where no suspicion ever occurred that screw dislocations with possibly accompanying spirals played any significant part whatsoever. He suggests that spiral formation is not always essential to growth but is a late incident in growth due to vortices or eddies which would impress on the uppermost surface a spiral character.

Neither uni-molecular growth steps, nor a spiral pattern of growth lines have been observed yet on the octahedral faces of diamond, but this may be due to the spacing between the octahedron planes being only 2·05A^{o}. However Griffin (1951) considers that there is evidence for the formation of multi-molecular layers, on the octahedron faces of diamond: he suggests that if crystal faces consistently exhibit multi-molecular layers, uni-molecular steps will not always be found on these faces, and the direct evidence for growth will not therefore be available.

More recently Omar, Tolansky and Pandya (1954) and Pandya and Tolansky (1954) have given some evidence by etching the diamond at different stages that growth has proceeded by layer formation. They were supported in their views by the fact that all attempts to find a spiral on diamond have failed so far.

In view of existing uncertainties the possibilities for enlarging our knowledge about crystal growth processes are enormous.

Extension of the growth characteristics of diamond surfaces would seem necessary to a more satisfactory solution of the problem and the work described in this thesis gives more information about the study of growth features on some octahedron and dodecahedron surfaces of diamond.

A description is given of microscopical studies on various diamond faces asserted by the use of multiple-beam interferometry.

PART II

EXPERIMENTAL TECHNIQUES.

CHAPTER I

MULTIPLE - BEAM INTERFEROMETRY

Multiple-beam interference between plane parallel surfaces was first investigated theoretically by Airy (1831) and practically by Boulouch (1896) and by Fabry and Perot (1897). Tolansky was the first to recognize the potentialities of the method for the study of microtopography. He and his co-workers (Tolansky et al 1943 - 1955) developed it in several forms and have greatly contributed to the knowledge of the surface structure of crystals, e.g. mica, selenite, quartz, calcite, diamond etc. and the present work takes place in this series.

A full account of this technique is described by Tolansky (1948) in his book in which reference to original papers is made. A review of the subject is also given by Kuhn (1951). Consequently only a brief description of a few points of special interest to this thesis will be given.

In multiple-beam interferometry the two surfaces involved should be coated with a partly transparent metal film of high reflecting coefficient by evaporation in vacuum. If such reflecting surfaces are plane and parallel, then the expression controlling the transmission fringe shape in such an interferometer may be written as follows:-

$$I = \frac{I_{max}}{1 + F \sin^2 \delta/2} \quad \ldots \quad \ldots \quad (1)$$

where $\delta = \frac{2\pi}{\lambda}(2\mu t \cos\phi)$ is the constant phase lag.

I = intensity at any point in the fringe system

I_{max} = peak intensity of the fringe = $\frac{T^2}{(1 - R)^2}$

F = $\frac{4R}{(1 - R)^2}$

where R = $\sqrt{R_1R_2}$, R_1 and R_2 are the reflectivities of the front and back surface of the interferometer.

μ = refractive index of the gap of the interferometer

λ = wavelength of the light

t = the wedge thickness

ϕ = angle of incidence of light

(T = 1 - R when there is zero absorption in the film)

The factor F controls the sharpness of the fringes.

For sharp fringes sin δ can be replaced by δ.

$$\therefore I = \frac{I_{max}}{1 + F\frac{\delta^2}{4}} = \frac{I_{max}}{1 + \left\{\frac{R}{(1 - R)^2}\right\}\delta^2} \qquad (2)$$

At half width I = $\frac{1}{2}$ Imax

$$\therefore \delta = \frac{1 - R}{\sqrt{R}} \qquad (3)$$

The fringe phase angle corresponding to the fringe half-width is

$$= 2\left(\frac{1 - R}{\sqrt{R}}\right) \qquad (4)$$

The phase interval between successive orders is 2π, hence the fringe half width as a fraction of an order is

$$W = \frac{1 - R}{\pi\sqrt{R}} \quad \text{(Tolansky 1948)} \qquad (5)$$

It is to be noted that the above equations apply strictly to plane parallel surfaces in which all the effective beams are used. In practice this cannot be secured because of

(a) surface imperfections.

(b) lack of perfect parallelism

(c) finite aperature.

It follows that all the surface imperfections are integrated and cause broadening for every fringe. Formula (3) shows that is particularly sensitive to changes of R, when R is in the neighbourhood of unity. δ is a minimum when R is a maximum. To achieve a maximum value of R it is essential to reduce the absorption coefficient as much as possible. The contrast or visibility of the fringes also depends upon the absorption (in the reflected system only).

The contrast of the fringes in transmission is not affected by a change of absorption coefficient when R is in the neighbourhood of unity, so that extremely sharp fringes can be readily achieved by having R as high as 94 per cent.

Because of these considerations the process of depositing metallic films of high reflecting coefficient and low absorption is essential for the practice of multiple beam interferometry. Tolansky (1948) has already established that for work in the wavelength region 5 - 7000A^o, silver when evaporated in a high vacuum can give high reflectivities (some 95 per cent) with low absorption (below 5 per cent). The silver film necessary to produce such reflectivity is about 500A^o thick and this contours faithfully surface details which have height changes even only as small as 10A°, provided the details are not too small in extension across the surface (say not below 1/250 mm across).

The properties of the reflected system in multiple reflection interference are more complicated. Hamy (1906) studied these interference phenomena in reflection thoroughly, both theoretically and experimentally, for chemically deposited films but these fringes received little attention until Tolansky (1948) and Holden (1949) repeated Hamy's experiments for vacuum deposited films, mainly with a view to applications to surface topography. The experimental conditions for good reflection fringes are more critical than in transmission. The reflectivities of the surfaces of the interferometer must be critically matched for the best results.

Wedge Interferometer

If the two highly reflecting surfaces are inclined making a small angle θ, the Airy summation is modified for there is no longer equal path difference between successive beams. The beams therefore gradually get out of step, so that the retardation ultimately becomes $\lambda/2$, which tends to destroy the condition for the formation of sharp fringes. Tolansky (1946a) and Brossel (1947) have shown that when the fringes are viewed at the surface, the path difference between the first and n^{th} beam is $2\,nt - \frac{4}{3} n^3 \theta^2 t$, where t is the thickness of the film considered. When $\frac{4}{3}n^3 \theta^2 t = \frac{\lambda}{2}$, the first and n^{th} beams are out of phase and thus the fringe definition will suffer.

If X is the number of fringes per cm on the wedge surface, $\theta = \frac{\lambda}{2} X$ and therefore $t = \frac{3}{2n^3 \lambda X^2}$

For the Airy condition to be approximated to, t should be less than this.

In practice the important fact is that t should be as small as possible (not exceeding a few wave-lengths of light). Also in a wedge, the linear displacement of the successive beams is a matter of considerable importance and must be kept within the lateral resolving limit of the objective. Therefore again t must be as small as possible and it is preferable to use normal incidence of illumination for which objectives must be large enough to collect a sufficient number of beams. Again a broadening of fringes will occur if the beams incident on the interferometer are not parallel. For this purpose the light from the source is focussed on an iris diaphragm which is stopped down to within the tolerance limits (1 - 3°) and this acts as the source.

Thus the fundamental conditions for the production of highly sharpened multiple-beam Fizean fringes are:-

(1) The surface must be coated with a highly reflecting film of minimum absorption

(2) This film must contour the surface exactly and be highly uniform in thickness

(3) Monochromatic light, or at most a few widely-spaced monochromatic wavelengths should be used.

(4) The interfering surfaces must be separated at most by a few wave-lengths of light.

(5) A parallel beam should be used (within a 1 - 3° tolerance)

(6) The incidence should be preferably normal.

Practical Application of Fizean Fringes.

The practical importance of the Fizean fringes will now be considered.

In an interferometer formed by the correctly silvered diamond surface and an optical flat the interference fringes obtained may be interpreted as a "contour map" of the non-plane surface, each fringe representing a change of $\frac{\lambda}{2}$ from the thickness of the adjoining fringe. However there are two notable differences between geographical contour lines and those formed by interference. In geographical contours, the intersecting planes are parallel to the matching flat, whilst in optics the reference flat can be tilted. As this is tilted differences emerge. It is to be noted that when high magnifying powers are used, the tilt must be increased to bring the fringes closer together so that several can be seen in the small field of view of the objective. For this purpose a selected cover-slip has been used (as will be discussed later) since an ordinary optical flat (of 1 mm. or 3 mm. thick) would limit the working distance and thus the power of the objective.

Localised multiple-beam fringes obey the formulae

$$n\lambda = 2\mu t \cos$$

where n is the order of interference and an integer, λ is the wavelength of light, μ is the refractive index of the medium between the interferometer plates, t is the thickness of the interferometer gap and θ is the angle of incidence. For normal incidence and an air gap

$$\cos\theta = 1 \quad \text{and} \quad \mu = 1$$

$$\therefore \; n\lambda = 2t \quad \text{or} \quad t = \frac{n\lambda}{2}$$

Thus this method is absolute and measures surface contours in terms of light waves. The chief advantage is that it gives the interferogram of an extended area of the surface especially when low power objectives are used.

The large majority of multiple-beam Fizean fringes interferograms were carried out in reflection for it is well to realise that for even a transparent diamond crystal does not often have a plane surface at its reverse face.

The experimental arrangement for observing the fringes in reflection is shown in figure (3).

A metallurgical microscope is adapted so that the image I of the light source is formed in the back focal plane of the objective O, thus enabling the objective to direct a parallel beam of light at normal incidence on to the interferometer X.

Usually only the green mercury line 5460A^{o} was used for the interferometric examination, so that the separation

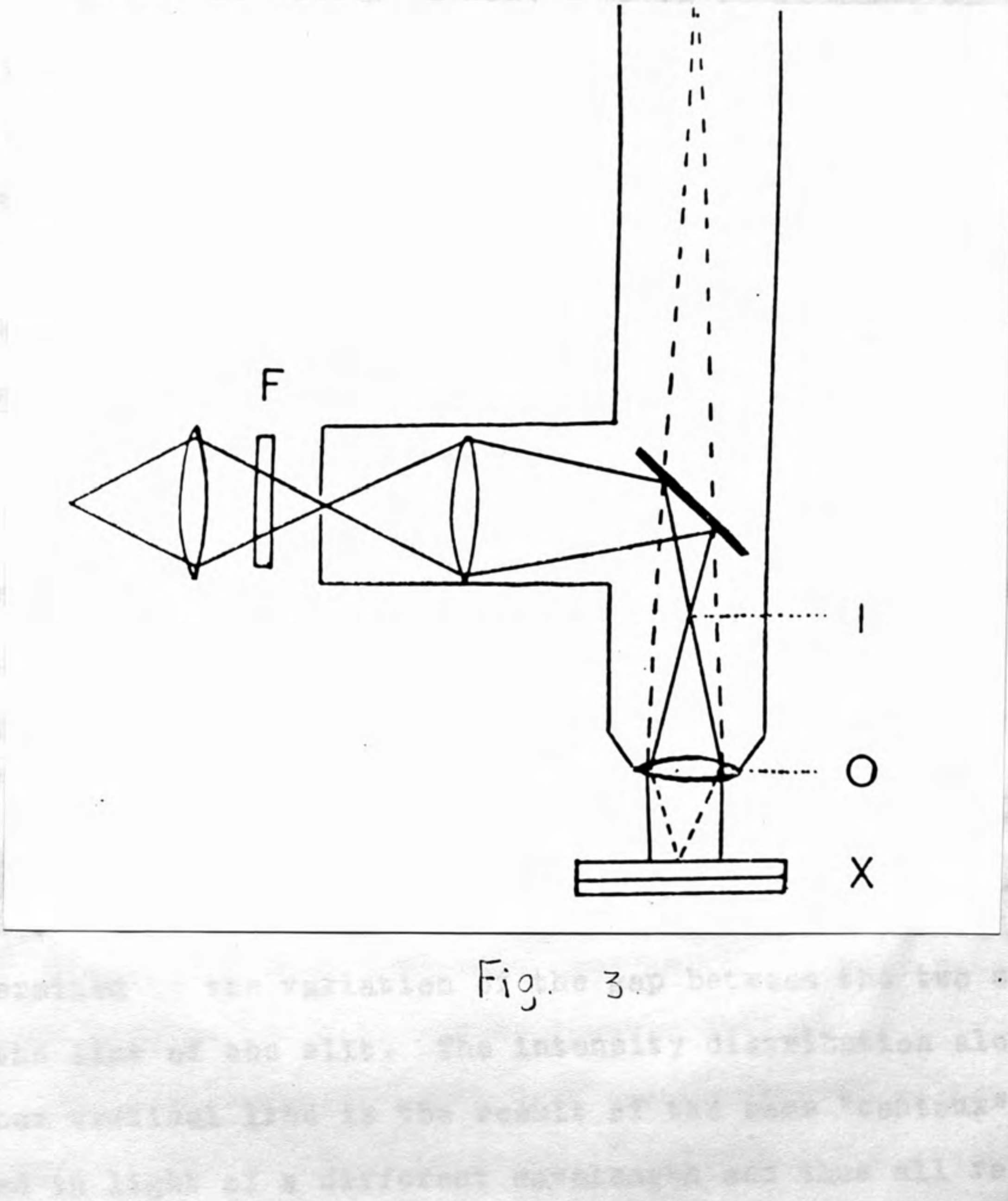


Fig. 3.

between fringes corresponds to 2730A°. Occasionally it was desirable to use the green line in conjunction with the yellow lines of 5770A° and 5790A° especially for the preliminary inspection of the surface. At other times unfiltered mercury has been used (effectively this consists of the above three, plus the 4358A° and 4078A° groups). It is to be emphasized that high definition multiple-beam Fizean fringes are only obtained when all the necessary optical conditions are critically obeyed.

A supplementary technique has also been used (in Tolansky's nomenclature) "fringes of equal chromatic order".

Fringes of Equal Chromatic Order.

This is an alternative technique to multiple-beam Fizean fringes and forms another powerful tool for the accurate measurement of optical distances. Thus if the image of a section of an interferometer wedge is projected on the slit of the spectrograph, white light being used, fringes of equal chromatic order are observed in the focal plane of the spectrograph. The intensity distribution along any vertical line is that of interference of equal thickness produced in monochromatic light. It is determined by the variation of the gap between the two surfaces, along the line of the slit. The intensity distribution along any other vertical line is the result of the same "contour" observed in light of a different wavelength and thus all refer to the one region on the surface under study. Although this method is limited to a line "contour" only, it has the important advantage of the immediate recognition between up and down directions which is sometimes difficult when using Fizean fringes.

It is of interest to note that, if an extended area of an object is to be inspected, this can be quickly carried out visually merely by scanning the image across the spectrograph slit with a slow motion screw. Also the measurements of wavelength can be made either directly from the wavelength drum of the spectrograph, or from photographic plates, on which are exposed both the fringes of equal chromatic order and the mercury spectrum.

However, the same considerations that apply to multiple-beam Fizean fringes apply equally to the multiple-beam fringes of equal chromatic order except that, the precision of measurements in the latter is not affected by local variations in dispersion which is a restricting feature of Fizean fringes. Thus high-power objectives can safely be used without the fringes suffering.

A simple optical set-up which can be used for examining reflection fringes with either pure monochromatic light or white light, is shown in figure (4).

The source A is a mercury arc; either a very wide slit can be used or the slit may be removed entirely.

One then, sees, fringes from the surface XY in the spectrograph at PQ, as shown in figure 4 (A). L,M,N,O are the patterns of the yellow doublet (LM), the green line N, and the blue line O. An advantage of this system is that an alternative

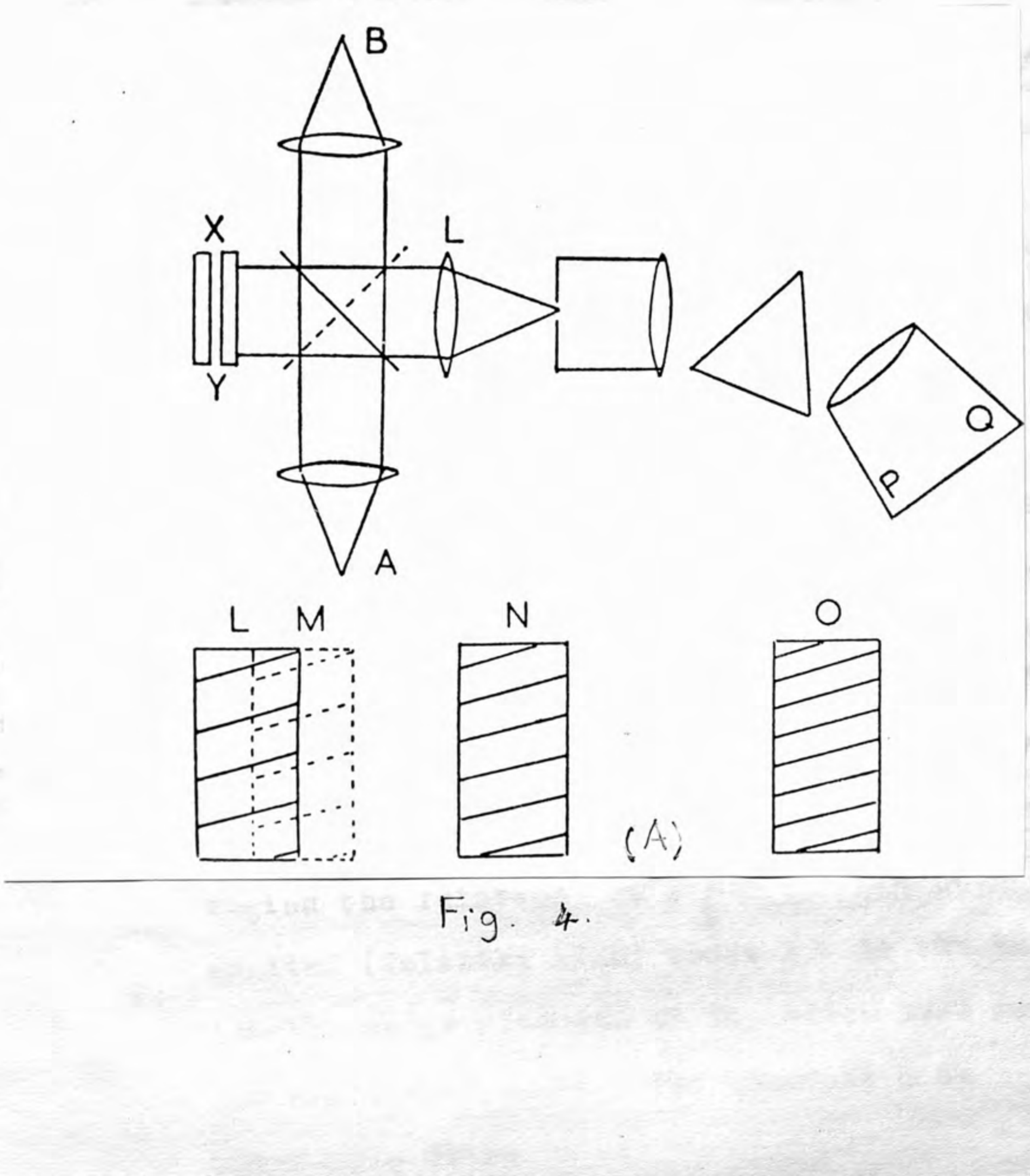


Fig. 4.

white-light source at B permits fringes of equal chromatic order to be observed by a quick change-over of the reflector between lens and interferometer, followed by suitable adjustment of the lens L.

Measurement of step-heights.

For an air gap and normal incidence we may write

$$n \lambda = 2t$$

(i) For small spaced fringes where there are many fringes in the field of view the simple relation $dt = dn \times \frac{1}{2} \lambda$ is applicable (dn is a small fraction of an order).

However, in this case it is only necessary to measure the fraction of an order displacement dn at one wavelength. A displacement towards the violet corresponds to a step towards the optical flat.

(ii) For widely spaced fringes where possibly no more than three or four fringes appear in the visible region the relation $dt = \frac{n}{2} d\lambda$ can be applied (Tolansky 1948) where $d\lambda$ is the wave-length change produced by dt, which need not necessarily be small. The quantity n is obtainable since

$$n \lambda = (n + 1) \lambda_1 ,$$

for two adjacent orders, giving

$$n = \frac{\lambda_1}{\lambda - \lambda_1}$$

with similar expressions for other pairs of orders. Since n is a small number, it can always be determined without ambiguity when high dispersion is used. Since both n and d λ are now determined these give dt.

High Dispersion Interference Fringes.

It has already been stated that the spacing of the Fizean fringes can be adjusted by the tilt of the optical flat and may be adapted to the particular purpose. If the two surfaces concerned forming a small wedge angle are brought as near as parallel as possible and illuminated with monochromatic light high dispersion interference fringes are formed. On removal of the colour filter a high dispersion complex pattern is obtained as shown in figure (5). This exhibits a wealth of structural detail not obtainable by ordinary micrographic methods, i.e. there is a condition of high "interferometric contrast".

Tolansky (1948) has established that the high sensitivity of the method depends on the reflectivity of the surfaces. With 95% reflectivity, a visually detectable change of 10% in intensity transmitted is produced by a step a mere 3A° in height.

It is to be emphasised that the intense interference contrast obtained by this technique is at least equal and in many ways superior to that given by phase contrast equipment. The advantage of the interferometric method over phase contrast is that while both reveal details of structure as a contrast picture, a slight adjustment of the interferometer gives precise

Fig. 5 X110

numerical information on the depths of the surface details.

An extension of the above method is the "crossed-fringe" technique developed by Tolansky and Wilcock (1946) in which they have combined the advantages of both low and high dispersion multiple-beam fringes by superimposing several fringe patterns of the same surface area by taking successive photographs with different tilts of the optical-flat. But, it is well to realise that such a technique is suitable only for transparent surfaces which do not lie far from a mean plane.

CHAPTER II

THE DESIGN OF THE INTERFEROMETER

The interferometer used for the present investigation was designed for the use with the Vicker's Projection Microscope. It consisted of two main parts as shown in figure (6). The upper part of the jig is a brass disc of about 22 inches in diameter with a central portion for resting the mount for the diamonds. The diamonds were mounted on a glass flat of about 1 inch diameter using gelva cement which has a low melting point of about 60°C and has a further advantage of permitting the stone under study to be viewed in transmission. The diamond after being correctly silvered on this holder was then held in position to the upper part of the jig by means of small screws so that the surface of the diamond to be examined faced downwards.

The lower part of the jig is a brass disc of about 2.2 inches in diameter fitted with three equally spaced arms of about 2.5 cm. in length, and the lower section of each arm being surrounded by a spring. The optical flat after being correctly silvered is held in position on the central portion of the lower part of the jig with its surface facing upwards. The screws attached to the stage of the microscope allowed the whole jig to be rotated without it being touched by hand so that the area to be examined is seen in the field of view of the microscope.

The upper part of the jig can be fitted on to the lower part so as to rest on the tops of the springs by inserting the three arms into the corresponding holes on the top part of the jig. The adjustment of the interferometric gap between the diamond surface and optical flat was then obtained by means of three nuts threaded on the arms. After practice great sensitivity and control were easily achieved for obtaining the required tilt between the two surfaces. This arrangement proved to be very stable, even at high dispersion the fringes showed no perceptible creep over periods as long as twenty minutes, much longer than the photographic exposures needed.

Optical Flats.

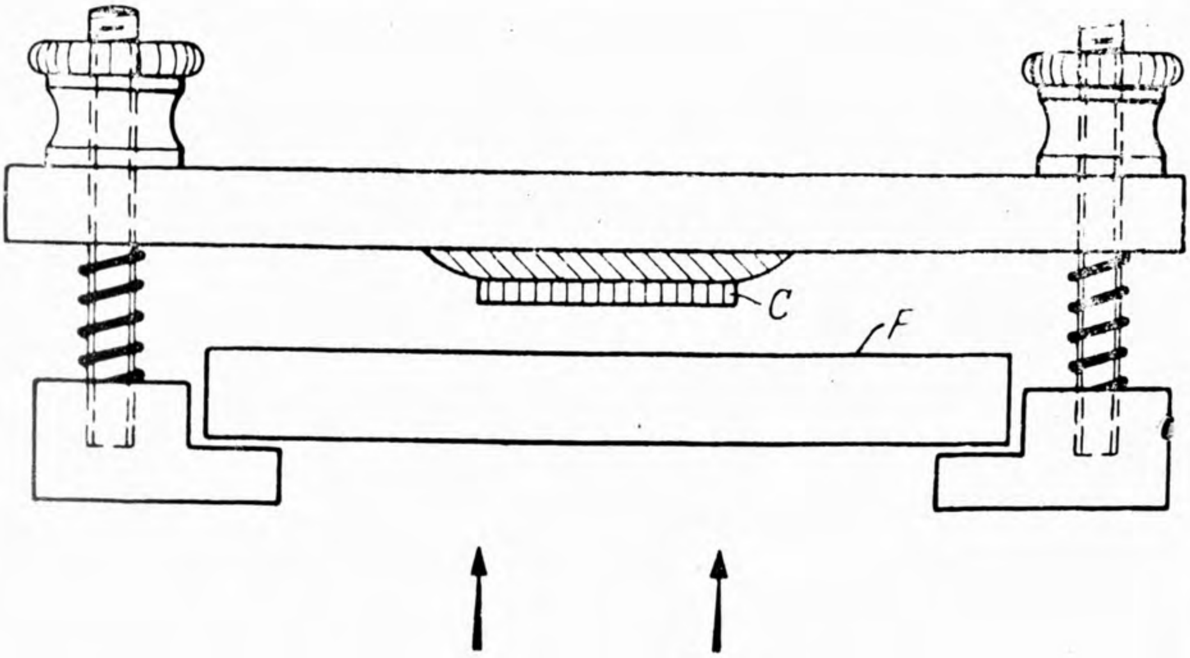
Three types of optical flats were used depending upon the power to be used and the surface to be studied.

(a) Optical Flats. For nearly perfect surfaces of diamond and when low powers down to 16 mm. to be used, very high-grade optical flats 3 cms. in diameter and 3.5 m.m. thick especially made by Hilger were used, of which the central 1 cm. disc has been worked flat better than $\frac{\lambda}{40}$ (Hg green light). Locally, over appreciable areas, these flats are likely to be smooth and flat to within at least $\frac{\lambda}{200}$, probably much better. For the majority of work flats in the form of a square 2.5 cm. in length and about 2 mm. thick cut from photographic plates were satisfactorily used with high powers up to 8 mm.

(b) Micro-flats. For the study of surface topography of very rough surfaces of diamonds where the required close approach necessary for high-precision multiple-beam interferometry is not obtained with ordinary optical flats, micro-flats as devised by Tolansky and Omar (1953) were used. These were in the form of truncated cones with flat tops of less than 1 mm. in diameter and were prepared by the author in the laboratory with different thicknesses in the following procedure.

An optical flat with the required thickness is selected and coated with gelva cement to protect the upper surface of glass from being scratched. Carborundum powder was then spread over the gelva with some drops of water and a cylindrical piece of about 5 mm. in diameter is carefully cut. The cylindrical piece was then mounted by gelva cement to the top of a metal rod which was fixed to a lathe. The grinding was then carried out by the use of carborundum powder spread over a copper strip until the required shape and size is obtained. In this manner truncated cones of different thicknesses were made.

The cone, after being cleaned thoroughly and silvered, is mounted centrally in a simple manner on a brass ring which sits on a special jig to hold the crystal and micro-flat with convenience of moving the surface of the specimen in two perpendicular directions on the stage, and can be brought as near to the cone tip as is desired. Also the specimen can further be tilted to the plane of the tip in order to secure any required interference fringe direction or dispersion. This is



Line diagram showing the jig
C–crystal ; *F*–optical flat

Fig. 6.

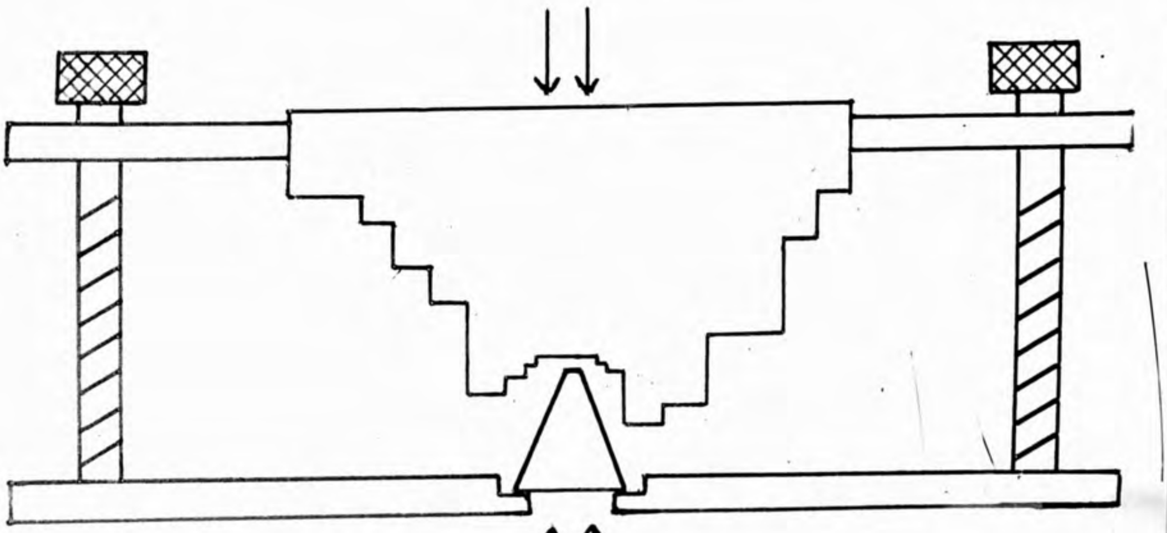


Fig. 7.

similar to the type described by Tolansky and Omar (1953). A schematic diagram of the crystal and micro-flat mounted on the jig is shown in figure (7).

With a 5 mm. cone there is no difficulty in using a 25 mm. objective and a slightly shorter cone permits the use of a 16 mm. lens, both of which give best results for multiple-beam interference.

(c) <u>Cover-slip</u>. For the use of high powers ordinary flats are usually too thick and limit the working distance. To overcome this difficulty selected cover-slips were used. In this case a 3 mm. objective, N.A. 0·95, with correcting collar for the cover-glass thickness was employed. (This will be discussed in detail later).

CHAPTER III

THE SILVERING TECHNIQUE

The practice of multiple-beam interferometry requires the coating of two surfaces involved with highly reflecting thin layers of metal films having very small absorption losses for visible light. This is conveniently done by the thermal evaporation of silver in a high vacuum. Since the technique has been adequately described by Tolansky (1947,1948), Strong (1946) and others, a relatively brief description of the technique and apparatus used in the present work will be given.

The first requirement for successful evaporation is thorough cleansing of the specimens to be coated. Oil and impurity films reduce the reflection coefficient somewhat and increase the absorption a great deal, both of which are undesirable for the visibility of the fringes, especially in the reflected system. The cleaning treatment to be used depends upon the nature of the surface to be silvered. Optical flats of glass are washed with soap and water to remove gross amounts of grease contamination and then cleansed with hydrogen peroxide and rubbed gently with dry cotton wool until no breath figures are seen. For cleaning of crystal surfaces a similar process may be adopted. But for diamond which is very resistant to chemical action the crystals can be treated with nitric acid and washed with water several times and then cleaned as above. Final cleanliness is achieved by mild ionic bombardment from a discharge passed at a pressure of about 1 mm. in the silvering plant.

A commercial evaporating unit manufactured by Edwards and Co. (type E_3) was used. The general form is shown in figure (8) a,b. It consists of a vacuum chamber in the form of a large pyrex bell jar 60 cm. in height and 40 cm. in diameter resting on a horizontal metal base-plate. The chamber is evacuated by a large three-stage silicon oil diffusion pump backed by a rotary oil pump. A number of vacuum-tight insulated electrodes are fastened into the base-plate, between which the evaporation filaments and electrodes for high tension discharge are connected. The backing vacuum and the final vacuum can be read directly by the Pirani gauge and Pilips ionization gauge supplied in the unit. At a pressure of about 1 mm. of mercury the high voltage discharge cleaning can be started. When 10^{-5} mm. pressure is reached the silver can be evaporated by heating the molybdenum filament using a current of 120-150 ampere. While the silver is fusing a moveable shutter covers the filament to protect the substrate from possible contamination. Experience shows that rapid deposition gives best results; this has recently been proved by Sennet and Scott (1950). The thickness of the silver layer and hence the reflectivity is judged visually by viewing through the top of the bell jar; in this way reflectivities may be estimated to within a few per cent and no important differences are found between the results of successive evaporations.

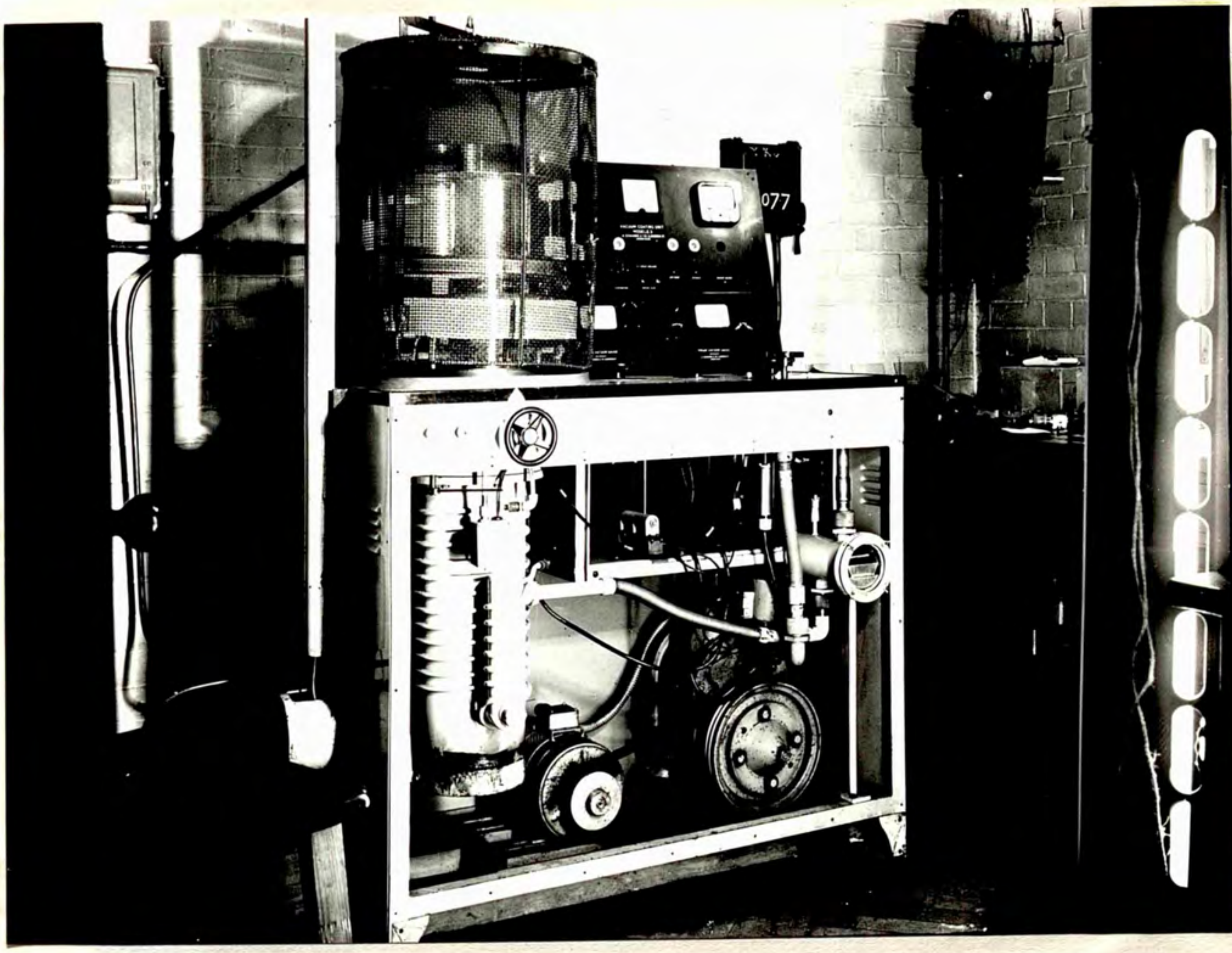


Fig. 8 (a)

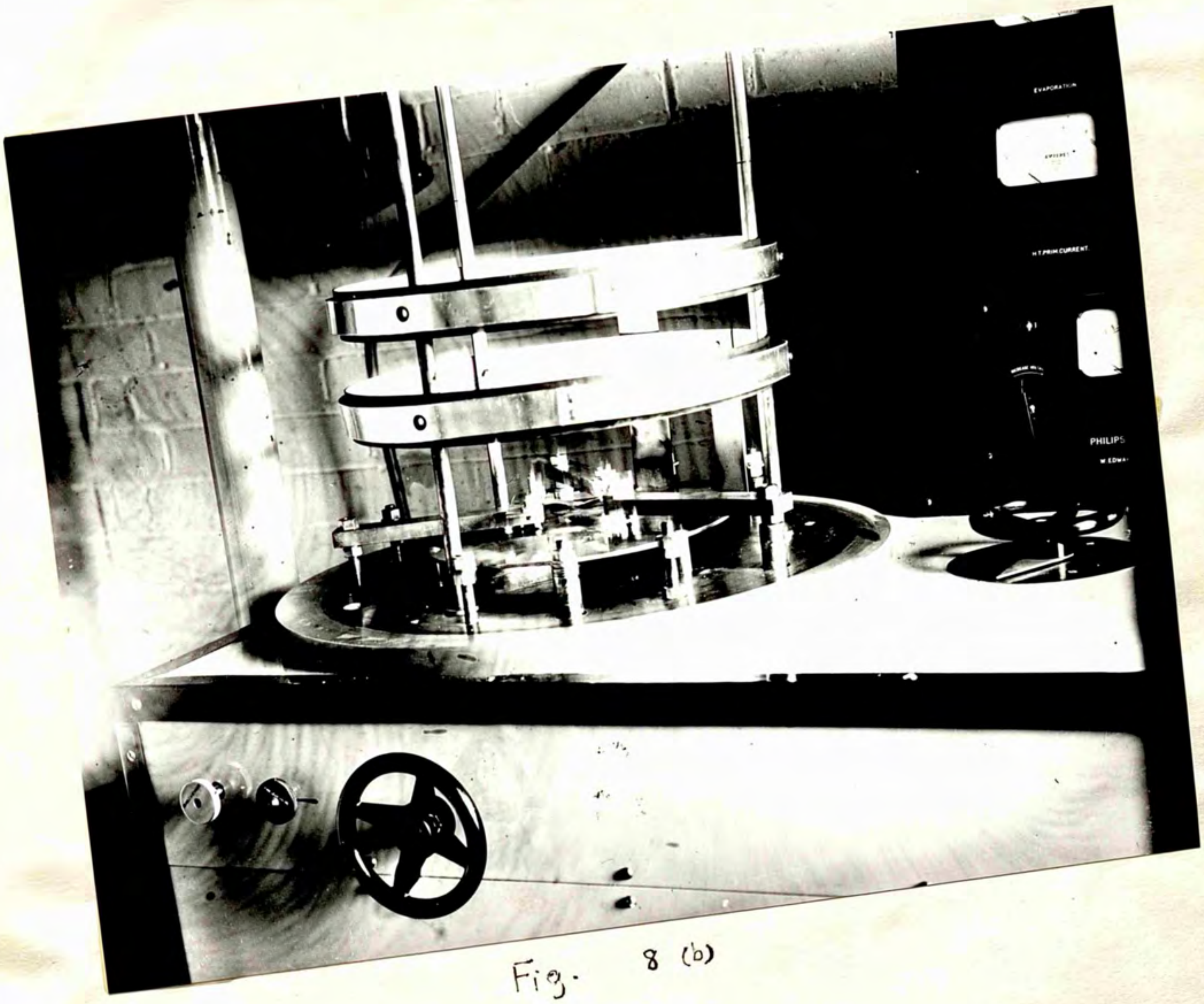


Fig. 8 (b)

CHAPTER IV

THE MULTI-LAYER TECHNIQUE

In addition to thermal evaporation of silver films on to the surface of the specimen, dielectric multi-layer films are found to be useful in some cases, especially when applied to the study of the (110) faces of diamonds (as will be seen later). These films were first produced in the U.S.A. (1942) for use as beam splitters which would reflect approximately 50% of the incident light and transmit the rest. An extensive bibliography has been given by Cotton and Rouard (1950) and by Kuhn (1951) and their application to interferometry described by Jacquinot and Dufour (1950) and later by Turnbull and Belk (1952) and Belk, Tolansky and Turnbull (1954).

These multi-layer films consist of alternate deposits of high and low refractive-index layers, each of optical thickness (μt) either one quarter of the wavelength of the light to be employed for first-order films, or three quarters of the wave-length for second order films. Deposits of alternate layers of zinc sulphide ($\mu = 2.37$) and cryolite ($\mu = 1.36$) of thickness $\frac{\lambda}{4}$ each on the optical class ($\mu = 1.5$) were successfully used.

The principle of multi-layer films is most easily understood by considering initially a single film. If a single film having an optical thickness $nt = \frac{\lambda}{4}$, where t is the metrical thickness and λ is the wavelength of light in vacuo, is deposited on glass, the reflectivity of the surface is increased if the refractive index n of the film is greater than that of the glass. The light reflected at the dielectric-air surface suffers a phase change of π and is in phase with that reflected at the dielectric-glass surface which has traversed an additional optical path $2\ nt = \frac{\lambda}{2}$, this being equivalent to a phase change of π. Since the light reflected at these surfaces is in phase it is reinforced and an increase in reflectivity takes place. A simple calculation shows that a single $\frac{\lambda}{4}$ layer of zinc sulphide on glass increases its reflectivity from 4% to 31%, whereas a similar film of cryolite reduces the reflectivity of the glass from 4% to 1%. The reflectivity of a single quarter wave film is given by

$$R_{max} = \left(\frac{n_2 - n_1^2}{n_2 + n_1^2} \right)^2$$

where n_1 is the refractive index of the film and n_2 that of the substrate. The reflectivity is a maximum for the wave length at which the film is a quarter wave thick.

By using a number of films of alternately high and low refractive index and each of optical thickness $\frac{\lambda}{4}$, various reflectivities may be attained. Thus with 1,3,5,7 and 9 dielectric layers (ending with zinc sulphide) reflectivities equal to 31,67,87,94,97 per cent respectively can be achieved. Jarret (1952) reports that for a 7-layer film (4 of zinc sulphide and 3 of cryolite) the reflectivity is 94% and the absorption is 1%, while Tolansky (1946) has established that a silver film of similar reflectivity has an absorption of some 5%. It is to be noted that as the number of layers is reduced the reflectivity and absorption decrease and for this reason the absorption for low reflecting multi-layer films is negligible.

The technique employed for the production of thin dielectric films is similar to the silvering technique; the same commercial evaporating plant can be adapted for the purpose. The main difficulty lies in the control of the thickness of each layer as the material is deposited without breaking the vacuum. Therefore two molybdenum filaments are used to hold the two dielectric materials for alternate operations.

In producing multi-layer films it is necessary to measure the thickness during evaporation as accurately and as simply as possible. The method of thickness control by colour change of the reflected light originated by Banning (1947) is employed and successful results are obtained. It is of interest to emphasise that in addition to the high reflectivities given by dielectric multi-layer films (which indeed can be almost attained by silver films) the following advantages are almost attained:-

1. The chief is that they have a low absorption.
2. The ease of obtaining a useful range of reflectivities, with low absorptions is valuable.
3. There is the possibility of obtaining a range of reflectivities for a range of different wavelengths.
4. The high reflectivity of second order films is fairly sharply localized at one wavelength.

5. The high durability and resistance to corrosion of the layers is a valuable advantage.

In addition, the good contouring properties of the multi-layer films has been well established in this laboratory. For steps down to as small as $\frac{1}{60}$th of the multi-layer thickness, the contouring is satisfactory; for there is at any rate, exact agreement with the silver values (within experimental limits) down to steps as small as 90 A^o. However, this conclusion applies only to step heights over regions which have relatively enormous lateral extension compared with the step height itself. Belk, Tolansky and Turnbull (1954) have shown that if the structure of the specimen is more than three times greater in lateral extension than in depth, multi-layers may safely be used.

In the succeeding sections supplementary microscope techniques which have also been used will be described.

CHAPTER V

THE PHASE CONTRAST MICROSCOPE.

Zernicke's phase contrast microscope has become a powerful and comparatively simple means of revealing in sharp contrast very small path differences in objects, provided they are on a small enough scale to produce marked diffraction. The technique does not lend itself to numerical evaluation but is rapid, convenient and useful as an exploratory method.

The principles of phase contrast microscopy were first given by Zernicke, (1934, 1935) and a detailed mathematical account of the theory together with its application in practice has been given by various workers including Kohler and Loos (1941), Burch and Stock (1942), Payne (1947), Taylor (1947, 1949). An excellent bibliography of the principles and applications of this technique is also given by Bennett, Jupnik, Osterburg and Richards (1951). For this reason the present treatment will be restricted to a brief survey of the technique and the apparatus used.

The method is somewhat distantly related to the dark-ground illumination, in which the direct beam is stopped out completely. In phase contrast this beam is only weakened, but its phase is also affected. This may easily be understood if we suppose a diffracting object under view in a microscope. This can be seen by a combination of light viewed as a direct beam and diffracted beams (spectra). When viewing amplitude features, the different diffracted intensities combine to make a visible pattern. Zernicke has established that the diffracted beams from an optical phase structure differ from those of a corresponding amplitude structure by a phase difference of a quarter of the wavelength of the light used. Thus, retarding the direct light by one quarter of a wavelength brings the direct and diffracted waves into phase, giving rise to a negative phase contrast image. Portions of the object giving greater retardation are rendered bright against a darker background. Equally, advancing the direct waves by one quarter of a wavelength, or (what is the same thing) retarding them by three quarters of a wavelength, puts the direct and diffracted waves out of phase by half a wavelength. This again gives rise to destructive interference, known as positive phase contrast. Portions of the object giving greatest retardation are now rendered dark against a lighter background.

A diagram of the light path through a phase - contrast microscope is shown in figure (9).

The apparatus used in the present work was the Cooke, Troughton and Simms phase contrast equipment for incident illumination which can be fitted on the Vicker's projection microscope. In this device an annular disc is placed in the position of the normal iris, and an image of it is therefore formed in the back focal plane of the objective and through this image passes all the direct light from the object. In

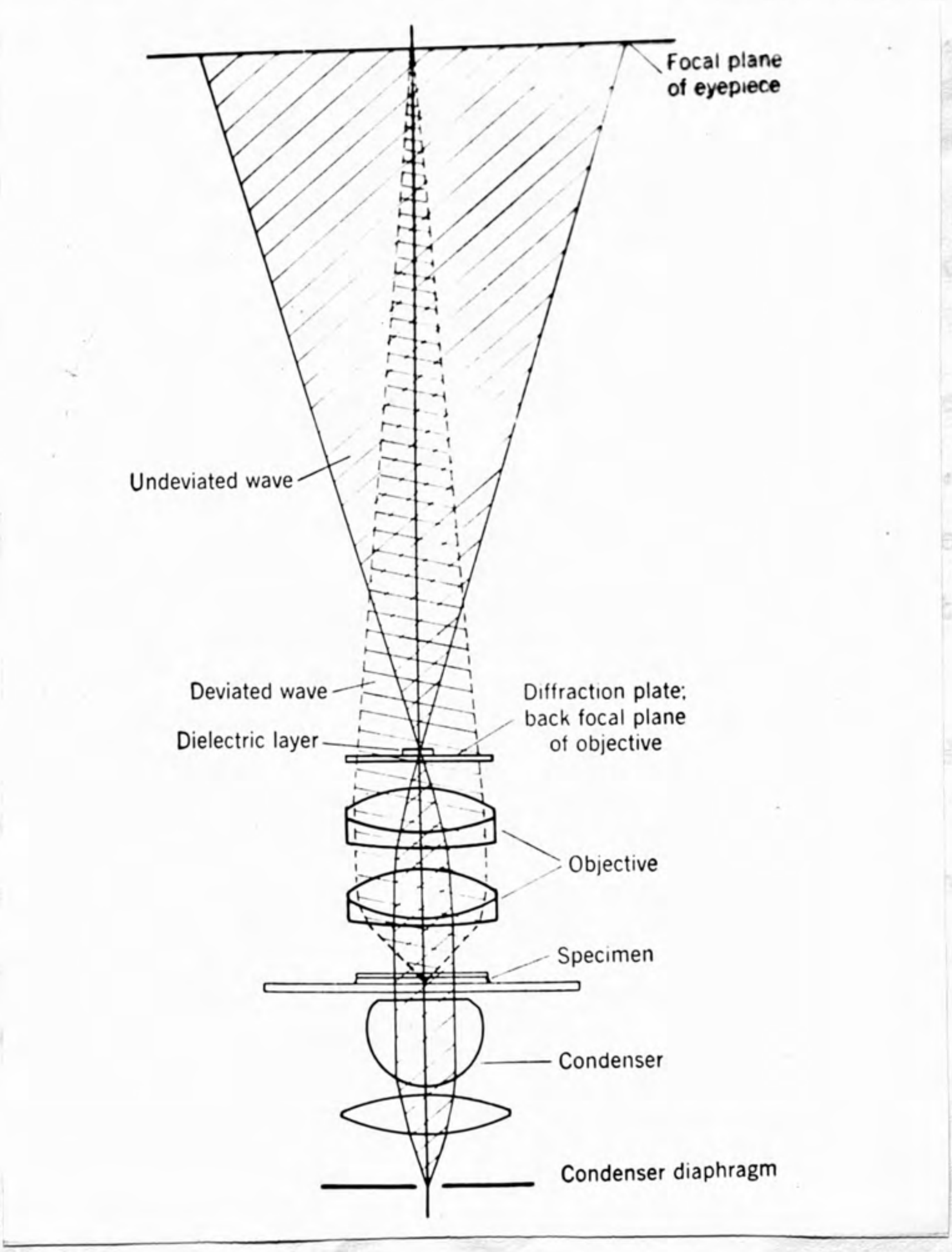

Focal plane
of eyepiece
Undeviated wave
Deviated wave
Diffraction plate;
back focal plane
of objective
Dielectric layer
Objective
Specimen
Condenser
Condenser diaphragm

Fig. 9.

this plane is inserted a phase plate (having an absorption of 80%). It takes a form of a disc of glass in which an annulus is cut, corresponding in size to the image of the condenser annulus and of such a depth as to advance the direct waves by one quarter of a wavelength in relation to the diffracted light passing through the remainder of the plate. We therefore achieve a <u>positive phase-contrast</u> image.

A diagramatic scheme of the instrument is shown in figure (10).

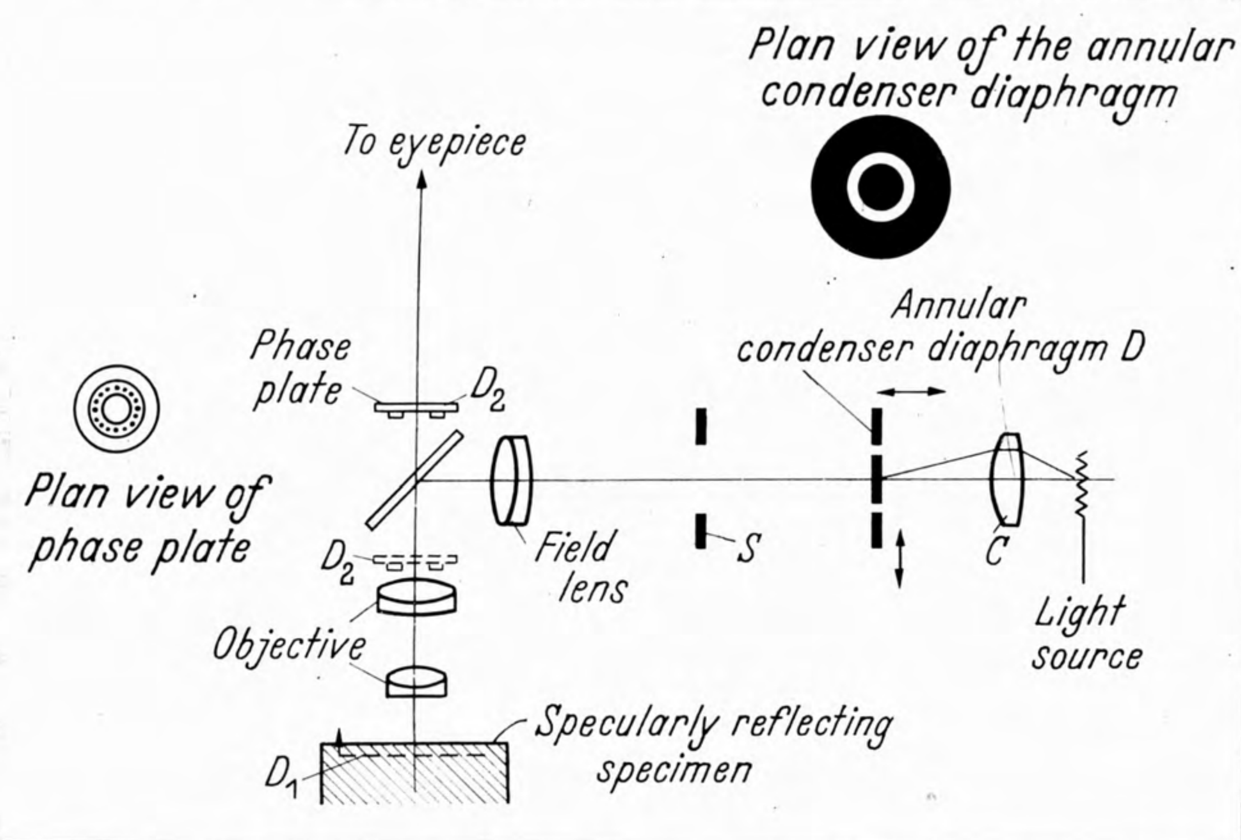
D is an annular diaphragm which serves as the entrance pupil of the optical system consisting of a field lens, the microscope objective, and the reflecting surface of the specimen.

C is a condenser lens which focuses the light source on D.

The field lens and the objective form an image D_1 of the field stop on the specularly reflecting surface of the object specimen. The light is reflected from the surface of the specimen and is then passed through the objective again to form a real image D_2 of the diaphragm D.

The optical assembly consisting of the microscope objective lenses, the beam splitter, and the phase plate are mounted on the objective.

The surface to be observed must be adjusted perpendicular to the optical axis of the microscope so that the image of the diaphragm is centred upon the optical axis when



Plan view of the annular condenser diaphragm
To eyepiece
Annular condenser diaphragm D
Phase plate
D_2
Plan view of phase plate
D_2
Field lens
S
C
Light source
Objective
Specularly reflecting specimen
D_1

Fig. 10.

the condenser diaphragm has been centred. For this purpose an auxiliary microscope is provided, which can be inserted in place of the normal eyepiece. This enables the back focal plane of the objective to be examined so that the image of the diaphragm can be made to coincide exactly with the phase plate. However, objects mounted on the stage of the microscope may produce changes in amplitude or changes in the phase of the transmitted light. In the former case the direct and scattered rays arriving in the back focal plane of the objective are in phase and a well contrasted image is produced in the field of view of the microscope by interference. In the latter case the direct and scattered rays arrive in the back focal plane of the objective out of phase by $\frac{\lambda}{4}$ and a well contrasted image can be produced. Ideally, contrast is at its best when both diffracted and direct beams have the same intensity. In phase contrast microscopy there is practically no decrease in resolution.

For finally improving the contrast very contrasty slow photographic plates (Kodak B_{20} or B_4) can be used and then developed in a contrasty developer such as D_8 caustic developer; still further contrast is achieved in printing by using extra hard photographic paper.

CHAPTER VI

THE LIGHT-PROFILE MICROSCOPE.

This technique which has been developed by Tolansky (1952) is a modified form of Schmaltz light-cut method (1936). Within recent years it has assumed value in many fields, in particular in the evaluation of metal finish, finish produced by machine tools, and by lapping and also for the studies of surface characteristics of crystals. Diamond is one of those crystals whose surface features are being studied by this technique. The method described is simple, inexpensive, and non-destructive and it has the advantage of giving magnifications of up to 2000 with corresponding resolutions of the order of 0.25 μ both in extension and in depth. The Schmaltz light-cut has been adequately discussed by Räntsch (1945). It is a microscope technique which reveals a line profile of a metal surface with magnifications up to about 400 in extension and 650 in depth but it suffers from various defects. In the original method, an image of a slit is projected with a microscope on the surface under study at an angle of incidence of 45°. The specularly reflected beam is then viewed with a separate microscope. It thus requires a special double microscope. The effect of the arrangement is to convert a profile in depth into a line pattern in extension. Working distances prevent the use of high powers.

Methods have been proposed by Busch (1943), Frischmuth (1945) and Menzel (1951) to permit the use of a single high power lens to increase the magnification but resolving power and definition suffer considerably. The four distinct defects in these methods are:-

1. A serious difficulty is that the profile is a bright line on a dark background which makes identification of the area under study difficult.
2. Absence of specular reflection at rough regions gives a false representation and may well give quite wrong estimates of roughness, especially if non-specular parts lie deep or project high.
3. Diffuse regions produce scatter and local image broadening.
4. Apart from Menzel's method only a single-line profile appears, and thus many separate photographs may be required to survey an area.

To overcome all these defects and to achieve high resolution and magnification Tolansky (1952) has adapted the Vickers Projection Microscope, by simply reversing the condition of illumination by using an opaque line on a bright field before the field iris instead of a slit. In fact this simple principle can be applied to any standard metallurgical microscope, by placing a piece of glass with a scratch on it in the focal plane of the field iris using an off-pencil beam of illumination. This acts as a shadow and a line is then thrown on to the object.

The schematic arrangement of the light-profile microscope is shown in figure (11).

A is a monochromatic light source with wratten 77A filter to give the green 5461A° line.

S_1 is a diaghragm

S_2 is the field iris in the universal illuminator near to which the profile is kept so that the image of the profile can be projected on the surface X under study.

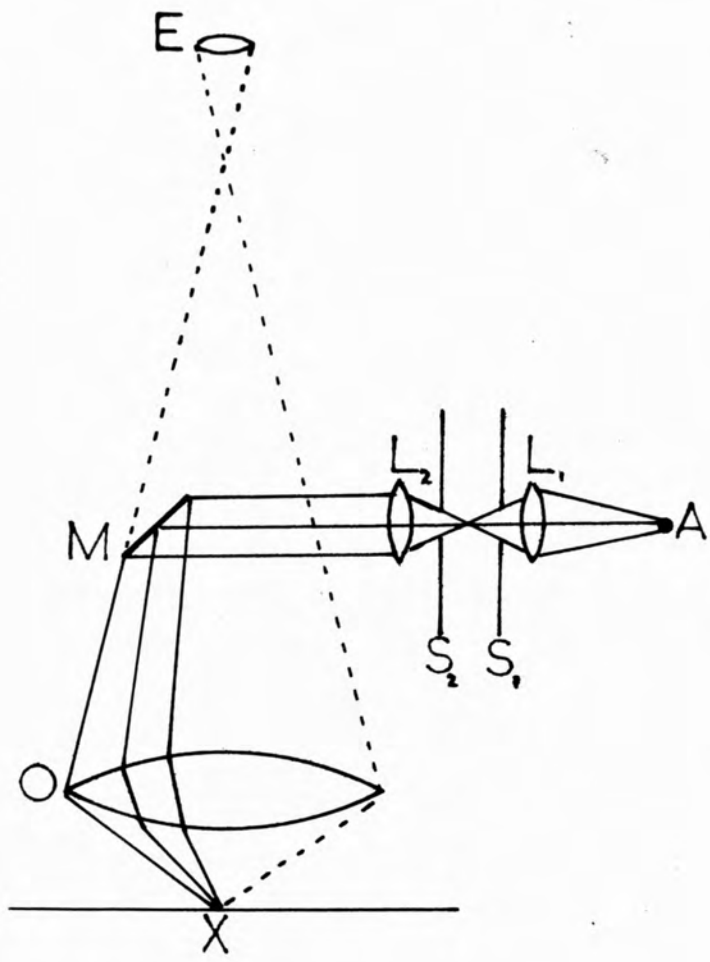
M is a metal tongue sector reflector which gives the off-centre illumination and practically the full aperature of the objective O is made use of.

E is an eyepiece where the image can be seen.

In practical work the specimen is focussed first with a small diaphragm and then the profile is adjusted so as to give its image on the surface of the specimen.

It is essential to calibrate the system to convert observed displacements into real heights and depths and this can easily be achieved either by a supplementary observation using interferometry or with a standard depth-graticule. A step or trough is cut into glass and the depth measured by interferometry. The profile picture is taken and calibration is affected.

The profile magnification with a single lens system is readily shown to be $M' = M \tan i/n$ where M is the linear magnification in extension of the microscope, i is the effective angle of incidence of the off-centre pencil and n is the refractive index of the medium between the specimen and the



OPTICAL SYSTEM
FOR
PROFILE MICROSCOPE

Fig. 11.

objective.

The above equation is usually written in the form.

$$K = \frac{M^{1}}{M} = \frac{\tan i}{n}$$

where K is called the "light-profile constant". This has been evaluated by Tolansky (using interferometric means) for the 2 mm. (oil immersion), 3,4,8 mm. objectives used in this laboratory. If the oil-immersion objective is to be used and if the specimen is not a metal it is advisable to silver the surface studied, for this leads to maximum contrast. As a rule adequate power can be obtained with a $\frac{1}{8}$th inch dry objective and if such is employed silvering is not essential. It is however necessary to use lower powers on coarser structures because of the depth of focus.

The light-profile microscope finds ready use for measuring depths or heights which are coarse for interferometry. It also decides the direction of the step. Further, it gives the direction of the wedge, for if the step direction is known and the area including this step is afterwards studied by interferometry the wedge direction can be found.

The multiple-light profile.

By replacing the single opaque line by a series of near parallel lines one obtains a multiple-profile picture which gives profile contours over a whole area.

Both the single and multiple-profile techniques are now regularly used for measurements of depths of etched features, heights of twinning bands, cleavage steps on metal crystals fine machined finishes, studies on hardness tests, growth features on diamond surfaces etc. in this laboratory. Frequent applications of the light-profile will be met later

CHAPTER VII

MULTIPLE-BEAM INTERFEROMETRY WITH HIGH LATERAL MICROSCOPIC RESOLUTION.

The use of optical interference methods for observing macroscopic surface topography is quite old, but its use in conjunction with a microscope for studying detail of smaller size is of more recent origin.

Linnik (1933) was the first to describe an interference microscope for interferometric investigations of small reflecting objects.

Ruhle (1943) and Timms (1945) have also described simple arrangements for micro-interferometric studies of surfaces using ordinary microscopic equipment with a vertical illumination. The interference patterns in all these instruments were formed between the light reflected from the surface of the specimen and that reflected from a partially reflective coating evaporated upon the front surface of the objective lens.

Kayser (1944) has also given a similar method which uses instead of the lens surface, a thin microscope cover-slip semi-aluminized on one side as the reference surface.

Tolansky (1948) discussed in detail the main optical difficulties which may arise in attempting to combine high resolution microscopy with multiple beam interferometry. On account of these difficulties most of the multiple-beam topographical interferometric studies published by various workers have generally been restricted to the use of microscope objectives of lower power than that of a 16 mm. objective.

More recently Grube and Rouze (1954) have applied a modified form of the two-beam interference microscope of the type described by Linnik for the study of microstructural details on the surfaces of metals. Their instrument is essentially a Michelson interferometer, operating at zero order, and incorporated into a microscope. This method suffers from some defects, mainly that the fringes have a $\cos^2$ intensity distribution, i.e. the intensity maxima are as broad as the minima and this restricts accuracy.

Tolansky and Emara (1955) have succeeded in developing an interference technique which overcomes those defects from which the two-beam interference microscopes suffer. The technique to be described gives multiple-beam Fizeau fringes of high interferometric precision yet associated simultaneously with the high lateral microscopic resolution and magnification of a good quality 3 mm. dry objective of N.A. 0.95. With this lens and a suitable eyepiece a lateral magnification X 1500 can be produced on the photographic plate. Such an objective when correctly illuminated with converging light ($\lambda = 5460 A^o$) should resolve some 0.35 μ . Since the illumination is with parallel monochromatic light a lateral resolution of the order of 0.7 μ may at least be reached. It will be shown by a simple illustration that this microscopic resolution of the objective has been obtained.

Apart from considerations involving small working distance and depth of focus restrictions, the two primary difficulties in securing high interferometric fringe definition with such an objective are:-

(a) The strict necessity for a small gap between the two surfaces involved.

(b) The desirability of having as low a wedge angle as is possible.

These are apparently related conditions.

As to (a) it is self evident that the spacing between the surfaces increases with the fringe order. So severely does this affect the phase condition that observation must largely be restricted to the first or second orders. Thus the experimental conditions must be arranged such that viewing takes place near an effective region of contact between the two surfaces. Such a region will be descriptively called the "zero" order region. It may, according to circumstances, cover a large or small portion of the field of view.

As to (b) it has been established by Tolansky (1948) that the phase retardation which tends to reduce good definition is proportional to the square of the wedge angle between the two surfaces. Now the use of a high power objective necessarily imposes a large wedge angle, since fringes must be very close together on the surface if even only one fringe pair is to fill the field of view. In the example given here, fringes used for measurement are some 15 mm. apart on the photographic plate at X 1500, i.e. some $\frac{1}{100}$ mm. apart at the surface. This requires a wedge angle $\tan^{-1} 0.0273$, i.e. almost $1\frac{1}{2}^{\circ}$, which from the view point of precise multiple beam fringes, is quite a large angle. Indeed with such a wedge angle a high numerical aperature collecting lens is essential for good fringe definition merely from the viewpoint of adequate collection of a sufficient number of effective beams. Thus a high aperature lens is needed both for lateral surface microscopic resolution and also for good interferometric fringe definition. Furthermore it seems possible that lateral microscopic resolution might well be improved by the existence of the wedge angle and it may be somewhere intermediate between that of parallel illumination and that of correct convergent illumination. For each succeeding illuminating beam approaches the object at the higher and higher angle of incidence.

As an illustration of the procedure an example from some studies on the topography of a natural dodecahedral face of a diamond will be given. (Many examples of the application of this technique will be met later in Part IV of this thesis). This face was slightly cylindrically curved, a point of much value in that it was possible to rest the diamond on the matching flat so as to be effectively in contact and thus to secure the important condition of a region of "zero" order.

The observations were made on the Vickers Projection Microscope, the objective itself acting as a condenser of sufficient numerical aperature.

The key to the success of the observations lies in the use of an objective corrected for cover-glass thickness. It is to be emphasised that one would fail to secure anything like comparable definition from the normal metallurgical type of objective designed for uncovered work-pieces. In this case a 3 mm. objective, N.A. 0.95, with correcting collar was employed.

The diamond surface was correctly coated with multilayer reflecting films, and all observations were made in reflection.

This condition is necessary, for the diamond bulk and shape affects illumination and thus effectively destroyed definition when attempts were made to use transmission fringes. Figure (12) X 1500 shows a portion of the surface under study. It consists of a curious pattern of parallelograms. It will be seen that by examining this surface with this technique high definition fringes are obtained, such that surface lateral resolution persists.

The fringes are produced by using as a matching flat a standard microscope cover-glass, correctly coated with multilayer films. The objective correcting collar is set for the specific thickness of the cover-glass. The objective is functioning to give good resolution under this arrangement.

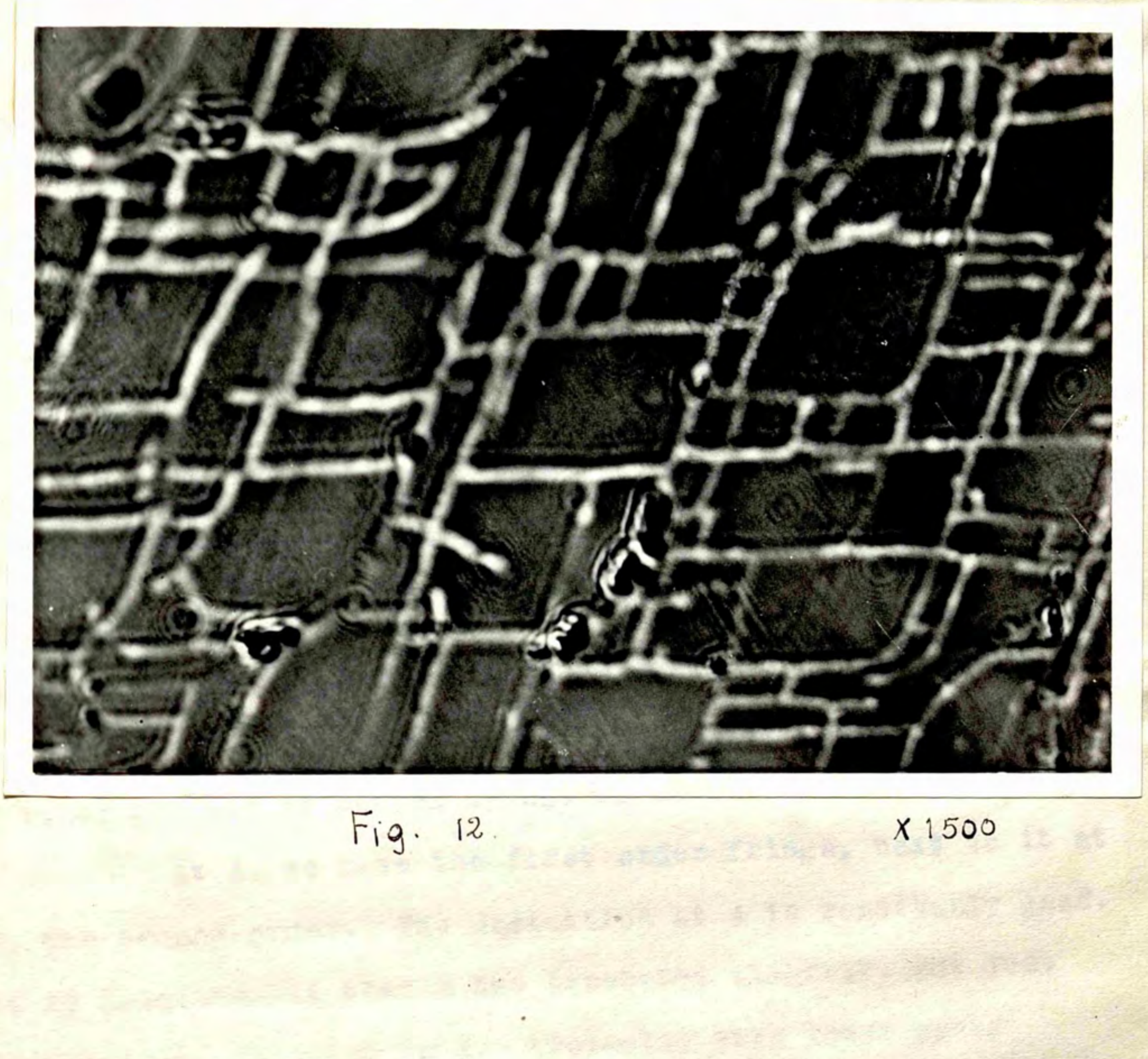


Fig. 12 X 1500

There is no difficulty in selecting a suitable cover-glass.

The small field of view (perhaps 3 or 4 hundredths of a millimeter) make it easy to find regions effectively flat over the field to within an extremely small fraction of a light wave.

It is essential to manipulate the contact between diamond and "flat" to bring a zero order region either in or very close to the field of view. The interferogram secured is shown in figure (13) X 1500. The interpretation is as follows:

One sees a large "zero" order region, over which the path difference at every point is below $\frac{\lambda}{2}$. The interference pattern in this "zero" region is analogous to the high dispersion system. Here there is a condition of interferometric highly enhanced contrast. The parallelograms can be identified and from the intensity pattern within each it is evident that each shows an independent curvature from the boundaries, but whether concave or convex cannot be decided from this alone.

At A, we have the first order fringe, next to it at B, the second order. The definition at A is remarkably good. It is recognisable that B has broadened slightly, but just perceptibly, relative to A. (Normally with lower power cylindrical fringes one would expect B to be slightly sharper than A). This difference is due to the fact that the gap of value λ for B is making its influence felt compared to the

Fig. 13 x 1500

gap value of $\frac{\lambda}{2}$ for A.

It is in these highly sharpened fringes that the combined high resolution in microscopy and interferometry is obtained. Fringe definition is adequate even for exact measurement.

At X 1500 the suggested microscope resolution of 0.7μ corresponds to about $\frac{1}{2}$ mm. on the plate. Comparison between micrograph and interferogram shows that indeed the fringe pattern is certainly revealing the topography of surface detail extending over no more than a $\frac{1}{2}$ mm, possibly less.

The parallelograms are shown thus to have convex faces a small fraction of a light wave high and all the dimensions can be evaluated. Where they meet these are sharply defined depressions. (A detailed discussion will be given later in Part IV of this thesis). There is very little evidence for false diffraction images even in these shallow regions.

There is not the slightest doubt about the considerable superiority of the fringe pattern illustrated here over those seen with the two-beam instrument (even with a good Linnik-type) which have, of course, only the familiar $\cos^2$ intensity distribution.

It is to be emphasised that the unique character of the interferograms in figure (13) is not the fact that there is good microscope lateral resolution, but the fact that the fringes are so sharp and contour the surface pattern so faithfully. This has always been a difficulty in the past with such high powers.

It is of interest to compute roughly the kind of volume element resolvable with the present system. Taking generous limits it is clear that one can certainly resolve an area element of say $1\mu \times 1\mu$ and in this, detection of a fringe displacement of $\frac{1}{50}$th order is unquestionable. (On a correctly exposed negative this would correspond to a fringe displacement by the whole of a fringe width. We consider that with straight fringes we can detect even $\frac{1}{5}$th of this). Such a volume element is some 5×10^{-15} c.c. and this may well be cover-estimated by a factor of as large as 5, because of the generous tolerances considered. With such a volume resolution many important fields such as those of corrosion, etching, polishing, crystal boundaries etc. are amenable to exploration.

<u>High Power Fizeau Fringes Using Oil immersion objective</u>.

An extension of the above technique is the use of the oil-immersion objective (2 mm.) and N.A.1.30. It has been already established by Tolansky (1948) that where possible, the highest-powered objectives that can be tolerated should be used. On the other hand, he pointed out that very high powers cannot be employed with Fizeau fringes especially when oil-immersion is to be used owing to some difficulties which may arise mainly due to restrictions of depth of focus and small working distance.

The depth of focus for a typical oil immersion 2 mm. lens approximates to $\frac{1}{2500}$ mm., and the working distance of such lens is $\frac{1}{4}$ mm.

It is of considerable interest to note that these difficulties were finally solved in a simple manner by selecting a suitable cover-glass as a matching flat. The fringes were produced in the same way as mentioned in the above procedure. As an illustration of the success of the technique two examples are given from the studies made on some natural dodecahedral faces of diamond (Part IV in this thesis). The first example is an interferogram of the same surface figure (12) and is shown in figure (14) X 1500. The second example figure (15) X 1500 is an interferogram of a striated face of another crystal. It is clearly seen that the fringe pattern is certainly revealing variations of ruts on the surface to within 100A.

There is no doubt that these high power fringes are strikingly good even though they are of higher power than any previously obtained.

Although it is always preferable to use the high power dry objective 3 mm. for cleanliness of the specimen under study, yet it appears that there is no objection whatsoever in using oil-immersion when further high resolution is to be required.

Fig. 14 X 1500

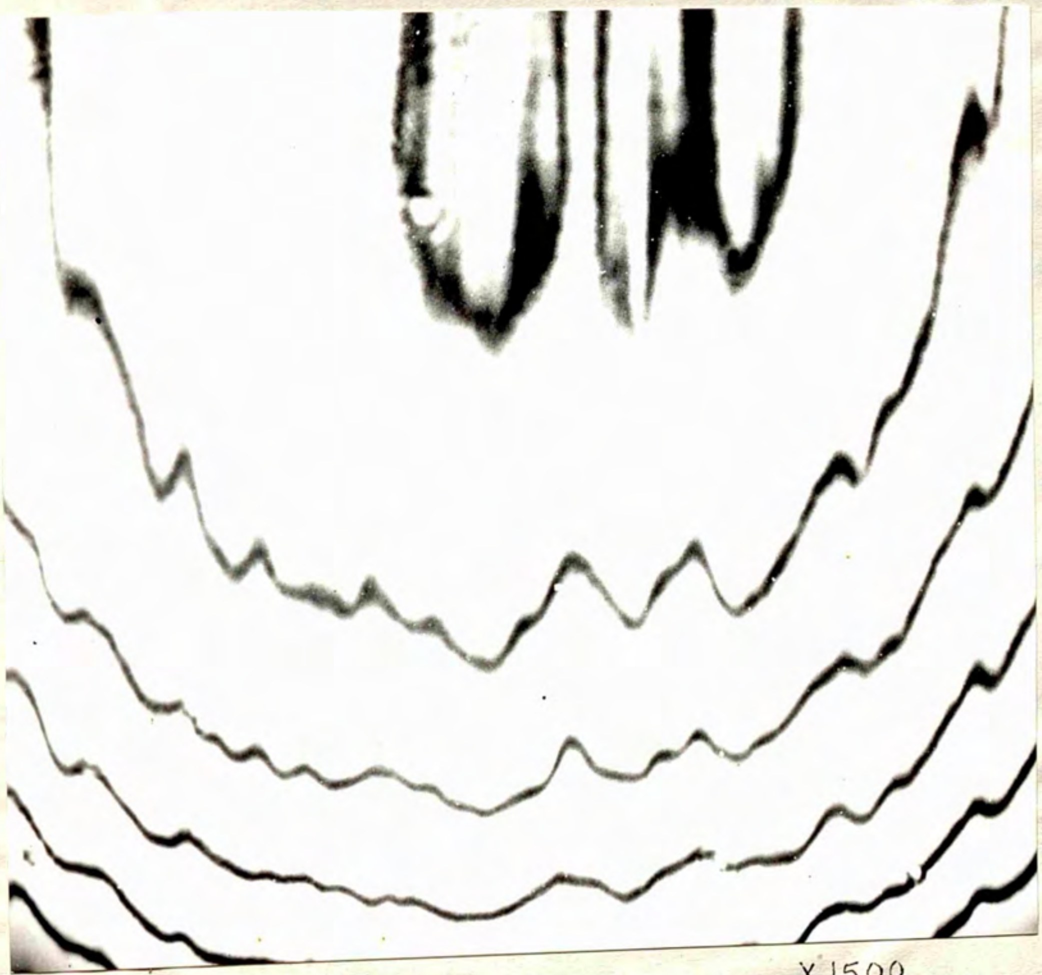


Fig. 15. X1500

CHAPTER VIII
MICROSCOPE TECHNIQUES.

The instrument used for all the observations carried out in this thesis is the Vickers Projection Microscope of the inverted metallurgical type, which can be equipped for any or all of the following systems.

1. Normal incident illumination.
2. Dark-ground illumination with catoptric condenser.
3. Phase contrast for incident light, incorporating positive phase contrast, normal incident, and dark-ground illumination.
4. The Tolansky techniques for the study of minute irregularities in the surfaces of crystals and of machined, ground or lapped metal surfaces:

(a) A high resolution surface profile technique which can readily resolve about 2000A^0 and is particularly suitable for opaque specimens in which a bright field image is crossed by one or a series of parallel lines to yield in the latter case a multiple profile picture.

(b) A simple interference method suitable for opaque specimens whereby a series of interference fringes are formed between a reference surface and the surface under test.

(c) Multiple-beam interferometry for transparent or opaque objects, where by a series of Fizeau fringes are formed between a reference surface and the surface under test.

(d) Fringes of equal chromatic order for transparent or opaque objects whereby the optical separation between the reference plate and the surface of the specimen can be accurately determined, even if the fringes are discontinuous.

5. Polarised light.

The microscope was set for the particular problem in hand, and photomicrogrphy was taken by means of ½ plate (or ¼ plate) bellows camera resting on a separate stand upon which the microscope is attached.

Figure (16) shows the microscope adjusted for reflection.

Most observations were carried out in reflection, either by direct microscopy or by a variety of illumination techniques. Occasionally, transmission microscopy was used, particularly when polarised light is to be employed for the possibility of detecting an internal strain.

For photography, Kodak orthochromatic plates O.250 were used for green mercury line 5460 A^o and further contrast achieved by developing in a contrast developer (Kodak D.19b). For fringes of equal chromatic order and high dispersion, Kodak panochromatic plates P.1200 which are particularly sensitive to the green line 5460 A^o and also the yellow lines

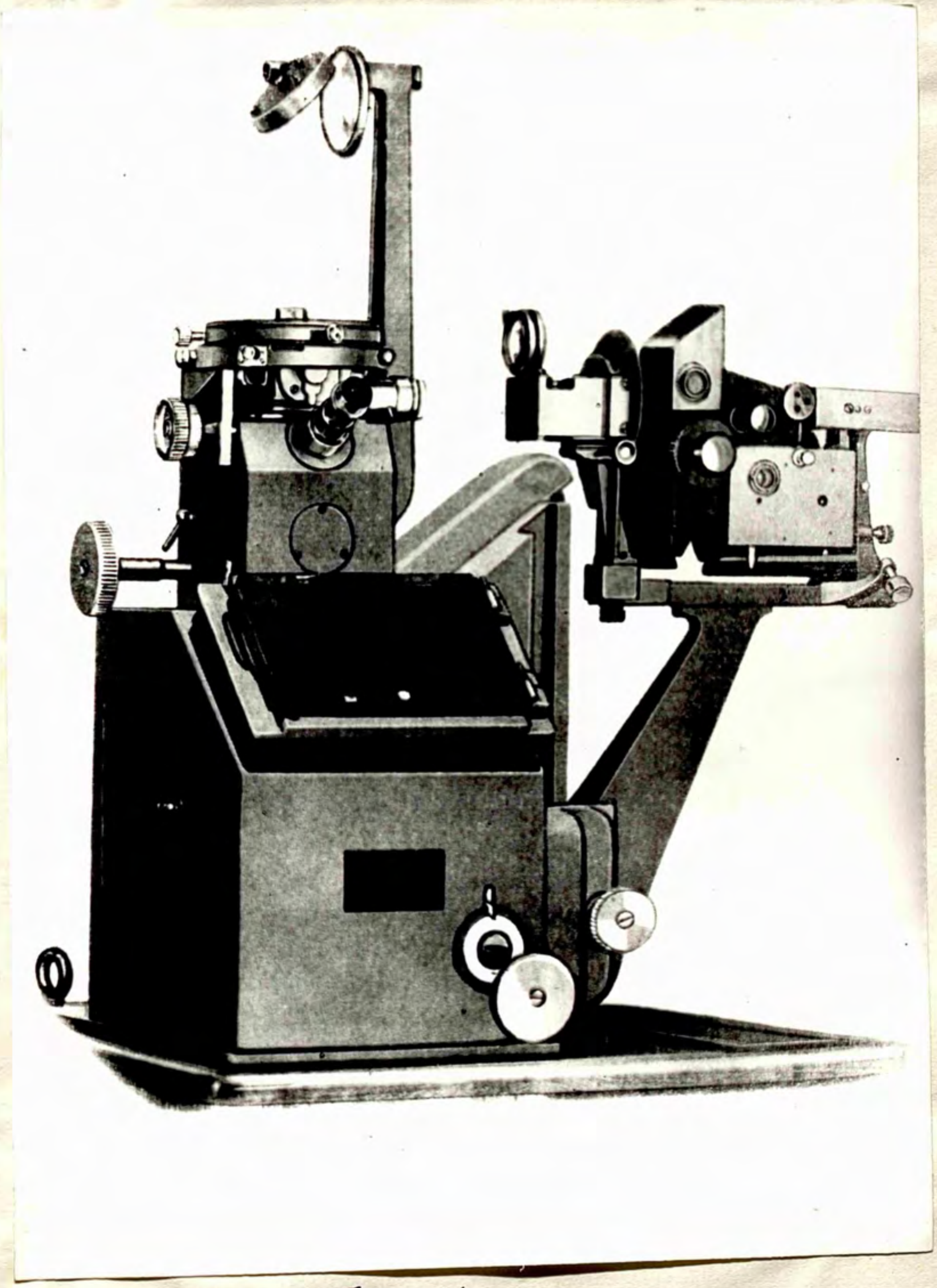


Fig. 16

5770 A° and 5790 A° were used: further contrast was obtained by using the same developer D.19b.

It will be seen in the following chapters how the availability of these optical techniques have revealed a great deal of topographical surface features on diamond.

P A R T III

OPTICAL STUDIES OF GROWTH FEATURES ON OCTAHEDRON FACES.

CHAPTER I

OPTICAL STUDIES OF GROWTH FEATURES ON OCTAHEDRON FACES

Introduction.

Diamond crystallizes in many forms in the "cubic" system, which has the most perfect symmetry known. The most common shape in diamond is that of the octahedron. Observation shows, however, that in very few cases has the growth been free. Hence approximations to other forms have been assumed as well as the octahedron crystals of irregular habit. Very few diamonds crystallize as mathematically perfect octahedrons; in fact very few perfect crystals of any of the possible forms are ever found. In very few cases, moreover, are the four pairs of opposite faces equidistant, the crystal thus tending to flatness in one or two directions. With the flattening carried to the extreme we have the tabular crystal known as the "portrait stone" because it can be used for glazing small miniatures. It is to be noted that whatever the flattening the inclination of any given octahedron face to another on the same crystal is always a constant angular quantity. However, the diversity of irregularity in diamond is infinite, and one would not be wrong in affirming that no two crystals of diamond are exactly alike. This would happen generally if the crystal had not had room in which to grow freely in all directions. Under constraint the crystal would tend to assume a shape conforming to that of its environments. It is also well to realize that each diamond mine produces diamonds bearing certain characteristics peculiar to that mine. It does not follow that all diamonds of one particular mine are different from those of another mine, but each mine taken as a whole has a type of diamond not found in other mines. This difference is shown by one mine having a high percentage of large rounded octahedra while another mine will have very few large diamonds, and again another mine will produce mostly sharp-edged octahedral diamonds. It is therefore difficult to derive general rules which apply uniformly to all diamonds. For the most part the edges of the best octahedrons are not sharp, and there is a trend to curvature towards the corners giving a rounded outline to the whole.

Many octahedra have a groove or furrow in place of the octahedral edge. This may be due to some peculiarity in their growth, or it may be an effect of twinning. If a supplementary twin of two tetrahedra have their projecting corners truncated by the face of the inverse tetrahedron, the twin crystal will have the appearance of an octahedron with grooved edges. Twinned crystals are flattened parallel to the twin plane of an octahedron face and are usually called "macles". Twinned octahedroid crystals are quite common. They may be derived geometrically or physically in the same way from the simple crystal. But there is an important distinction between the typical macle and the ideal macle determined by the hemitropic rotation of two halves of a simple regular crystal. It is that the former tends to a tabular habit, its thickness being much less than that of an octahedron of the same spread; moreover, its central plane ("composition plane") is scarcely ever a plane at all. Sutton (1928) describes a twin as though it were formed from two flakes not necessarily of equal thickness, broken roughly from two faces of a plastic octahedron and after due rotation being squeezed together.

Macles are rounded exactly like simple crystals; composite and irregular forms occur in about the same ratio to regulars, as is the case with simple crystals. A nearly complete crystal may have a small block macled into one corner. However, it is curious and certainly important fact that the majority of macles have flawed edges (Sutton 1928). The flaws show as feathery lines of a brown tint, from nearly white to nearly black running inward at right angles to the edges. It often happens that the two components of a macle do not fit closely i.e. either they have not come into or have been forced away from justaposition.

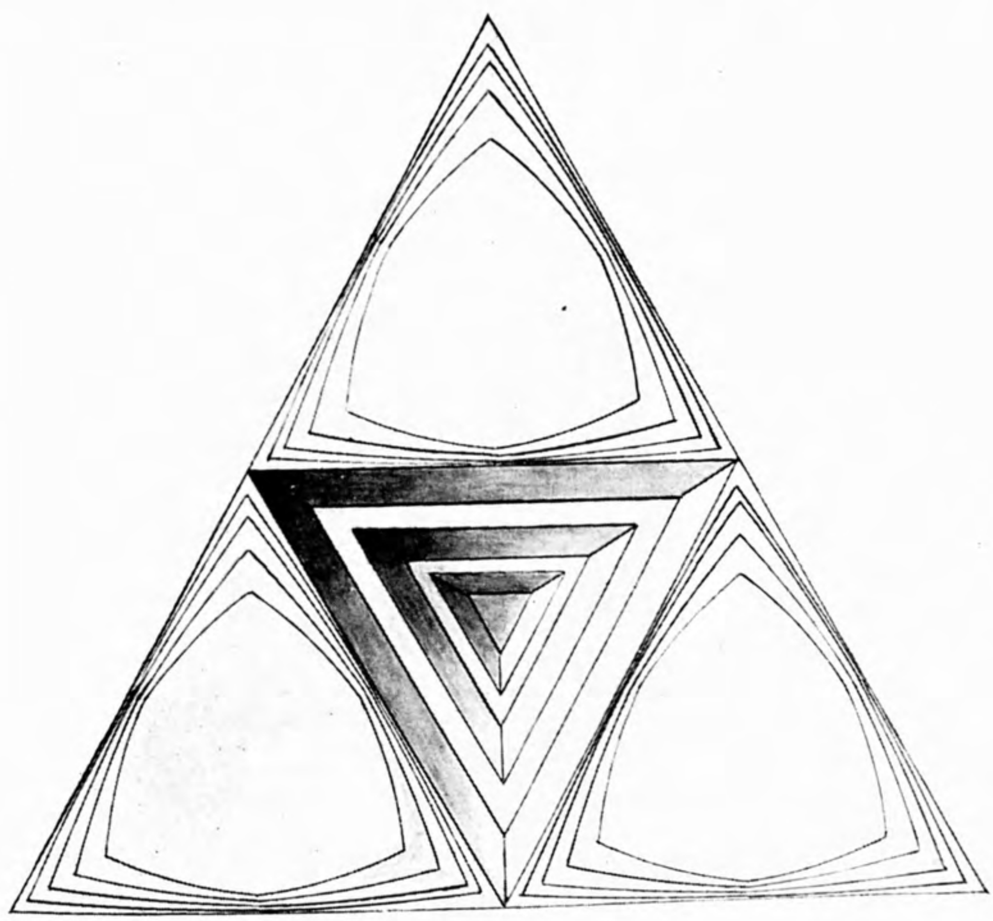
Natural octahedron faces of diamond are characterised by well defined triangular depressions which are called "trigons" after Sutton. These trigons are always strictly uniformly oriented on untwinned faces having their angles directed to the octahedron edges. They are usually distributed at random over the octahedron faces and are of all sorts and sizes, and also varying in number considerably from one crystal to another even on face to face of one crystal.

For long there was much speculation about their origin and formation. Numerous extensive studies were carried out by several workers to account for these features.

Miers (1902) attributed the triangular markings on the natural octahedron faces to etch and considered them to be a solution phenomenan. He drew his conclusions from the fact that they take the position of etch marks on the octahedron faces of other crystals such as alum and cuprite.

Crookes (1905) who repeated Gostav Rose's experiments by burning diamonds before the blowpipe considered the natural triangular depressions to be due to growth. Fersmann and Goldshmidt (1911) suggested that the rounding of faces and edges are due to partial dissolution in accordance with the usual knowledge that all crystals get rounded after some dissolution. Although they make the general assertion that all diamonds show signs of solution, they do qualify it by saying that growth structure, generally occurs on the faces of the octahedron. Moreover, they believed that the grooves along the edges were caused by solution, and further the triangular hillocks bounding the triangular depressions, which always show bent edges, were also produced by solution.

Van der Veen (1913) drew special attention to the triangular depressions so noticeable on the octahedron faces, and was of the opinion that they were produced by growth. The method of growth he illustrates is shown in the sketch Figure (17). This sketch shows that at the side of the depressions are the hillock growths, of which there are three in the illustration.



GROWTH STRUCTURE ON THE OCTAHEDRAL FACES OF THE DIAMOND (VAN DER VEEN).

Fig. 17

Each hillock growth consists of elementary plates to which six arched segments give ditrigonal form. The plates are all bounded differently, and resemble more or less an equilateral triangle. Van der Veen says that the newer elementary plates possess somewhat curved outlines, whereas the older ones possess straight sides and conform more nearly to the equilateral triangles of the octahedron face. He also claimed that all irregularities of the diamond crystals e.g., their curved surfaces and notched edges can be explained by a growth in layers according to the octahedron. These growth layers sometimes produce notched edged octahedrons, but it is no longer necessary to regard the diamonds with notched edges as twins.

Mohr (1924) using geometrical analysis was of the opinion that the triangular depressions arise during crystal growth.

Honess (1927) who made a careful study of etch figures on many crystals also attributed the pits on diamond to be due to growth phenomena.

Sutton (1928) was also in favour of the growth phenomena. He considers the trigons to be a result of growth at different rates, growth at accelerated rate forming hills and at retarded rate trigons. He also attaches importance to the suggestion of Friedel (1924) that the curvature is a reflection stage of plasticity through which diamonds pass during crystallisation.

Williams (1932) strongly advocated the growth phenomena basing his conclusions on morphological and etch characters that appear on diamond surfaces especially on the faces and edges of the octahedron. He shared the views of Van der Veen (1913) that the triangular depressions have been produced by building the diamond layer upon layer on the face of the octahedron. He also believed that the curvature was due to the steady diminution in the sizes of the plates away from the edges of the crystals and that the grooves are formed on the edges of the plates if the eight faces fail to join.

Kucharenko (1946) suggested that the curvature is attributed to minute crystal facets whose inclination to one another is very small.

Raman and Ramaseshan (1946) after examining several diamond crystals came to the conclusion that the curvature of the faces and edges is by crystallisation from a liquid drop of carbon.

It is concluded, therefore, that although these writers have expressed their opinions as to the cause of the triangular depressions and curvature observed on the natural octahedron faces, only a few have provided experimental evidence in support of their views. This uncertainty remained until the work of Tolansky and Wilcock (1947).

Recent Studies on Trigons.

Tolansky and Wilcock (1947) used multiple-beam interferometric techniques for their studies on some selected octahedrons of diamond. The "crossed fringe" technique gave conclusive evidence to support the view that curvature of diamond faces and the occurrence of the triangular pits were attributed to growth.

In their studies they observed that some growth sheets are almost truly plane, whilst others are distinctly convex. They argued that there is no reason to suppose that any solution process has taken place, particularly in view of the strict rectilinearity of the boundary edges. Furthermore, they believed that it is quite unreasonable to suppose that solution could attack the upper region and yet fail to attack an adjacent lower layer when the difference in height is merely 200A°. They concluded therefore that the curvatures of the faces arise during growth. They also showed that the trigons are a growth phenomena and they proposed for their formation that growth takes place by means of sheets or wave fronts, advancing in three possible directions inclined at 60° to each other. Then when one layer is held up over a section of its front by some disturbance a step would be formed which would increase in height as succeeding layers arrived at the stationary front. Secondary growth would then start from the edges of the layers, proceeding from either side of the stationary part of the intial front and when the secondary fronts met a flat-bottomed trigon is enclosed.

However, this growth mechanism explains only the flat-bottomed trigons; it does not account for the pyramidal trigons which are of more frequent occurrence on the octahedron faces of diamond.

Therefore, it was felt that further studies on the nature and form of trigons was necessary.

Wilks (1952) continued the work of Tolansky and Wilcock on the trigons using the interferometric techniques. She concluded from her observations that trigons could be classified under three headings although there were noticeable variations within the groups.

(a) Shallow trigons - these are mostly small and their depths are proportional to surface area.

(b) The tetrahedral form - the minotity of the deep tetrahedra are regular i.e. sometimes the sides had two slopes. In many cases the larger trigons overlapped with their neighbours, and some contained within their boundaries smaller, shallow trigons.

(c) The flat-bottomed trigons - these were very rare.

With regard to (a) if the area in shallow trigons is depth then the length of the side is $\propto$ (depth)$^{\frac{1}{2}}$ and this is a parabolic relation which means that the trigons are steeper than that which is necessitated by the linear relation, length of the side $\propto$ depth, for the trigons are generally shallower at the bottom than at the top.

Concerning (b) her conclusions were not clear for in some cases the slope flattened near the bottom of the trigon although the bottom was pointed, and further she could find no relation existing between the surface area of the trigons and their depths.

As to (c), as these trigons were rare she was unable to get any relations existing between length of the sides of the trigons and their depths.

Therefore, it seems that her observations were not sufficient to give a general conclusion.

Tolansky (1953), Omar (1953) after examining several octahedron faces, including some nearly perfect stones, have established that in fact all (111) faces so far examined reveal trigons, and that many of them are less than 50A° deep.

Omar (1953) also found that large trigons can be as shallow as small ones. On some stones he observed a number of deeper trigons which enabled him to make a statistical survey of the relation between size and depth of trigons but his survey was so limited that it cannot be accepted as a general rule until more evidence is given.

He also put forward a suggestion for his observations on the trigons, in particular the pyramidical type, basing his ideas on an experiment made on iodine crystals grown from solution. These crystals grow as indendintric trees with limbs which arrange themselves in rows of growth hillocks and enclose geometrical depressions similar in nature to the trigons.

He concluded that on octahedron faces of diamond the process of formation of trigons is similar. He, therefore, considered that growth starts by means of triangular plates which can be small in size. From the tips of these triangular plates other triangular plates are developed. From the tips of these secondary plates other tertiary plates are developed and so on. This kind of growth he called "growth from the corners outwards". If, however, the triangular plates are in conformity with the octahedron face they can enclose triangular spacings between their branches in the exact position of the trigons. Thus, he considered that growth is a continuous wave front that is advancing, only that it is dissected wave front full of corners and steps in three mutual directions and the whole group will build up as a pyramid full of triangular depressions.

This explanation cannot be accepted, as the process of growth of diamond is much more complicated than he had assumed.

Halperin (1954) who also made some studies on natural octahedron faces of diamond observed on one crystal a sequence of trigons at different stages of formation and proposed a possible explanation for its formation. He explained these stages by postulating that the main direction in which growth advances is away from the centre and perpendicular to the edges of the growth sheets. Along each of these edges there is only one main direction of growth and when the growth wave approaches a trigon, the process is as follows:-

(i) At first the growth wave approaches the edge of the trigon which is parallel to the growth front.

(ii) On reaching this edge (where this trigon should be formed) growth is arrested along it.

(iii) Growth proceeds on both sides of the obstacle, propagating round the corners, and finally, by inward growth, the sheets form the other sides of the trigon.

When neighbouring trigons disturb the completion of a trigon from the side, growth propagates around all the obstacles and finally the trigons may be completed.

He therefore based his final conclusions for the formations of trigons on the theory of dislocation due to Frank (1949) and Burton, Cabrera and Frank (1951). He assumed that the obstacles which arrest the growth and cause trigons to be formed are faults in the lattice which are mainly dislocations created on the octahedron surfaces of diamond under certain conditions. For the formation of these dislocations, interstitial faults are first formed by misfitting of individual atoms in the lattice points. These faults accumulate from layer to layer in the growing crystal until their density on a certain surface area becomes so high that the surface energy may be lowered by stretching out of the new oncoming layer into the next mechanically stable configuration of the lattice. Thus, an imperfect sessile dislocation ($\frac{1}{3}$a,$\frac{1}{3}$a,$\frac{1}{3}$a) suggested by Frank (1949) on face centred cubic lattices is formed on the boundary which should pass along the (111) twinning lattice planes cutting the surface. With the advance of the growth sheet this process is completed, leaving what he calls a "tribase" with an imperfect step along its boundary. It is separated from the perfect lattice by three octahedral twin-lattice planes cutting the growing face. In this way the "tribases" are obtained, and in certain conditions of growth, the advancing layers will be arrested on the boundaries forming triangular growth pits or trigons.

He also tried to explain why small trigons are deeper than larger ones but this is not always the case as large trigons can be deep.

In fact, all the above opinions remain as speculations and no definite answer can be given as to the mechanism of formation of trigons until the problem of how a diamond grows is solved.

CHAPTER II

ANOMALIES IN TRIGONS.

Introduction.

As indicated in the previous chapter extensive studies made by previous workers on natural octahedron faces have revealed the existence of beautifully shaped equilateral depressions, the trigons, which arise during growth. On many crystal faces most of the trigons are very shallow sometimes less than 50 A° deep (Tolansky 1953). In other instances the crystal faces are covered with much deeper trigons, often inconveniently deep for an interferometric approach. These were measured to be sometimes 4 microns using the shadow casting technique developed by Tolansky (1954).

In the present investigation nearly a hundred octahedron faces of different crystals have been examined, some of these are quite small but regular whilst others are larger and convenient for the interferometric study. It was observed in every case that trigons are always present on the surfaces although in some cases they were only seen with high magnification and critically correct illumination. These trigons vary considerably in number from one crystal to another and even from one face of the same crystal to another. Furthermore, they are mostly shallow with their bottoms flat, especially in nearly perfect crystals, while on imperfect crystal faces they are usually deeper and occasionally their sides are extended down to meet a point, like an inverted pyramid. It is of interest to note that an attempt has been made to find out if there is any relation existing between depths and sizes of trigons and it was not easy to get any correlation which could be considered as a general rule.

On the faces of many diamonds trigons are randomly distributed as shown in figure (18).

In addition to these equilateral depressions some anomalies have been observed. These will now be described and discussed.

Interferometric Study of Anomalous Features.

The features now to be described were observed on one face of a well formed good natural octahedron, the average side of an edge being 4 mm, thickness 3 mm. and weight 0.63 carats. Similar but few of these have also been observed on faces of other crystals. All the features were examined using both Fizeau fringes and fringes of equal chromatic order. This has been done by intially obtaining Fizeau fringes and projecting the image of a particular anomalous trigon on the opened slit of the constant deviation spectrograph: so that one of the edges of the irregular trigon was at right angles to the slit. The wedge angle of the interferometer was then adjusted so that Fizeau fringes were observed at right angles to the above edge of the irregular trigon and passing through one of its corners.

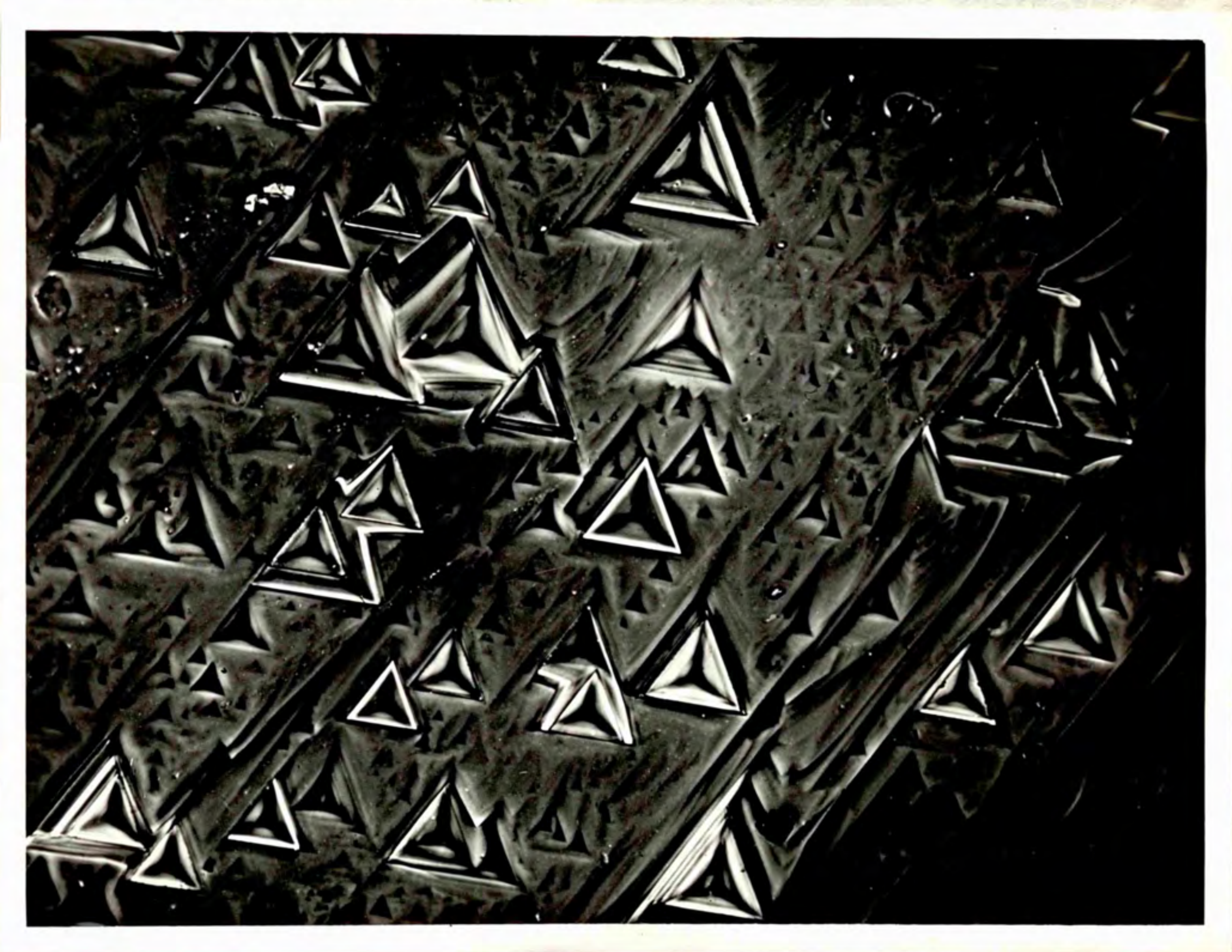


Fig. 18. ×110

The slit was then narrowed and the mercury lamp was replaced by carbon arc. By this use of Fizeau fringes and fringes of equal chromatic order all the features were identified and their depths were measured. For each feature both Fizeau fringes and fringes of equal chromatic order were taken on the same photographic plate and measurement were carried out with an accuracy of about 1%.

The anomalies involve a form of truncation of the trigon. The truncation takes place either in one corner and these will be called "single truncated" trigons or in two corners of the feature, and these will be called "double truncated" trigons.

In most cases the truncation was straight and crystallographically oriented, but in very few cases it tends to show a slight curvature. Also in all cases growth has taken place inside the features.

Single truncated Trigons.

An example of a singly truncated trigon is shown in the photomicrograph figure (19a) X 970. It is clear that one of the corners has been split into two parts each of which is straight and crystallographically oriented. Examination of the feature using fringes of equal chromatic order figure (19b) X 230 shows that it is a depression with depth about 1900 A°. A second example of this type is shown in figure (20a) X 1150. In this case the truncation is parallel to the base of the feature. Figure (20b) X 250 shows the fringes of equal chromatic order for

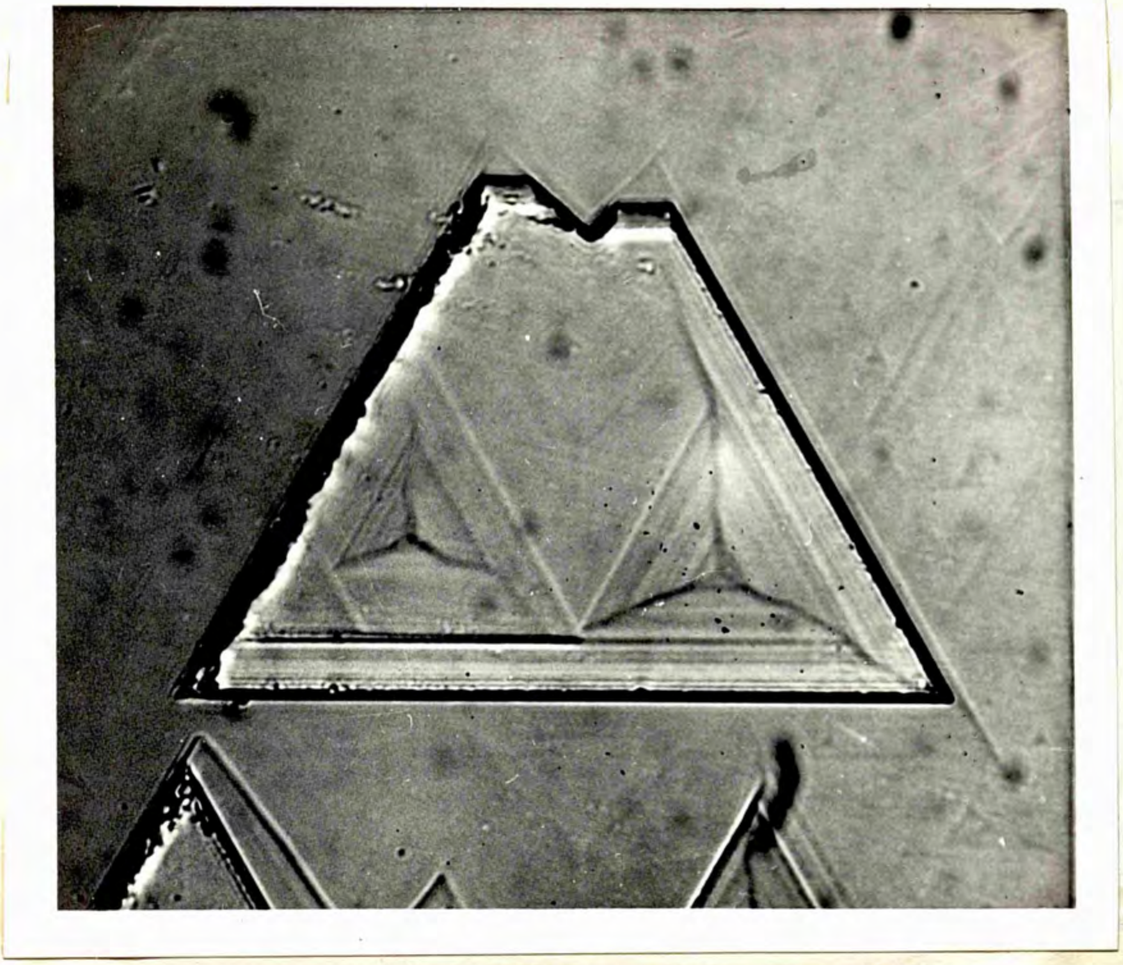


Fig. 19 (a) x 970

Fig. 19 (b) x 350

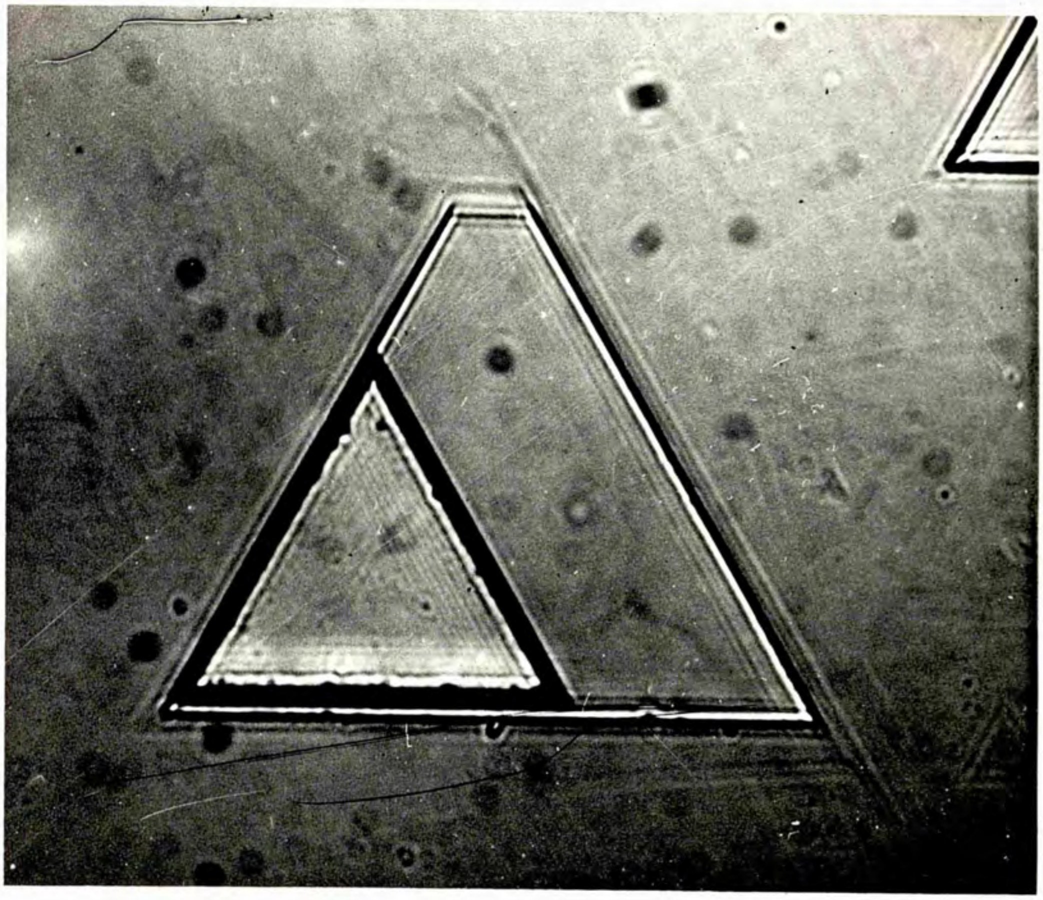


Fig. 20 (a) x 1150

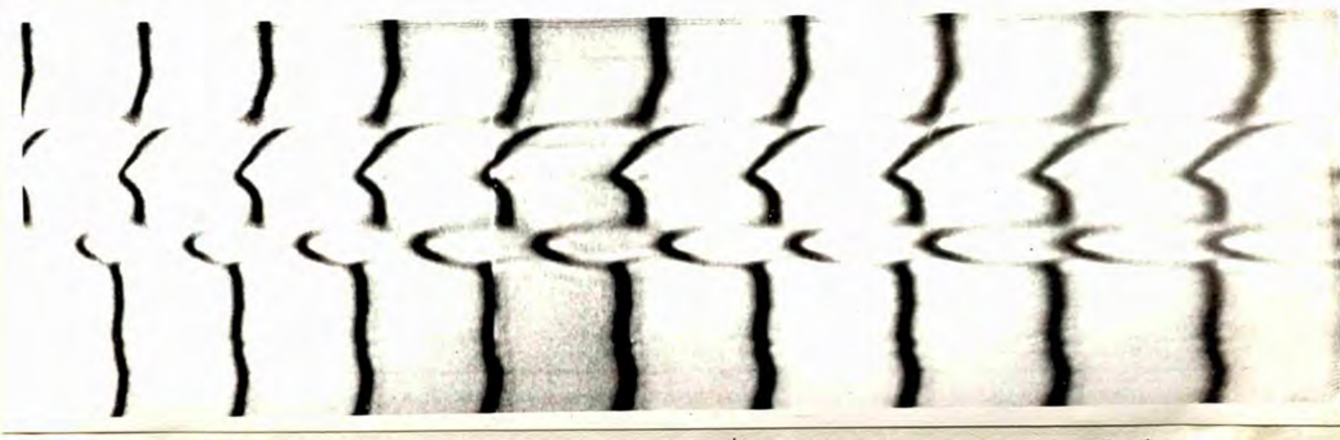


Fig. 20 (b) x 250

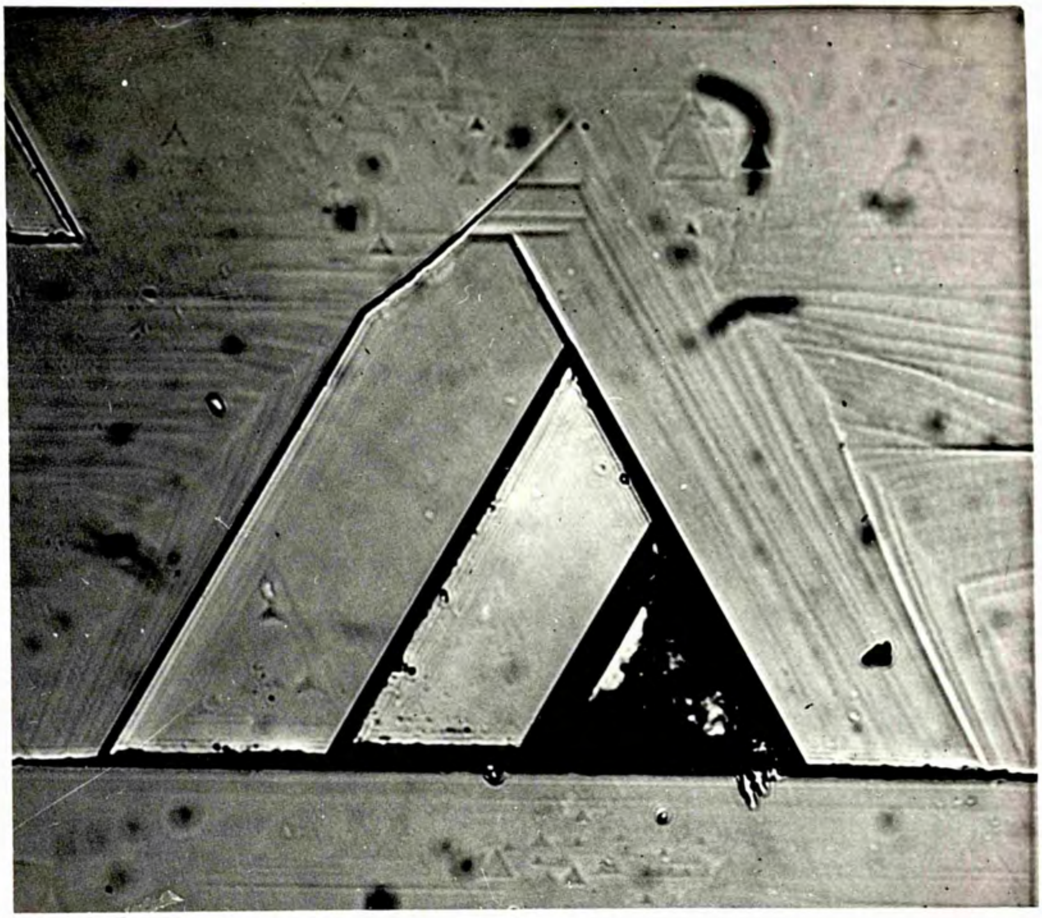


Fig. 21 (a) X 860

Fig. 21 (b) X 350

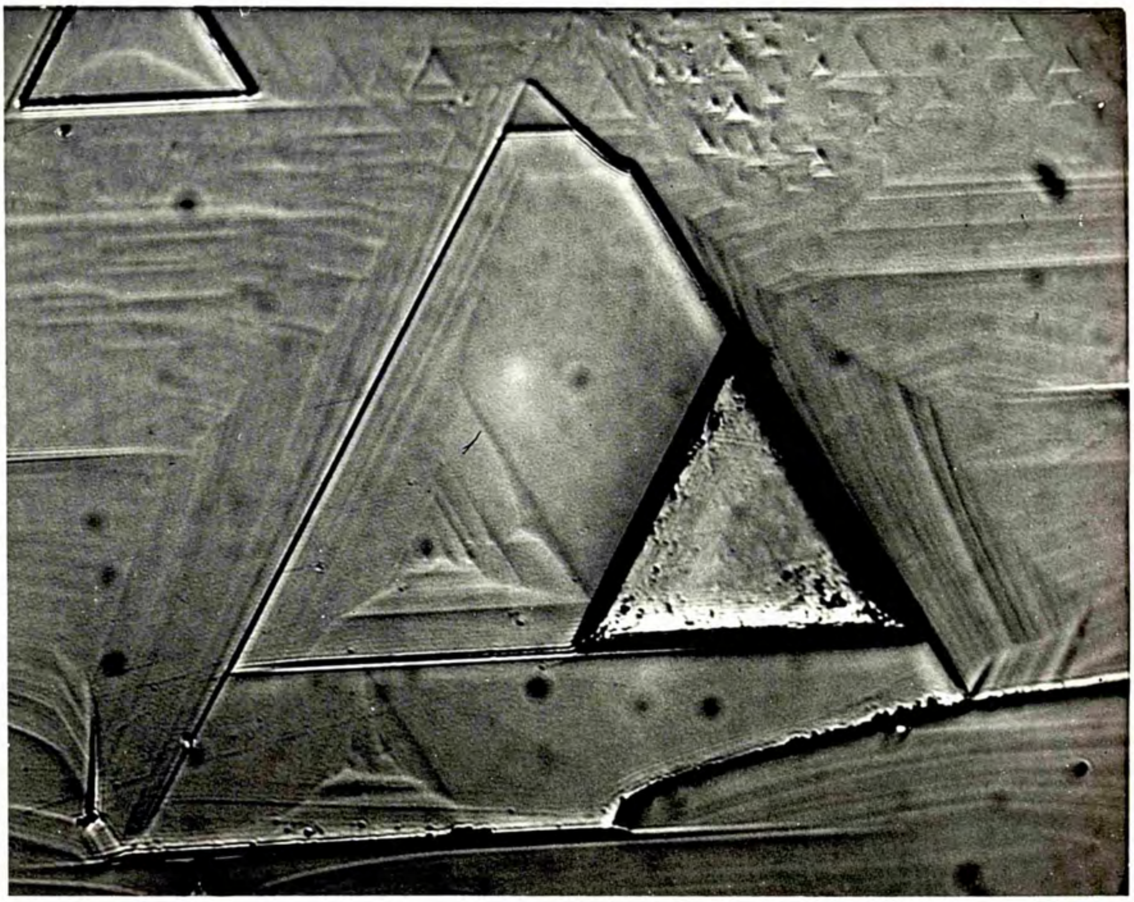


Fig. 22 X790

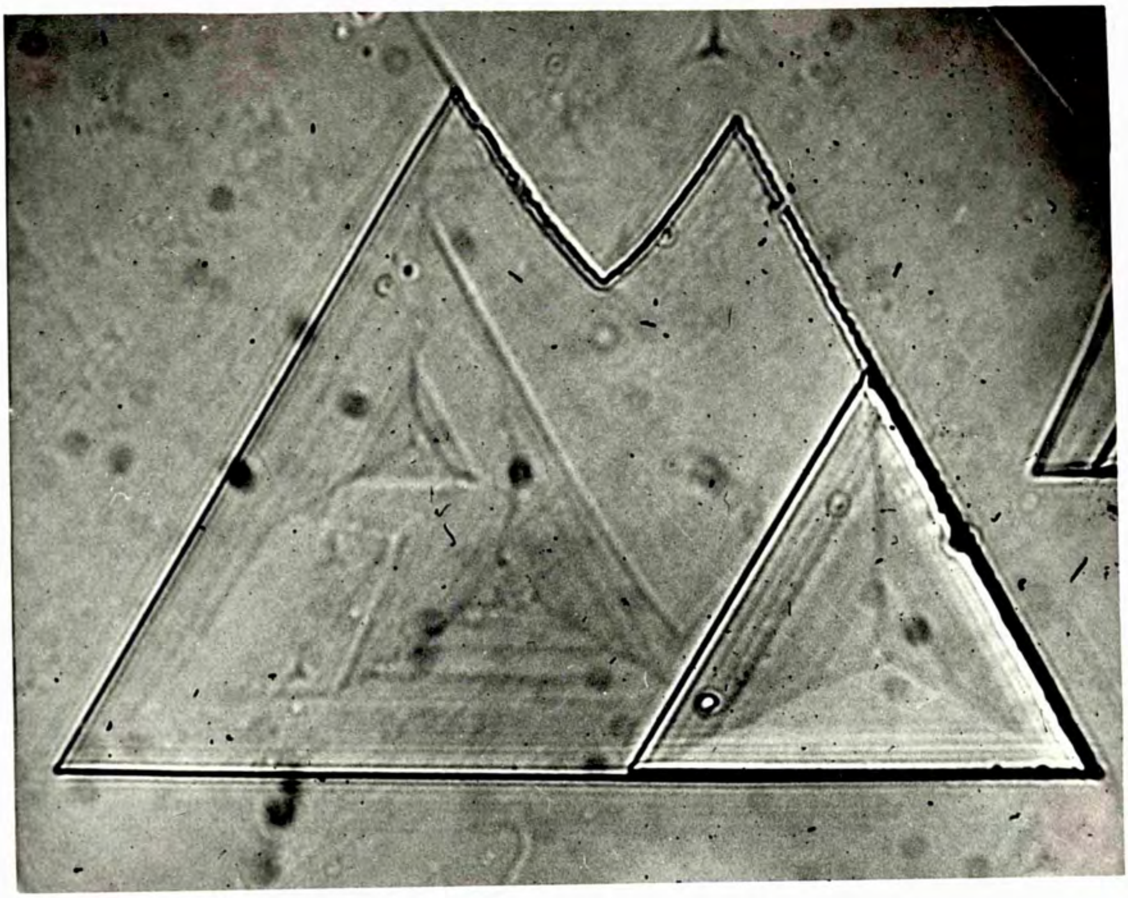


Fig. 23 (a) X1080

Fig. 23 (b) X350

one line section passing through the truncated corner. Measurement shows that the depth of this feature is about 1230A°.

A third example is striking for the truncation in the corner has taken place in two steps in one of them the truncation is straight while in the other it is irregular.

This is shown in Figure (21a) X 860. Figure (21b) X 350 shows that the depth of such feature is about 3000 A°. A fourth example of this type is shown in Figure (22) X 790. This photomicrograph shows that the truncation has taken place in two steps. In the first part it is slightly curved.

A last example is one of the common truncation with one slightly curved edge as shown in Figure (23a) X 1080. Figure (23b) shows the fringes of equal chromatic order for one line section passing through the middle of the truncated corner. The depth of such feature is found to be about 2400A°.

Doubly Truncated Trigons.

The first example shows a typical truncation which has taken place at two corners, with straight truncations crystallographically oriented, giving the appearance of the trigon as a six sided figure as shown in Figure (24a) X 1500. Fringes of equal chromatic order have been taken along three different directions. Two of these are shown in Figures (24b) X 240, (24c) X 350. The fringes show that there is a slight curvature and also reveals the overlapping of the growth trigons inside the feature. The depth of this feature is about 3300A°.

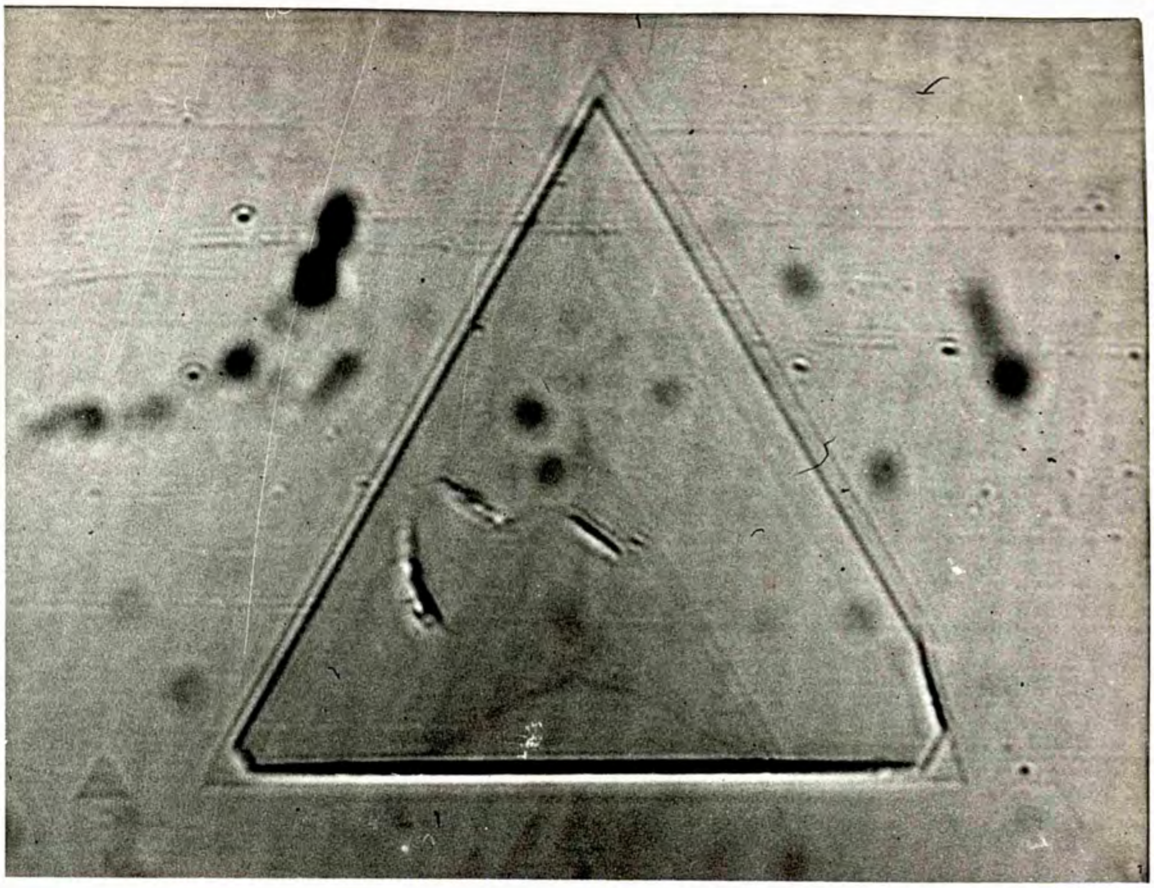


Fig. 24 (a) ×1500

Fig. 24(b) ×240

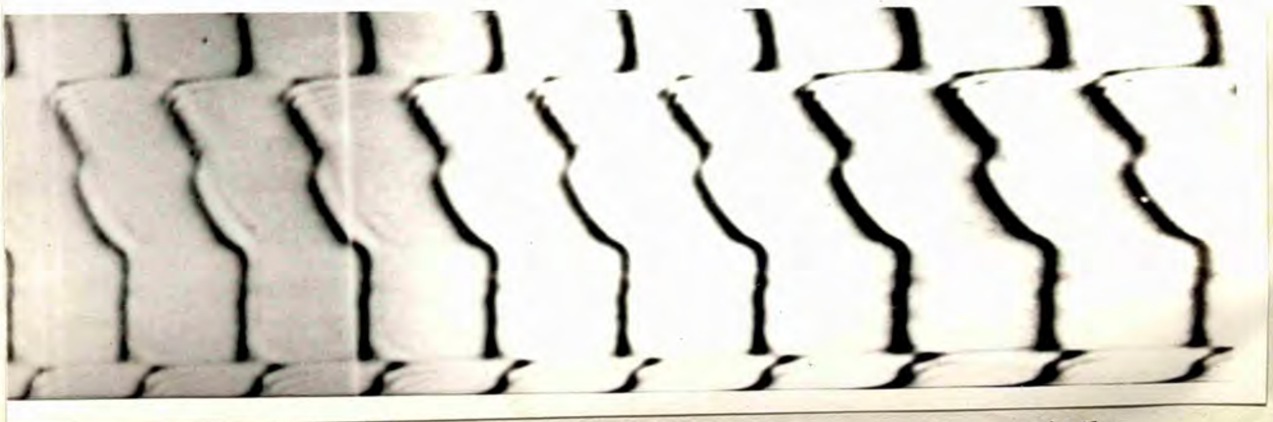


Fig. 24(c) ×350

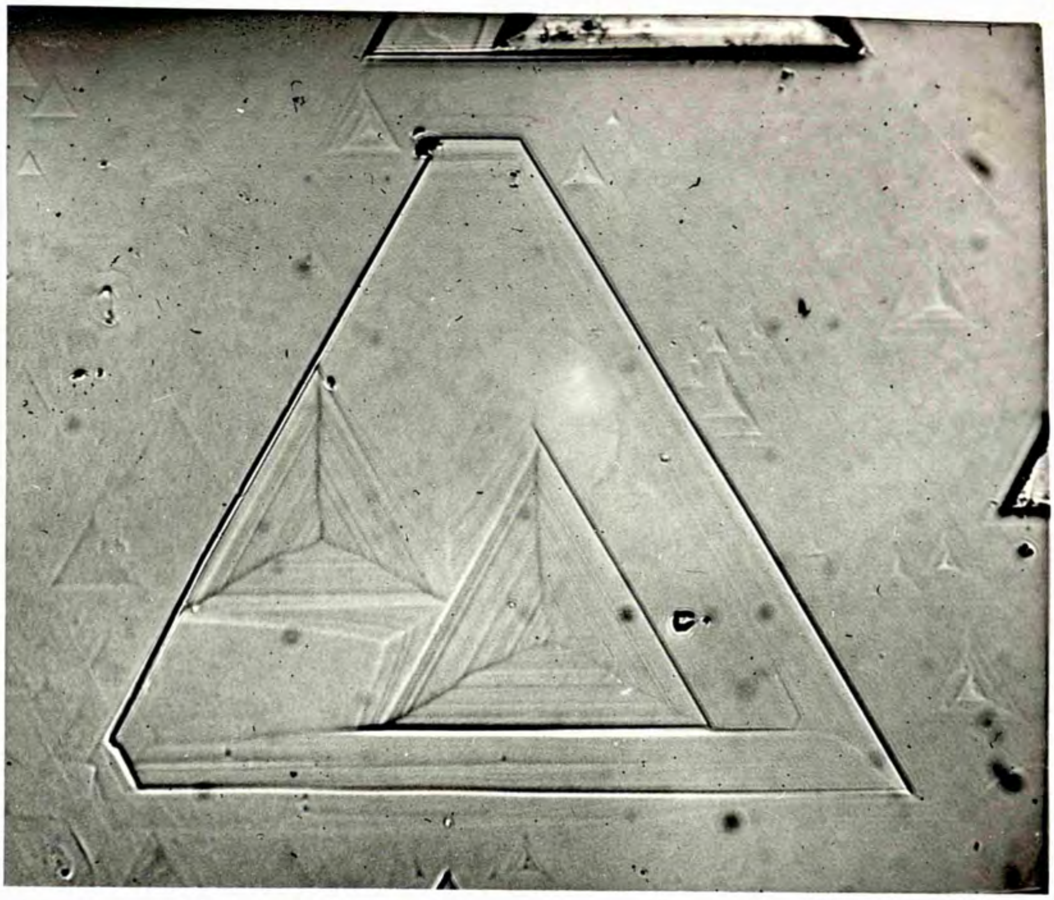


Fig. 25 (a) x610

Fig. 25 (b) x 200

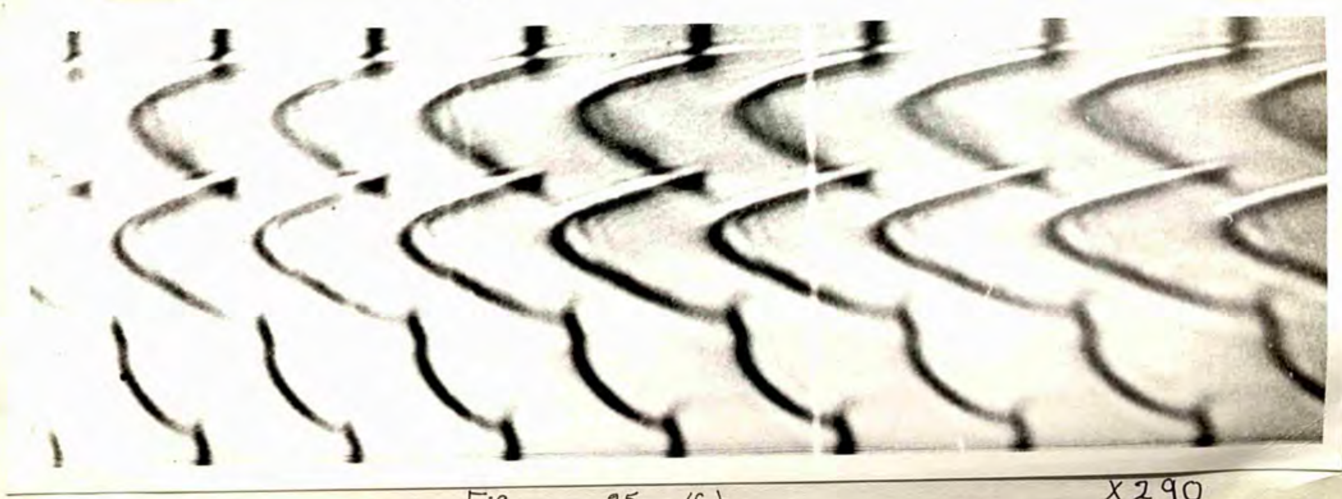


Fig. 25 (c) X290

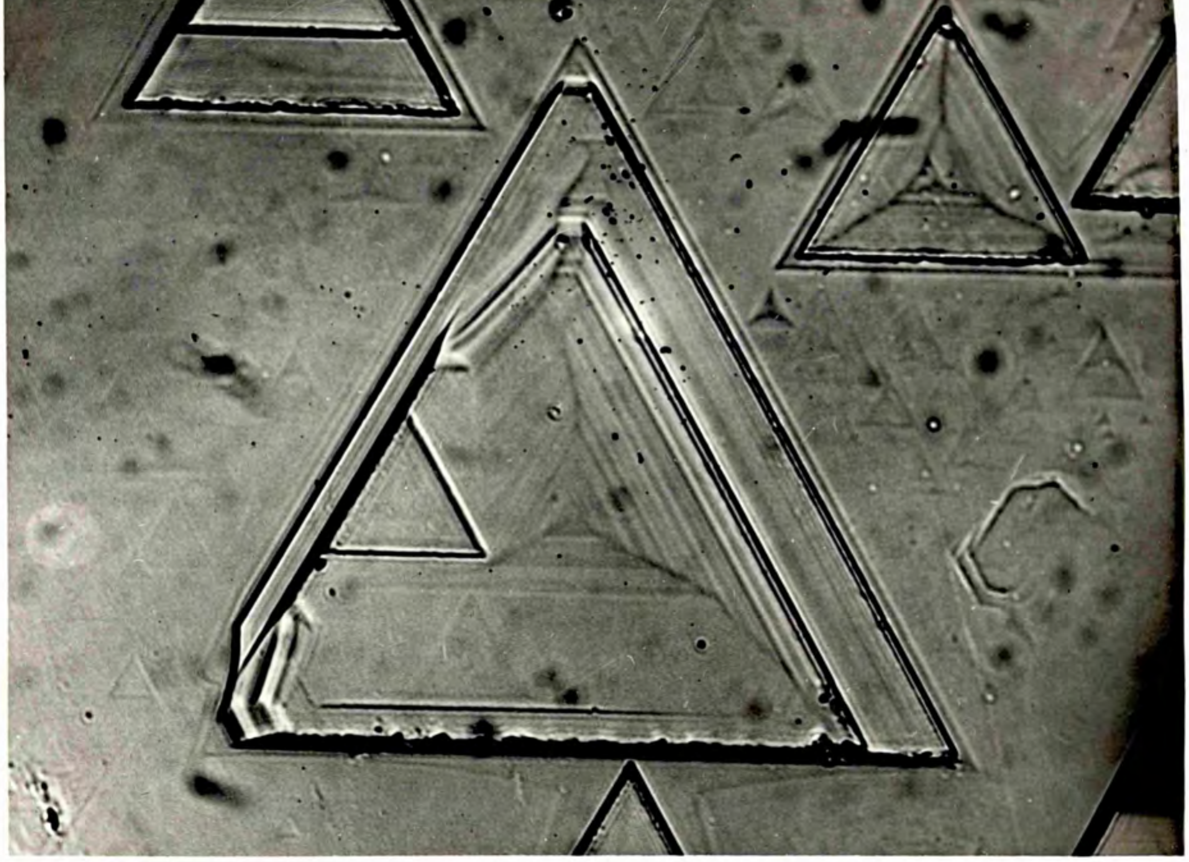


Fig. 26 (a) x 860

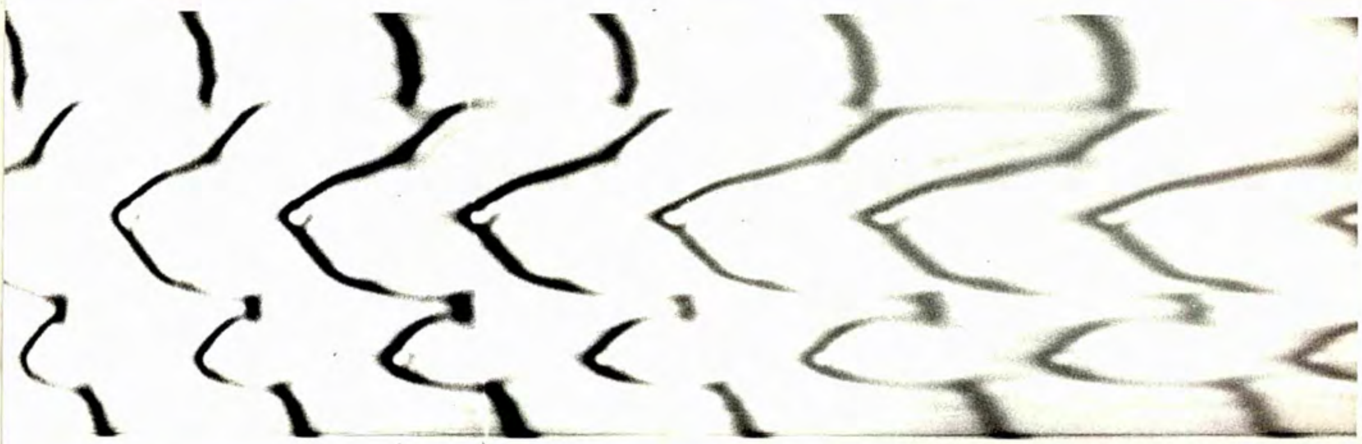


Fig. 26 (b) x 320

A second example is shown in Figure (25a) X 610. Here again two corners have been truncated with edges crystallographically oriented.

Figures (25b) X 200 and (25C) X 290 show the fringes of equal chromatic order of a line-profile of a section passing through the corners A and B of the feature. The curvature is here much more pronounced in figure (25C) X 290. Calculation revealed that the depth of such feature is about 2160A^{o}.

A remarkable example of this type of truncation is shown in Figure (26a) X 860. It is clearly seen from this photomicrograph that the truncation in one of the corners is shown to be strictly straight while in the other corner truncation has taken place in two steps and each step is crystallographic although there appears a slight curvature. Also it is easily seen that growth has taken place inside such feature. Figure (26b) X 320 is the fringes of equal chromatic order for a line-profile of a section passing through the top corner of such feature. The fringes also show a little curvature at the base of the feature, and calculation revealed that its depth is about 2200A^{o}.

A fourth example is shown in Figure (27a) X 720. Both truncations at the two corners are strictly straight and crystallographic with one of the corners showing linear steps. The fringes of equal chromatic order in Figure (27b) X 250 revealed that its depth is about 1400A^{o}.

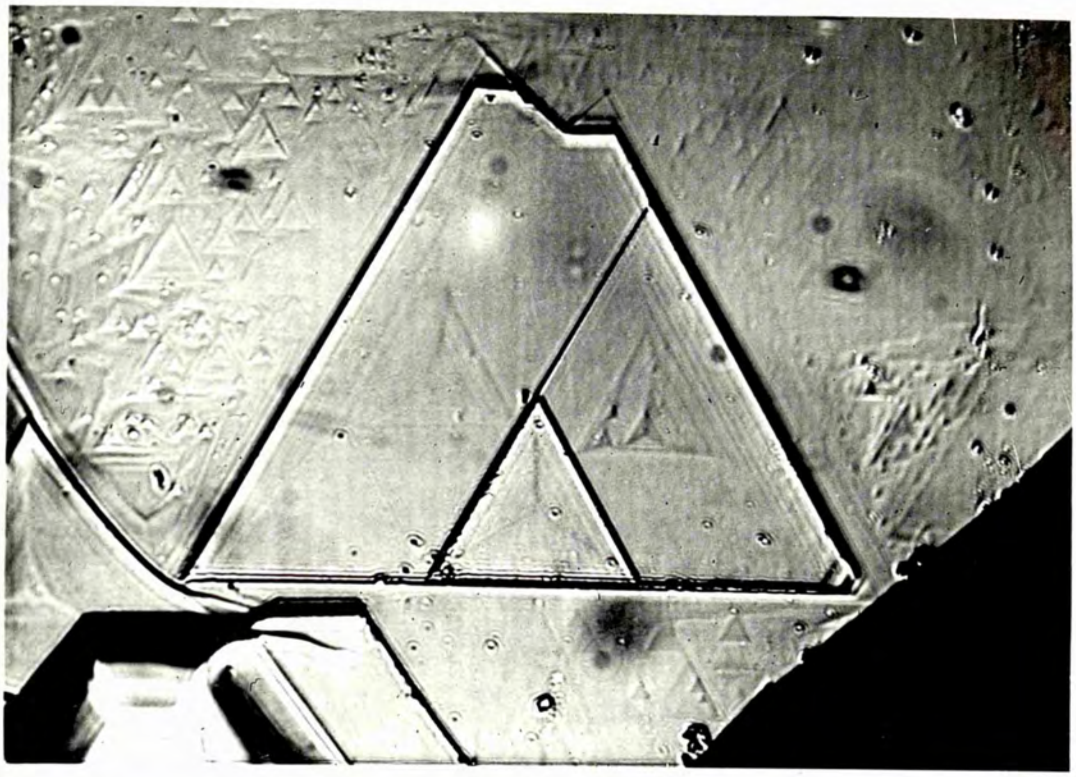


Fig. 27 (a) X720

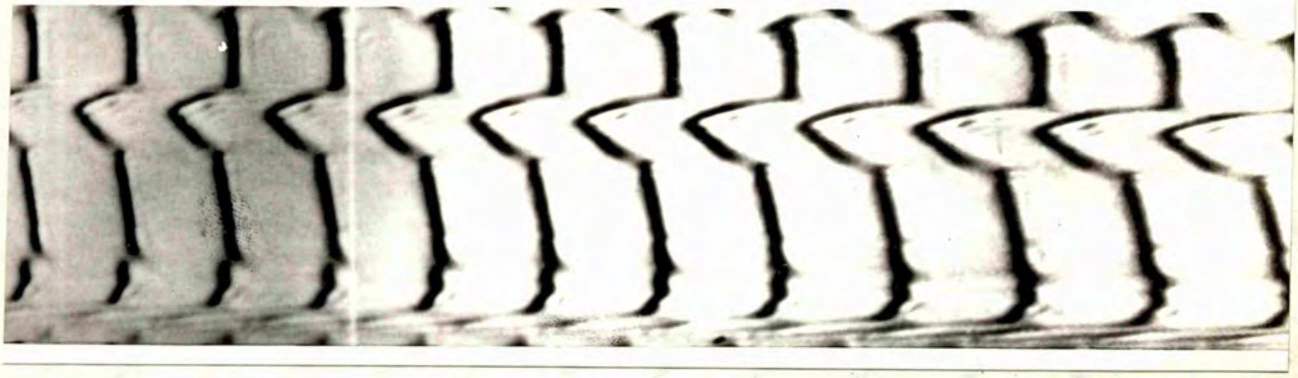


Fig. 27 (b) X250

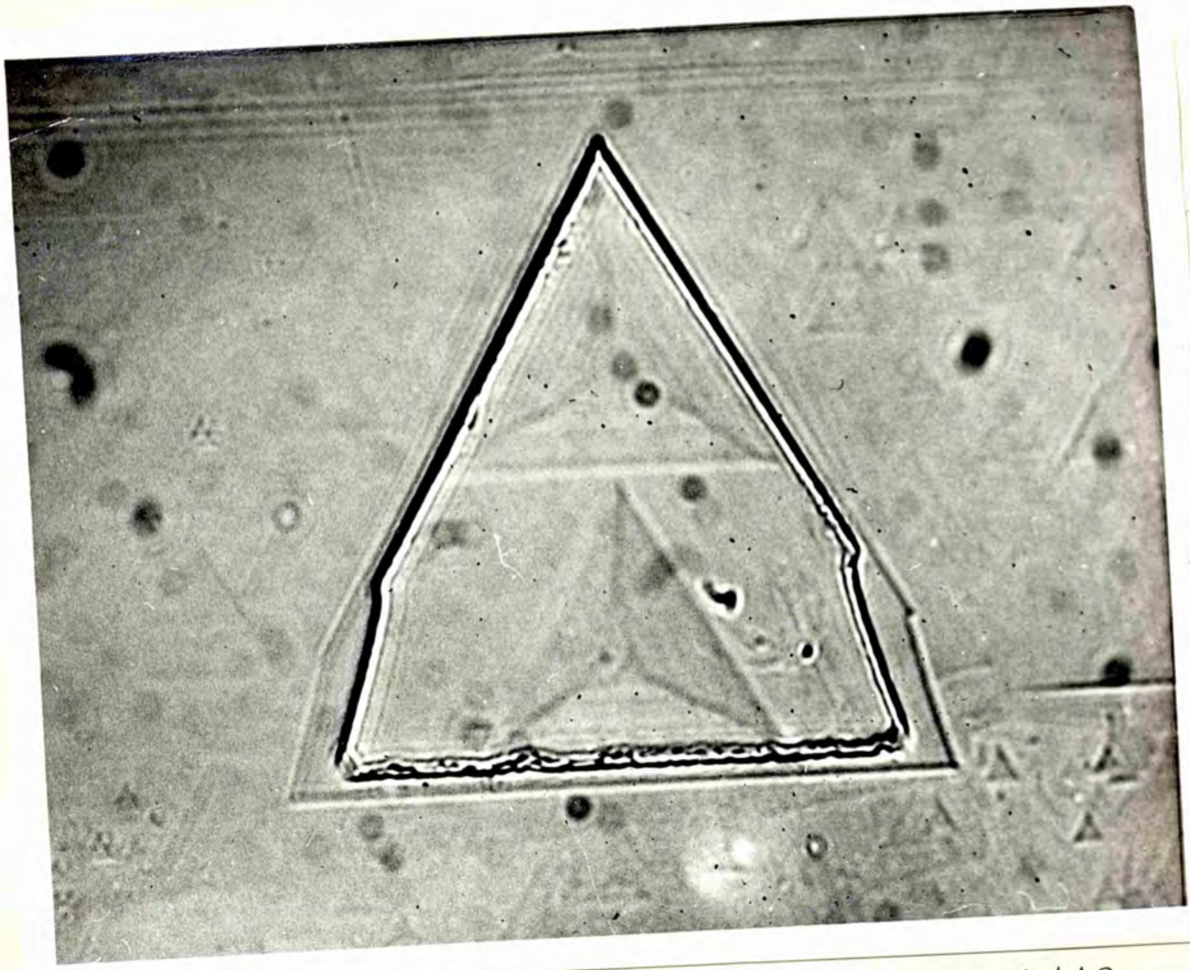
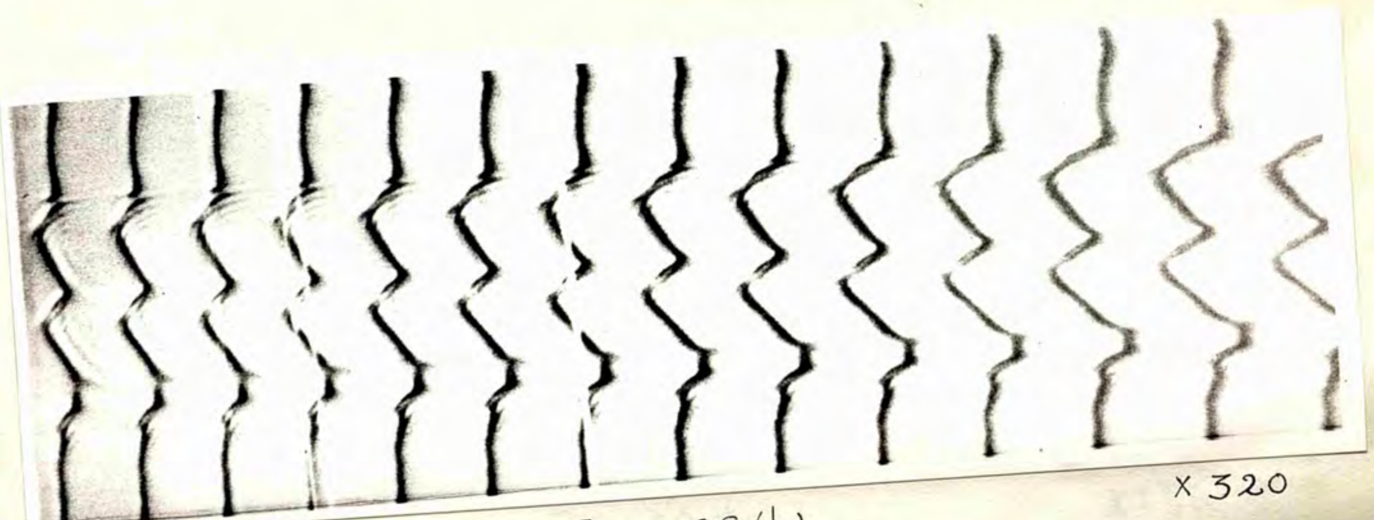


Fig. 28 (a) x 1120



x 320

Fig. 28 (b)

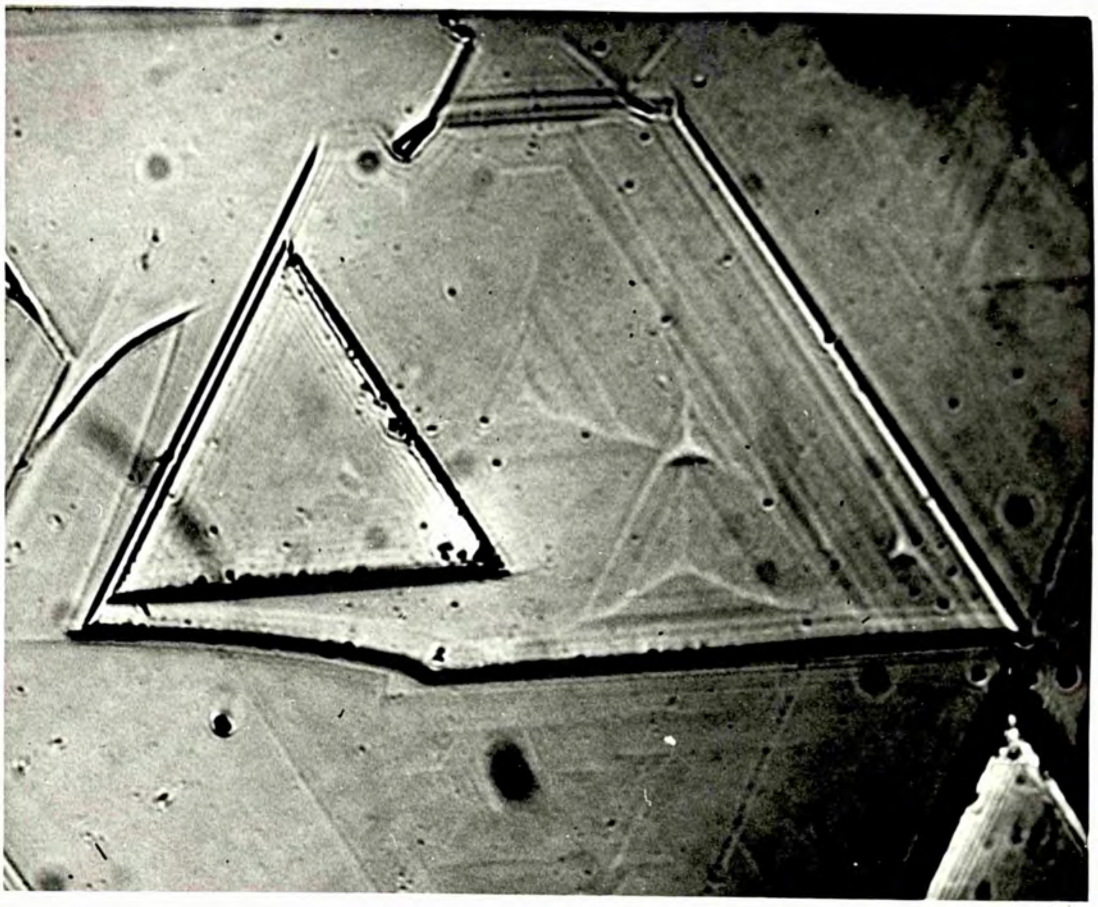


Fig. 29 (a) X1080

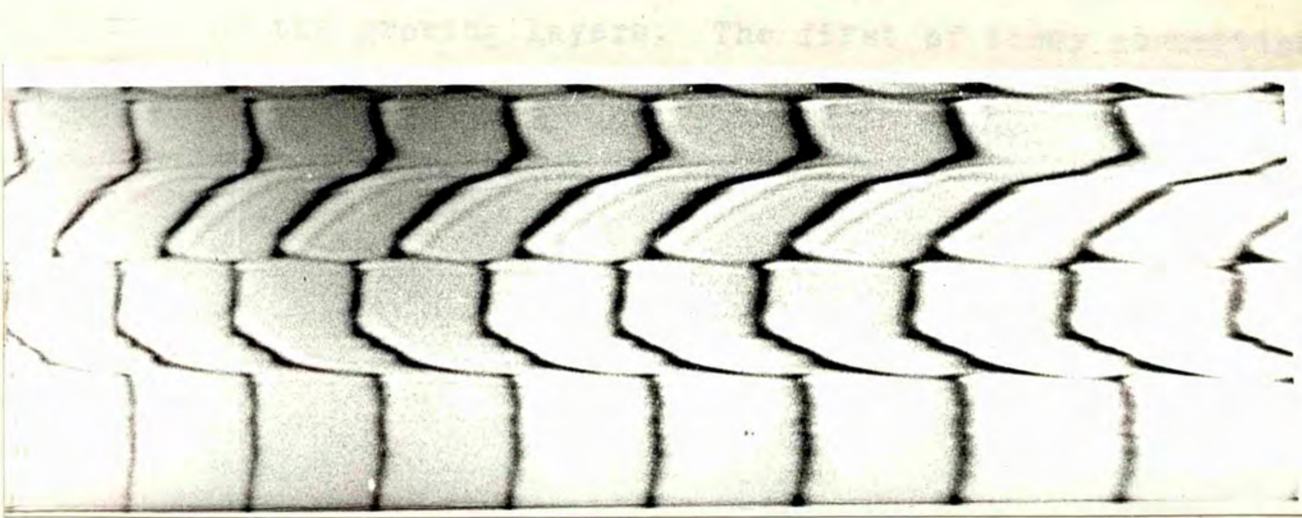


Fig. 29 (b) X186

A fifth example is shown in Figure (28a) X 1120. Here again the truncation has taken place at two corners. The depth has been calculated from the fringes of equal chromatic order to be about 1120A$^{\circ}$ as illustrated in figure (28b) x 320. The fringe pattern shows also the overlapping of growth trigons inside the feature.

A final example is shown in figure (29a) x 1080. It is one of the features with more complex irregularities. Figure (29b) x 186 shows the line-profile of a section passing through the middle top region and calculation revealed its depth to be about 600A$^{\circ}$. The fringe pattern revealed also the overlapping of growth trigons inside the feature.

Discussion.

These anomalies could be accounted for by two suppositions. First, that growth proceeds in layers spreading in succession over the crystal from comparatively few centres. Second, that disturbances are present on the surface to impede the forward progress of the growing layers. The first of these assumptions is quite in accord with the modern views on crystal growth, which have been revived by Buckley and by Mott (1949), and which conceive growth to take place in layers of molecular thickness. These theories are valid for growth from solution. The principal difficulty encountered by the layer growth theory, when it is applied to close-packed surfaces, is to account for the existence of appreciable continued growth at low supersaturation.

Under these conditions a layer already in existence will grow until it covers the whole surface, but the initiation of a new layer requires a two dimensional nucleus greater than a certain critical size, and the calculated rate at which such nucleation occurs is negligibly small unless the supersaturation is much higher than any experimentally observed value. Frank (1949) has pointed out that this difficulty is avoided if the crystal surface is not perfect. It is well known that the mechanical strength of actual crystals is far less than the theoretical strength of a perfect crystal, and this discrepancy is attributed to the presence of lattice imperfections. It is possible that these features are built on linear dislocation regions in the crystal lattice. Growth progresses until a linear dislocation is reached and then growth sweeps round this so that the feature will be filled in. Yet even if filled in from behind the linear dislocation can be left in the body of the crystal. This view has been favoured by Tolansky (1955), and there is a great deal of evidence which indicates that most crystals are very imperfect in structure. The tensile strengths of actual crystals are only small fractions of what they would be for perfect crystals, and the intensities of X-ray reflections indicate that the precise structure which exists in small regions is not continued uninterrupted throughout the crystal. There are discontinuities at intervals of the order of 100A°. The discontinuities are not at regular intervals, the idea of a regular secondary structure due to fundamental causes, which at one time put forward by Zwicky (1929), (1932) is not now accepted: as Smekal (1930) has shown by measuring mechanical properties of rock salt crystals, and Lonsdale (1947) by divergent beam X-ray photography of various crystals. It seems likely that these imperfections rise (at any rate partly) from the manner of growth by the spreading of layers across the faces. Successive layers do not necessarily join up perfectly with each other. Champion (1953) has been exploring specimens of diamond with nuclear radiations of differing penetrations. He reports local imperfections in diamond.

Again changes of pressure and supersaturation might also affect the formation of trigons and it seems likely that reduction in pressure should enhance the faults in the lattice, the changes of supersaturation affecting the rate of growth. It might be that the combinations of these factors cause these anomalies.

As to the slight curvature which is observed in some of the features. This could be attributed to the high temperature at which diamond is formed (Burton, Cabrera and Frank (1949), (1951)). The binding energy in diamond is great. According to a known relation depending on concentration of kinks this should result in nearly straight edges, unless the temperature is high.

The existence of anomalies on one crystal face where linear discontinuities has been observed (this will be discussed later) suggests that the local distortions in the lattice which may have caused "slip" to occur may have affected the formation of trigons during their growth and cause these irregularities.

Furthermore, it has been established by Tolansky and Emara (1955) that there exists on this crystal growth features (discussed in the next chapter) which can be explained to be due to the intersection of (221) with the (111) face, and there is a probability that the interaction of the (221) planes with the (111) planes may cause these anomalies.

CHAPTER III

OCCASIONAL MODE OF GROWTH IN DIAMOND

Introduction.

It has been established by previous workers that by far the great majority of octahedron faces of diamond grow by means of plane sheet growth which leads to trigon formation and to oppositely oriented growth pyramids. In both **trigons** and triangular growth pyramids the edges are strictly parallel to the three edges of the normally triangular face constituting the (111) natural octahedral face of the diamond. It is shown that in rare instances a plane-sheet mode of growth, operates on the octahedral faces of diamond which leads to the formation of six-sided growth features containing alternate angles of approximately 90^{o} and 150^{o}. It is also shown that the edges of these are effectively parallel to the directions $\langle 431 \rangle$. Quite a number of examples have been found of an oriented growth pattern and those of particular interest will now be described in detail. Three of these occur on different octahedral faces of diamond and the other two on another two good octahedrons. Interferometry establishes that all the features are elevations, i.e. growth hillocks with their heights not exceeding $1000A^{o}$.

Observation

Case I.

The first example is remarkable for its approximate

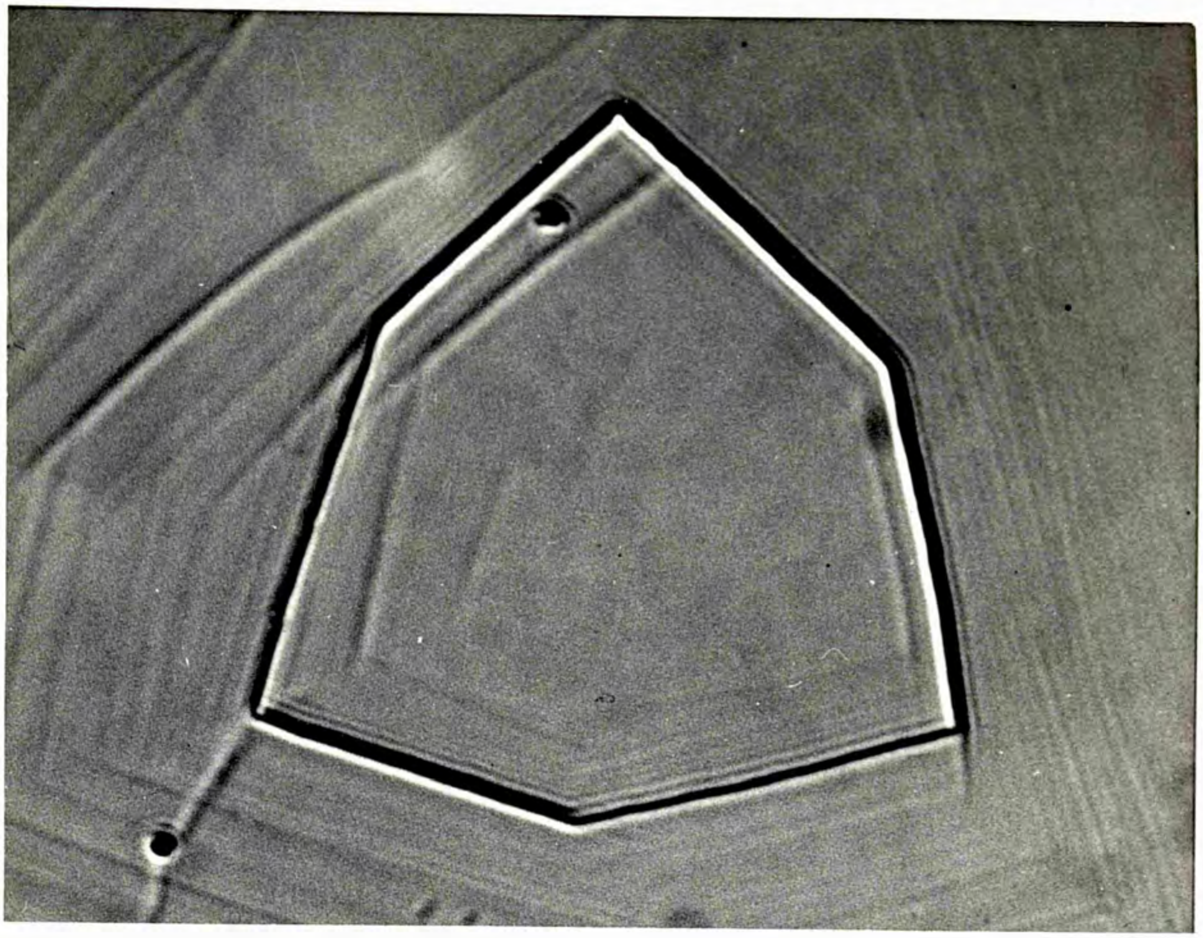


Fig. 30 (a) X2000

Fig. 30 (b)

symmetry and gives the clue to the others. It appears on one face of a good transparent octahedron from South Africa, of weight 0.63 carat and length of side 4 mm. and thickness 3 mm. The feature is quite small indeed and is shown in figure (30a) X2000. It consists of a hexagonal pattern and measurement reveals that the alternate angles are respectively approximately some 90° and 150°. The sides are almost, but not quite, equal in length. The angles are difficult to evaluate with any precision because the sides are not quite straight. The angles can be measured to within a little better than $\frac{1}{2}^\circ$. They are respectively, in degrees, $89\frac{1}{2}$, 150, $92\frac{1}{2}$, 144, 95, 150. Their sum is $721\frac{1}{2}$ and the excess is $1\frac{1}{2}^\circ$ over a rectilinear figure is undoubtedly due to curvature of the sides and not due to faulty estimation of the angles.

Estimation by fringes of equal chromatic order figure (30b) establishes that this feature is a plateau standing merely some 1000A° high above a more extensive growth pyramid. It is certainly a growth feature for there is no evidence for the existence of any etch effects whatsoever on this diamond.

Case II.

Figure (31) X 1400 shows the second example. As before, it is a six-sided figure enclosing within the familiar 60° growth trigons and measurement reveals that the alternate angles are respectively approximately some 90° and 150°, but the sides have different lengths leading to some distortion of shape. The angles measured in degrees are, 90, 153, 92, 150, $92\frac{1}{2}$, 151.

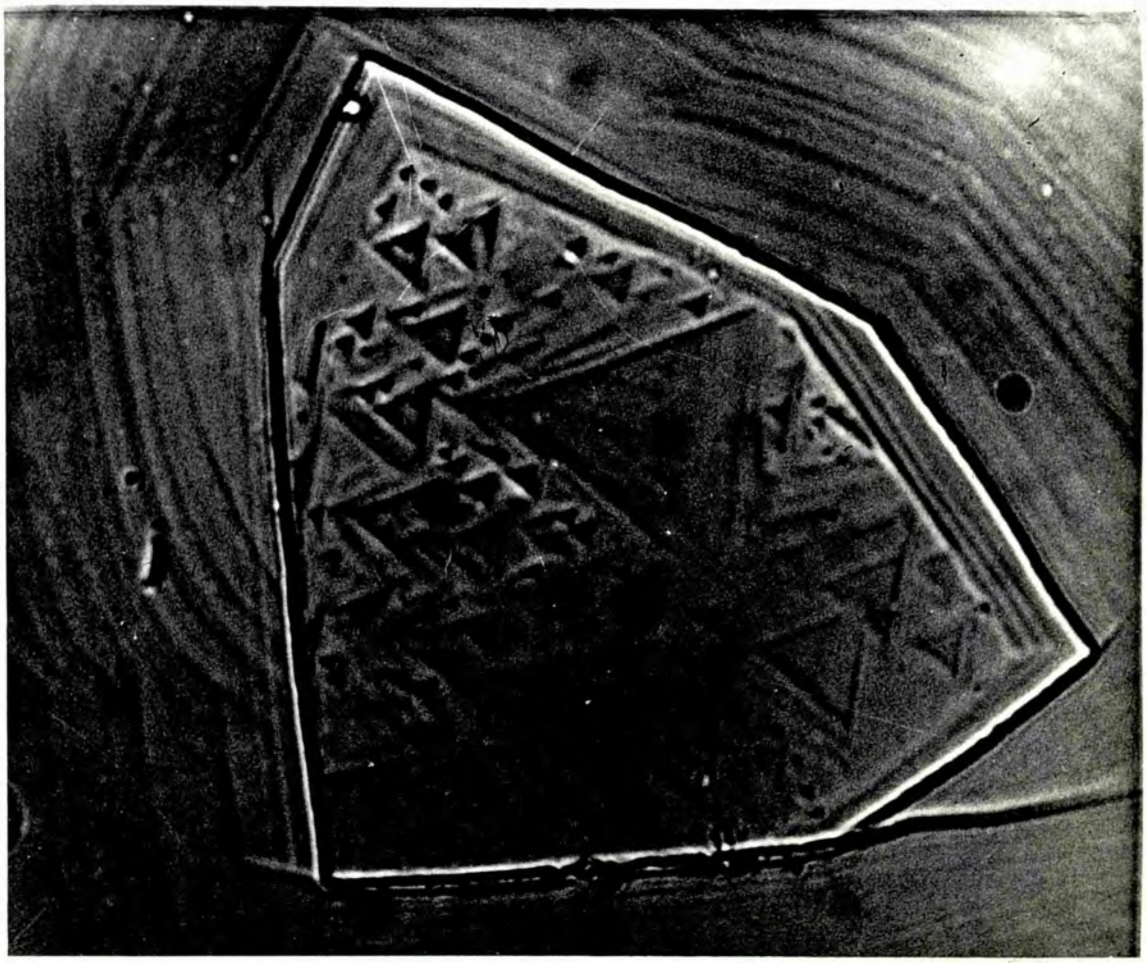


Fig. 31.   X 1400

The sum of these is $728\frac{1}{2}^{o}$ and the excess ($8\frac{1}{2}^{o}$) over that for a rectilinear figure is undoubtedly due to curvature of the sides and not due to faulty estimation of the angles.

Case III.

This example figure (32) X 600 at first seems a most irregular pattern but can be classified along with the two previous ones. The key lies in the appearance of alternate angles, approximating once more to some 90^{o} and 150^{o} which establish that this is just another distorted example. The angles measured are 89^{o}, 153^{o}, 93^{o}, 149^{o}, 90^{o}, 151^{o} with sum 725^{o}, and the excess is attributable to curvatures. Here again within the hexagon is the familiar 60^{o} growth trigon.

It is noteworthy that these three features, each on a different face of one crystal, cover a relatively insignificant fraction of the total area. Despite the numerical differences in angles, these features are undoubtedly similar and are clearly related.

Case IV.

In this example figure (33) X 30, the mode of growth under consideration is on a much bigger scale and dominates the whole growth of the face. The stone is a clear octahedron mined in South Africa. There is a good deal of deviation from the ideal case shown in figure (30), nevertheless the relationship is evident. It is clearly a relatively rare example of a crystal face which has grown primarily both in this manner as

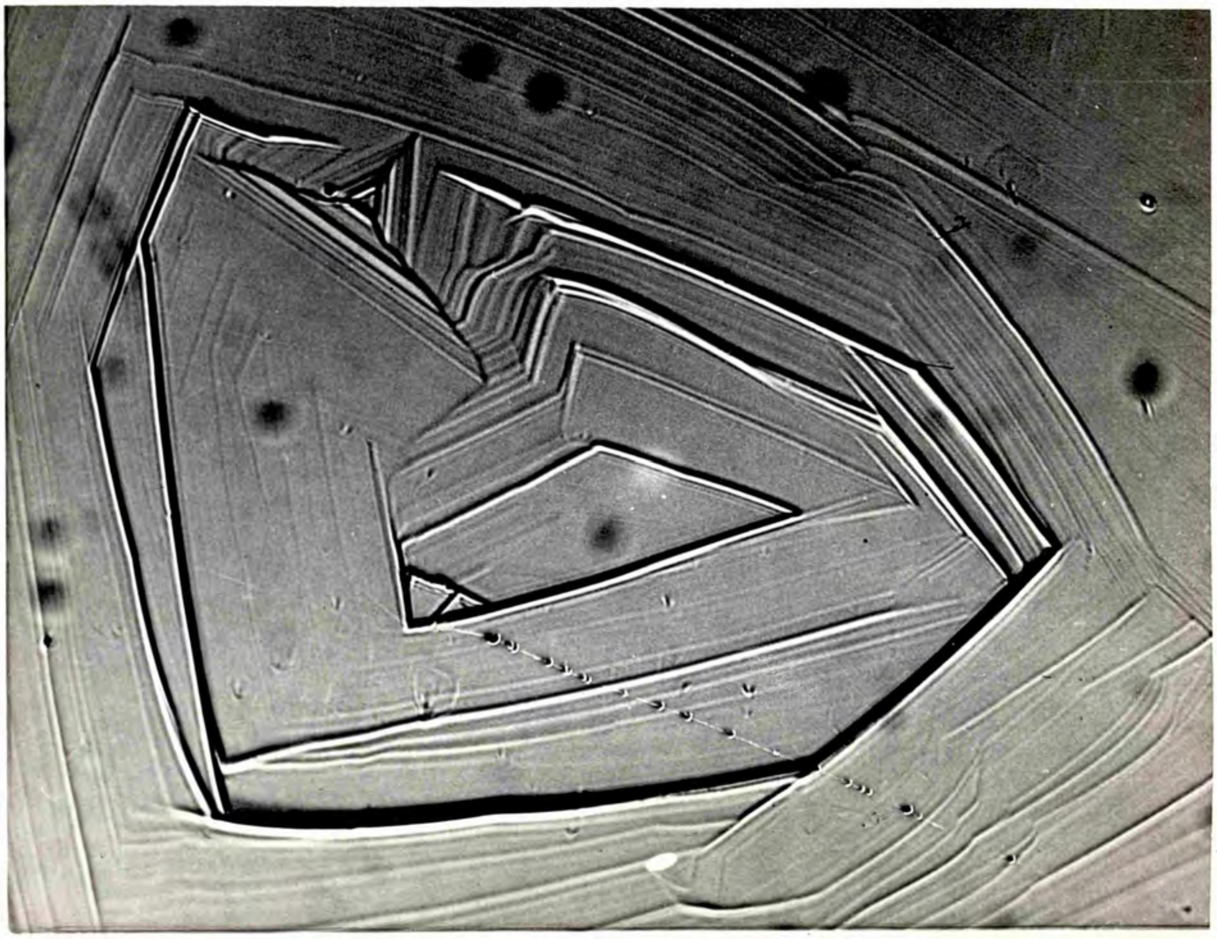


Fig. 32. X600

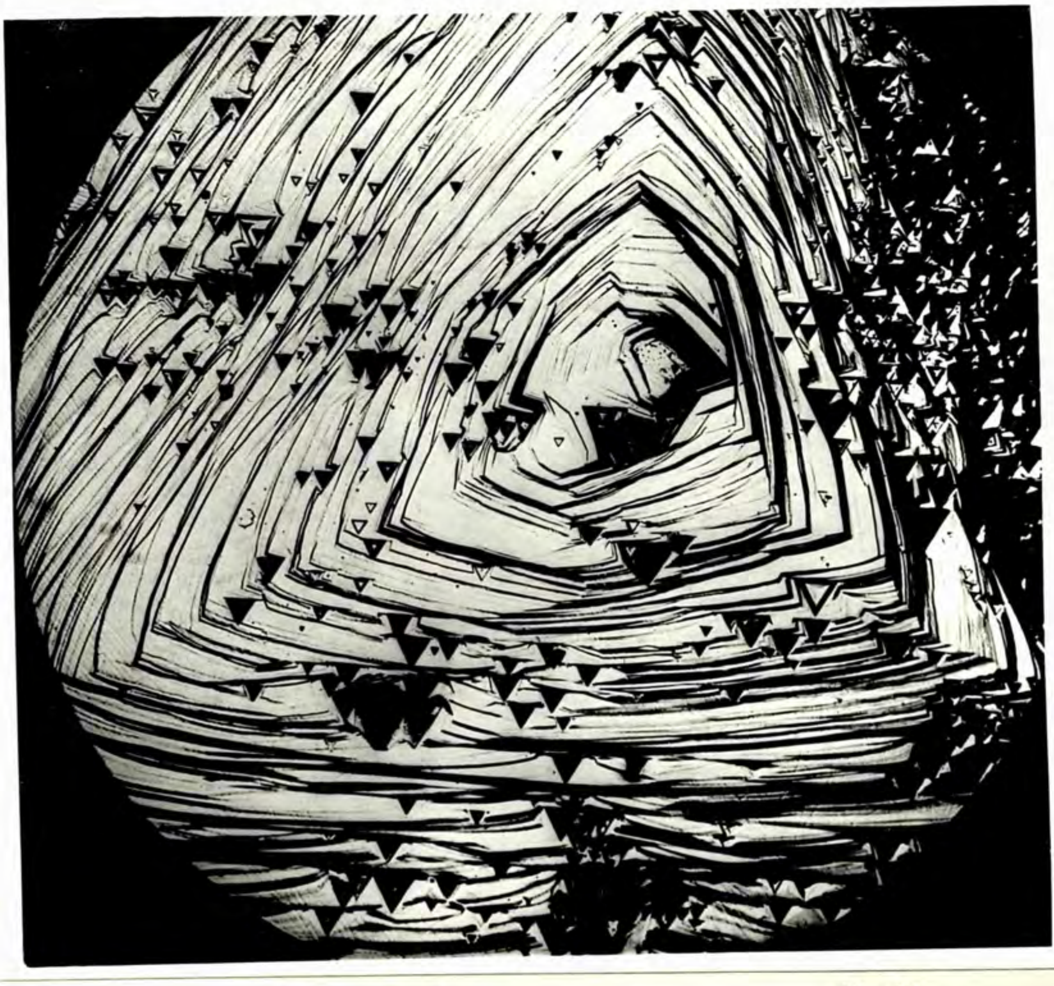


Fig. 33.　　　　X 30

Fig. 34. x 160

well as by trigon formation. The strongly outlined hexagonal central feature, which seems to start off with angles near 90° and 150°, quickly transforms its character on moving to the edges, tending to become a crude 60° equilateral triangle.

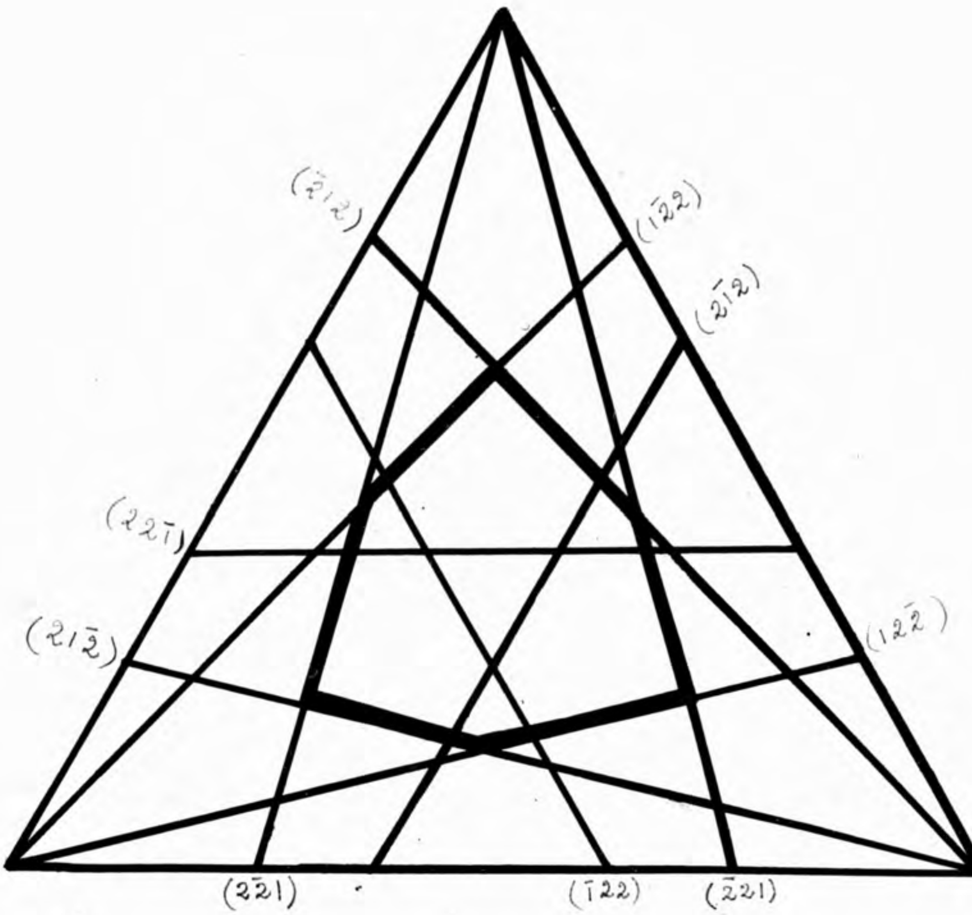
A similar example is shown in figure (34). x 160 This has also been observed on another clear octahedron mined in South Africa.

Discussion.

The observed hexagonal patterns can be crystallographically described as having their growth edges more or less parallel to the directions <431> . The first example for its approximate symmetry has given the clue to the others. The calculated angles for a hexagon in these directions are respectively 87°, 47′ and 152° 13′ . The values in the observed figure are somewhat similar. Although there is only a crude parallelism to <431> the main fact is the differentiation from the general mass of growth features on octahedral faces, which consist of trigon or pyramidal growth features in which the three sides are, almost invariably, inclined to each other at angles very near to 60°.

The lines which form this hexagon could arise from intersection of (111) with any of many planes which include for example (221), (430), (103), (014) etc. Of these, there is much in favour of (221) for the following reasons:-

It is the only set of planes which can produce simultaneously



$(\bar{2}12)$
$(1\bar{2}2)$
$(2\bar{1}2)$
$(22\bar{1})$
$(21\bar{2})$
$(12\bar{2})$
$(2\bar{2}1)$
$(\bar{1}22)$
$(\bar{2}21)$

Fig. 35.

on each of all the (111) planes of the crystal both the hexagonal pattern and equilateral triangles. as shown in figure (35), and both patterns appear simultaneously on three faces of the crystal. Further, (221) is the most close packed of all the possible forms giving the hexagonal pattern and might be favoured during growth. Again it has been established by etching experiments (Omar, Pandya and Tolansky 1954) that the most important planes produced by etching (111) on diamond are (221). This evidence is far from decisive but favours (221) a little.

It is worthwhile to point out that these particular hexagonal growth patterns have not been recorded by any of the other previous workers. Although Williams (1932) who had the opportunity of inspecting many thousands of stones yet he never, it seems, noticed this special mode of growth, despite its appearance in one of his published photographs. It is certainly of infrequent occurrence.

CHAPTER IV

CRYSTALLOGRAPHIC SLIP (?) IN DIAMOND.

Introduction.

It has long been known that plastic deformation in a metal is usually accompanied by the appearance of step-like patterns of "slip lines" on the surface of the separate crystal. It was concluded from this and other evidence that the essential process in plastic deformation is the slipping of microscopically observable layers of the crystal over each other. This process has often been linked to the sliding of cards in a pack over one another. Analysis has shown that slip occurs more readily along certain crystal planes and directions than along others. Many investigations have established that the slip directions and planes depend on the crystal structure, and in some cases on the temperature. However, the slip direction is almost that along which the atoms are most closely packed. In single crystals of most metals slipping is intiated at quite low stresses. The corresponding shear strains are much too small to cause simultaneous sliding of one part of the crystal over another. The only alternative explanation is that slipping occurs progressively across the plane of the slip. This process requires the existence of lattice imperfections of the type known as dislocations.

The idea that slip occurs by movement of dislocations was first introduced by Taylor, Orowan, Polanyi (1934), although concepts similar to that of slip dislocations were used earlier by Prandtl (1928). More recently some modifications of the theory were discussed by Frank (1949), (1951), Barrett (1952), Seitz and Read (1952) and Mott (1953). It has been concluded that two alternatives may account for the imperfections which may cause slip in crystals. The first is that dislocations are already present in the crystal, in which case the yield strength is the stress needed to move them; the second is that cracks or intercrystalline boundaries are present from which slip can be started easily. In this second case the yield strength is either the stress needed to start slip at these defects, or to propagate the slip away from them across the rest of the slip plane. In both cases some parts of the slip plane are required to slip before others, so that slip takes place by movement of dislocations. Strong evidence for dislocations in crystals has now been established by various workers, Griffin (1950), Verma (1951), Dawdson and Vand (1951), Amelenckx (1951), (1952), Forty (1952) and many others. Also some interesting investigations of unit slip lines have been observed by Forty and Frank (1953) on silver crystals, Anderson and Dawson (1953) on n - nonatriacontane crystals and by Verma (1955) on palmitic acid.

The observation of multiple lines on the surface of diamond having the character of slip lines is of considerable interest. These may well be interpreted as crystallographic slip and will now be described.

<u>Description of the crystal.</u>

The stone on which the linear discontinuities were observed is a clear well formed crystal from South Africa, of weight 0.63 carats, length of the side or edge 4 mm. and thickness 3 mm. with two of its corners missing.

Experimental.

The optical techniques employed for the study of the surface topography is described in Part II of this thesis.

All the eight faces were photographed using direct microscopy with a 33 mm. objective. On five of the faces were observed related and interconnected straight lines parallel to the edges of the octahedron faces. In order to obtain a clearer nature of these multiple-linear processes a model has been constructed by enlarging the microphotographs of the faces and combining them into a cardboard model. A photograph of this model is shown in figure (36) and the oriented and correlated "slip" lines with their associated trigons can be seen clearly. Another arrangement is shown in figure (37). Here the diamond is, so to speak, opened out, adjacent adges being in contact. One sees now how the lines pass right through the diamond since for example faces third from the top and third from the bottom are opposite. It is striking the way in which lines meet terminate on one another.

For the interferometric study the crystal was cleaned and a suitable silver film was deposited on it by evaporation in vacuo. It was then matched against a correctly silvered

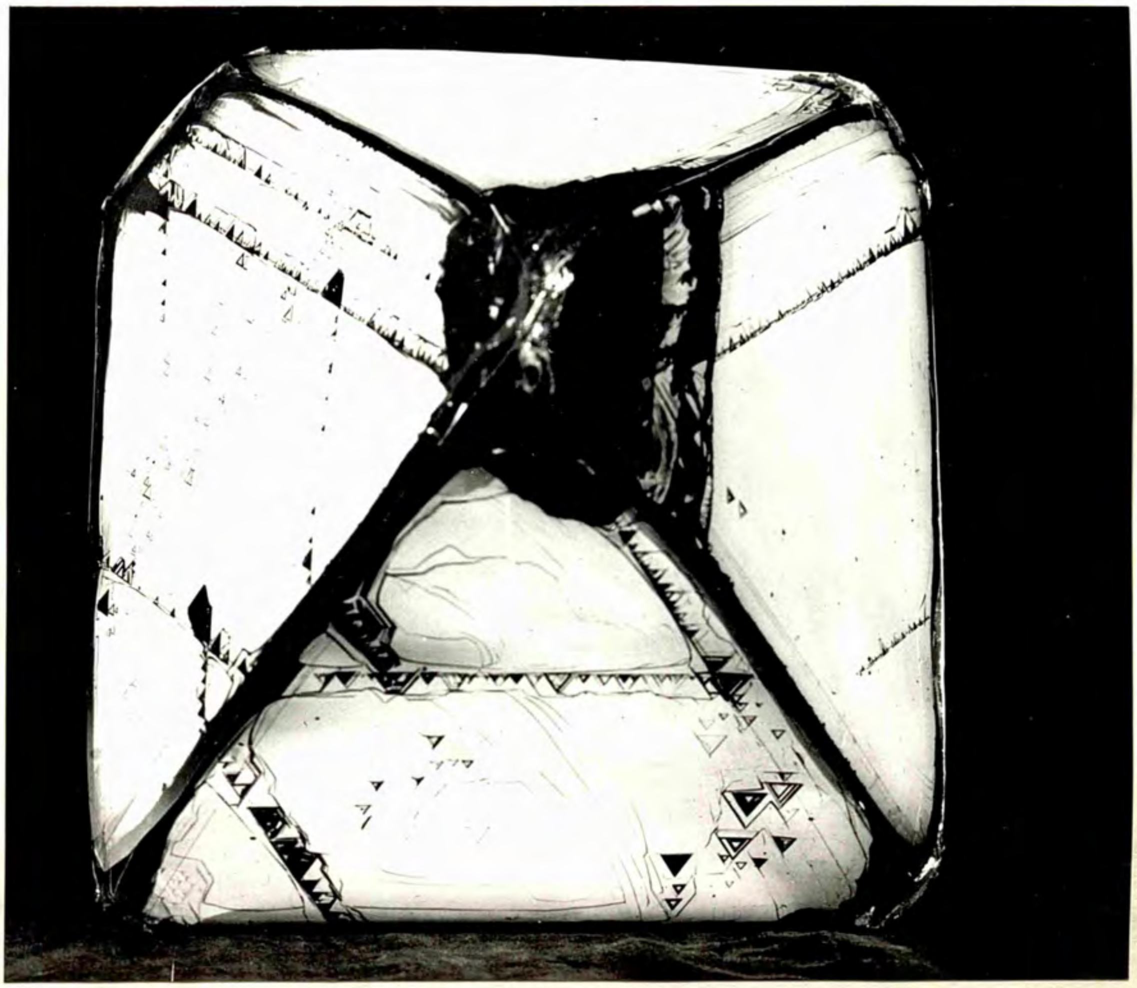


Fig. 36

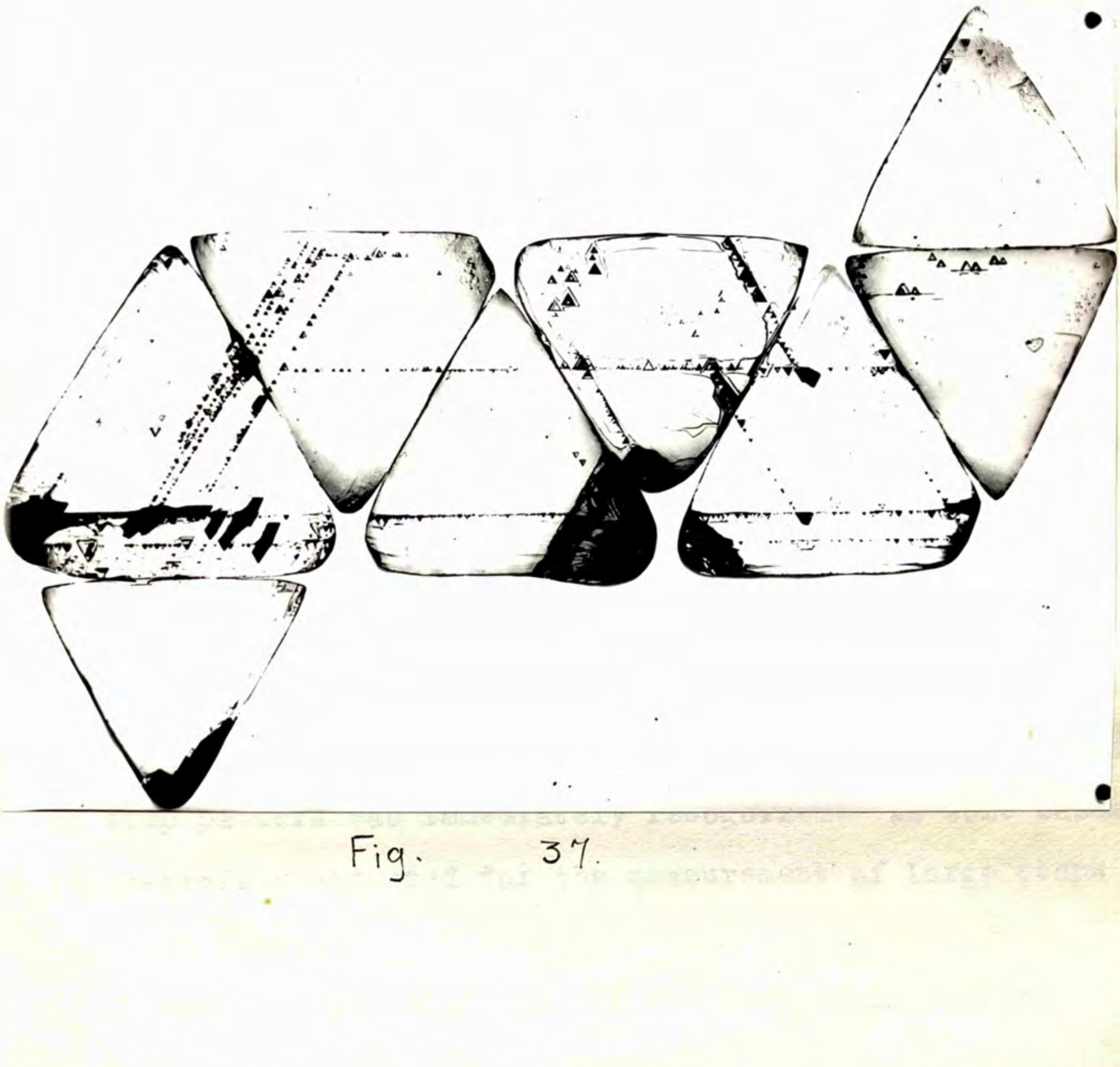


Fig. 37.

optical flat and most observations were carried out in reflection. Occasionally high-dispersion Fizeau fringes with unfiltered mercury arc were used. The heights of the steps along each "slip" line for the five faces were measured using fringes of equal chromatic order. This has been done intially by obtaining Fizeau fringes, and projecting the image of a line section of the slip line across the spectrograph slit; measurements of step-heights were then either made "in situ" from the spectrograph drum, or the fringes together with the mercury arc spectrum were photographed, and the steps were computed from measurements made on the photographic plates. With the former method the accuracy was about 1%, but with the photographic method this was improved to less than 1%. The accuracy could not be further improved owing to the low dispersion of the constant deviation spectrograph. In this way approximately 400 steps over 27 lines on the different faces of the crystal were readily estimated. The advantage of the fringes of equal chromatic order may be noted at this point for by their use, distinction of hills and valleys and true direction of step pattern was immediately recognized. In some cases the light-profile was used for the measurement of large steps as will be seen later.

The detailed study of all the faces will now be described.

Face 1.

On this face the "slip" appears as eight lines parallel

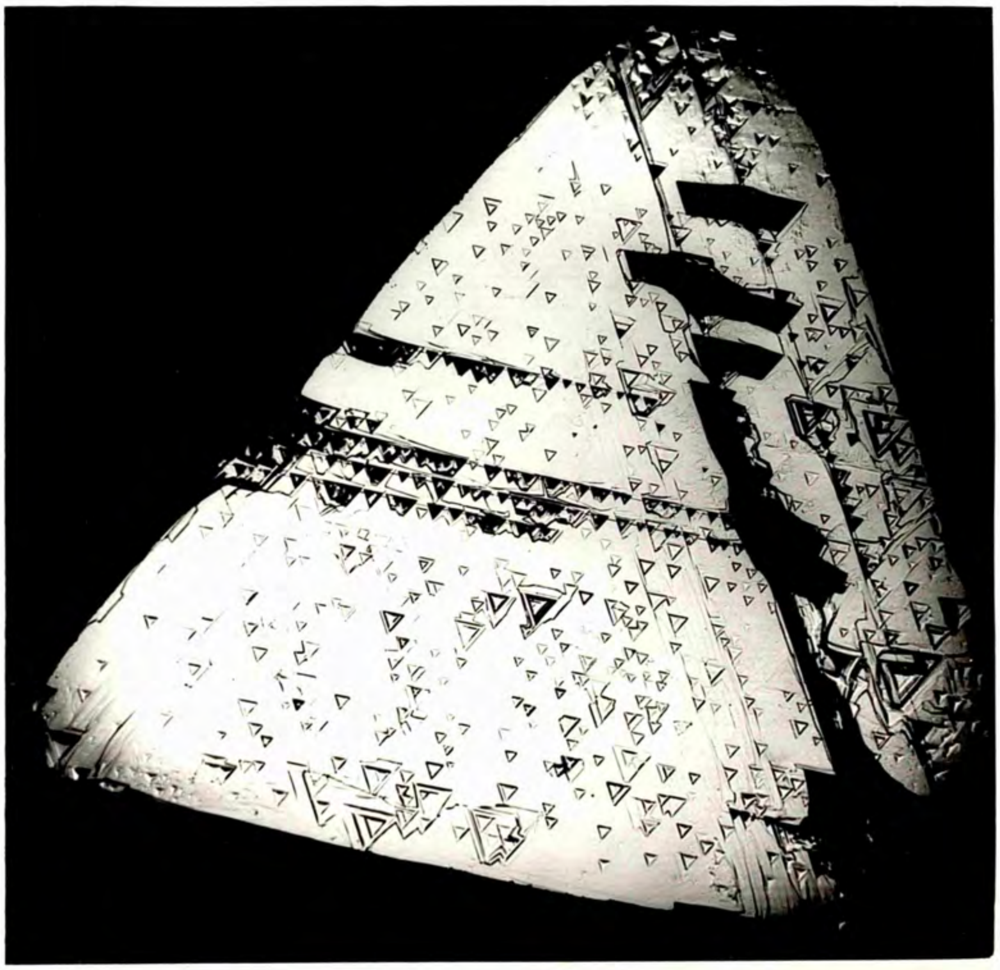


Fig. 38.   X30

to the edges of the octahedron. Of these, two lines were interrupted by a groove in the face of more than 6 · deep and figure (38) x 30 shows the microphotograph of the whole face. In spite of the existence of this groove the lines are observed to continue running right through the growth features as is clearly seen in the phase contrast photomicrograph figure (39) X 100. The high magnification revealed a large concentration of small shallow trigons all probably less than 50 A° deep. The topography of this region is shown by the high dispersion interferogram of figure (40) X 100. In this high contrast interference photomicrograph one sees growth trigons sitting in the deep groove.

In most cases the "slip" lines are straight, but occasionally they kink slightly and continue again in the same direction. A typical example is illustrated in figure (41) X X940 where one of the lines is in fact double with the two components separated by a distance of 5×10^{-4} cm. The trigons near the groove are seen to be less regular than those which lie away from it. The surface topography in the vicinity of the other "slip" lines is shown in figure (42) X 110. Measurements show that the most strongly outlined trigons sitting on the "slip" lines are very deep up to about 5 μ.

For measurement of the heights of steps use was made of both Fizeau fringes and fringes of equal chromatic order. Figure (43) X 95 is an interferogram for part of a "slip" line

Fig. 39. X100

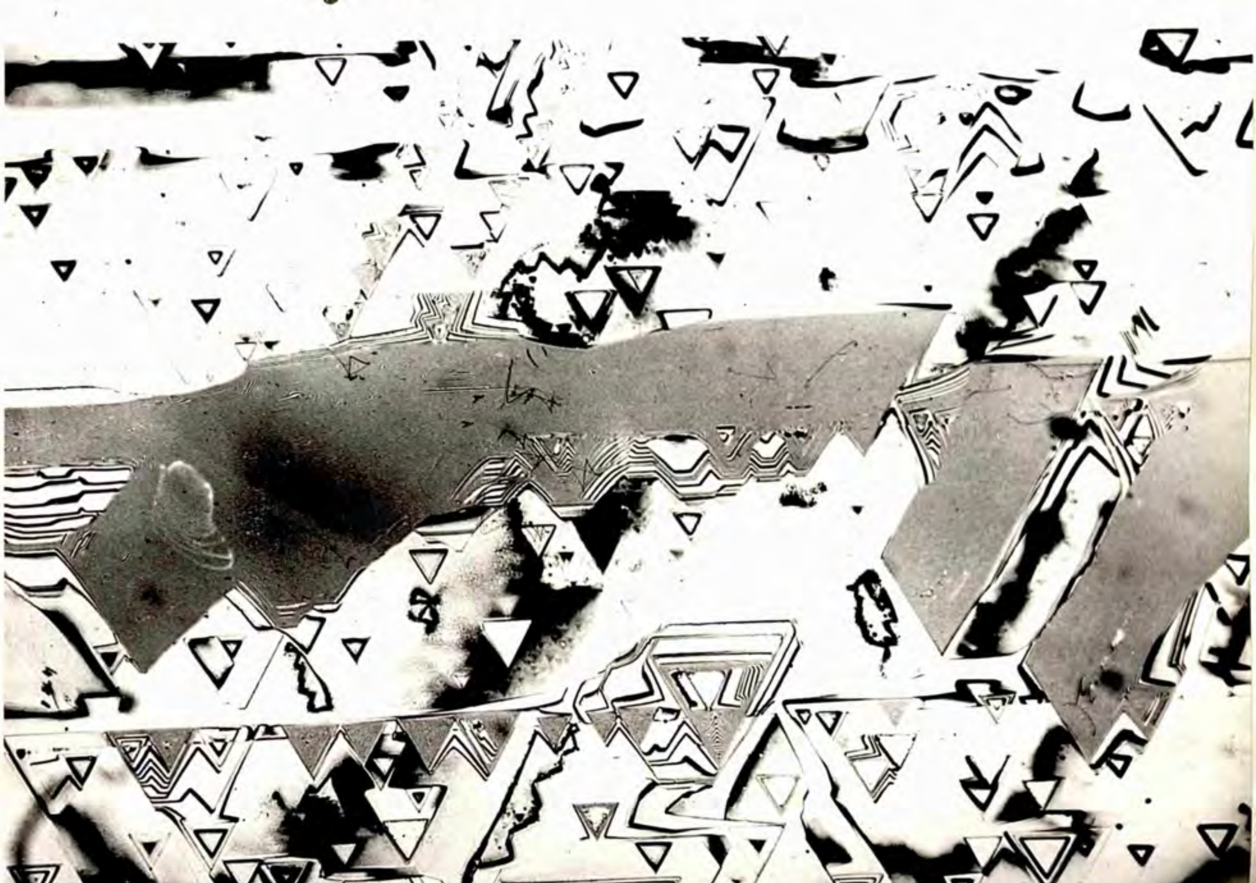


Fig. 40 X100

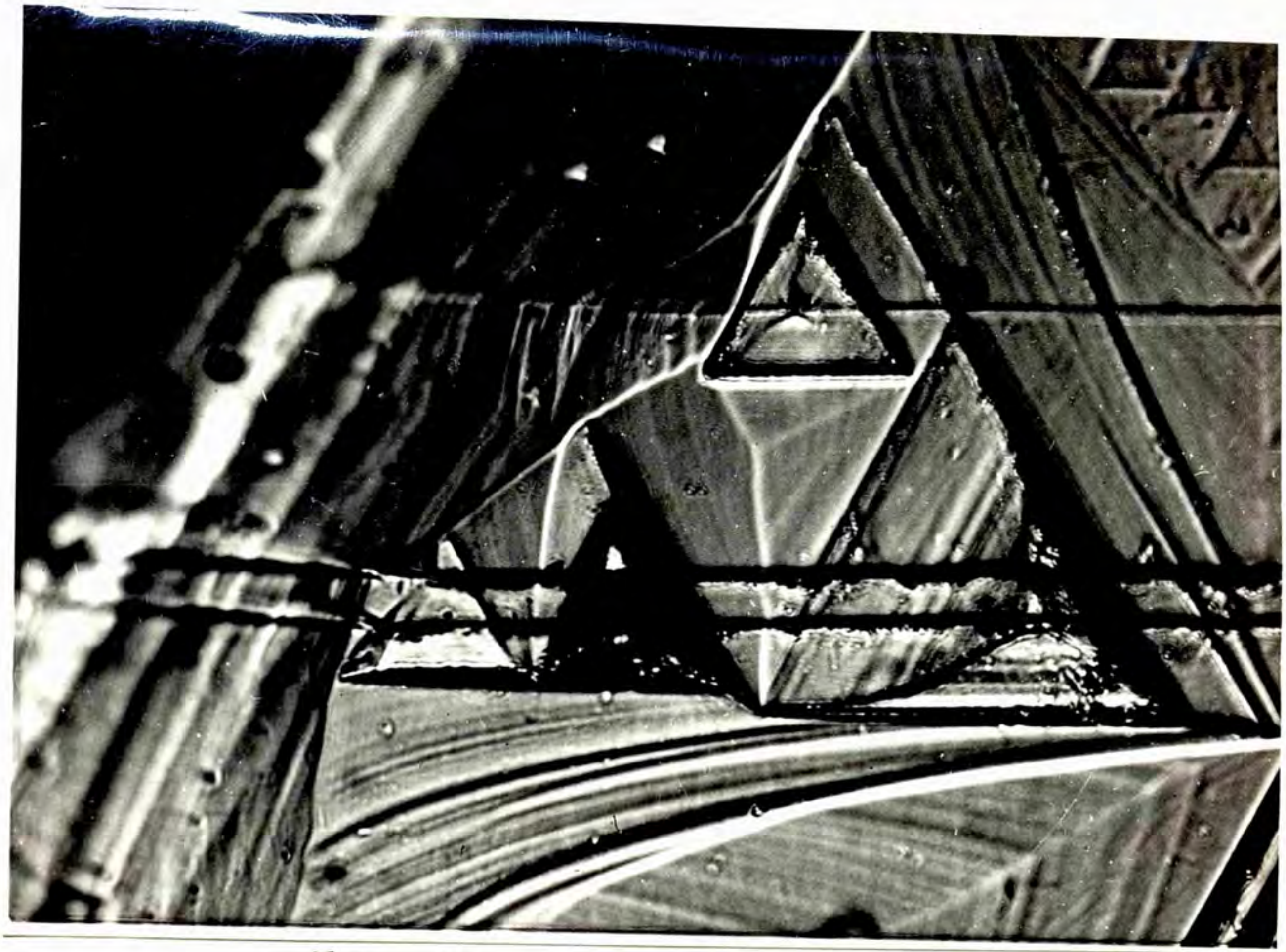


Fig. 41. X940

Fig. 42 X110

and it is clearly seen that the heights of the steps along the line are not regular and that there is an ambiguity as to the directions too. This point has been clarified using fringes of equal chromatic order and measurements show that they vary from one line to another and even on the same "slip" line. However, in the case of two "slip" lines crossing the groove the heights of the steps range from 1200A° up to about 900A°; while in the case of the other six "slip" lines the case is similar except that the heights of the steps are much less. Thus in one line the step is about 1000A° at one end and becomes progressively less, down to zero at the other end of the line. On all the other five lines the heights of the steps varied between 1500A° at one end down to about 600A° at the other end of the line. An example for one of the measured steps using fringes of equal chromatic order is shown in figure (44) X 140. The measured step is about (800 ± 10) A°.

It is important to note that in all the slip lines measured, the lower level is the side nearer to the base of the trigon parallel to the "slip" line. The light-profile was sometimes used for the measurement of large step heights and figure (45) X 2300 shows one of the multiple slips where the step heights are about 8000A° and 4000A° respectively.

Face 2 (Opposite to Face 1.)

On this face the "slip" appears in four lines. Three of them are parallel to one edge of the face while the fourth

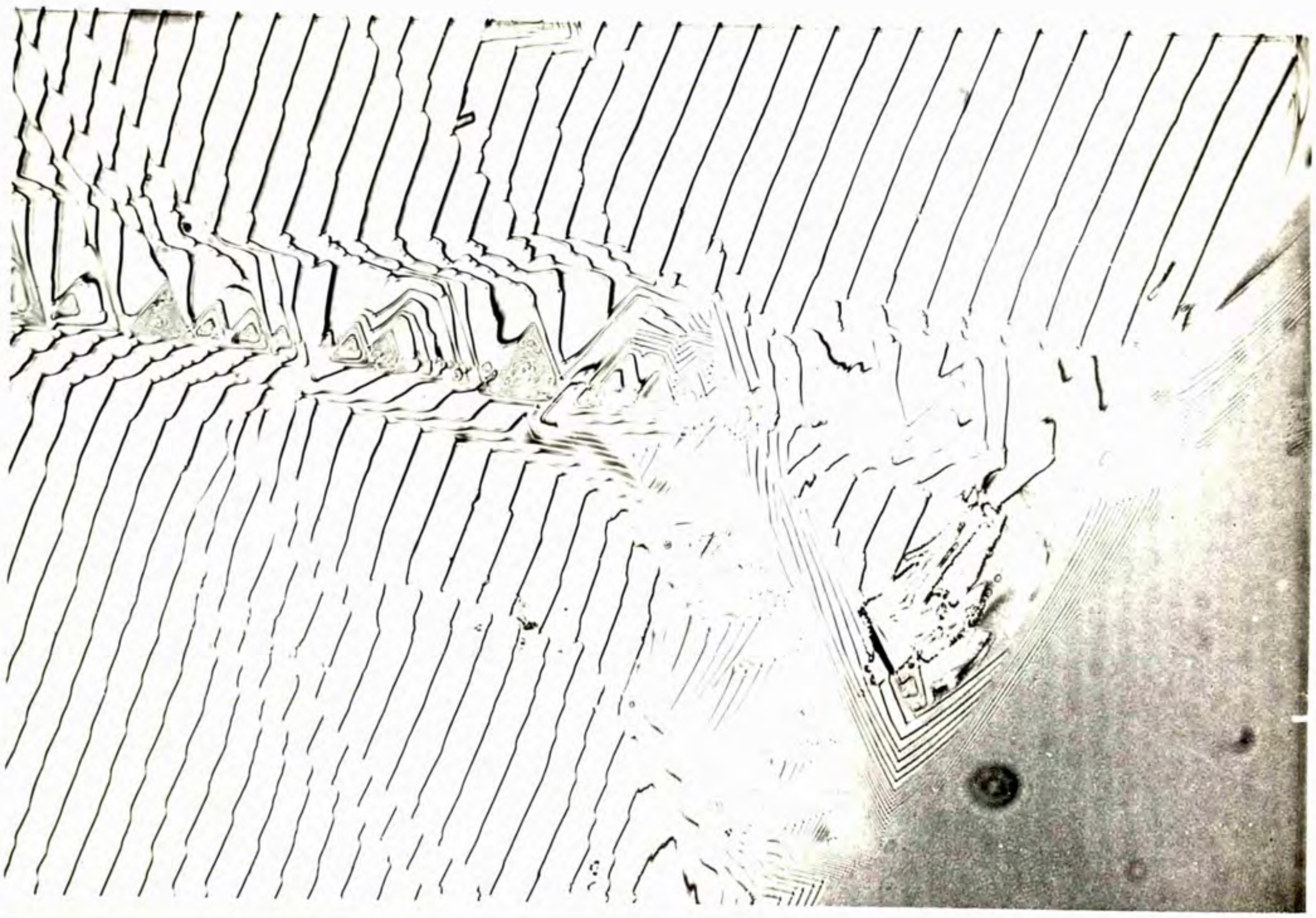


Fig. 43 x95

Fig. 44. x140

Fig. 45. X2300

cuts two of them at an angle of 60°. Figure (46) X 30 shows the photomicrograph of the whole face. High magnification revealed that all the lines on this face are single, and that there is a high concentration of linear groups of trigons sitting on the "slip" lines, with growth sheets advancing from both sides of each line. A typical example is shown in the phase contrast photomicrograph figure (47) X 110. In this photograph one can also recognize the faint outlines of the small shallow trigons.

The topography of this region is vividly revealed in the high dispersion interferogram shown in figure (48) X 110. Here the wealth of contrast shows the great depths of the rows of trigons along the "slip" lines and also the great heights of growth pyramids as well. Not only that but the various tints show the very slight variations of level across the surface. Using high power, the trigons were found to sit with their growth centres just on the "slip" lines. This is easily seen in figure (49) X 600.

The study of growth features along the "slip" lines was carried out using high dispersion Fizeau fringes as illustrated in figure (50) X 95. Here again from the fringe pattern the trigons along the "slip" lines are clearly seen to be much deeper than those lying on the rest of the surface. The estimated depths of these deep trigons is up to about 4μ.

For the measurement of step heights along each line use was made of the fringes of equal chromatic order and it was

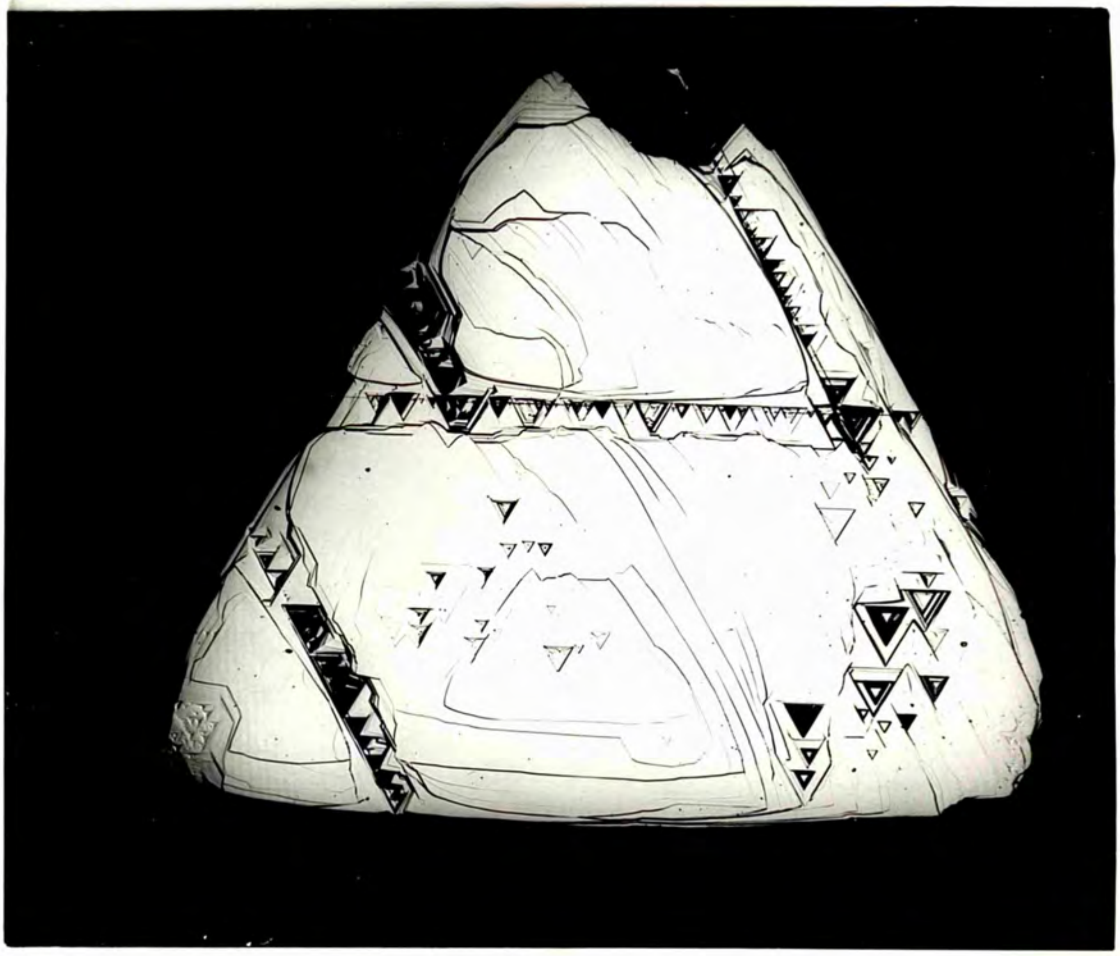


Fig. 46. X30

Fig. 47.   X110

Fig. 48. X110

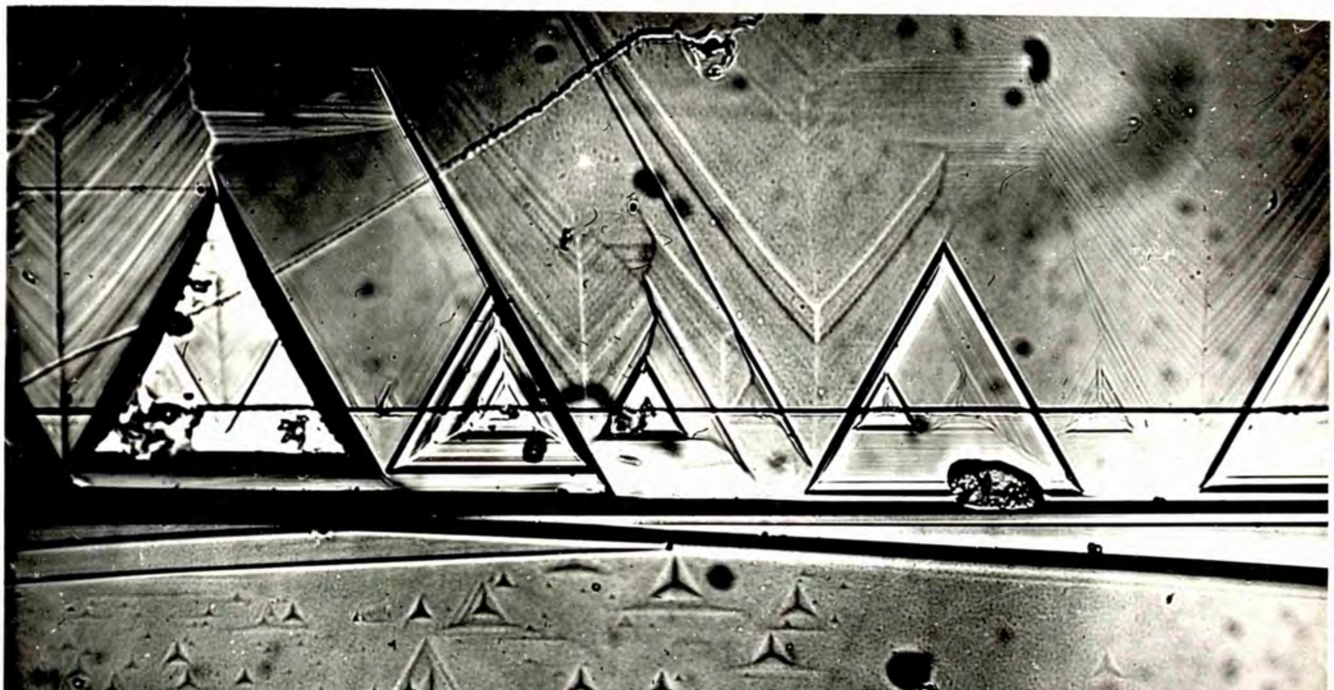


Fig. 49. X600

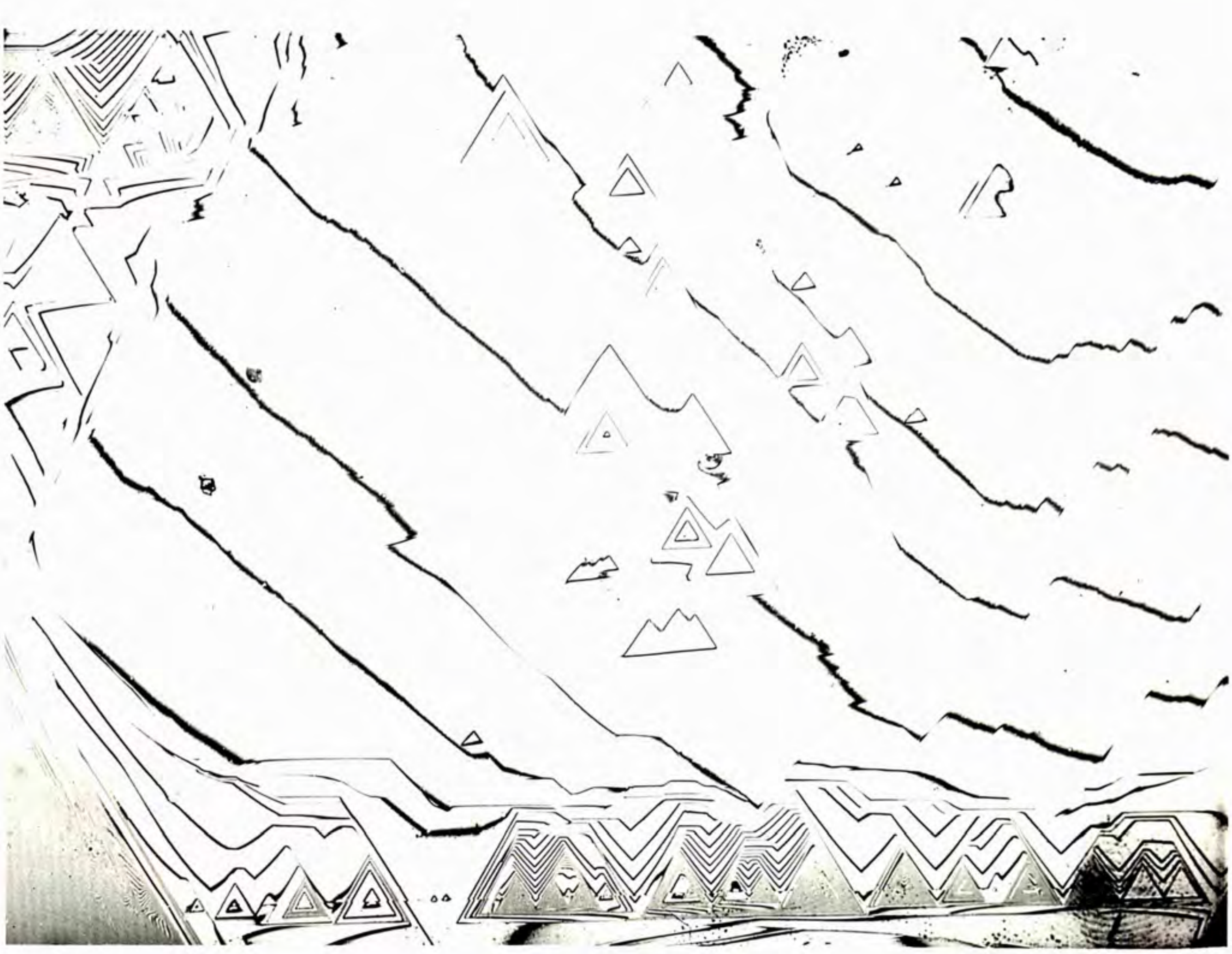


Fig. 50 x95

Fig. 51. X240

found that the heights of the steps are not uniform along the lines, but all the lines gave similar results. Thus, at one end the step is about 1100A° and then decreases irregularly down to about 800A° and in all cases the apex region of the trigons is higher. An example of one of the steps is shown in figure (51) X 240 where the heights of the step is about 1900A°.

Face 3.

On this face the "slip" appears in six lines. Of these three are parallel to one edge of the face and are crossed by the three others which are parallel to another edge of the face. The lines when crossing each other make an angle of 60° as is shown the photomicrograph of the whole face figure (52) X 30. The 4 mm. objective revealed that each of the bottom "slip" lines seen on the face is in fact composed of two fine lines separated by a distance of some 5×10^{-4} cm. as is illustrated in figure (53) X1000. It is of considerable interest to note that these double lines when traced were found to be connected to those already mentioned for Face 1. Also the trigons sitting on the "slip" lines are observed to be elongated as if some disturbance had occurred during their growth. The interferogram for the top region where two "slip" lines cross is shown in figure (54) X 110 where the heights of the steps are observed to vary along the whole line.

As before, for the accurate measurement of step heights, use was made of fringes of equal chromatic order and it was

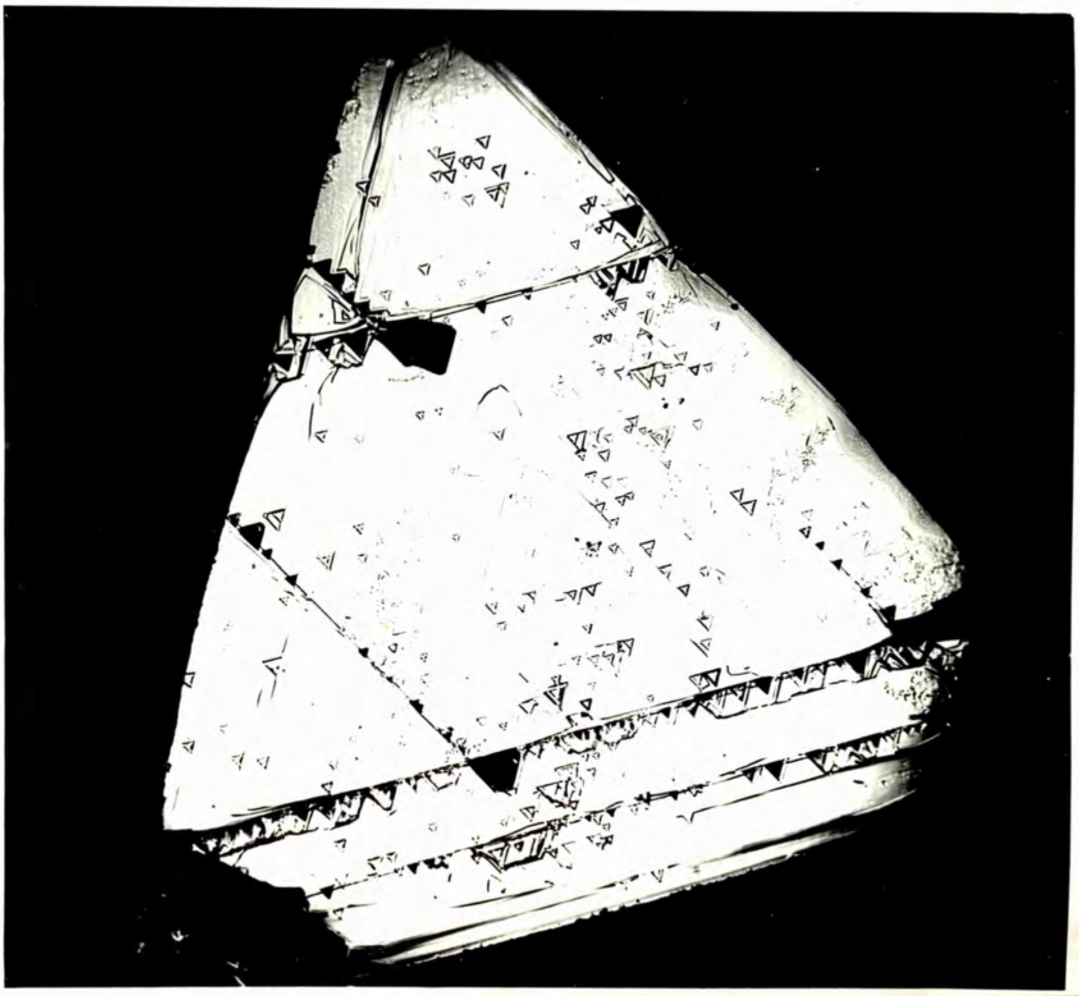
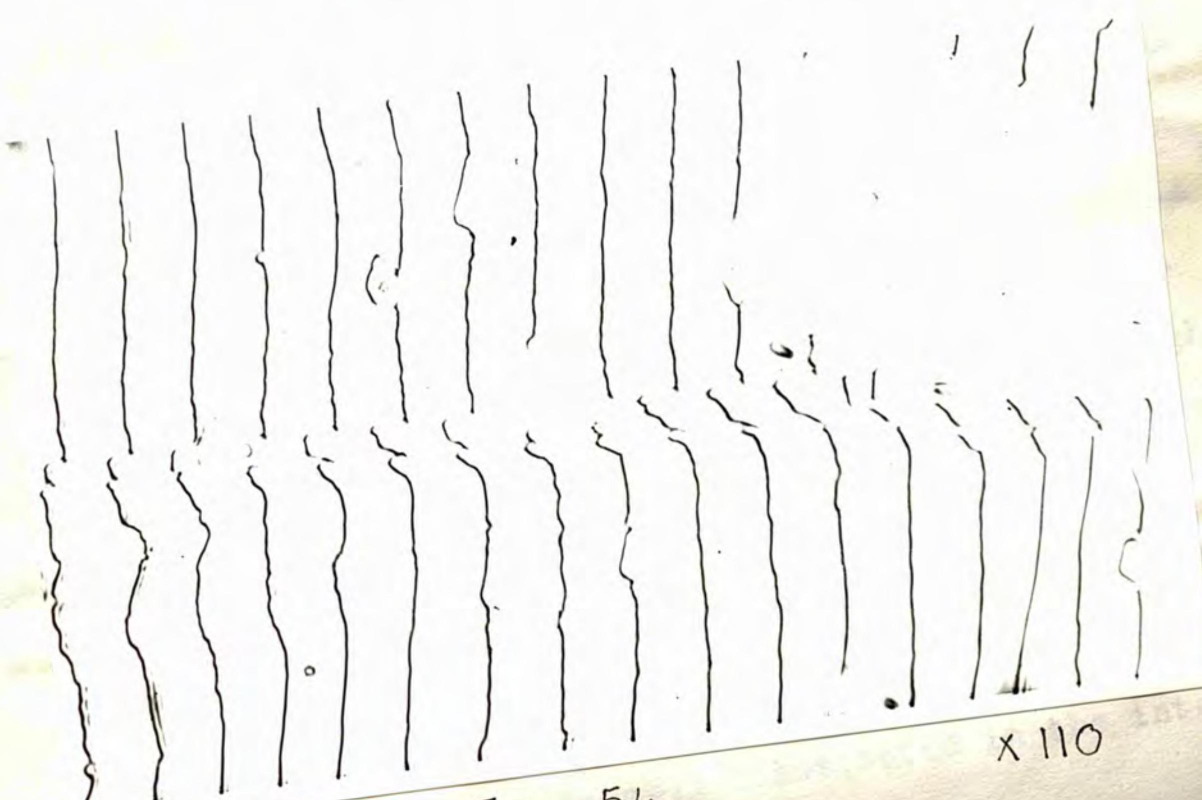


Fig. 52. X30

X1000

Fig. 53.



x 110

Fig. 54

concluded that most of the steps are not uniform along each line. Thus, in the case of the two bottom sets of "slip" lines the steps are large and usually start at one end at about $6500A^{o}$ and then decreasing progressively down to about $1000A^{o}$. In the case of short "slip" lines the step at one end is about $1500A^{o}$ and then decreases irregularly down to zero. For the rest of the "slip" lines the variations of heights of the steps vary between about $1000A^{o}$ and $4000A^{o}$. The light-profile was also used for the measurement of the larger steps and one example is shown in figure (55) X 1800 where the measured values for the upper and lower steps are about $6500A^{o}$ and $3000A^{o}$ respectively.

Face 4. (Opposite to Face 3).

On this face the "slip" appears as eight lines. Of these, five are parallel to one edge of the face and are crossed by the other three which are parallel to another side of the face. All the "slip" lines when they meet one another make an angle of 60^{o}. Also the "slip" lines run right through the trigons. Figure (56) X 30 shows the photomicrograph of the whole face. The majority of lines are observed to be discontinuous and some of these lines were revealed under high magnification to be multiple lines with a separation of about 5×10^{-4} cm. This is clearly seen in the photomicrograph figure (57) X 200. It is striking to note how the trigons are arranged in linear groups along the "slip" lines. The topography of this region is well illustrated in the inter-

Fig. 55. X 1800

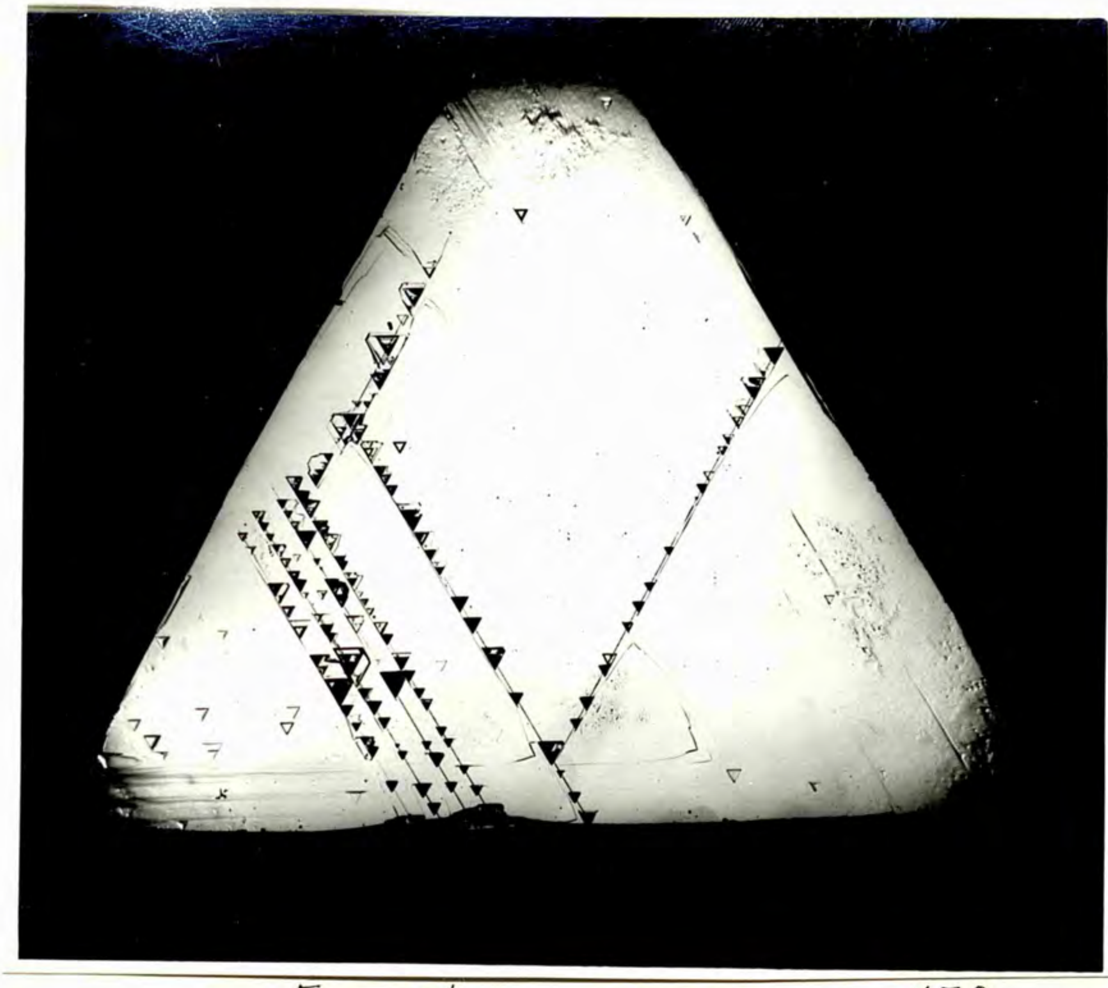


Fig. 56. X30

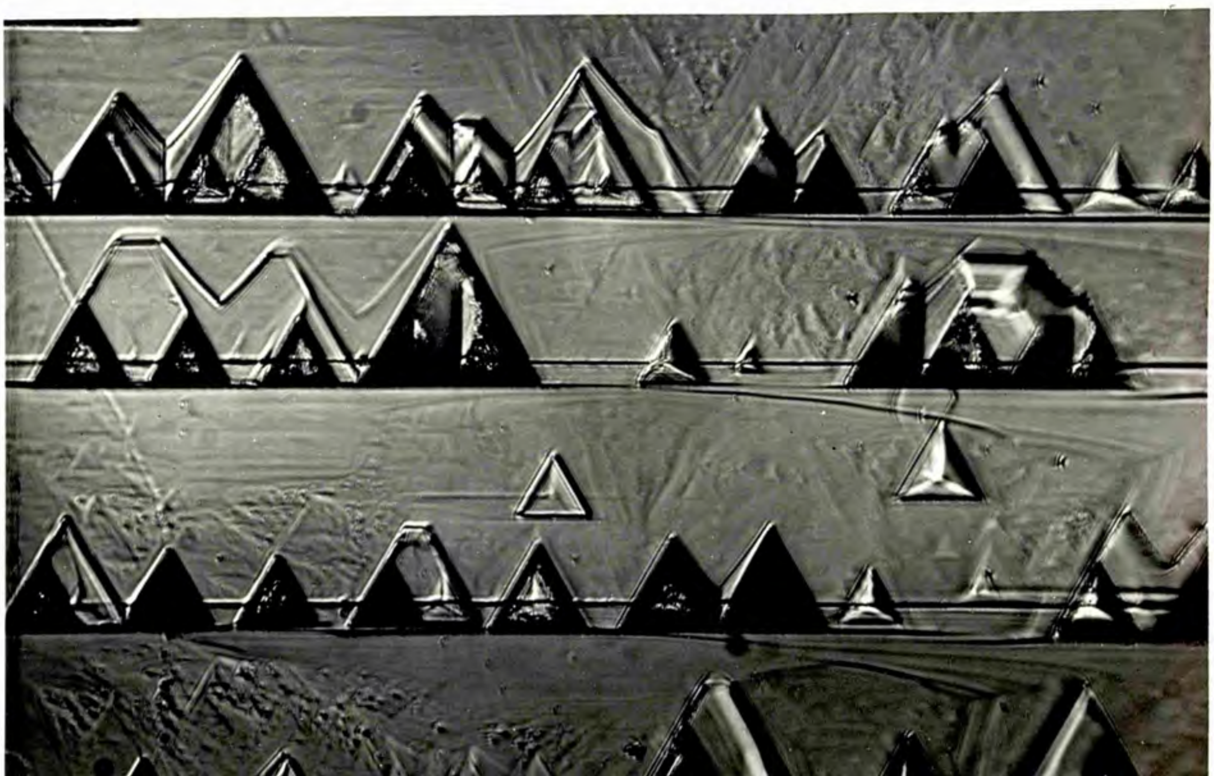


Fig. 57. X200

ferogram of figure (58) X 240. Here one sees differences in tint revealing very small variations in level across the surface, and also the considerable depths of the trigons are revealed. Furthermore, the heights of the steps along each line are variable. Figure (59) X 200 is an interferogram for one of the "slip" lines. To decide the directions of steps from this fringe pattern is difficult and therefore use was made of fringes of equal chromatic order for estimating the heights of the steps along each line. It was found that in the case of the six discontinuous lines the step at one end is about 1400A° and then decreases progressively down to zero at the other end whereas in the case of the other two lines the step at one end is about 1000A° then increasing up to about 4000A°.

The apex region of the trigons is the higher, as always.

Face 5.

On this face the "slip" appears when seen under low power, as two lines about 1.7 mm. apart and parallel to one edge of the face as shown in the photomicrograph of the whole face figure (60) X 30. However higher magnification reveal that the longer "slip" at the bottom of the face is in fact composed of at least three parallel lines with separations of 5×10^{-4} cm. and 6×10^{-4} cm. respectively and probably a fourth. This is clearly illustrated in the phase contrast microphotograph figure (61) X 650. Here again the trigons are arranged in linear groups as if anchored to the "slip" lines at their centres. These

Fig. 58. X240

Fig. 59. X200

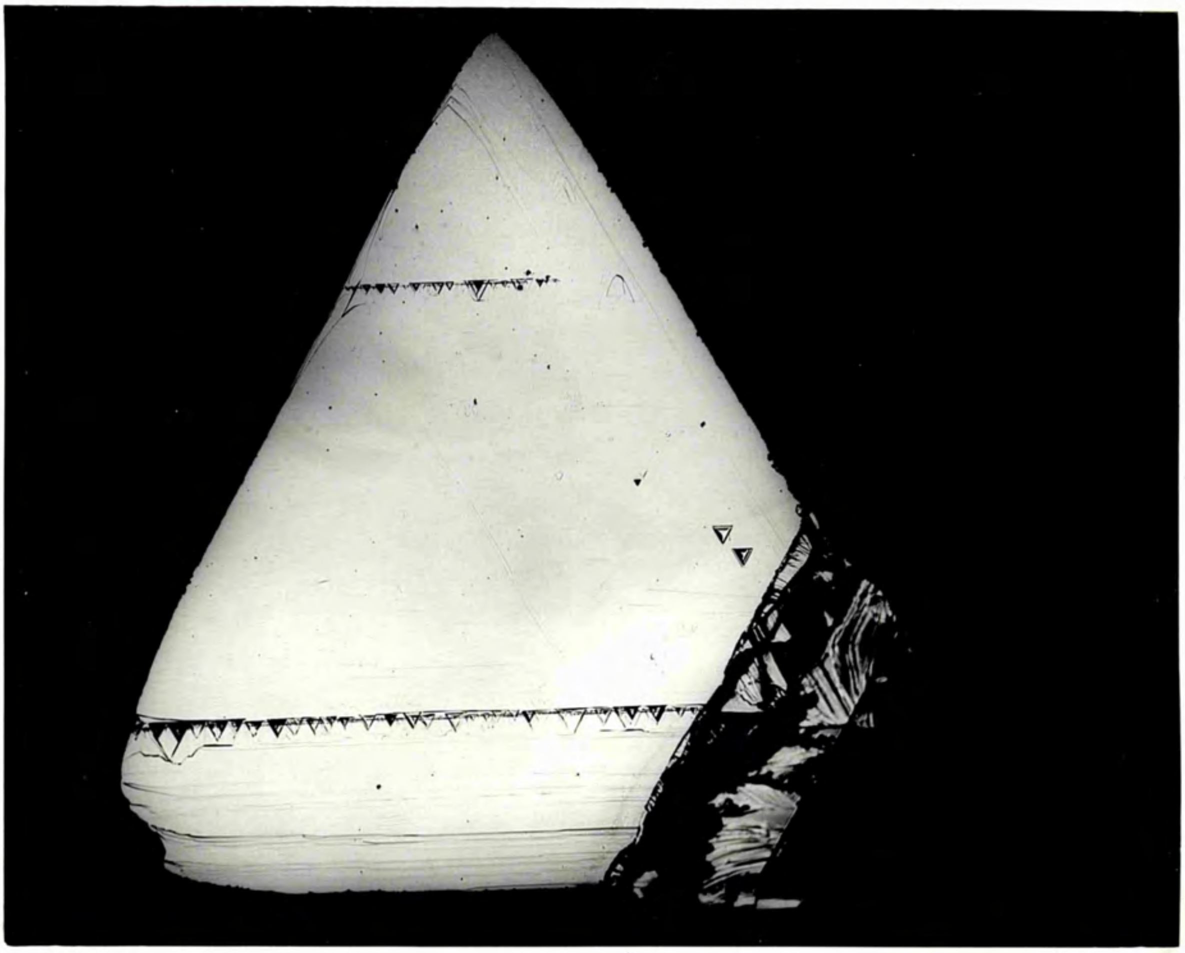


Fig. 60 X30

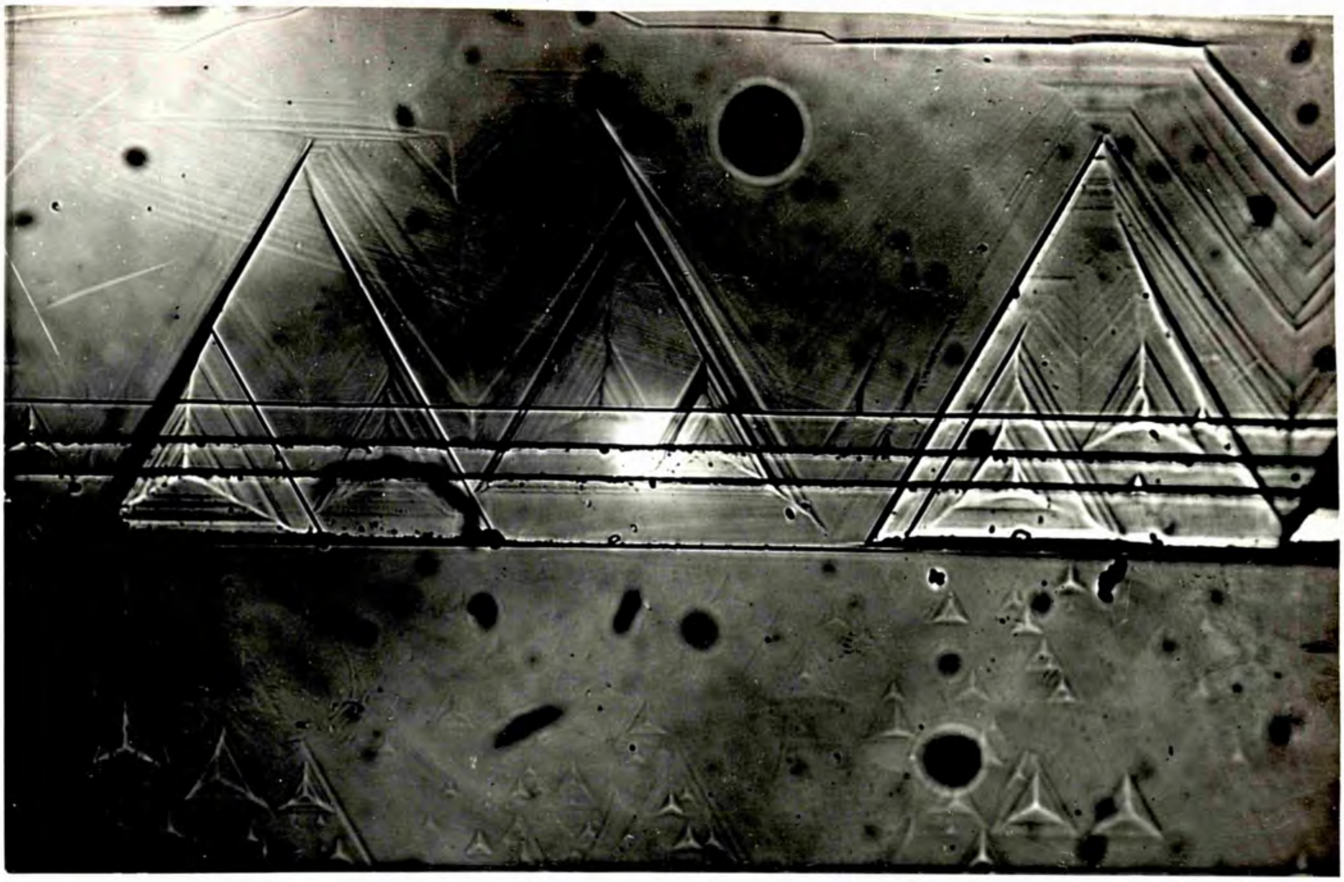


Fig. 61. X 650

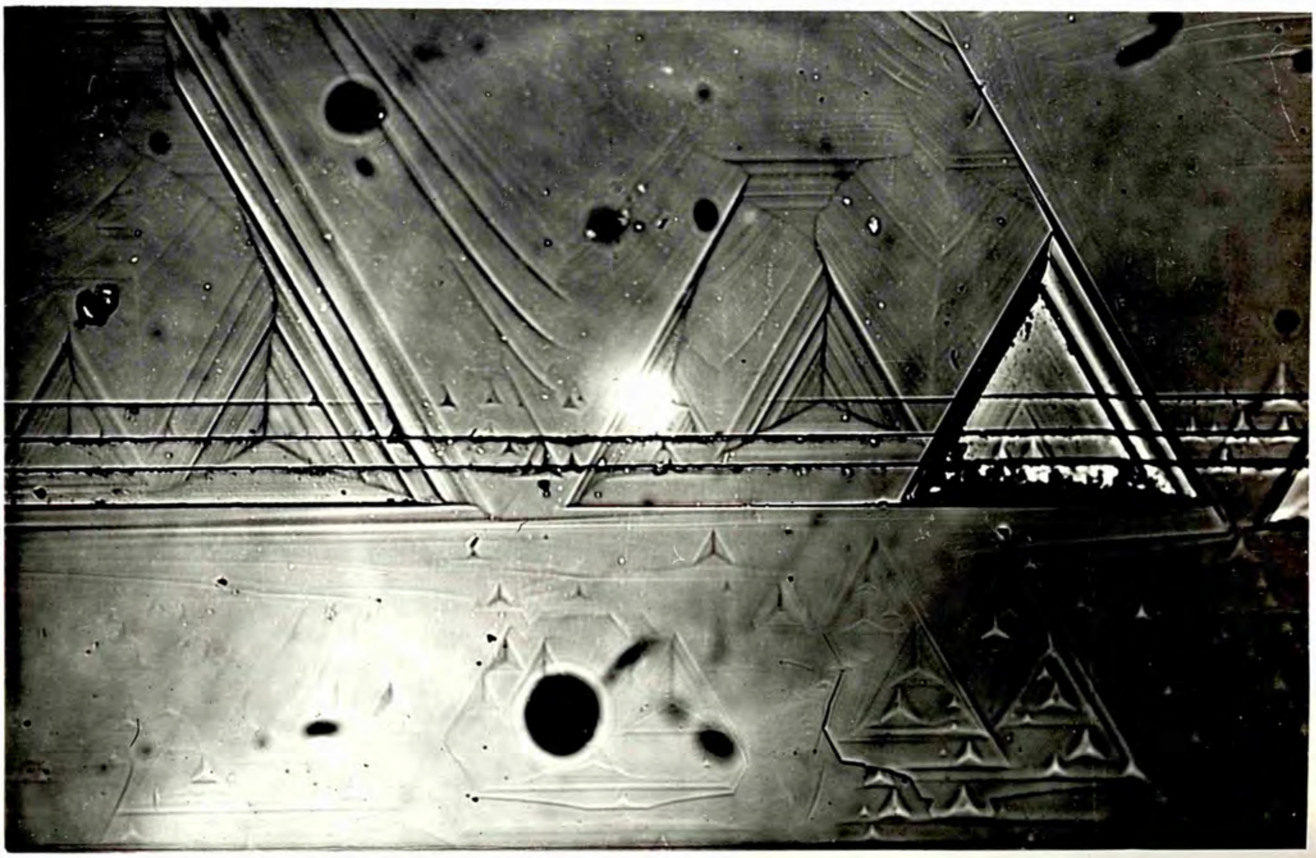


Fig. 62 X 650

triple lines which are not seen along their whole length appear to have been partly obscured by the later stages of growth. A typical example is shown in figure (62) X 650. In this photograph one sees that the middle portion of the top line is very faint as if covered up but in its place there exists a chain of small shallow trigons of the order of 50A° deep. Also striking the way in which the trigons sit with their centres just on the "slip" lines. This is further illustrated in figure (63) X 800.

Multiple-beam Fizeau fringes reveal that the heights of the steps on each line vary irregularly. Figures (64) X 120 and (65) X 120 are the interferograms for part of the short and long lines respectively. For accurate measurements of step heights fringes of equal chromatic order were used and the results were as follows:-

For the shorter "slip" the steps at one end are about 2900A° and then decrease progressively down to zero at the other end.

For the long "slip" where the lines are tripled the heights of the steps are not uniform and vary on two of the lines between about 1800A° and 2200A° while in the case of the third line the heights of the steps are much larger varying between about 6000A° and 7000A°.

As on the other four faces the apex regions of the trigons are always the higher.

Faces (6), (7), (8).

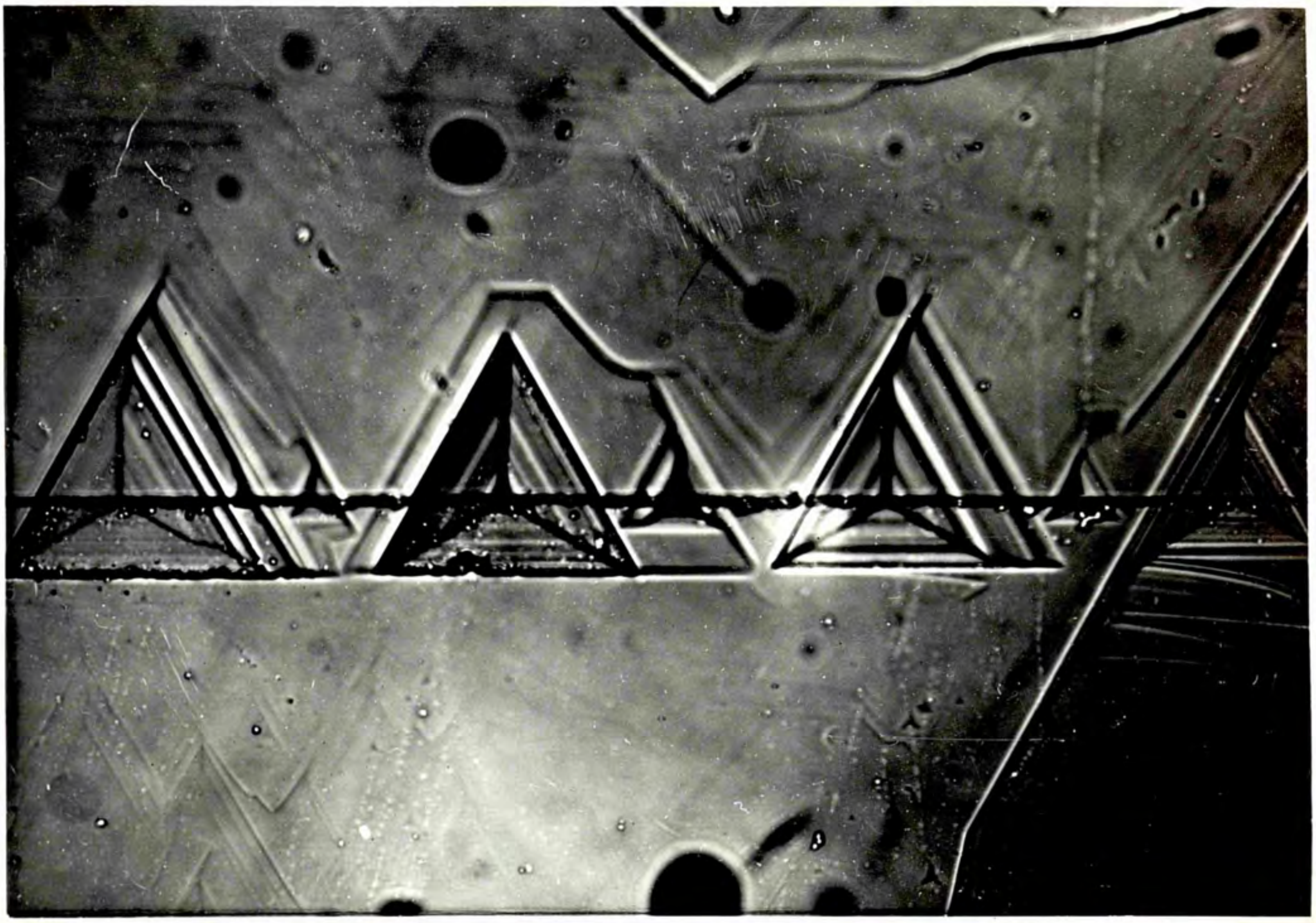


Fig. 63. X 800

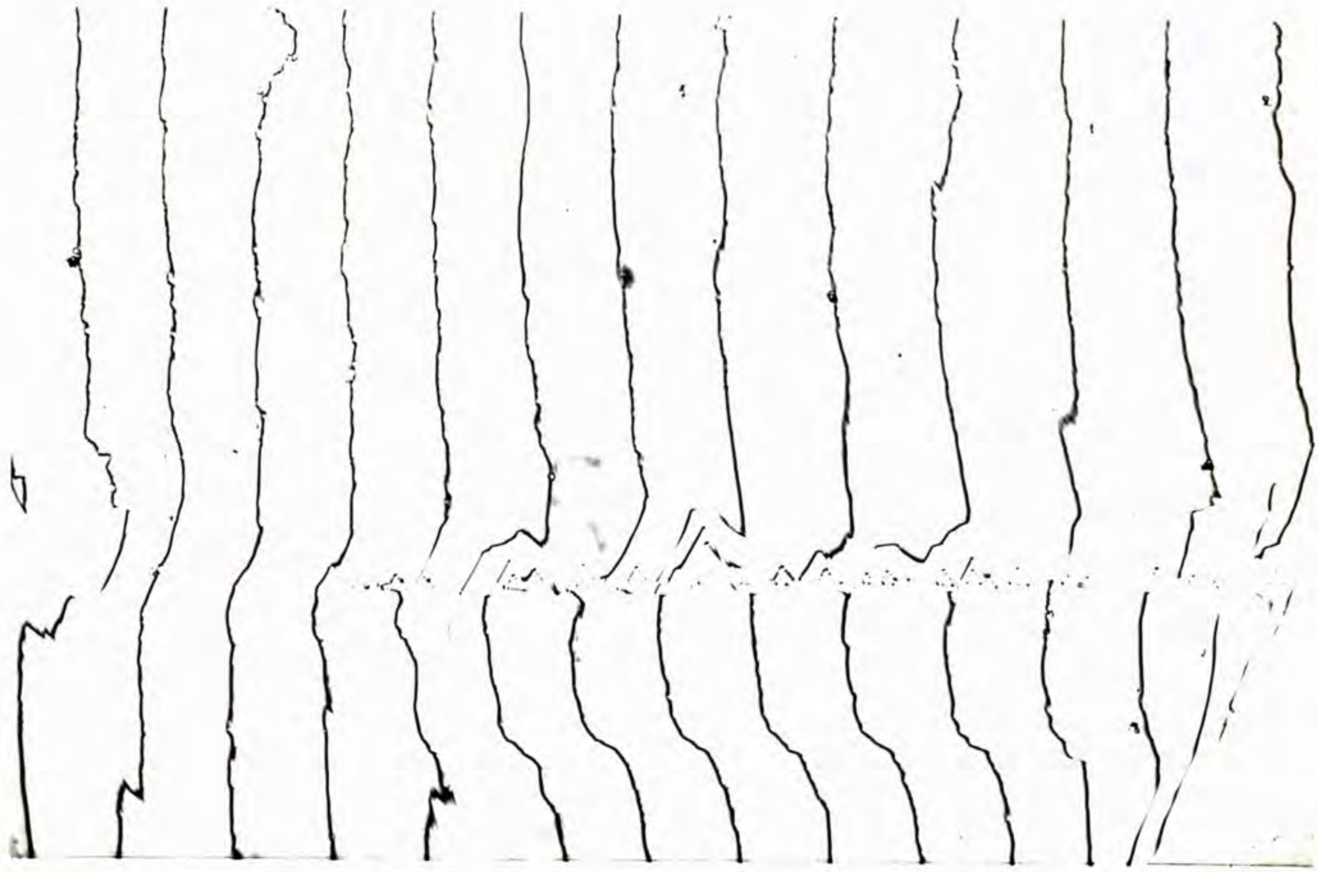


Fig. 64.   X120

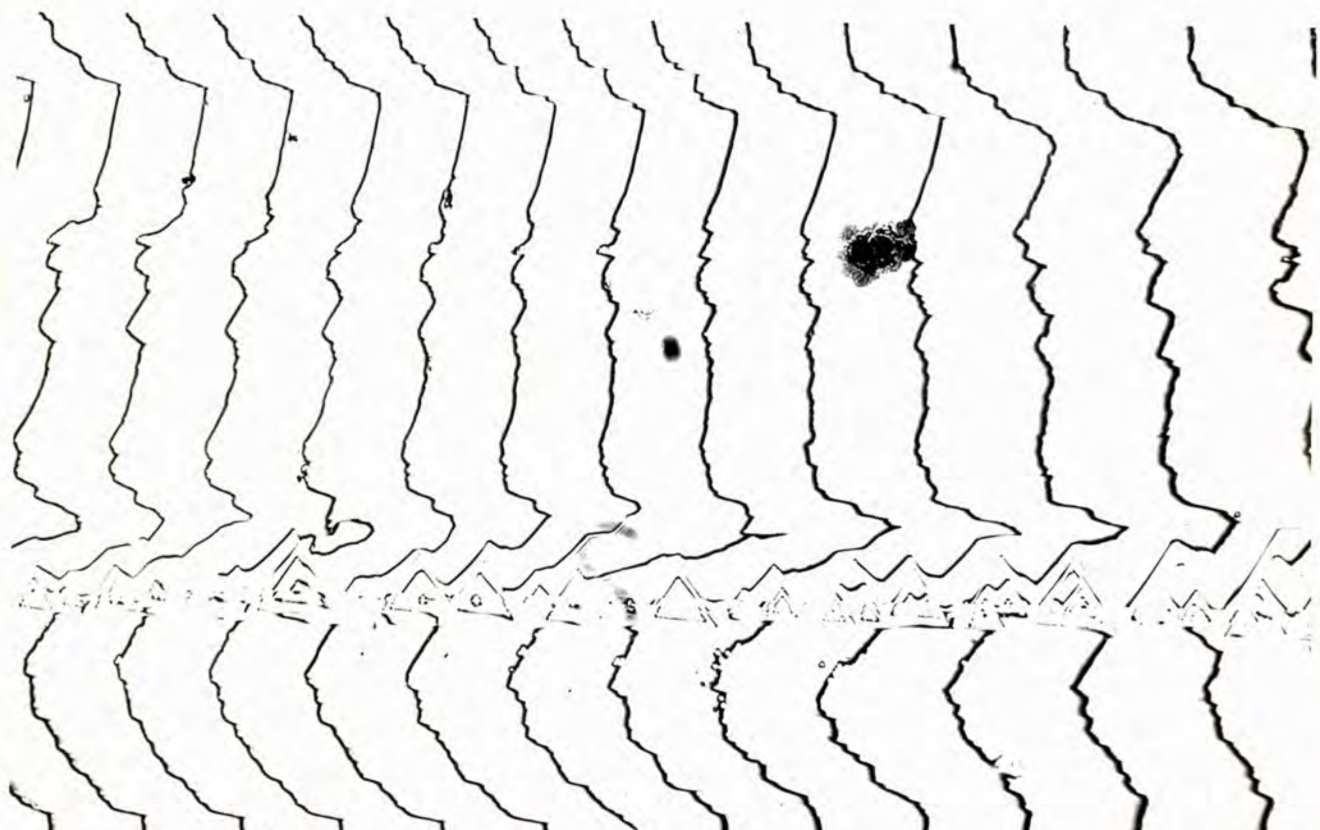


Fig. 65.   X120

No clear traces of "slip" lines could be observed on these faces. Figures (66) X 30, (67) X 30, (68) X 30 show the photomicrograph of faces 6, 7, 8 respectively. It is most interesting to note that all these faces exhibit an enormous number of small shallow trigons and interferometric study revealed that in most cases their depths is less than $50A^{o}$.

Figure (66) shows the familiar characteristic reported so often by Tolansky of a linear projection (linear dislocation?) at the base of some trigons.

A construction similar to that of figure (37) was made by tracing the "slip" lines (27 in all) and measuring the heights of more than 400 individual steps. This is shown in figure (69)[a] where the step-heights are expressed in Angstrom units, and the direction of the steps are also indicated. On the faces 3, 1, 6 multiple lines with large step heights of the order of $7000A^{o}$ are found to exist.

Table (1) shows the relations existing between the variation of step heights together with their directions when traced on consecutive faces of the crystal as shown in figure (69)[a,b]

The index of the letters denotes the number of face as described before).

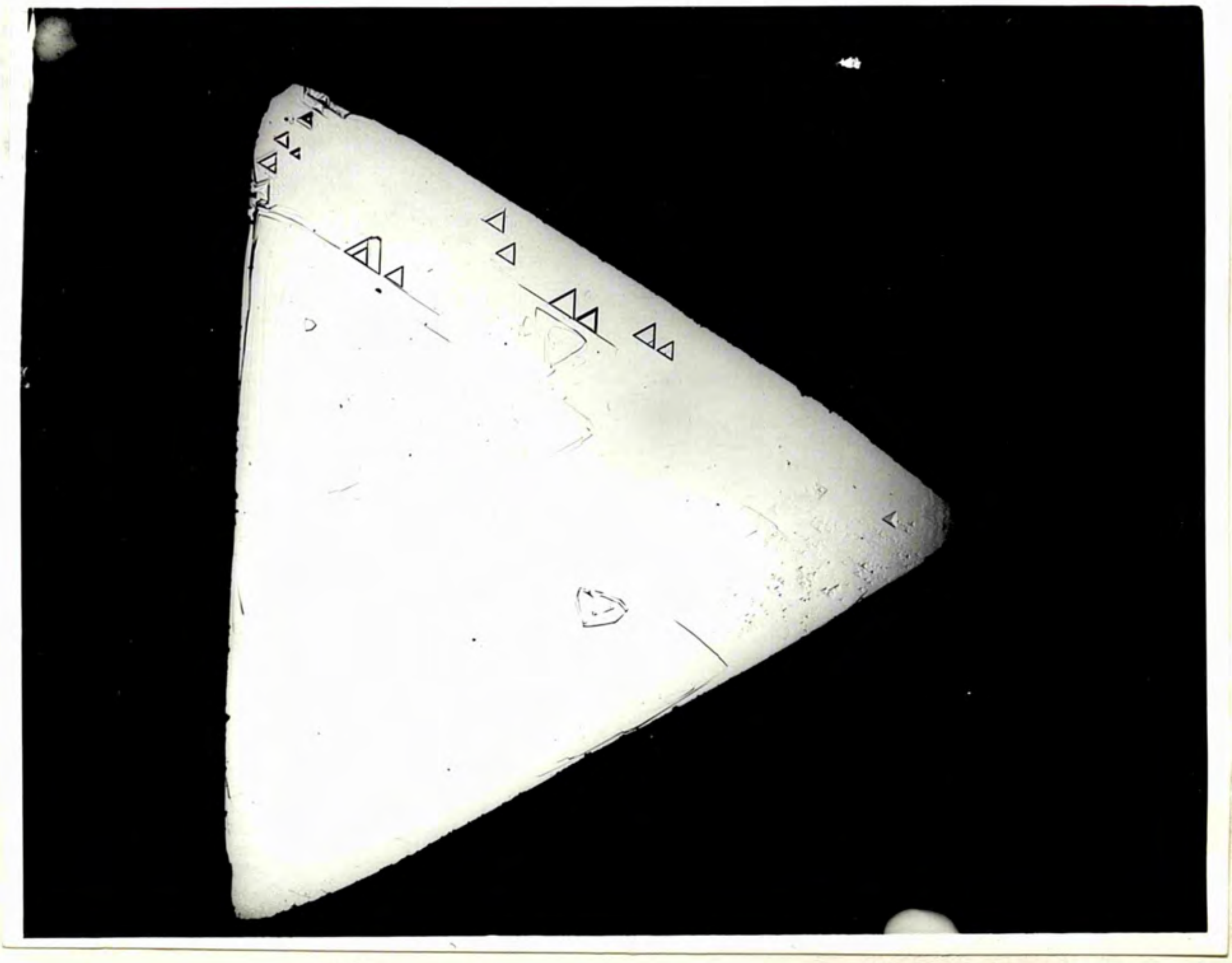


Fig. 66. X30

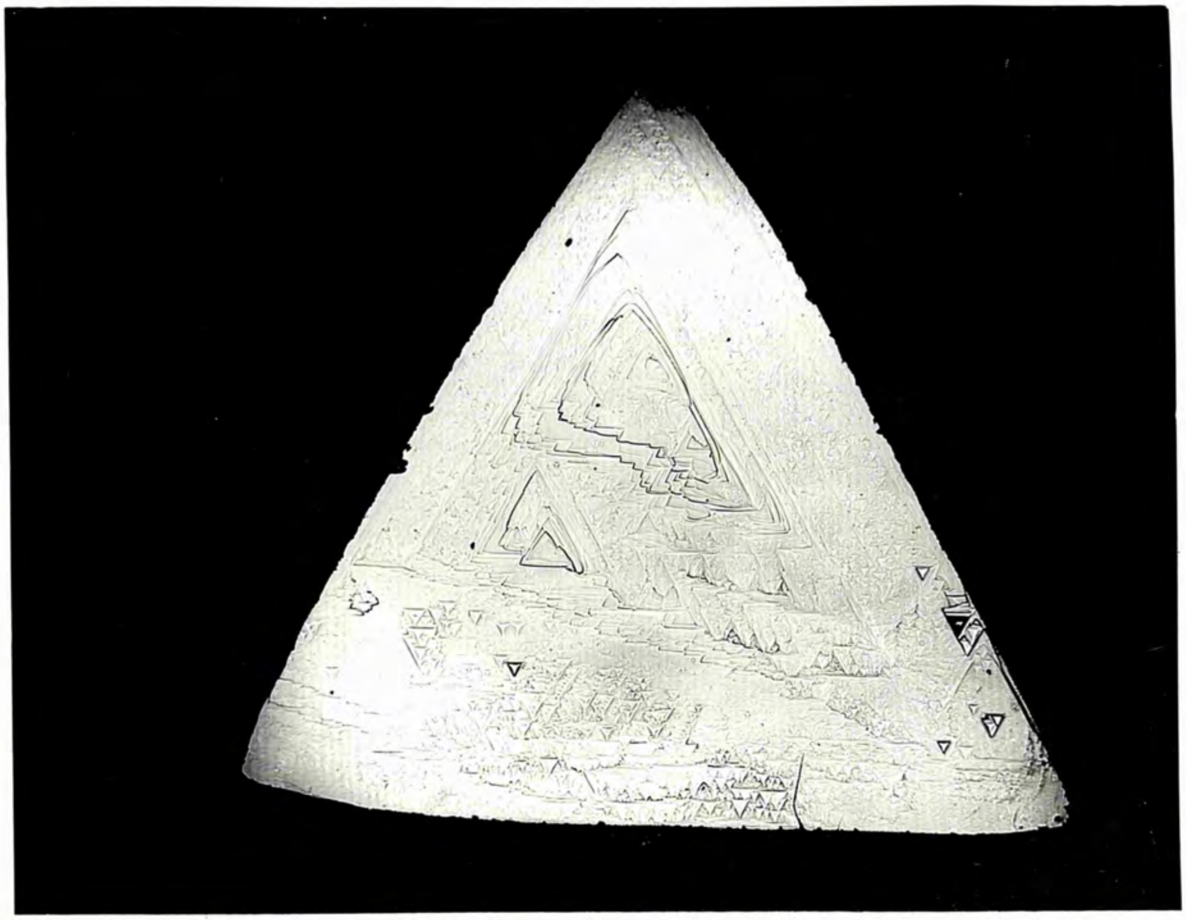


Fig. 67. X30

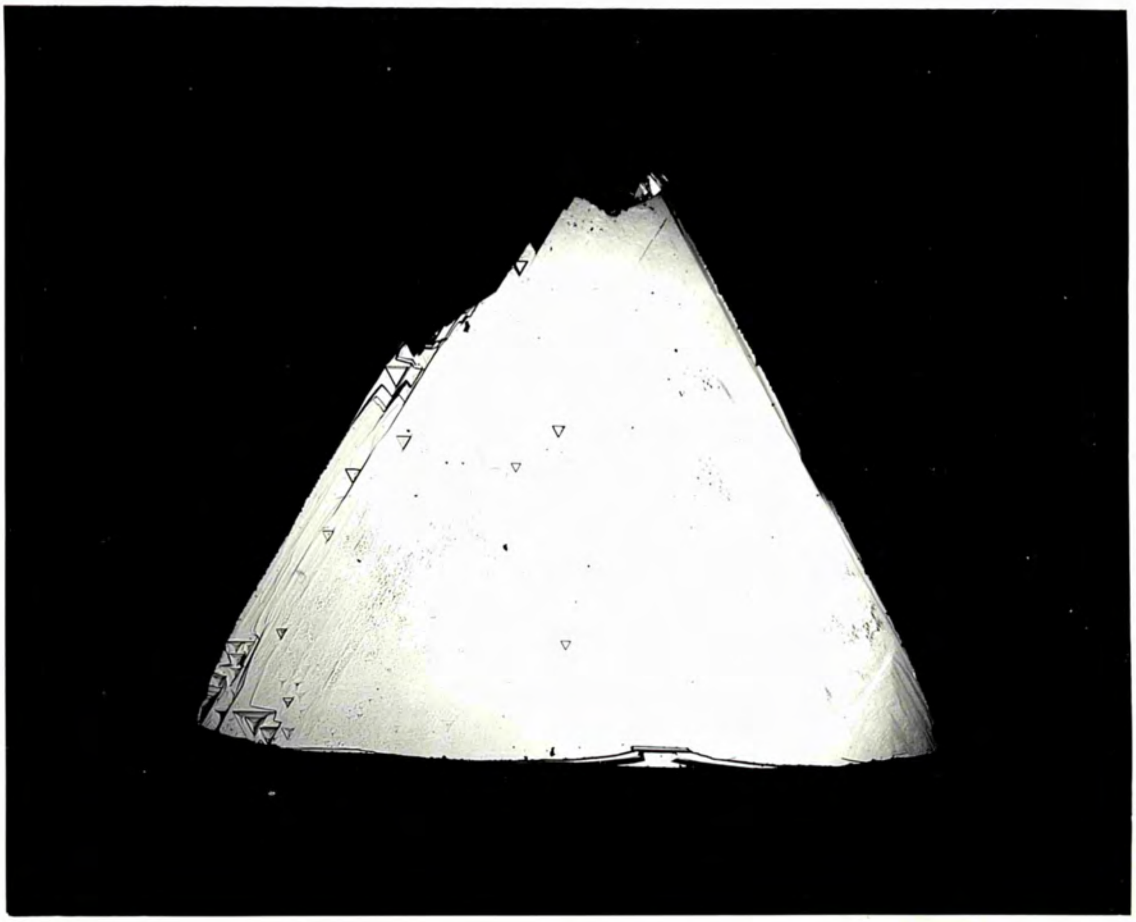
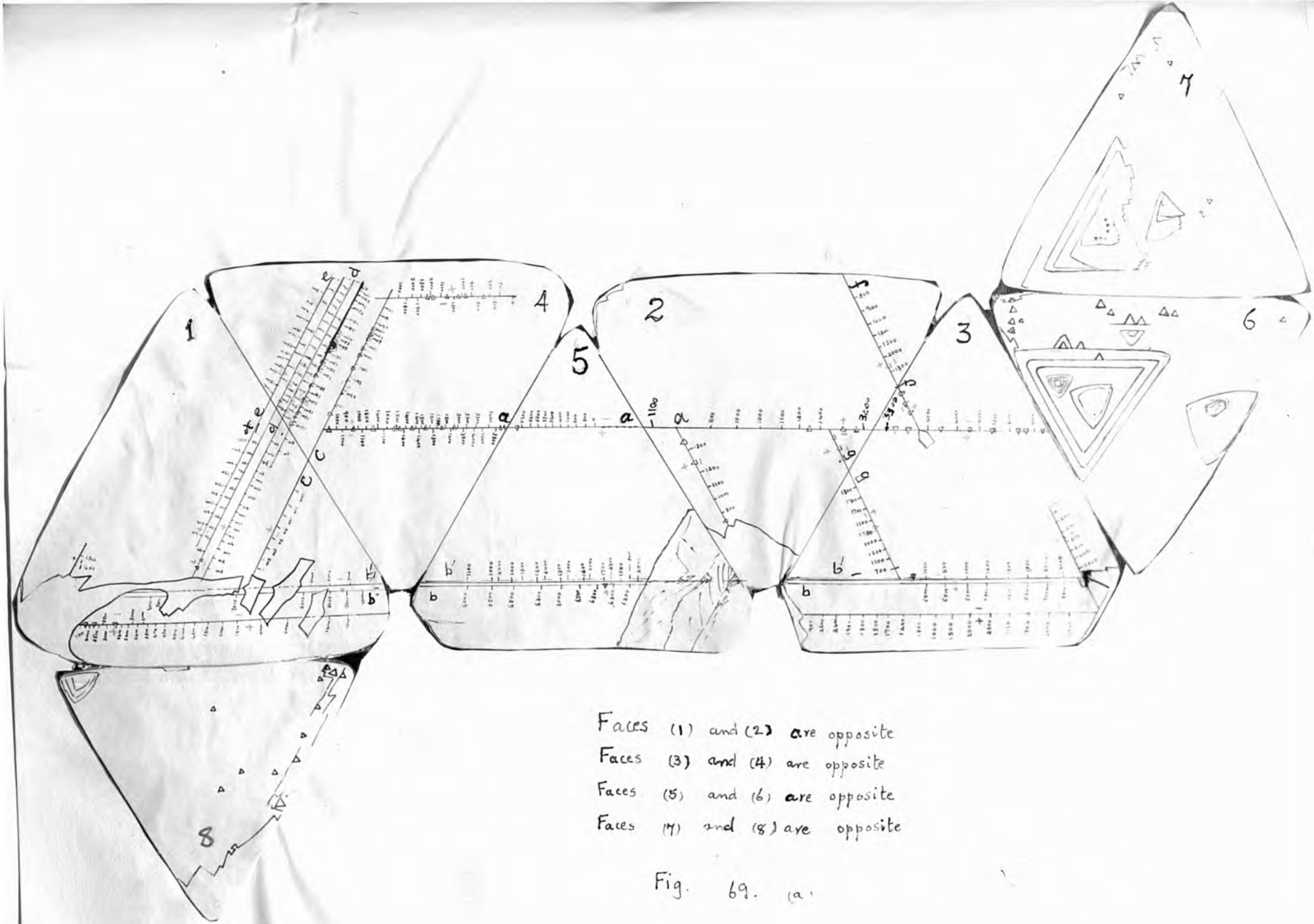
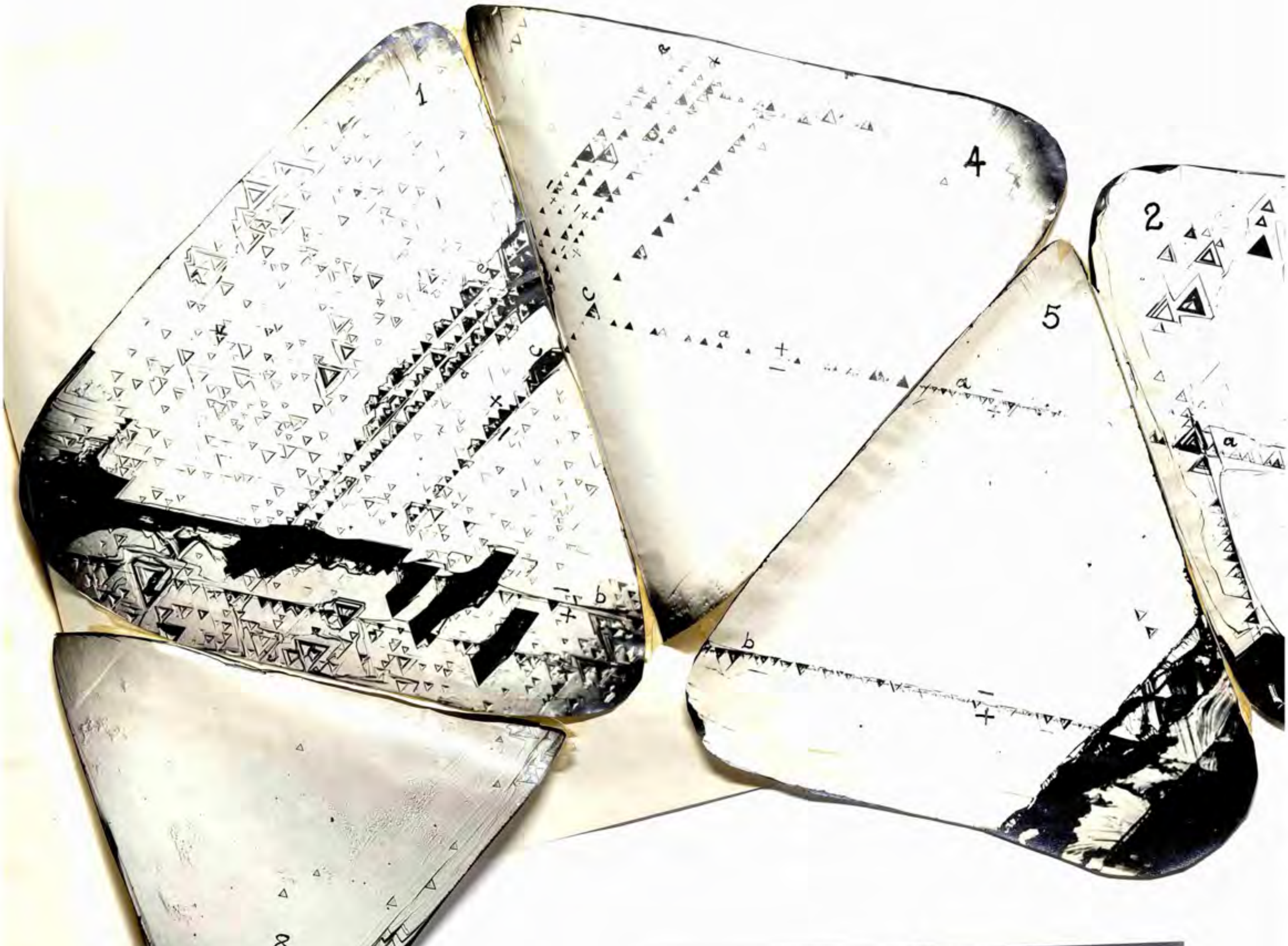


Fig. 68. X30



Faces (1) and (2) are opposite
Faces (3) and (4) are opposite
Faces (5) and (6) are opposite
Faces (7) and (8) are opposite

Fig. 69. (a)


1
4
2
5
8
a
b
c


2
3
5
a
b

Table 1

"slip" line (a)	a_4 + / − 1000A° − 3000A°	a_5 − / + 2900A° − 0	a_2 + / − 1100A° − 3200A°	a_3 − / + 3300A° − 3000A°
"slip" line (b)	b_1 − / + 1700A° − 7000A°	b_5 − / + 6500A° − 6300A°	b_3 − / + 6500A° − 7500A°	
"slip" line (c)	c_1 + / − 0 − 1000A°	c_4 − / + 1200A° − 1500A°		
"slip" line (d)	d_1 + / − 1500A° − 1000A°	d_4 − / + 1200A° − 0		
"slip" line (e)	e_1 + / − 1500A° − 800A°	e_4 − / + 1000A° − 900A°		
"slip" line (f)	f_2 − / + 1400A° − 900A°	f_3 + / − 1000A° − 700A°		
"slip" line (g)	g_2 − / + 900A° − 1700A°	g_5 + / − 1800A° − 700A°		

The results in this table show that in most cases the value of step-heights at the termination of each line when traced on consecutive faces of the crystal is of the same order.

Figure (70) shows that the planes which contain the "slip" lines when traced on consecutive faces are the (111) planes (the shaded plane in the figure).

Summary of Experimental Results.

A number of general conclusions may now be drawn from the detailed study of all the eight faces of this crystal. The main conclusions are as follows:-

1. All "slip" lines are parallel to the edges of the octahedron, i.e. they are following the directions $\langle 110 \rangle$ and the slip planes are found to be the (111) planes.
2. Linear groups of trigons sit with their centres exactly on the "slip" lines.
3. Most of the trigons along the "slip" lines are comparatively "deep" being up to about 4 μ in depth.
4. All the faces of the crystal exhibit an enormous number of shallow trigons of depths of the order of 50A°.
5. The lines are discontinuous steps and on whichever face they occur the lower level is the side nearer to the base of the trigons, parallel to the "slip" line.
6. In some regions there are multiple lines, which in parts are faint as if covered up but even on the

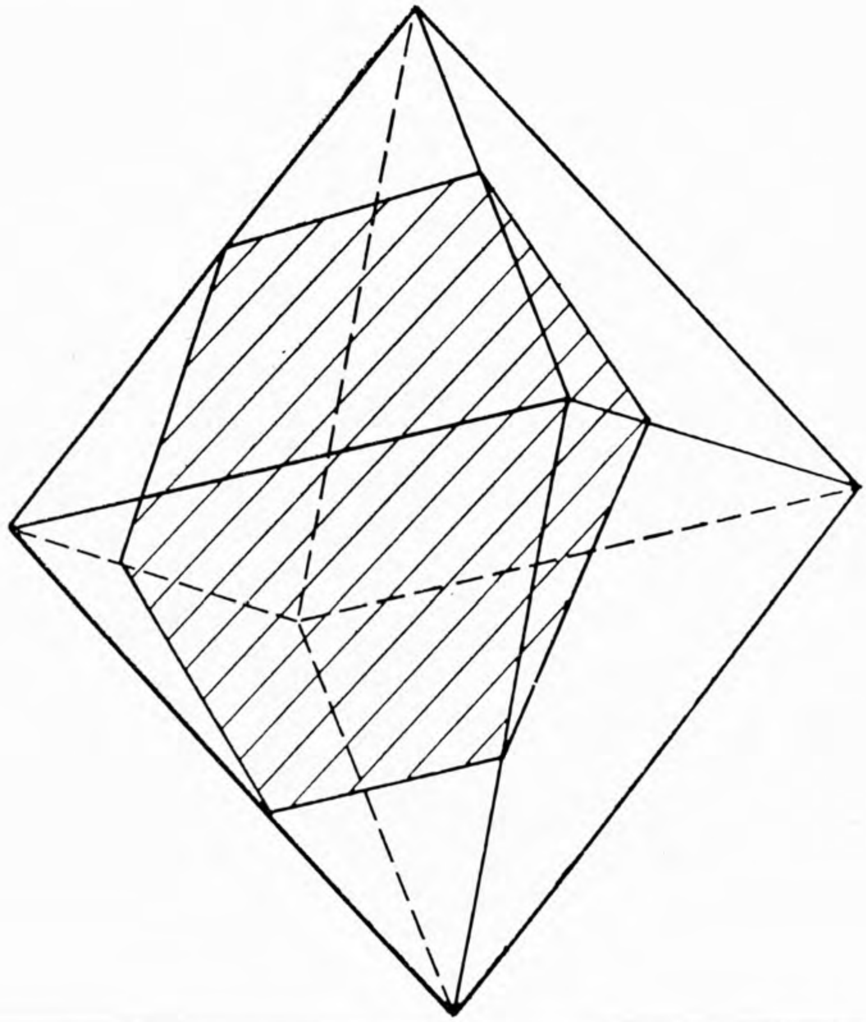


Fig. 70

fainter parts there exists chains of small shallow trigons.

7. The height of the step varies along the length of any given line.

8. The heights of the steps vary from line to line.

9. The spacing in the case of multiple lines is usually of the order of 5×10^{-4} cm.

Discussion.

The following alternative three possible explanations will now be discussed.

(a) A form of twinning.

(b) Etching.

(c) Slip.

If the mechanism were due to twinning one might frequently expect analogous results to those which occur on the common macles: i.e. the common twin type in diamond. It follows from twinning that the orientation of growth features should appear as shown in figure (71). One sees from this photomicrograph of a twin that where one side of a growth trigon forms on the twinning plane of one half of the crystal another growth trigon of exactly the same size appears on the other half of the crystal whereas the observations on the crystal under consideration do not show this characteristic of twin crystals.

If the mechanism were due to etching we would expect that the crystal faces would show the familiar etch pits and cavities oppositely oriented to the growth trigons, i.e. their sides should be parallel to the edges of the faces of the octahedron. Further the etch pits will have rounded edges as illustrated in figure (72).

(Omar, Pandya and Tolansky 1954).

We are considering then a good clear octahedron exhibiting linear discontinuities, with no evidence for either twinning or etching. It is therefore reasonable to interpret these linear discontinuities as being due to crystallographic slip. There is much in favour of this view. First, the linear groups of trigons with their centres just on the "slip" lines. Second, in some regions there are multiple lines, which in parts are faint as if partly covered up even though a chain of small shallow trigons are present. This suggests that "slip" must have occurred before the final growth of the diamond was completed. Third, almost all the faces of the crystal exhibit an enormous number of the small shallow trigons which are usually present on natural octahedron faces of diamond. Most of the linear groups of trigons sitting on the straight lines are very deep up (to about 4 μ) and have strictly straight edges. Growth sheets are observed to be blocked on meeting the "slip" lines, (figure 47) as if at some later time growth must have re-established itself so that growth trigons were formed by filling-in processes, approaching from both sides of the "slip" lines. This would fit in both with the linear distribution and with the existence of the high regions on the apex side of the lines. The second

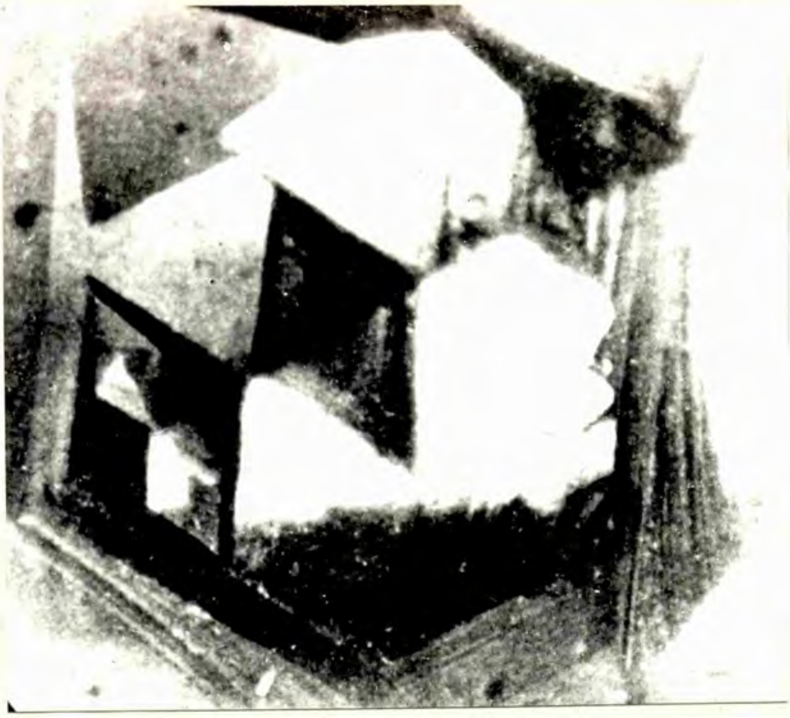


Fig. 71.

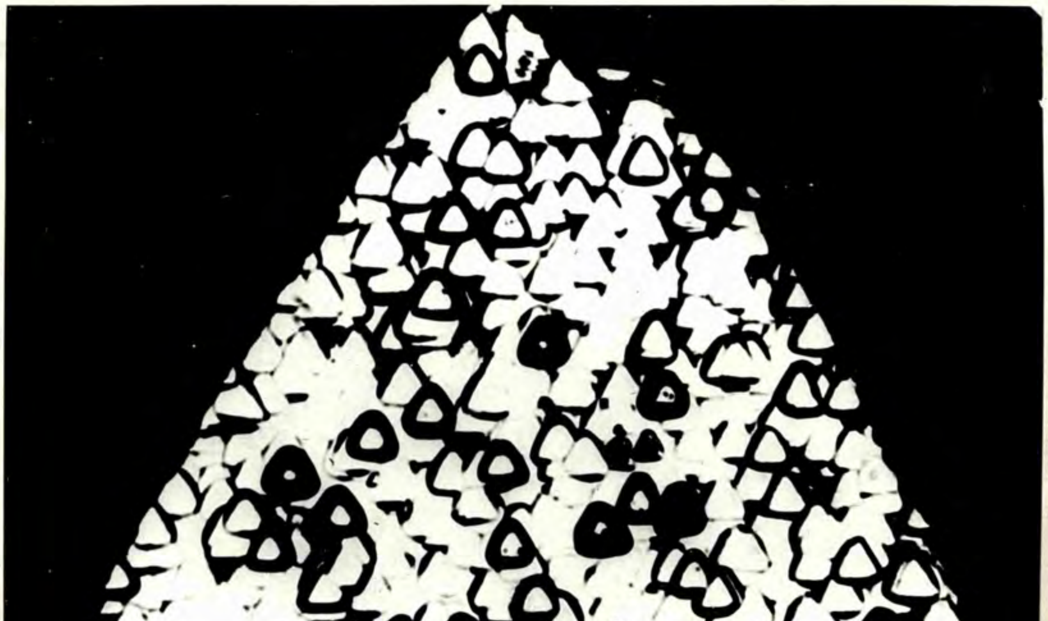


Fig. 72.

stage of growth suggests that the original "slip" occurred under temperature and pressure conditions not very different from those required for growth.

As to the original amount of slip nothing can be known as it should be realized that the observed step-heights at the lines, after the new growth need bear no relation whatsoever to the original height of the "slip" step. Indeed the latter may even have been of lattice dimensions. It is therefore not in the least surprising that considerable variation in step height should appear on the final crystal. This is precisely what would be expected.

As to the irregularities of trigons in some regions this may also suggest that they are due to local distortions in the lattice caused by the "slip".

Now let us consider the possibilities which may have caused "slip" to occur. There may be dislocations already in the crystal (theory of Mott and Nabarro 1948), or alternatively these may be imperfections of other kinds which may be created under stresses (theories of Kochendorfer (1938), (1941) and Laurent (1945)). However, strong evidence is in favour of the dislocation theory by the studies of crystal growth as described previously. Therefore, we shall assume the sources of slip are dislocations. The difficulty previously with this view has been that the formation of large slip bands implies that each active source supplies many dislocations, and it was not clear how this could happen when the sources are single dislocations. This difficulty has now been overcome with the realization of Frank and Read (1950) that virtually unlimited amounts of slip can be produced by the repeated rotation of a single dislocation line about its points of emergence. Frank (1950) has suggested that most stable configurations are those in which the dislocation lines are linked together in a three-dimensional net work, rather like that formed in a foam by the lines where three bubbles meet. Also Heidenreich and Shockley (1948) have pointed out that the presence of dislocations should cause a crystal to behave as if it consisted of independently reflecting blocks. According to this view Gay, Hirsch and Kelly (1953) calculated the density and distribution of dislocations in unworked crystals and found that if at least one dislocation is needed to define a block, the block size cannot be smaller than $(\rho)^{\frac{1}{2}}$ where ρ is the density of dislocation. They also pointed out that if the crystal contains a network of dislocation lines as suggested by Frank, the characteristic spacing of the lines would be about 10^{-4} cm. and in this case the value for ρ would be 10^{8} cm.$^{-2}$

At this stage it is of interest to note that the observed spacing between the multiple-lines on the faces of the crystal is of the order of about 5×10^{-4} cm. which might favour the concept of slip a little.

Finally, it is worthwhile pointing out that some other lines having similar slip line character have been observed by earlier workers, Sutton (1928) and Williams (1932) but no attempts have been made to explain the phenomena. More recently Tolansky and Omar (1953) have described a case of possible slip on opposite octahedron faces of a twinned diamond. Also shortly afterwards Seale and Menter (1953) reported the observation of a slip line character on polished diamonds and suggested that these were caused by plastic deformation initiated by the extremely high local pressures produced whilst polishing.

However, in the work described above it is seen that, for the crystal under investigation the surface topography is of particular rarity and interest. For slip to occur in diamond such special conditions of stresses and temperature combinations are needed as to make this occurrence unusual. In addition for slip to be followed by further growth makes the event even more rare.

P A R T IV

THE MICROSTRUCTURE OF THE DODECAHEDRAL (110) FACES.

CHAPTER I

THE MICROSTRUCTURE OF THE DODECHEDRAL (110) FACES.

INTRODUCTION.

Although the most common form of diamond is the octahedron, rarely however, dodecahedra occur. A rhombic dodecahedral crystal is usually bounded by twelve faces, each of which meets two of the axes at equal distances and is parallel to the third axis. Each face is a rhomb with plane angles of $70^{o}\frac{1}{2}$ and $109^{o}\frac{1}{2}$ and has the general symbol (110). The faces of the dodecahedron are parallel to the six auxiliary, or diagonal planes of symmetry. A perfectly shaped dodecahedron is very rare. Sutton (1928) considered that the dodecahedron figure can be created if we imagine that the rounded edges and corners of the octahedron are more and more developed until its faces become smaller and smaller, and finally disappear. But the best way to visualize a dodecahedron, is to imagine triangular plates of diminishing size "deposited" on all the eight faces of the octahedron. The faces of the dodecahedron are usually lined with striations running parallel to the longer diagonal of the rhombs. It is conceivable that the edges of the diminishing triangular plates need not exactly fit to give plane new faces. Curvature would then be the rule in such a process, and whether the new faces turn out to be convex or concave would depend on the thickness of these layers, and how closely they approach each other. Generally the faces turn out to be slightly convex. When the convexity is noticeable they are called "rounded dodecahedra". In general, the dodecahedral surfaces are either striated, or exhibit a patchy, flaky appearance. No detailed study of the microtopography of any dodecahedral faces has yet been established in the whole literature of diamond by any of the previous workers.

Fersmann and Goldschmidt (1911) illustrate dodecahedral striations by means of rough drawings. They believe that practically every diamond has at some time of its history suffered solution. In other words, very few diamonds are found which continue to grow from start to finish without some interruption, during which the diamonds were partially or wholly dissolved. Generally speaking they contend that diamonds exhibiting bent or uneven planes owe these characteristics to the action of solution, while sharp edged crystals represent a growth structure. Also they reported that since solution has a rounding effect on crystals and since the striations on the dodecahedral faces are usually rounded, they used this fact as a support for their solution hypothesis. Thus they concluded that dodecahedral stria emerge as a consequence of the flow of solution currents down the octahedral edges. All their conclusions have been formed from interpretations of readings with the goniometer. They conjecture that growth structure appear in the goniometer reflex pictures as points and straight lines, while dissolution structures are bent lines. The whole of this interpretation therefore turns on whether bent lines do indicate dissolving action and straight lines growth. They claim that, with but few exceptions, the the rhombic dodecahedron form of the diamond is produced by solution. They actually do not place the rhombic dodecahedron as a crystal of a commencing form, but they say that it can be produced as a growth structure by the gradual building up of a retarding structure of sharp edged triangular plates on the faces of the octahedron. Fersmann and Goldschmidt give very few examples of a sharp-edged rhombic dodecahedron, as they consider that the rhombic dodecahedron is generally the product of solution. They do show three drawings which they claim to be octahedra changing over to rhombic dodecahedra which they contend have been produced by a process of solution.

Van der Veen (1913) considered that the dodecahedron is a separate form appearing in combination with octahedra and cubes. Its surfaces are only flat by way of exception, being mostly concave or convex, and in addition often separated into two triangular compartments along the shorter diagonal.

Sutton (1928) stated that dodecahedroid faces which are generally rhomb shaped are lined with striations running parallel to the larger diagonals of the rhombs. Such variation in aspect as there is in these striations depends mainly on the particular mine from which the crystal came. Thus the striations on the Bulfontein crystals are close and somewhat rough, as as though scratched with a fine needle. Those on yellow crystals from Dutoitspan are bolder and smoother. De beers crystal striations tend to gentle rippling, imparting a kind of satiny sheen to the surface. Some other crystals exhibit a patchy, flaky appearance. In addition to drawings, six low-power microphotographs (magnifications 20 X and 30 X) were given by Sutton. Three faces show striations and three a flaked surface pattern. No detailed study was made.

Williams (1932) has established in his comprehensive book on diamond that sharp-edged rhombic dodecahedron approaching the geometrically perfect crystal are exceptionally rare, much more so than the perfect sharp edged octahedron. He also described cases of the octahedron changing over to a rhombic dodecahedron by the building up of straight-edged superimposed growth plates, and also the same change due to the building up of shield-like plates with straight and curved edges. Both structures would produce a crystal of a rhombic dodecahedral character. Williams also illustrates with six micrographs of dodecahedroid faces (at magnifications of X110 and X140) two of which show striations and the remainder the flaky pattern. Little comment was made on the structures.

The diamonds to be described here are five dodecahedral crystals from South Africa selected from large stocks. All five are transparent with slightly convex surfaces. Two of these are small of weight 0.25, 0.35 carats while the other three are of weight 0.642, 0.70 and 0.75 carats respectively. The mines of origin are not known. All exhibit surfaces good enough to tolerate examination by interferometric methods.

It will be shown how the detailed study of a number of faces on these crystals have revealed some new topographical features of considerable interest.

CHAPTER II

Experimental.

The microstructures of the dodecahedral faces were studied using

(a) high-power optical microscopy.

(b) multiple-beam Fizeau fringes.

(c) fringes of equal chromatic order.

(d) the light profile microscope.

For the interferometric study the usual method for producing the fringes is by matching the silvered crystal against a silvered optical flat. In most cases multi-layer films of zinc sulphide and cryolite were employed. Both the optical flat and the diamond surface were coated with the correct number of layers and observations were carried out in reflection. Some of the observations were repeated with silver films of reflectivity exceeding 0·90.

For the micro-interferometric study of the surfaces an improved multiple-beam interference technique has been developed for this purpose, whereby it has been possible to obtain precision multiple-beam fringes with high lateral microscopic resolution (full details of the method has already been described in Part II of this thesis). Indeed full use has been made of the resolving power of a 3 mm. dry lens objective N.A. 0·95 with a correcting collar for a cover glass thickness. The diamond surface was coated with multilayer film and fringes were produced by using as a matching flat a microscope cover glass of thickness 0.020 cm. Fringes of high definition were obtained at magnification of X 1500. This technique has been valuable for the measurement of curvature, surface irregularities etc.

In most cases confirmation has been made by using fringes of equal chromatic order. For surfaces which are too coarse for the interferometric study the light profile was employed.

Although all the faces on each crystal have been studied in detail only a few of special interest are described here. Of the faces studied some are striated and some exhibit the so called flaky appearance. In two rare cases patterns of a network structure have been observed on one crystal. On another patterns of parallelograms, crystallographically orientated have been found.

Since the striated faces are usually the commoner these will be discussed first.

1. Striated Faces.

Crystal A: Face 1.

This crystal is of weight 0.35 carat, is transparent but of a yellow colour enclosing a black inclusion possibly carbon.

Figure (73) X 85 shows the whole of one striated face on the crystal.

Figure (74) X 100 is an interferogram of most of the

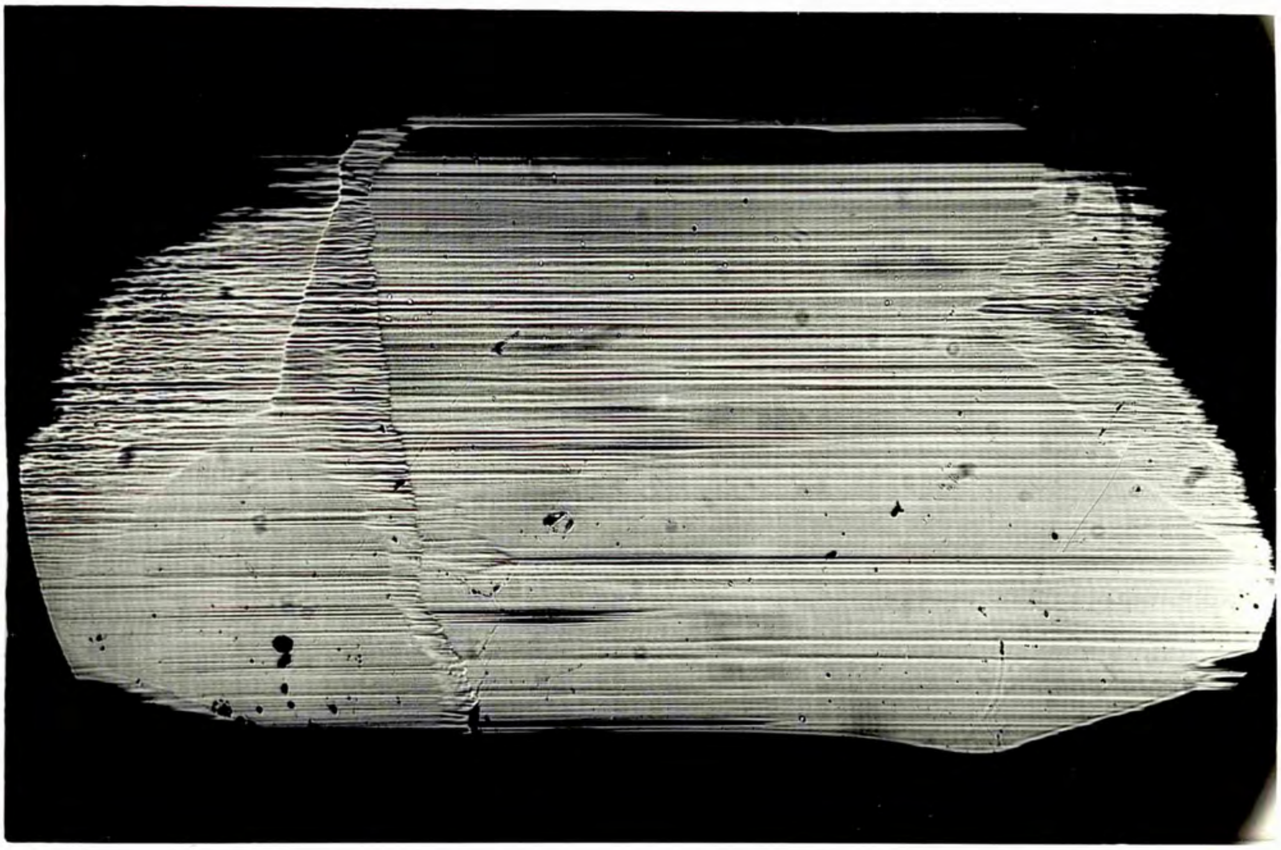
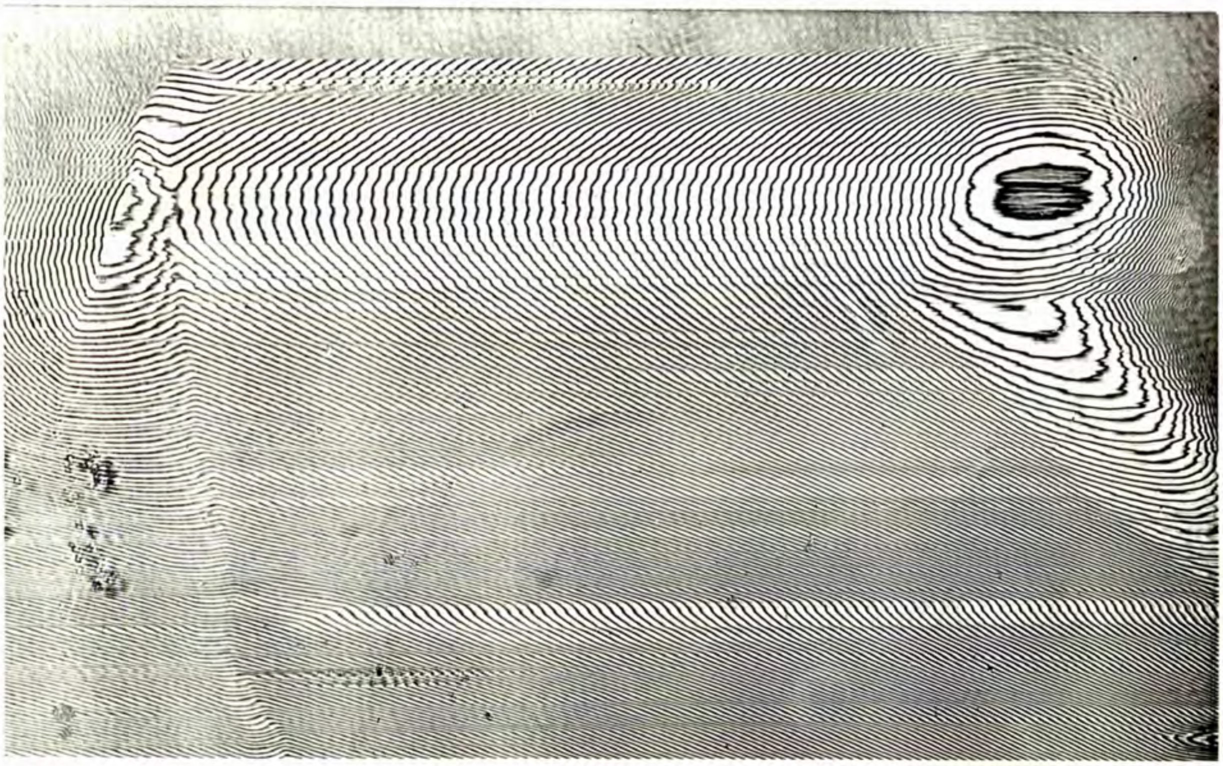


Fig. 73. X85



A

Fig. 74. X100

face, showing a peak A which is a region at which vicinal faces meet.

The nature of this region is revealed by the interferogram in figure (75) X 400. Region A is shown to be the flattest part on the surface. The region is somewhat conical, with a radius of curvature approximating to 0.3 cm. The character of the striations is clearly revealed by the ripples in the fringes. Moreover, the fringe patterns in both figures (74), (75) show that the striations are shallow ruts with rounded upper ridge regions. It appears that each rut maintains its character virtually unchanged along the length of the crystal face and that the ruts represent the last stages in the growth of this particular surface. A striation can run straight across the main hillock. Figure (76) is one of the high power interferograms taken with a 3 mm. objective N.A. 0.95.

The fringe sharpness is exceptionally good when the high power used is taken into consideration. Measurement shows that some of the striations are similar in depth, this being of the order of 500 Å. However, there is an appreciable variation in the numerical value of the irregularities along the striations. The deepest striation measured is only some 1100Å deep. Furthermore the fringe pattern shows that the striations are in the form of sharp V-ridges.

The results of measurements obtained using Fizeau fringes were confirmed using fringes of equal chromatic order.

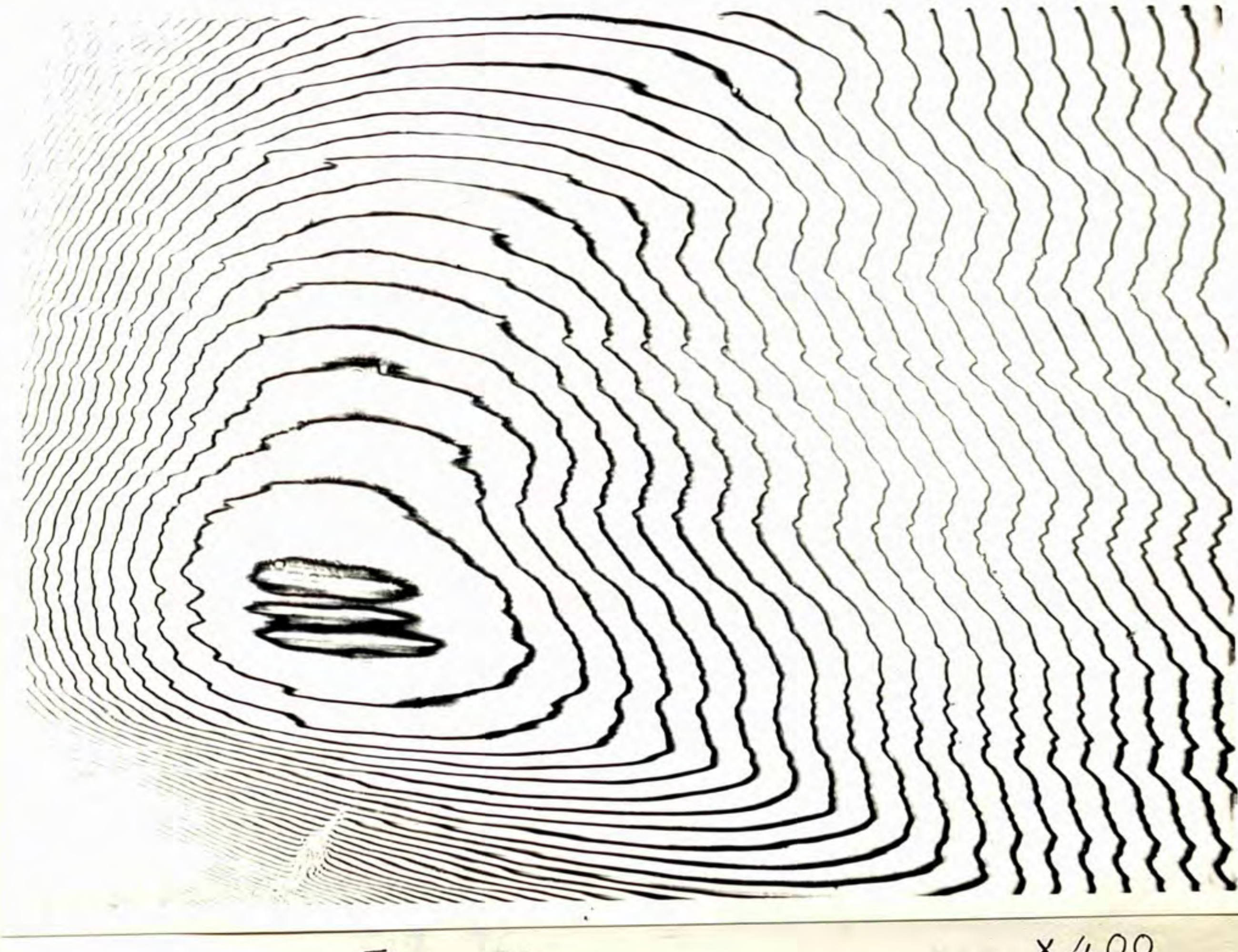


Fig. 75. x 400

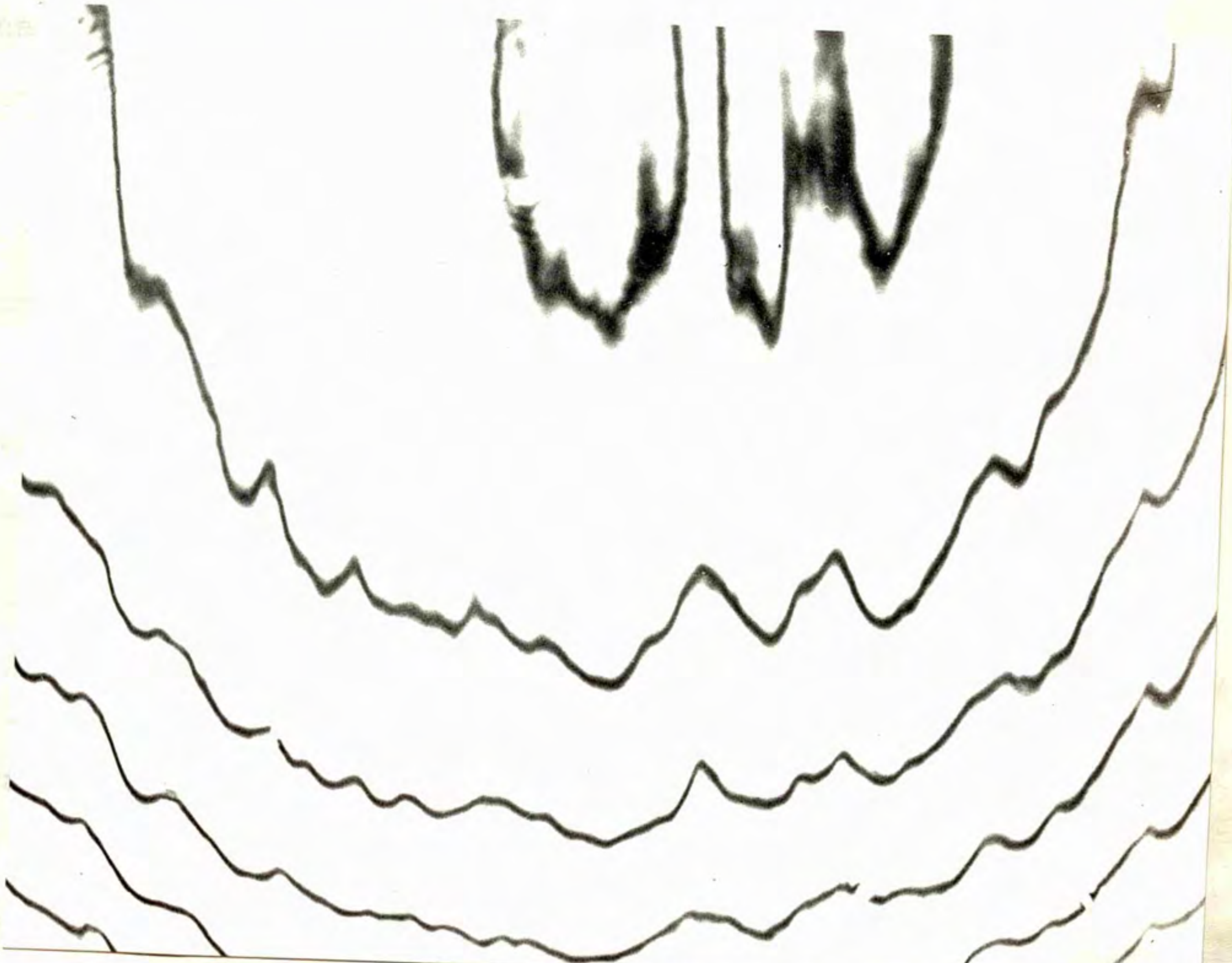


Fig. 76. X1500

Figure (77a) X 200 illustrates one example of the fringes of equal chromatic order for a line profile on one of the striations showing two hills and two valleys of heights and depths of the order of $500A^{0}$ and $600A^{0}$ respectively.

Figure (77b) X 200 illustrates another example for the V-character of the striations.

Crystal A: Face 2.

Crystal A has one other face which is good enough for the micro-interferometric study, although this surface, Face 2, is more rugged than that of Face 1.

Figure (78) X 110 shows effectively the whole face which is also striated. Here again there are peak regions at which vicinal faces meet.

The topography of the whole face is shown by the interferogram figure (79) X 110, where the fringe pattern indicates that the surface consists of a series of broad, somewhat curved, parallel ridges. The striations are again sharp ruts with rounded curved upper ridge regions with extreme uniformity in depths along the entire length. It appears that each rut does not change its character along the length of the crystal face. The striated character is revealed in detail by the fringe pattern in figure (80) X 180 where the V-ridges are similar in character to those described on Face 1.

The distinction between ridges and valleys is made by employing fringes of equal chromatic order. Figure (81) X 200

Fig. 77 (a) X200

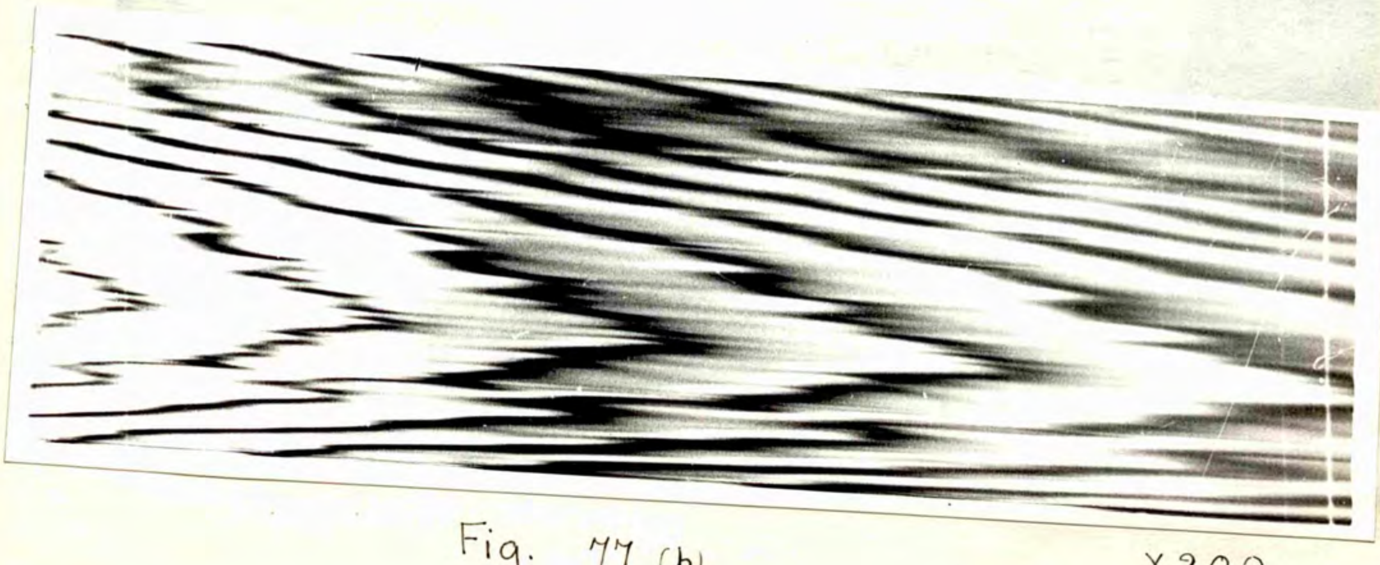


Fig. 77 (b) X200

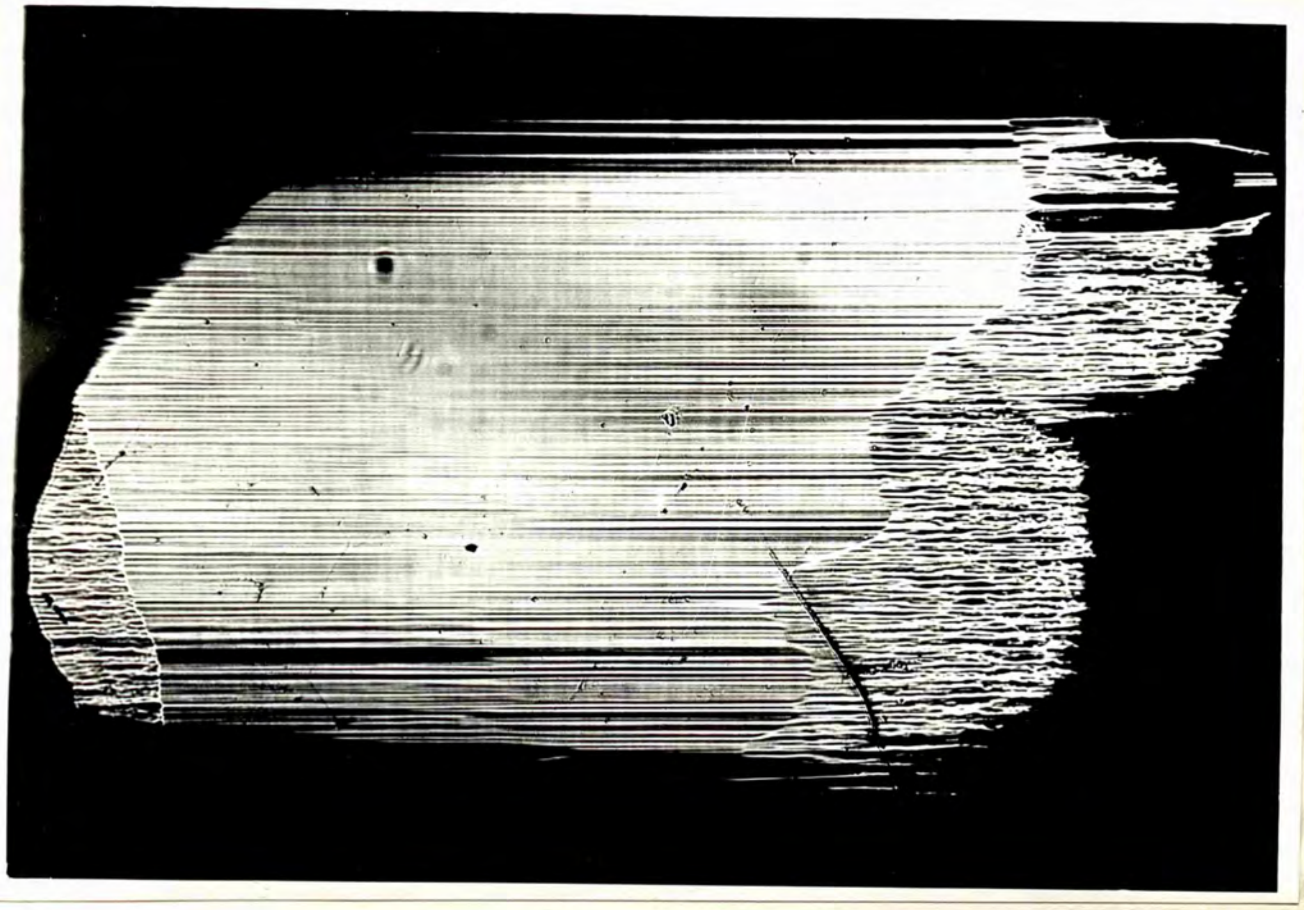


Fig. 78. x110

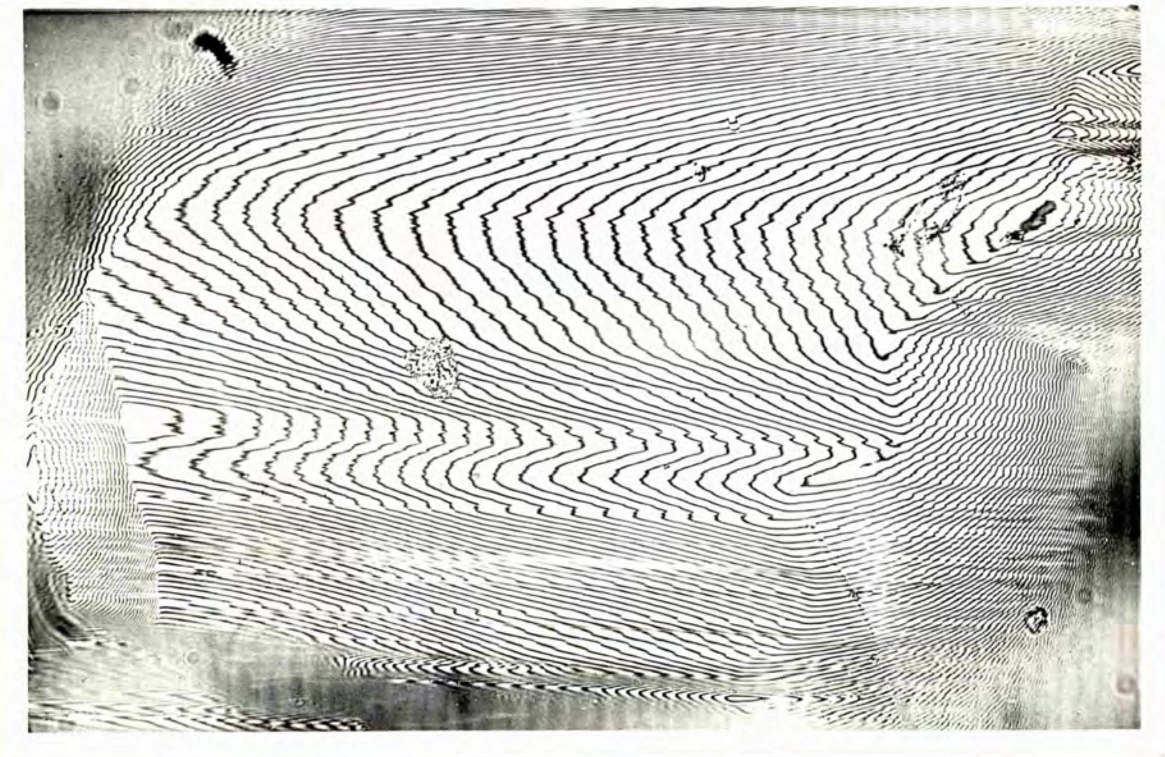


Fig. 79. X 110

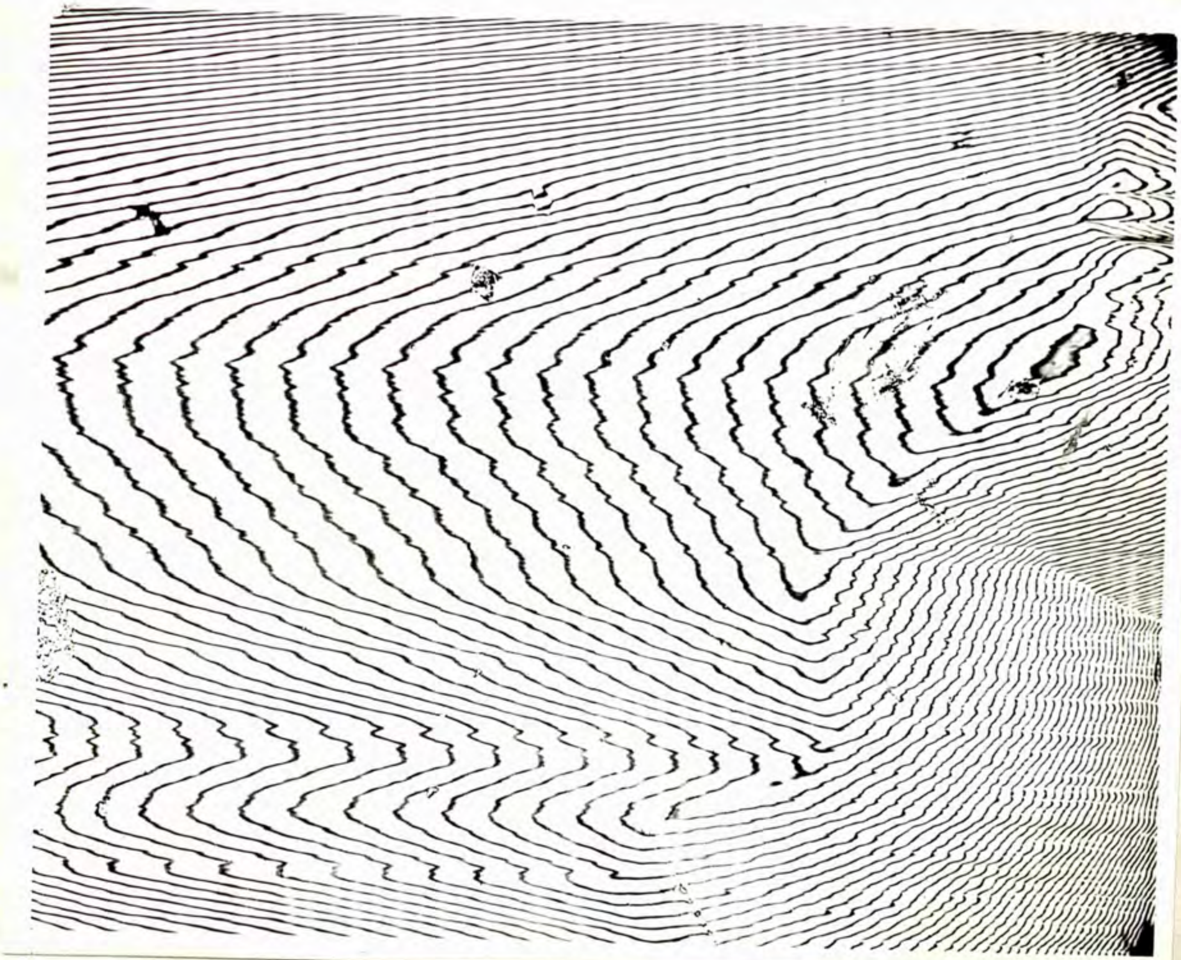


Fig. 80. x 180

is an example of high dispersion fringes of equal chromatic order for a line section for one of the striations where the V-shaped character is clearly seen. Measurements show that the successive elevations and depressions are of the order of about 200A° and 500A° respectively.

Figure (82) X 200 is another example of the high dispersion fringes of equal chromatic order for another line section illustrating once more the V-shaped character of the striations. Measurement reveals that the successive elevations and depressions are here of the order of about 3000A° and 2000A° respectively with variations in the depths of the ruts of about 600A°.

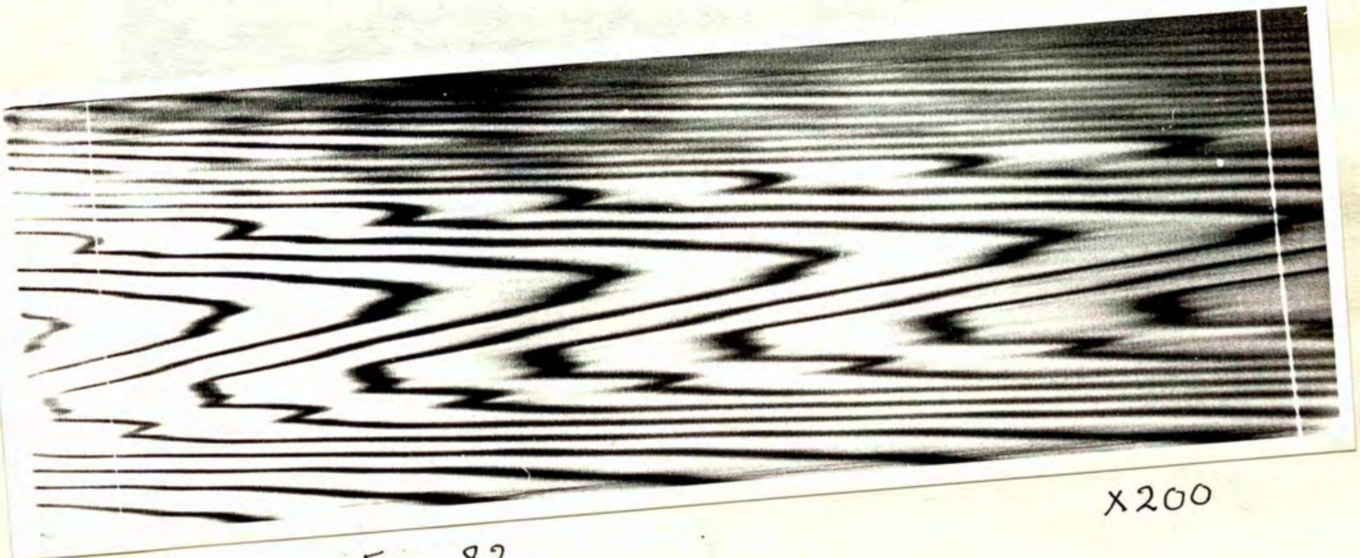
Crystal A: Face 3.

Crystal A has on it another much more irregular face. This is shown in figure (83) X 120. Here again the surface has striations which are deep in some regions towards the edges of the face. There is also what looks like a flaky area to the left and there are some undisturbed regions as is clearly seen in figure (84) X 160.

The character of the striations on this face is well illustrated in the interferogram figure (85) X 160 as is shown in the lower section of the pattern. A transmission fringe pattern at 600X is shown in figure (86) for a selected peak region in figure (84). In this photograph one sees once more the V-shaped ridges, but this time on a somewhat bigger scale than on the other two faces already described. The depths of

x200

Fig. 81.



x200

Fig. 82.

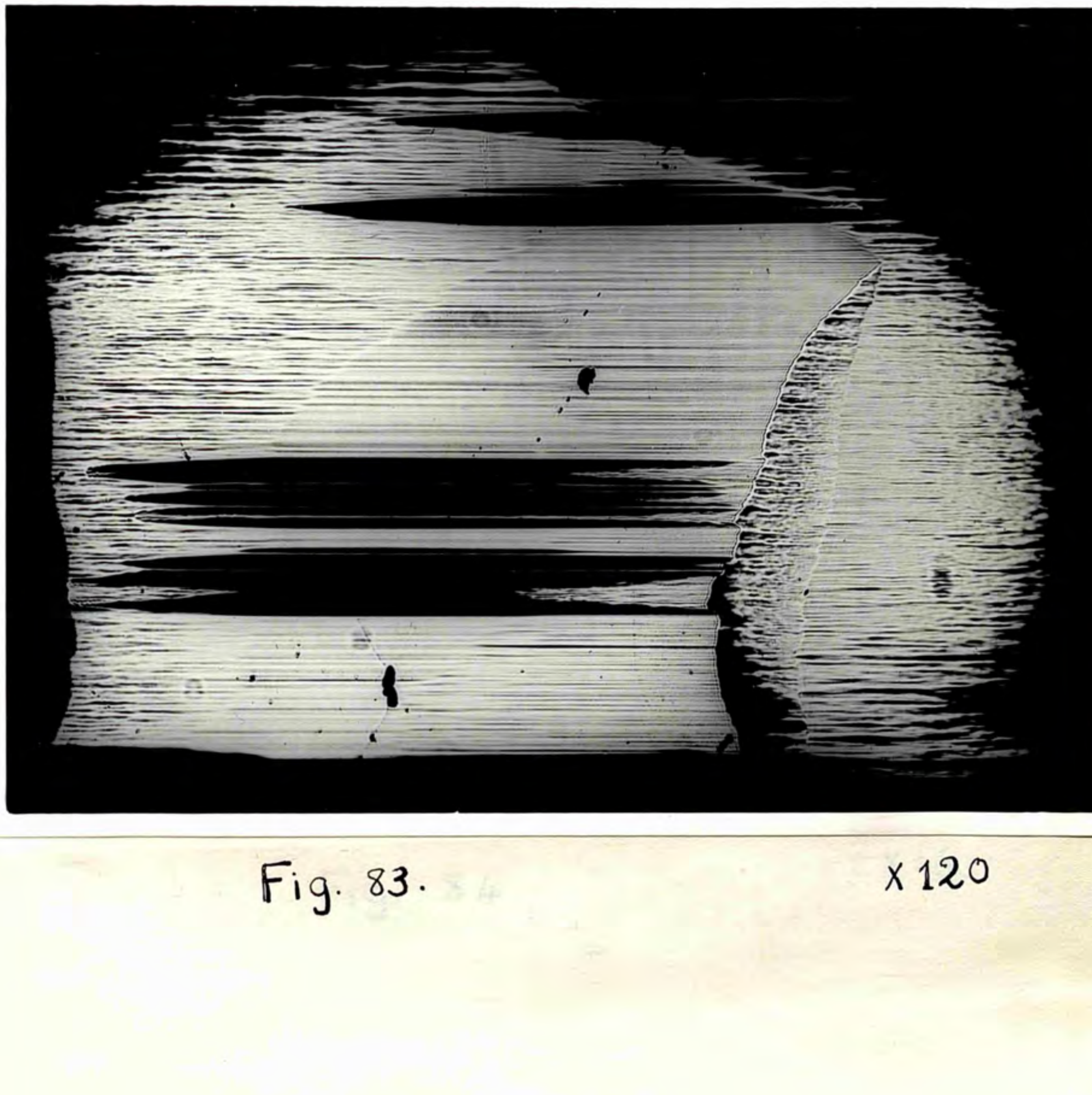


Fig. 83. x 120

Fig. 84. X160

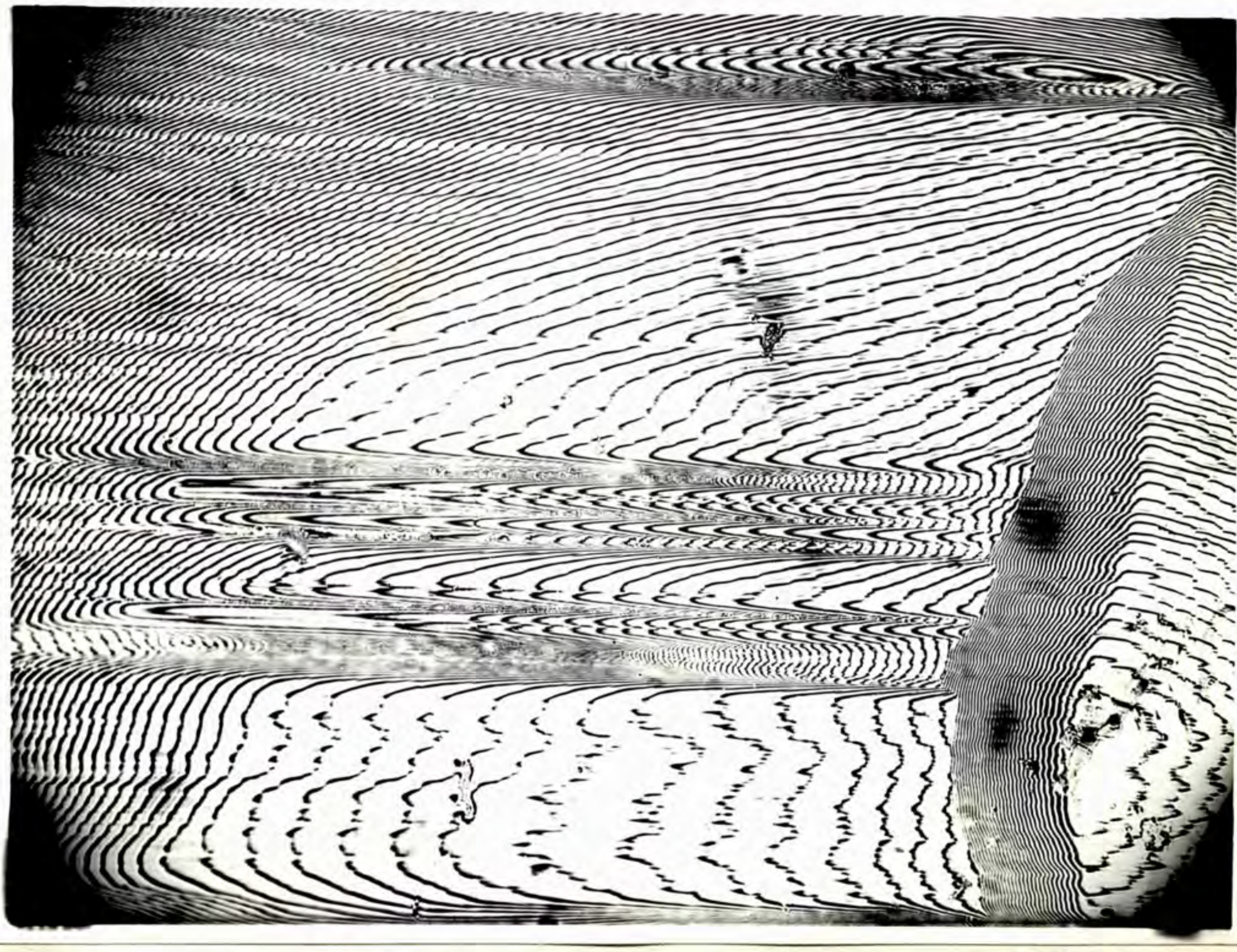


Fig. 85. X 160

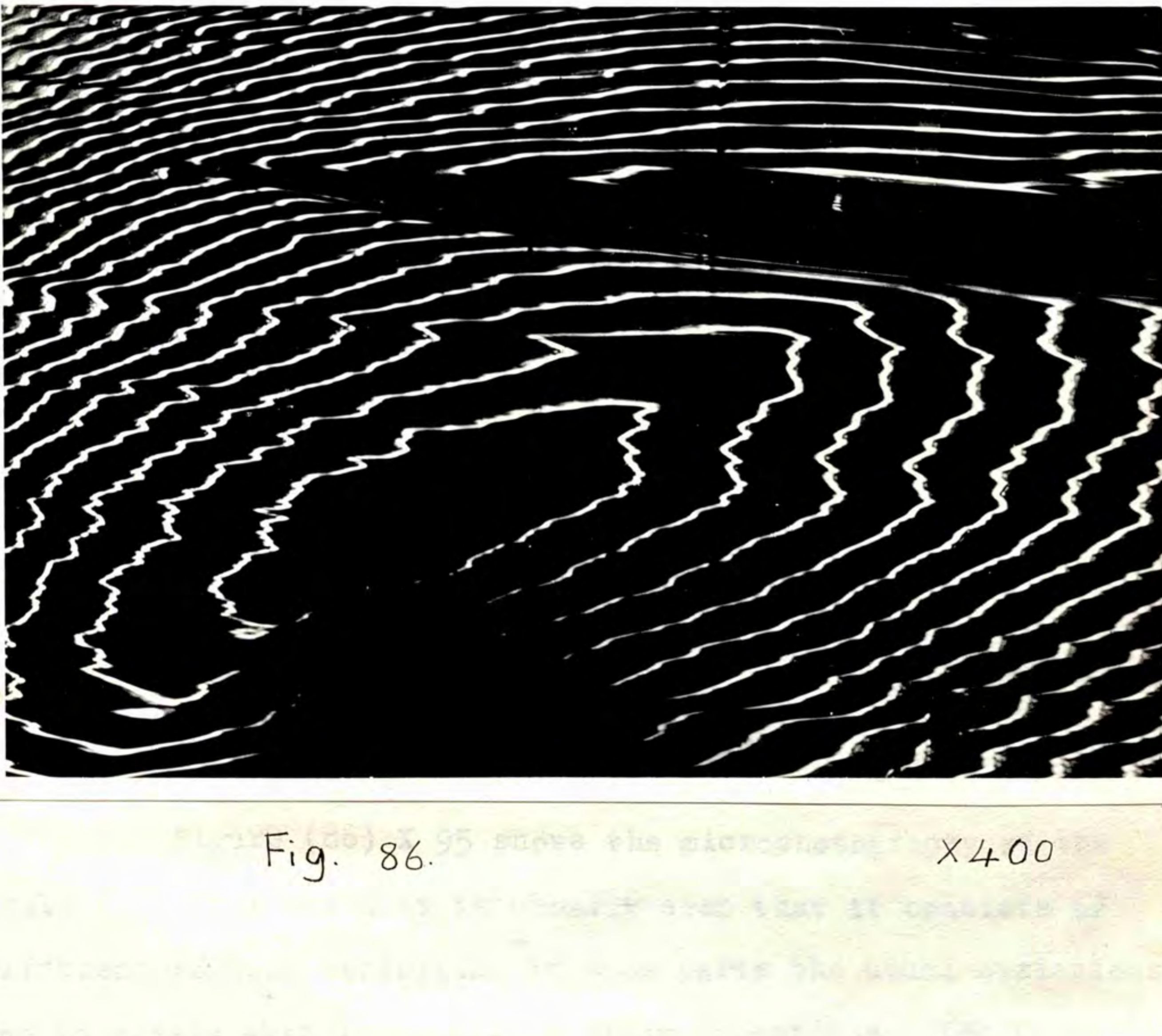


Fig. 86. X400

the ruts vary from some 270A° up to about 2000A°. Moreover the number of deeper ruts is greater than on the two other faces of the crystal.

Confirmation of measurements has been made using fringes of equal chromatic order. A high dispersion pattern of fringes of equal chromatic order for a typical region is shown in figure (87a) X 200 where the V-shaped ridges are clearly illustrated. The successive elevations and depressions for this region are of the order of 800A° and 1800A° respectively. Figures (87b) X 200 and (87C) X 200 are two other examples showing the V-shaped character of the striations.

It is of interest to note that the character of most of the ruts on this face does not continue unchanged along the whole length of the ridge but they seem to disappear in some cases.

<u>Crystal A: Face 4</u>.

Crystal A has on it a fourth face which is tolerably good although this surface Face 4 is much more rugged than the other three faces just described.

Figure (88) X 95 shows the microphotography of the whole face from which it is clearly seen that it consists of different regions exhibiting in some parts the usual striations and in others what looks like a flaky appearance. The topography of this face is revealed by the interferogram illustrated in figure (89) X 140. Here again the V-shaped character of the striations is clearly seen. Also in this photograph five hillocks

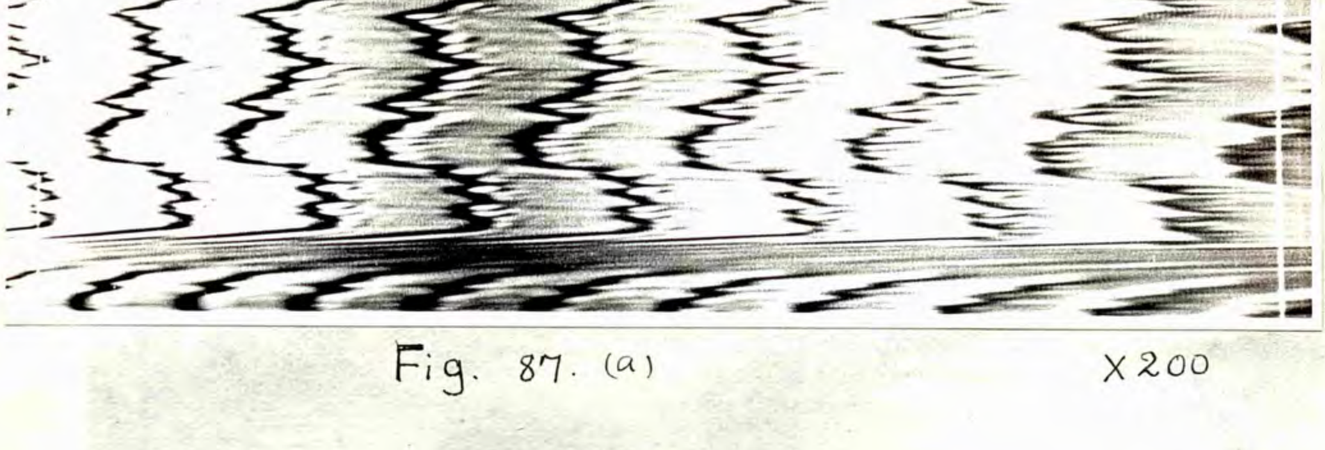


Fig. 87. (a) X200

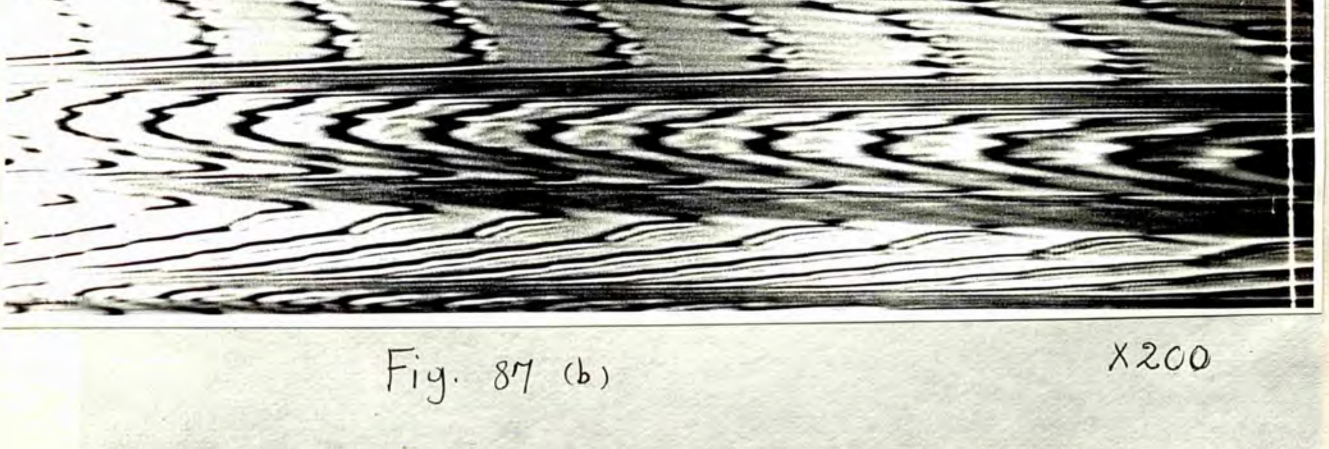


Fig. 87 (b) X200

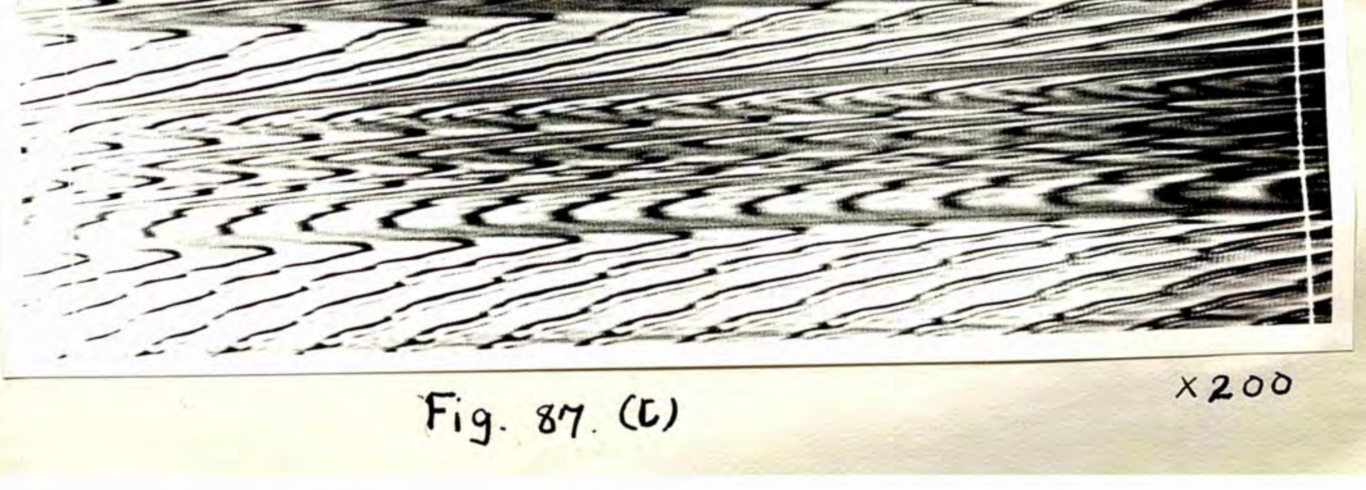


Fig. 87. (c) X200

Fig. 88.　　　　　　x95

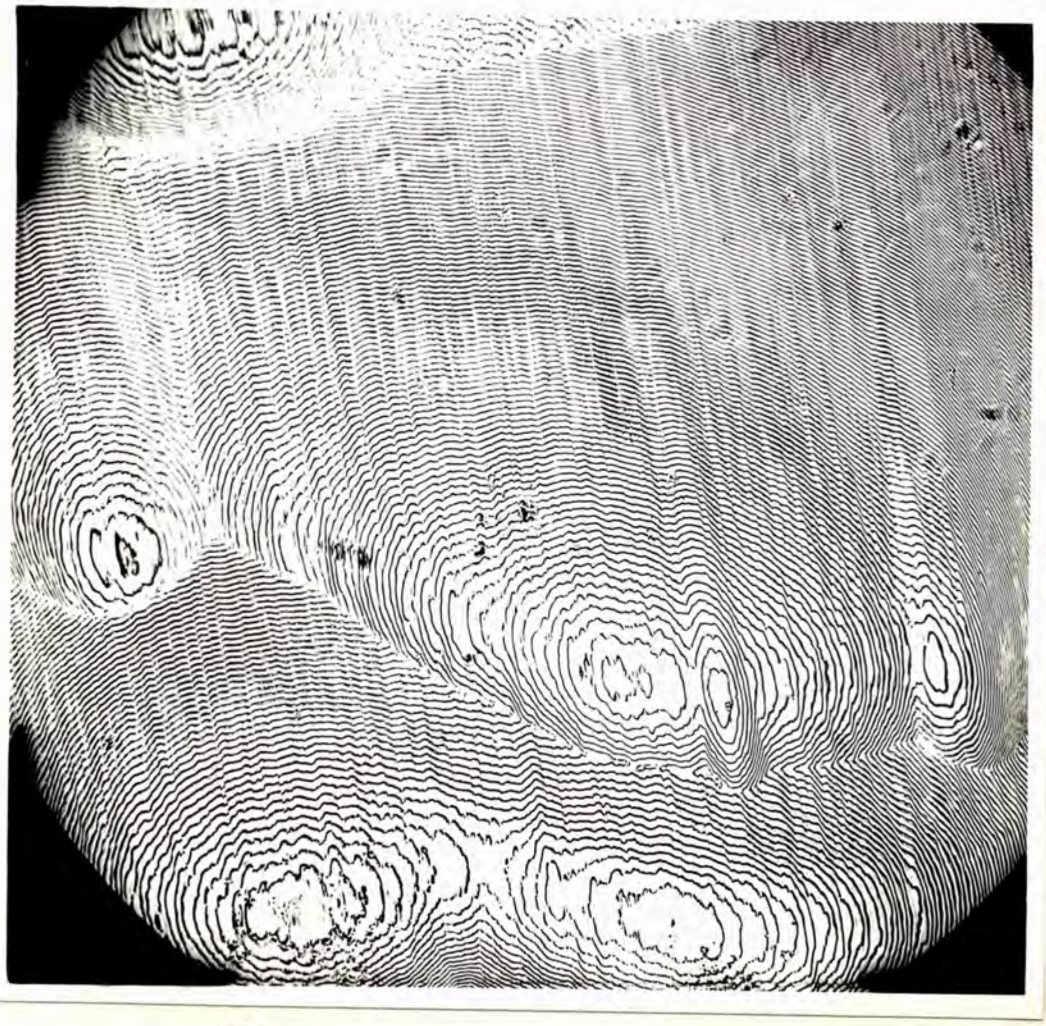


Fig. 89. X 140

can be distinguished with the striations running across them. Moreover, it appears that there is not much variation in the numerical value of the depths of the ruts on this face. The deepest is about 1200A°.

The other faces of this crystal are very similar to those already discussed and will not be described.

Crystal B.

This crystal is of weight 0.642 carats, is transparent and also has striated faces.

Figure (90) X 85 shows one of the faces of this crystal. Under low magnification the striations cannot be identified. However, the high power microphotograph figure (91) X 720 has revealed the nature of the striations on the surface. Those are discontinuous and in parts very deep, up to about 2 μ .

Figure (92) X 470 is a high power interferogram for part of the surface where the fringe pattern indicates that the major part of the surface consists of curved ridges and that the depths of the ruts on the surface is small of the order of 600A° deep.

Other faces of the crystal are similar and will not be described.

The Network Structures.

Crystal C.

This crystal, of weight 0.70 carats, is transparent and exhibits a curious pattern of network structures which are

Fig. 90 X 85

Fig. 91. X720

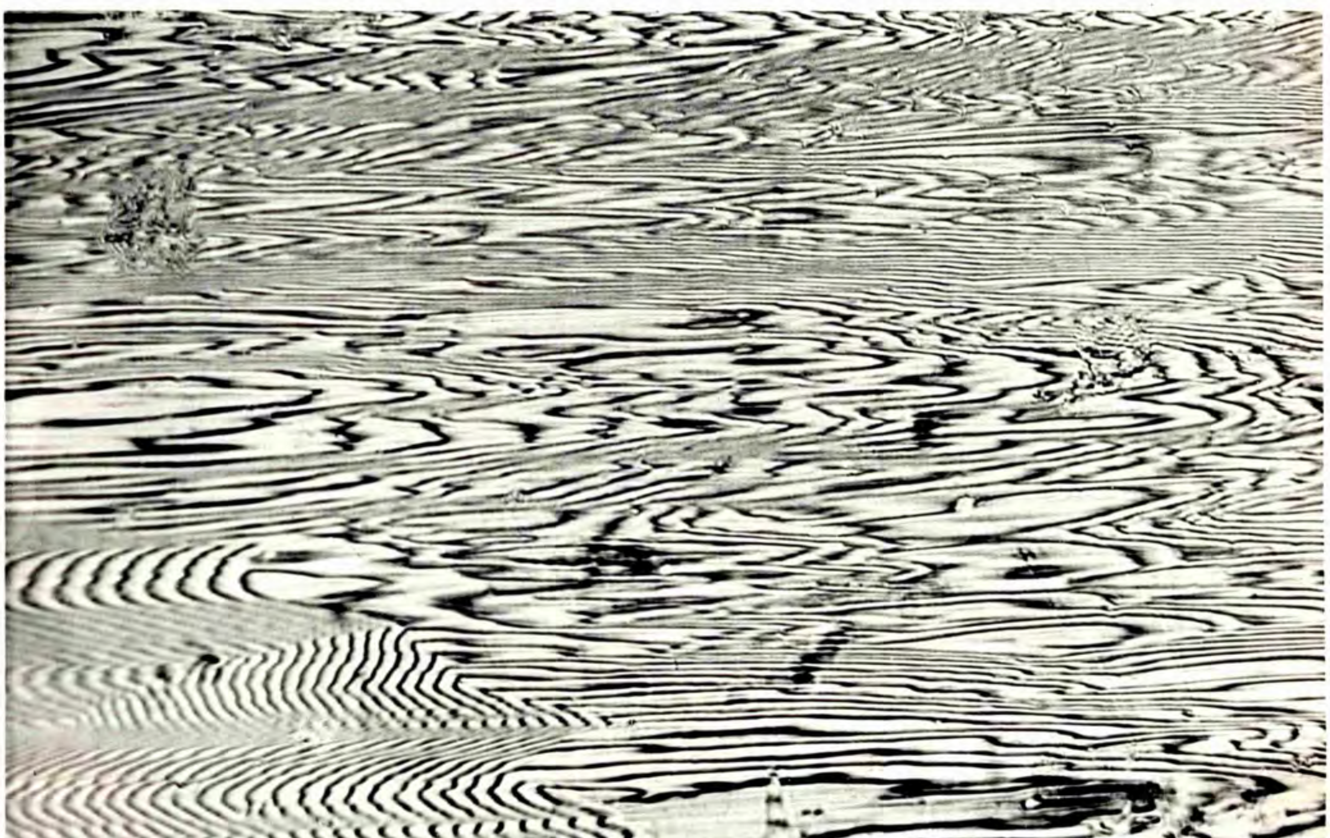


Fig. 92 X470

it seems rare.

Figure (93) X 55 shows effectively one face of the crystal. The nature of the surface structure is revealed by a higher magnification illustrated in figure (94) X 370. Here one sees that the surface consists of irregular patterns. The features are small and ranging in area from some 5×10^{-4} sq cm. to 2×10^{-2} sq cm. They mostly exhibit curved boundaries. Figure (95) shows the interference fringe pattern secured at X 200. The fringes contour the features in the form of closed loops with heights in most cases less than 3000A° as confirmed by the fringes of equal chromatic order. The features are rounded hillocks.

Figure (96) X 2000 shows a light-profile passing across one of the features. It is an elevation with somewhat curved edges and rough estimation of height about 4000A°. The profile shows also that the features are rounded hillocks. The other faces of the crystal are very similar and will not be described.

Crystal D.

This crystal, is of weight 0.75 carats, is transparent and exhibits a network structure much more complicated than that observed on crystal (c) but which is yet good enough for the interferometric study.

The major part of one face of this crystal is shown in figure (97) X 85. The surface consists of irregular features crossed by straight sheets crystallographically oriented. This is also clearly seen in figure (98) X 140. The enclosed linear

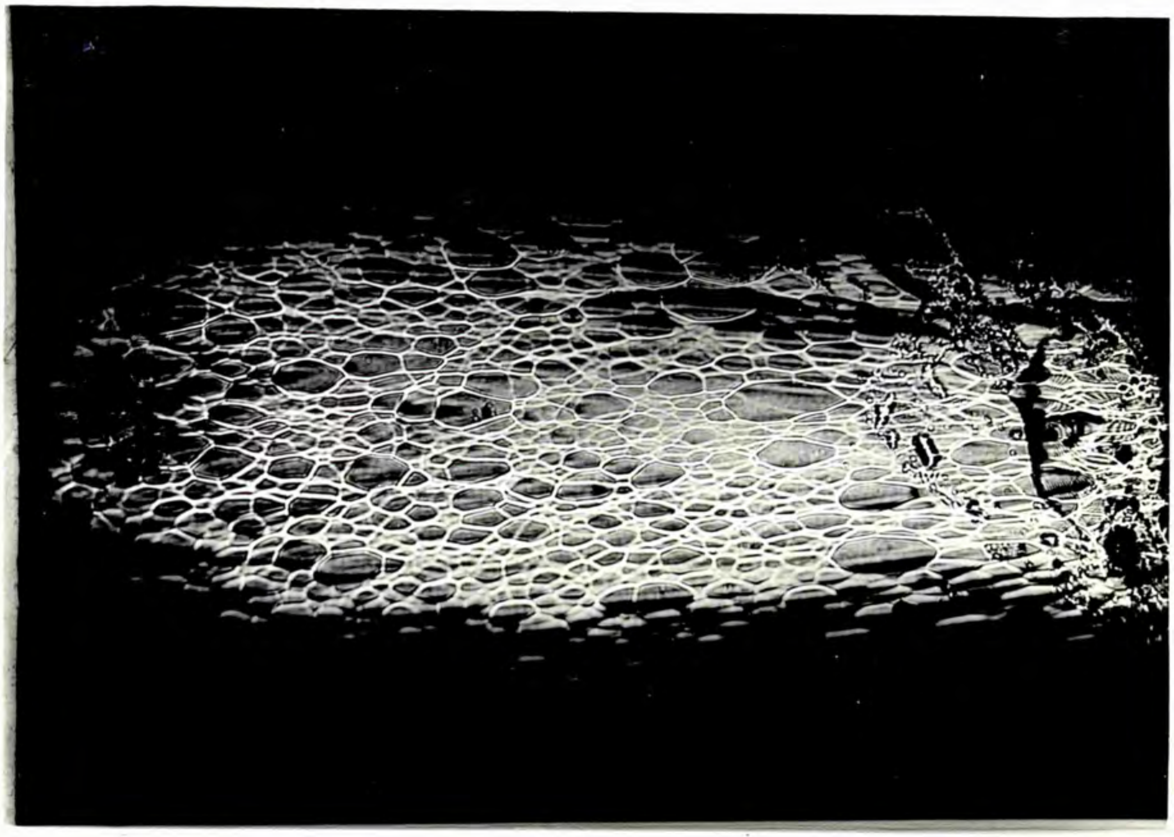


Fig. 93. X55

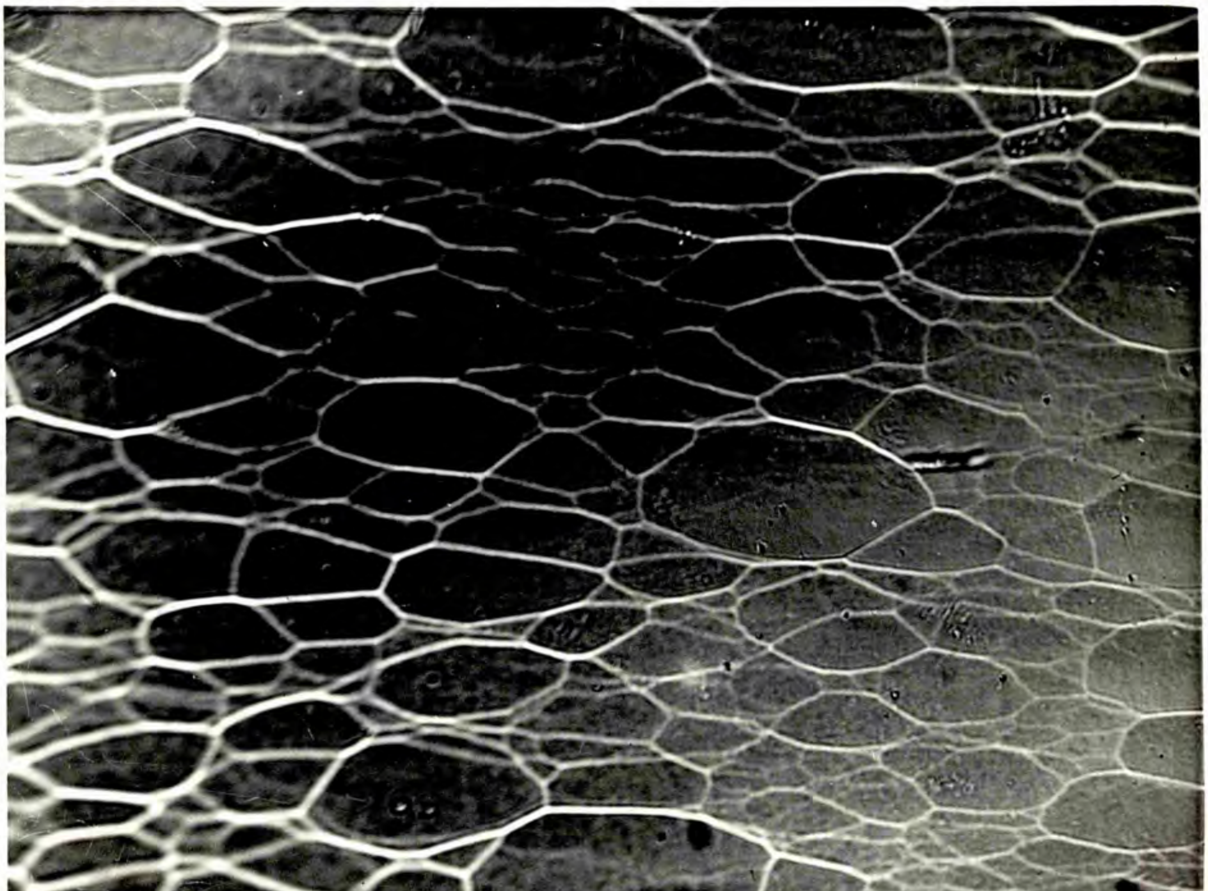


Fig. 94. X370

Fig. 95. X200

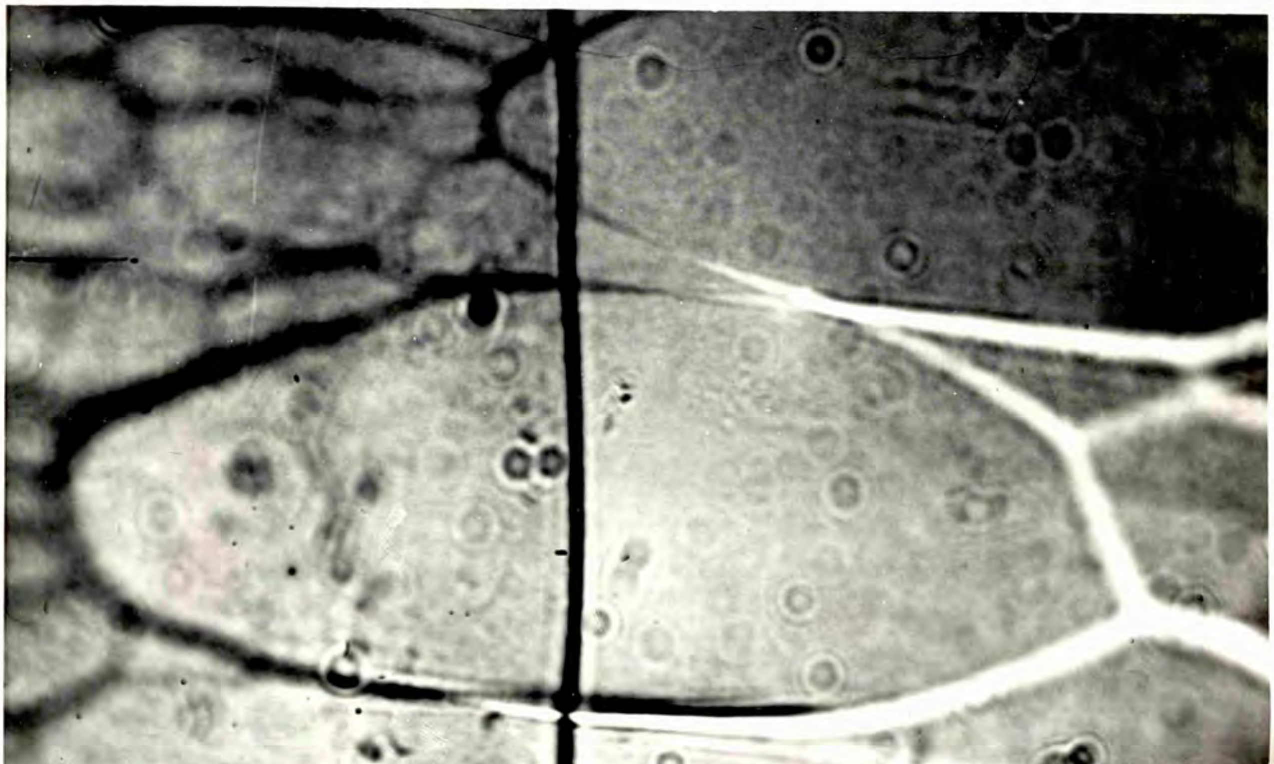


Fig. 96 X2000

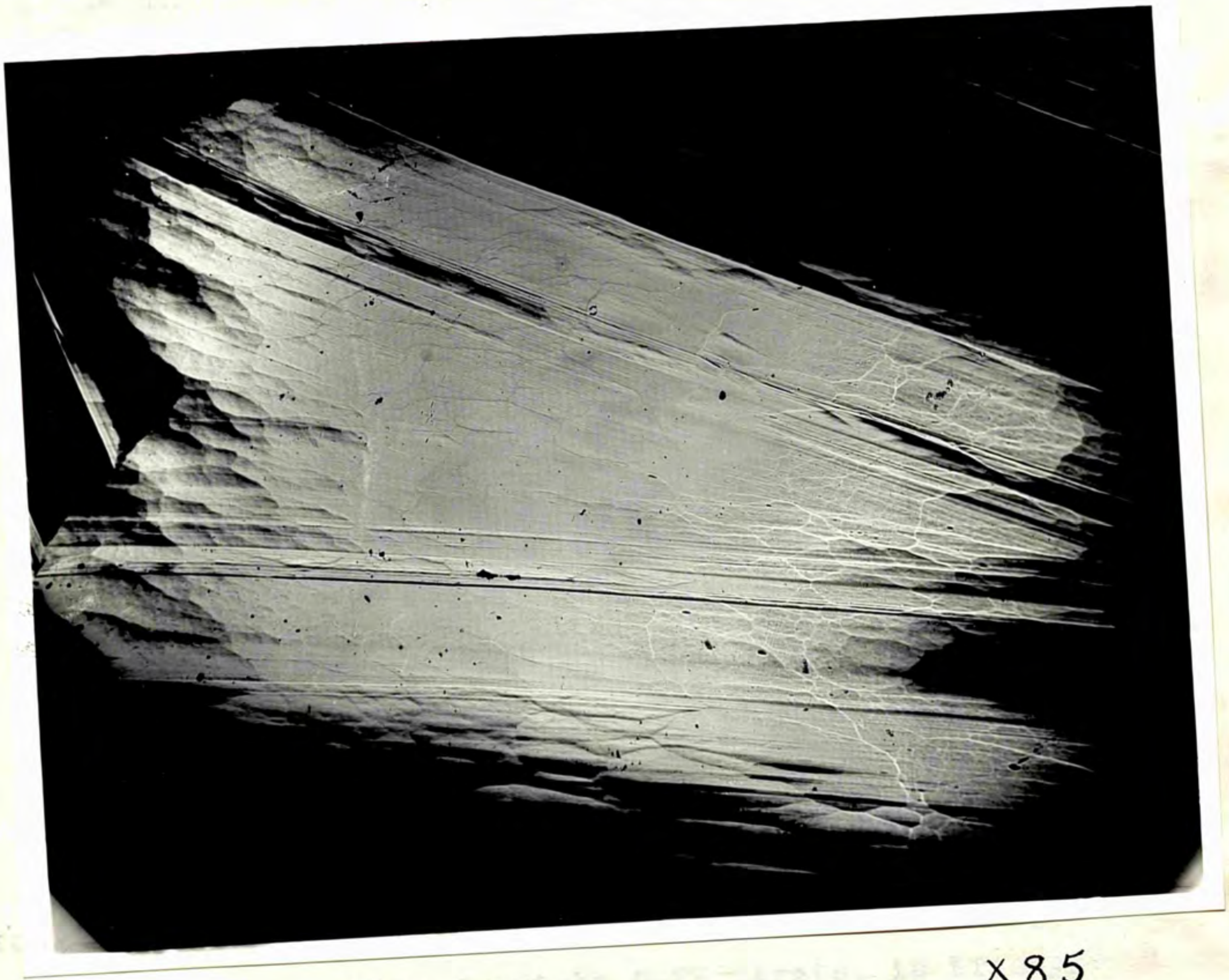


Fig. 97. X85

pattern in parts resembles the first stage etch pattern produced by Pandya and Tolansky (1954) on dodecahedral faces by artificial etching. But figure (97) shows that the pattern on this crystal is triangular and not hexagonal as revealed by etching. This suggests that there is some doubt that the pattern is due to etch.

The topography of the surface is revealed by the interferogram shown in figure (99) X 160. The fringe pattern shows some peak regions all lying in the central portion of the crystal.

Two examples of the high dispersion fringes of equal chromatic order are shown in figures (100) X 200 and (101) X 200. The first for a line profile of the central region of one of the features and the other for one of its edges. From the second example it is clearly seen that the boundaries are irregular showing successive elevations and depressions, bounded from both sides by some fairly flat regions.

3. Parallelogram Structure.

Crystal E.

This crystal exhibits a most unexpected novel topographical features of particular interest.

The crystal of weight 0.25 carats, is transparent and has two well developed faces.

Figure (102) shows the microphotography for part of one surface secured at a magnification of X 1500 with a 3[illegible] mm. lens. The surface is seen to consist of a striking pattern of small parallelogram regions, each enclosing angles of $70\frac{1}{2}^{\circ}$ and $109\frac{1}{2}^{\circ}$.

Fig. 98. x 140

Fig. 99. x 160

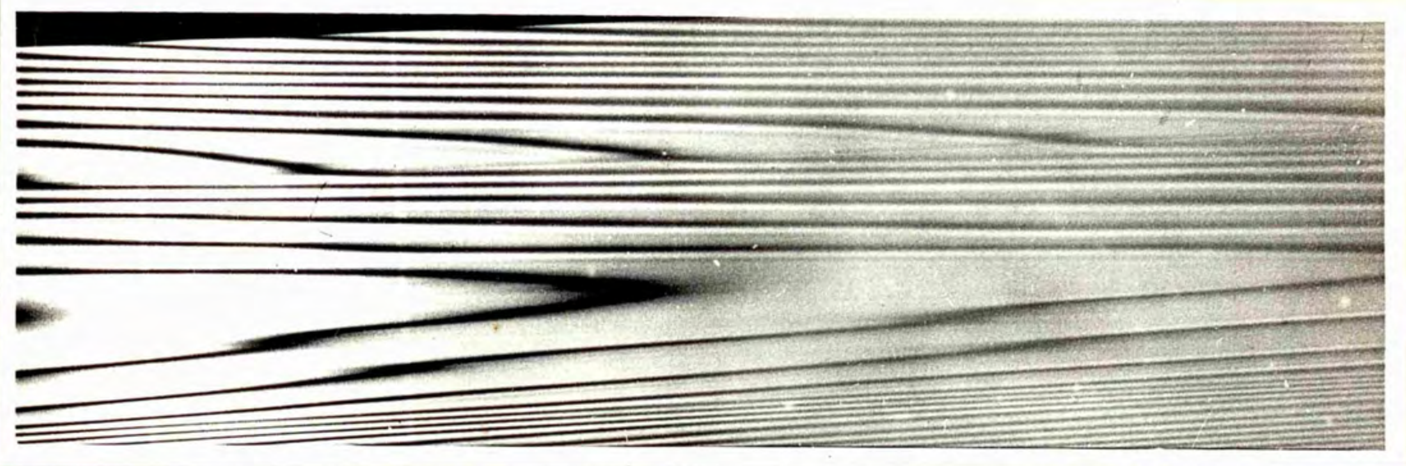


Fig. 100 x200

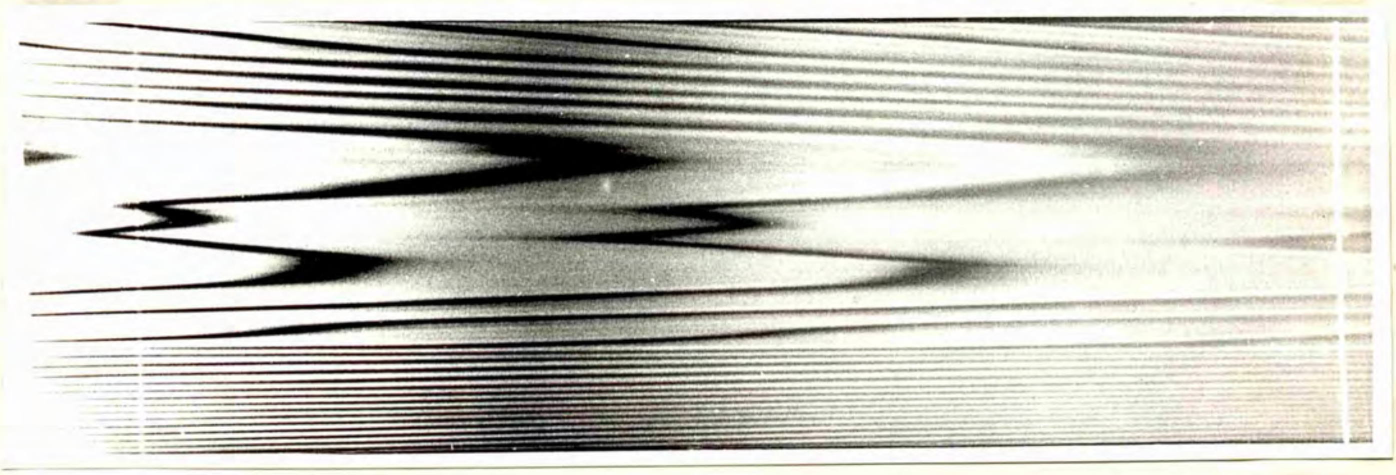


Fig. 101 x200

The sides are therefore crystallographically oriented. The parallelograms are very small indeed ranging in area from some 5×10^{-8} sq. cm. to some 2×10^{-6} sq. cm. Figure (103) X 270 is an interferogram for a small region on the surface. It shows a central patch region of "zero" order interference surrounded with what are the equivalent of the multiple-beam Newton's "rings" for an approximately cylindrical or elliptical surface. It is near this zero-order region which is that to be examined with the high power.

Figure (104) shows the interference fringe pattern secured at X 1500 with the 3 mm. lens. In the upper half of the picture is the zero order region. This consists of a pattern of high-dispersion fringes running over the parallelograms of figure (102). The extremely high contrast in the fringe pattern is, as formerly shown, primarily due to the low absorption in the multi-layer reflector.

In the lower half of the picture are two fringes, respectively, the first and second orders of the multiple-beam "Newton's ring" system. The fringe definition in the first order is exceptionally good. It is just recognizable that the second order has broadened slightly, but appreciably relative to the first order. This difference is due to the fact that the gap for the first order is $\frac{\lambda}{2}$ and that for the second order is λ.

The interferograms reveal that the parallelogram features are small convex units. They vary in height from about

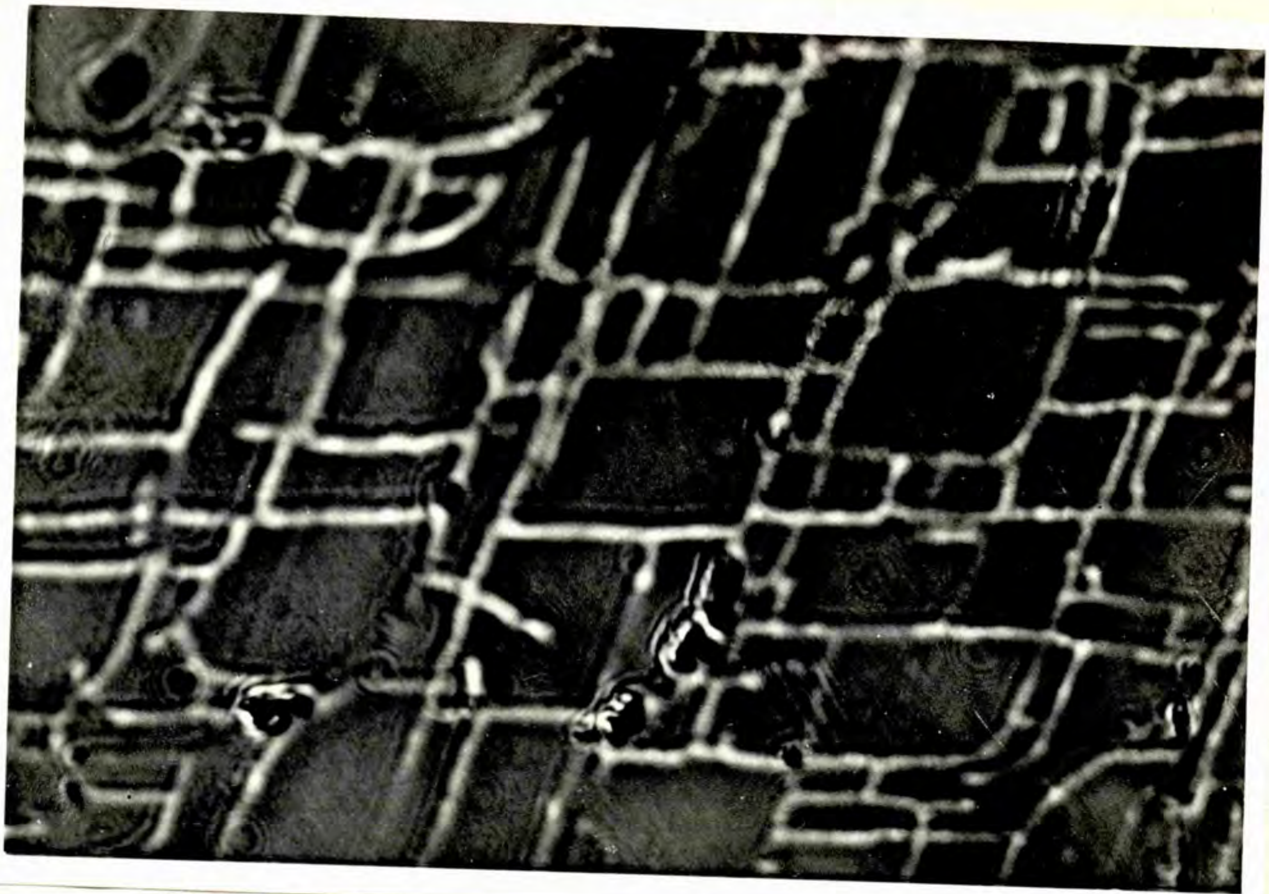


Fig. 102. X1500

Fig. 103. X450

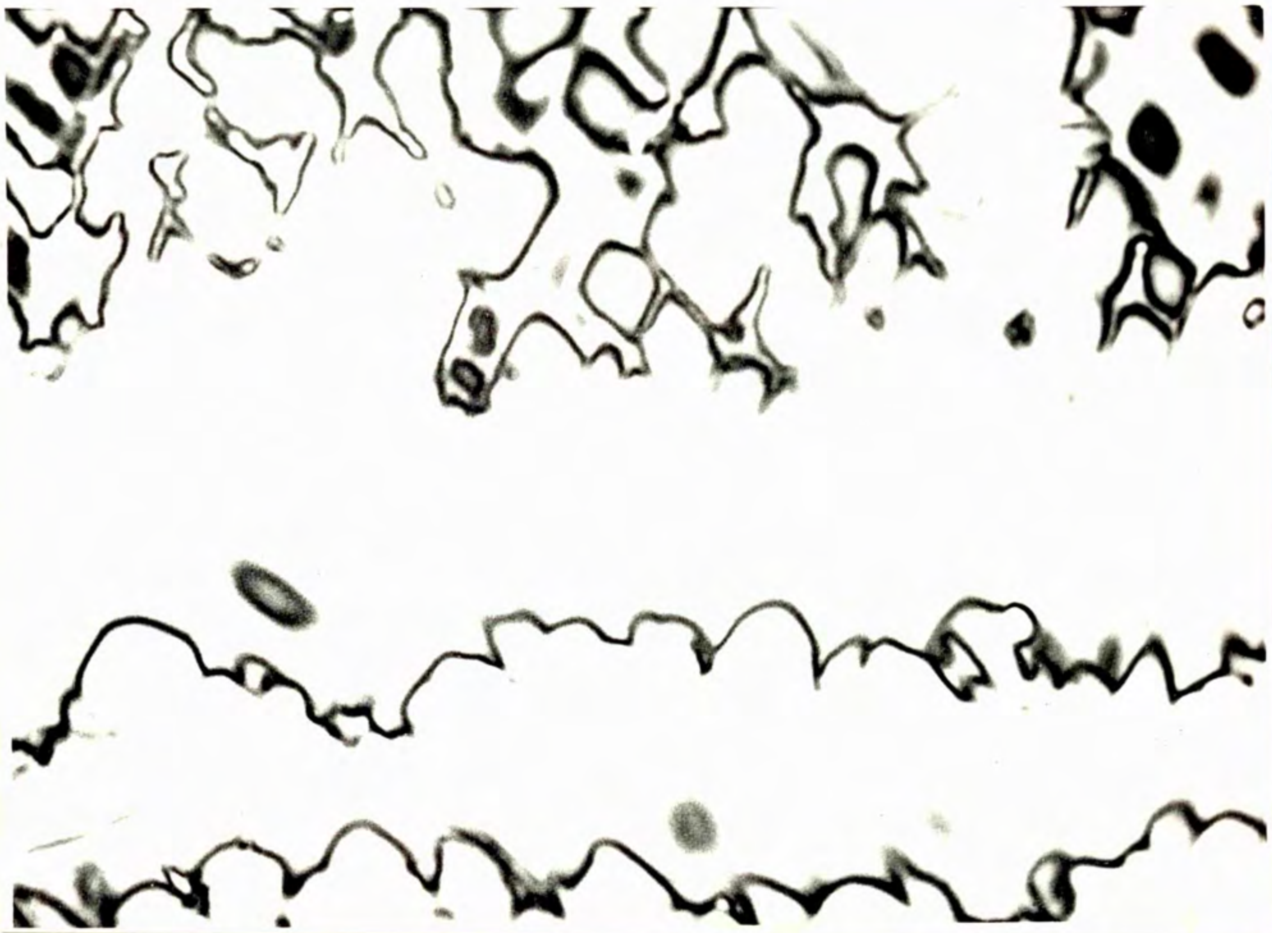


Fig. 104. X 1500

260A° to some 900A°. The boundaries of the features are sharply defined ruts or channels. Furthermore, the fringe patterns show that most of these separate parallelogram regions are highly curved. Approximate curvatures have been calculated by assuming that the elements are spherical segments. This has been done for different regions on the surface leading to the result that the radii of curvatures vary from about 0.67 mm. to 0.02 mm.

Table (1) shows the result of measurement which has been carried out on the interferogram figure (104).

Table (1)

Points on the Surface	Radius of curvature
A	.022 cm.
B	.012 "
C	.026 "
D	.006 "
E	.002 "

This table shows that the radii of curvatures for the selected region are very small indeed and vary from about .02 mm. to .02 mm.

It is worthwhile to note that the parallelogram features described do not at all resemble any of the etch patterns which have been produced recently in this laboratory by Pandya and Tolansky (1954) on dodecahedron faces of diamond.

Since there appear to be no etch features on this crystal it is reasonable to conclude that the parallelogram pattern is a growth feature.

CHAPTER III

Conclusion

A general conclusion may now be drawn from the detailed study of the different faces of the five crystals already described. Each crystal exhibits a structure of its own.

In the present investigation we may classify the different structures observed under three main headings.

1. Striated Faces.

These include

(a) Surfaces which exhibit smooth striations and are good for interferometric techniques (Crystal A)

(b) Surfaces which exhibit rough striations which are too coarse for interferometric study (Crystal B)

(c) Surfaces which exhibit striations either smooth or coarse and are characterized by some flaky regions.

These variations in the character of the striations may well depend on the particular mine from which the diamonds have been extracted. Usually the striated faces are quite common. Each little ridge on a striated surface is enclosed by two narrow planes more or less regular. These planes often correspond in position to different faces of the crystal, and these ridges may have been formed by a continued oscillation in the operation of the causes that give rise, when acting uninterruptedly, to enlarged faces. By this means, the surfaces are marked in parallel lines, with a succession of narrow planes meeting at an angle and constituting the ridges referred to.

From the studies made on all the faces of crystal A it is concluded that the striations are sharp ruts and it appears that each rut maintains its character virtually unchanged along the length of the crystal face.

2. Network Structure.

This type of structure is one of the rarest ever reported on diamond. All the features on the surface are convex elements.

Now this irregular structure may well be interpreted in terms of dislocations as a row or lattice of dislocations as was first proposed by Burgers (1940) who has pointed out that two crossing systems of dislocations were a possible model for a boundary between crystals differing in orientation by a small rotation about an axis normal to the boundary. Strong evidence that the lineage boundaries consist of a row of dislocations has been offered chiefly in the form of observations on etch pits on sub-grain boundaries by Lacombe (1948) and by Read and Shockley (1950). Further support has been given recently by Vogel et al (1953) who have studied the boundaries between nearly perfect crystals of germanium grown from the melt, the growth direction being < 110 > . But the crystal had to be etched in a suitable reagent to reveal the end points of the edge dislocations which serve as nuclei for etch pits (Lacombe and Beaujard (1947)).

Support for Burger's model has been given by Vema (1954) who observed the mosaic structure on the natural surfaces of a highly perfect germanium crystal by interferometric techniques without etching the surface.

Moreover, Hedges and Mitchell (1953) describe patterns of lines revealed by photolytic silver in the interior of silver bromide crystals, which show the arrangement of dislocations resulting from strain in the process of production followed by annealing. The dislocation lines in these networks join each other exclusively at three-line nodes. In some regions the resulting network is essentially three-dimensional, but predominantly the dislocations are arranged in surfaces which divide the crystal into cells of an average diameter of the order of magnitude 10 microns; justifying application of the term "mosaic structure" to this particular case. In some cases the arrangement of dislocations in a cell wall is essentially a grid of parallel lines, corresponding to the dislocation models of a boundary between crystals differing in orientation by a small rotation about an axis lying in the boundary, which have been discussed by a number of authors (Burgess 1939, Bragg 1940, Van der Merwe 1950. Read and Shockley 1949, 1950). In other cases, the pattern seen in a cell wall is fairly uniform network of hexagons (not necessarily regular hexagons, though the nodal angles appear to be close to 120°). The pattern observed on the crystal is somewhat similar in some regions. Frank (1954) has discussed such hexagonal patterns observed by Hedges and Mitchell by generalizing Burger's model. He pointed out that the patterns in which dislocations run in more than one direction in the surface are anticipated in the case of a mosaic boundary. He added that the unique relationships between net pattern, axis of rotation and plane of net depends on the non-existence of far reaching strains, and that dislocation nets may be forced out of their equilibrium planes, or the uniformity of their net patterns may be disturbed by stresses. Occasional dislocations may be present, producing far reaching strains, anywhere else in a crystal. Such dislocations will be only weakly bound into the net. This view can explain why the observed patterns on diamond are sometimes irregular.

The network structure may also alternatively be attributed to other imperfections in the lattice. Addink (1947) has established that not only mosaics but also holes in a lattice or ions at interstitial places will contribute to make a crystal "imperfect". He calls a crystal with these flaws "incomplete" and works out a set of degrees of "incompleteness" for a number of crystals including diamond.

Further support for the presence of such imperfections in the lattice is given by Champion (1953) who also reported local imperfections in diamond. He stated that variations in the texture of diamond can be regarded as variations in the relative thicknesses of the layers of perfect crystalline material and of the imperfect barrier layers which make up the specimen. His view has been supported by Hall (1952) who studied the growth of germanium crystals and found that a wide variety of texture may be affected by changing the shape and the amplitude cycles. After each surface layer of the crystal is covered by a new layer, its composition will tend to approach the equilibrium value for the solid, but if the new layers are added too rapidly the imperfections have insufficient time to exchange with the surface and material having a non-equilibrium composition will be grown.

Now germanium has essentially the diamond structure, and it may be supposed that in natural diamond a similar situation occurs. Variations in the rate of growth lead to the formation of interior surfaces, the ultimate natural surface representing merely the last and final surface to be formed. According to Champion these surface or barrier layers consist of aggregates of vacant sites and interstitial atoms in varying properties.

Of course there remains one point namely, if the network is indeed a growth mechanism, why does it only appear rarely on a few dodecahedra? An answer may be that no enough dodecahedra have yet been studied. If the network is due to solution, it is necessary to postulate that dodecahedron faces are more easily dissolved than octahedral faces because etch is rare on natural octahedra.

3. <u>Parallelogram Structure</u>.

As to the regular pattern of parallelograms observed on crystal E, this does not resemble any of the etch patterns produced by any of previous workers. This is probably a growth characteristic. It may be well interpreted in terms of the dislocations as before only in this case the rows of dislocations form regular patterns.

It might be expected that the conditions for the growth of the type shown by the regular pattern of parallelograms is rarely achieved. Since the most difficult conditions to achieve in crystal growth are those of uniformity in the temperature, pressure and concentration. As variations in these properties or in their rate of change lead to imperfections in crystal texture, the conditions of natural growth of diamonds would generally be expected to lead to a surface structure which is more commonly that described in crystals A and B while those of crystals C, D and E is surely of rare occurrence.

It must be concluded that a firm answer as to the origin of the networks cannot yet be given.

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An Occasional Mode of Growth in Diamond

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Abstract. It is shown that in rare instances a mode of growth by plane sheets operates on the octahedral faces of diamond which leads to the formation of six-sided growth features containing alternate angles of approximately 90° and 150°. It is shown that the edges of these are effectively parallel to the directions ⟨431⟩. These may possibly arise through intersection of {221} with the (111) face.

§ 1. INTRODUCTION

IN this laboratory an intensive systematic optical study is being made of growth characteristics on natural diamond faces. In this study several hundred octahedral faces have been subject to detailed examination by the microscope, by interferometry and by the light-profile microscope. It has been established that by far the great majority of these diamond faces grow by means of plane sheet growth which leads to trigon formation and to oppositely oriented triangular growth pyramids (for a recent discussion see Halperin (1954)). In both trigons and triangular growth pyramids the edges are strictly parallel to the three edges of the normally triangular face constituting the (111) natural octahedral face of the diamond.

In two exceptional instances we have found again a plane-sheet mode of growth, but this time the edges of the growth sheets are parallel to ⟨431⟩ and it is the object of this brief note to describe these relatively infrequent growth features which we have found on four separate faces. Three of these occur on different octahedral faces of one diamond and the fourth on another diamond.

§ 2. OBSERVATION

Case I.

The first example is remarkable for its approximate symmetry and gives us the clue to the others. It appears on one face of a good transparent octahedron from South Africa, of weight 0·63 carat. The feature is quite small indeed and is shown (×1000) in figure 1 *a* (Plate). It consists of a hexagonal pattern and measurement reveals that the alternate angles are respectively approximately some 90° and 150°. The sides are almost, but not quite, equal in length. The angles are difficult to evaluate with any precision because the sides are not quite straight. The angles can be measured to within a little better than $\frac{1}{2}$°. They are respectively, in degrees, 89$\frac{1}{2}$, 150, 92$\frac{1}{2}$, 144, 95, 150$\frac{1}{2}$. Their sum is 721$\frac{1}{2}$.

Examination by fringes of equal chromatic order (figure 1 *b*) (see Tolansky 1948) establishes that this feature is a plateau standing merely some 1000 Å high above a more extensive growth pyramid. It is certainly a growth feature for there is no evidence for the existence of any etch effects whatsoever on this diamond. This observed hexagonal pattern can be crystallographically described as having its growth edges more or less parallel to the directions ⟨431⟩. The calculated angles for a hexagon in these directions are respectively 87° 47′ and 152° 13′. The values in the observed figure are somewhat similar. Although there is only a crude parallelism to ⟨431⟩ the main fact is the differentiation from the general mass of growth features on octahedral faces, which consist of trigon or pyramidal growth features in which the three sides are, almost invariably, inclined to each other at angles very near to 60°.

The lines which form this hexagon could arise from intersection of (111) with any of many planes which include for example (221), (430), (103), (014), etc. Of these, we tend to conjecture in favour of (221) for the following reasons: It is the only set of planes which can produce simultaneously on each of all the (111) planes of the crystal both our hexagonal pattern and equilateral triangles, as in figure 2, and both patterns appear simultaneously on three faces of our crystal.

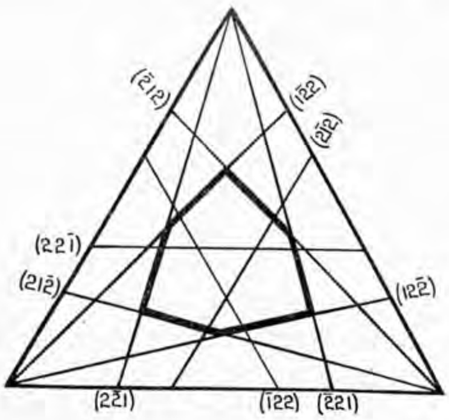

Figure 2.

Further, (221) is the most close packed of all the possible forms giving our hexagons and might well be favoured during growth. Again, it has been established by etching experiments (Omar, Pandya and Tolansky 1954) that the most important planes produced by etching (111) on diamond are (221). This evidence is far from decisive but favours (221) a little.

Case II.

In the second example, figure 1 *c* (×650), interferometry once more demonstrates that this figure lies on a growth pyramid. This pyramid reflects the feature, but there are distortions because of interference from surrounding growths.

As before, we have a six-sided figure, the angles being 90, 153, 92, 150, $92\frac{1}{2}$, 151°. The sum of these is $728\frac{1}{2}$° and the excess ($8\frac{1}{2}$°) over that for a rectilinear figure is undoubtedly due to curvature of the sides and not due to faulty estimation of the angles. Within the hexagon are the familiar 60° growth trigons.

Case III.

This example (figure 1 *d*) (×300) at first seems a most irregular pattern but can be classified along with the two previous ones. The key lies in the appearance of the alternate angles, approximating once more to some 90° and 150° which establish that this is just another distorted example. The angles measured are 89, 153, 93, 149, 90, 151, with sum 725°, and again the excess is attributable to curvatures.

It is noteworthy that these three features, each on a different face of one crystal, cover a relatively insignificant fraction of the total area. Despite the numerical differences in angles, these features are undoubtedly similar and are clearly related.

Case IV.

In this example (figure 1 *e*) (× 15), the mode of growth under consideration is on a much bigger scale and dominates the whole growth of the face. The stone is a clear octahedron mined in South Africa. There is a good deal of deviation from the ideal case shown in figure 1, nevertheless the relationship is evident. We have here a relatively rare example of a crystal face which has grown primarily both in this manner as well as by trigon formation. The strongly outlined hexagonal central feature, which seems to start off with angles near 90° and 150°, quickly transforms its character on moving to the edges, tending to become a crude 60° equilateral triangle.

We have sought through microphotographs published by other observers to see whether any examples of this particular hexagonal mode of growth have been recorded and overlooked. We have indeed found one clear example amongst 86 excellent micrographs of (111) faces recorded by A. F. Williams in his comprehensive book on diamond published in 1932. (There is amongst these photographs what may possibly be a second example but the evidence here is rather uncertain.) Although Williams had the opportunity of inspecting many thousands of stones yet he never, it seems, noticed this special mode of growth, despite its appearance in one of his published photographs. It is certainly of infrequent occurrence.

Acknowledgment

One of us (S. H. E.) wishes to express thanks to Ein Shams University, Cairo, for a grant of study leave enabling this work to be carried through.

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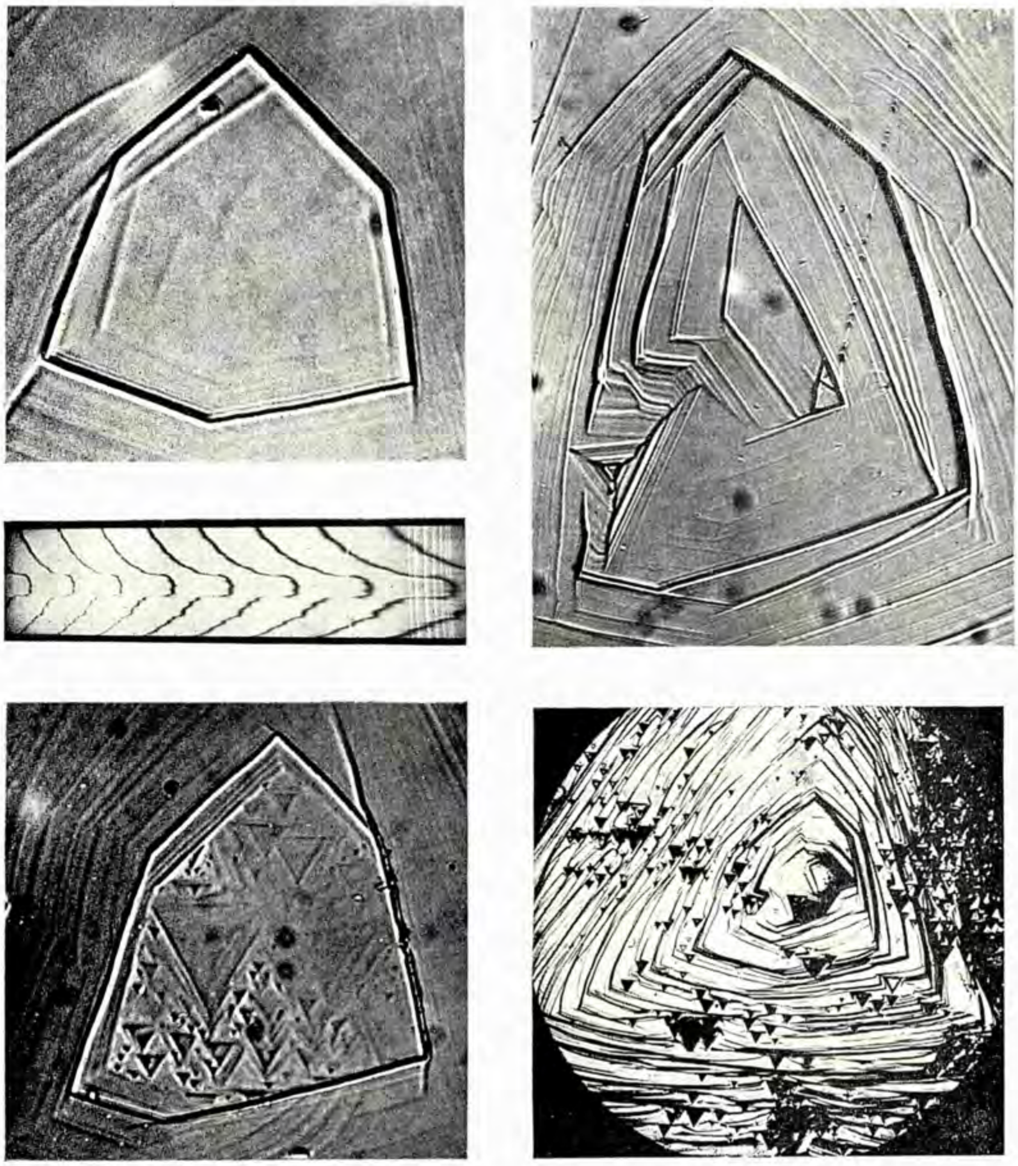

a *b* *c* *d* *e*

Figure 1. *a*, ×1000; *b*, ×50; *c*, ×650; *d*, ×300; *e*, ×15.

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Precision Multiple-Beam Interference Fringes with High Lateral Microscopic Resolution

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It is shown that very sharp multiple-beam interference fringes can be produced with a high-power 3-mm lens of numerical aperture 0.95. The optical conditions necessary to secure high definition in the fringes are discussed. The arrangement described is used with lateral magnification of $\times 1500$. It can resolve in extension about 0.7μ and in depth about 50 A. The technique is illustrated by topographical studies on a dodecahedron face of a diamond. The fringes obtained are much superior to the best given by high-power two-beam interference microscopes. Volume elements as small as 5×10^{-15} cc can be resolved.

IT has usually been considered[1] that any attempt to combine high-resolution microscopy with high-definition multiple-beam interferometry is likely to involve optical difficulties. The reasons for this have been adequately discussed. As a consequence of experience, most of the multiple-beam interferometric topographical studies, published by various workers in different laboratories, have generally been restricted to microscopes with a power not exceeding that of a 16-mm objective. The result has therefore always been that the interferograms have shown very high resolution in depth (at times approaching molecular dimensions) but have only exhibited mediocre lateral resolution at best.

It is the purpose of this note to describe how we now produce multiple-beam Fizeau fringes for topographical studies which not only have high interferometric sensitivity and precision but also have good lateral microscope resolution and magnification of a high-quality 3-mm dry objective with numerical aperture 0.95. With this lens and suitable eyepiece and bellows magnification, we have secured very fine fringe definition with a lateral magnification of $\times 1500$. When correctly used, with converging light, this lens can resolve laterally 0.35μ. Since necessarily our interferometric illumination requires a parallel beam incident on the object, we might anticipate at least a lateral resolution of 0.7μ. We shall show that with this good lateral magnification and resolution we are still able to maintain fringe definition at a very high standard, a matter not formerly thought possible.

Apart from such considerations as the difficulties associated with small working distances and depth of focus restrictions, the two primary difficulties involved in securing good multiple-beam Fizeau fringes with such an objective are (a) the strict necessity for a small gap between the two surfaces and (b) the desirability of having as low a wedge angle as is possible. These conditions are together related in determining the phase lag of successive beams which is the principal factor affecting definition. As to the first condition, it is self-evident that the spacing between the surfaces increases with the numerical order of the interference fringe observed, hence to reduce phase lag to a minimum, observation should be restricted to very low orders of interference, indeed only to the first two or three. So severe is the condition of small gap imposed at these high powers that the experimental conditions must be arranged such that the region under examination is close to a region of effective contact between the two surfaces. Such a region of contact we shall descriptively call the "zero" order and in such a region the separation between the two surfaces is everywhere less than $\lambda/2$. According to the curvatures of the matched surfaces, this zero-order region may cover a large or small portion of the field of view, depending on the arrangements used.

As to the second condition, that of a small wedge angle, it has already been established[1] that the phase retardation which leads to the fringe broadening is proportional to the square of the wedge angle between the two surfaces producing the fringes. Now the use of high magnification with Fizeau fringes (although not with fringes of equal chromatic order) necessarily imposes a wedge angle which can be considered quite large from the viewpoint of multiple-beam interferometry. The reason is clear, for it is evident that the fringes viewed must be sufficiently close together on the surface studied for at least one pair to be included in the field of view. However, in accordance with the phase condition, the wedge angle should be restricted to the minimum possible. This means that fringe dispersion should therefore be as high as possible. This condition we have scrupulously obeyed here. In fact, since the first factor, already discussed, restricts observation to but very few orders, the two conditions can be simultaneously met by arranging to have high dispersion fringes in the field of view (and therefore very few in number) and selecting those fringes to be the first and second fringes following a zero-order position.

This is the condition we adopt. In our example illustrated here, fringes are some 30 mm apart on the plate (quite a high dispersion) which is viewed at $\times 1500$, from which it follows that the fringes are 1/50th mm apart on the actual surface. For this to happen, a wedge angle of some 0.75° is required and, although relatively large, this is the smallest we can tolerate. It is note-

[1] S. Tolansky, *Multiple Beam Interferometry* (Oxford University Press, New York, 1948).

worthy that with such an angle the total effective cone of all the emerging beams, which contribute appreciably to the sharpening of the fringes, is considerable, for with our high reflectivities at least 60 beams are effective. The emerging light to be collected for adequate definition therefore fills a considerable fraction of the lens aperture even when the N.A. is 0.95. Indeed, with so large a wedge angle a high numerical aperture collecting lens is an absolute essential if high fringe definition is to obtain. We have long been aware of the fact that high wedge angles and low-aperture lenses give very poor definition. Thus we have the fortunate coincidence that a high numerical aperture lens is essential both for the high lateral resolution sought and for the high interferometric fringe definition aimed at. (It is just possible that the emerging wide cone of rays may improve the lateral resolution. For although the initial incidence is by a parallel beam, the collected beam diverges to such an extent that lateral resolution may well be greater than that for incident parallel light and lie nearer to the optimum value for correct convergent illumination. A detailed analysis of this would assuredly be very complex.)

As an example of the application of our procedure we will illustrate from some studies we are making on the topographical features of a natural dodecahedron face of a diamond. Such faces are frequently found striated. This particular face has on it unique features. It was somewhat cylindrically curved and this enables us to isolate a zero-order region to suit our convenience. It is merely necessary to rest the diamond on the matching flat to be effectively in contact and so secure the important condition of zero order in the field of view. These observations were made with a Vickers projection microscope, which is of the inverted metallurgical type for surface illuminating, the objective itself acting of course as a condenser of adequate numerical aperture. Multiple-beam interference fringes taken with a medium power lens, ×187.5, are shown in Fig. 1. This shows that there is a central patch region of zero order, surrounded with what are the equivalent of the multiple-beam Newton's "rings" for an approximately cylindrical surface. It is near this zero-order region which we proceed to examine with the high-power lens.

The key to the success of our observations lies in the use of an objective which has a correcting collar for correcting for cover glass thickness, the correct cover glass being used as the matching flat for producing the fringes. We have failed completely to secure anything like comparable fringe definition from the uncorrected type of objective normally employed for uncovered workpieces. In our case the 3-mm lens, N.A. 0.95, was set with correcting collar for a cover glass thickness 0.02 mm of which we possess adequate stocks. Observations were to be made in reflection a condition imposed by the nature of the diamond available. A cover glass was selected and both diamond and cover glass coated with multilayers (seven) of alternate films of magnesium fluoride and zinc sulfide. As has already been discussed such multilayers are highly advantageous for reflection fringes.[2] We have also repeated our observations satisfactorily with silver films of reflectivity exceeding 0.90. There is no difficulty in selecting a cover glass which is adequately flat over the very small field of view, which is a square of side a mere three-hundredths of a millimeter. It is easy enough to find regions as small as this which are flat to within a very small fraction of a light wave. Furthermore it is the repeated experience of this Laboratory that glass which is fire-polished can exhibit an astonishing perfection of smoothness locally.

Figure 2, is a direct microphotograph (×1000) without interference, illustrating the nature of the surface of the diamond, taken with the 3-mm lens. The surface is seen to consist of a striking pattern of small parallelogram regions, each enclosing angles of

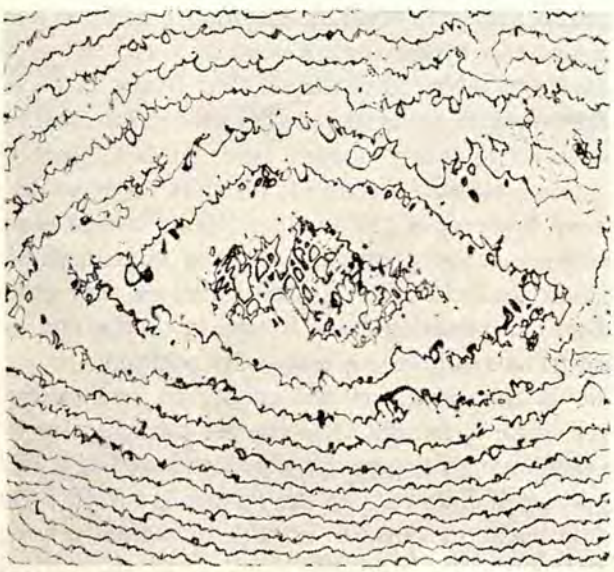

FIG. 1. Multiple beam interference fringes of diamond taken with medium power lens, ×187.5.

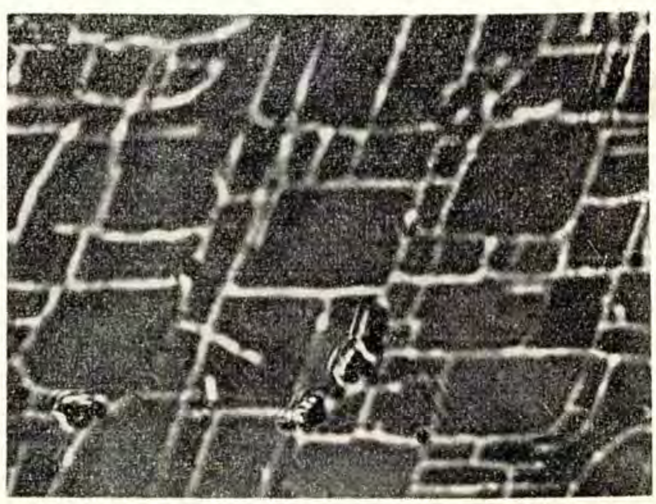

FIG. 2. Microphotograph (×1000) of diamond taken with 3-mm lens.

[2] Belk, Tolansky, and Turnbull, J. Opt. Soc. Am. 44, 5 (1954).

FIG. 3. Interference fringe pattern of diamond (×1000) taken with 3-mm lens.

$70\frac{1}{2}°$ and $109\frac{1}{2}°$. The sides are therefore strictly crystallographically oriented. We believe this form of growth in diamond has not previously been described. The parallelogram elements are small, ranging in area from some 5×10^{-8} sq cm to some 2×10^{-6} sq cm.

Figure 3 shows the interference fringe pattern secured at ×1000 with the 3-mm lens. The interpretation is as follows. In the upper half of the picture is the zero-order region. This consists of a pattern of high-dispersion fringes running over the parallelograms of Fig. 2. The path difference being here below $\lambda/2$, therefore this is an interference pattern of very high dispersion. There exists the condition of highly enhanced contrast due to the interference, a condition closely similar to that used in the crossed fringe technique,[1] although here we deal with reflection fringes. The extremely high contrast in the fringe pattern is, as formerly shown, primarily due to the low absorption in the multilayer reflector.[2]

In the lower half of the picture are two fringes, respectively, the first and second orders of the multiple-beam Newton's "ring" system. The fringe definition in the first order is exceptionally good. On the original it is recognizable that the second order has broadened slightly, but appreciably, relative to the first order. This difference is due to the fact that the gap for the first order is $\lambda/2$ and that for the second order is λ. So sensitive is the definition to the gap at these high magnifications that this slight increase in gap value makes a noticeable difference to the definition.

It is in these very sharp first and second orders that we have the combined high resolution both in lateral extension and in fringe definition. The fringe definition is of the best, being adequate even for very exacting measurement. At ×1500 the expected microscope resolution of 0.7μ corresponds almost exactly to 1 mm on the photographic plate. Comparison between micrograph and the interferograms show that indeed the fringe pattern is precisely contouring the surface detail to within the predicted resolution. It so happens fortuitously, that with the dispersion and fringe width adopted the widths of the fringes are themselves somewhat just below 1 mm. Fringe half-width is certainly less than 1/30th order, much nearer 1/50th order in fact.

The interferograms reveal that the parallelogram features are small convex units. They vary in height from a mere 200 A to some 900 A. The boundaries are revealed to be sharply defined ruts or channels. It is not our purpose here to discuss the crystallographic interpretation of these observations. It is of course clear that the interferograms contain a good deal of crystallographic interest and this is under active study. Most of these separate parallelogram regions are highly curved. The approximate curvatures can be computed from the fringe patterns by assuming that the elements are spherical segments. This is, of course, quite justified when the difference in scale in depth and in extension is recalled. Radii of curvatures vary from 0.67 mm to as little as 0.02 mm.

These features do not at all resemble any of the etch patterns which we have recently produced experimentally in this Laboratory on dodecahedron faces of diamond. They are without doubt an intriguing growth characteristic.

We make a special point of drawing attention to the considerable superiority of the fringes of the kind shown in Fig. 3 over those obtainable with high magnification two-beam interference microscopes of types, for example, such as the Linnik interference microscope. We have in this Laboratory used a Zeiss-Linnik interference microscope equipped with 4-mm lenses and operating at a magnification of ×750. The two-beam $\cos^2$ distribution fringes given by this instrument are of an altogether much lower order of sensitivity than are our multiple-beam fringes given with the 3-mm lens. This same superiority of our fringes is also clearly evident when they are matched with the numerous excellent two-beam fringes, recently shown by Grube and Rouze,[3] taken with a Bausch & Lomb variant of the Linnik instrument. Grube and Rouze exhibit a considerable range of interferograms with magnifications from ×150 to ×1250. For two-beam fringes these are good, yet we regard such interferograms as crude when compared with corresponding multiple-beam fringes, such as those illustrated here.

It is of some interest to make a rough computation of the smallest element of volume resolvable with our present simple system. Taking generous limits, it is

[3] W. L. Grube and S. R. Rouze, J. Opt. Soc. Am. 44, 851 (1954).

clear that we can resolve an area element of say $1\mu \times 1\mu$, and in this detection of a fringe displacement of 1/50th of an order is a modest claim. (On a correctly exposed negative this would correspond to a whole fringe width. Experience demonstrates that one can always do better than this, but we shall adopt this as a safe upper limit.) Such a volume element is some 5×10^{-15} cc. This quantity may well be overestimated by a factor of 2 or more, because of our generous tolerances. With the ability to resolve such small volumes, many important fields such as those of etching, corrosion, polishing, crystal boundaries, etc. become amenable for exploration. In these fields the early stages are frequently the most important, and the ability to detect and measure minute pits will certainly prove useful.