

OPTICAL STUDIES ON SURFACES OF NATURAL

AND SYNTHETIC CUBIC DIAMONDS.

THIS THESIS SUBMITTED TO THE UNIVERSITY OF
LONDON FOR THE DEGREE OF MASTER OF SCIENCE.

BY

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C7 6FEB1964

February, 1964.

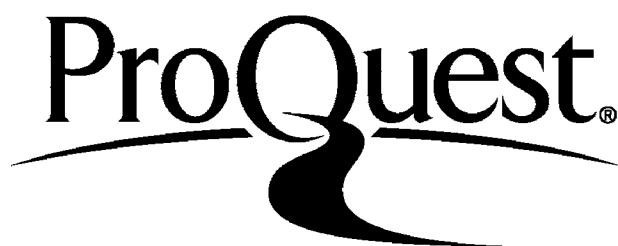
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ABSTRACT

The importance of diamond in modern technology, and crystal structure (with emphasis on diamond) are discussed. Theories of crystal growth are briefly reviewed. After describing previous work on the surface topography of diamond, that of diamond of the cubic habit is described in detail for the first time.

A brief review is given of etch studies on diamond surfaces. Etch figures obtained on natural cubic diamond surfaces and on polished sections of both cubic and octahedral diamonds are described. Two different types of etch pits were obtained on polished surfaces, and also observed on surfaces of synthetics, and the nature of these is discussed. Arrays of etch pits obtained on sections of cubes are described and related to the strain patterns.

Etch patterns obtained on sections of octahedra reveal that the diamonds are made up of three dimensional layers of different character. Ultra-violet absorption studies show that these layers are of type I and type II material. We have estimated, from observed etch pit densities, the number of dislocations in type I material to be in excess of 4×10^8 per mm^3 and in type II material as low as 6×10^4 per mm^3 .

Some evidence is given, drawing on our own observations of etch patterns and the work of others, to suggest that many diamonds may have grown around a central core. An attempt is made to explain the origin of etch pits on the natural faces and polished sections of cubic diamonds, and the parallel curved (convex and concave) layers within an octahedral diamond.

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CHAPTER I.

THE TECHNOLOGICAL IMPORTANCE OF DIAMOND

I.I. Introduction.

Diamond is a crystalline form of carbon. It is colourless and transparent in the pure ^{and structurally perfect} form. Since earliest times it has been prized as a gem stone, not only because of its rarity and beauty, but perhaps more particularly because of its great hardness and permanence. It owes its beauty to its high refractive index of 2.42, as compared with about 1.5 for glass, and to its high reflectivity of 18%, as compared with 4% for glass. It is ~~by far~~ the hardest material known to man being chosen as 10 on Mohs' scale of hardness and having a Vicker^os hardness number in excess of 10,000, as compared with about 800 for hard tool steels. The permanence of diamond is due in part to its resistance to abrasion, being abraded only by diamond itself, and also to its extreme resistance to chemical attack, being acted on only by strong oxidising agents at temperatures in excess of about 525°C.

Diamond occurs in a number of crystal habits (figure I.I). As with other natural crystals these shapes are in many instances far from ideal, very often for example the faces may be markedly curved. Of those crystals which are reasonably well shaped, by far the

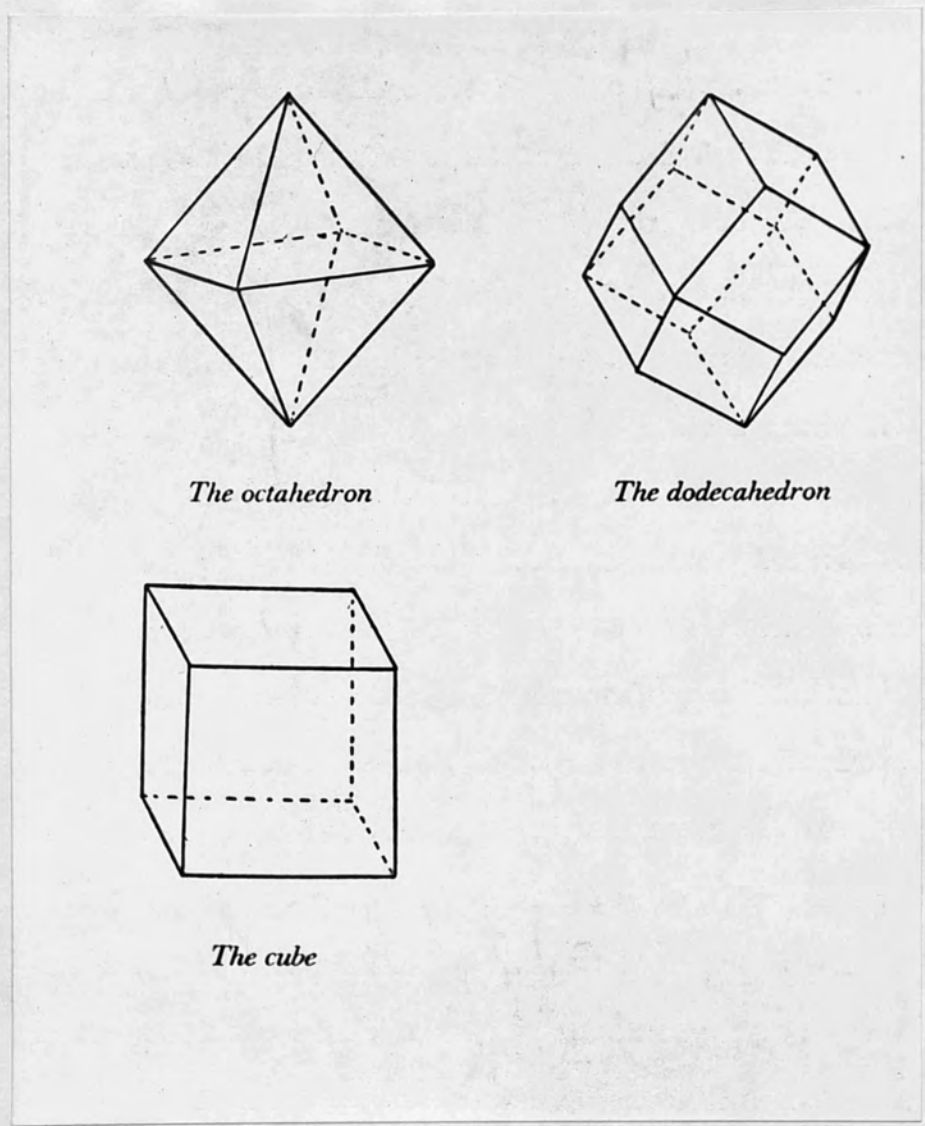


Figure I.I.

most common are those of forms related to the octahedron. It is crystals of this habit indeed which most nearly approximate to the ideal crystal shape. There are too a number of well known variants of this habit which occur from time to time. Such are the flat portrait stone in which two opposite octahedral faces have developed preferentially and the more common "macle" which is also more or less flat but has a twinning plane parallel to the two more prominent faces. Rhombic dodecahedra also occur commonly but they are rarely if ever found with flat faces. Cubes are rarely found and when they do occur their faces, though reasonably flat on a macro scale, appear to be frosted. These faces are in fact made up of numerous crystallographic facets, many of which may be quite flat. The form of the cube faces will be discussed in detail in chapter 5.

Diamond is an important technological material. An idea of the extent to which it is used may be gained from recent production figures. In 1954 (Moyar, 1955) world production was slightly in excess of 20 million carats, of which about 85% was estimated to have been marketed as industrial diamond. According to Tolansky (1962a) the annual production of diamond from all sources

is 25 million carats, of which about 2 million carats is synthetically produced.

Diamond is found either in alluvial deposits such as in Brazil and the Congo or in volcanic pipes as in the Kimberley mines of South Africa and in Tanganyika. (De Beers 1961; Tolansky, 1962a). It is believed that diamond was formed deep in the earth under high temperature and pressure, and subsequently brought to the surface in the volcanic pipes, in which it is present in about one part in 25 million. The alluvial deposits presumably originated from such pipes by weathering and subsequent transportation by water to their present sites. The nature of the diamonds varies from pipe to pipe and deposit to deposit. The small natural cubic diamonds which form part of the study of this thesis come from surface alluvial deposits in the Congo where they are found in small numbers. They are of uniform size and similar stones are not found elsewhere.

Because of the large potential demand for diamond as a cutting tool and the relatively limited supplies of natural diamond, production of synthetic diamond on a commercial scale was undertaken about 1951 by General Electric in the United States of America. The first announcement of their success was in 1955 (Bundy et al., 1955)

and they were subsequently produced also at the Adamant Research Laboratories of the Diamond Corporation in South Africa. While the diamond produced up to the present time is suitable only for use as "powder", it represents an appreciable part, namely 10%, of all diamond used industrially. Research on the production of synthetics is proceeding at these and other laboratories.

I.2. Properties of Diamond.

The carbon atoms composing diamond consist of a nucleus and two shells of electrons, the inner being a complete shell has two electrons and the outer has four. A complete second shell requires eight electrons. The atoms combine by sharing electrons in such a way that each may be considered to have a complete set of eight. How this is done may be illustrated by reference to figure I.2 (Custers, 1956). In a crystal each atom is surrounded by four nearest neighbours and by sharing two electrons in a co-valent or homopolar bond with each neighbour, each supplying and receiving one, a total complement of eight electrons is associated with each atom. The crystal may then be considered as a huge molecule made of many atoms, This arrangement of atoms in a crystal is known as the diamond structure and is found also in silicon, germanium and grey tin. This arrangement of the atoms in diamond was positively

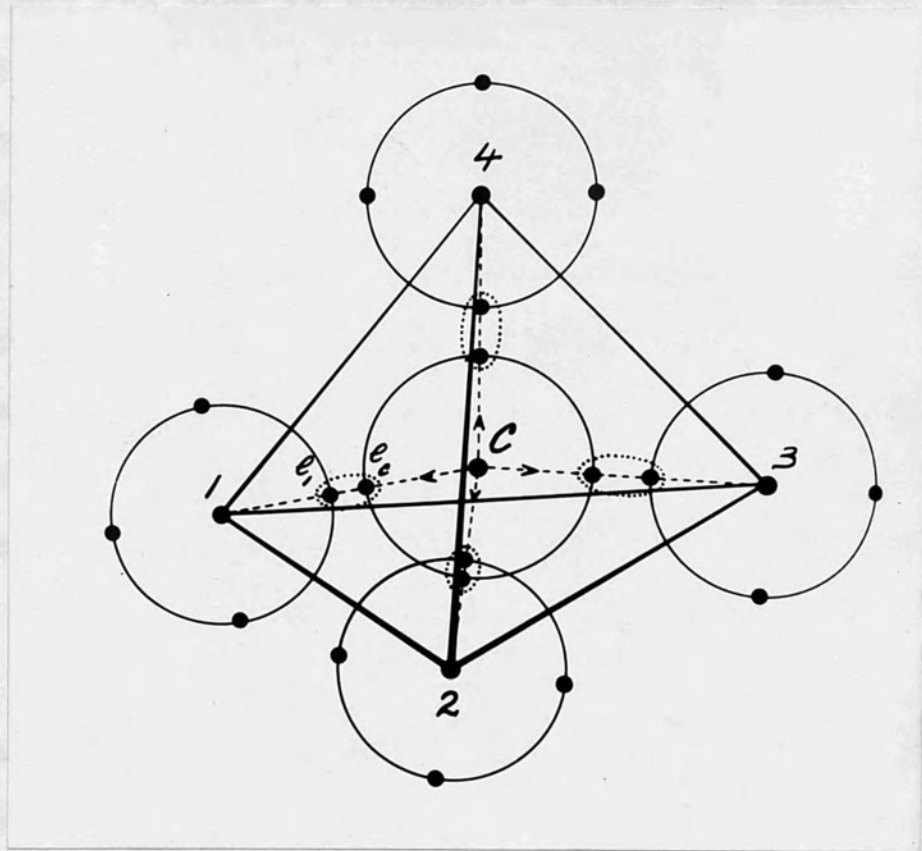


Figure I.2. (Custers, 1956).

established by W.H. & W.L. Bragg (1913). It is the most close packed crystal structure of all and, particularly in diamond, the bond is extremely strong and once formed it is difficult to break. This accounts for the extreme hardness of diamond and its resistance to abrasion.

Crystalline substances are anisotropic as regards many of their physical properties. This is so as far as the hardness of diamond is concerned. Some faces are more readily worked than others and certain directions on the faces are preferred. The dodecahedral and the cube faces are appreciably softer than the octahedral faces. In the industry diamond is said to have "grains", that is directions in a crystallographic plane in which abrasion is difficult. The dodecahedral plane has two such grain directions, the octahedral three and the cubic four. This is shown diagrammatically in figure I.3 (Grodzinski, 1953). It is because of the presence of these hard and soft directions that diamond can be ground and polished. Normally when a material is ground an abrasive which is somewhat harder is chosen. In the case of diamond no such harder material is available. However some of the hard "directions" of the abrasive diamond powder or paste, when presented to a softer face against the grain, that is in a soft direction, are able to cut.

As well as being hard, diamond is also brittle. While it will resist huge pressures, comparatively modest impacts blow are sufficient to shatter or cleave it. The brittleness of diamond is due to its crystal structure. It is a very hard material, but it is also very brittle. This is because of its crystal structure. It is a very hard material, but it is also very brittle. This is because of its crystal structure.

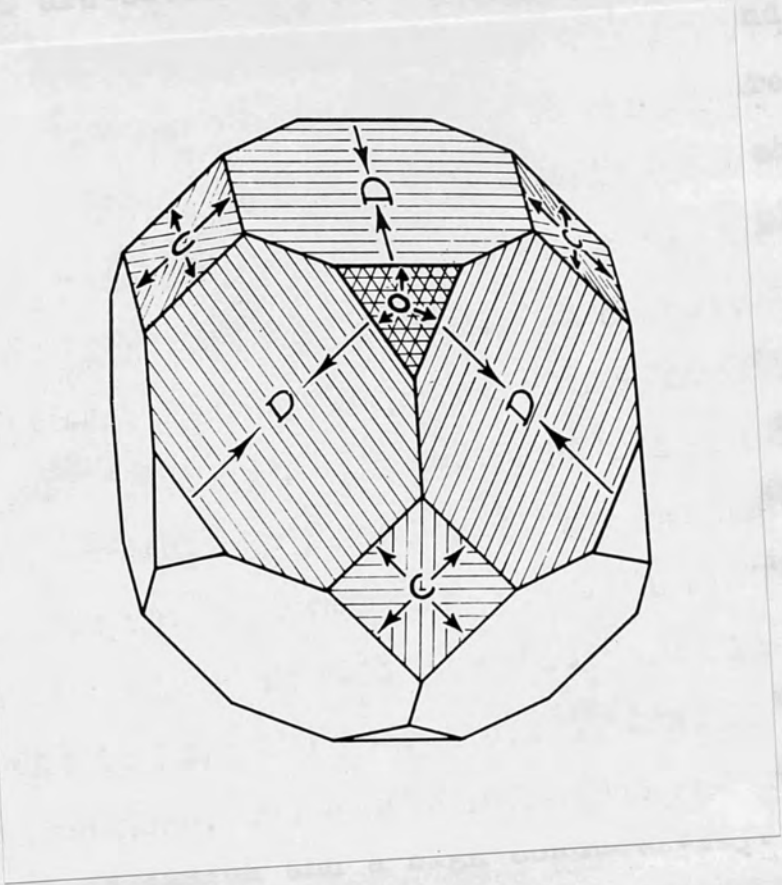


Figure 1.3. (After Grodzinski, 1953).

... per degree Celsius as compared with about 12 p.p.m. for steel, for tool steels and 3 p.p.m. per degree for glass. It is of the same order as that of lava which however is only extremely small at ambient temperatures (Clave & Laby, 1957). The thermal conductivity of diamond is much the same as that of aluminium. This is due to its resistance to thermal shock and withstanding the high

As well as being hard, diamond is also brittle. While it will resist huge pressures, comparatively modest impulsive blows are sufficient to shatter or cleave it. The brittleness is made use of when crushing diamond to form an abrasive powder and poorly shaped stones are frequently cleaved to produce more satisfactorily shaped ones. Diamond cleaves parallel to the octahedral planes. There are thus four cleaving directions.

Because of its hardness, low compressibility and ability to resist abrasion diamond is useful as a cutting tool, for indenting hardness testers, stylos and the like, But because of its brittleness care is necessary not to subject it to mechanical shocks.

The thermal properties of diamond have an important bearing on its use as a cutting tool. It has a very low coefficient of expansion and a high conductivity. The coefficient of expansion is 1 p.p.m. (part per million) per degree Celsius as compared with about 12 p.p.m. per degC. for tool steels and 3 p.p.m. per degC for pyrex glass. It is of the same order as that of Invar which however is only extremely small around ambient temperatures (Kaye & Laby, 1957). The thermal conductivity of diamond is much the same as that of aluminium. Thus it is that it is resistant to thermal shock and withstands the high

temperatures developed in the high speed cutting of metals. Its thermal properties together with resistance to wear make diamond tools eminently suitable for precision machining.

Except for relatively few specimens, diamonds are good electric insulators, having a resistivity of between 10^{14} and 10^{16} ohm cm. Custers (1952, 1954) reported ~~con-~~
~~ductivities~~ ^{resis} of 10^8 to 25 ohm cm for diamonds of relatively low ~~conduc~~ ^{resis} tivity and suggested they be placed in a special category to be called type IIb. These diamonds show phosphorescence when irradiated by light of wavelength 2500A and have other semi-conducting properties which have been the subject of a number of research papers (e.g. Champion and Wright, 1959; Dyer and Matthews, 1958; Goldsmid et al, 1959).

1.3 Diamond as a Cutting and Forming Tool

In the production of engineering components it is necessary for them to be made efficiently and consistently with an appropriate degree of dimensional control and with surfaces whose characters are suited to their function. One important factor influencing the cost of machining is the life of the tool between "dressings" and the greater the demand on dimensional control and surface finish the shorter the tool life tends to be. Not only is the dressing of the tool usually relatively expensive but production

necessarily comes to a halt while the dressing is done and the tool re-set or while a replacement tool is set. Particularly during World War II and since, with the development of fast revving engines and bearings and the increased use of high precision equipment, there has been a tendency for increased use of diamond tools. They retain their shape and the quality of their cutting edges because of their resistance to abrasion, and this leads to long life without the need for reforming them. The economies effected by this increased efficiency very often more than off-set the high initial costs as well as the high costs of reforming. There are of course some machining processes such as the machining of hard metal carbides where diamond is the only appropriate cutting agent.

Diamond used industrially is classified and graded in many ways (e.g. Grodzinski, 1953; Freeman, 1956). The most important factors taken into account are size, crystal habit, absence of impurities, opacity, soundness and texture. What really matters of course is how much work can be obtained without re-dressing and without fracture. Obviously the requirements for material used as abrasive are less stringent than those for single point tools. While the very best diamonds are selected for gem stones, those used for dies are only little inferior. Perhaps only colour is of less importance in this instance.

We may consider diamond tools as divided into four classes as follows:

1. Single stones, of high quality, used as dies.
2. Single stones used as cutting and forming tools such as are used for turning and boring, and for dressing grinding wheels.
3. Small stones, multiply set, such as are used in drills.
4. Diamond grit, made from crushed diamond boart and synthetics, which are used either as free abrasive powder or paste or in bonded tools.

Even a superficial outline of the properties and uses of diamond serves to show its importance in modern technology. It explains why a country like the United States of America considers diamond of strategic importance and is interested in the production of synthetics. The importance is an increasing one as engineering processes call for closer geometrical tolerances and for finer surface finishes and for the use of hard materials now being developed for specific purposes.

CHAPTER 2.CRYSTAL STRUCTURE AND HABIT WITH SPECIAL REFERENCE
TO DIAMOND.2.1 The Crystalline State.

A crystal was once considered primarily in relation to its outward form. For example Dana (1898) defined a crystal as a "regular polyhedral form bounded by smooth surfaces, which is assumed by a chemical compound, under the action of its inter molecular forces, when passing, under suitable conditions, from a state of a liquid or gas to that of a solid". Many naturally occurring crystals do not have smooth faces and this is the case with diamond of cubic habit as will be discussed in chapter 5. The external form of many crystals grown from the melt in the laboratory is almost entirely dependent on the physical shape of the apparatus and the conditions in which they are grown. It was early recognised that the regular geometric form which a crystal tends to acquire, results from its definite internal structure, a crystal being built up of a large number of identical three-dimensional unit cells, and by the tendency for it to grow in many cases by the deposition of sheet layers.

Although the internal structure is the essential feature of a crystal, nevertheless much information about this structure can be determined from the external form,

i.e. from its habit and surface topography. Early crystallographers were able in many cases, through studies of crystal symmetry and the optical properties of crystals, to determine the basic crystal structure. Even since the powerful X-ray techniques were introduced by Friedrich, Knipping and Laue in 1912 and W.L. Bragg in 1913 and many uncertainties about the structure of crystals of a number of materials were removed, the older techniques still have their place in the study of crystal structure.

When a substance crystallizes it always does so in one of perhaps several definite crystal classes peculiar to its atomic or molecular configuration. The angular relationships between the crystal faces of any one of these crystal types is always the same although some faces may be suppressed and the habit of the crystal may vary. Crystallographers have classified crystals into 32 different crystal classes (or point groups) within 7 crystal systems distinguished by their external symmetry characteristics. The way in which these point groups may be repeated is not unique for all of them and the patterns in which they repeat themselves are called the space lattices (or Bravais Lattices) of which there are 14 and these give rise to 230 possible space groups.

Carbon crystallizes in two allotropic forms, diamond and graphite, and the arrangement of the carbon atoms in the crystal lattice is different in the two cases. In section 1.2 it was shown how the carbon atoms combine in diamond to form a crystal which may be considered as a large molecule. The unit cell of the diamond lattice is shown in figure 2.1. It may be considered as a face-centered cubic lattice with four additional carbon atoms B within the cell in such a way that each is equally spaced from four other carbon atoms A (a corner atom and 3 neighbouring face-centered atoms), there being only 1 carbon atom on each cell diagonal. Although 18 atoms are involved in a unit cell, in fact a cell is composed of only eight atoms, all but the four atoms B in the body of the cell are shared. Those on the faces are shared with neighbouring cells so that only half the atom may be considered as belonging to each, while those at the corners are shared between eight cells, so that only one eighth may be considered as belonging to each. In graphite the carbon atoms are arranged in nearly plane layers, each of which is a hexagonal network. The sheets are so superposed that every second atom lies vertically above a carbon atom in the sheet below. A comparison of the arrangement of

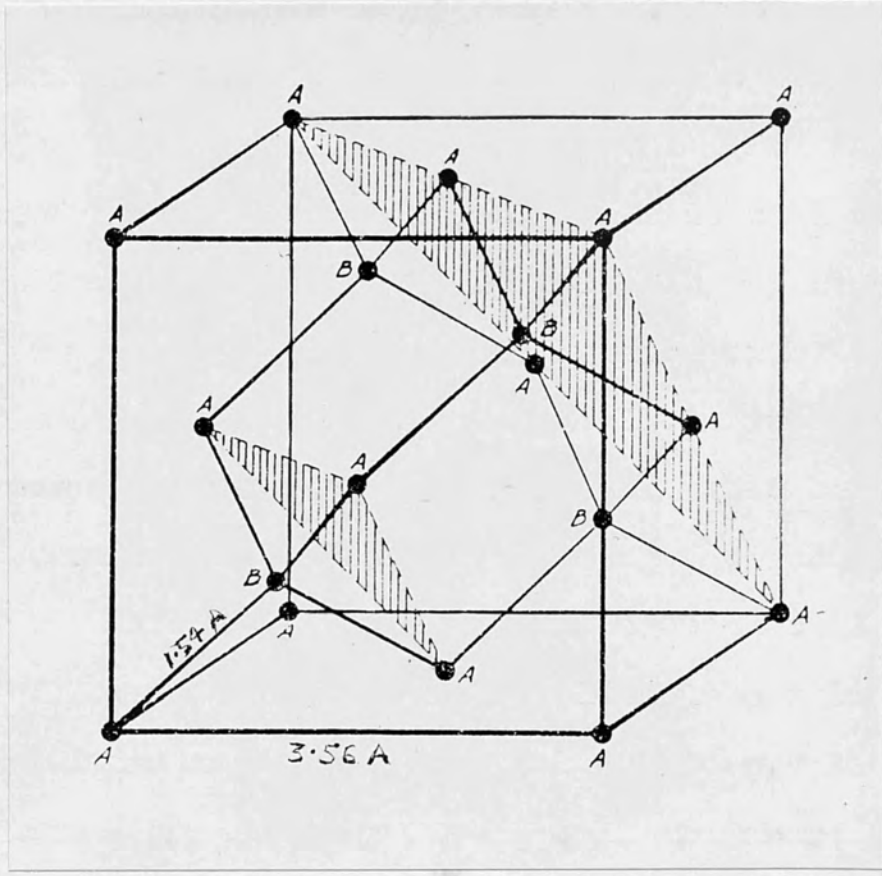


Figure 2.1. Unit cell of diamond crystal lattice.

(After Bragg, 1937).

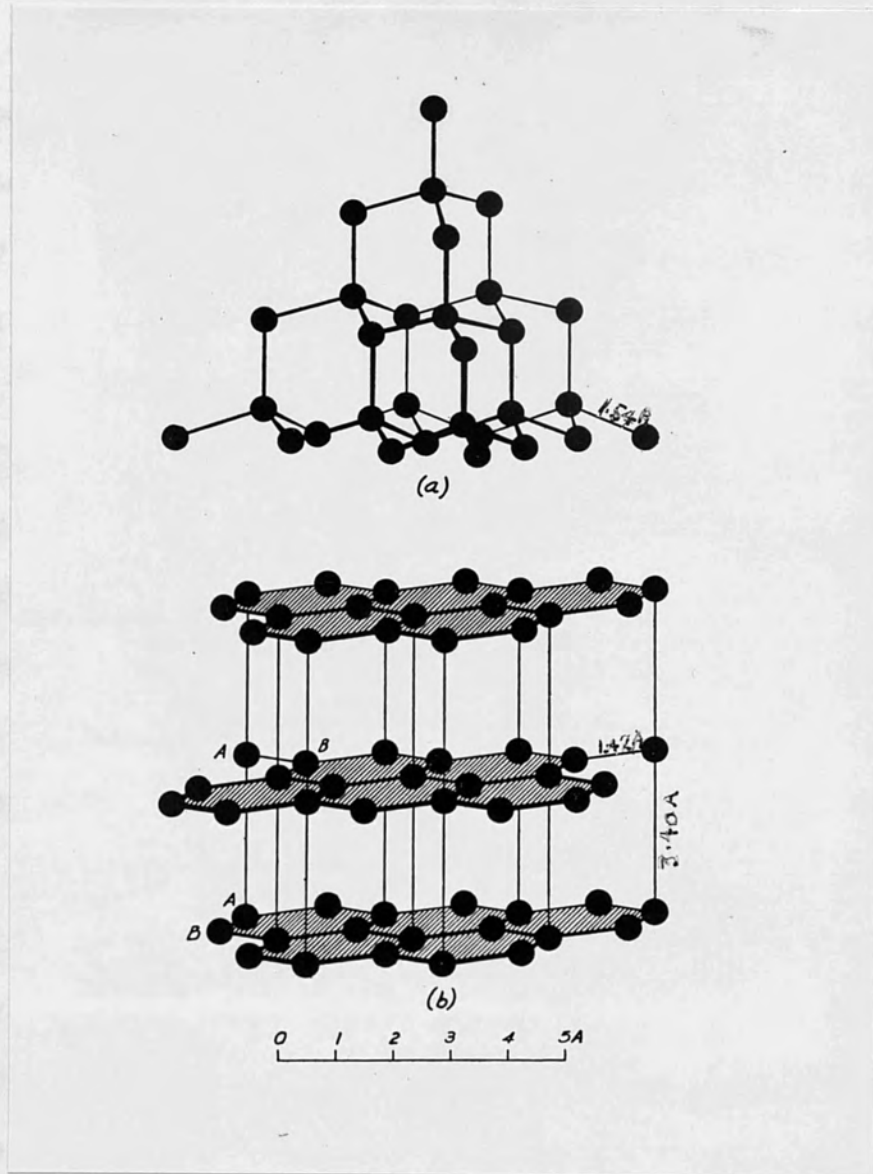


Figure 2.2. (a) Structure of Diamond.

(b) Structure of Graphite.

(After Bragg, 1937).

the atoms in diamond and graphite is shown in figure 2.2. The atoms in the hexagonal layers are linked by strong homopolar bonding and are closer even than the carbon atoms in diamond. The links between the rows are by van der Waals forces, and these are very much weaker.

Although the crystal structure of diamond is always the same, it is found in a number of crystal habits as shown in figure 1.1. Very often of course the crystal habit contains more than one form, e.g. the cubic diamonds to be discussed below in chapter 5 have, as well as six cubic faces, twelve dodecahedral faces and occasionally octahedral faces are present. Modifications of habit which occur are dependent on the conditions of growth.

The faces of crystals, as stated above, are at fixed angles to one another. The directions of the faces may be described by the Miller indices $(h k l)$ and for perfect crystals the Miller indices of the faces are all small numbers and are known as low index faces.

Not all actual faces are low index faces. Often a crystal will have bright well-formed faces which are not. Such are the vicinal faces which sometimes replaces a low index face. They are symmetrical in accordance with the symmetry of the crystal. A face may not be a flat continuum but be made up in fact of a number of small facets. Such is the case, as stated above, with the cubic

diamonds to be described in chapter 5.

An atom consists of a small nucleus of atomic number Z and of diameter $\sim 10^{-5} \text{A}$, and a surrounding series of shells of Z electrons, the atom having a diameter of $\sim 1 \text{A}$. It is chiefly the electrons in the outermost shell which take part in chemical bonding. Four types of bonding are recognised between atoms: ionic, homopolar, metallic and van der Waals.

In the ionic (or heteropolar) bond the bonding results from electrostatic attraction between oppositely charged ions. NaCl is a typical example of this type. The structure of an ionic crystal is determined largely by geometrical considerations (the number of ions of one charge which can assemble around an ion of the opposite charge) and also by the necessity for the crystal to ~~retain a~~ ^{remain} neutral ~~charge~~. The distance between atoms is large relative to the diamond lattice in which atoms are linked by homopolar bonds. In ionic crystals the ions are kept apart by the repulsive forces between the shell electrons, each ion retaining its identity without any over-lapping of electron shells. The large separation of the ions is reflected in the relatively low hardness, melting point, thermal expansion and electrical conductivity.

The homopolar bond is due to the sharing of electrons as in the case of diamond as discussed in section 1.2 (see figure 1.2). The number of configurations which the atoms of a crystal can take up is strictly limited by the bonds being disposed in some characteristic spatial configuration. In the electron sharing the electron systems overlap and the atoms are brought into relatively close proximity. Because of this, the strength of the bond is very great compared with the ionic bond in the case of atoms of small atomic diameter such as carbon (atomic number 6). Tin (atomic number 50), on the other hand, where the bond is weaker, has many of the properties of a metal.

The atoms of a metal may be considered to ionize, giving rise to positive ions and free electrons. The type of bond to be found between these metallic atoms differs from the ionic bond in that the bonding forces in general are non-directional. This tendency leads to simple packing of atoms in regular arrays which have a tendency to acquire a minimum volume. Thus many metal (and alloy) crystals tend to be in the close packed face-centred cubic and hexagonal close-packed systems. Most of the physical properties of metals (thermal and electrical conductivity, opacity and high reflecting power) derive from the presence of the free electrons. The maleability

of metals is due to the undirected nature of the metallic bond which allows close-packed layers to glide one over the other with relative ease.

The van der Waals (or residual) bond is usually much weaker than other types of bond. It is of importance in the case of the inert gases in solid or liquid form, in organic crystals, and is responsible for the linkages between the close-packed hexagonal planes of graphite. The effect is due to the fact that a neutral atom can acquire a polarisation under the influence of an electric field and even two neutral isotropic atoms will induce weak dipole moments in one another due to the fluctuating moments they possess due to the existence of virtual excited states.

2.2. Imperfections in Crystals.

The crystals we have considered so far are perfect or ideal ones. The continuous ordered lattice does indeed exist over small distances which are yet large compared with the inter-atomic spacings. A number of defects in crystal lattices have been recognised. Many properties (e.g. optical) of crystals can be discussed satisfactorily in terms of the ideal lattice but some properties (e.g. strength) do not agree with the theoretical by a number of orders of magnitude unless the lattice defects are taken into account.

The assumption of the presence of crystal defects is necessary to make theories of crystal growth quantitatively satisfactory. This will be discussed further in chapter 3. Frank (1951) classed as "good", crystals in which the strains and density of atomic defects are small enough to allow unmistakable correspondence with the ideal lattice and all other crystals as "bad". Defects are classified as point, line and plane defects depending on the number of dimensions over which they extend.

Point defects include "vacancies" and foreign and interstitial atoms. In point of fact the crystal lattice may be disturbed over a region of a number of atomic spacings. A number of point defects may occur together to give "divacancies" or "melted" regions. In the latter the number of atoms is the same as for the ideal lattice but they are strongly disordered.

In line dislocations the bad crystal forms a line. The idea of the edge dislocation was introduced by Taylor (1934) and Orowan (1934) to account for the large discrepancies in theoretical and observed strength of crystals. Burgers (1939, 1940) introduced the idea of the screw dislocation and showed that the low-angle grain boundaries in metal crystals could be explained in terms of arrays of dislocations. Frank (1950) extended the area of application of dislocations by showing that a suitable

network of dislocations can account for any type of mis-orientation in any direction of a mosaic structure. The simplest types of line dislocation are the edge dislocation, which is normal to the slip vector, and the screw dislocation, which is parallel to the slip vector. Diagrammatic illustrations of these two types of dislocation are shown in figures 2.3 and 2.4.

A Burgers circuit is a path which closes on itself in a real crystal. If the closed Burgers circuit in the real crystal has an associated path which in the ideal or reference crystal does not close on itself then the circuit encloses one or more dislocations, and the vector required to complete the circuit is called the Burgers vector. Frank claims that because a Burgers circuit can be displaced continuously along a dislocation line without change in its Burgers vector, a dislocation cannot terminate within the crystal. If a number of Burgers vectors meet at a point their total Burgers vector is zero.

Planar defects include "stacking faults" and "grain boundaries". Stacking faults occur when two regions of good crystal are displaced by less than a lattice spacing whereas grain boundaries separate regions of different orientation.

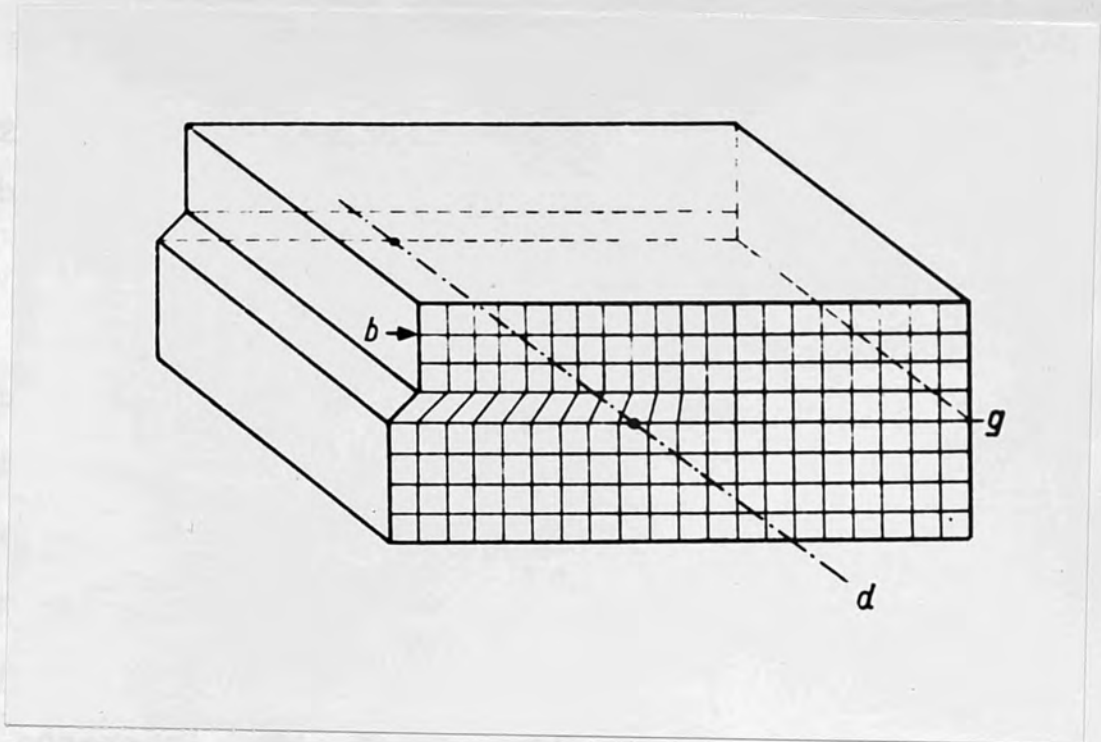


Figure 2.3. Edge dislocation (After van Bueren, 1960)

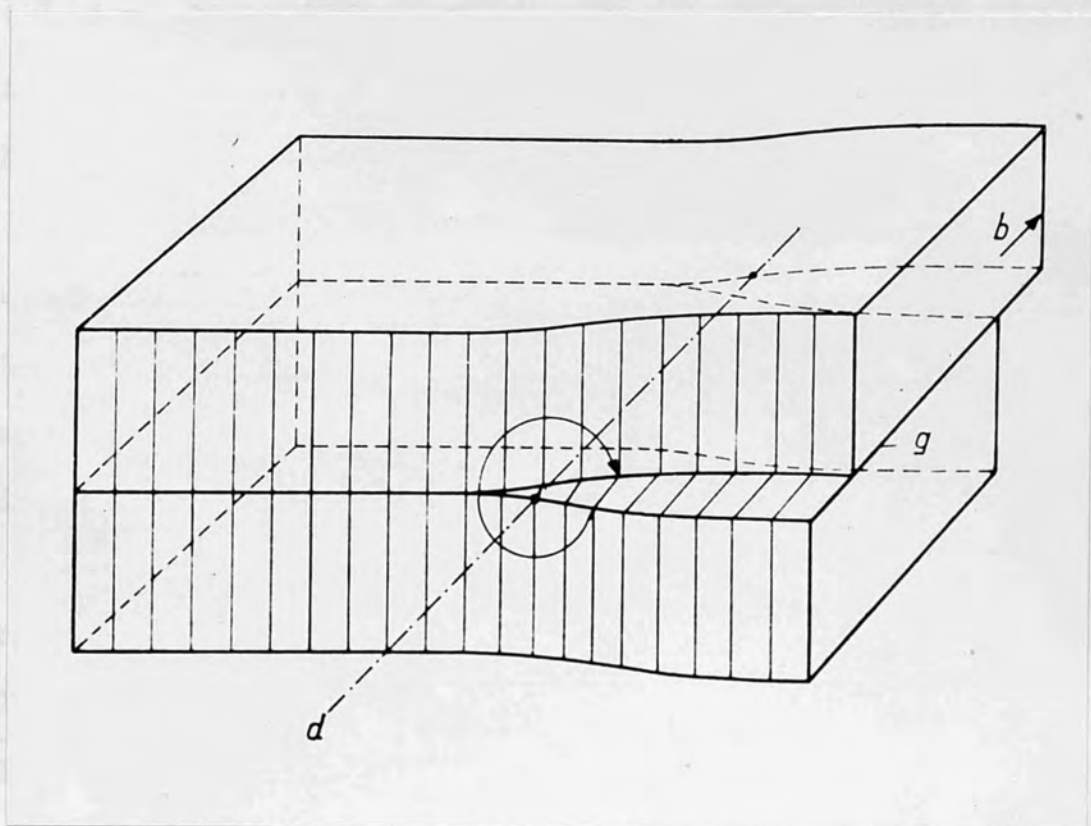


Figure 2.4. Screw dislocation (After van Bueren, 1960)

2.3 The Crystal Structure and Habit of Diamond.

The crystal structure of diamond was discussed in section 2.1 and is illustrated diagrammatically in figures 2.1 and 2.2. The nature of the co-valent bond is shown in figure 1.2. The X-ray analysis by W.H. and W.L. Bragg (1913) finally resolved a controversy which had been going on since the nineteenth century. A small number of crystals having the tetrahedral habit had been found, and this led some crystallographers to believe that the diamond possessed tetrahedral symmetry. Miers (1902) for example argued that because of the grooves found in many octahedra along their edges, the octahedral form was in fact due to supplementary twinning of tetrahedra. The etch patterns on the cubic sections shown in figures 7.30 to 7.40 below show in fact that these grooves are due to dissolution and re-growth. Finally X-ray analysis showed the diamond structure to be highly perfect, and established it as having octahedral symmetry, having 9 reflection planes as well as 13 axes of symmetry (3 tetrad, 4 triad and 6 diad).

In section 1.1 it was stated that diamond crystallised in a number of habits, octahedral, dodecahedral and cubic. Of these only the octahedral is found to occur naturally having anything like a perfect crystal habit. Some synthetics recently seen by us and

discussed in chapter 8 have a near perfect habit which consists of both the octahedral and cubic forms, and sometimes in addition the dodecahedral form much suppressed. (see figure 8.1).

Even amongst octahedra, more often than not the crystal faces are found to be curved. It is rare indeed to find a dodecahedral face which is not grossly curved, and of course cube faces are multi-faceted as will be discussed in chapter 5.

2.4. Some Effects of Lattice Defects in Diamond.

Robertson, Fox and Martin (1934) recognised differences in the absorption of infra-red and ultra-violet by various diamonds and divided them into type I, opaque at 8μ in the infra-red and below 3000\AA in the ultra-violet, and type II, transparent at 8μ in the infra-red and beyond 3000 to 2250\AA in the ultra-violet. They also observed differences in the appearance and morphology of the two types, type I exhibiting faces with coarse oscillation steps whereas type II showed a finer laminar structure (spacing 1 to 10μ) parallel to octahedron faces, type II being much more nearly isotropic optically; and differences in photoconductivity, type I showing very little photoconductivity while that of type II was marked.

Diamonds having relatively high electrical conductivity were discovered by Custers (1952,1954). They showed absorption spectra similar to type II diamond. He suggested they be placed in a new class to be called type IIb, to distinguish them from old type II, now to be called type IIa.

It is expected that some other properties of diamond might show a correlation with the absorption spectra. Wilks (1952) for example has found a difference in the cleaving properties, type II diamonds exhibiting cleavage which is more nearly perfect.

Champion (1952) established that there is a good correlation between the electrical counting properties of diamond and the wavelength of the ultra-violet transmission limit. In further studies (Champion, 1953) he came to the conclusion that good counters are composed of layers of highly perfect crystalline material (preferably 10μ thick) separated by relatively few and much thinner partial barriers of imperfect material. Wide barrier layers lead to poor counting properties. These ideas were carried further and a theory using the concept of a defect bond was developed (Champion, 1956) to explain many of the physical properties of diamonds. The theory leads to the suggestion of a new classification of diamonds based on the number and type of defects present.

CHAPTER 3.

CRYSTAL GROWTH.

3.1 Introduction.

In the laboratory under suitable conditions crystals may be grown from supersaturated solutions, from the vapour, from the melt, by electrodeposition, or by thermal diffusion. By an appropriate annealing process some crystal lattices may be changed from one type to another, and strain-anneal cycles have been used to annihilate crystal boundaries and so produce large crystals. Crystallization may be associated with chemical reactions of association and dissociation. From solution or from the vapour it may take place under suitable conditions of supersaturation, or from the melt when the molten liquid is under-cooled by an appropriate amount.

Two main theories of crystal growth are current. The one is a molecular kinetic theory due largely to Volmer and Weber (1926), Kossel (1927), Stranski (1928), Volmer (1932), Kaischew and Stranski (1934) and Becker and Doring (1935), and deals with ideal perfect growth. According to this approach supersaturations of 50% are necessary for growth from the vapour or from solution. In practice crystal growth can take place at supersaturations much less than this, in fact less than 1%.

The dislocation theory of Burton, Cabrera and Frank (1949,1951) seeks to resolve this difference and their theory of imperfect growth incorporates the idea that lattice defects, mainly as screw dislocations, introduce steps and kinks on the crystal surface and these act as sites of crystallization even at low supersaturations.

3.2 Ideal Perfect Growth.

If the vapour pressure above a liquid phase is greater than the saturation vapour pressure, the tendency for large size clusters of atoms or molecules to form increases. Unless, however, they reach a critical size where they become stable they will disperse again and the vapour will remain supersaturated. Volmer and Weber (1926) worked out a theory of nucleation of liquids from the vapour but the arguments may be extended in principle to include nucleation of solids from the vapour and from solution. Frenkel (1945) has shown that a saturated vapour contains clusters of more than 1000 molecules, the number and size increasing with supersaturation.

Once a stable nucleus has formed growth may continue. According to Volmer (1932) crystallizing particles may nucleate on the surface to form an adsorbed layer. When such a particle arrives at the surface it loses part of its latent heat and becomes bound to the

surface about which it can migrate. It subsequently becomes incorporated in the crystal lattice. The idea of an adsorbed layer has since been modified but not entirely rejected. It is now believed that once an atom or cluster becomes attached to the surface it can migrate across it but nevertheless nucleation can still occur without assuming mobility.

For growth to take place the theory requires that when crystallizing particles reach a surface there must be two dimensional nucleation at a site on the surface. The attractive and repulsive forces depend on the state of the surface and size of the crystallizing cluster. For a surface in which the sites in a layer are all filled the size which the cluster must reach before it can become attached is very much greater than where there are steps on the surface and hence a much higher supersaturation is necessary. For atomically smooth surfaces it is probable that the growth rate depends very largely on the rate of nucleation. Once a nucleus has formed, growth of a sheet layer on a face is probably rapid. This is the idea of Kossel's (1927) "repeatable step". Because for high index faces the rate of growth of a sheet layer is less than the time required for nucleation, the latter controls the rate of growth. For high index faces, which may be considered to be

stepped, nucleation will be easier but, because of their fast growth rate, these surfaces will generally tend to disappear.

3.3 Ideal Imperfect Growth.

Frank (1949) has pointed out that the above method of ideal perfect growth requires for crystal growth from the vapour supersaturations of a factor of ~ 10 for self nucleation, ~ 5 for new liquid drops, and ~ 1.5 for the formation of two-dimensional monolayers. It is found in practice that crystals will grow at supersaturations of less than 1%. For example iodine crystals will grow at a supersaturation of 0.8% (Volmer and Shultze, 1931). To explain the discrepancy between the theory and practice Burton, Cabrera and Frank (1949, 1951) suggested the presence of dislocations. Imperfections, mainly as screw dislocations, are considered to occur in the earliest stages of growth, giving rise to steps on the crystal faces. Growth can then take place without the necessity for two-dimensional nucleation. If a single screw dislocation emerges normally at a crystal face and nucleation takes place there, the step persists and growth may continue without interruption, the direction of the step spiralling around the crystal face. If there are a pair of dislocations, right and left handed, a family of outward growing closed loops results. In the case of

random distributions of dislocations, more complicated interactions occur. If however the solution concentration is low, so that there is competition for crystallizing particles, only one, usually the largest, will grow.

The thickness of these layers is of course on an atomic scale and they are not visible. The fact that visible advancing steps occur may be explained by "bunching" which is assumed to occur where advancing atomic layers are held up behind stationary ones.

On a microscopic scale a growth spiral should take the form of a flat cone with its surface inclined at an angle depending on the supersaturation, about 1 minute for 1% supersaturation. Taking into the account the dependence of the rate of advance of the step on its direction we should expect to see, not a flat cone, but a sharply defined pyramid with symmetry appropriate to the crystal face.

Calculations show that according to this theory the growth of crystals from the vapour will take place for supersaturations of the order of 1% (Frank, 1949). Agreement with practice is thus quite good. Frank further suggests that agreement should also be obtained for growth from solution, and perhaps for growth from the melt.

3.4 Growth from the Melt.

Growth of crystals from the melt occurs when conditions are arranged for atoms of an under-cooled liquid to "freeze out" on to a seed crystal. Such a seed may be introduced or may occur spontaneously. Usually in the latter case many potential nuclei are formed and one seed will tend to grow at the expense of the others. An important problem in crystal growth from the melt in the laboratory is the controlled removal of the latent heat which is given up at the crystal face as crystallization occurs. This is usually transferred by conduction along the growing crystal but when the melt is under-cooled it may be conducted into the melt. The rate of crystal growth is governed by the rate at which the latent heat is conducted away from the solid-liquid interface.

The form of the liquid-metal interface is usually governed by the rate of diffusion of latent heat and of rejected soluble impurities away from the interface (Hurle, 1962). The surface is usually rough on a coarse scale and without crystallographic significance, but step-like and cellular structure, as well as dendritic

forms, do occur. In the case of some semi-conductors and semi-metals, e.g. gallium, bismuth, germanium and silicon, faceted growth has been observed (e.g. Hurle, 1962). Evidently some surfaces tend to be smooth. Jackson (1958) has examined the conditions for which the surfaces of a number of substances tend to be smooth or rough by evaluating the surface free energy of an atomically smooth surface, and surfaces on which newly deposited atoms are randomly arranged as a function of atomic sites occupied, and comparing these. He concludes that all surfaces of melt grown crystals should be rough with the possible exception of a number of marginal cases including gallium, germanium and silicon. These are surfaces on which faceted growth has been observed.

3.5 Modification of Crystal Habit.

The number of large crystals which occur with uniform simple shapes, with smooth flat faces, and in which the angles between the faces are repeated for similar sets of faces, and from crystal to crystal lead us to the belief that crystals tend to grow in a standard shape. Stranski (1949) has considered, from the crystal structure and the character and magnitude of the bond forces, crystal shapes which should occur with minimum surface energies for a given volume. In

most cases actual crystals acquire these forms if grown under appropriate conditions of purity and low supersaturation. The fact that certain faces appear on a crystal indicates that growth on these faces (i.e. perpendicular to them) is slow relative to growth on other faces. In other words fast growing faces tend to grow out. The faces which appear are usually the more close packed. For example the most close packed of diamond faces is the octahedral and the octahedron is the standard shape.

But many crystals grow in shapes which are different from the standard in that faces with indices different from those of standard shapes occur. Not only may additional faces be present but some or all of the faces of the standard shape may be suppressed. The crystal faces, in some cases, are curved or irregular. Factors which are known to influence the shape are the degree of supersaturation, the solute and impurities which may or may not become incorporated in the lattice.

The presence of certain impurities even in minute traces has long been known to influence and often completely change the crystal habit by preferential adsorption on some faces, or by inclusion in the lattice and in so doing in some cases altering the growth rate.

Any factor which affects the relative rate of growth of the faces will on this very account tend to change the habit. For example, faces which grow only slowly at low supersaturation, and therefore are dominant faces, may grow more readily under conditions of high supersaturation.

CHAPTER 4.

SURFACE TOPOGRAPHY OF DIAMOND.

4.1 Introduction.

Many diamonds occur having rough, uneven and curved faces. On octahedra flat faces occur more frequently than on the other forms. Dodecahedral faces, except in rare instances, are markedly curved. Cubic faces are never smooth and flat and always have a frosted appearance.

On the surfaces of almost all natural diamonds characteristic features and figurings occur. Whether these figures are growth feature or whether they are due to dissolution or etch has been debated for many years. They have been studied in the hope that they would give information about the conditions and manner of diamond growth.

Fersmann and Goldschmidt (1911) believed that practically all diamonds have at some time during their life history, suffered extensive dissolution, giving rise to the curved faces so frequently found. However they believed that the trigons, characteristic of octahedron faces, are growth features. They thought that dissolution was responsible for "etched projections" on dodecahedral faces and for the "etched bore holes" on cubic faces.

Williams (1932) disagreed with the conclusions of Fersmann and Goldschmidt believing that diamond was not subject to dissolution. He reasoned that growth stopped if the magma, in which the diamond grew, solidified or if the carbon init became exhausted. He allowed that if conditions of temperature and pressure in the magma just below the crystallization point of diamond were reached dissolution was a possibility. A study of the carbon phase diagram (figure 8.2) which was not available to Williams, would lead to the belief that some dissolution or graphitisation would not be unlikely as a diamond passed from the conditions of its formation to normal temperatures and pressures. But there is, on the other hand, strong evidence to indicate that some of the surface figures are true growth features. Williams argued that etch features produced in the laboratory are oriented differently to those found on actual crystals. A comparison of the orientations of the characteristic figures found on the various diamond faces with the etch figures produced in the laboratory is given in figure 6.1 in chapter 6 where the etching of diamond is discussed in some detail.

4.2 Characteristic Features on Natural Octahedral Faces.

Triangular shaped depressions, or trigons, are

found on almost all octahedral faces. An octahedral face from a cubic diamond is shown in figures 5.62 and 5.63. The trigons are conspicuous. Two types are identified, shallow ones with flat bases and deeper ones with usually flat sloping sides and meeting in a point at the base (Tolansky and Wilcock, 1947). Intermediate and mixed forms also occur.

Many trigons have one side which projects beyond the pit at one or both ends, where they appear as sharply defined discontinuities. (Tolansky and Wilcock, 1947; Wilks, 1952).

Wilks (1961) measured the angle of a number of steep-sided trigons and reported that they coincided with that of a true octahedral plane.

As well as trigons, triangular growth hillocks oriented oppositely to them are found. These are usually made up of a number of distinct sheet layers. Other layer-like formations also occur. (Tolansky and Wilcock, 1947).

An interesting multiple beam interference pattern is reported by Tolansky and Wilcock (1946). This showed a fringe on the flat base of a trigon to lie in line with another on a flat plane area nearby, strongly suggesting that the area at the base of the trigon and

the plane area were part of the same crystal plane. They consider that the chance of this occurring due to etch was very slight and put it forward as evidence that trigons are growth features.

4.3 Characteristic Features on Natural Dodecahedral Faces.

Two main types of features appear on dodecahedral faces. Either the faces have close parallel striations or "geometrical network of patterns". (Emara and Tolansky, 1957). On the dodecahedral faces of cubic diamonds (figures 5.58 to 5.60) parallel striations (sometimes modified) of a nature similar to, but coarser than, those reported by Emara and Tolansky are to be found. The network patterns, which are sometimes described as having a "shield-like" or a "flaky" appearance, were found by these workers to be slightly curved hillocks. While most of these networks are rather irregular, being bounded by crude polyhedra having rectilinear sides, they reported a crystal in which the outlines were on a very fine scale and in the form of parallelograms with angles equal to the angles of rhombic dodecahedral faces.

They concluded, largely as a result of etching experiments, that the striations are natural growth features whereas the network patterns are the result of a mild solution process.

CHAPTER 5.

SURFACE TOPOGRAPHY OF NATURAL CUBIC DIAMONDS.

5.1 General Description

For the study of the surface topography of cubic diamonds fifty cubes were made available by Dr. Custers of the Adamant Research Laboratories. These came from surface alluvial deposits in the Congo where they occur in small numbers. They are of uniform size, of edge about 2mm, weighing about 0.1 carat. Almost without exception they are clear but have internal defects. In colour they vary from white to deep yellow.

As well as these, nine stones of uncertain origin were available. Seven of them bear such a strong resemblance to the Congo cubes in habit, size and colour that it is likely that they too originated in the same region. The other two are somewhat larger, being of edge about 4mm and 5mm respectively. These appear to be coated stones but have similar surface characteristics to the other 57 cubes.

The surfaces of these stones were examined and a number of surfaces were selected for critical study. On superficial inspection the faces of the cubes appear to be frosted but more careful examination under the microscope reveals that they are made up in fact of a multitude of

small facets. As well as the six major cubic faces other less developed faces are present. Without exception at the intersection of two cubic faces there is a small but definite dodecahedral face, so that the edges of the cube appear to be bevelled. These dodecahedral faces are also multi-faceted. Occasionally at a corner of a cube there is a definite octahedral facet which is flat but on which trigons are present.

A study of the absorption spectrum of a selection of five of these diamonds showed them to be of type 1. The crystals are opaque in the ultra-violet from about 3100A down.

5.2. Methods of Examination.

Because of the faceted nature of the surfaces, light incident on them is specularly reflected from the facets and observation by direct reflection microscopy is generally very difficult. Many of the features do not show up at all. It is often more satisfactory to study such a surface, however, by means of a replica viewed in transmission. Replicas were made in "Perspex" acrylic sheet, 3/16 inch thick, heated to 140-160°C and sufficient pressure applied to reduce the thickness of the softened Perspex to about 1/8 inch. To ensure minimum residual strain the replicas were returned to the oven for about 15 minutes after the pressure had been applied and then

allowed to cool very slowly over a period of several hours. A jig was used for applying the pressure and a diagram of this is shown in figure 5.1. Replicas of two opposite faces of a diamond can be made in such a jig at the one time. The diamond is held by four quadrants which are clamped between two annuli as shown in figure 5.2.

Although reports in the literature (e.g. "Engineer", 1959) indicate that plastic replicas may be faithful to very high accuracies and the type of replica used in this work has been shown by Faust (1949) to reproduce both in extension and depth to an accuracy of 1%, tests were made to ensure that the exact technique employed produced replicas which were faithful enough for the present purpose. The distance between a pair of graticule lines ruled at a spacing of about a millimetre was compared with a replica of them. Magnified images were obtained on photographic plates at a magnification of approximately 40. The mean measured separation of the lines was as follows:

Graticule.....33.64 mm.

Replica33.38 mm.

The edge of a glass cover slip about 0.2 mm in thickness was replicated and the height of the step so formed on the replica compared with the thickness of the cover slip.

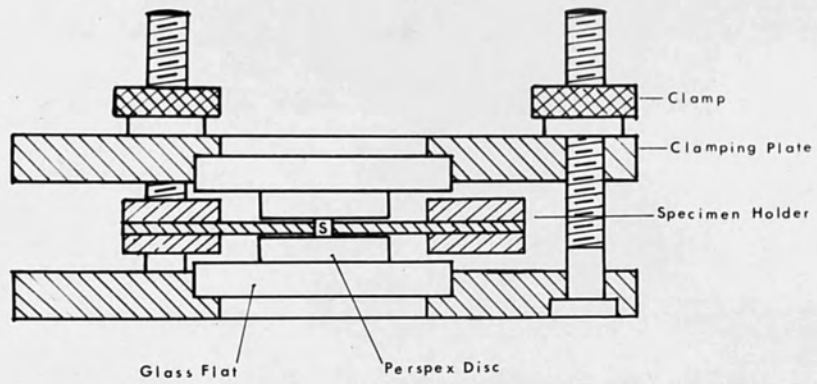


FIGURE 5.1. JIG FOR MAKING REPLICAS.

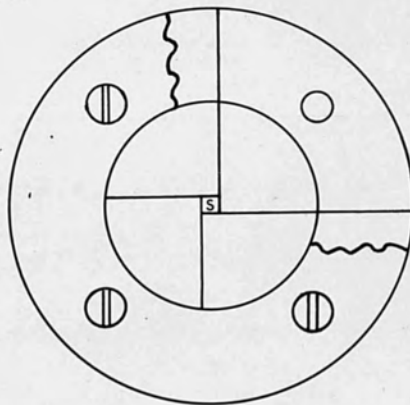


FIGURE 5.2. SPECIMEN HOLDER.

The thickness of the cover slip was measured with a 0-25 mm Moore and Wright micrometer, type 961M. The step height on the replica was measured with the micrometer held in a stand with the spindle vertical and the Perspex disc resting on the lower anvil. A cylindrical needle of diameter uniform to within the accuracy of reading of the micrometer, 0.001 mm, was placed in turn on the lower and upper levels of the step and micrometer readings taken. The accuracy of this measurement was estimated to be ± 0.005 mm. The results of the measurements were as follows:

Mean thickness of cover slip at edge0.174 mm.

Mean step height on replica0.171 mm.

These results indicate that in extension the replica reproduced to within 1% and in depth to within 2%. Although the reproduction obtained was apparently not as faithful as that obtained by Faust, it is considered to be adequate for the present purpose. Interferometric studies in some cases were carried out on the surfaces directly but because of the rough character of the surfaces it was impossible to obtain true multiple-beam fringes. The two-beam type fringes obtained directly on the surface gave some useful information about the cubic type facets but two-beam transmission interferograms obtained from replicas gave a better idea of the relation of the cubic

facets to the rest of the surface structure. The distance between the replicated surface and the reference flat was reduced in order to reduce the order of interference. This was done by filing away unwanted high material with a ground glass plate.

Polished sections through the surface of one diamond were prepared in order to examine its faceted nature. One section was made by polishing off an edge of the cube to give an approximately dodecahedral plane. The intersection of this polished face and the natural cubic faces which cut it at 135° were examined. The diamond was parted by sawing through two opposite edges to give two approximately equal parts. The sawn faces were polished and the intersection of the resultant polished dodecahedral faces with the cube faces which meet them at 90° were examined for surface features. Fortunately it is possible to polish diamond on a scaife using free diamond abrasive powder to give a sharp edge. In the case of the intersection between the planes at 135° , the edges were in fact quite sharp and free from chipping. In the case of the intersection between the planes at 90° the edges were only a little inferior making the interpretation of some of the very fine detail a little doubtful.

5.3 Cube Faces.

Sutton (1928) briefly described cubic diamond, stating that it deviates from true crystal form more than other forms do, its cube faces departing from planar and its edges always rounded off to form faces which are dodecahedral but such a face very often has a ridge along its length. He pointed out that the rectangular depressions, present in profusion on the faces were in many cases complete inverted pyramids and noted that their orientation was 45° to the cubic face. These he called "tetragons" by analogy with the trigons found on octahedral faces.

Some typical cubic faces are shown in figures 5.3 to 5.6 (x 60) inclusive. The most obvious features of the surface are the rectangular shaped depressions which Sutton called tetragons and the large total area of nearly flat facets of cubic or near cubic orientation. Indeed these two types of feature make up the entire surface of figure 5.3. On the surface shown in figure 5.4 there some rather irregular facets running more or less parallel to the cubic edges. These will be shown below to have indices like $(h\ 1\ 0)$ and may be considered as "dodecahedral-like" facets.

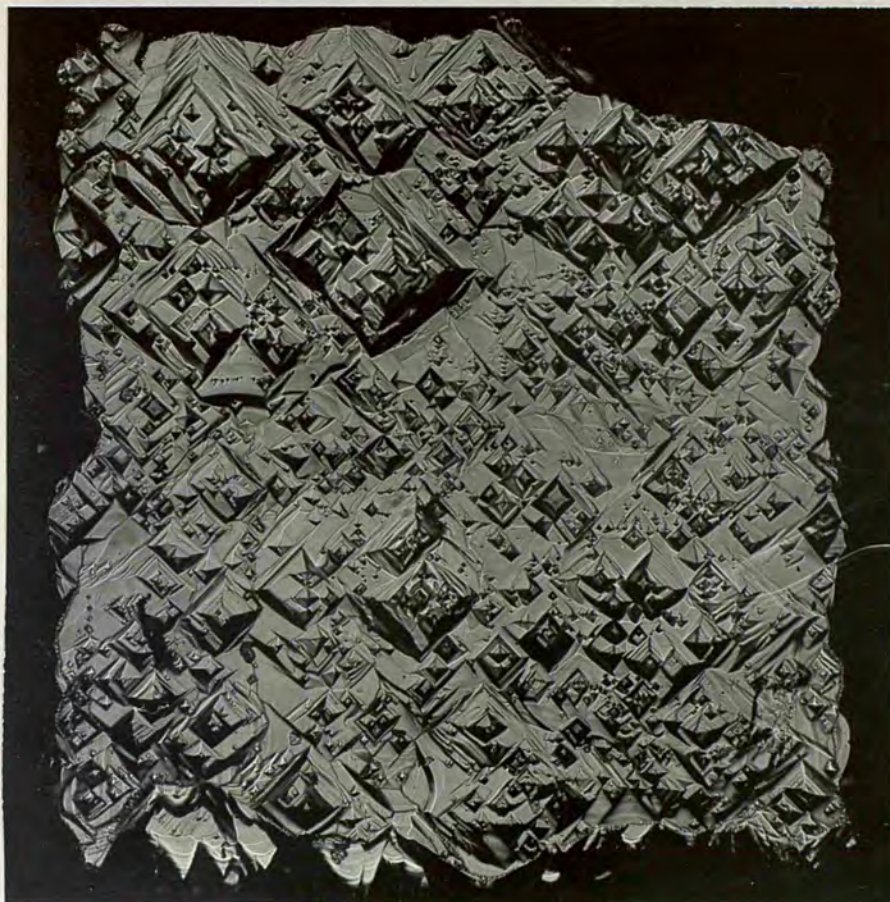


Figure 5.3. Diamond H4, 010 face. (x 60)

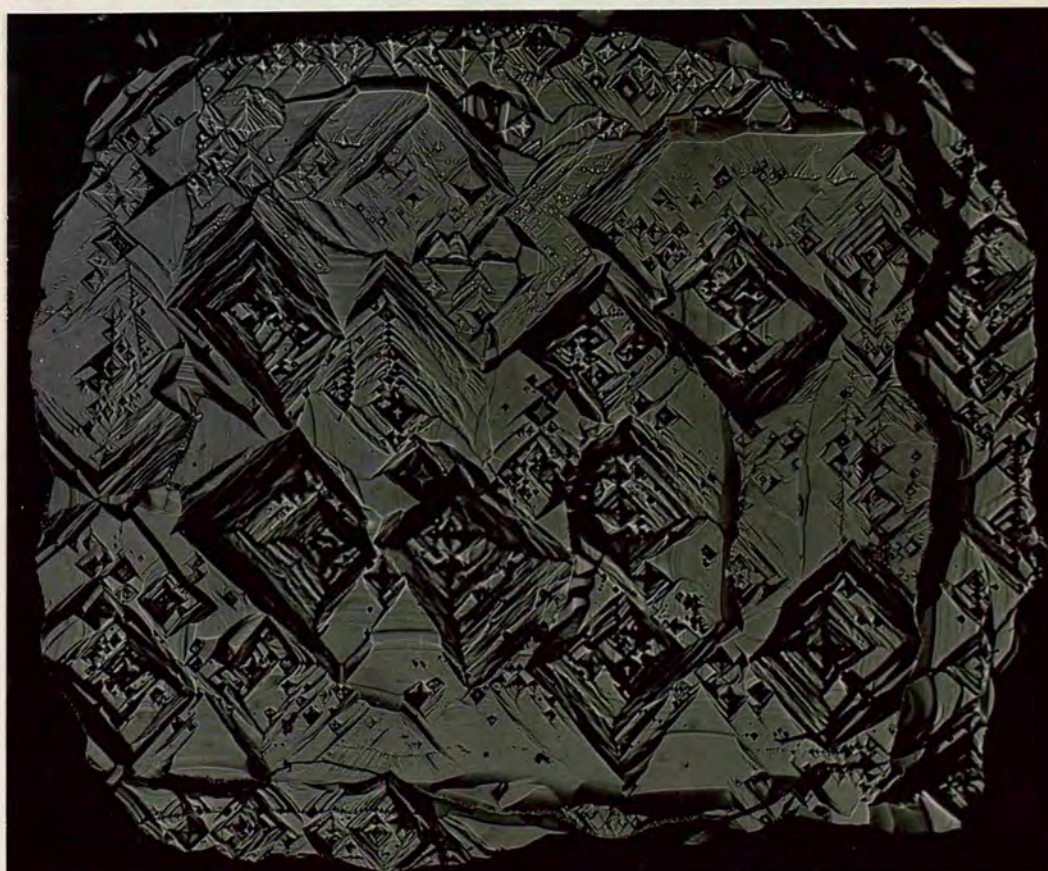


Figure 5.4. Diamond H6, 010 face. (x 60)

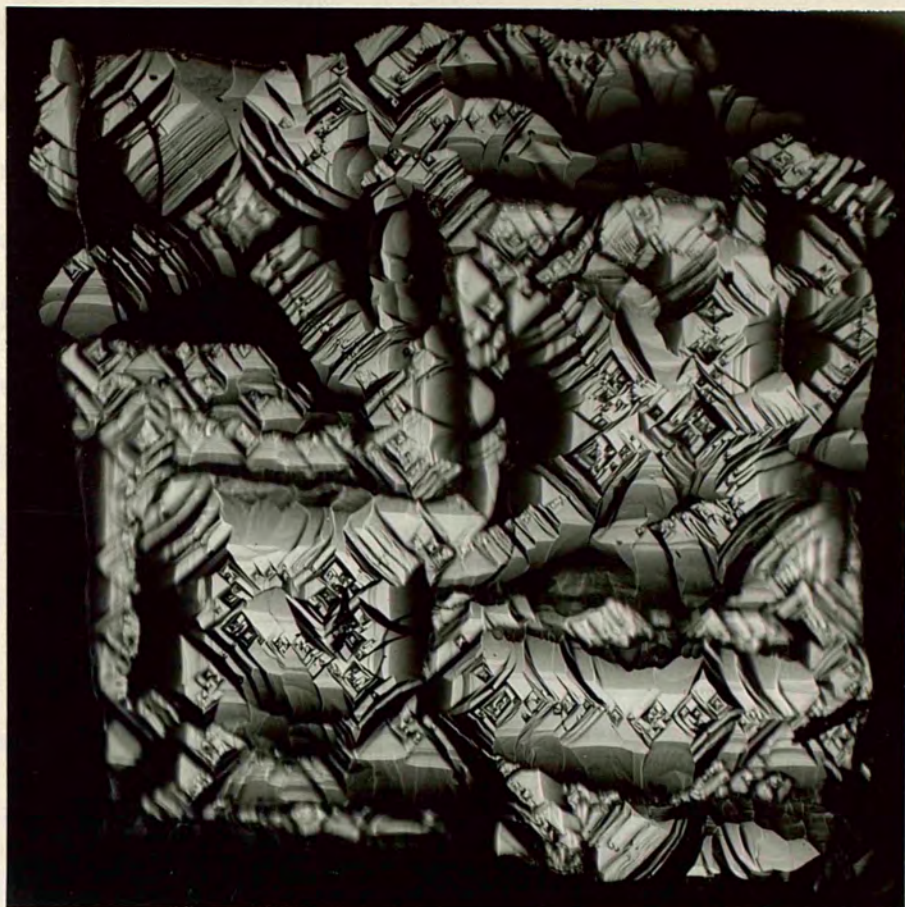


Figure 5.5. Diamond H2, 001 face. (x 60).



Figure 5.6. Diamond H10, 001 face, (x 60).

The tetragons are rather complex features, many smaller ones occurring within a larger. Enlarged views of two relatively simple tetragons are shown in figures 5.7 and 5.8 (x 200) and more complex structures are shown in figures 5.9 and 5.10 (x 300). The sides are made up of relatively flat "cubic-like" facets alternating with "octahedral-like" facets having indices like (h 1 1). The more prominent cubic-like facets of part of a large tetragon can be readily identified on the two-beam interferogram of figure 5.11 (x 450).

Near the centre of figure 5.7 a number of well-formed nearly flat facets can be seen. On all of these tetragons are visible. Several of the facets appear to be made up in fact of two or more vicinal facets. Similar features can be observed in figure 5.8. Here, as in figure 5.7, banding, which can be seen on some of the cubic facets running at 45° to the edges of the tetragons, suggests alternating cube and poorly developed dodecahedral facets. On the ~~left~~^{right} there is a more developed feature of the same nature. The centre of the large tetragon in figure 5.9 (x 300) also shows similar features but the number of small tetragons within it make it quite a complicated pattern. The feature shown in figure 5.10 (x 300) is also composed of a number of small tetragons and cubic-like facets.



Figure 5.7. Tetragon. Diamond H6,
 $\bar{1}00$ face. (x 200).



Figure 5.8. Tetragon. Diamond H6, $\bar{1}00$ face.
(x 200).



Figure 5.9. Diamond H6, 010 face. (x 300)

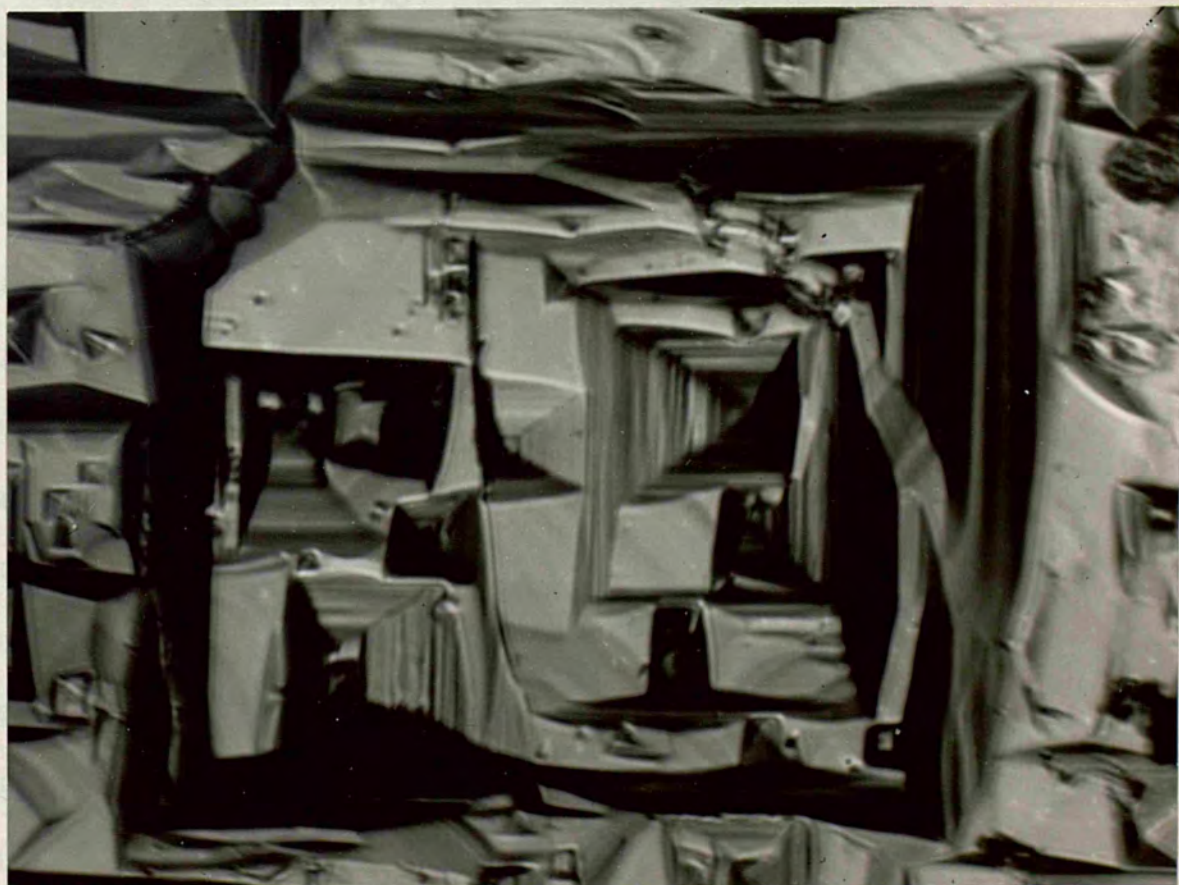


Figure 5.10. Diamond H4, 010 face. (x 300)

There is evidence of "tails" associated with most very small tetragons, these tails being extensions of edges of the tetragon and are connected with discontinuities in the surface of the cubic facet on which they occur. Such "tails" are apparent in the interferogram of figure 5.11 (x 450). A change in level of the cubic surface on which they occur is very frequently associated with them. The height of these surface steps in this interferogram varies considerably being in some cases less than 100\AA , the fringes merely changing in direction, and in others as much as one micron. They can however be very much larger than this.

Figure 5.12 (x 300) is a good example of the way small tetragons form on the small cubic facets on the side walls of the larger tetragons, and in clusters, in a line and singly on the larger cubic facets. At the top, ~~of~~ the dark line running across the picture is a dodecahedral-like facet associated with a change in level of the cubic face. Figure 5.13 (x 200) shows similar features. In addition there is a roughly triangular feature showing banding similar to the one noted in figure 5.8. It too appears to be made up of cubic-like facets and dodecahedral-like facets. Several such features are also visible in figure 5.14 (x 200) and 5.15 (x 200). An interesting feature of these micrographs

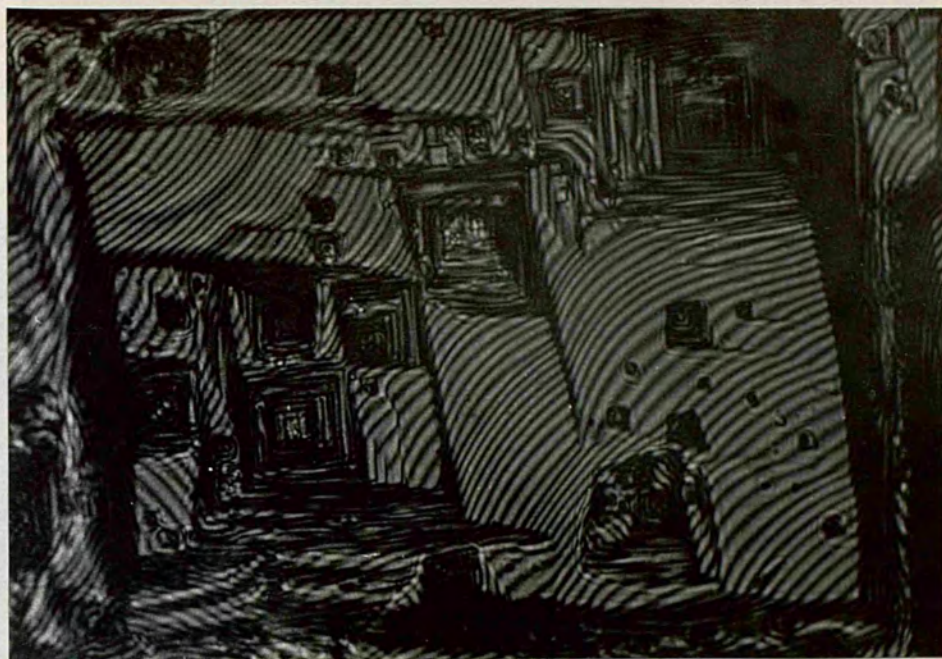


Figure 5.11. Cubic Diamond, (010) face. (x 450)



Figure 5.12. Diamond H6, ($\bar{1}00$) face. (x 300)



Figure 5.13. Diamond H6, 0 0 $\bar{1}$ face. (x 200).

Figure 5.14. Diamond H6, (010) face, (x 200)

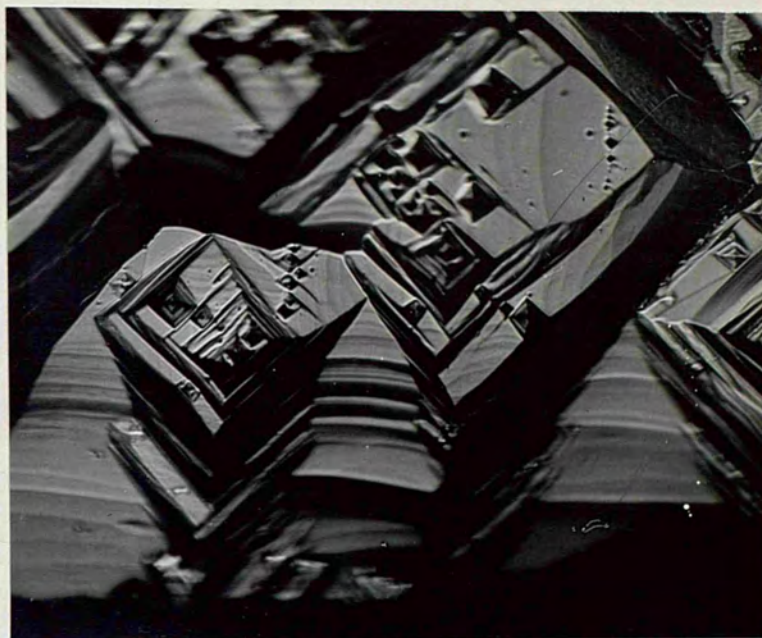


Figure 5.14. Diamond, (010) face, (x 200)

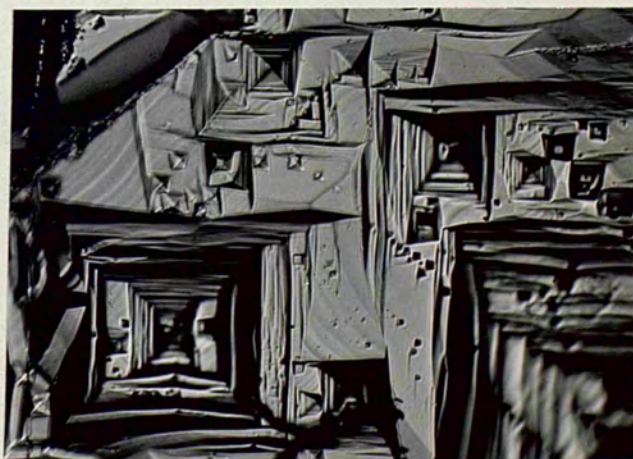


Figure 5.15. Diamond H6, (010) face, (x 200)

are the lines of small tetragons on the well developed cubic facets. Such lines of small tetragons occur frequently not only on cubic facets but down the corners or along the walls of large tetragons as in figure 5.16 (x 300). Figure 5.17 (x 150) shows the centre of a very large tetragon which has been modified by dodecahedral-like facets to give an eight-sided depression. The formation of small tetragons arranged more or less in lines is well illustrated. Figure 5.18 (x 300) shows several lines of tetragons on a cubic-like facet. The interferogram in figure 5.19 (x 300) of the same area shows a complicated pattern of tetragons and cubic-like facets, some of the smaller of which are nearly flat while some of the larger ones are markedly curved. The nature of the cubic-like facets will be discussed further below.

The walls of some of the small tetragons are smooth enough for interference fringes to be observed on them. An example is shown in the interferogram of figure 5.20 (x 800). Around the walls of the larger tetragons there is a series of concentric fringes in the form of squares. The angle which each of the walls makes with the reference mirror is about 12° . Thus each is very nearly a plane with indices close to (7 1 1). By comparison the



Figure 5.16. Diamond H6, 010 face. (X 300).



Figure 5.17. Diamond H2, $00\bar{1}$ face. (x 150).



Figure 5.18. Diamond H6, (010) face. (x 300)

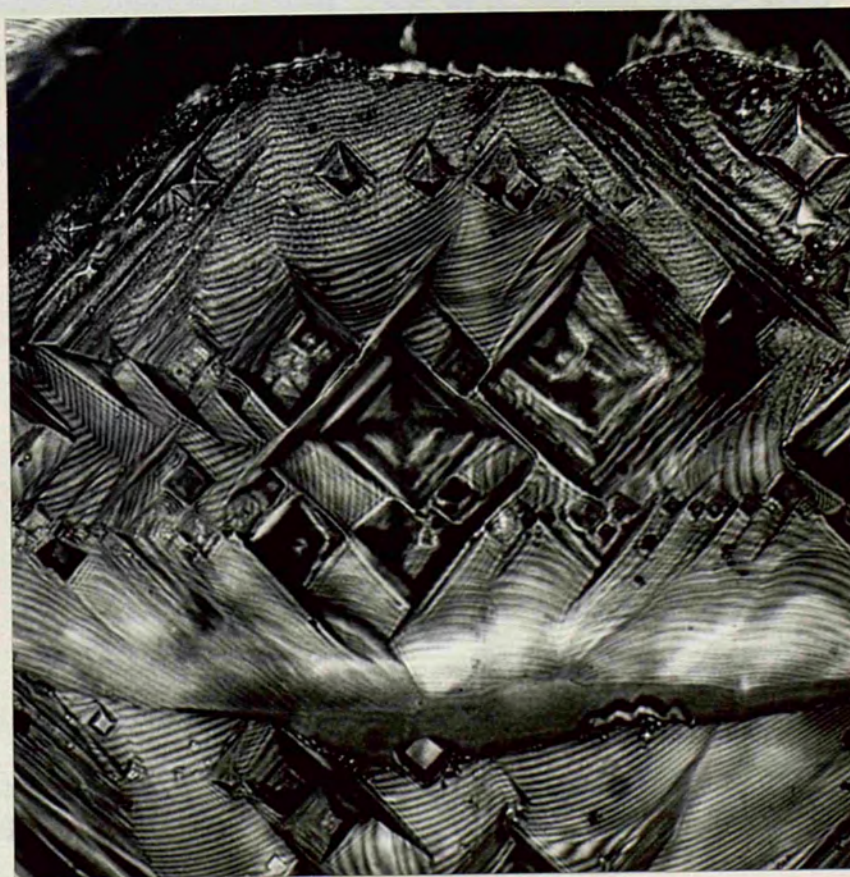


Figure 5.19. Diamond H6, (010) face. (x 300)

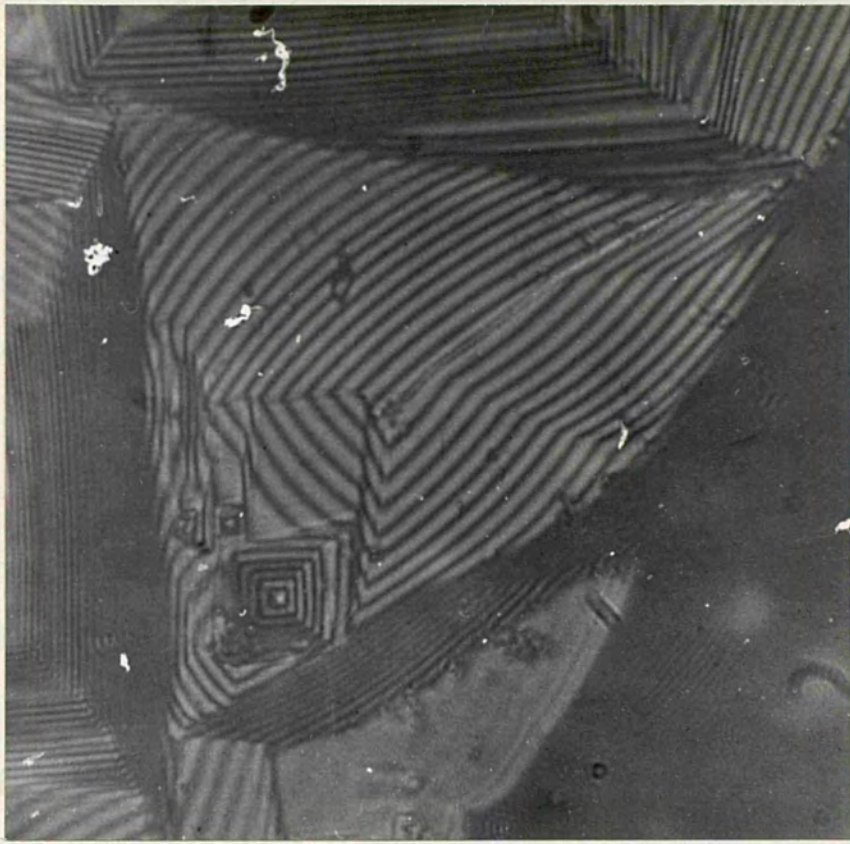


Figure 5.20. Diamond H4, $\bar{1}00$ face. (x 800).

angles, which the three more developed vicinal facets of the feature on which this tetragon occurs make with the reference flat are about 5° , 5° and 4° respectively.

Very rarely small flat facets with shallow flat bottomed tetragons are seen. Only two such examples were observed and these are shown in figures 5.21 (x 1000) and 5.22 (x 1000). On the former small straight steps not associated with tetragons are visible. These steps are small indeed the largest being about 200A deep and resemble the "tails" associated with tetragons.

The most striking feature of a cubic face is undoubtedly the abundance of tetragons on it. Another interesting feature is the large total area of facets of near-cubic orientation. Figure 5.23 (x 50) is a two-beam interferogram taken in reflection directly on a cubic face. It shows the large number of well developed near-cubic facets of linear dimensions of the order of 0.1 mm. As well as these there are a large number of very small facets which alternate with octahedral-like facets to make up the tetragon walls. These do not show up in the picture.

Figures 5.24 (x 50) and 5.25 (x 50) show interferograms of two cubic surfaces taken on perspex replicas viewed in transmission. In these pictures the

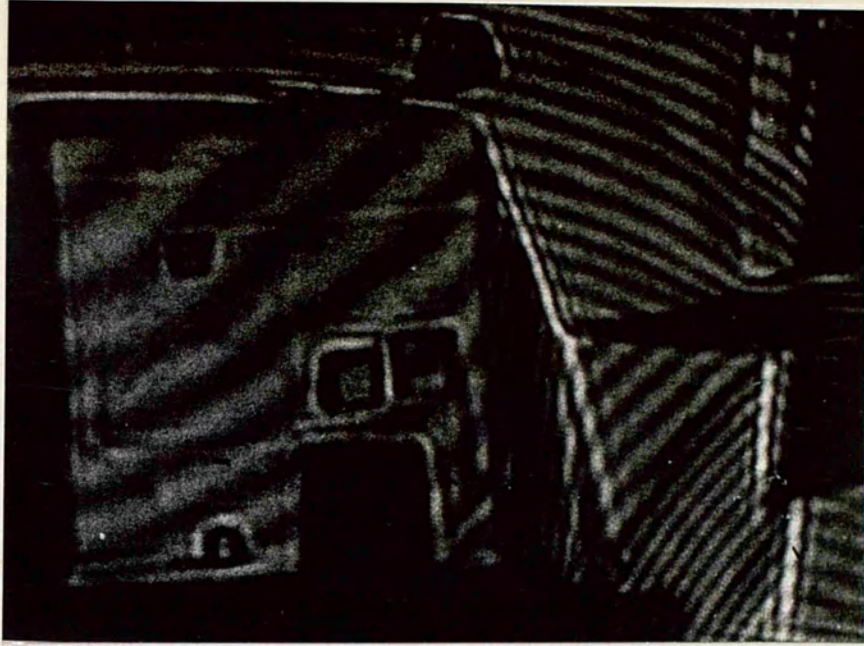


Figure 5.21. Diamond H1, 100 face. (x 1000).

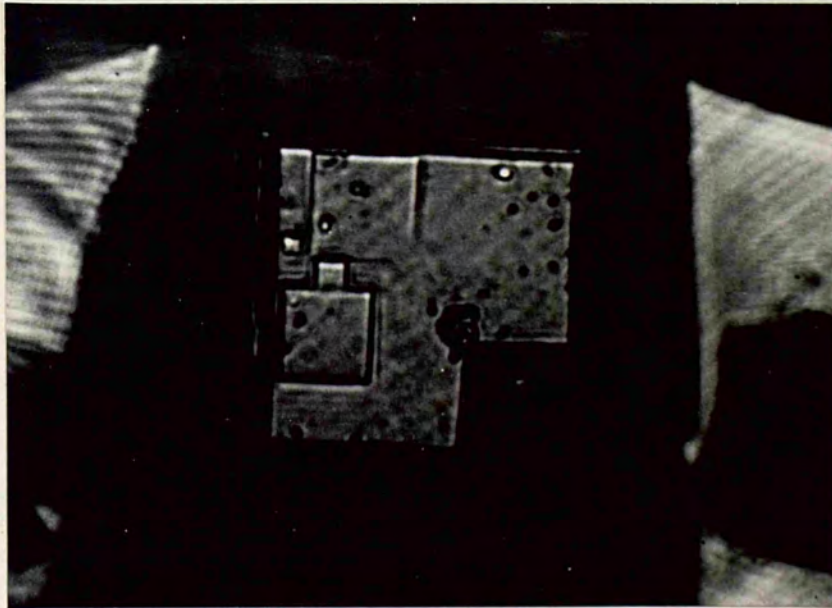


Figure 5.22. Diamond H1, 100 face. (x 1000).

relationship between the tetragonal and the cubic
facets can be seen to better advantage. The small

subid face
in many cases

1.2) and (2.3, 4.4)

The angles
facets vary

about 3.0
degree to

deteriorate
give the

the wedge
and it is

nearly
reasonable

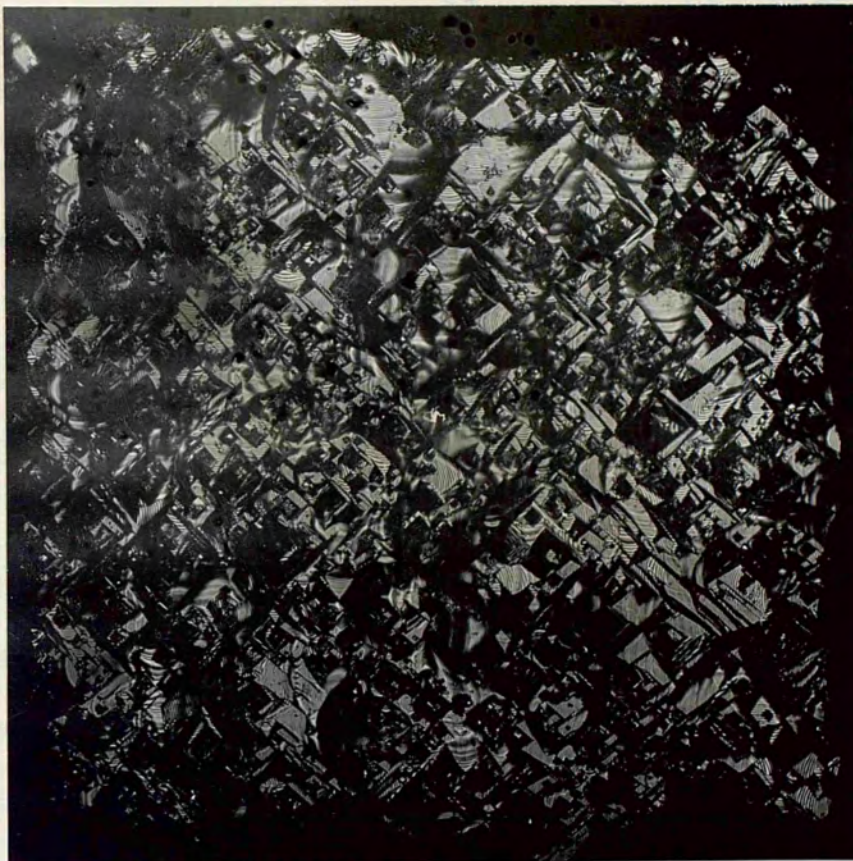


Figure 5.23. Diamond H4, 100 face. (x 50).

of the cubic-like facets is quite small. It is

Figure 5.26 (x 200) is a micrograph of a Parapex replica. In order to obtain a closer
approach between the diamond surface and the tetragonal
flat, some of the higher features of the replica, like
the features that would be at the bottom of depressions
on the diamond itself, were filed off. Several such

relationship between the tetragons and the cubic facets can be seen to better advantage. The small cubic facets on the tetragon walls can be identified in many cases, e.g. in figure 5.24 at positions (2.3, 1.2) and (2.1, 0.7) and in figure 5.25 at positions (2.5, 0.4), (3.3, 1.3), (3.3, 2.6) and (2.4, 3.2). The angles between the reference optical flat and the facets varies in figure 5.24 from about $\frac{1}{2}$ degree to about 5 degrees, and in figure 5.25 from about 2 degrees to 5 degrees. The direction of the fringes determine the direction of the wedge axis but does not give the sense of the angle. It should be noted that the wedge axes are in some cases at 90° to one another and it is not unlikely that the sense of angles with nearly parallel axes is in some cases opposite. It is reasonable to say that the variation in orientation of the cubic-like facets is of the order of 5 degrees.

Figure 5.26 (x 200) is a two-beam interferogram of a Perspex replica. In order to allow a closer approach between the diamond surface and the reference flat, some of the higher features on the replica, i.e. the features that would be at the bottom of depressions on the diamond itself, were filed off. Several such

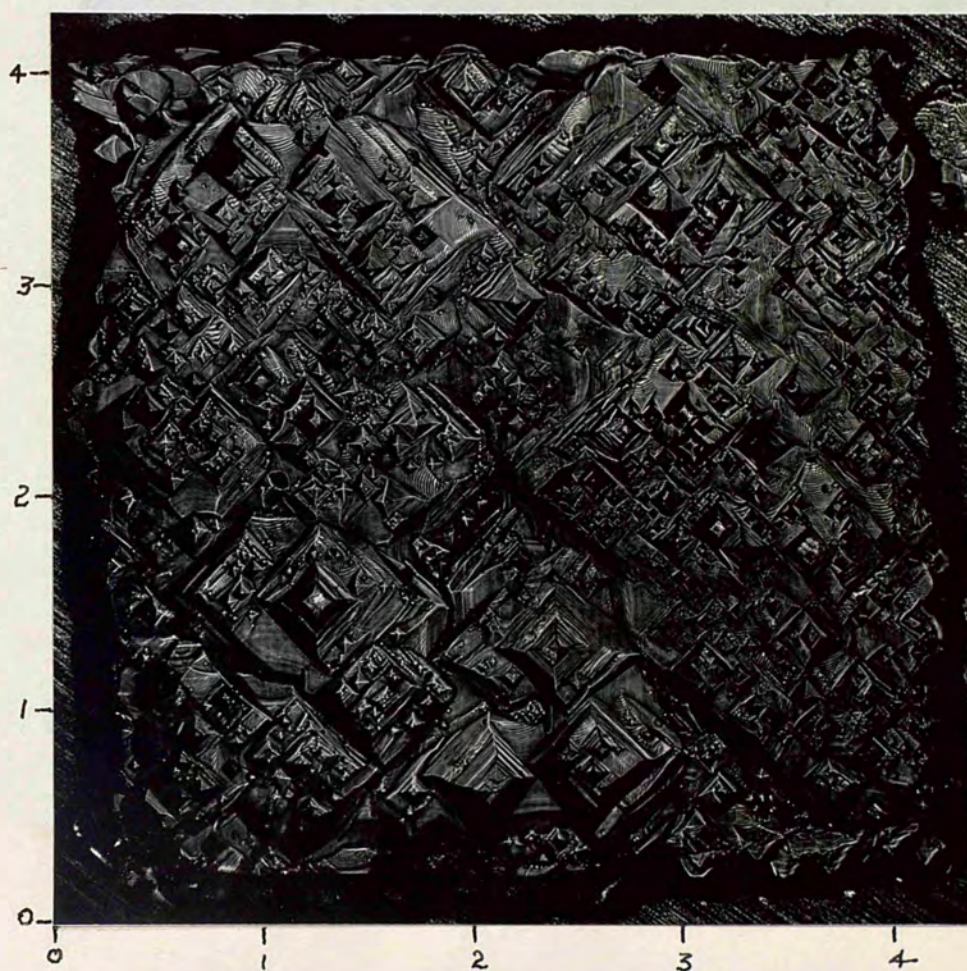


Figure 5.24. Diamond H4, 001 face. (x 50).

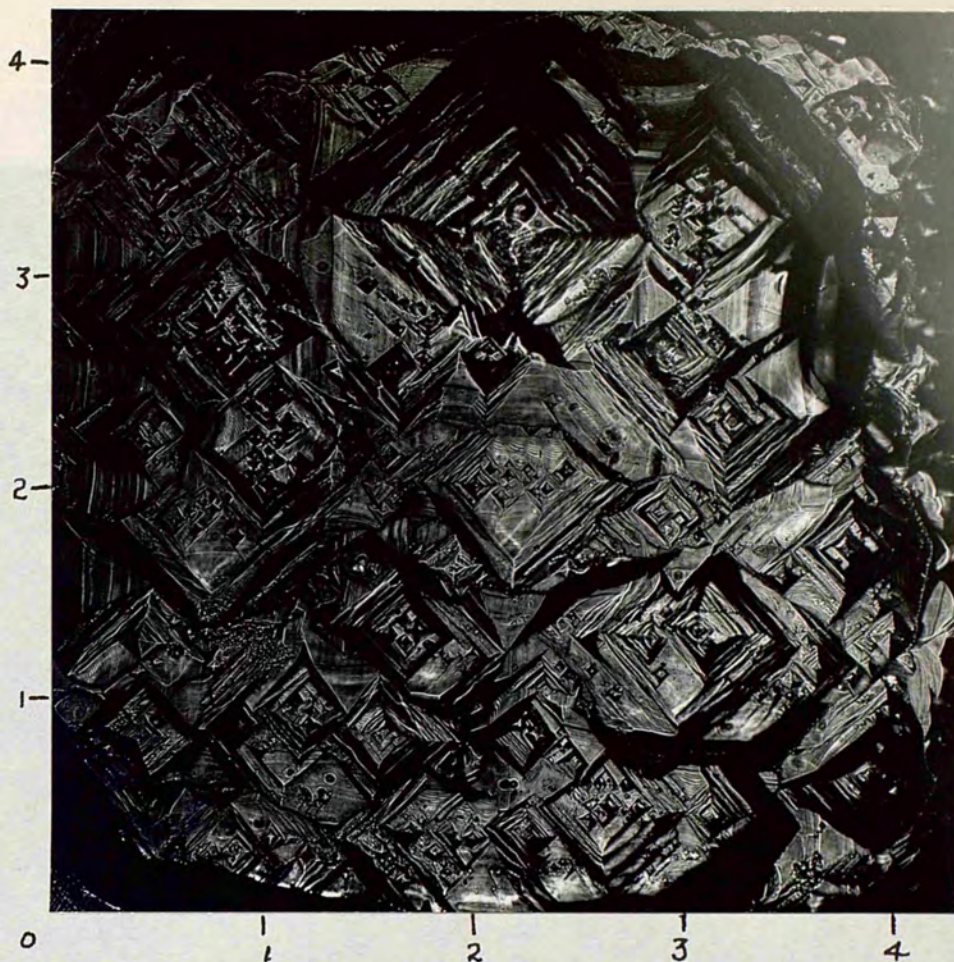


Figure 5.25. Diamond H6, 100 face. (x 50).

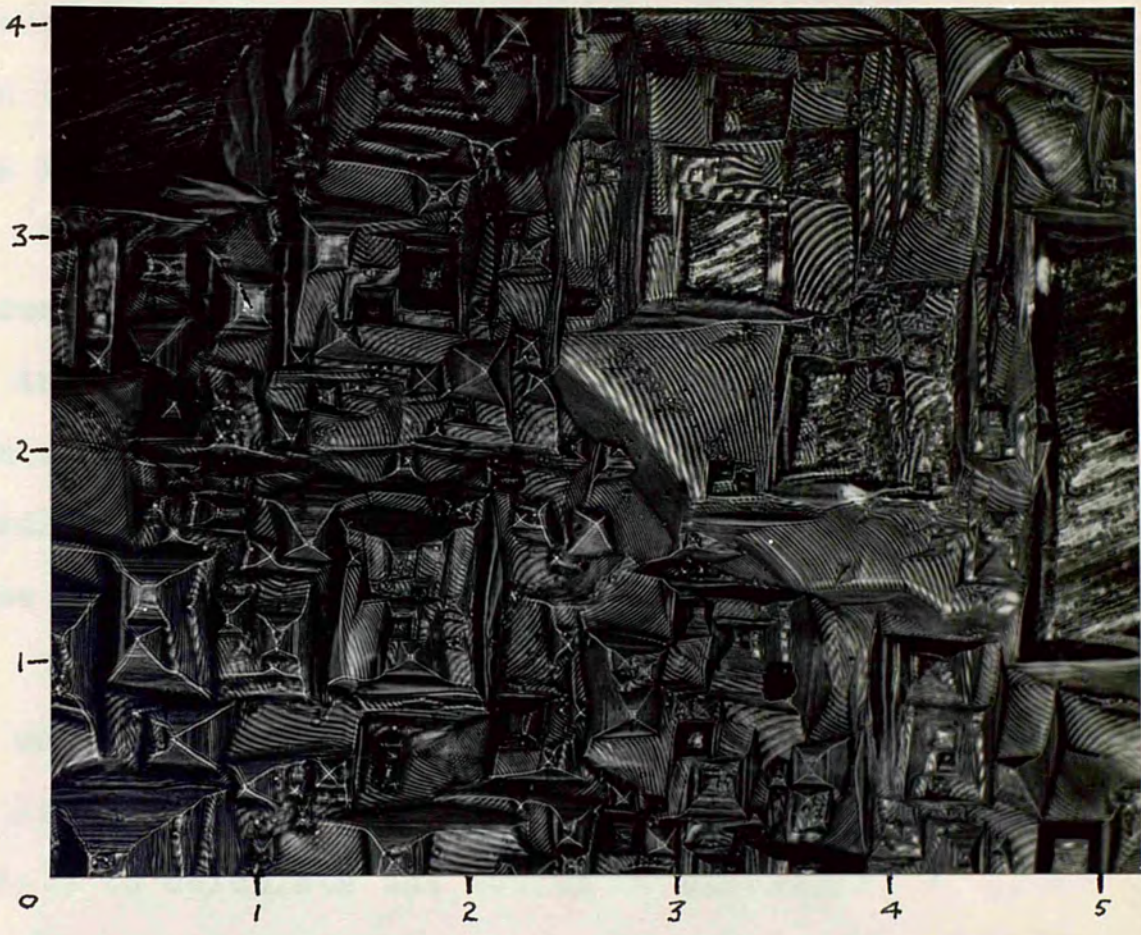


Figure 5.26. Diamond H4, 010 face. (x 200).

flat parts are visible on the picture at positions (5.0, 2.0), (3.2, 3.0) and (0.5, 4.0). The multi-faceted nature of the surface is well shown, the developed cubic facets, the small facets within tetragons and in many cases the fine cubic-like steps on the tetragon walls being visible.

The cubic-like facets are clearly shown in figures 5.27 (x 300) and 5.28 (x 300). Within the tetragons in figure 5.27 the small facets are numerous indeed. In this picture particularly the larger faces are markedly curved. An approximate estimate of the curvature may be made from a measurement of the fringes.

The fringe pattern obtained by resting a reference flat on a sphere would be a set of concentric circles. Even if only part of the fringe system is visible it is possible to calculate the radius of curvature, R , of the surface from the length of a chord, s , of a fringe and the number of fringes, a , between it and the fringe. Consider figure 5.29(a) in which the sagittal distance between chord and fringe is h .

$$\text{The radius of the } n\text{th fringe} = r = \frac{1}{2} \left(\frac{s^2}{4n} + h \right) \quad \dots\dots 5.1$$

$$\text{The radius of the } (n-a)^{\text{th}} \text{ fringe} = (r-h).$$

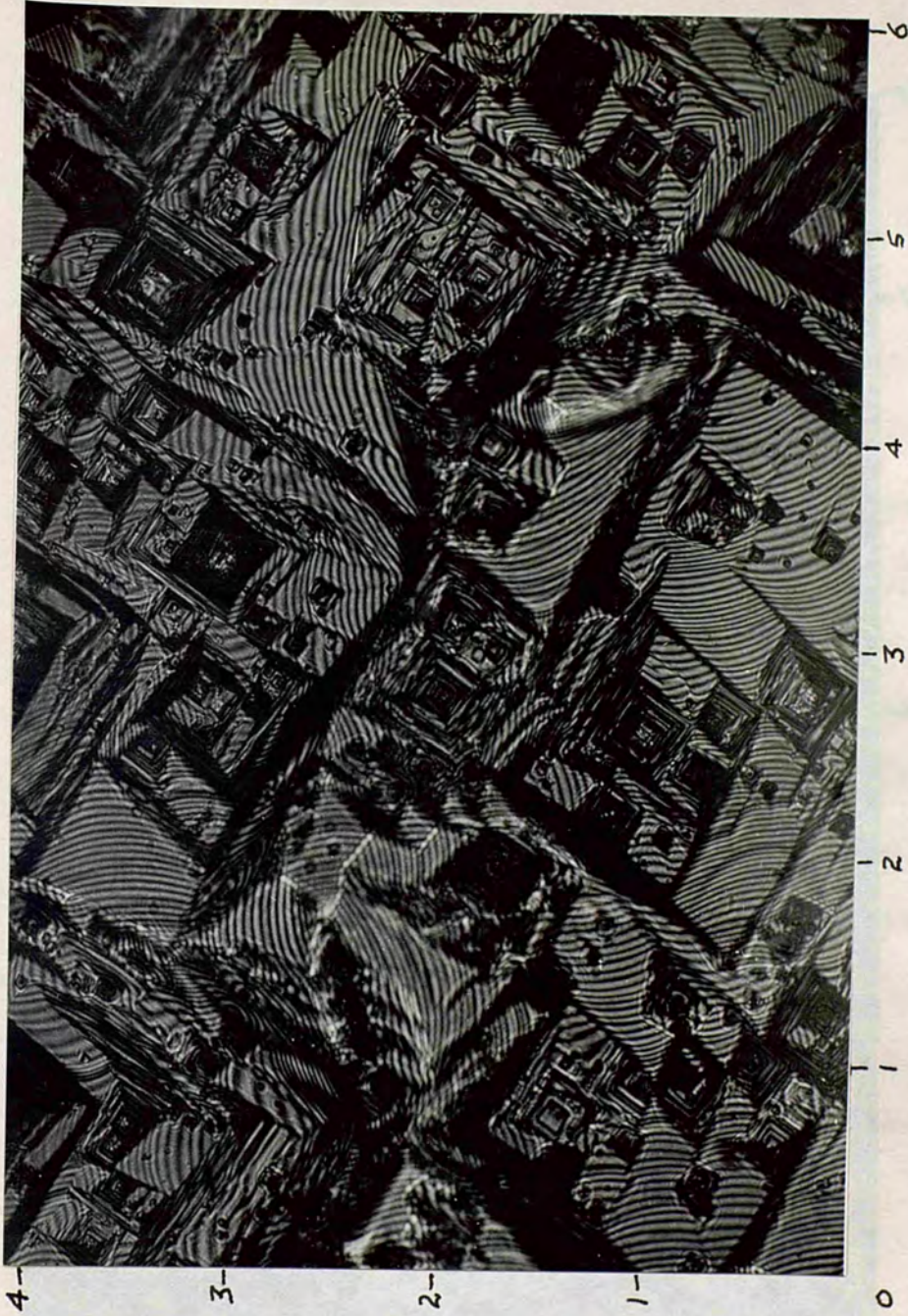


Figure 5.27. Cubic Diamond (010) face. (x 300)

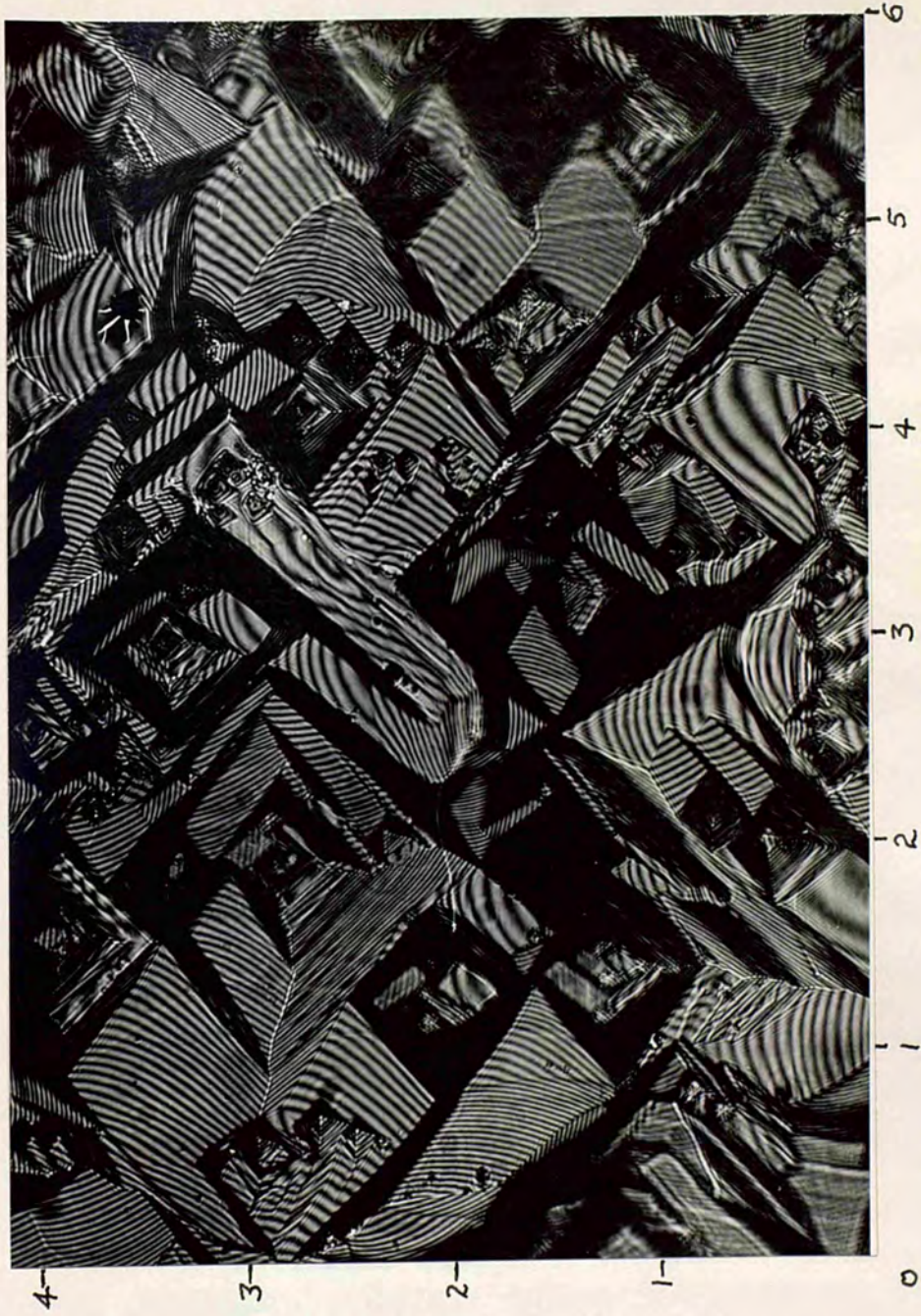


Figure 5.28. Diamond H1, (100) face. (x 300)

Figure 5.29(b) shows a cross section of the sphere perpendicular to the plane of the fringes. The diameters of the n^{th} and $(n-a)^{\text{th}}$ fringes are shown.

$$n\lambda/2 = R^2 - r^2$$

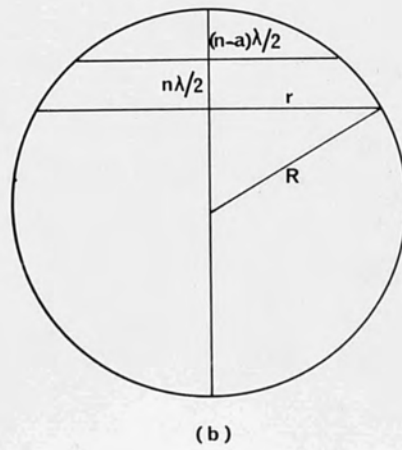
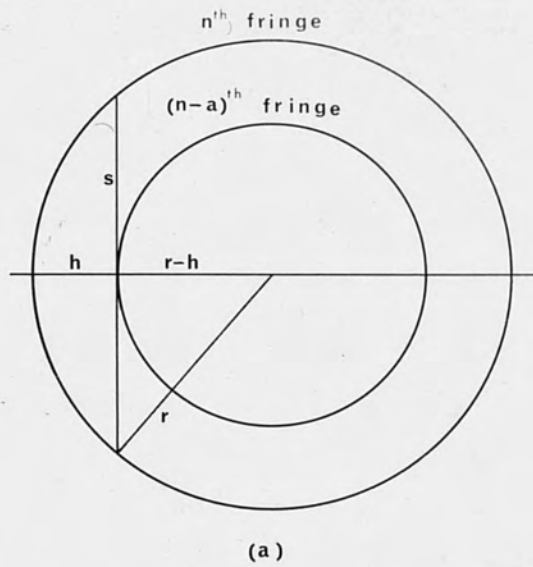


FIGURE 5.29.

From (a) which shows the geometry of the fringes, we have

Figure 5.29(b) shows a cross section of the sphere perpendicular to the plane of the fringes. The diameters of the n^{th} and $(n-a)^{\text{th}}$ fringes are shown.

$$\text{Now } n \frac{\lambda}{2} \cdot 2R = r^2$$

$$\text{and } (n-a) \frac{\lambda}{2} \cdot 2R = (r-h)^2.$$

Whence it follows that

$$R = \frac{h(2r-h)}{a\lambda}.$$

Substituting for r from equation 5.1 we have

$$R = \frac{s^2}{4a\lambda}.$$

For measurements made on an image of magnification M ,

$$R = \frac{s^2}{4M^2 a \lambda}.$$

The radius of a curvature of a number of facets have been calculated for the interferograms in figures 5.27 and 5.28. The results are given in table 5.1. The accuracy of measurement is not better than perhaps 20%. More accurate calculations are hardly possible and indeed are not worthwhile because large variations of curvature occur in a single surface. The values quoted as infinity simply indicate that the radius of curvature is greater than about 5mm.

Figure 5.30 (x 400) is an interferogram of a cubic facet on which there are a number of tetragons. Generally

Surface (Figure)	Approximate Co-ordinates. of Facet.	s (cm)	a	R (mm)
5.27	2.0, 3.5	1.8	2	0.8
		1.0	1	0.5
	0.6, 3.2	0.7	0.5	0.4
		-	-	∞
	4.5, 2.8	1.4	1	1.0
	0.3, 0.9	1.0	0.5	1.0
	3.5, 0.6	0.9	1	0.4
		1.0	1	0.5
5.28	0.9, 3.4	1.9	1	1.4
		1.2	1	0.7
	1.1, 1.6	1.0	0.5	1.0
	2.6, 1.1	0.9	0.5	0.8
	4.8, 2.6	1.7	4	0.3
	5.1, 3.0	-	-	∞
		1.0	0.2	2.5

Table 5.1 Approximate radii of curvature of cubic-like facets on figures 5.27 and 5.28.

the surface is curved, the radius of curvature being as small as 1 mm, but changes in the curvature occur where there are tails of tetragons. In addition there is a series of ridges (or perhaps depressions), about 2000 Å in height on the right hand side, only one of which seems to be associated with a tetragon.

An interferogram of a similar facet is shown in figure 5.31 (x 500). It may be considered as two parts divided by the tail (which is non-rectilinear in this case) from the large tetragon at the bottom of the picture. The difference in orientation of the two parts is about 2 degrees. On the left side of the picture the surface is extensively interrupted by tetragons and associated with the tails are the usual steps on the surface. On the right hand part, the surface is smooth but curved, the radius of curvature being about 2 mm. Where the group of tetragons occurs the surface is interrupted.

An interesting facet is shown on the left hand side of the interferogram of figure 5.32 (x 1000). This facet is in fact made up of four vicinal facets, each making an angle of about 5 degrees with the reference flat. the facet on the lower right is composed of two vicinal facets separated by a tail of the tetragon. One has a

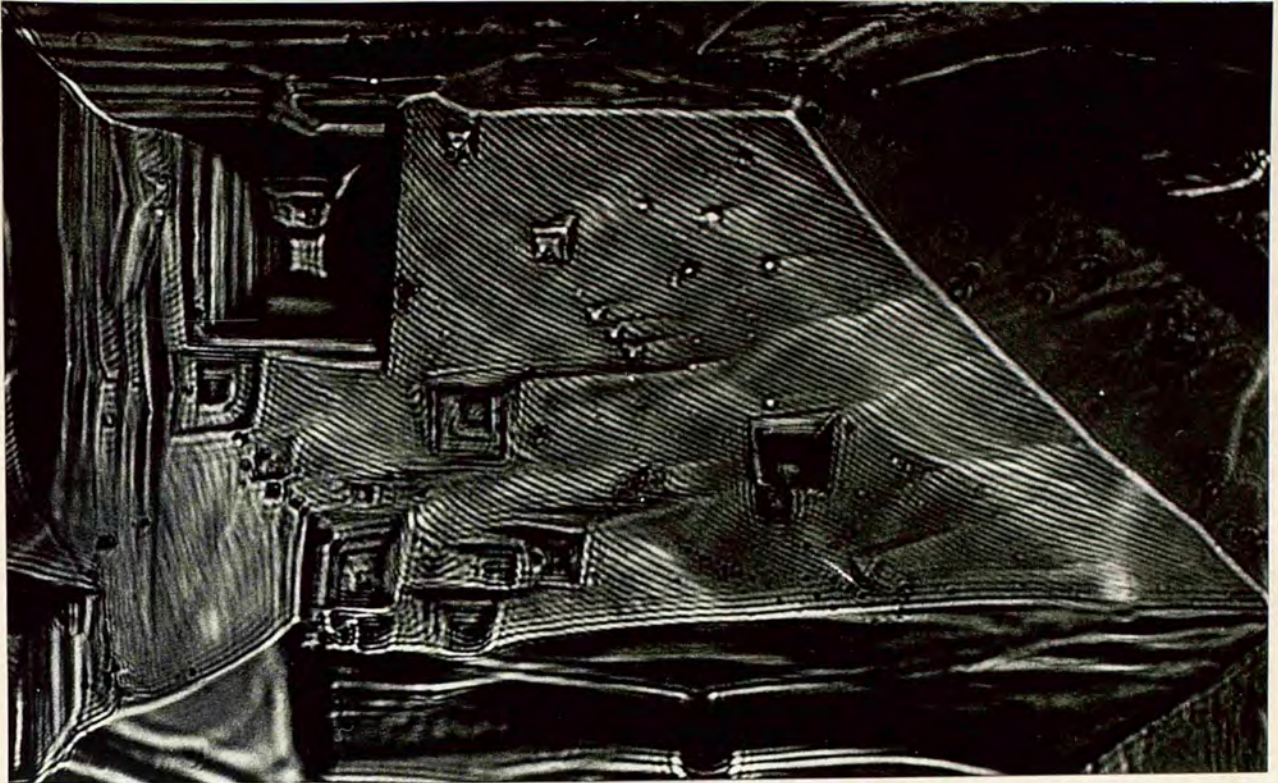


Figure 5.30. Diamond H6, 100 face. (x 400).

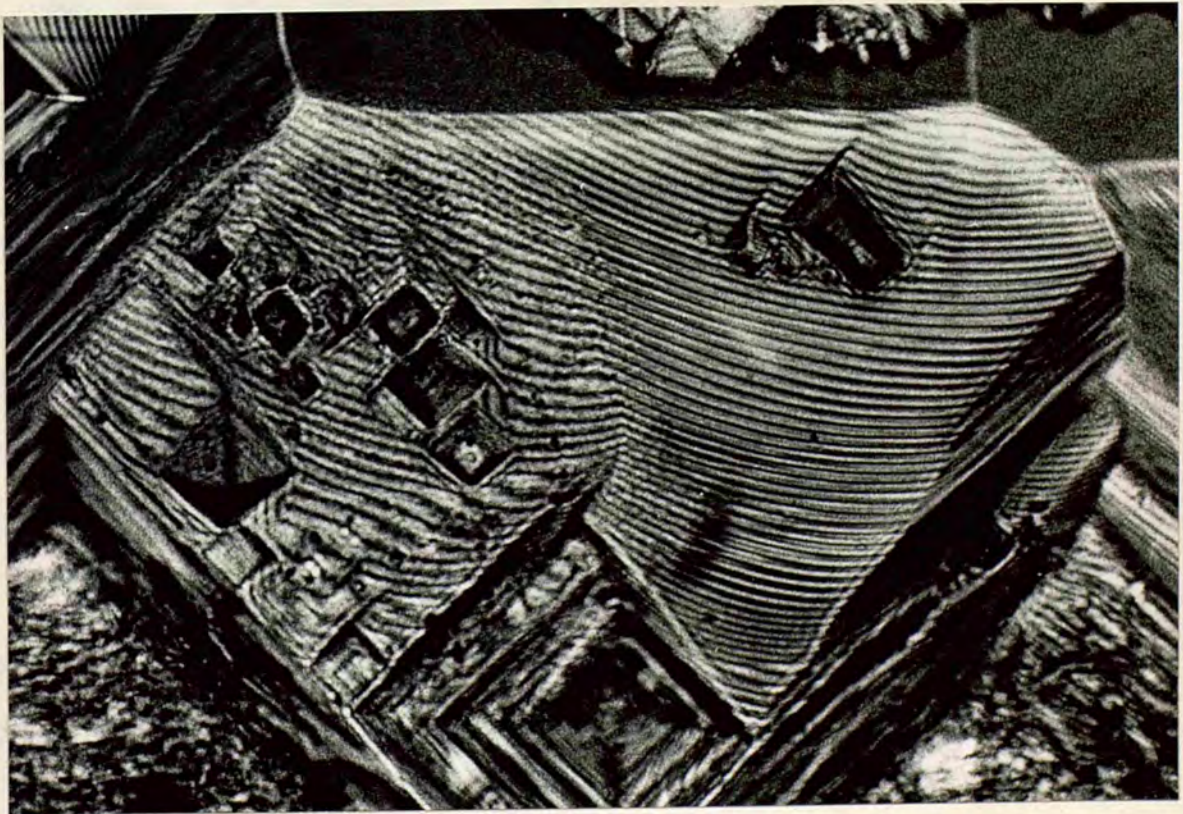


Figure 5.31. Diamond H6, 010 face. (x 500).

radius of curvature of about 1.4 mm, and the other of about 0.4 mm, the difference in general slope being about 2 degrees.

A group of facets of a type which occurs repeatedly is shown in figure 5.33 (x 1000). The differences in level on the faces and the differences in their orientation is associated with the tails from a line of tetragons.

The other feature which is characteristic of cubic faces is the presence of "dodecahedral-like" facets. They may occur where there is a change in level of the cube face. In figure 5.5 ridges of this type are quite prominent features and some have become associated with large tetragons so that these have been modified to eight sided depressions. Part of one of these features is shown at higher magnification in figure 5.17 (x 150). In figure 5.6 facets of a similar nature, but bearing the shield-like patterns associated with many dodecahedron faces, form the sides of rectangular hillocks. These are oriented at 45° to the tetragons. Sutton (1928) reported two specimens each of which appeared to be a cube enveloping a dodecahedron, and which he described as

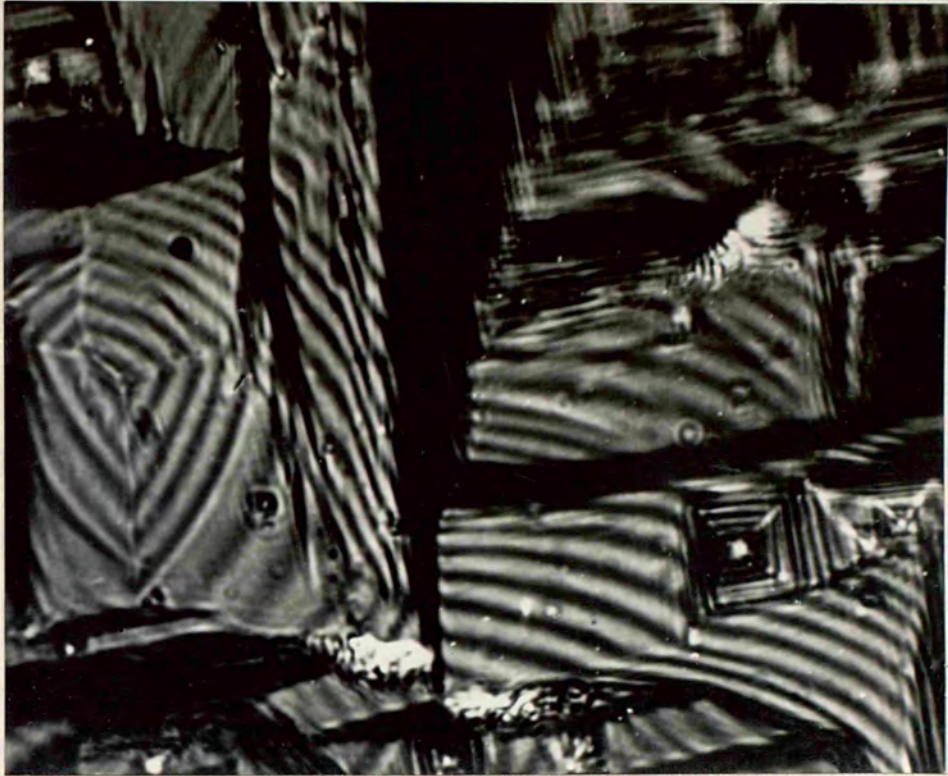


Figure 5.32. Cubic Diamond, (010) face. (x 1000).



Figure 5.33. Diamond H6, 001 face. (x 1000).

a hexahedroid-dodecahedroid combination. These would appear to be related in form to the cube just described but with the rectangular hillocks very well developed and centrally disposed on the surfaces.

The cube faces are in fact multi-faceted. The predominant facets are of a cubic nature, being oriented within say 5 degrees of true cubic orientation and being in most cases strongly curved, the radius of curvature frequently being less than 1 mm. Cubic-like facets in association with octahedral like facets, form the tetragons characteristic of these faces. Dodecahedral-like facets also occur in many cases being associated with a change in level of the surface.

Although the faces ^oif the cubic diamonds studied are made up of the same types of features the character of the surfaces differs a great deal from diamond to diamond. The general character of the faces of any one diamond is however very nearly the same. This is shown in figures 5.34 to 5.39 (x 60) and 5.40 to 5.45 (x 60) which show photomicrographs of Perspex replicas of the six faces from each of two diamonds, and figures 5.46 to 5.51 (x 60) which show pairs of faces from a further three diamonds.

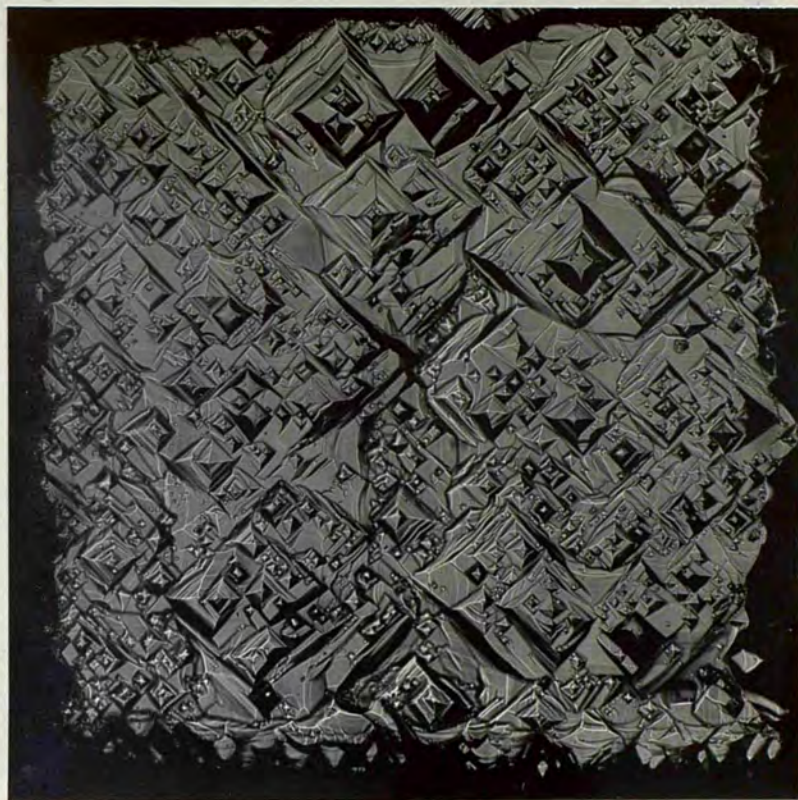


Figure 5.34. Diamond H4, 100 face. (x 60).



Figure 5.35. Diamond H4, 100 face. (x 60).

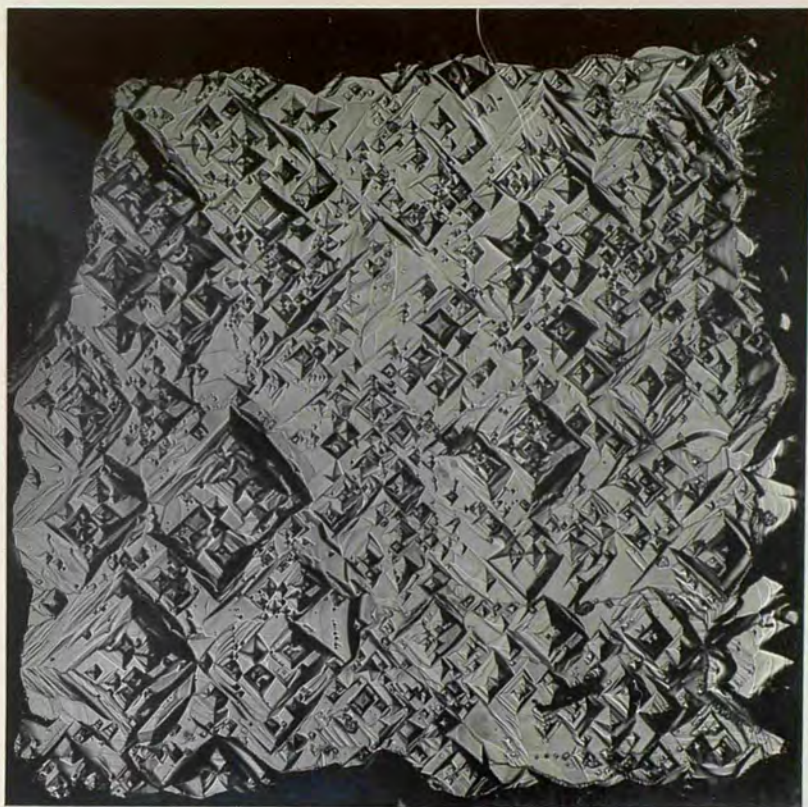


Figure 5.36. Diamond H4, 010 face. (x 60).

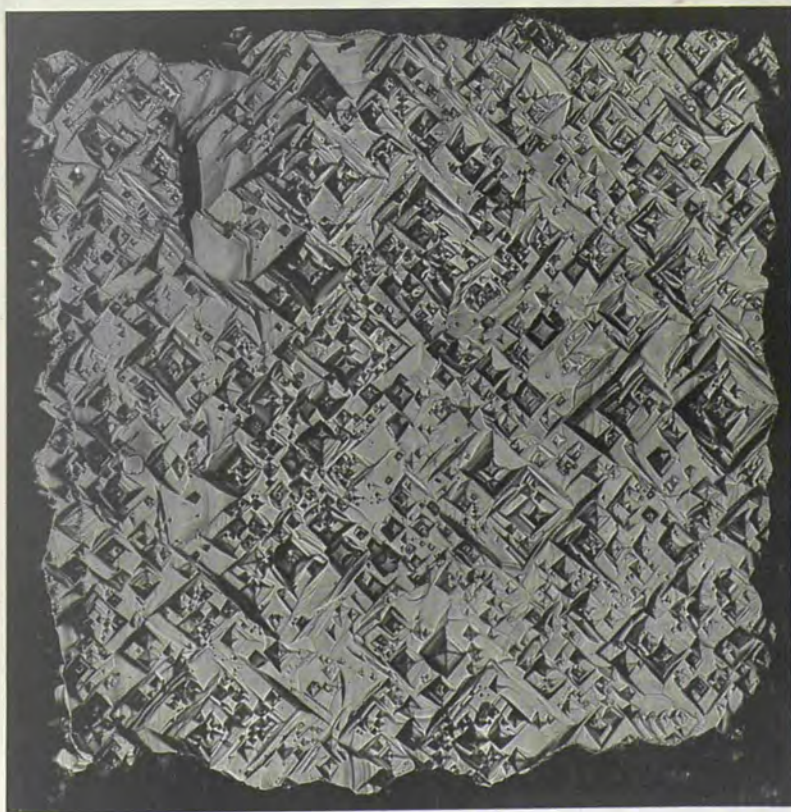


Figure 5.37. Diamond H4, $\bar{0}10$ face. (x 60).



Figure 5.38. Diamond H4, 001 face. (x 60).

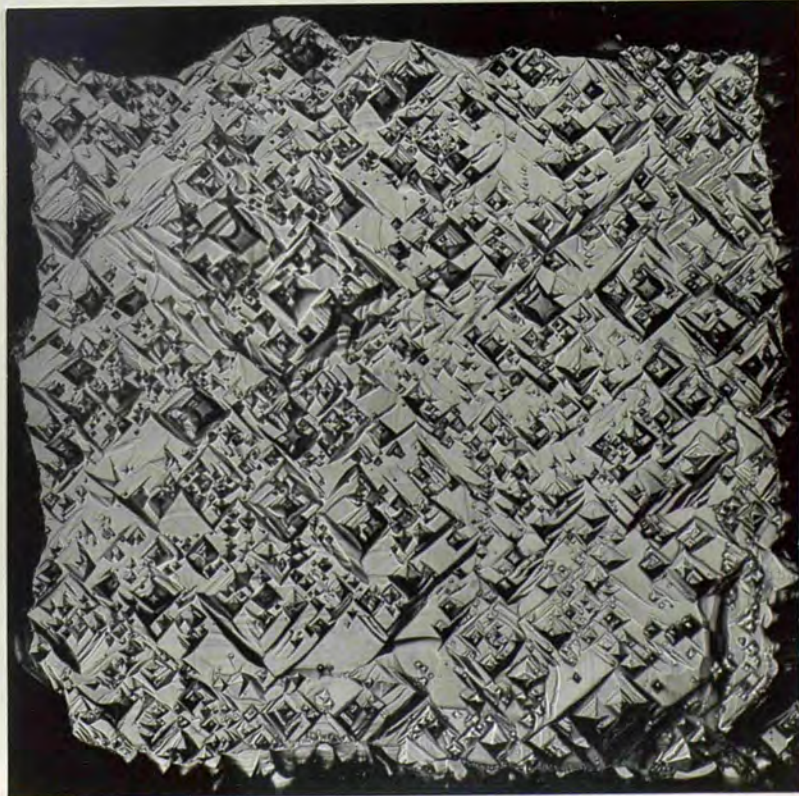


Figure 5.39. Diamond H4, $\bar{0}01$ face. (x 60).



Figure 5.40. Diamond H6, 001 face. (x 60).

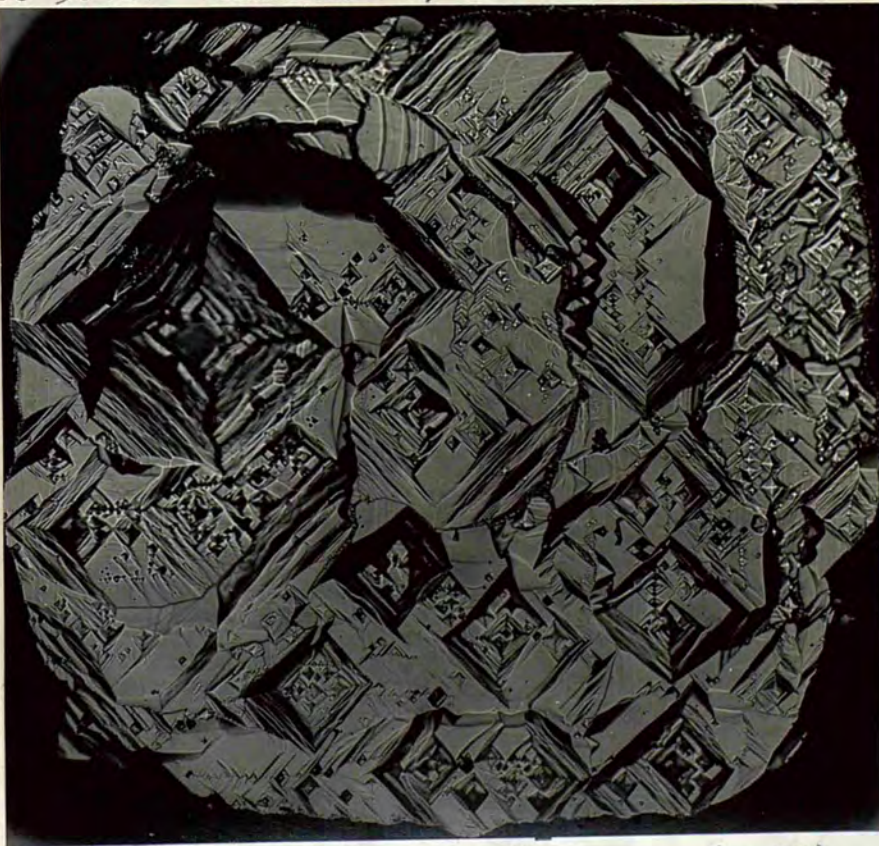


Figure 5.41. Diamond H6, 001 face. (x 60).



Figure 5.42. Diamond H6, 010 face. (x 60).

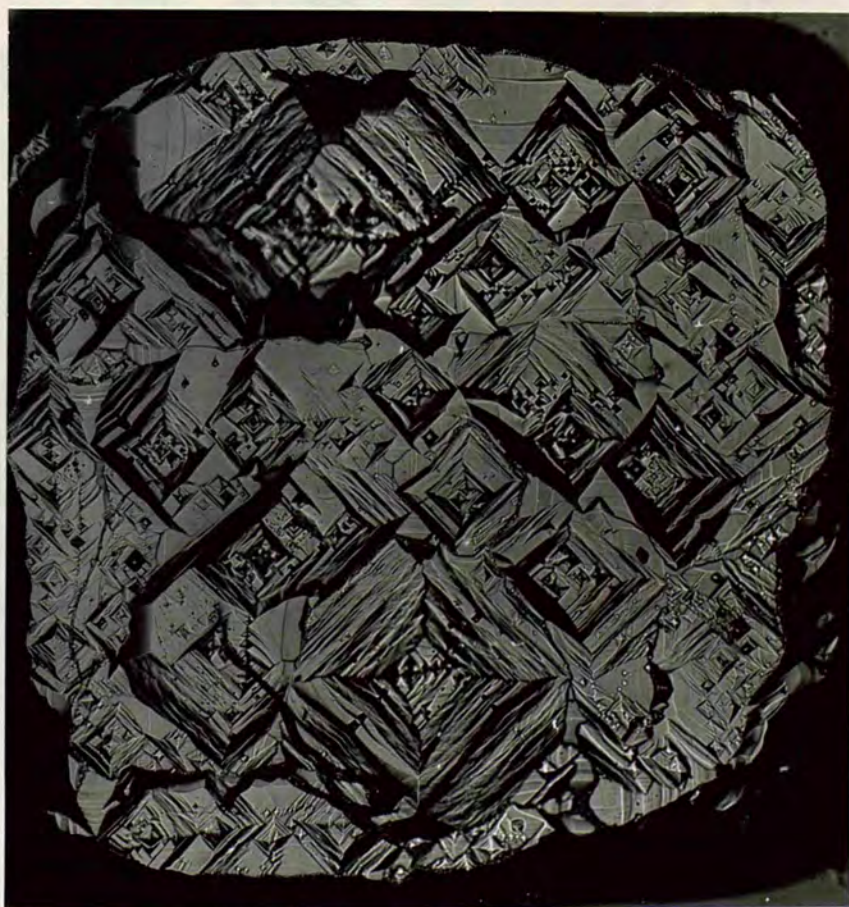


Figure 5.43. Diamond H6, $\bar{0}10$ face. (x 60).



Figure 5.44. Diamond H6, 100 face. (x 60).



Figure 5.45. Diamond H6, $\bar{1}00$ face. (x 60).

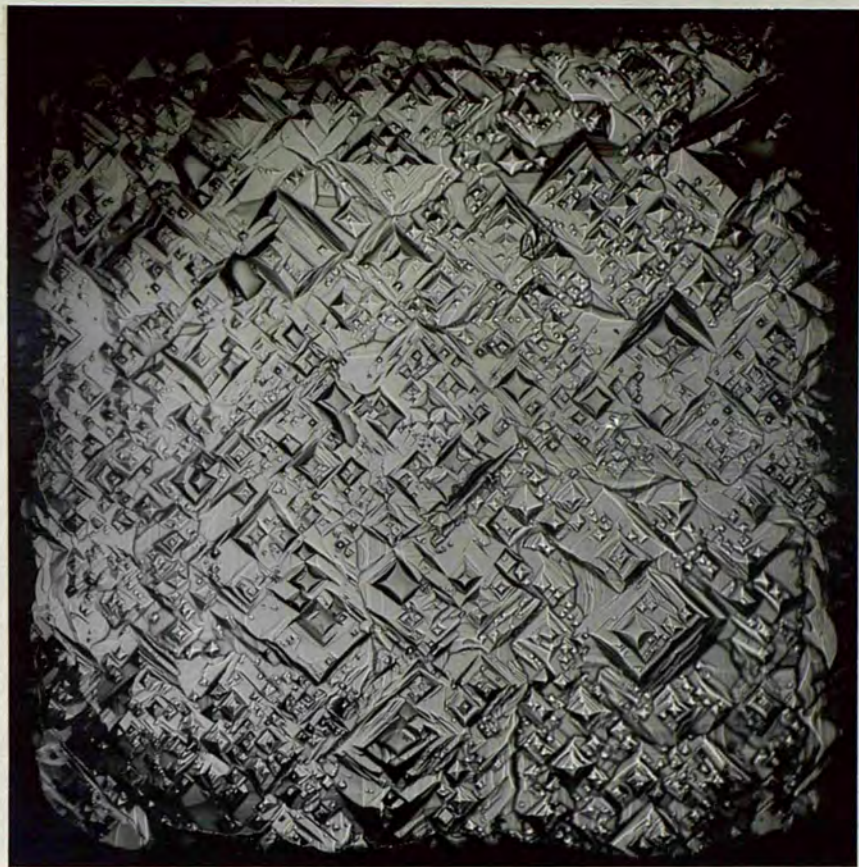


Figure 5.46. Diamond S2, 010 face. (x 60).

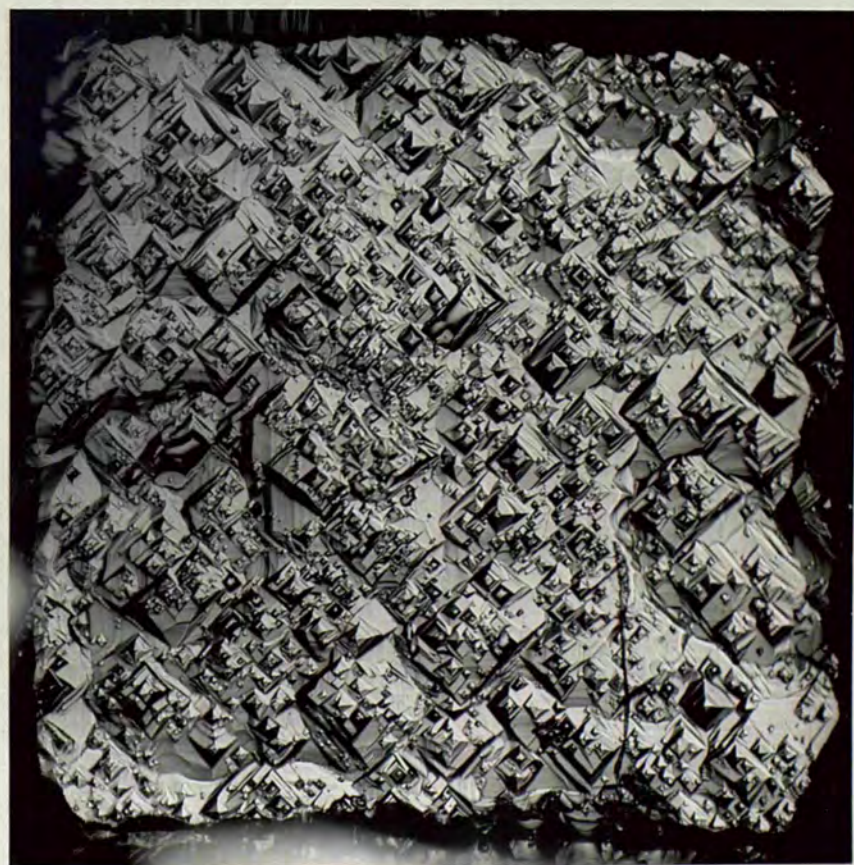


Figure 5.47. Diamond S2, $\bar{0}10$ face. (x 60).



Figure 5.48. Diamond H10, 001 face. (x 60).

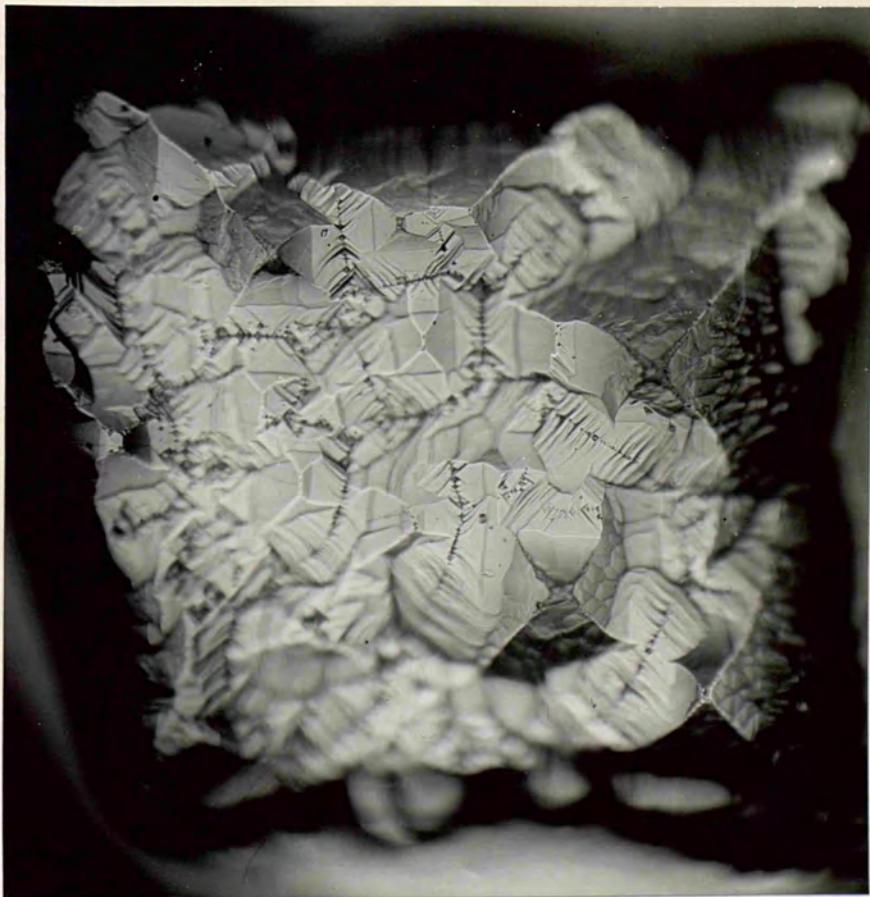


Figure 5.49. Diamond H10, $00\bar{1}$ face. (x 60).

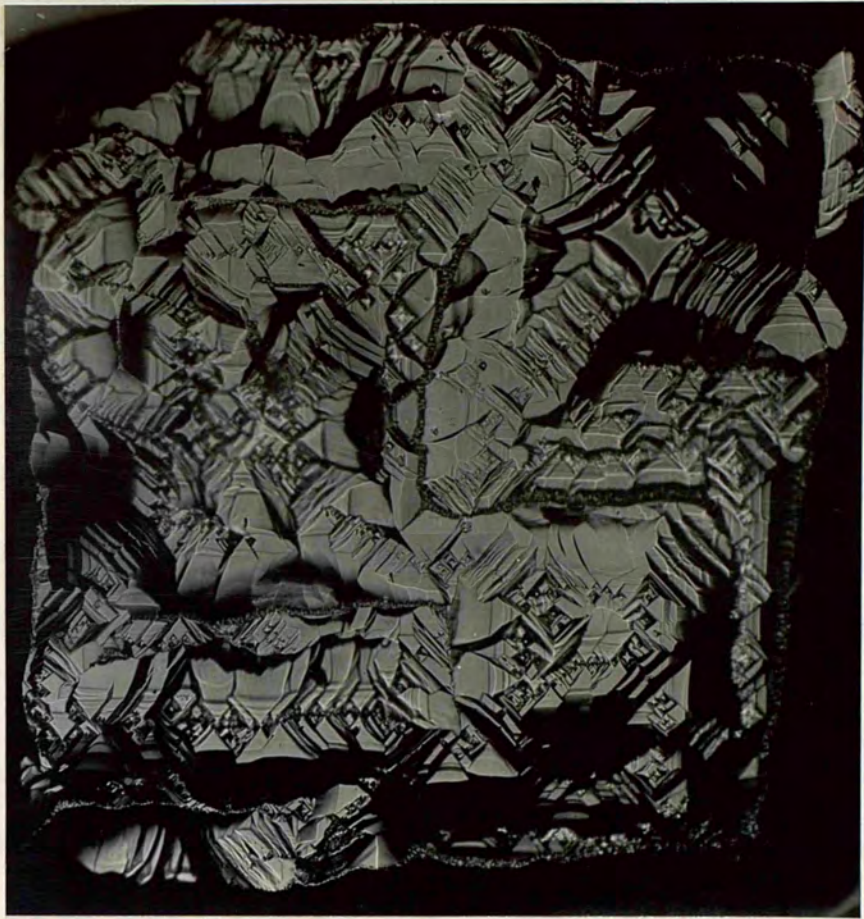


Figure 5.50. Diamond H2, 001 face. (x 60).

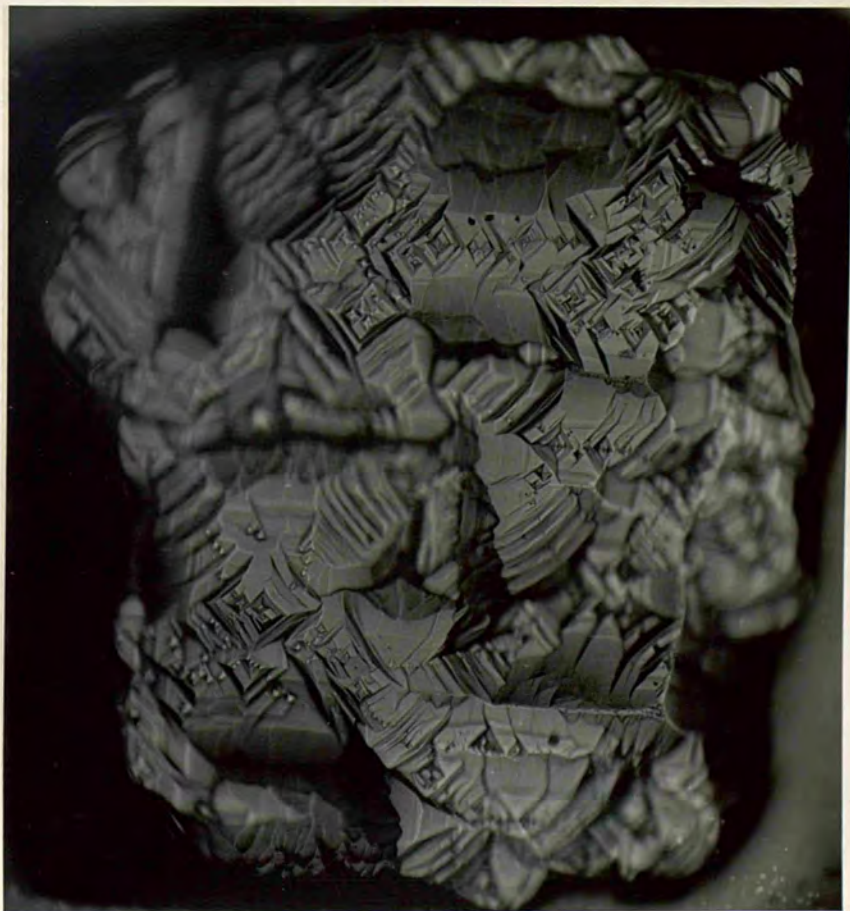


Figure 5.51. Diamond H2, $00\bar{1}$ face. (x 60).

5.4. Sectioned Cube Faces.

If a cube is polished along an edge to produce a plane of say dodecahedral orientation, features on the cubic surfaces at the intersection with the polished plane will cause the line of intersection to deviate from straightness. Figure 5.52 shows diagrammatically a cube so polished and indicates the effect on the edge of the polished plane due to a feature on one cubic face.

The angle ϕ between the plane ABDE and the cubic plane may be calculated from the angle α which the side AB makes with the edge at the intersection of the polished and cube faces, the angle γ which AE makes with the same edge, and the angle β which is the actual angle between the polished and cube faces.

$$\begin{aligned} \text{Then } \cot \phi &= \frac{Q'B}{QQ'} = \frac{A'P}{AA'} \cdot \frac{Q'B}{A'P} = \frac{A'P}{AA'} \cdot \frac{RP+PB}{RA'} \\ &= \frac{A'P}{AA'} \left(\frac{RP}{RA'} + \frac{PB}{AP} \cdot \frac{AP}{A'P} \cdot \frac{A'P}{RA'} \right) \\ &= \cot \beta (\cos \gamma + \cot \alpha \cdot \sec \beta \cdot \sin \gamma) \dots\dots 5.3 \end{aligned}$$

If the polished face is truly dodecahedral $\beta = \pi/4$
 and $\cot \phi = \cos \gamma + \sqrt{2} \cot \alpha \sin \gamma \dots\dots\dots 5.4$

Again if the feature on the cube face is a tetragon
 $\gamma = \pi/4$ approximately and
 $\cot \phi = 1/\sqrt{2} + \cot \alpha \dots\dots\dots 5.5$

If the feature is a dodecahedral-like plane $\gamma = \pi/2$ approximately and

$$\cot \emptyset = \sqrt{2} \cot \alpha \dots\dots\dots$$

Writing θ for \emptyset and re-arranging the relation may be written as

$$\tan \theta = 1/\sqrt{2} \tan \alpha \dots\dots\dots 5.6$$

The angle δ between a cubic plane and an octahedral-like plane, i.e. one having indices (h 1 1) and the angle ϵ between a cubic plane and a dodecahedral-like plane, i.e. one having indices (h 1 0) is given for a number of high index planes in the second columns of tables 5.2 and 5.3 respectively. In the third column is given the angle α between the facet edges as seen when viewing the polished dodecahedral plane normally.

The diamond whose cubic faces are shown in figures 5.40 to 5.45 was polished along the edge at the intersection of the faces $0\bar{1}0$ (figure 5.43) and $00\bar{1}$ (figure 5.41) to produce an approximately dodecahedral face with indices $0\bar{1}\bar{1}$. This face is shown in figure 5.53 (x 80). Its stepped edges reveal the nature of the neighbouring cubic faces which are shown after the polishing in figure 5.54 (x 60) alongside the neighbouring edges of the $0\bar{1}\bar{1}$ polished face. The crosses on this picture indicate that the edge was damaged during other experiments

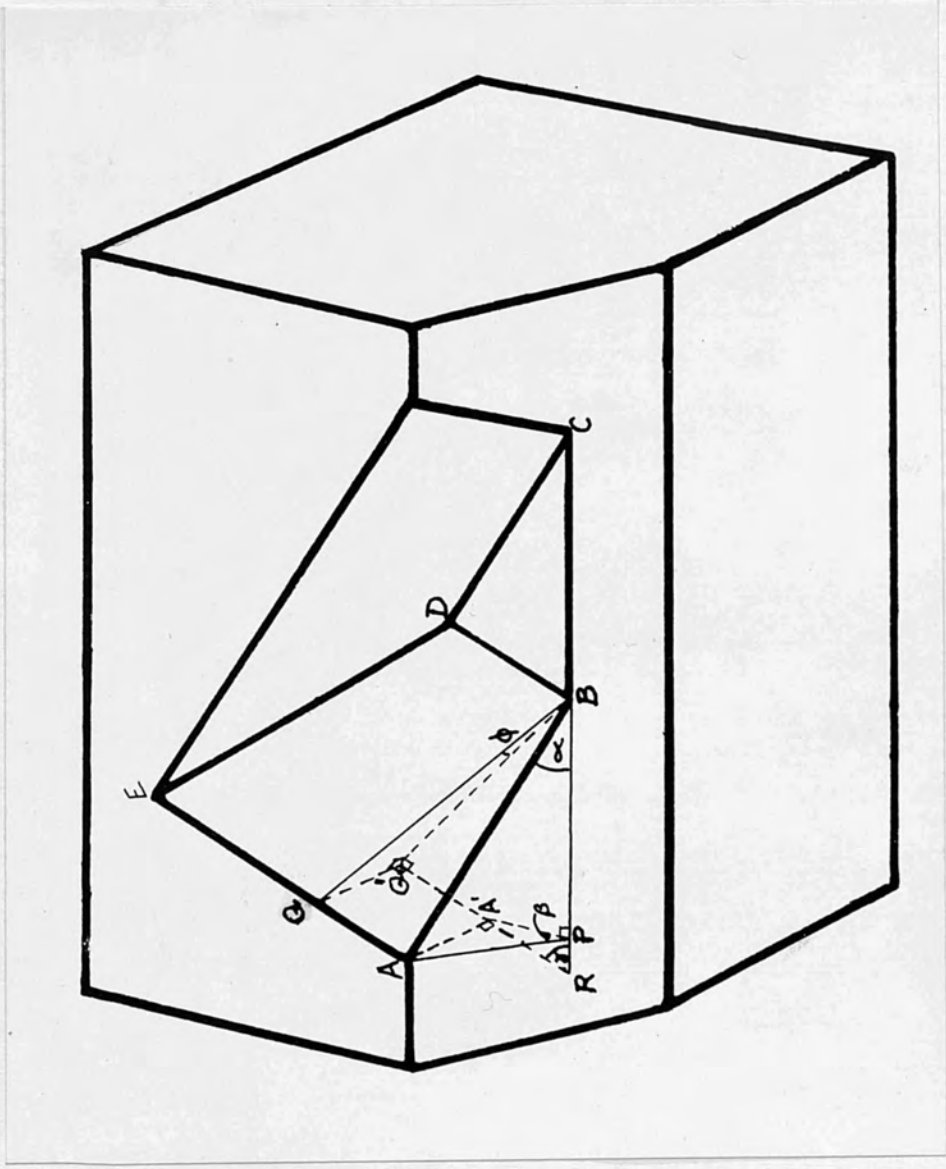


Figure 5.52.

Plane	δ	α
1 1 1	$54^{\circ} 44'$	90°
3 2 2	$43^{\circ} 19'$	$70^{\circ} 32'$
2 1 1	$35^{\circ} 16'$	$54^{\circ} 44'$
3 1 1	$25^{\circ} 14'$	$35^{\circ} 14'$
4 1 1	$19^{\circ} 28'$	$25^{\circ} 14'$
5 1 1	$15^{\circ} 47'$	$19^{\circ} 32'$
6 1 1	$13^{\circ} 16'$	$15^{\circ} 45'$
7 1 1	$11^{\circ} 26'$	$13^{\circ} 17'$
8 1 1	$10^{\circ} 2'$	$11^{\circ} 26'$

Table 5.2 Angles between cubic and octahedral -like planes.

Plane	ϵ	α
1 1 0	45°	$54^{\circ} 44'$
3 2 0	$33^{\circ} 42'$	$43^{\circ} 19'$
2 1 0	$26^{\circ} 35'$	$35^{\circ} 16'$
3 1 0	$18^{\circ} 26'$	$25^{\circ} 14'$
4 1 0	$14^{\circ} 2'$	$19^{\circ} 28'$
5 1 0	$11^{\circ} 19'$	$15^{\circ} 47'$
6 1 0	$9^{\circ} 28'$	$13^{\circ} 16'$
7 1 0	$8^{\circ} 8'$	$11^{\circ} 26'$
8 1 0	$7^{\circ} 7'$	$10^{\circ} 2'$

Table 5.3 Angles between cubic and dodecahedral-like planes.

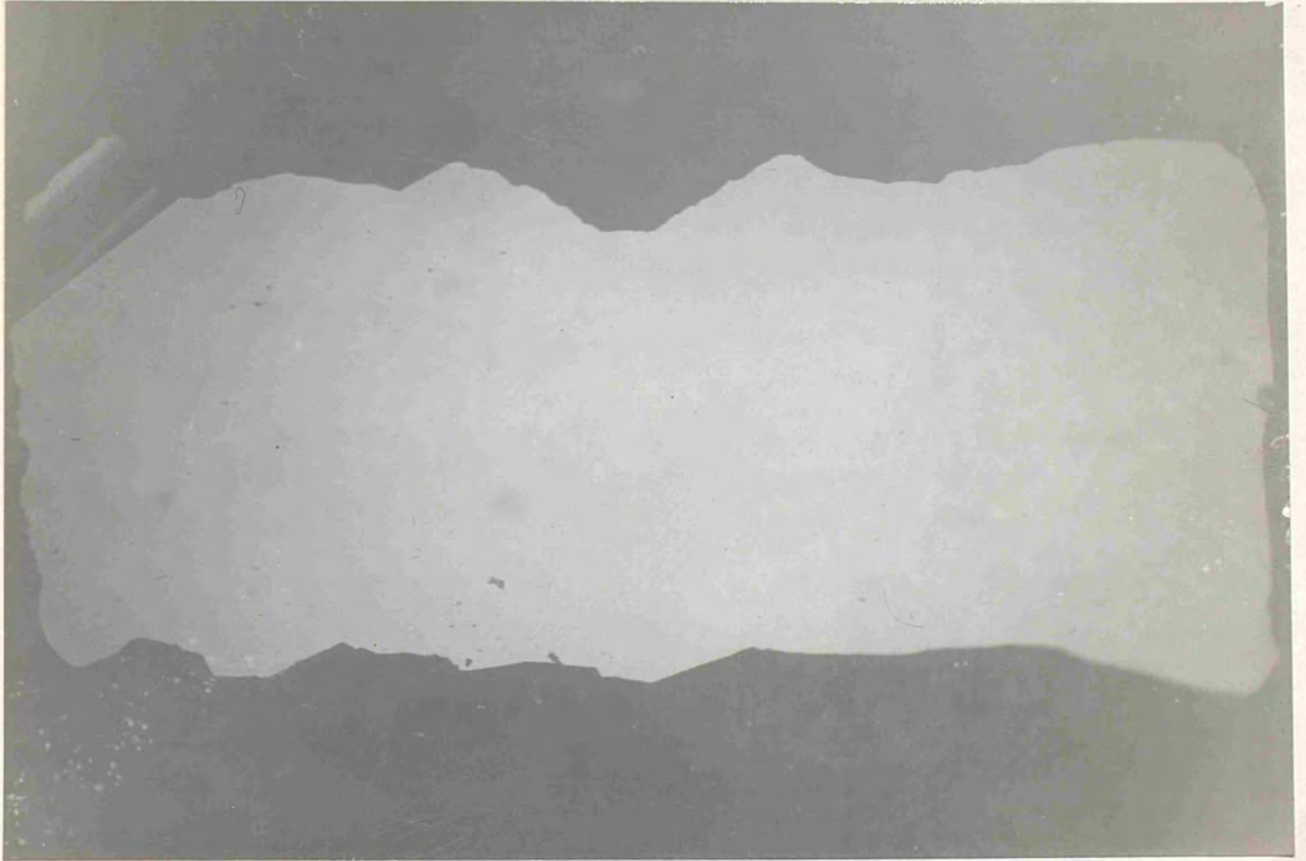


Figure 5.53. Diamond H6, Polished $\bar{0}\bar{1}\bar{1}$ face. (x 80).

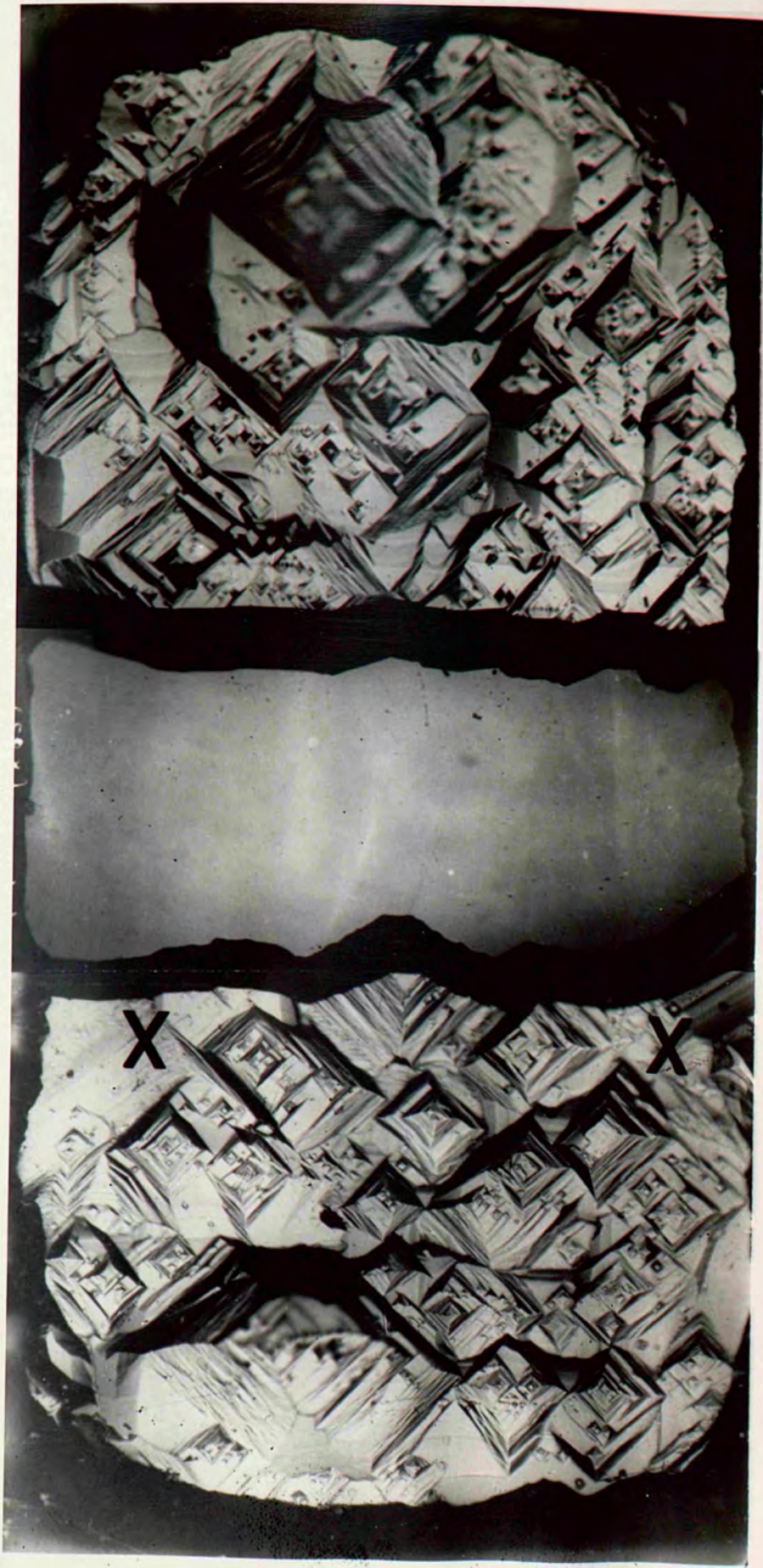


Figure 5.54 .

x60.

and therefore these portions must be ignored. It is possible to assign Miller indices to some of the facets and a number of these have been identified for several features on the edge of the $0\bar{1}\bar{1}$ polished face shown at higher magnification in figures 5.55 and 5.56 (x 200).

This same diamond was parted by sawing through the polished $0\bar{1}\bar{1}$ face and at right angles to it, cutting the crystal into two approximately equal parts. The resultant dodecahedral sawn faces were polished and the edges of these polished faces are normal sections of the original 100 and $\bar{1}00$ faces. Figure 5.57 (x 75) shows part of the $\bar{1}00$ face before polishing and alongside cross sections of the positions indicated by the lines drawn on the cube face. The feature indicated at A is a section of a cube plane on the side of a tetragon. At B a section through two small tetragons is shown. The angles between the facets are 110° in the one case and 130° in the other. The angle between two truly octahedral planes would be $109^\circ 28'$. The features shown at C and D are where the section passes through dodecahedral-like facets, the angles with the cube faces being about 22° , 30° and 45° . For true crystallographic faces the angle would be $35^\circ 16'$.

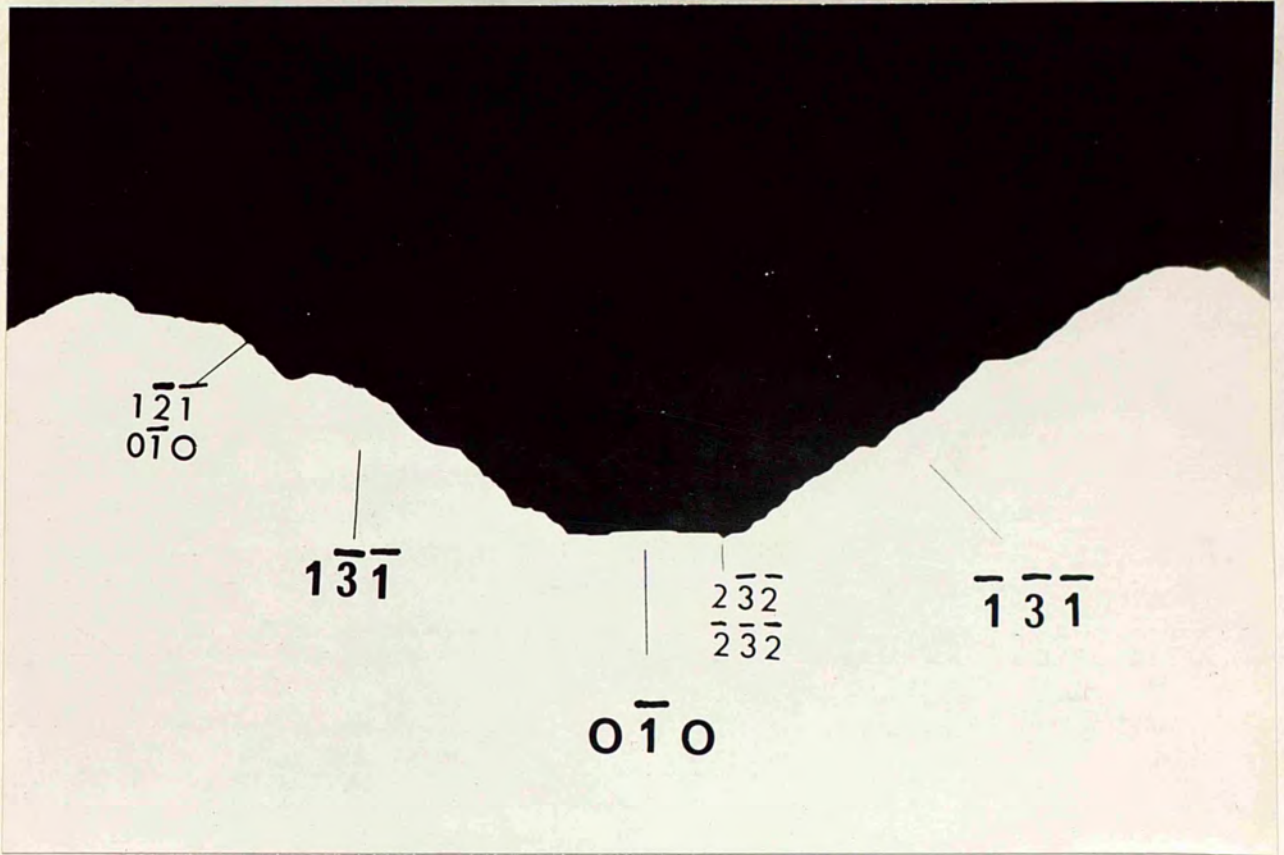


Figure 5.55. Diamond H6, Polished $0\bar{1}\bar{1}$ face. (x 200).

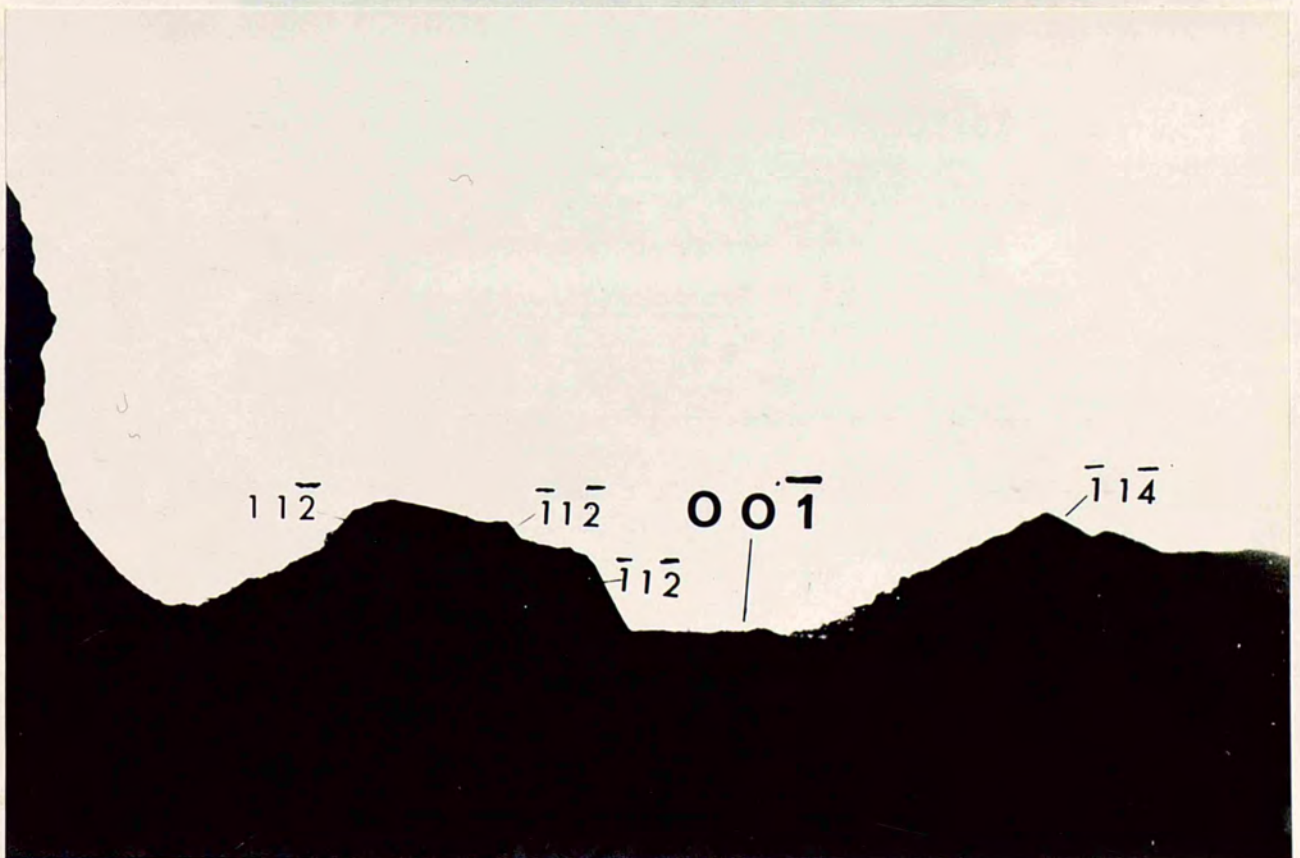


Figure 5.56. Diamond H6, Polished $0\bar{1}\bar{1}$ face. (x 200)

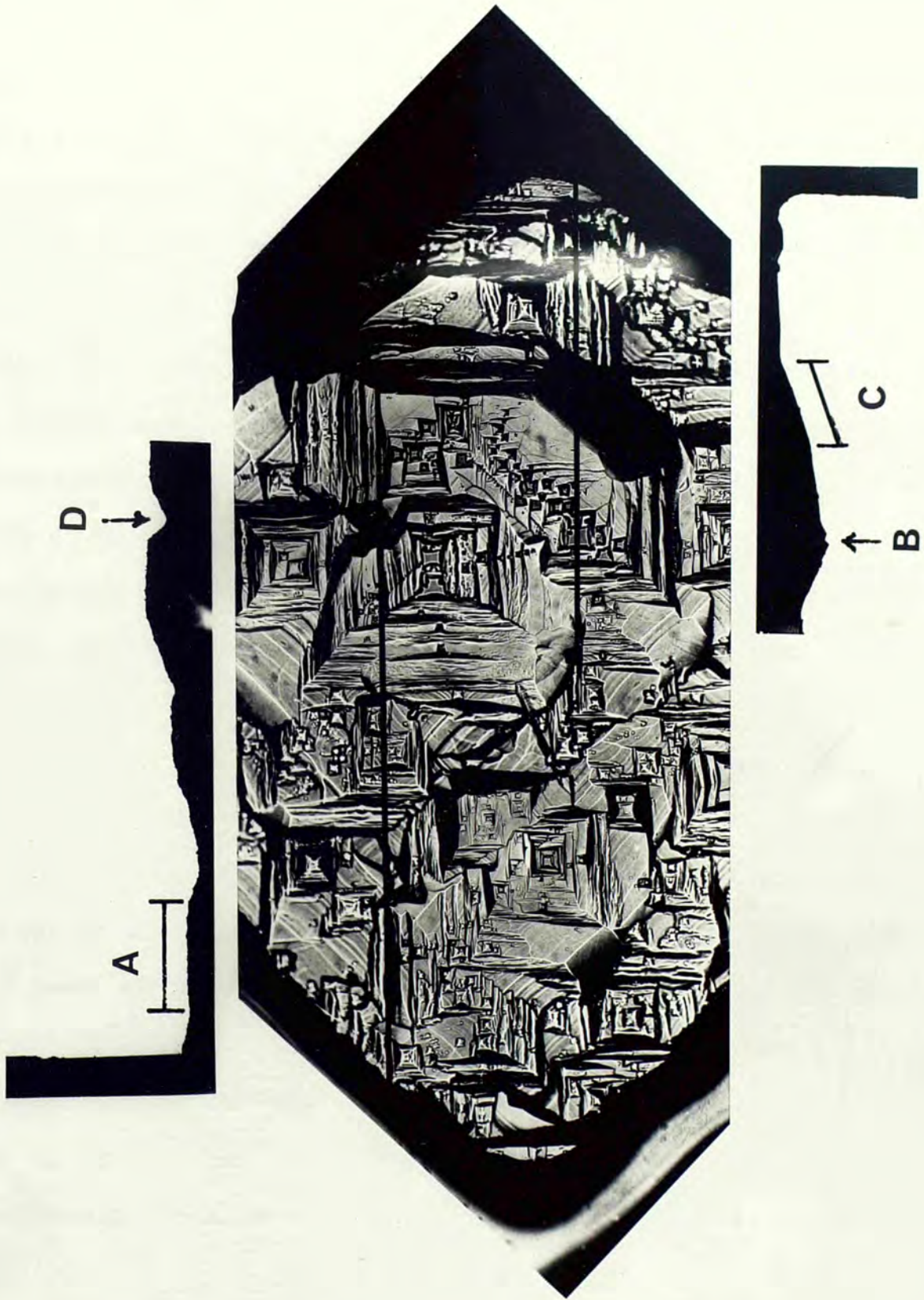


Figure 5.57.

x 75.

5.5 Dodecahedral and Octahedral Faces.

Without exception for the cubic diamonds studied there is , at the intersection of every pair of adjacent cubic faces, a small dodecahedral face about 0.2 mm in width. These faces, like the cubic faces, are characterised by faceted structure as shown in figures 5.58, 5.59 and 5.60 (x 60). The facets are inclined to the true dodecahedral plane about axes in the plane and perpendicular to the direction of the cubic edge, alternating in direction of inclination. In many cases, as in figure 5.59, there is a double row of facets, the rows being inclined to each other about an axis parallel to the cube edge. Figure 5.60 shows still further complexity.

Figure 5.61 (x 400) shows a photomicrograph of a small region on a dodecahedral face of another diamond. The diamond was tilted so that it was oriented approximately in such a way that an octahedral (1 1 1) plane on it would have been perpendicular to the optic axis of the microscope. Only one facet is in focus and trigons are clearly visible on it. Several others can be seen on some of the nearby but out-of-focus facets. The facets are clearly octahedral.

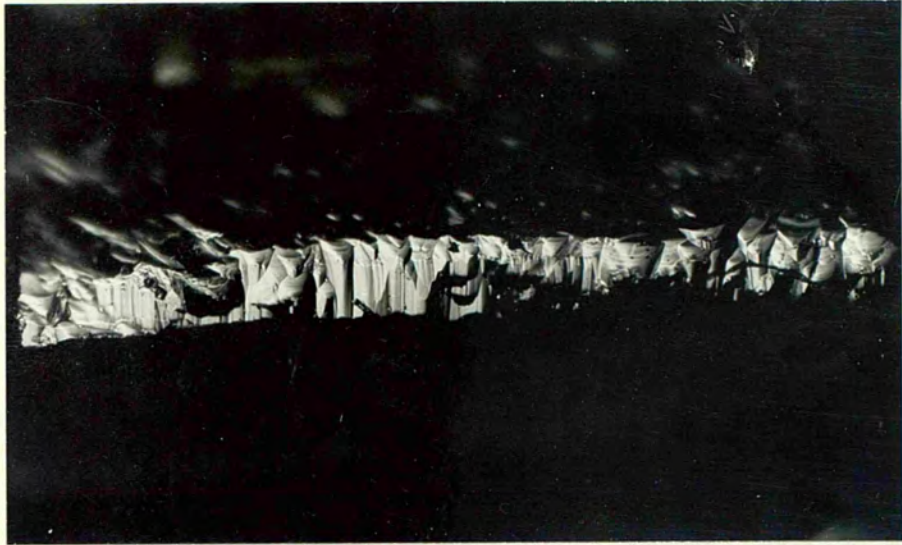


Figure 5.58. Diamond S2, 101 face. (x 60).

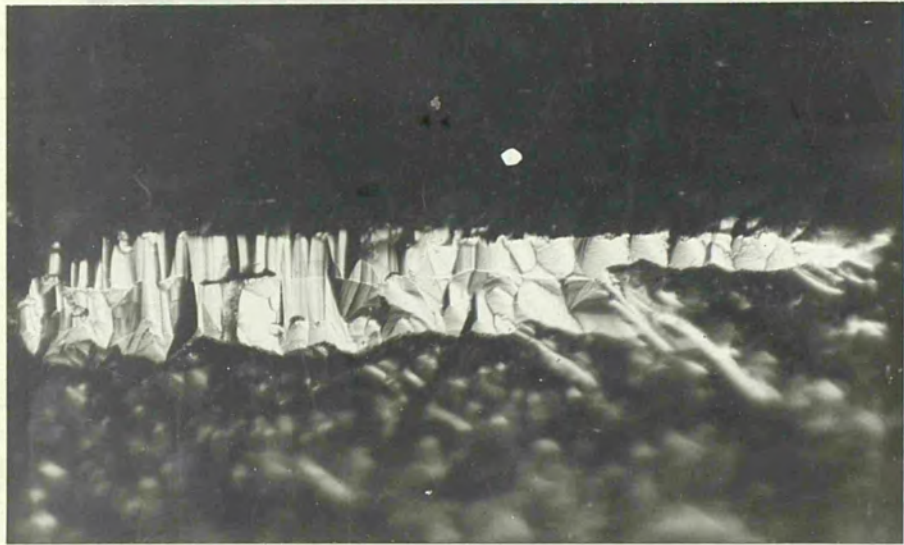


Figure 5.59. Diamond S2, $0\bar{1}\bar{1}$ face. (x 60).

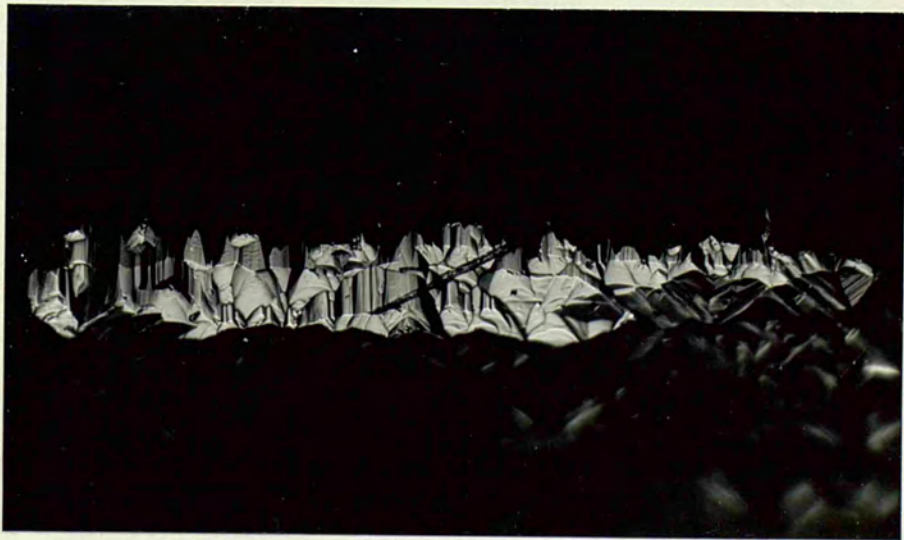


Figure 5.60. Diamond S2, $01\bar{1}$ face. (x 60).

of this face is a small, well-developed
 of linear dimensions about 2 μ and is located at
 one corner of the cube. A photograph of this face is shown
 in figure 5.55.

figure 5.55 (x
 those studied
 observed. No
 observed to be
 faces. On the
 stepped in cor
 also observed.



Figure 5.61. Diamond H5, 110 face. (x 400).
 cubic face. It failed to observe any such cases.

The stepped face shown in figure 5.55, though
 small, was well developed and by comparison with the
 other faces of the diamond was flat and smooth. The
 trisecting planes were well developed. In figure 5.57
 the layer-like structure of the dodecahedral face where
 it meets the octahedral face can be seen and one can well
 imagine the diamond in this region as consisting of
 layers of octahedral planes of increasing extent
 laid down successively one upon another.

On another corner of the same cube a hopper-like
 feature with conical faces and trigonal prisms was
 observed. This is shown in figure 5.54 (x 400).

On this same diamond a small octahedral face of linear dimensions about 1 x 0.5 mm was present at one corner of the cube. A picture of the face is shown in figure 5.62 (x 130) and at higher magnification in figure 5.63 (x 300). This diamond is the only one of those studied on which a true octahedral face was observed. Octahedral facets with trigons present were observed to be present as shown above on dodecahedral faces. On one other diamond where the surface was stepped an octahedral surface with trigons on it was also observed. Seal (1960) has reported a case of a trigon occurring on the side wall of a tetragon on a cubic face. We failed to observe any such cases.

The octahedral face shown in figure 5.63, though small, was well developed and by comparison with the other faces of the diamond was flat and smooth. The trigons present were well developed. In figure 5.62 the layer-like structure of the dodecahedral face where it meets the octahedral face can be seen and one can well imagine the diamond in this region as consisting of layers of octahedral planes of continued decreasing extent laid down successively one upon another.

On another corner of the same cube a hopper-like feature with octahedral facets with trigons on them was observed. This is shown in figure 5.64 (x 200).

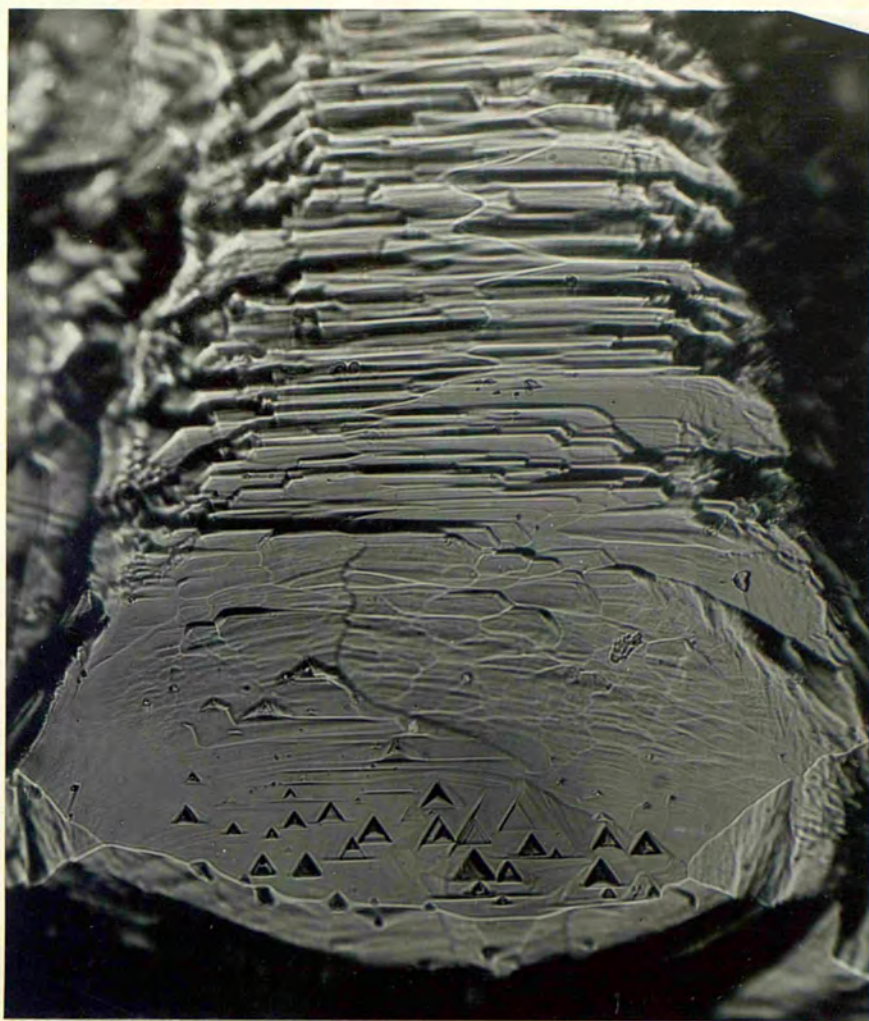


Figure 5.62. Diamond H5, $1\bar{1}\bar{1}$ face. (x 130).

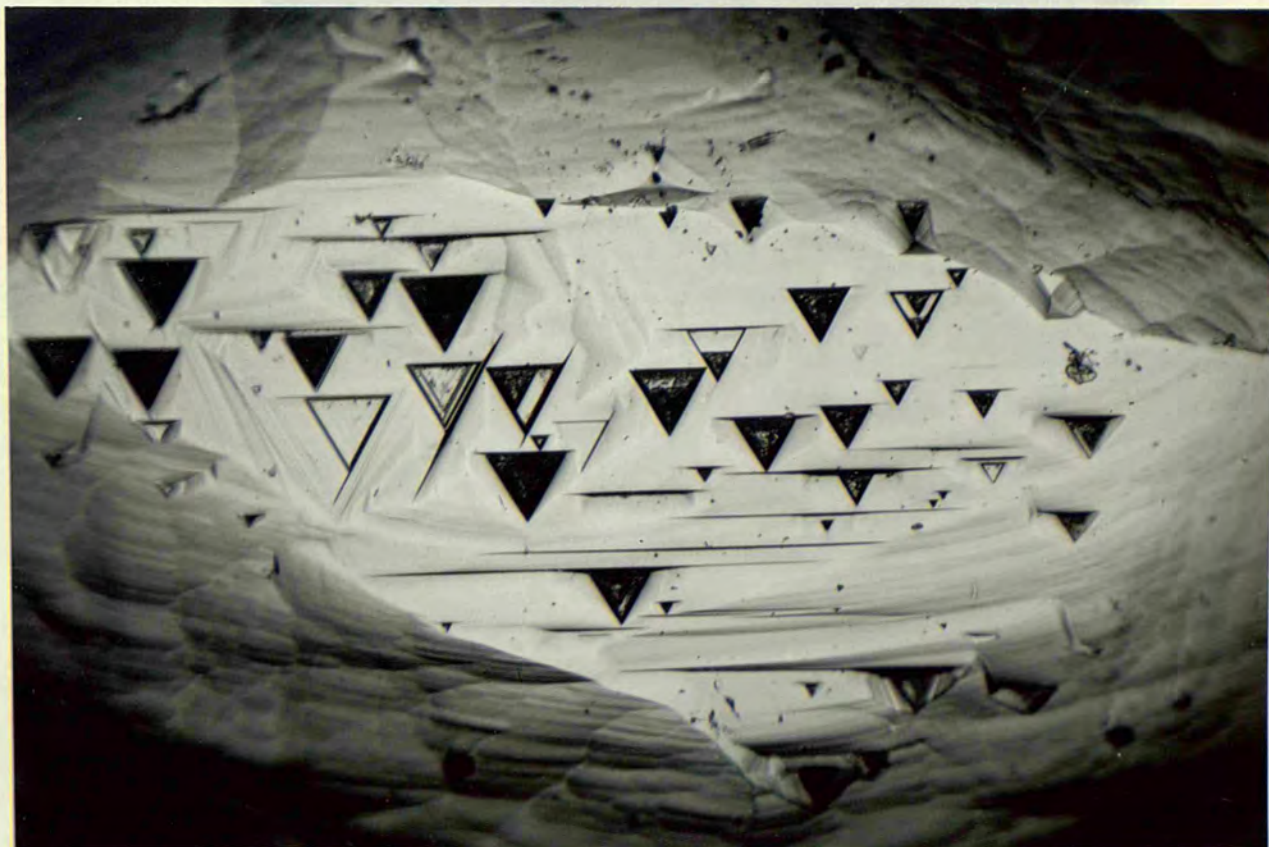


Figure 5.63. Diamond H5, $1\bar{1}\bar{1}$ face. (x 300).

5.6. Crystal Growth

The surface of a crystal of the diamond H5 is

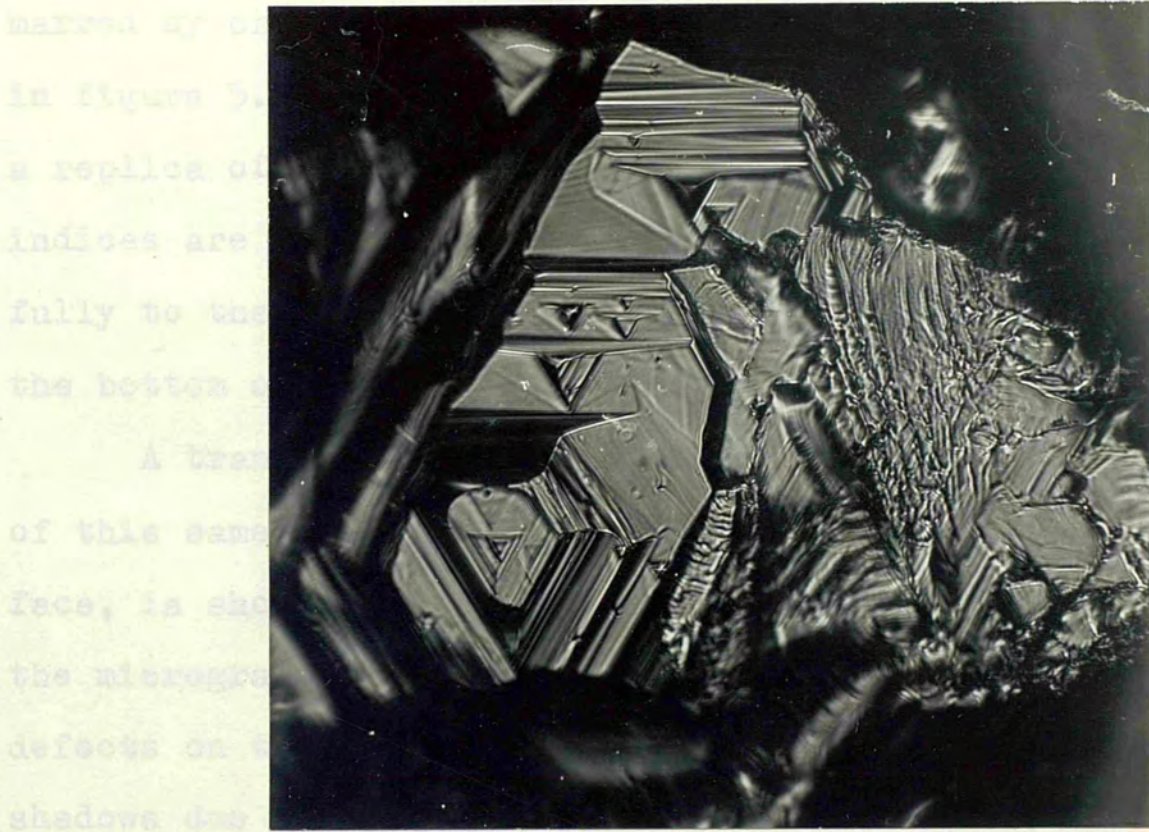


Figure 5.64. Diamond H5, 111 face. (x 200).

into two approximately equal parts. Figure 5.64 shows the same surface after being polished and etched to a mild etch by potassium nitrate at 500°C for one hour. There are three points of interest in the present connection. (1) The grain structure is shown in figure 5.65. (2) Additional cracks are observed in figure 5.66 as a result of etching. (3) In the lower part there are a series of holes with some or less crystalline boundaries approximately parallel to the surface.

5.6. Internal Defects.

The surfaces of a number of the diamonds are marred by cracks and furrows. An extreme case is shown in figure 5.65 (x 60) which is a transmission picture of a replica of a partially polished face, whose Miller indices are $(0\ 0\ 1)$. The Perspex has not been pressed fully to the bottom of the furrow although detail at the bottom of the deep tetragons is revealed.

A transmission picture of the opposite $(0\ 0\ \bar{1})$ face of this same diamond, taken through the polished $(0\ 0\ 1)$ face, is shown in figure 5.66 (x 60). The shadows on the micrograph are caused partly by the residual surface defects on the $(0\ 0\ 1)$ face but in addition there are shadows due to internal faults.

Figure 5.67 (x 50) shows a sawn face of a cube cut into two approximately equal parts. Figure 5.68 (x 50) shows the same surface after being polished and subjected to a mild etch by potassium nitrate at 580°F for one hour. There are three points of interest in the present connection. (1) Cracks are visible in figure 5.67. (2) Additional cracks are revealed in figure 5.58 as a result of etching. (3) In one corner there are a series of holes with more or less rectilinear boundaries approximately crystallographically orientated.

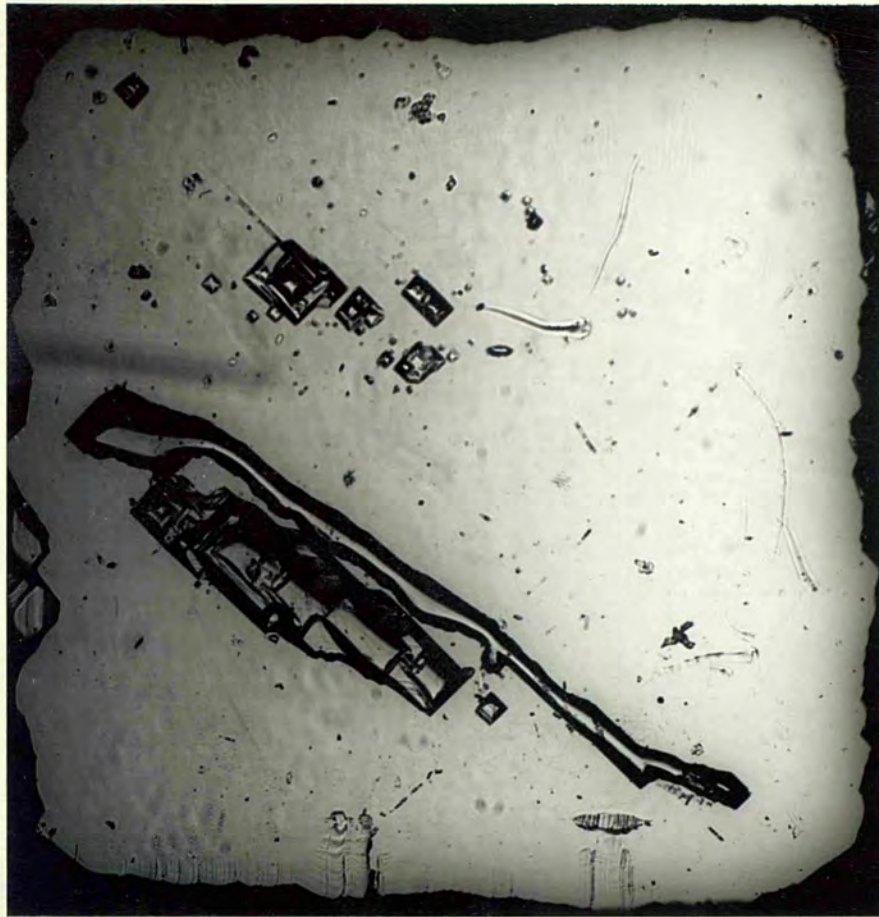


Figure 5.65. Diamond S2, 001 face. (x 60).



Figure 5.66. Diamond S2, $00\bar{1}$ face. (x 60)

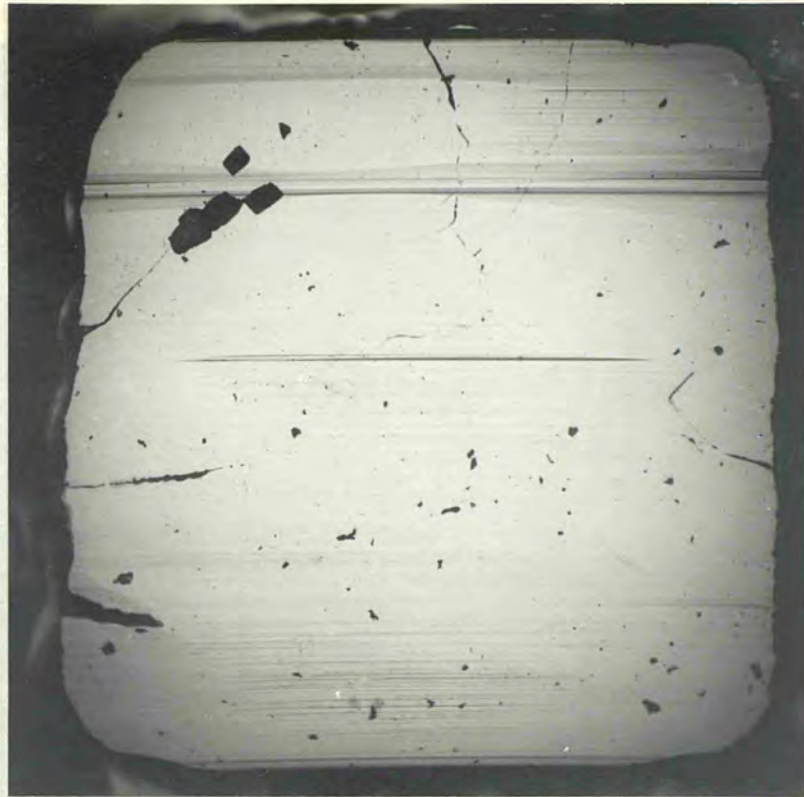


Figure 5.67. Diamond G1B, $00\bar{1}$ face. (x 50).

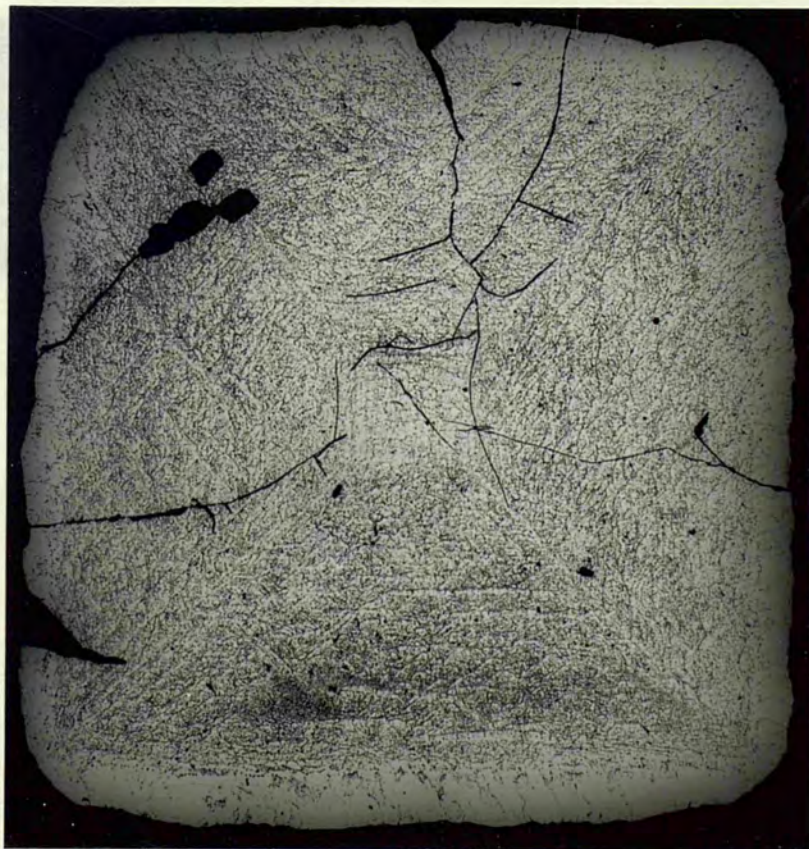


Figure 5.68. Diamond G1B, etched $00\bar{1}$ face.
(x 50).

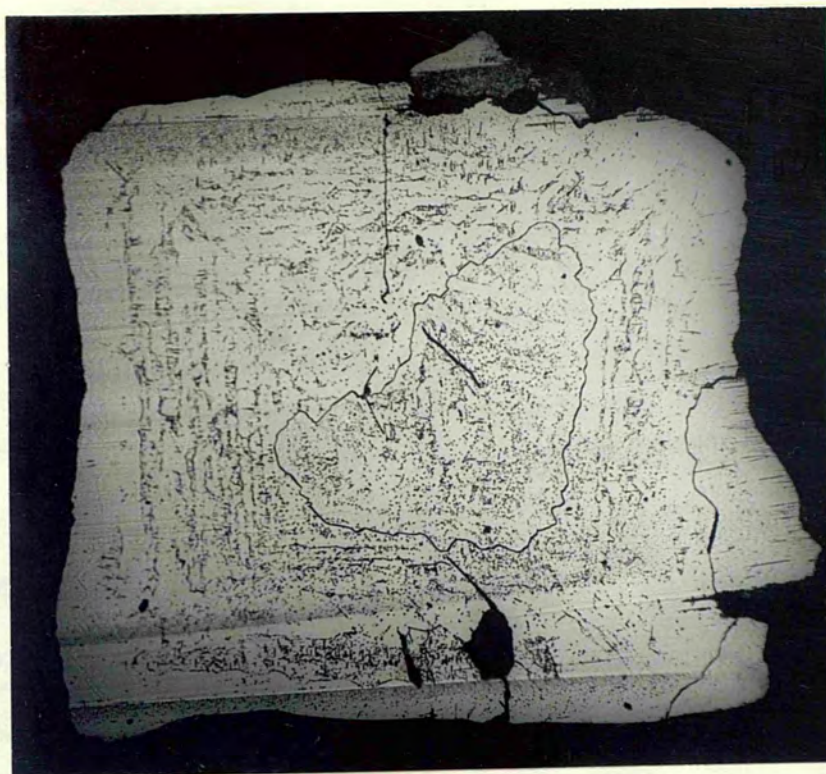


Figure 5.69. Diamond S3, etched 001 face. (x 50).



Figure 5.70. Diamond H6, polished 011 face. (x 500).

Similar features are shown in figure 5.69 (x 50). This is the etched surface of a diamond whose natural surface has been polished away.

A possible clue as to how the gas inclusions may occur is given in figure 5.70 (x 500) which shows a small part of a dodecahedral face of a diamond sectioned diagonally through two opposite edges. A hole opening into the neighbouring natural cubic face is visible. The sides of this hole are for a large part rectilinear and crystallographically orientated and there is evidence of bridging at the surface.

CHAPTER 6.ETCH FIGURES ON CUBIC DIAMONDS.6.1 Previous Etching Experiments on Diamond.

An interesting feature about the natural figures occurring on diamond is that they are oriented differently from the etch patterns produced in the laboratory. This is shown diagrammatically in figure 6.1. This and other observations have led a number of workers to conclude that the naturally occurring figures are growth features. Other workers however are of the opinion that they are in fact etch figures produced under conditions which are different from those produced in the laboratory. Quite a lot of work has been done on the relation between the natural figures and those produced by etch. Tolansky and his co-workers, from the study of block etch patterns obtained on the surfaces of sectioned diamonds, have shown that laminar structure exists within diamond crystals. They suggest that these etch patterns may reveal a history of growth and that the structure is strong evidence in favour of growth by successive deposition of rectilinear layers.

Early experiments on the etching of diamond were

carried out by ...
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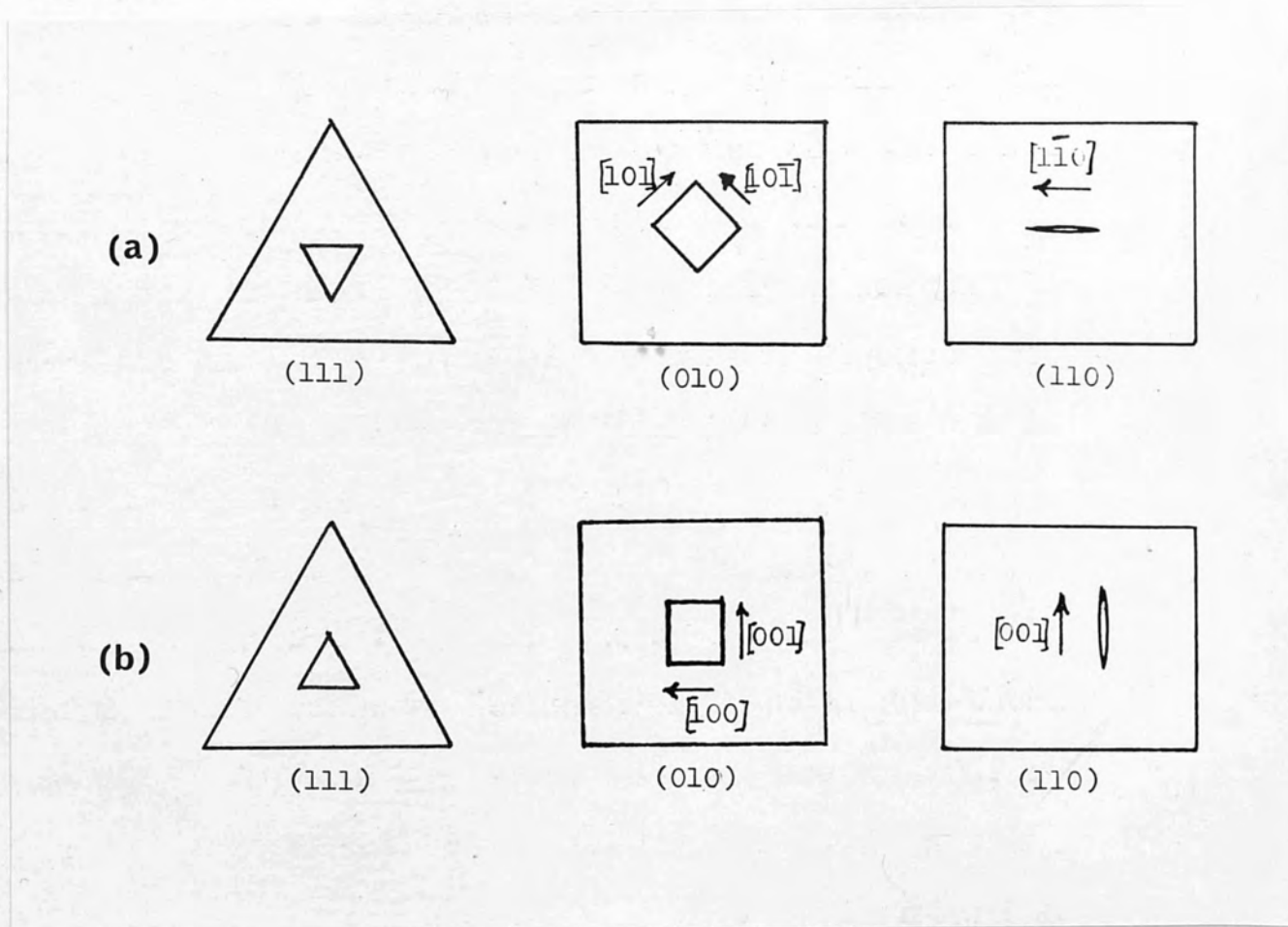


Figure 6.1. (a) Naturally occurring figures on diamond faces.

(b) Etch figures produced on diamond faces.

carried out by Luzi as early as 1892 when he heated diamond to temperatures as high as 1770°C . in blue ground. Fersmann and Goldschmidt in 1911 and Williams in 1932 etched them by heating in fused potassium nitrate to some 900°C . More controlled experiments were carried out by Omar, Pandya and Tolansky (1954) who etched in fused potassium nitrate commencing at quite low temperatures. They found for octahedral faces that etching commenced at 525°C along existing ring cracks and micro-ring cracks, and along scratches if these were present. It had of course been known since the beginning of the twentieth century that etching of crystals takes place preferentially along scratches and in strained regions. At the temperature at which they did their experiments well shaped etch pits were produced over most of the natural octahedral faces. Etching, for example, for one hour at 550°C produced small triangular shaped etch pits up to 4 microns across. They noted that etch inside trigons was notably less severe than elsewhere on the surface and considered this as evidence that trigons were growth features on the basis that dislocations encourage growth and that the relatively small number of etch pits within trigons was evidence of fewer dislocations in these regions.

They found that etching above 575°C caused the etch pits to increase in size so that ultimately they devoured neighbouring ones. There is a tendency for these pits to have rounded corners and flat bottoms. A third stage of etching was observed in which the flat bottomed pits tend to become pyramidal, finally giving remarkable block patterns. On the sides of such blocks secondary etch pits were observed.

Etching experiments were carried out by Sutton (1928) on a polished cube face of an octahedral diamond and on a natural dodecahedral face, and by Williams (1932) on a supposed naturally occurring cube face. Further studies were carried out by Pandya and Tolansky (1954) on cubic and dodecahedral faces polished on octahedra. On the cube (010) faces these workers reported square etch pits orientated so that their sides were parallel to the $[100]$ and $[001]$ directions, and on the dodecahedral (110) faces boat shaped pits orientated so that the keel of the boat lay parallel to the $[001]$ direction.

They etched a polished dodecahedral section of an octahedron. At 550°C numerous small micro-etch pits were observed to have formed. The density of these pits varied over the surface to reveal laminar structure within the diamond. The observed pattern was hexagonal,

the sides of the hexagon being approximately parallel to the edges of the section. The individual pits and the block pattern became more pronounced after etching at higher temperatures and for a longer time, showing up well at 600°C . The angles between the sides of the hexagon were considered to be reasonably close (within 3°) to the expected crystallographic angles but there were some irregularities. They also studied the effect of etch on a cubic section polished from an octahedron. Etching at 550°C for 2 hours gave square etch pits but also a striking rectangular pattern. They observed that the etch pits within a group were of uniform size. Further etching at 700°C gave a stronger pattern revealing laminations within the crystal.

Emara and Tolansky (1957) studied the etching of natural dodecahedral faces at 500°C and 600°C in fused potassium nitrate. They found etching faster for the dodecahedral than for the octahedral faces and that preferential etching took place along the so-called "solution channels". They concluded that these solution channels were probably due to etch because the original outlines on the surface were less resistant to etching than the rest of the surface, etching presumably taking place preferentially along dislocation networks. However as boat-shaped depressions were produced in their

experiments with more vigorous etching, they concluded that the natural etch would be very gentle indeed.

Etching studies by Patel and Tolansky (1957) on cleaved diamond surfaces revealed linear arrangements of etch pits. Moreover the patterns on pairs of matching cleaved surfaces were identical. Studies on a block cleaved from an octahedron showed that stratigraphy within the diamond occurred "in depth" and also indicated that growth had taken place by successive deposition of sheets. They postulated that the different degree of etching which occurred for the different layers was due to differing conditions of growth (temperature, pressure, concentration, impurities, etc.). They suggested that sheets with uniform etch characteristics may have been laid down at a fairly rapid rate but that there may have been considerable intervals between the deposition of successive layers.

Omar and Kenawi (1957) obtained well formed triangular etch pits in so-called positive (or etch pit) orientation by heating an octahedron to 1000°C on a molybdenum strip in a vacuum chamber at a pressure of some 2.5×10^{-3} mm Hg. Frank and Puttick (1958) heated octahedra in various agents such as steam, chlorine

and wet hydrogen at 800°C in an attempt to produce etch pits in the negative, i.e. trigon orientation, without success. By heating to 1450°C in blue ground, however, they reported evidence of the formation of etch pits in the negative (or trigon) orientation. These experiments were continued by Evans and Sauter (1961) who carried out etching experiments in air at reduced and atmospheric pressures at temperatures between 800°C and 1400°C . They found that there was a change in the orientation of the etch pits at higher temperatures. Thus on octahedral faces at etching temperatures above 1000°C they obtained etch pits in the negative, or trigon, orientation; on cubic faces at 1400°C etch pits in tetragon orientation; and on dodecahedral (110) faces at 1400°C boat-shaped pits in which the "keel" was in the $[110]$ direction as compared with the $[001]$ direction at temperatures of about 800°C . At the higher temperatures, surface layers of graphite had to be removed after etching in order to examine the surface. Following graphitisation experiments at 3000°C , and under 100,000 atmospheres pressure, Titova and Futergendler (1963) reported that with the graphite layer removed, triangular etch pits, inversely parallel to the octahedron faces were observed.

The pattern formed by etching a polished diamond

section (in potassium nitrate at 525°C for one hour) has been used by Stevenson (1962) in an attempt to reveal the growth history of a coated diamond of cubic habit from Sierra Leone. He suggested that the crystal commenced from a seed forming the core nucleus. The early stages of growth produced planar though stepped faces. The presence of twin components and complex banded structure were observed. There was evidence of partial dissolution.

Seal (1962) has produced patterns by etching, in potassium nitrate at 675°C for 15 minutes, polished cubic and dodecahedral sections of octahedral diamonds. He reported results on a single section of each of fifteen stones, five each from the Williamson mine, Tanganyika, the Premier mine, South Africa, and the Kimberly area, South Africa. The patterns obtained show the familiar layered structure, sometimes simple and sometimes quite complex, similar to those already reported by Tolansky and his students. Examination of the etched natural surface of one of the diamonds showed etch patterns extending over several faces. He also confirmed the findings of Omar, Pandya and Tolansky (1954) that the density of etch pits within trigons on natural faces was markedly less than elsewhere on the surface. Further stratigraphical etch patterns were reported by him (Seal, 1963) at the Bristol Diamond Conference.

Included were some specimens in which a cross-like structure was present in the centre. A striking pattern of such a feature was also reported by us at the same conference (Harrison, 1963) and further studies on the same diamond are reported elsewhere (Harrison and Tolansky, 1964) and in more detail below in chapters 7 and 9.

Patel and Ramanathan (1962) reported that etch can be initiated as low as 380°C . They carried out their experiments on natural and polished octahedral faces and on polished cubic faces using potassium chlorate (KClO_3) and sodium perchlorate (NaClO_4). Etch pits of both orientations were produced even at the temperature of 380°C .

Many measurements have been made on the depth and shape of trigons, many of which are low-angle triangular pyramids but some have steep sides and flat bases. An interesting set of observations on these latter was made by Wilks (1961) who showed that for the cases examined the angle of the sides coincided with that of a true octahedral plane to within the accuracy of her measurements (6 degrees). She concluded that these trigons could not be due to etch, although she attributed the low-angle pyramidal type as due to etch.

Ever since Taylor (1934), Orowan (1934) and others introduced the idea of dislocations in crystals and the idea was developed further by others (e.g. Burgers, 1939; Mott and Nabarro, 1948; Frank, 1948) it has generally been held that etch pits commence to develop at the sites of lattice defects such as dislocations, foreign atoms or vacant sites, along scratches, cracks and edges, or where strain exists within the crystal.

In the remainder of this chapter etch studies carried out on cubic diamonds will be described, first the nature of the etching produced on polished natural surfaces from which the existing surface structure has been removed, and secondly the nature on untreated natural surfaces. The nature of the etch patterns formed on cubic sections within the heart of the crystals will also be discussed.

Subsequently in chapter 7 etch patterns formed on cubic sections of octahedral diamonds will be described.

6.2 Etch Figures on Polished Cube Faces.

We considered that the natural structure on the surfaces of the Congo cubic diamonds studied could have arisen as growth features or due to natural etch subsequent to growth. If in fact the features were due to etch, i.e. the tetragons are large etch pits, we

considered that these etch pits would have been centered around lattice defects. Now as these tétragons are in many cases quite large bold features, then many at least of the defects possibly existed in depth as line dislocations of quite large extent. Subsequent etch may then proceed along the same dislocations, and for a lightly polished surface it might be that the new etch pattern would show some correlation with the original surface pattern.

The cubic faces of one of the diamonds, H4, were polished to remove most of the surface structure. It was decided not to remove the deepest features in order that the polished surface would not be too far removed from the original one. Remaining structure serves, in addition, the useful purpose of providing datum positions on the surface to assist correlating etch features with the original structure. Unfortunately during the polishing process some of the corners of the diamond were damaged due to inexperienced handling. Figure 6.2 (x 50) shows one of the natural surfaces while figure 6.3 (x 50) shows a multiple beam interferogram in reflection of the same surface after polishing. Although the surface shows some waviness the micro-finish is reasonably good. The vestiges of the original surface structure can be seen.

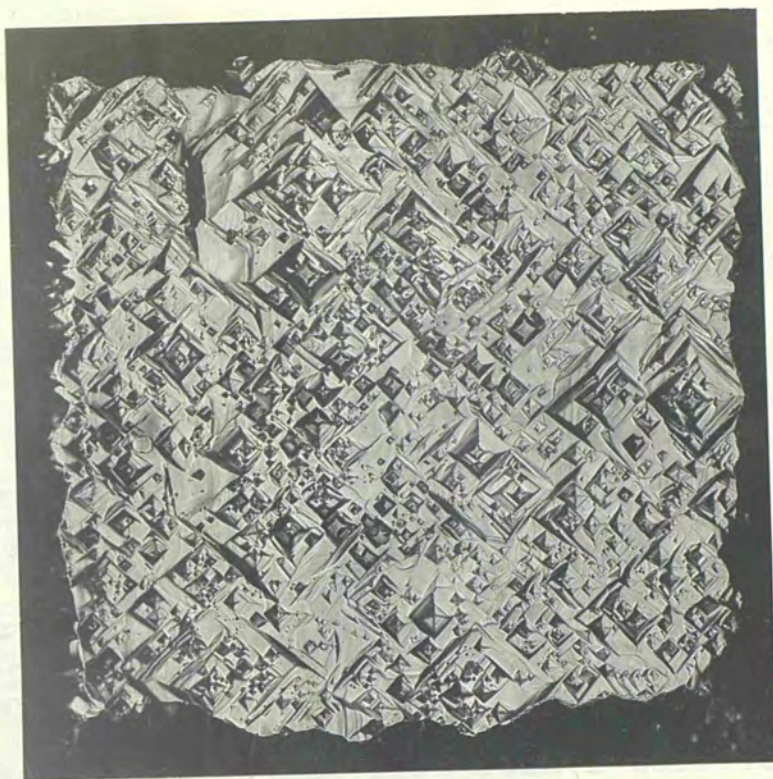


Figure 6.2. H4, $0\bar{1}0$ (x 50).

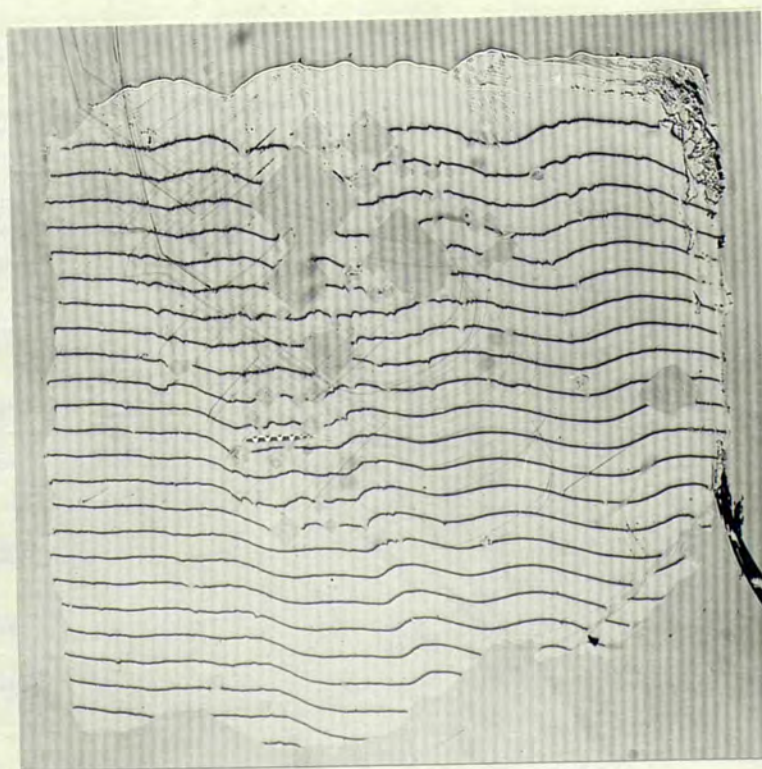


Figure 6.3. H4, $0\bar{1}0$ (x 50).

After polishing, the diamond was subjected to a mild etching treatment in fresh fused potassium nitrate. The etching temperature and time were somewhat arbitrary as the work was done before a satisfactory procedure had been settled upon by trial and error. The following treatment was given:

- Etch 1 - 525°C for 1 hour)
- + 650°C for 5 minutes,)
- Etch 2 - 590°C for 25 minutes,
- Etch 3 - 575°C for 14 hours.

The etch pits resulting from etch 1 were very small indeed. A part of the surface is shown in figure 6.4 (x 90). An exceptionally fine high dispersion multiple beam fringe passing across a number of pits is shown in figure 6.6 (x 100) and a portion of the same fringe printed at higher magnification in figure 6.7 (x 300). The square shape of the etch pits is just resolved in a number of cases.

For comparison with figure 6.4, the same area is shown after etch 2 in figure 6.5 (x 90). The whole surface after etch 2 and etch 3 is shown in figures 6.8 and 6.9 (x 50). At the resolution of these pictures, few if any new etch pits have been developed after the first etch. This is in agreement with the results of other workers who found that after initial attack prolonged etching merely enlarges existing pits.

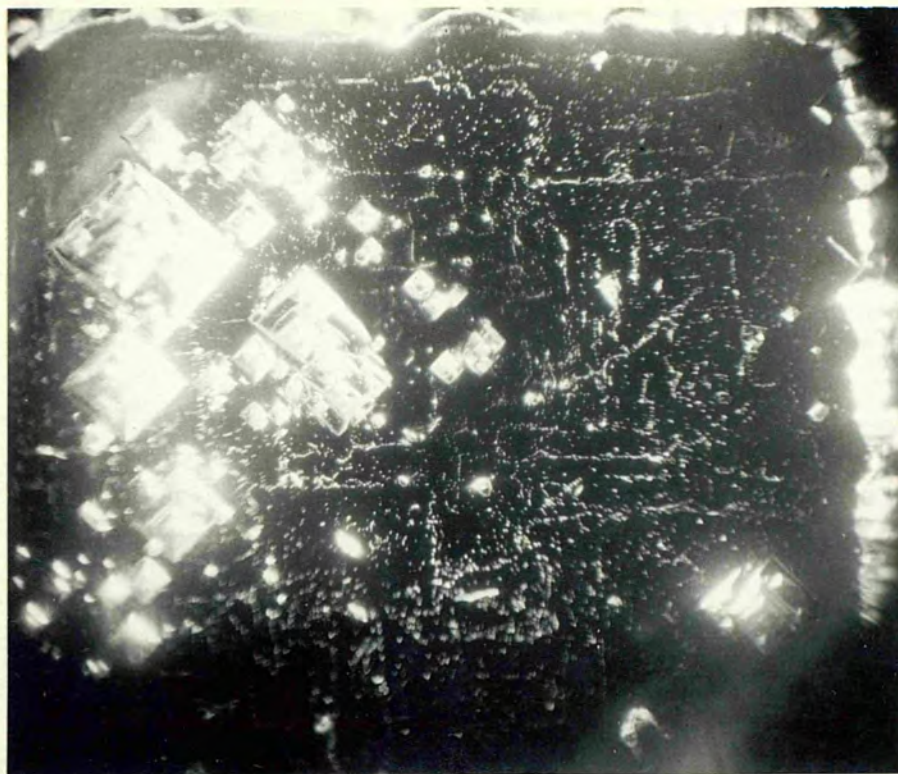


Figure 6.4. H4, $0\bar{1}0$ (x 90).

Figure 6.5. H4, $0\bar{1}0$ (x 90).

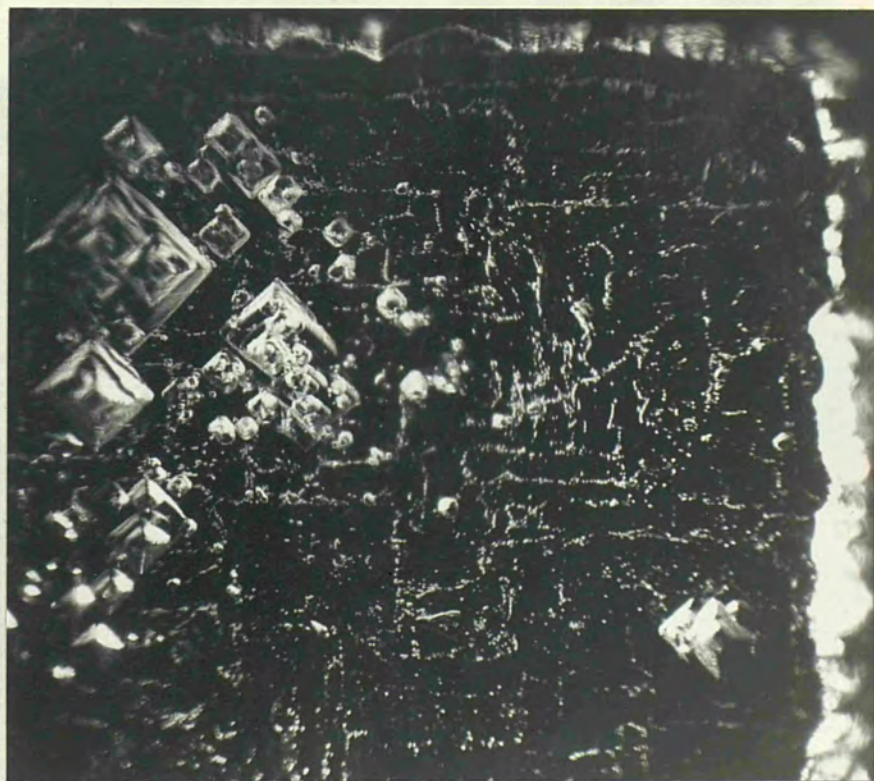


Figure 6.5. H4, $0\bar{1}0$ (x 90).

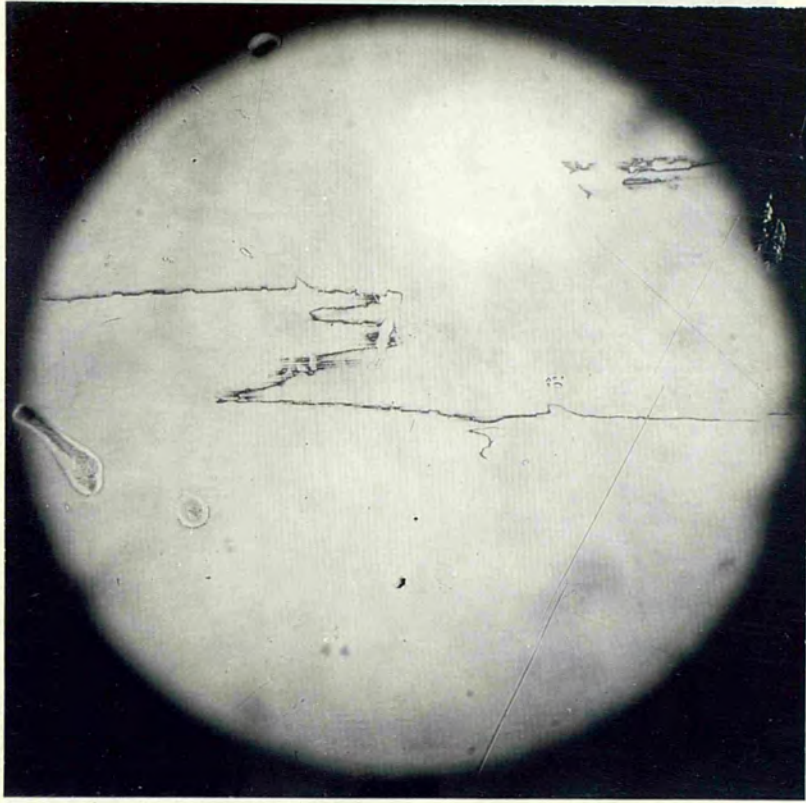


Figure 6.6. H4 $O\bar{1}0$ (x 100).

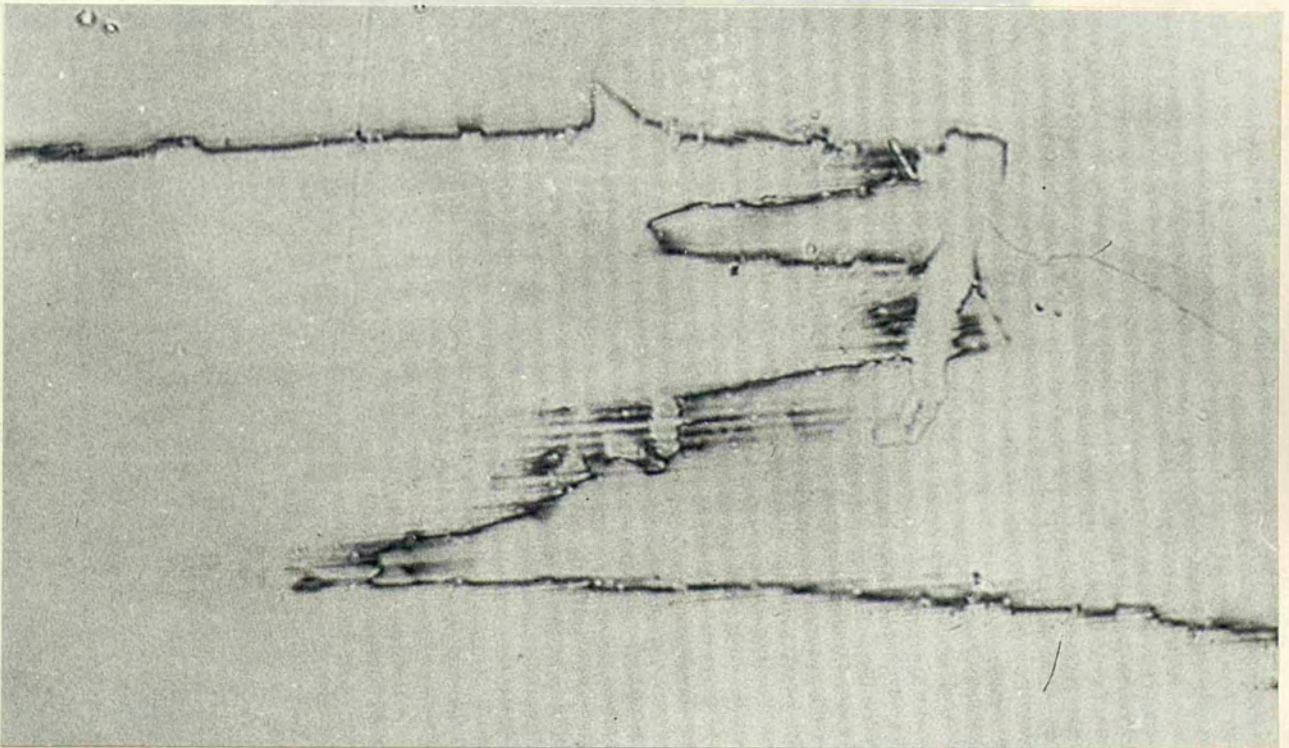


Figure 6.7. H4 $O\bar{1}0$ (x 300).

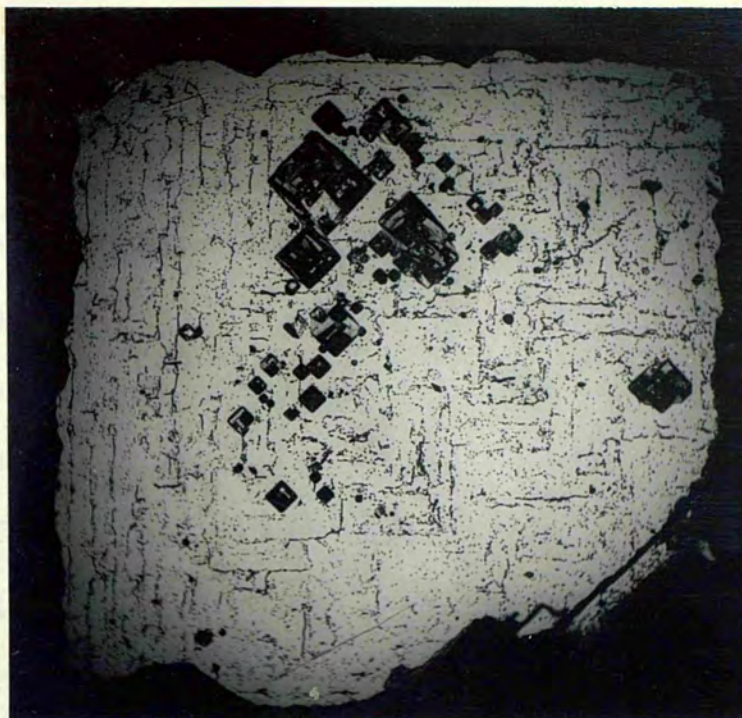


Figure 6.8. H4, $\bar{0}10$ (x 50).



Figure 6.9. H4, $\bar{0}10$ (x 50).

Another two faces before etching and after the final etch treatment are shown in figures 6.10 to 6.13 (x 50). Careful qualitative examination was made in an attempt to determine if there was any correspondence between the etch pits and the original pattern. It is interesting to note that the etch pattern on the polished surface is of the same character as the etching on cubic-like facets within tetragons. This can be seen from figures 6.34 and 6.36. Similar patterns are obtained on the cubic-like facets of unpolished natural surfaces as shown in figures 6.29, 6.31 and 6.33. These aspects will be discussed further below.

Other interesting results emerge however. We confirm the results of other workers that the etch pits are generally square and that they are mostly oriented at 45° to the naturally occurring tetragons. There are, however, some etch pits which are tending to be octagonal or are rounded. Indeed there are square pits in the tetragon orientation. As the etching proceeded high resolution micrographs show that in fact a few new etch pits have developed. These results may be seen from three sets of high magnification pictures taken using a 2.2. mm oil immersion objective and oblique illumination on the $0\bar{1}0$ face after various stages of etching. The first set in figures 6.14 and 6.15 (x 750) shows, after etch 1 and etch 2, a region in which



Figure 6.10. H4 001 (x 50).

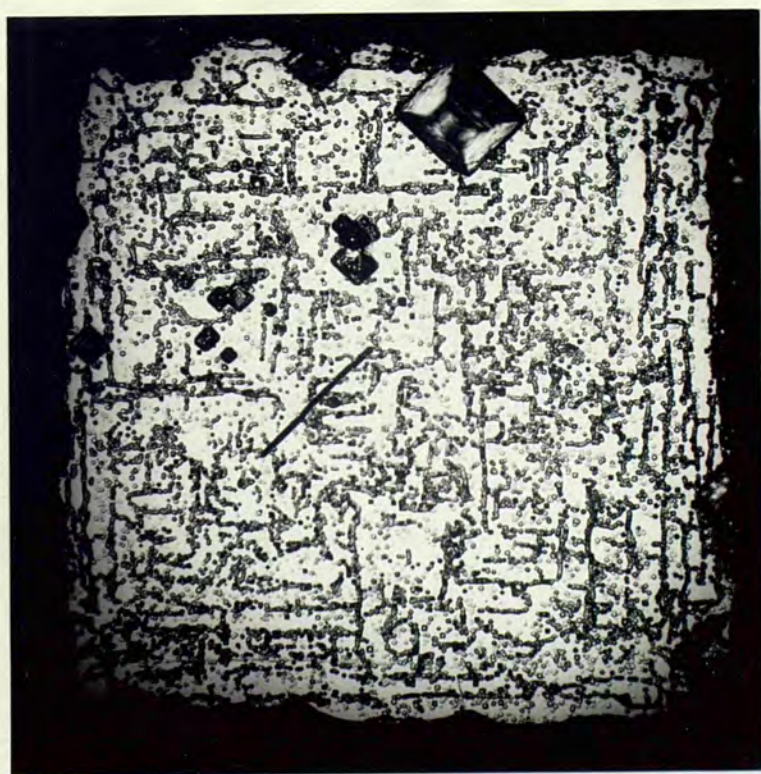


Figure 6.11. H4 001 (x 50).

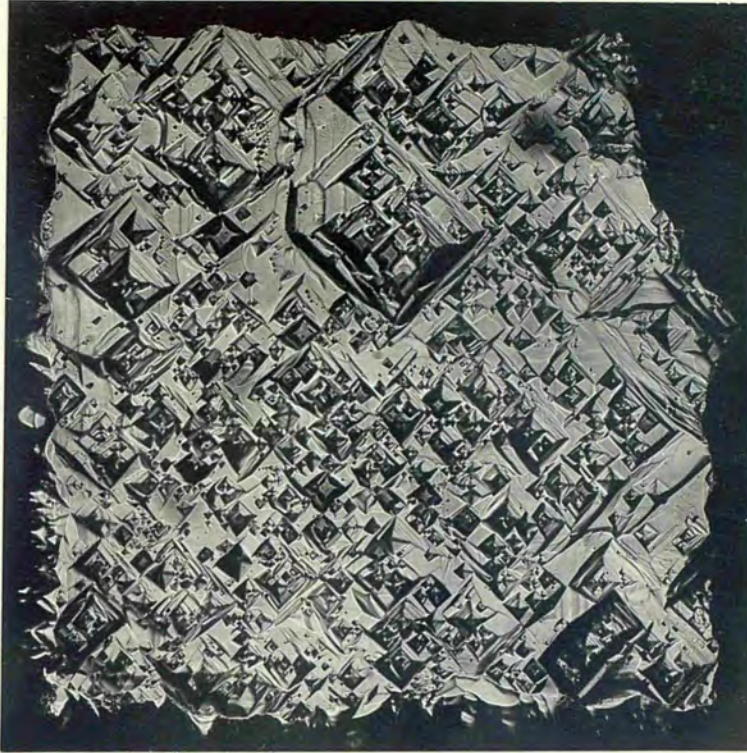


Figure 6.12. H4 $\bar{1}00$ (x 50).

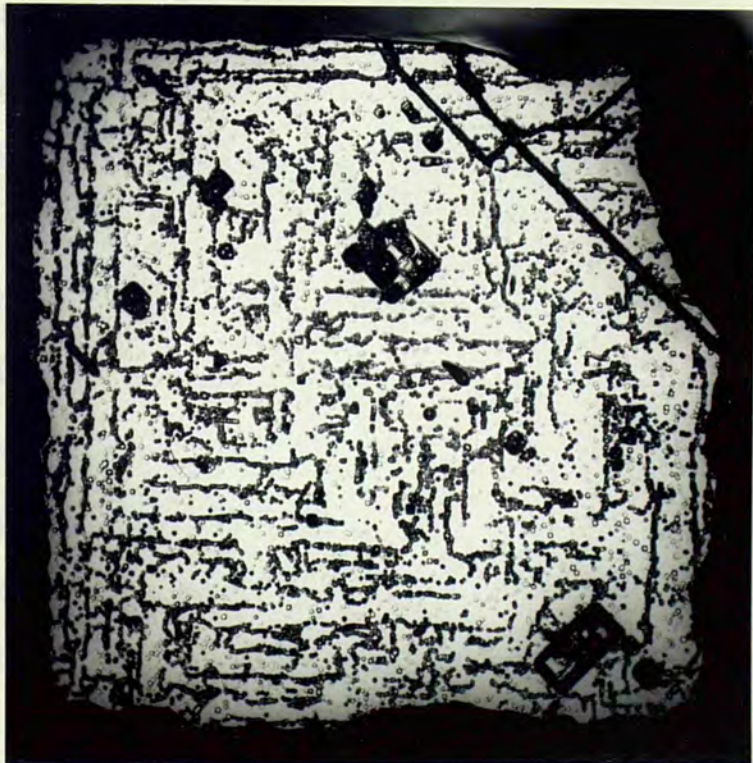


Figure 6.13. H4 $\bar{1}00$ (x 50).

there is a crack. Although the crack has etched up clearly the etch pits after etch 1 are very small whereas after etch 2 they have become much better defined. It should be noted that there are etch pits in both orientations and that some have more than four sides. Some of the pits appear to be pyramidal whereas others appear to be very shallow. Now almost without exception the etch pits in the tetragon orientation in figure 6.15 are very shallow, whereas the shadows cast by oblique illumination show that most, if not all, of the square pits in the "etch" orientation are pyramidal. Also it is worthy of note that all the flat-bottomed pits had not formed following the first light etch (figure 6.14) but only on subsequent etching.

The second set as shown in figures 6.16 and 6.17 (x 1000) shows part of the surface after etch 1 and etch 2. There is a scratch on the surface at about 45° to a dense line of etch pits. There are also some lines in which the pits are less closely spaced. The etch pits are of the same character as in the previous pair of pictures. Those in the dense line have merged into one another after the second etch, as have some of the others which were close together. As in the case of figures 6.14 and 6.15, we again find etch pits in figure 6.17 which were not apparent in figure 6.16, and again

they are flat bottomed and oriented at 45° to the pyramidal etch pits.

The third set of figures 6.18 to 6.20 (x 1000) shows a region of the surface after each of three stages of etch. By the third stage many of the smaller pits have been swallowed up in neighbouring ones. The original tetragons have also been attacked by the etch and their shape modified. The one at the top right shows, even in figure 6.18, a tendency to take on an octagonal form. This form is well developed by figure 6.20 where the feature is beginning to merge with other pits. Etch pits of both orientations are again apparent in figures 6.19 and 6.20. In figure 6.19 those in the "etch" orientation are pyramidal while those in the tetragon orientation are flat-bottomed. After 15 hours or so etching (figure 6.20) a few additional shallow pits, either rounded or in the tetragon orientation have formed. In general the shallow pits formed by etch 2 (figure 6.19) have retained their shallow nature.

One important observation can be made here about these two types of etch pits. Those in the arrays parallel to the cube edges are pyramidal while those along the scratch in figure 6.16 are flat-bottomed. In figures 6.19 and 6.20 a number of flat-bottomed pits form arrays

at 45° to a direction parallel to a cube edge. There is no obvious reason for this. They are certainly not in a polishing direction. A point of interest which arises here and later is that, while scratches and cracks etch preferentially, polishing marks in general do not do so.

Another very interesting feature about the etch pits on these surfaces is their arrangement in lines more or less parallel to the edges of the cube as shown in figures 6.9, 6.11 and 6.13. This seems to be characteristic of this sample of cubic diamonds.

A similar pattern of etch pits is shown in figures 6.21 to 6.23 (x 50) which show a polished face of another diamond, S3, after various stages of etch. This diamond was etched in potassium nitrate successively as follows:

Etch 1 - 575°C for 30 minutes,

Etch 2 - 575°C for 20 minutes,

Etch 3 - 575°C for 14 hours.

The photomicrographs of figures 6.21 to 6.23 were taken after each etch. High magnification pictures of the same region on the surface were also taken after each etch. These are shown in figures 6.24 to 6.26 (x 1200). To show structure within the etch pits better an area on figure 6.25 has been printed at higher magnification in figure 6.27 (x 3500).

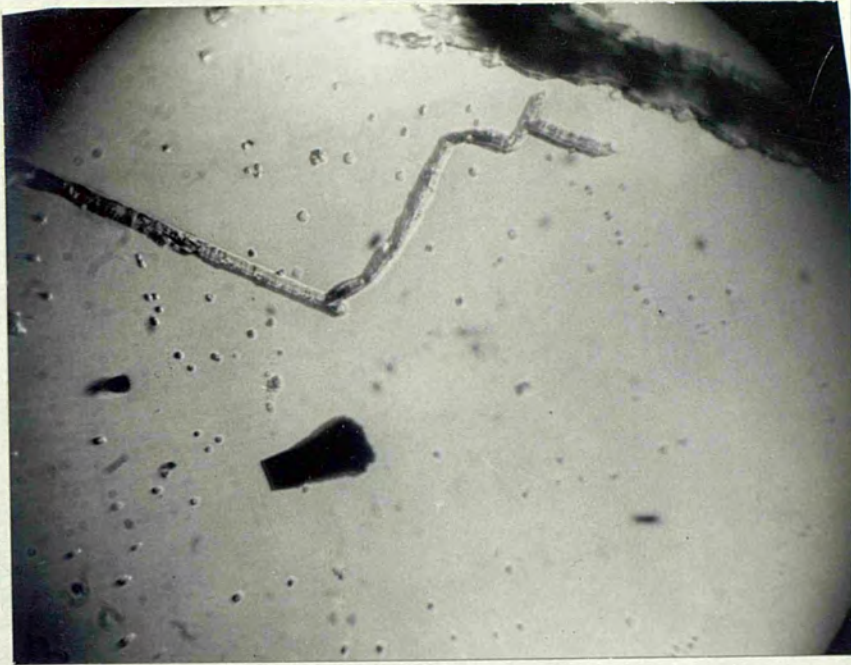


Figure 6.14. H4 $\bar{0}10$ (x 750)



Figure 6.15. H4 $\bar{0}10$ (x 750).

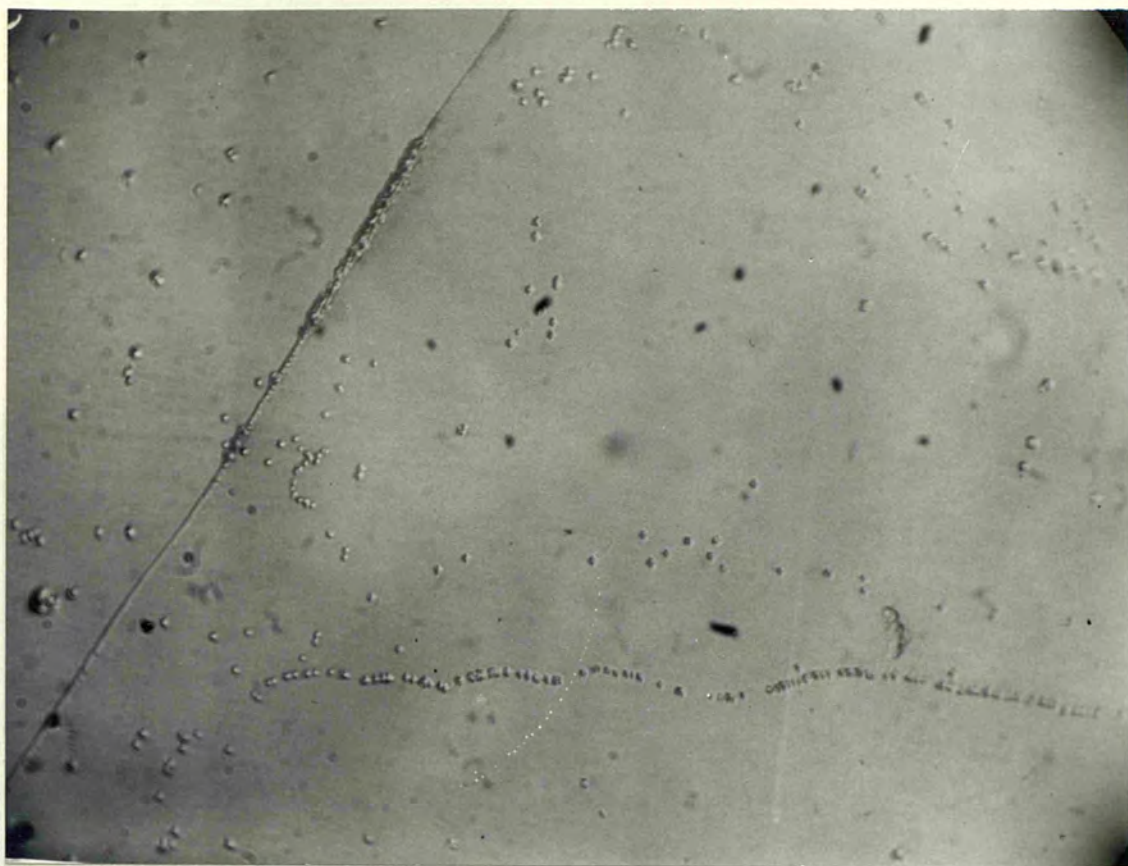


Figure 6.16. H4 010 (x 1000).

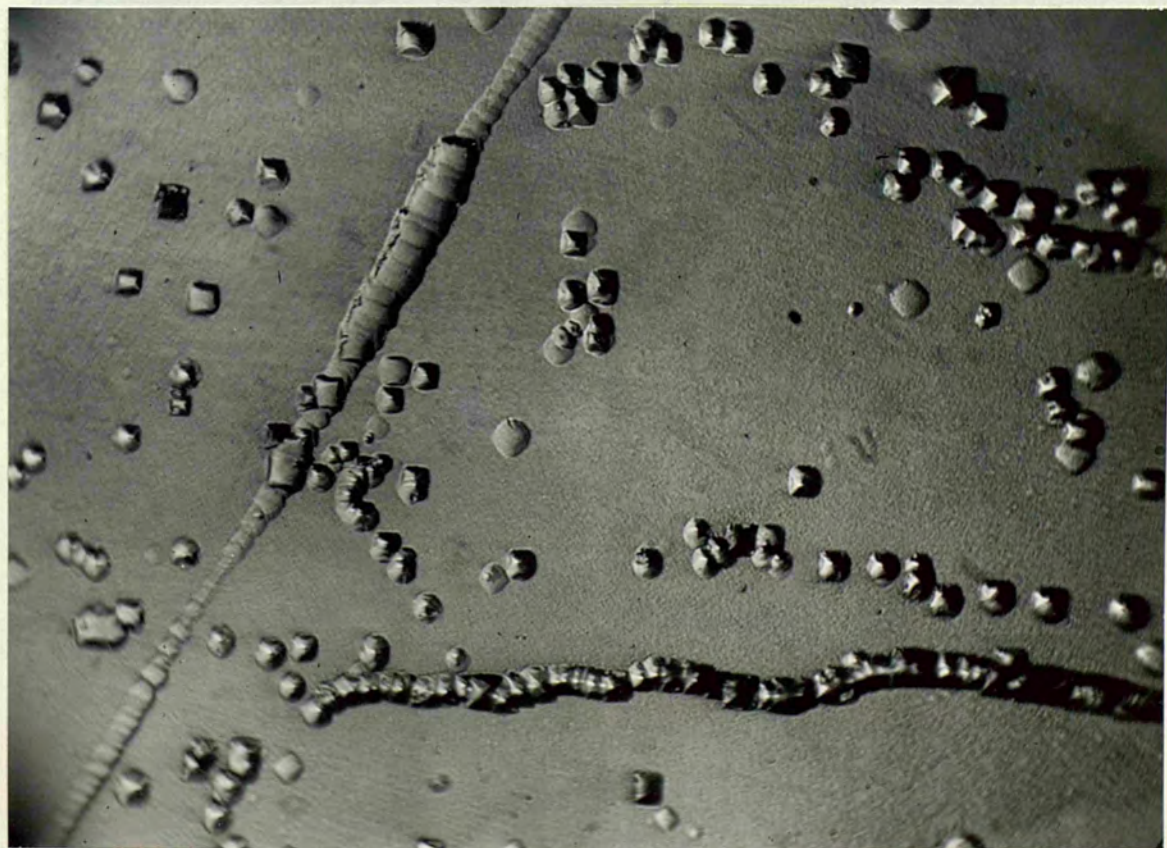


Figure 6.17. H4 010 (x 1000)

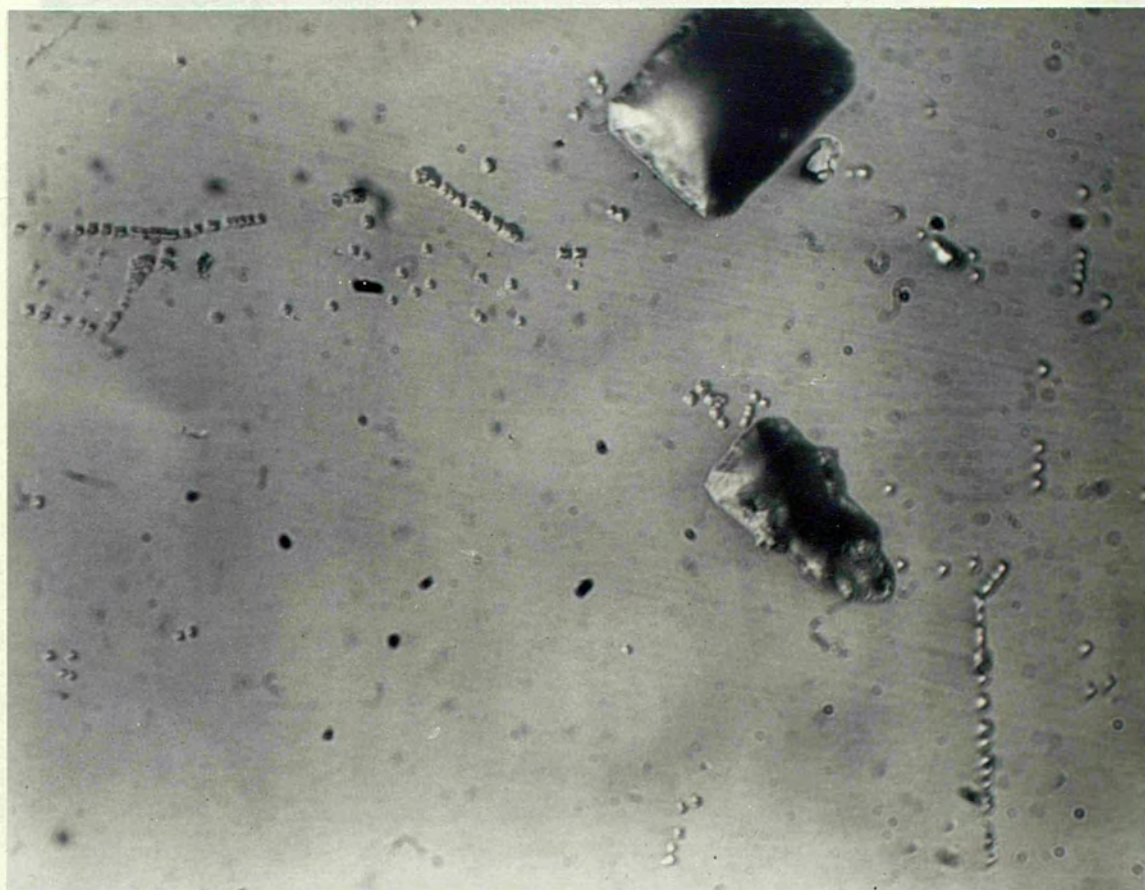


Figure 6.18. H4 O $\bar{1}0$ ($\times 1000$).

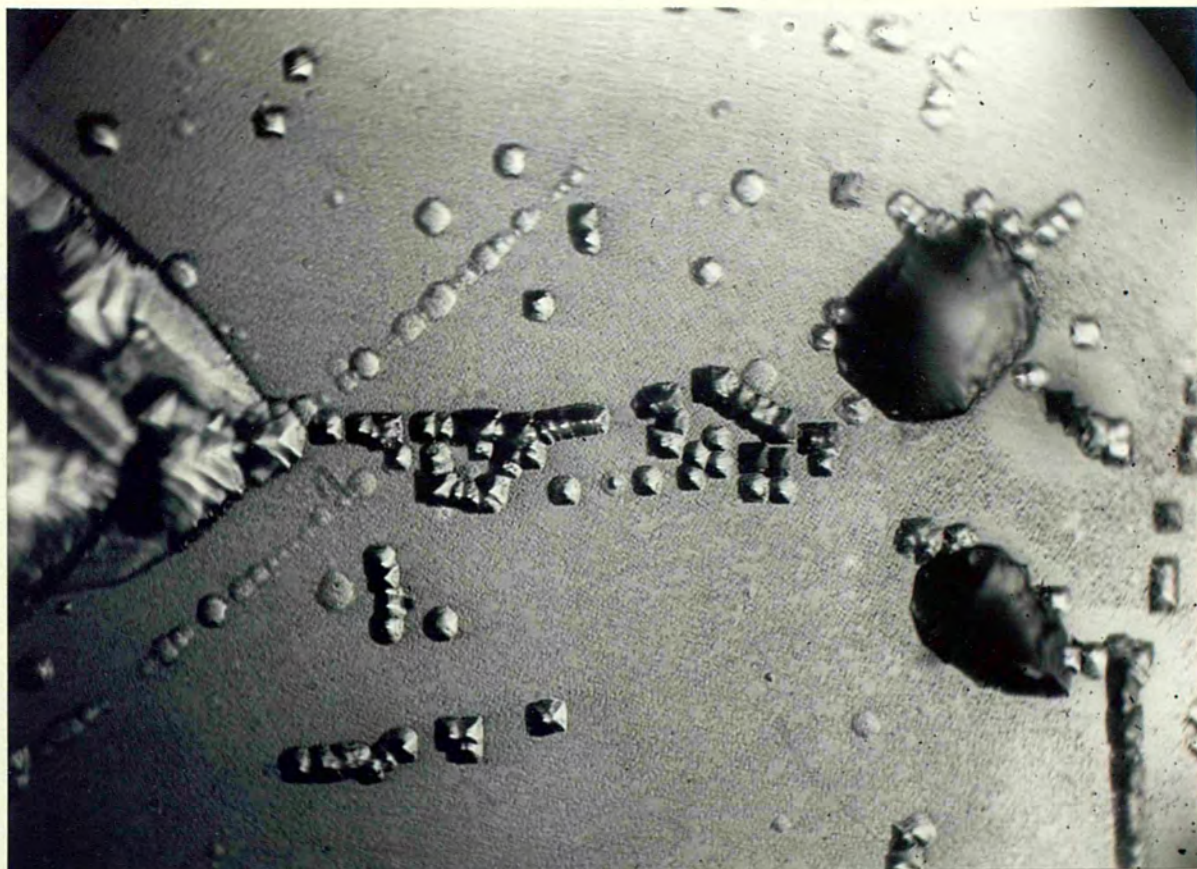


Figure 6.19. H4 OIO (x 1000).

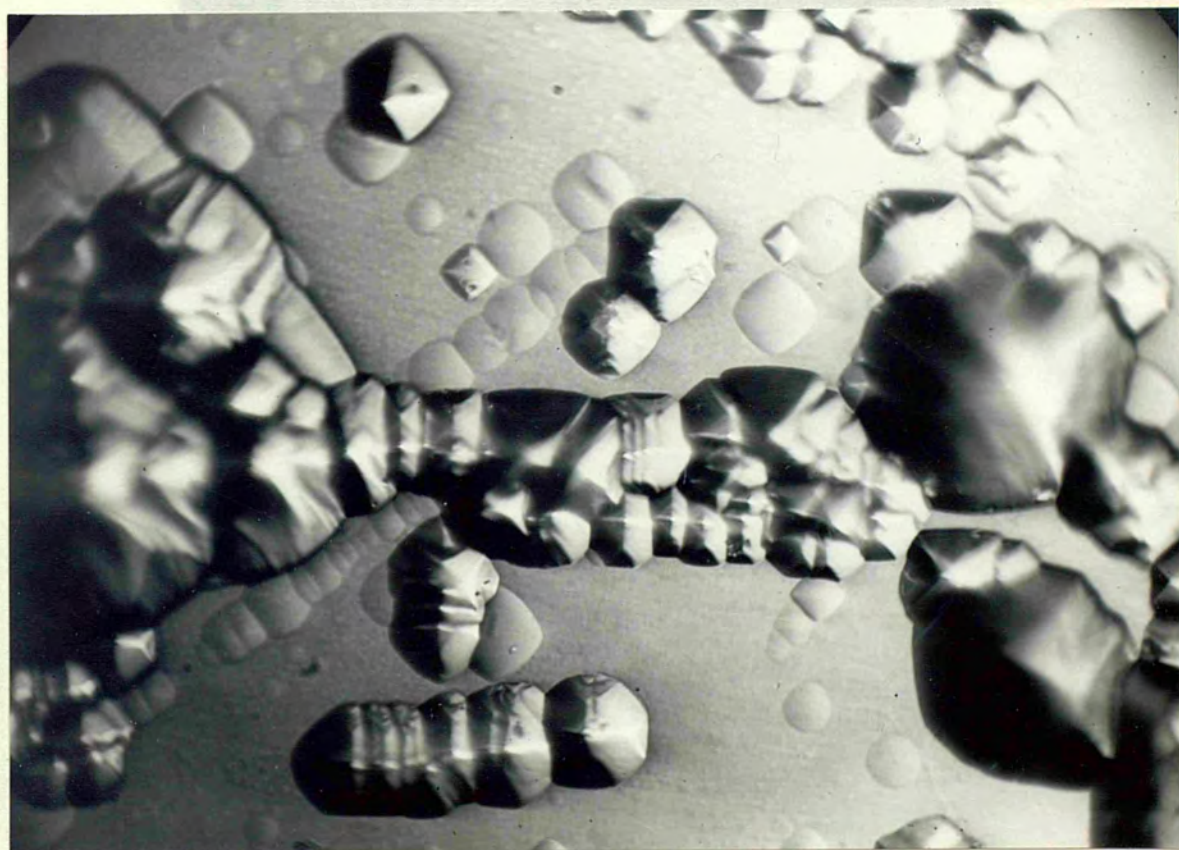


Figure 6.20. H4 O $\bar{1}0$ (x 1000).



Figure 6.21. S3 001 (x 50).

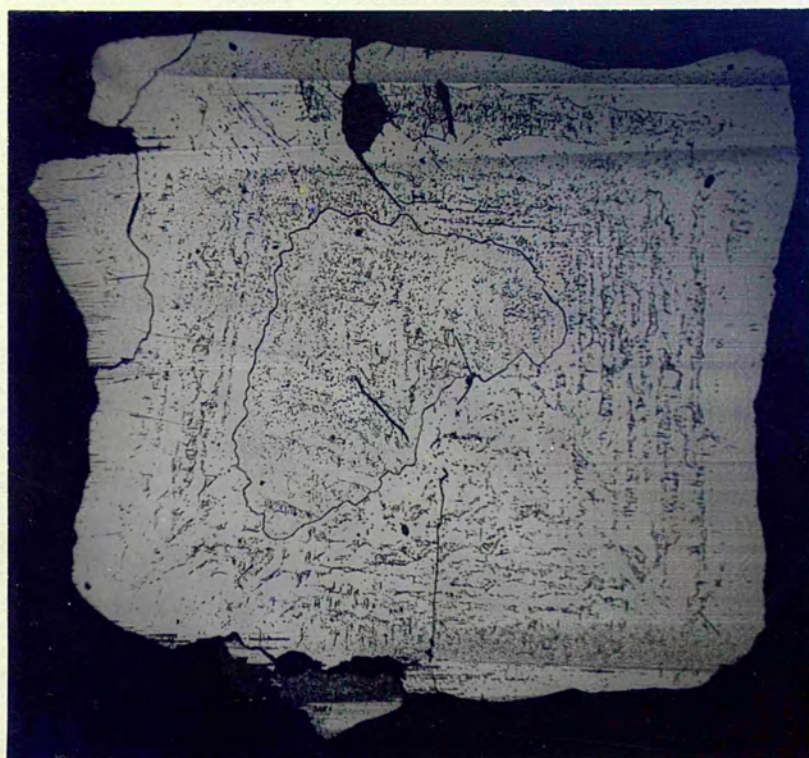


Figure 6.22. S3 001 (x 50).

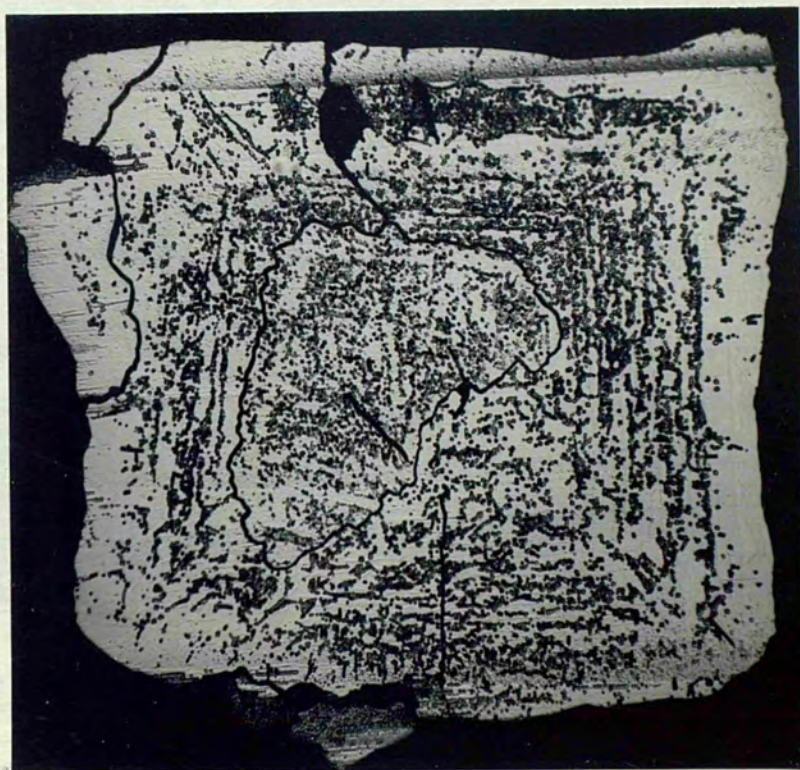


Figure 6.23. S3 001 (x 50).

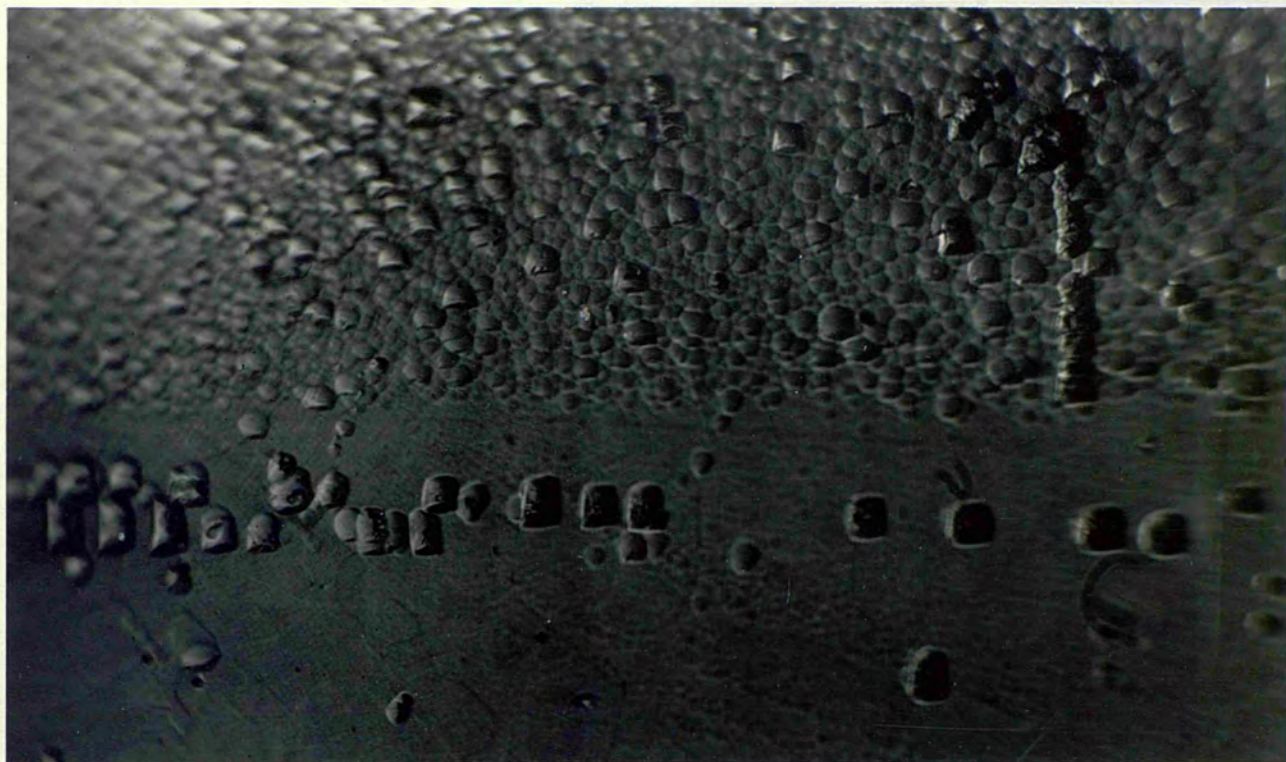


Figure 6.24. S3 001 (x 1200).

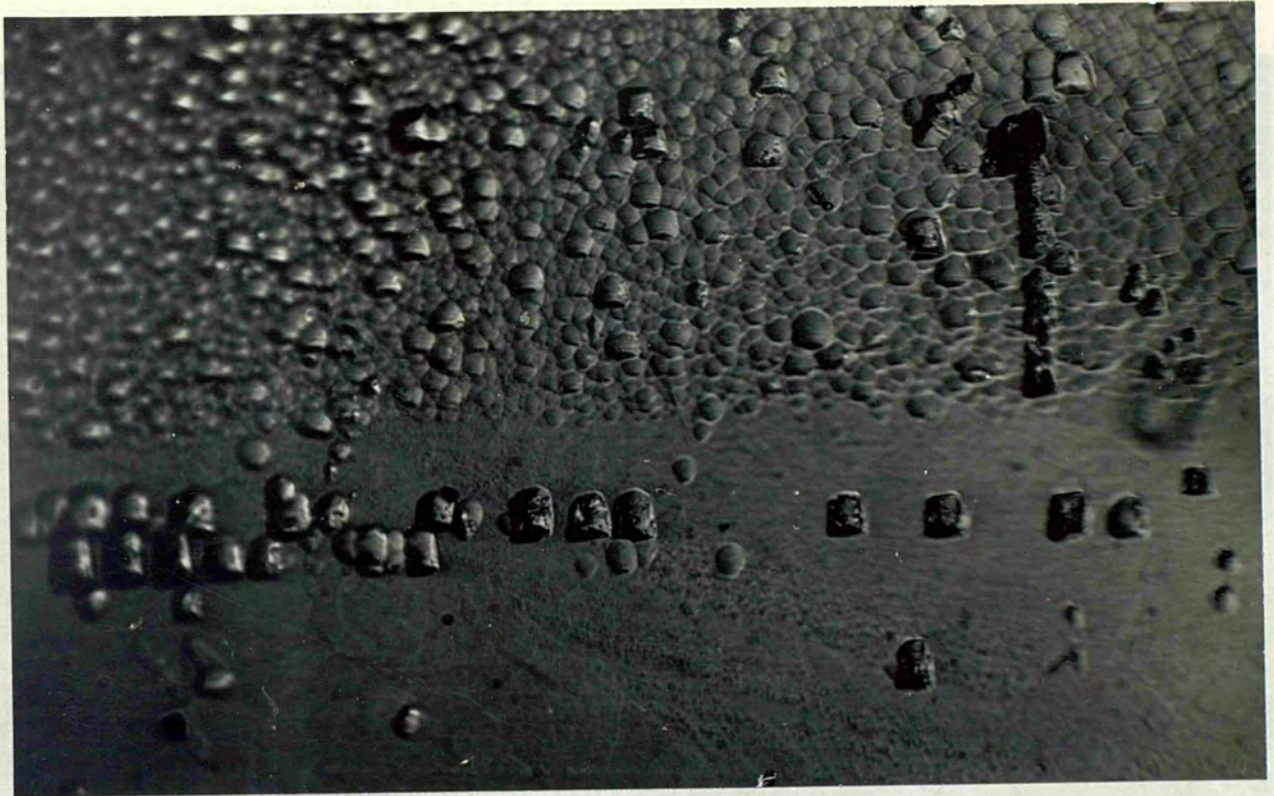


Figure 6.25. S3 001 (x 1200).



Figure 6.26. S3 001 (x 1200).

Section of the surface of the leaf.

In the present case, the surface of the leaf has been treated with a solution of potassium permanganate and it has been shown that the surface which has been only very lightly treated with the solution is further etching.



Figure 6.27. S3 001 (x 3500).

6.3 Etch Figures on Natural Cube Faces.

In the previous section findings of other workers have been confirmed, and in particular it has been shown that a cubic surface which has been only very lightly etched, when subjected to further etching, develops only very few new etch pits but the existing ones become larger and may merge. Now if the pattern on the surface of the cubic diamonds under study is due to etch we would expect that the lattice defects at the surface would have all been attacked and no new pits should be formed, provided of course no new defects had been introduced into the surface since the original etch had occurred.

Diamond S2 was etched in potassium nitrate at 585°C for one hour. Transmission pictures of Perspex replicas made before and after etching were taken. Pictures of the whole surface are shown in figures 6.28 and 6.29 (x 50). A multitude of small etch pits can be seen on the cubic-like facets. Pictures at higher magnification are shown in figures 6.30 to 6.33 (x 200) in pairs, before and after etch, of the positions near (2.5, 1.0) and (3.0, 3.0) in figure 6.28.

Etch pits on any but cubic facets cannot be seen in these pictures but etch may well have taken place.

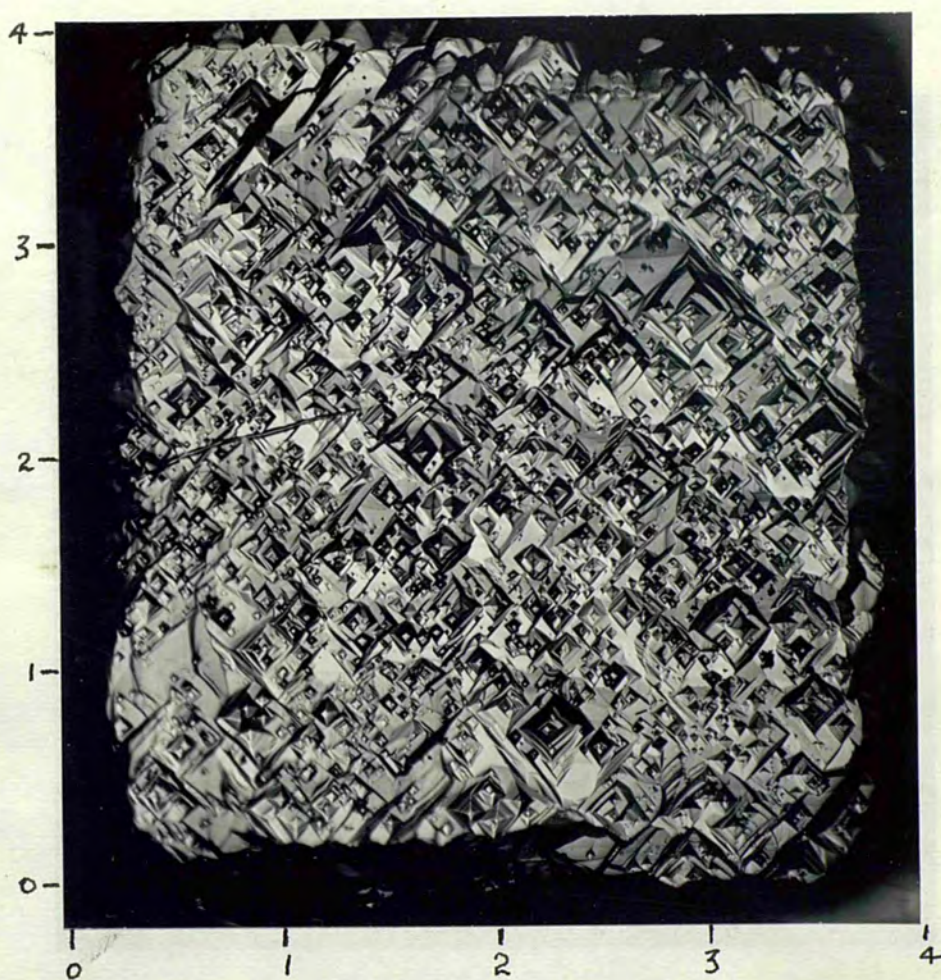


Figure 6.28. $s_2 00\bar{1}$ (x 50).

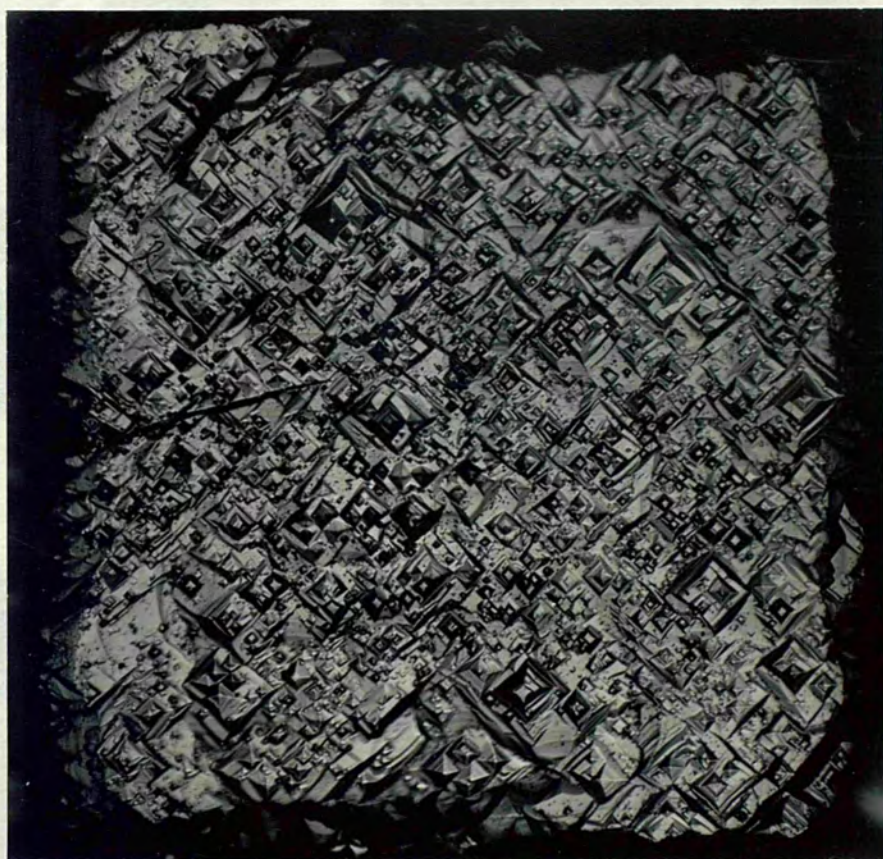


Figure 6.29. $S_2 00\bar{1}$ (x 50).

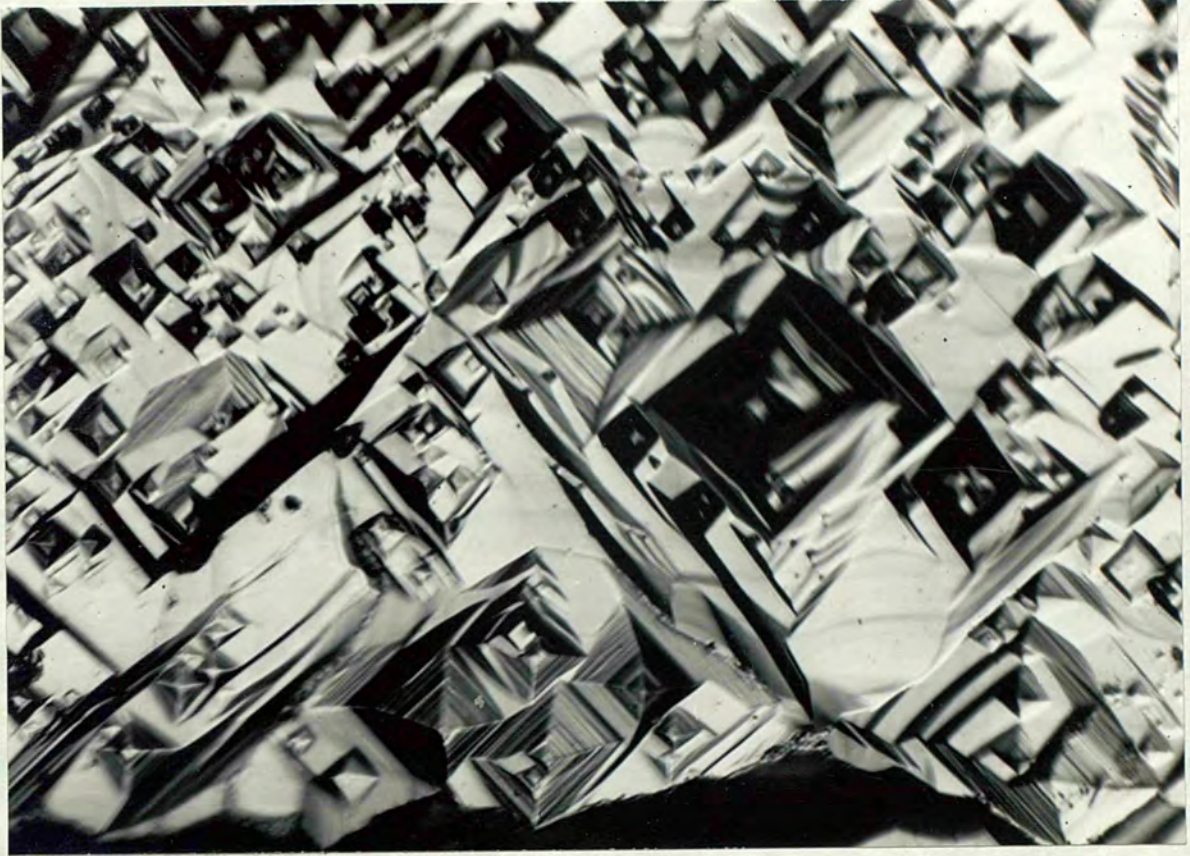


Figure 6.30. $S_2 00\bar{1}$ (x 200).

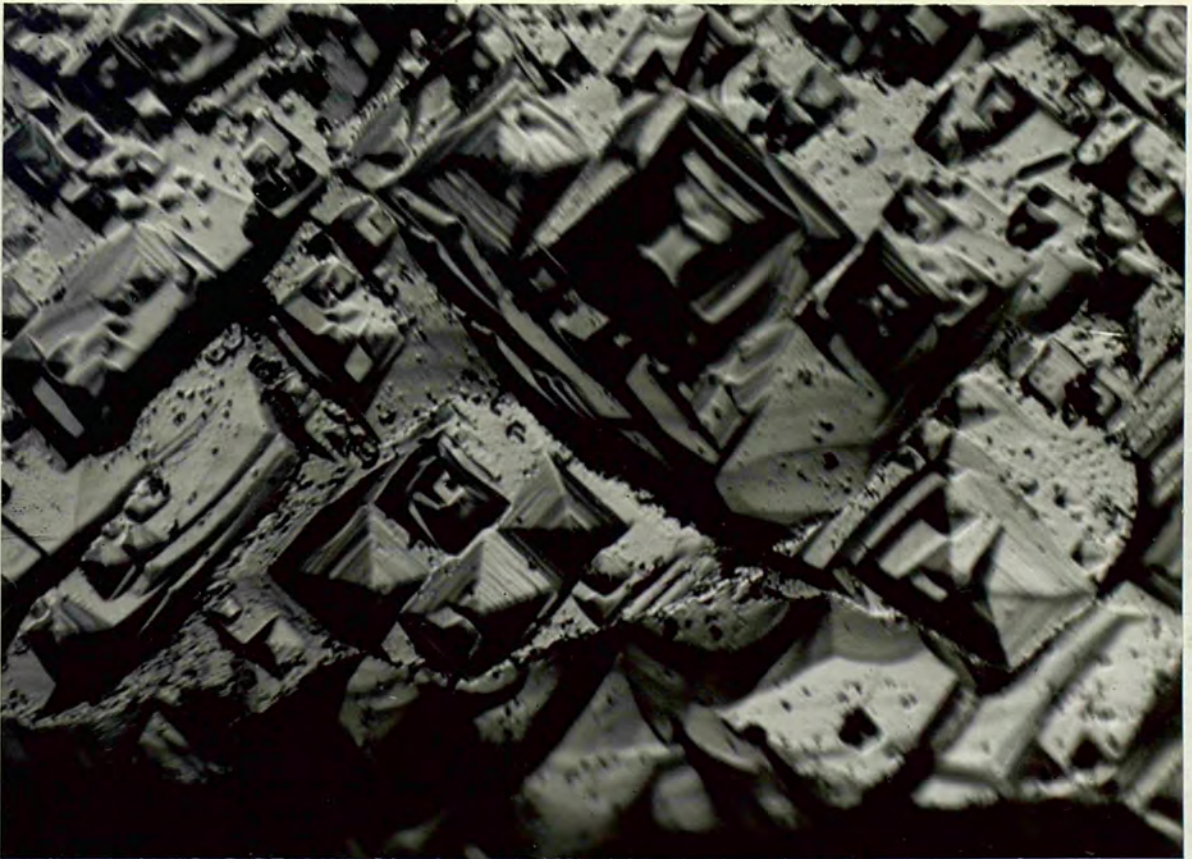


Figure 6.31. $S_2 00\bar{1}$ (x 200).



Figure 6.32. S2 00 $\bar{1}$ (x200).

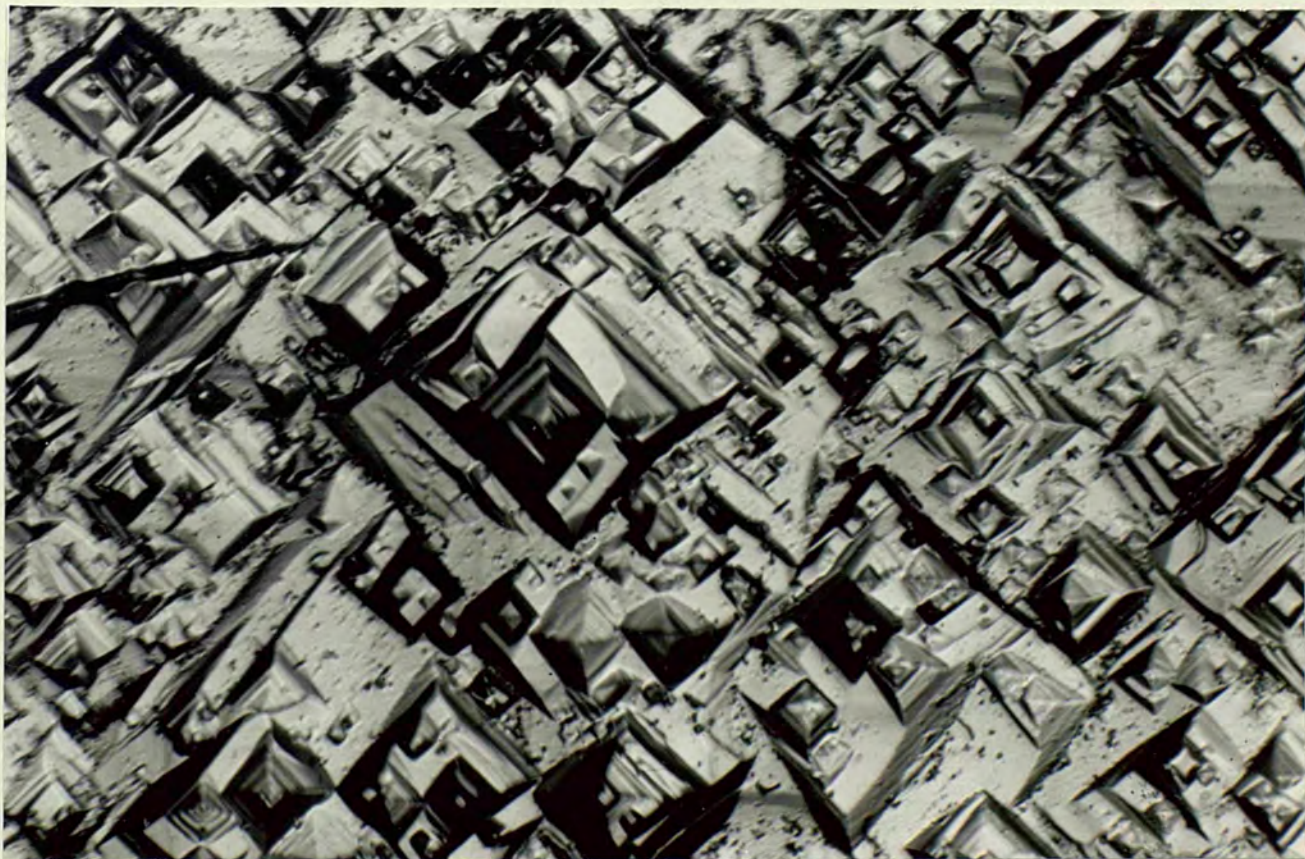


Figure 6.33. S2 001 (x 200).

Some interesting photographs of etch within tetragons are shown in figures 6.34 and 6.35 (x 200) showing bright field and dark field pictures of a region on the partly polished $0\bar{1}0$ face of diamond H4 after the following etch treatment in potassium nitrate:

525°C for one hour, 650°C for 5 minutes and 590°C for 25 minutes. Figures 6.36 and 6.37 (x 350) show part of the same area at higher magnification. It can be seen from these pictures, especially 6.34 and 6.36, that cubic-like facets within the tetragons have an etch pattern of the same character as the polished surface. The etch on the other facets is of a different character, appearing to attack the whole surface. The attack probably takes place at the edges of layers.

6.4 Etch Figures on Sections of Cubic Diamonds.

Three cubes were each sawn into two approximately equal parts by a cut parallel to a pair of cubic faces, the sawing being carried out by Messrs. Briefel and Lemer Ltd., London. Preliminary etching in fused potassium nitrate at 570°C for 1 hour showed an interesting array of etch pits suggesting a family of rectangular hyperbolae having the diagonals of the cube as asymptotes. Figure 6.38 and 6.39 (x 50) show



Figure 6.34. H4 O $\bar{1}0$ (x 250).



Figure 6.35. H4 O $\bar{1}0$ (x 180).

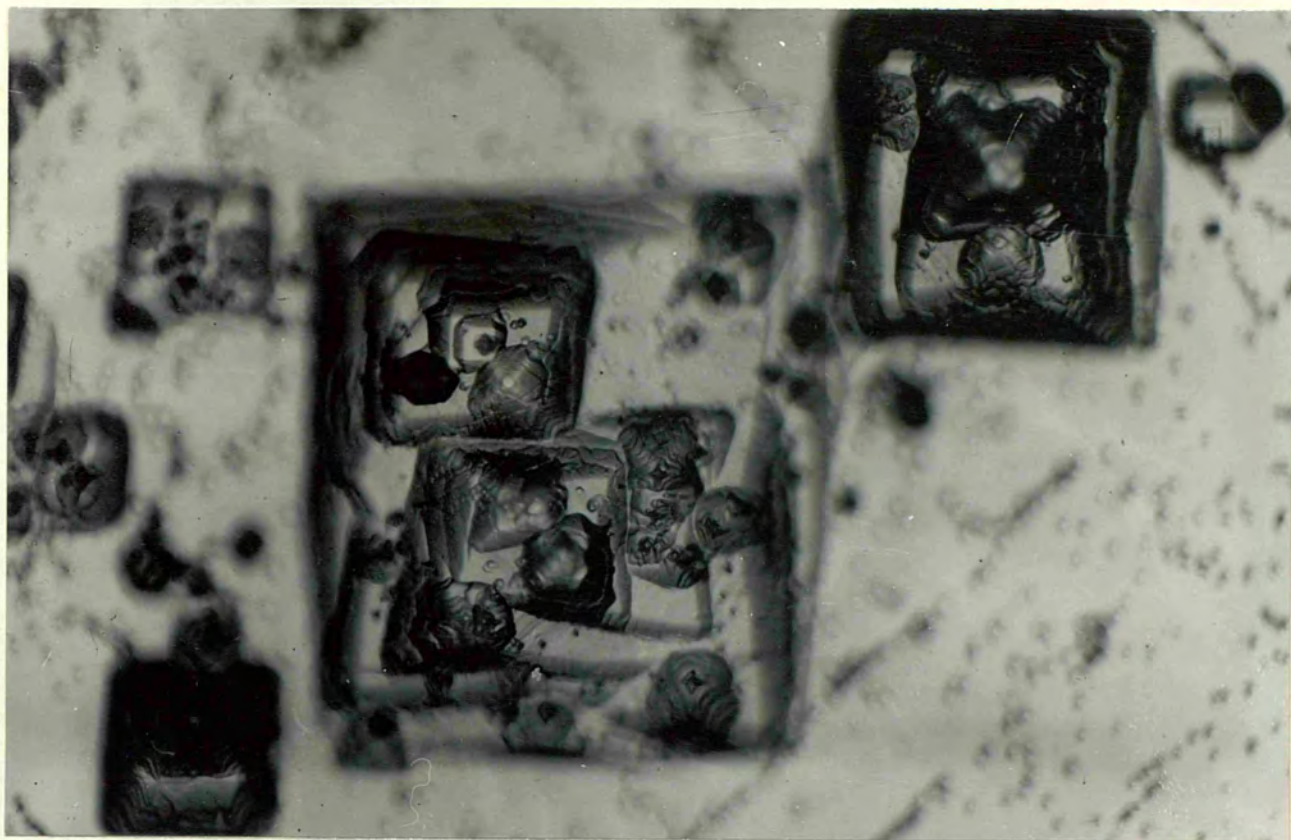


Figure 6.36. H4 O $\bar{1}$ O (x 375).



Figure 6.37. H4 O $\bar{1}$ O (x 300).

H4 O $\bar{1}$ O (x 50).

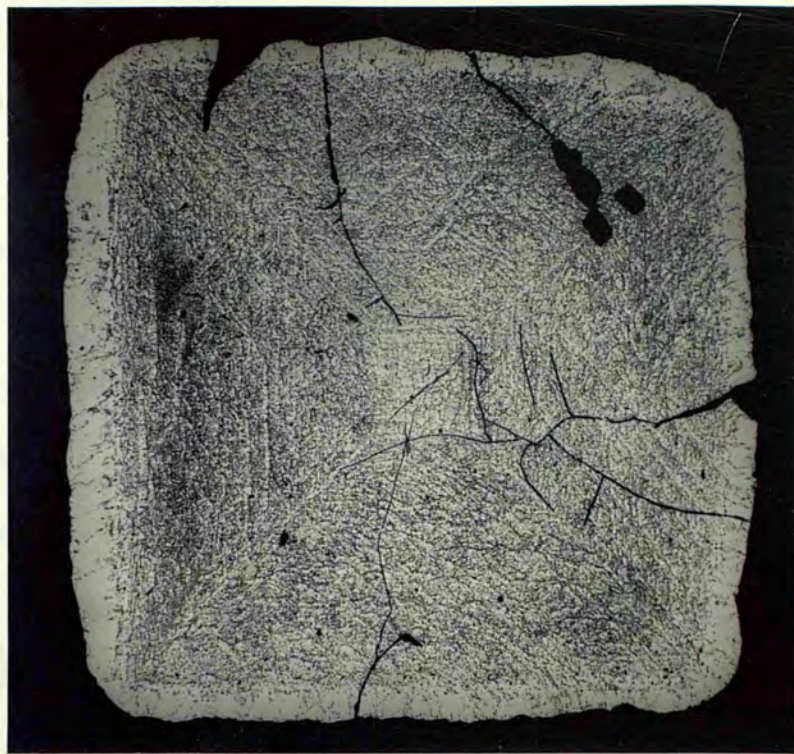


Figure 6.38. G1B $00\bar{1}$ (x 50).

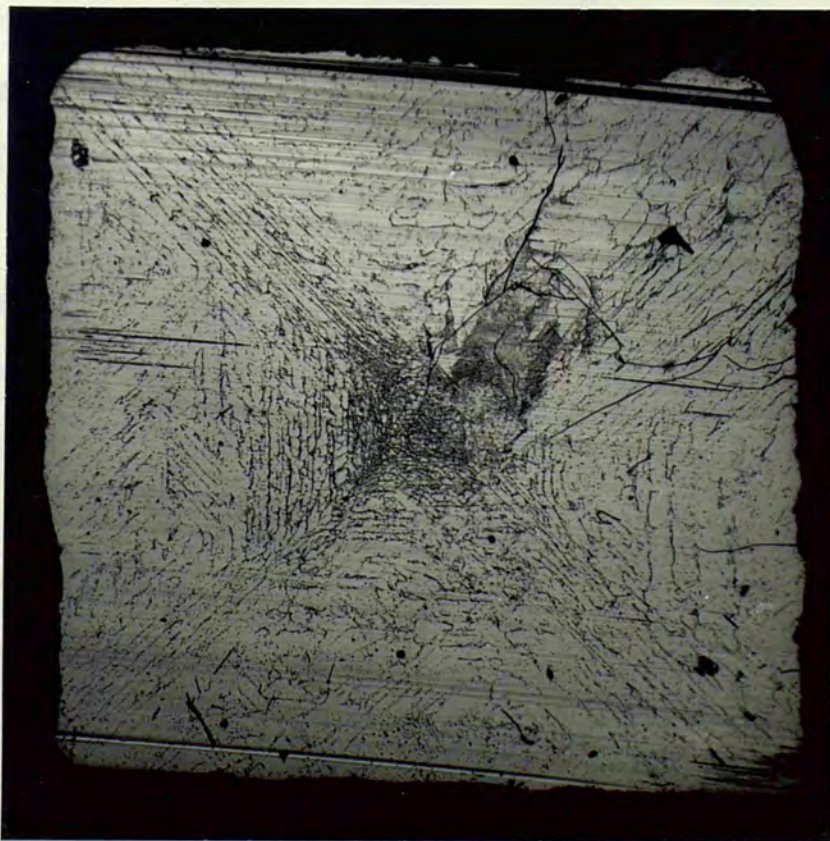


Figure 6.39. G3B $00\bar{1}$ (x 50).

the sawn surfaces of one half of each of two of the diamonds after polishing and a further etch in potassium nitrate at 580°C for one hour.

The two halves of the third diamond G2 were then polished on the sawn faces and also on the natural cubic faces opposite to remove the natural surface features. The polished slabs were then examined between crossed polars. Figure 6.40 (x 50) is a normal transmission picture for one half G2A of the diamond. It shows much gross internal defect and is included here to assist in the interpretation of the strain picture figure 6.41 (x 50) of the slab taken between crossed polars. A similar pair of pictures for the other half of the diamond G2B is shown in figures 6.42 and 6.43 (x 50). The slabs were etched in potassium nitrate at 575°C for one hour. The resulting etch patterns obtained on the surfaces from the middle of the diamond are shown in figures 6.44 and 6.45 (x 50).

When it is realized that the pictures between crossed polars are the result of an integration of the strain through nearly half of the thickness of a single diamond some 1 mm thick, and allowance is made for the effect of internal gross defects in the diamond, the correlation between the strain and etch patterns is very striking. It is apparent that most of the etch pits



Figure 6.40. G2A 001 (x 50).

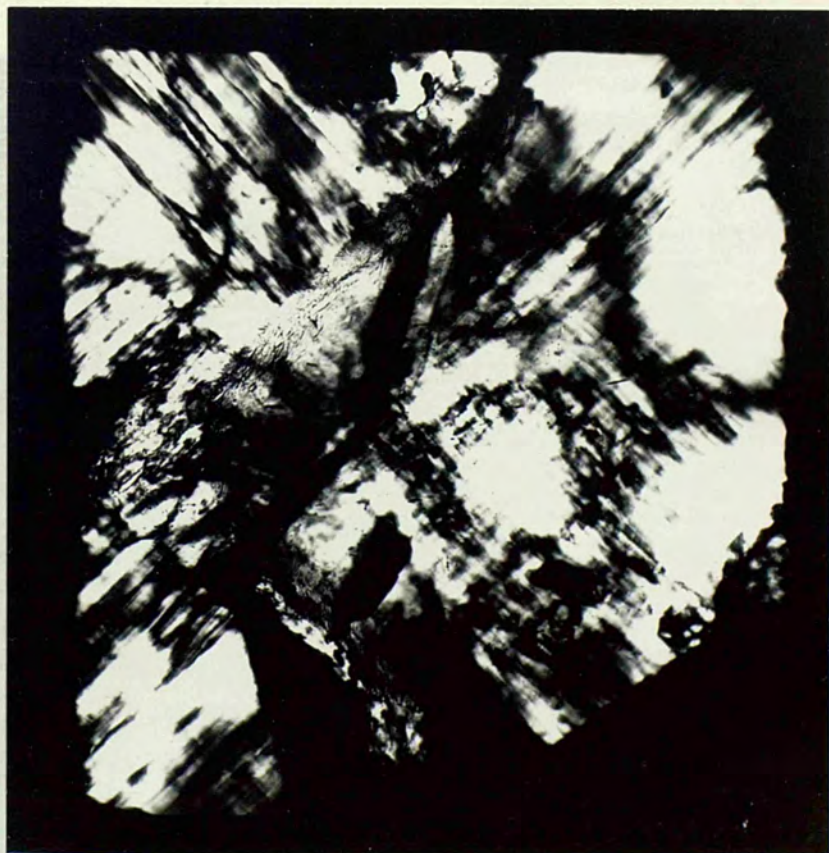


Figure 6.41. G2A 001. (x 50).



Figure 6.42. G2B 001̄ . (x 50).

Figure 6.42. G2B 001̄ . (x 50).

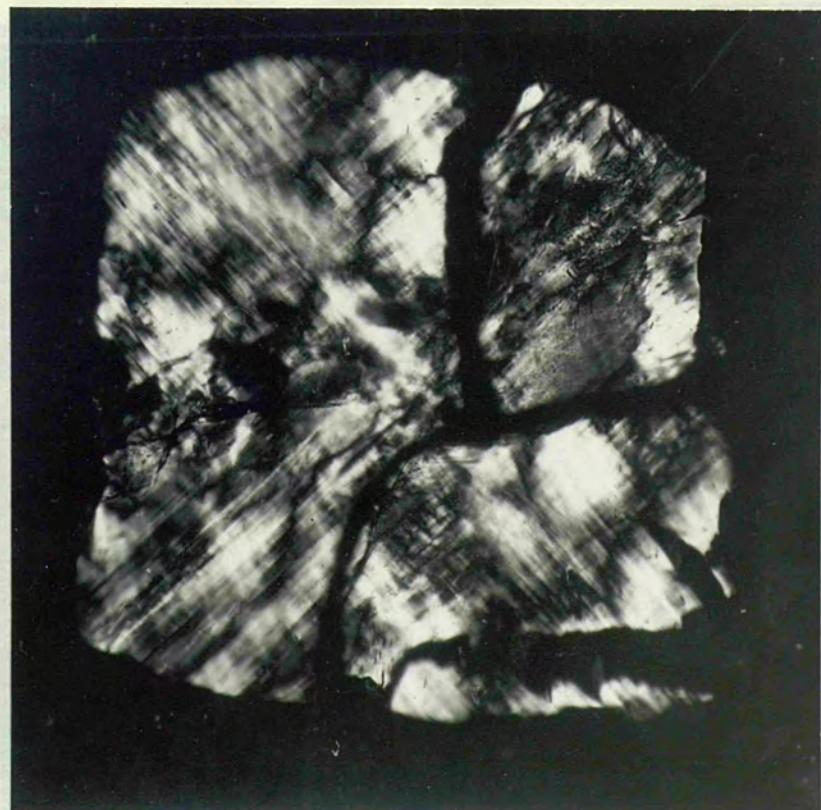


Figure 6.43. G2B 001̄ . (x 50).



Figure 6.44. G2A 001. (x 50).



Figure 6.45. G2B 001. (x 50).

CHAPTER 7.

produced on the cubic diamond surfaces are associated with strain induced dislocations. This will be discussed further in chapter 9.

Natural diamond has long been of interest to man. It has been assumed that high temperatures are required to give mobility to carbon atoms and high pressures to bring the atoms into a close bond. These are the conditions to be expected deep in the earth's crust or beneath it. Under pressures of some 100 000 atmospheres and at temperatures of about 3 000°C synthetic diamonds were first produced about 1955 (Bundy et al, 1955) by the General Electric Corporation in the United States of America. The work of Grenville-Halla and Lonsdale (1958) on these early synthetics indicates that they were grown from solution, nickel carbide molecules acting as crystallization centres. It is generally believed that the mechanism of formation of these synthetics is not the same as that of any naturally occurring diamond crystals and to this extent the production of synthetic diamond has so far not helped to show the mechanism by which diamond is formed in nature. It is not known for example whether it grows from solution or from the melt. It is hoped that a study of the etch patterns on diamond sections may

CHAPTER 7.

ETCH BLOCK PATTERNS ON CUBIC SECTIONS OF OCTAHEDRA.

7.1. Introduction.

The method by which diamond has grown in nature has long been of interest to man. It has been assumed that high temperatures are required to give mobility to carbon atoms and high pressures to bring the atoms into a close bond. These are the conditions to be expected deep in the earth's crust or beneath it. Under pressures of some 100 000 atmospheres and at temperatures of about 3 000°C synthetic diamonds were first produced about 1955 (Bundy et al, 1955) by the General Electric Corporation in the United States of America. The work of Grenville-Wells and Lonsdale (1958) on these early synthetics indicates that they were grown from solution, nickel carbide molecules acting as crystallization centres. It is generally believed that the mechanism of formation of these synthetics is not the same as that of any naturally occurring diamond crystals and to this extent the production of synthetic diamond has so far not helped to show the mechanism by which diamond is formed in nature. It is not known for example whether it grows from solution or from the melt. It is hoped that a study of the etch patterns on diamond sections may

help to reveal the growth history of diamond and possibly indicate the process of diamond growth.

That diamond with layers of different character occurs has been known for many years. Crystals of boart have been studied for example by Williams (1932) who showed a picture of a sectioned "hailstone" boart consisting of four more or less concentric layers of different colours readily discernable to the eye. The structure which Tolansky and his co-workers have described is of course much more subtle than this. Controlled etching techniques reveal this structure because of the preferential attack which the etchant makes on the crystal at lattice defect sites as will be discussed below.

It has been shown by Pandya and Tolansky (1954) and by Patel and Tolansky (1957) that a mild controlled etch which produces only micro etch pits on diamond sections often shows "stratigraphical" patterns. They believed these patterns revealed the growth layers laid down in sheets on octahedral planes. Because etch commences preferentially at lattice defect sites, such as dislocations, vacant sites ~~on~~ foreign atoms, the density of etch pits in a region is proportional to the number of such lattice defects. It was conjectured

by the above mentioned workers that the observed bands of different etch density were laid down under different conditions (e.g. pressure, temperature, concentration, impurities) of growth. It might be possible, they believed, with such patterns to follow the stages of growth of the crystal. Careful etch control, however is essential to show the maximum detail in the pattern. The etch pits must be large enough to be satisfactorily resolved but if etching proceeds too far the pits run together and much of the interesting detail may be destroyed.

7.2. Experimental Details.

The etched sections to be described in this chapter were all etched in freshly fused potassium nitrate at temperatures of about 575°C for periods of usually one hour.

To increase the contrast, as well as the total amount of light available for photography, an opaque film of highly reflecting silver was deposited in vacuo on to the etched sections.

Examination of the sections was carried out in reflection in general using a Vickers metallurgical microscope. In order to gain maximum resolution at low magnification, say x20, the microscope was used without

an eyepiece so that an objective with as high a numerical aperture as possible could be used. Some of the earlier pictures were taken using a Cooke, Troughton and Simms (C.T.S.) binocular microscope and in these cases resolution was not nearly so good although the photomicrographs obtained contain much useful information. Where this microscope has been used it will be clearly stated in the text.

The contrast obtained using normal illumination or the "oblique" illumination available on the Vickers microscope gave very poor contrast indeed. It was found that by appropriately adjusting the angle of incidence of oblique illumination from a subsidiary source at a suitable angle with respect to the normal to the surface (about 45°) and by rotating the specimen in a plane parallel to the surface being examined, it was possible to obtain pictures of the etch patterns of striking contrast although the patterns observed with normal illumination or the built-in "oblique" illumination were scarcely discernable. Figures 7.1, 7.2 and 7.3 (x 20) show pictures taken in turn with normal illumination, so called 'prism illumination, which may be described loosely as "off-axis normal illumination", and with the controlled oblique illumination. Somewhat

better contrast can be obtained with normal illumination if the surface is more heavily etched but of course some of the fine detail, as stated above, is destroyed by so doing. Figures 7.4 (x 20) shows a section after a total etch of seven hours viewed by normal illumination. Figure 7.5 (x 20) shows the same surface after a light polish to remove the existing etch pattern and re-etching for one hour. Unfortunately micro-ring cracks were produced during the polishing operation and these have etched up to mar the pattern. Figure 7.6 (x 20) shows the same surface examined with controlled oblique illumination.

A comparison of figures 7.4 and 7.6 shows a reversal of tone, the dark regions of one corresponding to the bright regions of the other. This is of course the normal effect obtained with illumination incident obliquely at large angles to the normal, and is the effect obtained with so called dark field illumination. In this instance the flat unetched areas of figure 7.6 specularly reflect the obliquely incident light away from the microscope objective whereas some of the light scattered from the etched regions is received by the objective. Thus, in the etch patterns to be described below, the dark regions are unetched or lightly etched

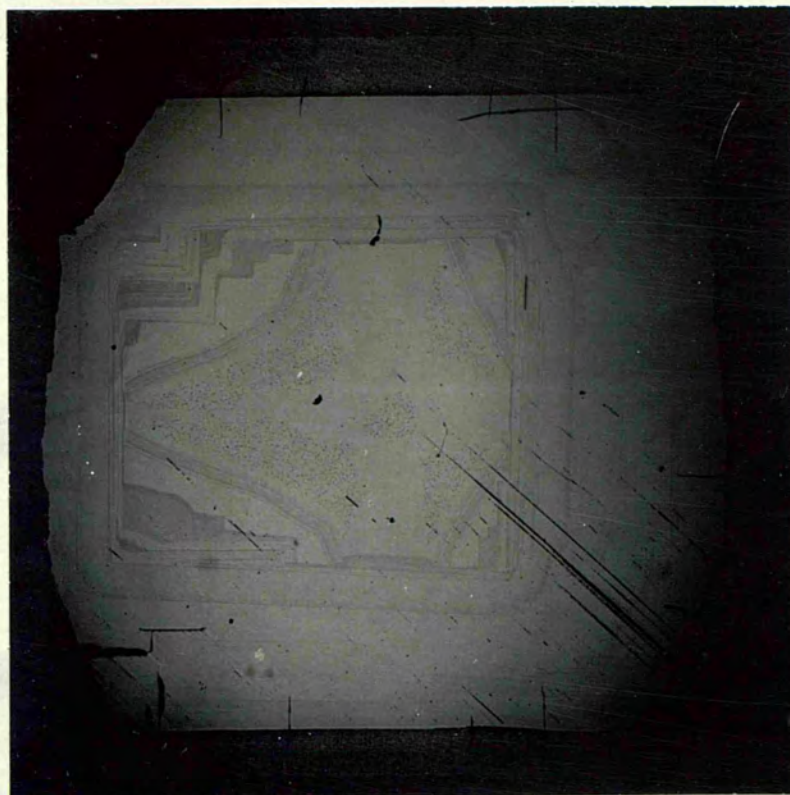


Figure 7.1. B, Section J. (x 20).

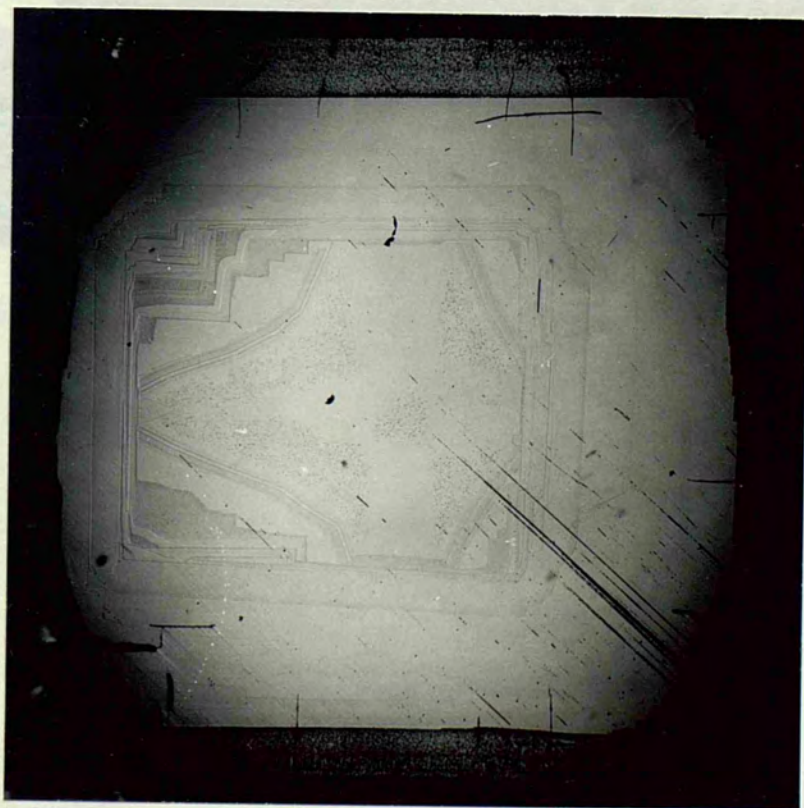


Figure 7.2. B, Section J. (x 20).

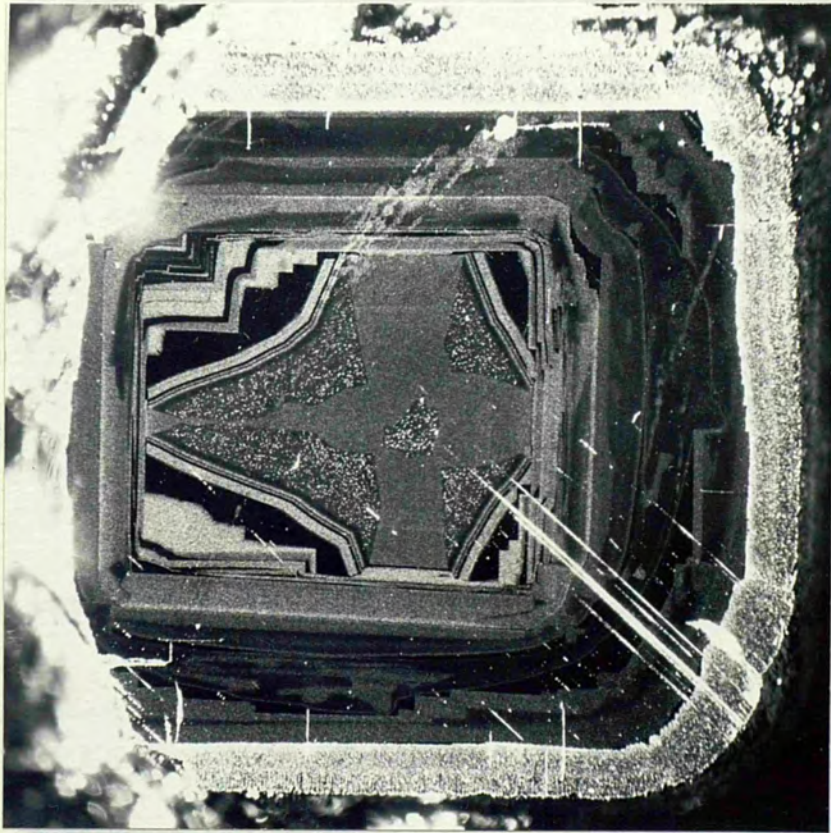


Figure 7.3. B, Section J. (x 20).

Figure 7.3. A, Section 2. (x 20).

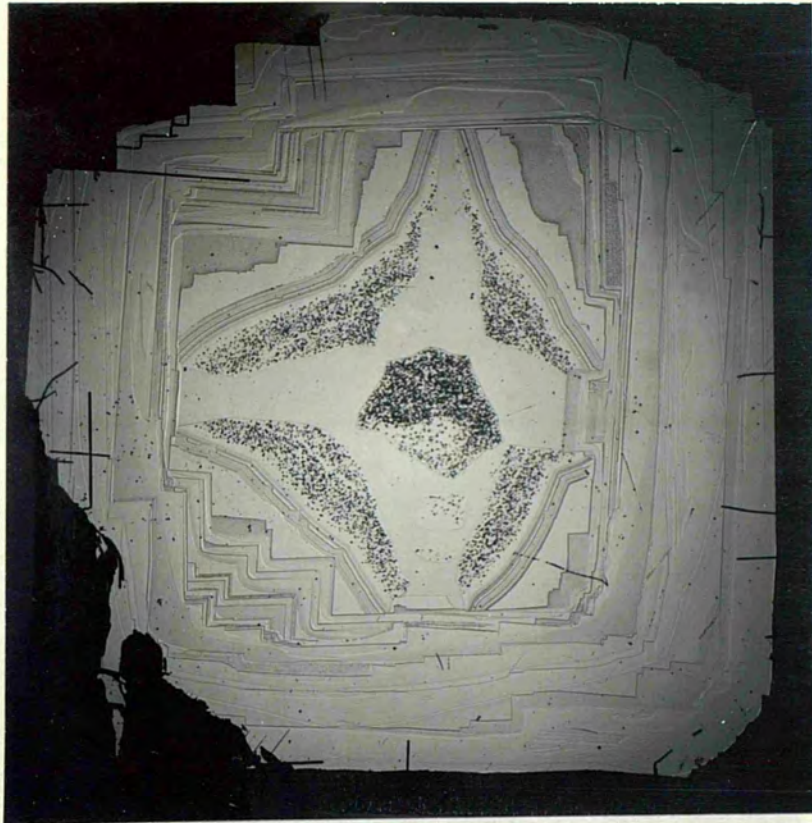


Figure 7.4. B, Section 2. (x 20).



Figure 7.5. B, Section 2. (x 20).

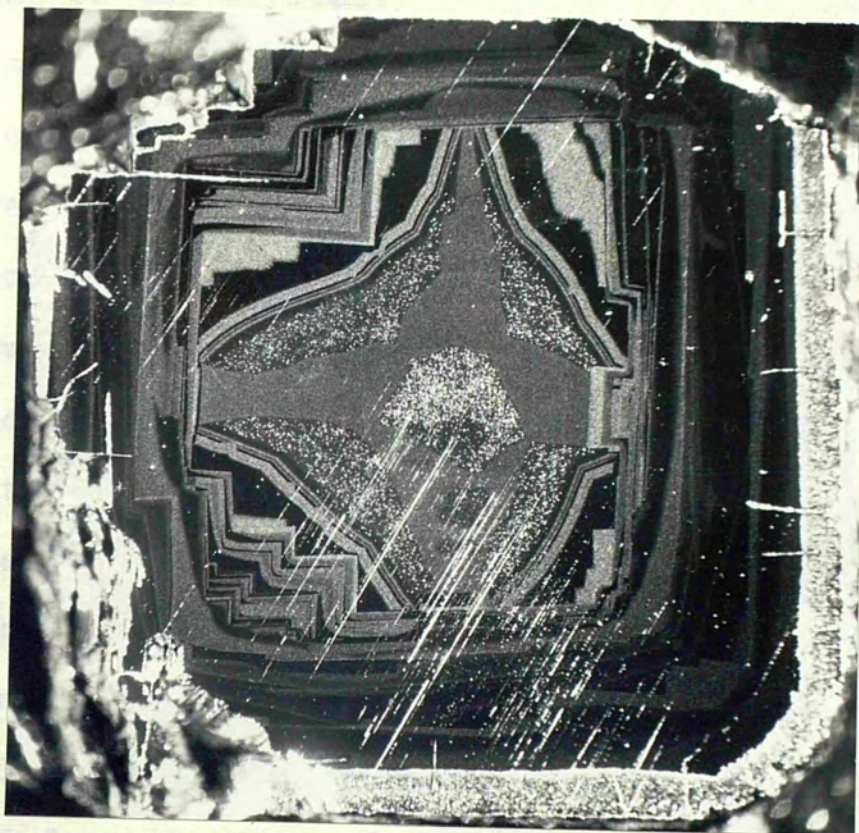


Figure 7.6. B, Section 2. (x 20).

Preliminary measurements of the absorption spectra of diamond II show that the ultra-violet absorption edge varied over the section, the cut-off in transmission varying between about 3000Å and 2500Å. A simple microscope was set up using a quartz objective. The slab was illuminated with ultra-violet light of wavelength

diamond whereas the bright areas are the more heavily etched regions of the crystal.

Cubic sections near the girdle of a number of diamonds of octahedral habit were examined. These diamonds were further studied by polishing away part of the diamond to produce further cubic planes. In particular two diamonds A1 and B1 were polished in this way to produce seven and nine sections respectively finishing with relatively thin sections of diamond. The final slab of diamond B1 was further studied by examination between crossed polars and by taking ultra-violet photomicrographs.

The thickness of diamond removed between sections was estimated from the mass of diamond removed and the area of cross section of the diamond sections as measured from enlarged photographic prints of known magnification, about $\times 50$, using a planimeter calibrated by us at the setting used.

Preliminary measurements of the absorption spectrum of diamond B1 showed that the ultra-violet absorption edge varied over the section, the cut-off in transmission varying between about 3000\AA and 2950\AA . A simple microscope was set up using a quartz objective. The slab was illuminated with ultra-violet light of wavelength

about 2966A obtained from a high pressure mercury lamp with the aid of a Hilger medium quartz spectrograph and photographed in transmission. A diagram of the set up is shown in figure 7.7. The resulting adsorption pattern to be described below shows regions of transmission and absorption. Diamond which is opaque in the ultra-violet wavelengths below about 3000A is classed as type 1 while that which is transparent below this wavelength is classed as type 11. Thus we have been able in the one diamond to distinguish regions of type 1 and type 11 (see figure 7.42).

7.3. Etch Block Patterns.

In all, halves of three diamonds (A1, A2 and A3) and both halves (B1 and B2) of a fourth diamond, each sawn at the girdle on a cubic (1 0 0) face, were studied. These diamonds were of unknown origin. Each was polished at the table to remove the saw marks and then etched as described above. Photomicrographs of the sections of the first three diamonds were taken using the C.T.S. binocular microscope and these are shown in figures 7.8 to 7.10 (x 20). Photomicrographs of the etch patterns on diamond B2 taken after sawing and after polishing using the Vickers microscope are shown in figure 7.11 and 7.12 (x 20). The patterns obtained on the other half of B, i.e. on B1, were similar. Now from these micrographs several observations can be made:

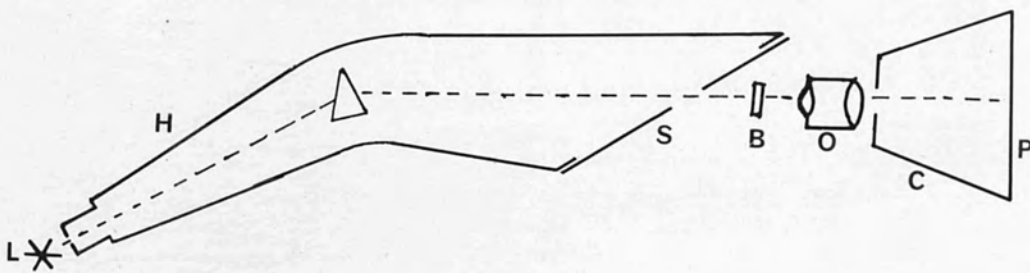


Figure 7.7. Diagrammatic sketch of Ultra-Violet
Microscope.
(B, diamond specimen; C, camera case;
H, Hilger medium quartz spectrograph;
L, high pressure mercury lamp;
O, quartz microscope objective;
P, photographic plate;
S, slit).

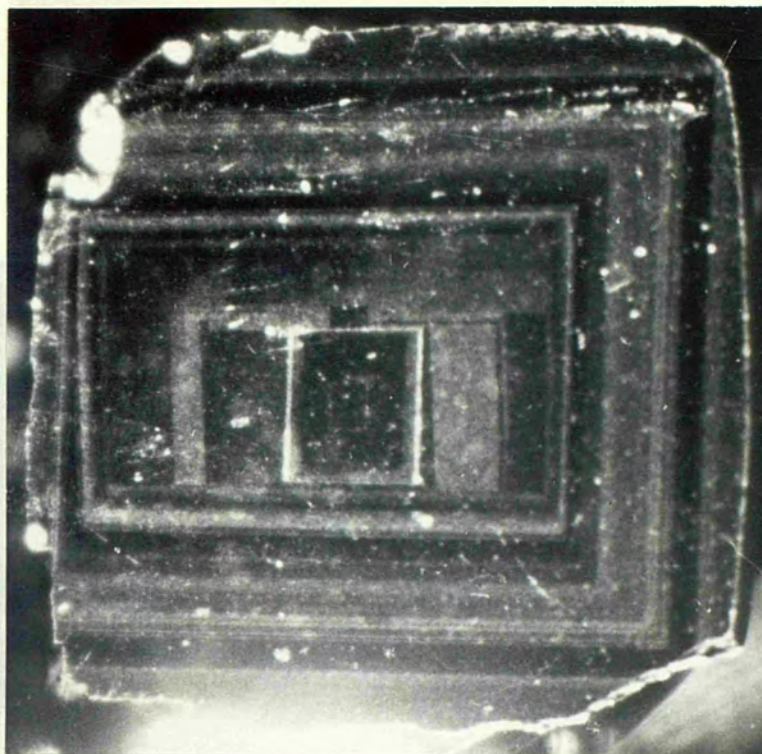


Figure 7.8. A1, Section 1. (x 30).

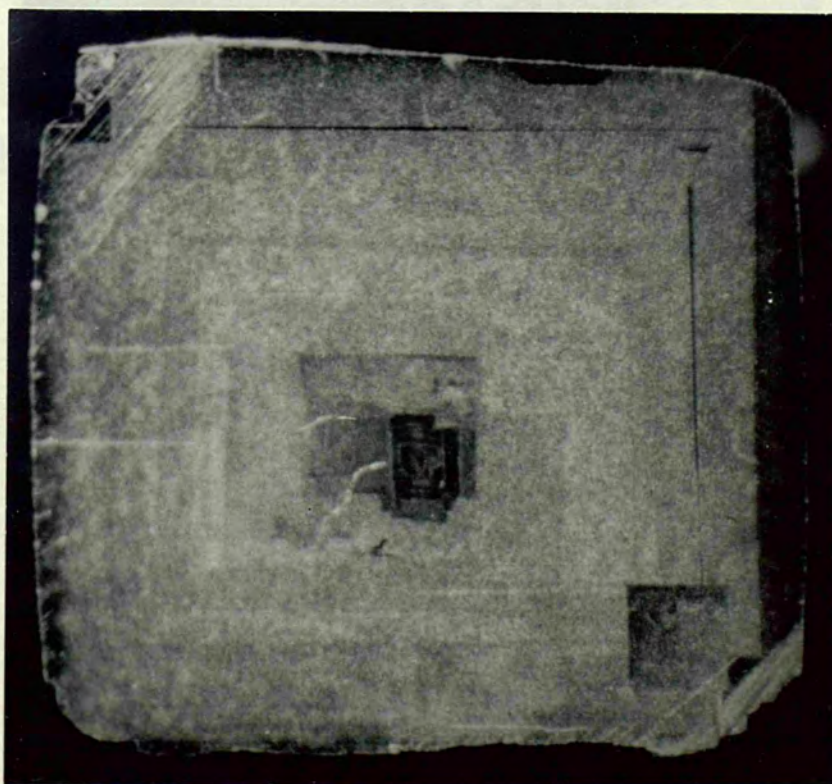


Figure 7.9. A2, Section 1. (x 20).

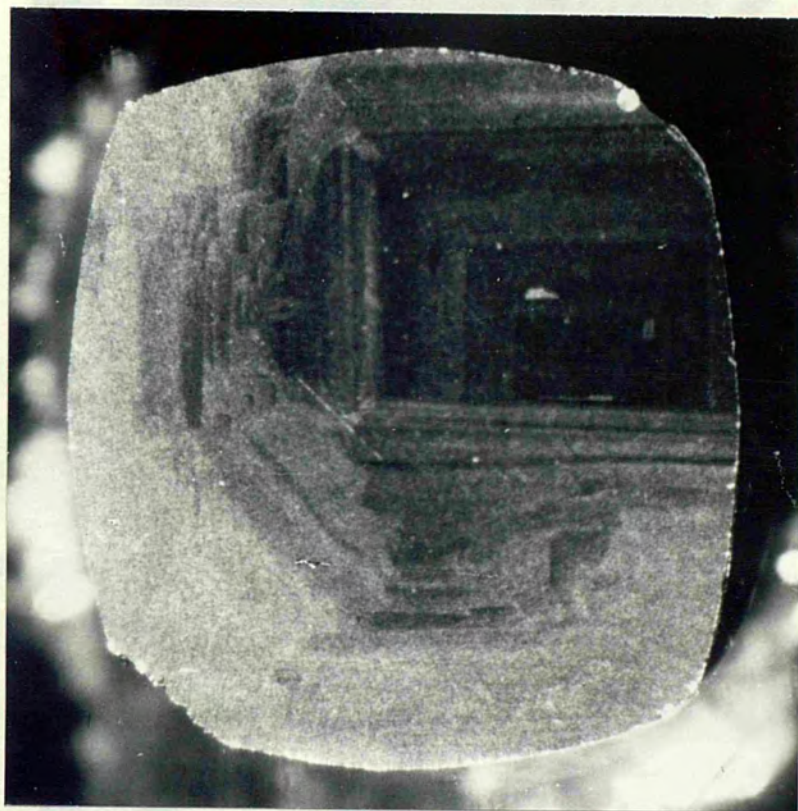


Figure 7.10. A3, Section 1. (x 20).

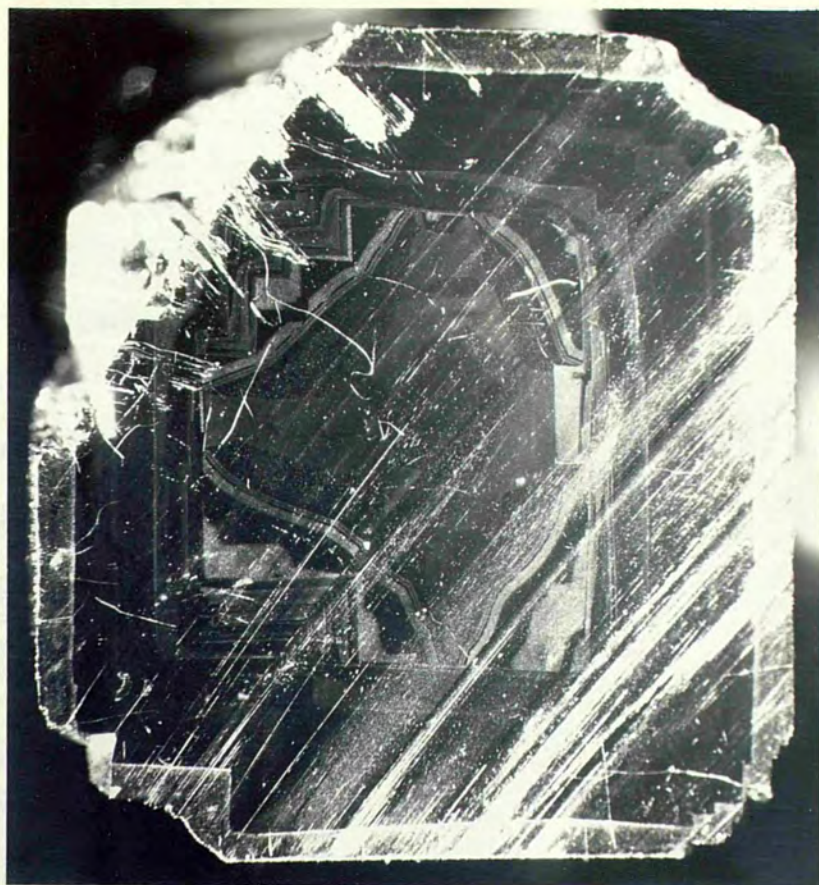


Figure 7.11. B2 $00\bar{1}$. (x 20).

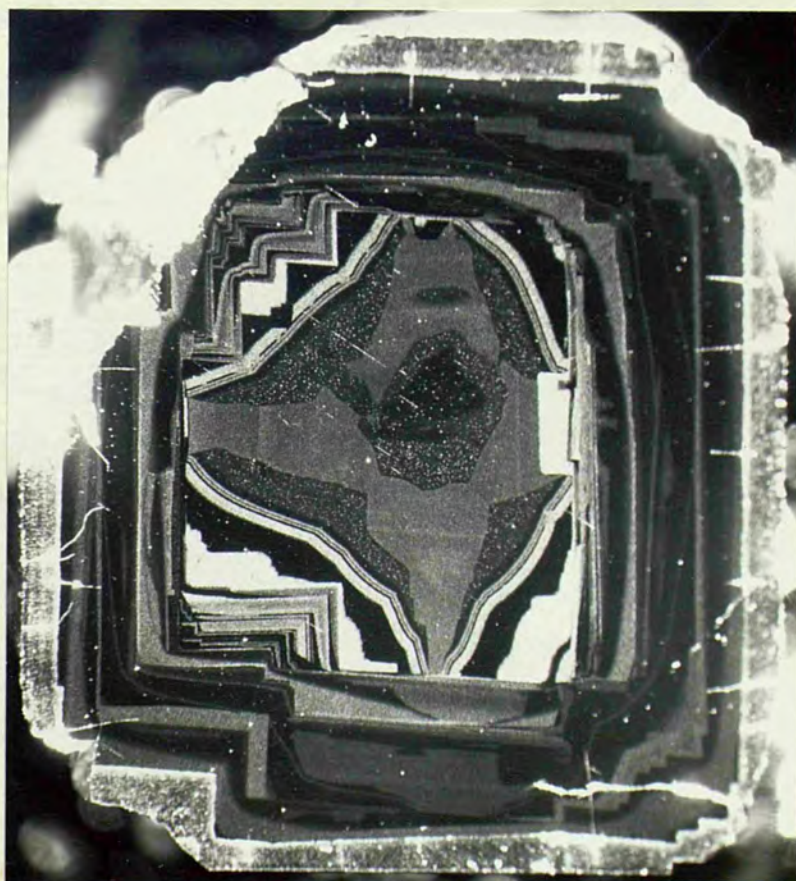


Figure 7.12. B2, $00\bar{1}$. (x 20).

1. In all cases there is some type of stratigraphical block pattern in which some regions are more heavily etched than others.
2. Much of the patterns are rectilinear and orientated closely crystallographically. But there are some notable departures from rectilinearity and crystallographic orientation.
3. There is at the centre of A2 and B2 a core of character different from the outer layers of the diamond crystals. This may apply also, but in a less pronounced way, to A1. There is also a difference in character in the region at the top left of A3 and it appears that the diamond structure is formed, though not symmetrically, about this region. It may be that there is a core to this diamond also, but, if so, it is by no means central.
4. The patterns on B1 after sawing and subsequent polishing show very close correspondence, allowing of course for the preferential etching at sawing lines and no micro ring cracks produced during the sawing operation. These obscure the pattern to some extent. The thickness of diamond removed by this polishing was of the order of 0.02mm on the

average. This indicates that the patterns are "in depth" in agreement with the results obtained by Patel and Tolansky (1957) on a block cleaved out of an octahedron. That the structure revealed by the etch patterns is three dimensional will be clearly demonstrated in the following sections.

7.4. Etch Patterns on Sections of Diamond A1.

This diamond showed particularly rectilinear etch patterns on the section shown in figure 7.8. These patterns are very closely crystallographic with some exceptions. Further sections were examined by polishing away the top section of the table and then by polishing in stages from the tip, T, in a $[1\ 0\ 0]$ direction towards the table. Seven sections in all were obtained. The approximate positions of these sections on the diamond are shown in figure 7.13, the final slab remaining between sections 2 and E being shown by cross hatching. The mean distances between the sections are as follows:

Lamina	Thickness mm
1 to 2	0.28
2 to E	0.74
E to D	0.04
D to C	0.19
C to B	0.19
B to A	0.03

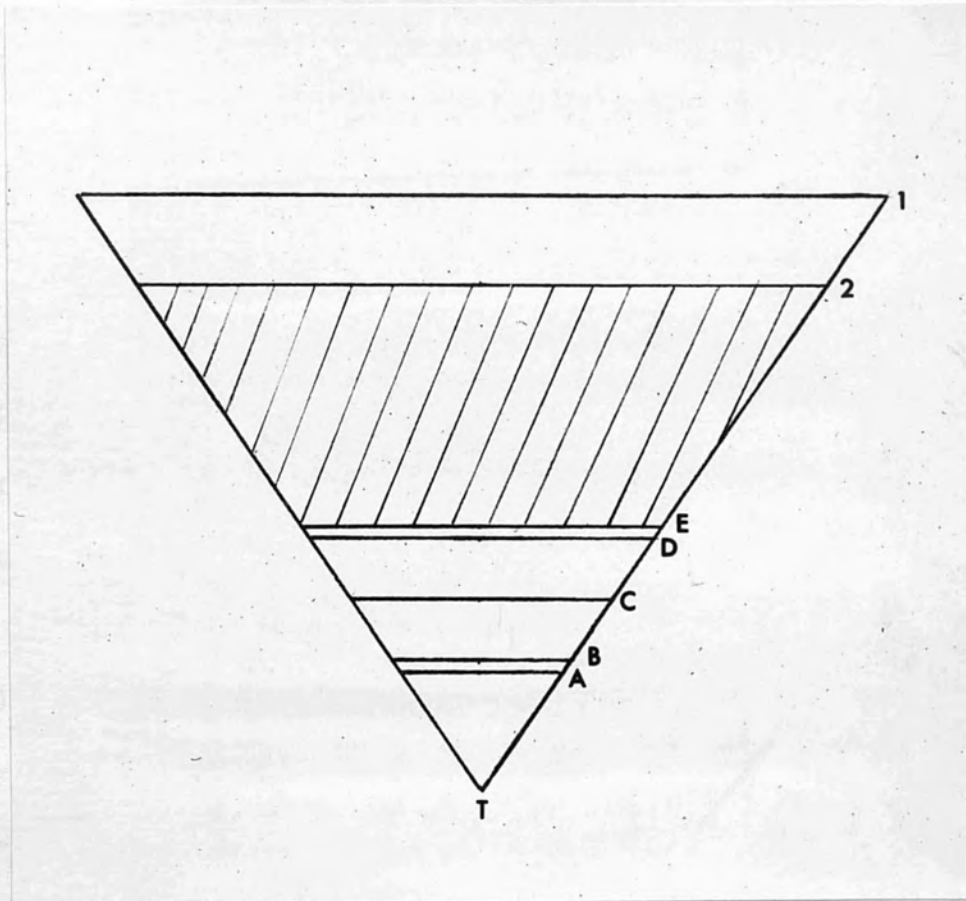


Figure 7.13. Diagram of diamond A1 showing sections studied.

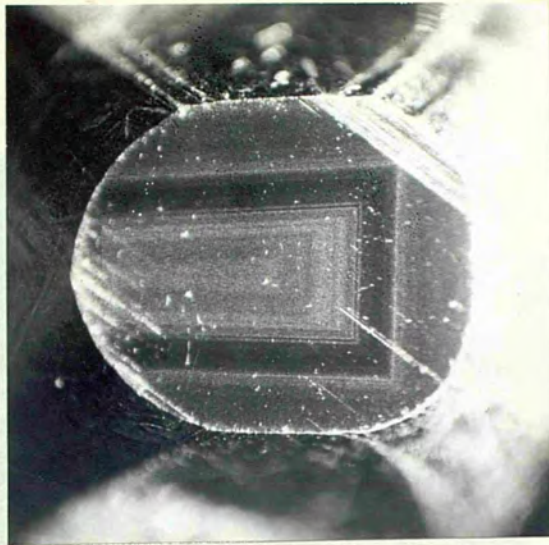


Figure 7.14. Al, Section A. (x 30).

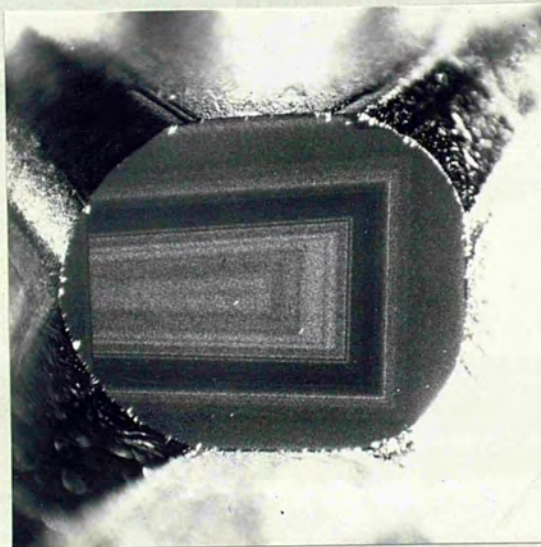


Figure 7.15. Al, Section B, (x 30).

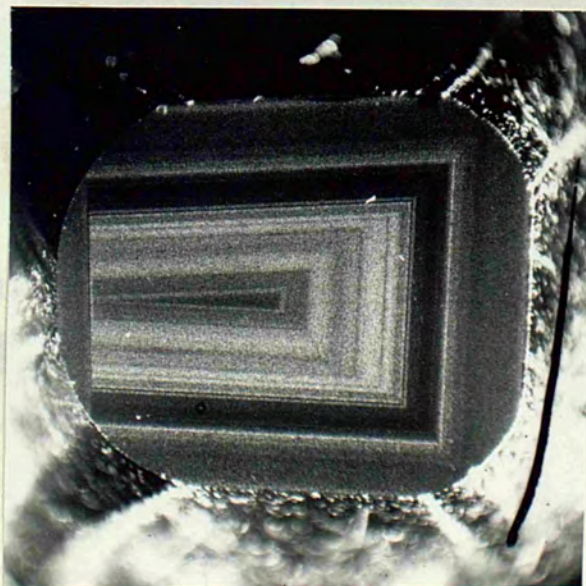
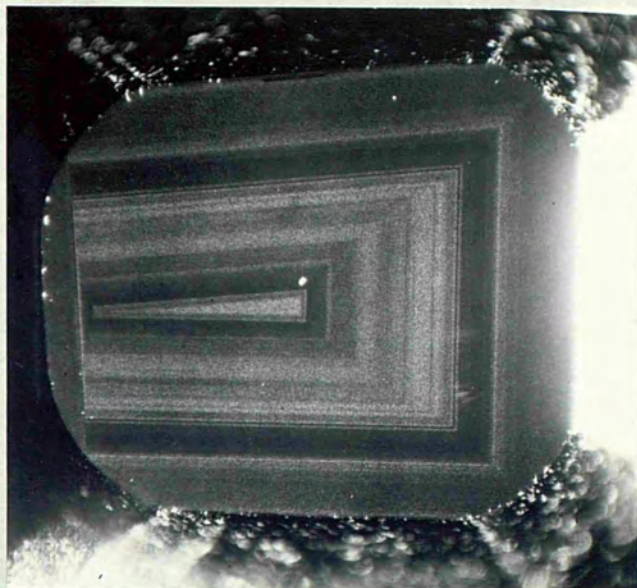
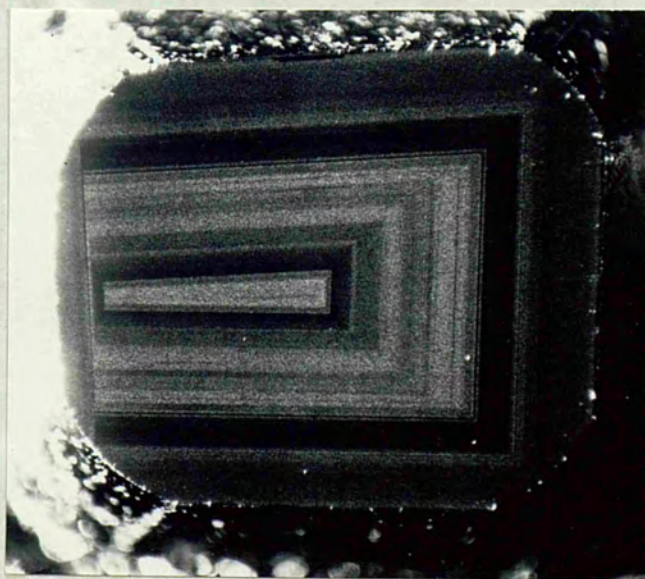


Figure 7.16. Al, Section C. (x 30).



Section 7.17. Al, Section D. (x 30).

Figure 7.18. Al, Section E. (x 30).



Section 7.18. Al, Section E. (x 30).

Figure 7.19. Al, Section F. (x 30).

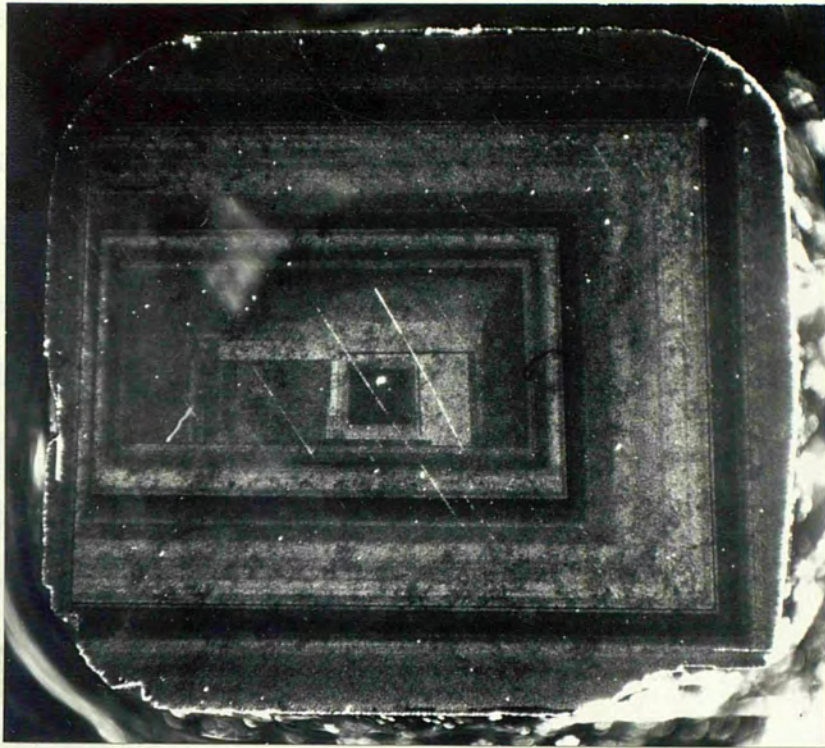


Figure 7.19. Al, Section 2. (x 30).

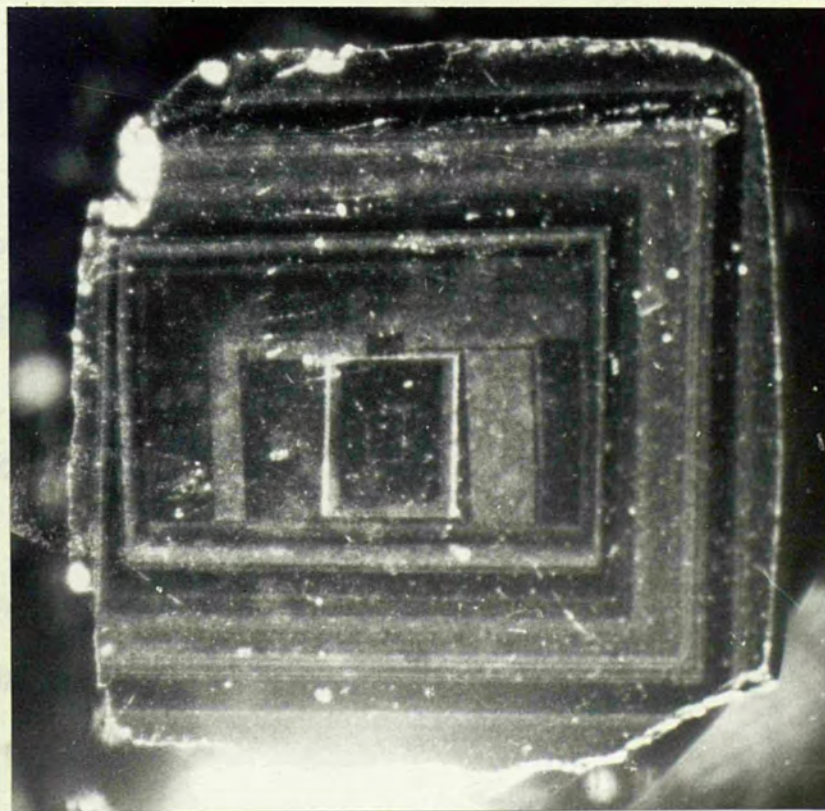


Figure 7.20. Al, Section 1. (x 30).

rectangular section has formed and growth has been by fairly uniform layers, giving the onion-like character. The correspondence between layers when regarded from the outside and going towards the centre is quite obvious, being repeated from section to section, layers disappearing at the centre, as it to be expected, as the tip of the diamond is approached.

Most of the layers have very sharp corners but as the outer layers are reached the corners of the crystal have become rounded, very much as though after growth had been completed dissolution had taken place, the rate of dissolution at the corners of the sections, i.e. along the edges of the octahedron, being very much greater than on the faces. Any dissolution at the faces away from the corners must have been very uniform as the block pattern has been preserved along the edges of the section for the most part but as the tip is approached the rounding of the two corners at the left side of the pictures increases until finally by section C they have met to give a smoothly rounded section.

The layers become visible on etching because of their different resistance to etch. The dark layers in the pictures are regions relatively free from etch pits and are presumably made up of diamond whose crystal

lattice is largely free of defects, or at any rate free of the type of defects which are attacked by potassium nitrate etchant under the conditions of etching used. The layers which appear light in the picture are regions of large etch pit concentration and the diamond in this region is therefore relatively rich in lattice defects. The character of the layering will be discussed in greater detail when considering diamond B.

7.5. Etch Patterns on Sections of Diamond A2.

The core of this diamond can be seen from figure 7.9 to be of different character to the rest of the diamond, being made up of blocks of largely rectilinear outline of diamond resistant to etch (dark in the picture) and of areas which have etched quite readily. Just outside the central core the pattern of rectilinear blocks of irregular size appears to continue but the contrast in density of etch pits from block to block is less marked. The outer layers, except for an odd block here and there and especially in two of the corners, is of similar character to that in diamond A1, the contrast between bands however not being nearly so marked.

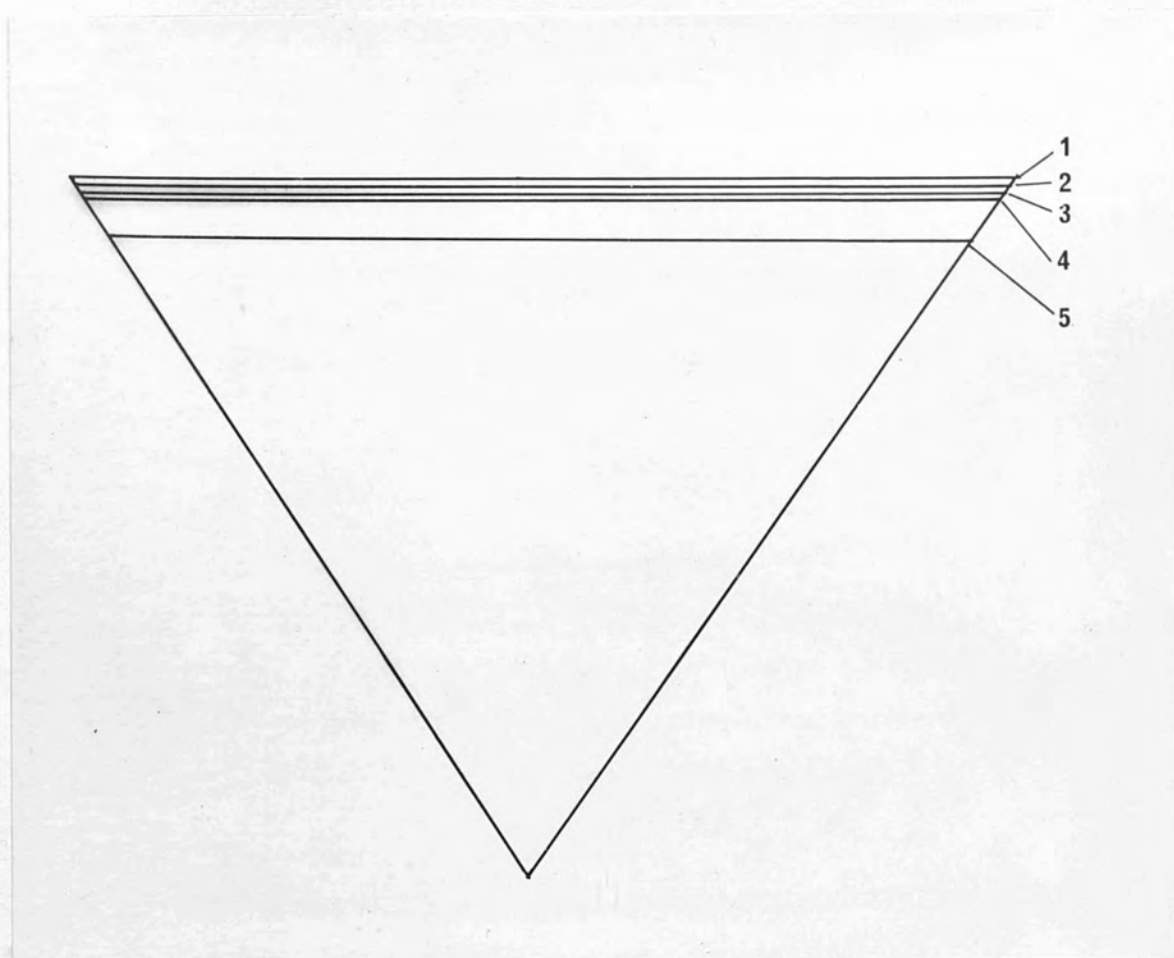


Figure 7.21. Diagram of diamond A2 showing
Sections studied.

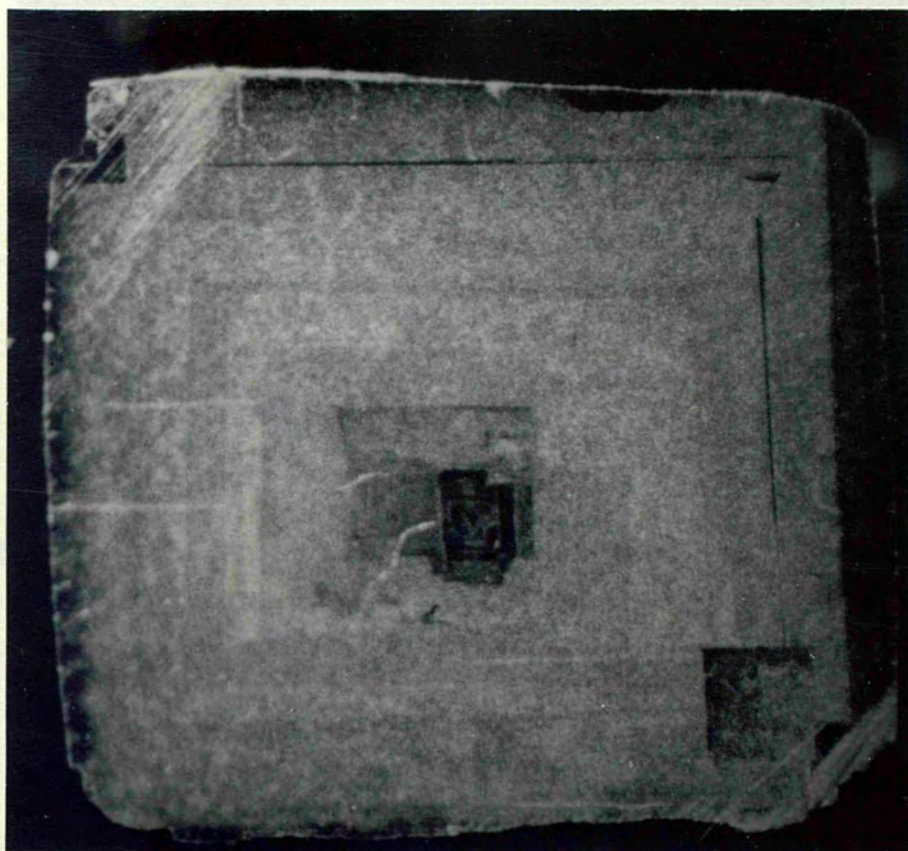


Figure 7.22. A2, Section 1. (x 30).

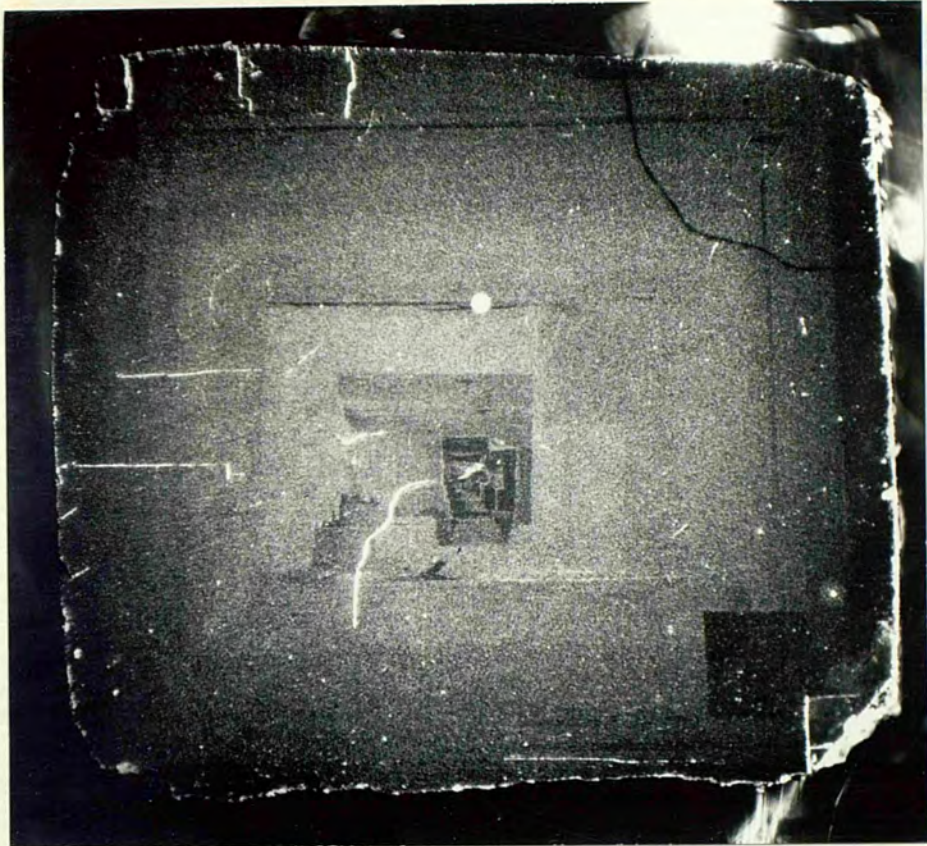


Figure 7.23. A2, Section 2 (x 30).

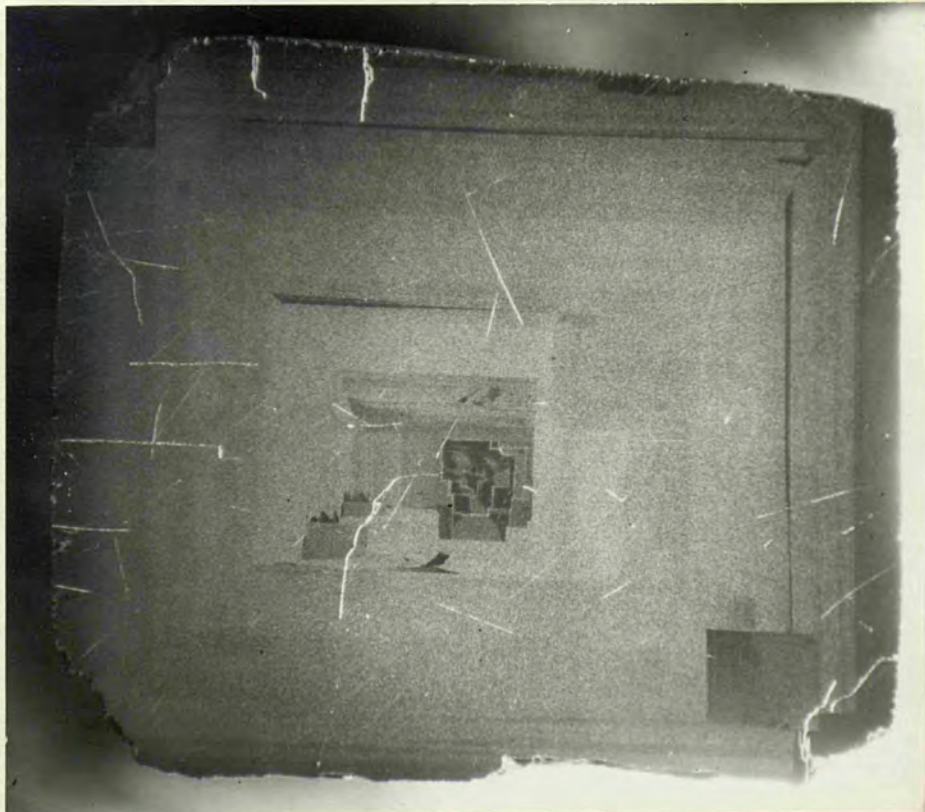


Figure 7.24. A2, Section 3. (x 30).

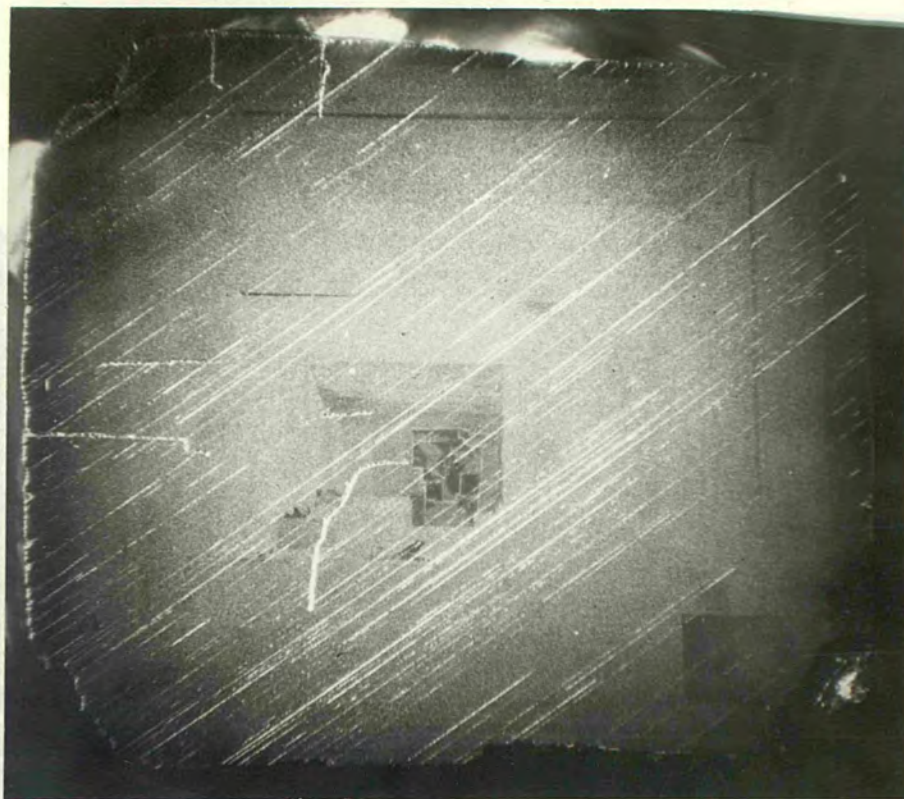


Figure 7.25. A2, Section 4.(x 30).

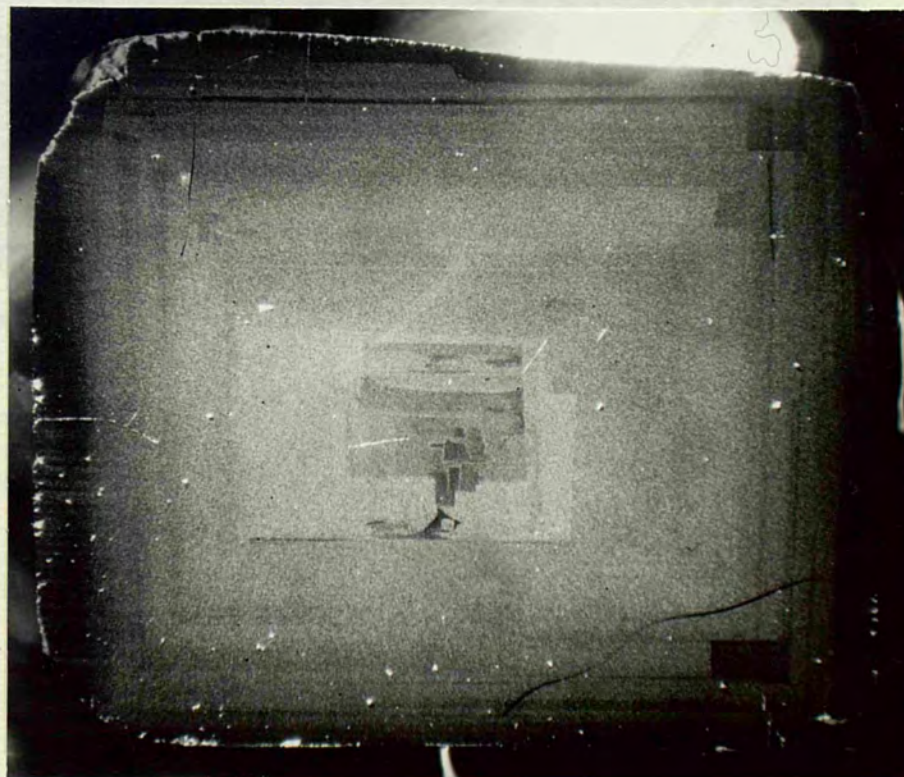


Figure 7.26. A2, Section 5. (x 30).

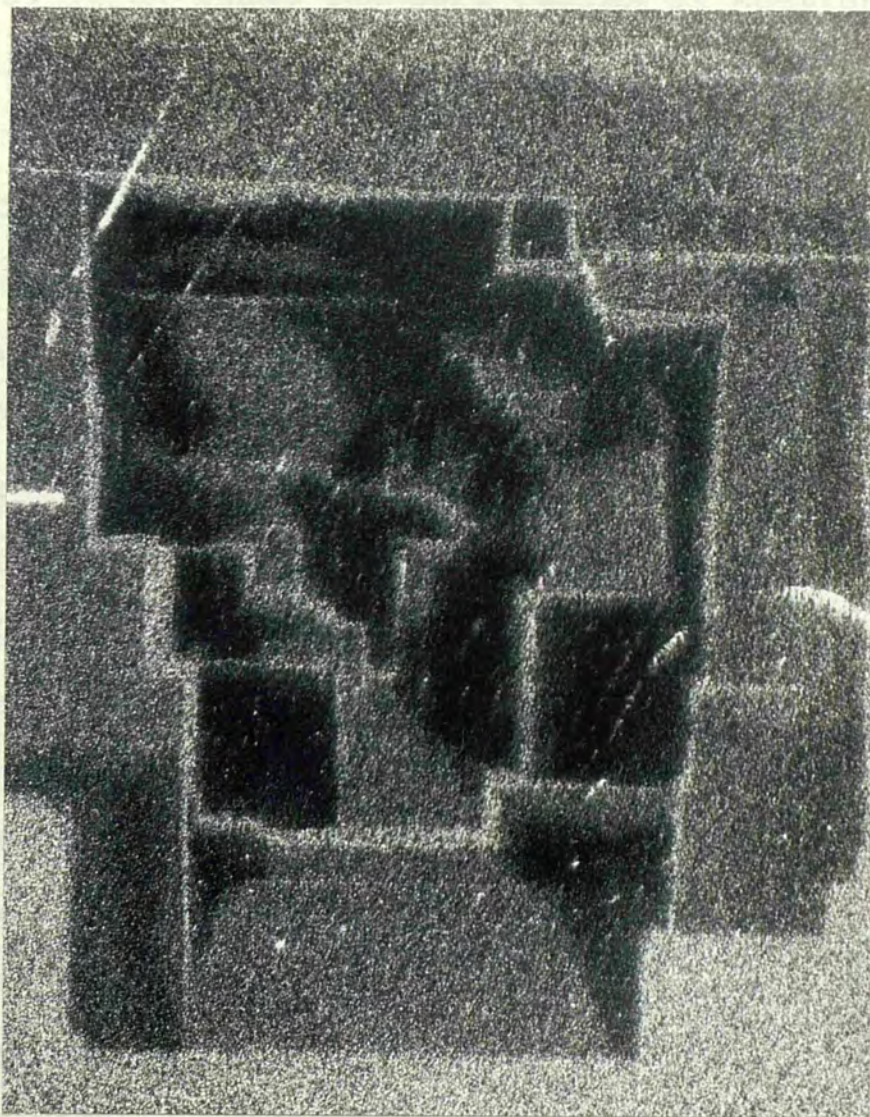


Figure 7.27. A2, Section 3. (x 250).

The nature of the central core is well illustrated by the high magnification photomicrograph of figure 7.27 (x 250) which shows the core region of section 3. The individual etch pits are resolved and the change in concentration of etch pits from region to region can be plainly seen. The general impression is of an agglomeration of small seed crystals (dark regions) all properly oriented in a matrix of slightly different material (lighter regions).

7.6 Etch Patterns on Sections of Diamond A3.

The diamond, of which a section is shown in figure 7.10, was lightly polished on the same face and the new section is shown in figure 7.28 (x 20). Etching of section 1 was at 525°C for 1 hour + 650°C for 5 minutes, while for section 2 it was at 565°C for 20 minutes. The etch block patterns reveal that on two faces either preferential growth has taken place or preferential dissolution has occurred on the other two faces. The rounded outline, in association with the rectilinear etch patterns which continue right to the edges of the section, indicate that dissolution, if it has occurred as appears likely, has certainly been severe. The possibility cannot be ruled out of course that in the final stages of growth layers of continued slightly decreasing extent have been laid down to

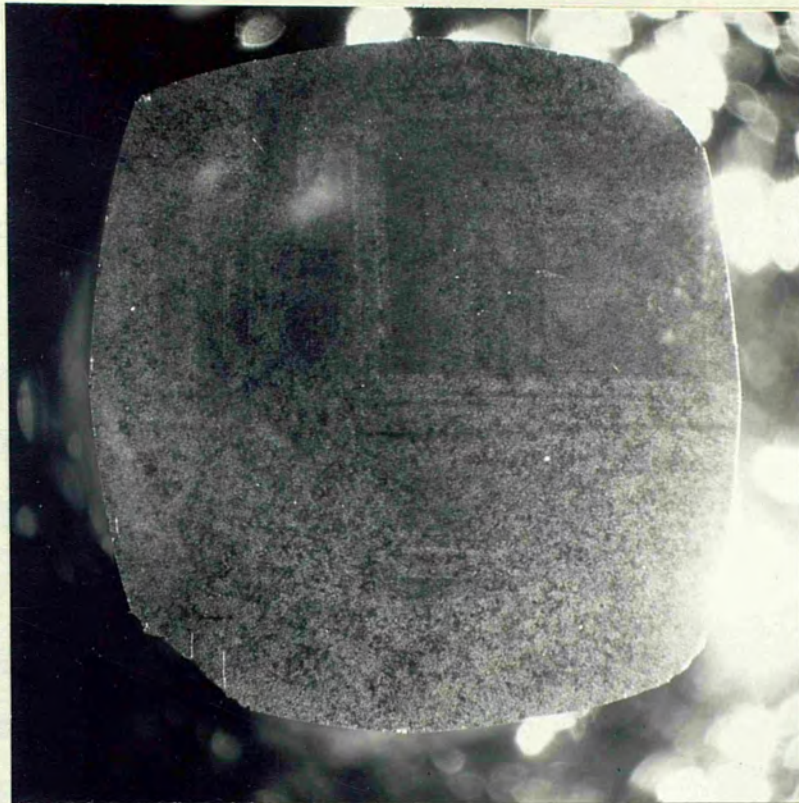


Figure 7.28. A3, Section 2. (x 20).

give a fairly smooth outline. If this diamond has commenced to grow from a core as diamonds A1 and A2 appear to have, then this core is certainly not now in the centre of the diamond and the true core may well not be revealed by the sections.

7.7. Etch Patterns on Sections of Diamond B.

Diamond B was a coated octahedral diamond, somewhat yellowish in colour. The outer coating was not clear but inside it the diamonds, apart from a number of flaws and a gas inclusion, was clear and of good quality. It was about 1.5 carat, of reasonably good octahedral habit. As received by us it was already sawn into two approximately equal parts, B1 and B2, at the girdle along a plane approximating to cubic (001). The tips of the two halves were somewhat rounded. Preliminary etching of the sawn faces showed a very complex etch pattern, that on one half B2 being shown in figure 7.11 and after polishing the same face is shown in figure 7.12. The average thickness of diamond removed between these two planes by polishing was about 0.02 mm. Similar patterns were obtained on the corresponding faces of the half B1.

Further sections on diamond B1 were obtained by polishing away from the tip T in successive stages, producing a further nine sections, A,B,CJ. Finally a thin slab bounded by faces 2 and J remained. The approximate positions of these sections of B are

shown in figure 7.29, the estimated difference between layers being as follows:

Lamina	Thickness mm
1 to 2	0.2
2 to J	0.75
J to H	0.48
H to G	0.32
G to F	0.32
F to E	0.34
E to D	0.08
D to C	0.38
C to B	0.58
B to A	0.2
A to T	0.25

After polishing, each section was etched in fused potassium nitrate at a temperature of approximately 575°C for one hour. The etch patterns obtained on these sections are shown in figures 7.30 to 7.40 (x 20).

Figure 7.41 (x 35) shows at larger magnification the etch pattern obtained on face 2. Firstly it can be seen that, while the laminae near the outside of the crystal are predominantly rectilinear, those near the centre are very strongly curved. Secondly and unexpectedly, are the complete changes in crystal habit which have apparently occurred during the growth. Near the centre of the section is a dark patch of irregular shape which is fairly heavily etched. It is surrounded by a cross-like feature 2, of lighter colour and therefore

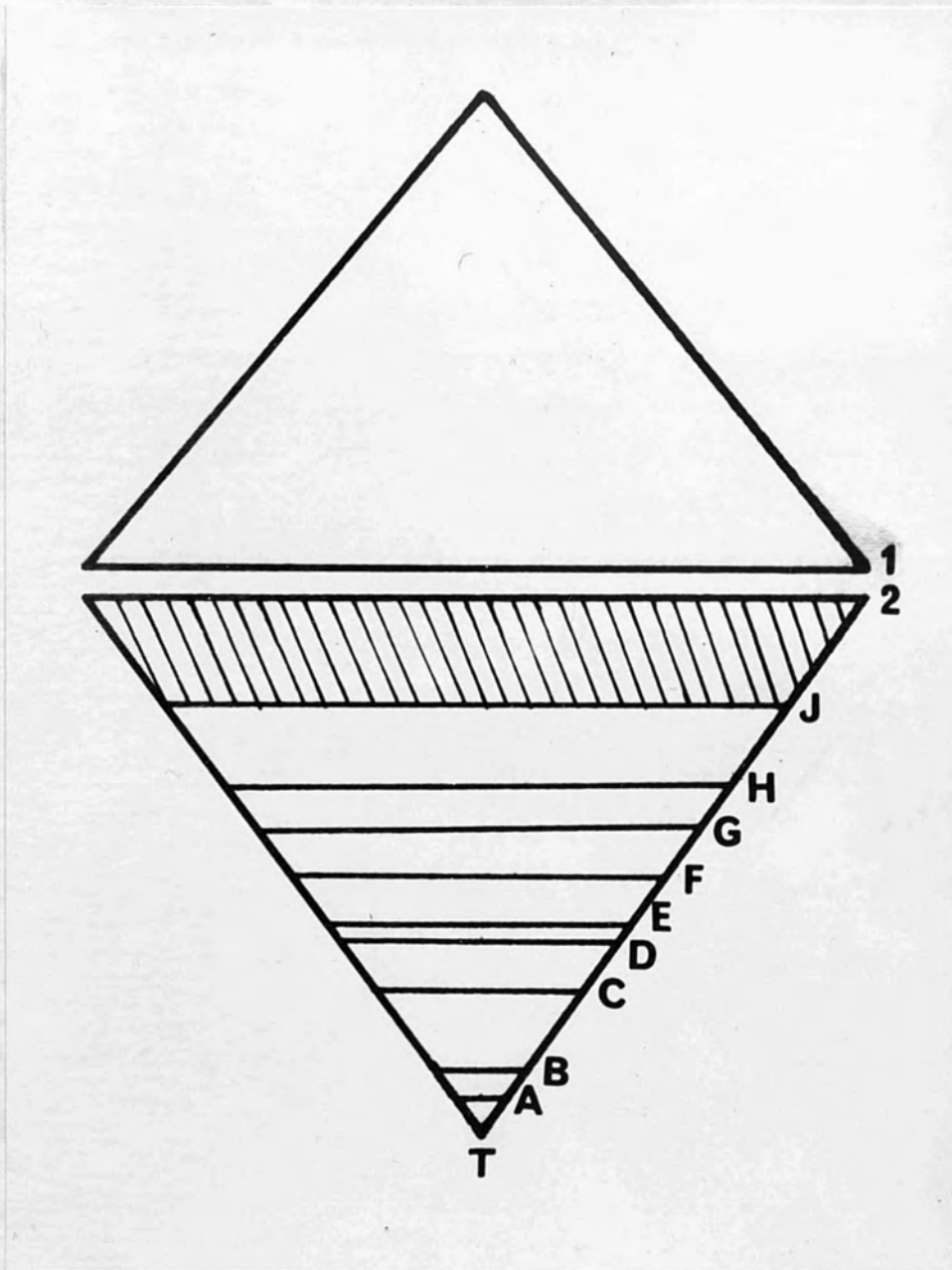
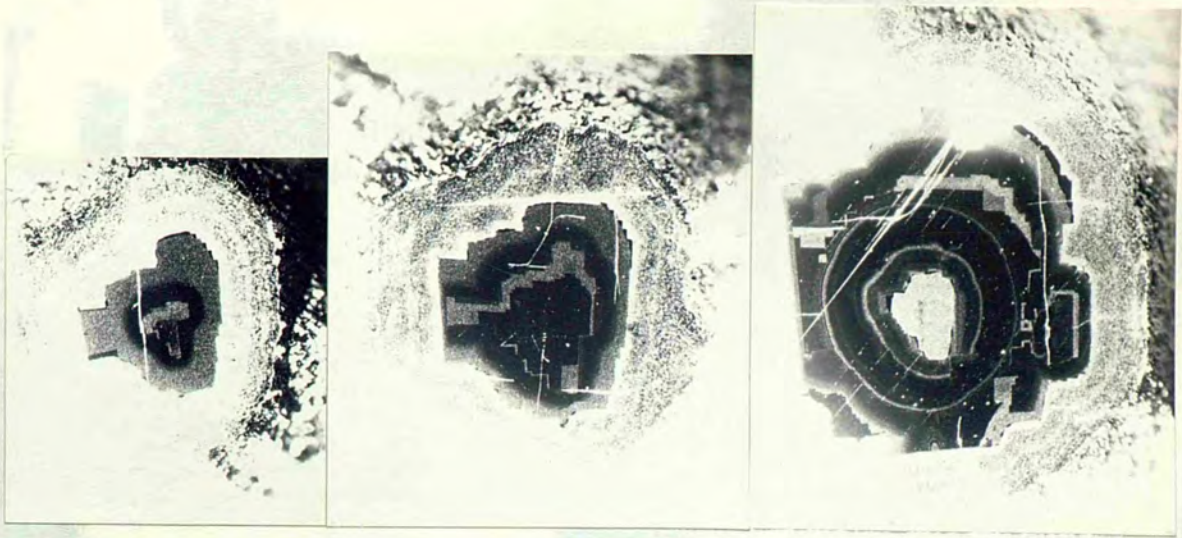
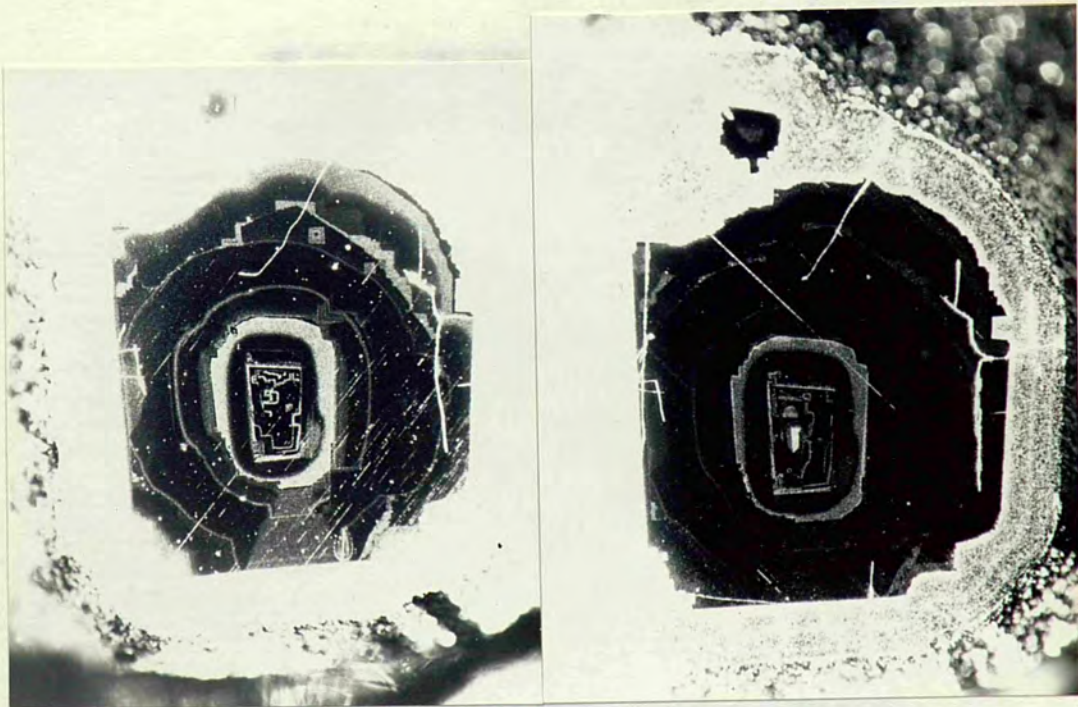


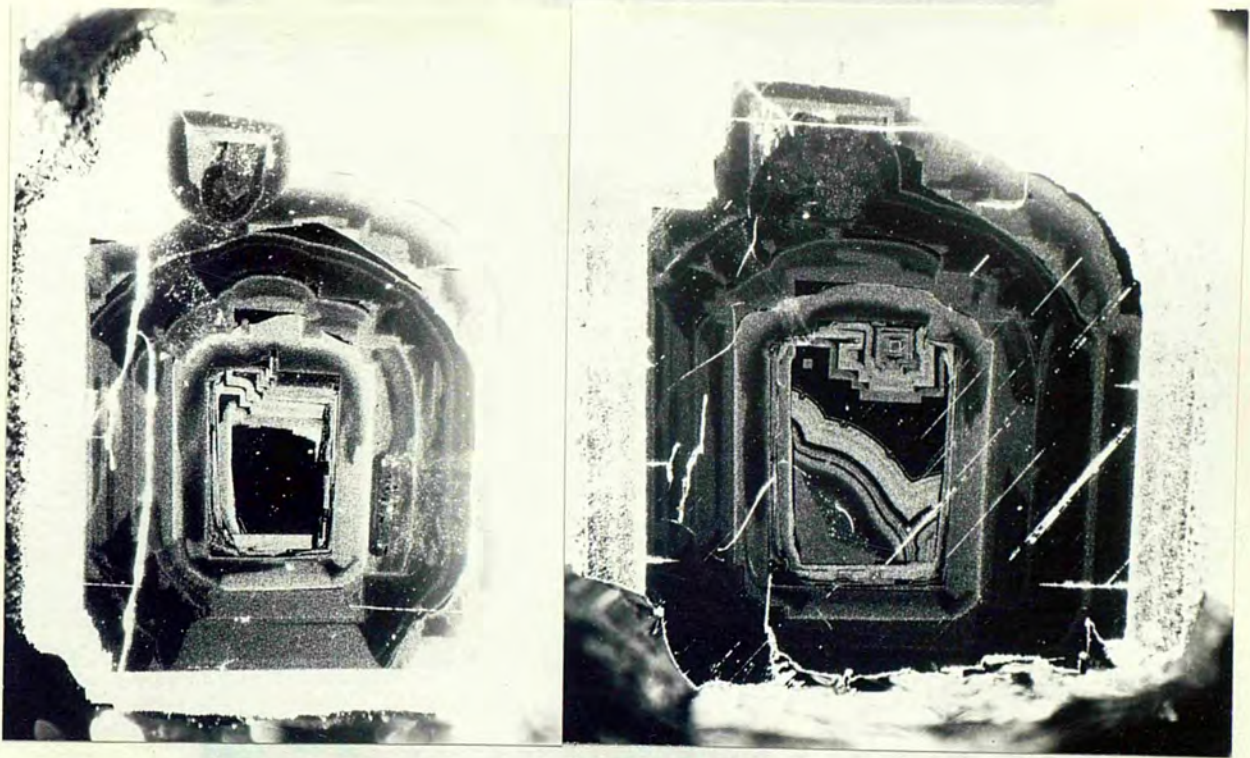
Figure 7.29. Diagram of diamond B showing sections studied.



Figures 7.30 - 7.32. B, sections A, B and C. (x 20).



Figures 7.33, 7.34. B, sections D and E. (x 20).



Figures 7.35,7.36. B, sections F,G. (x 20).

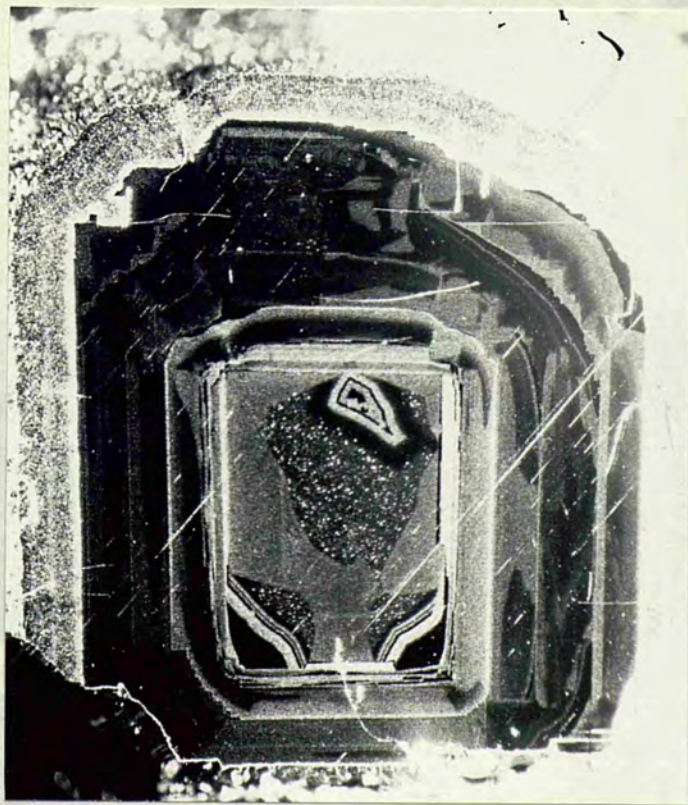


Figure 7.37. B, section H. (x 20).

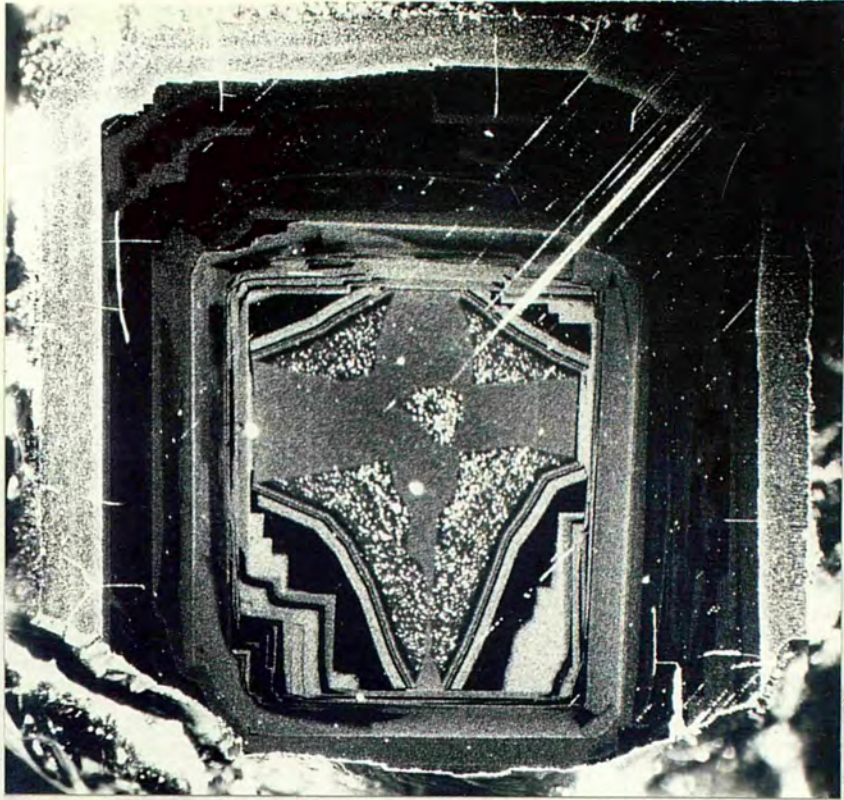


Figure 7.38. B, section J. (x 20).

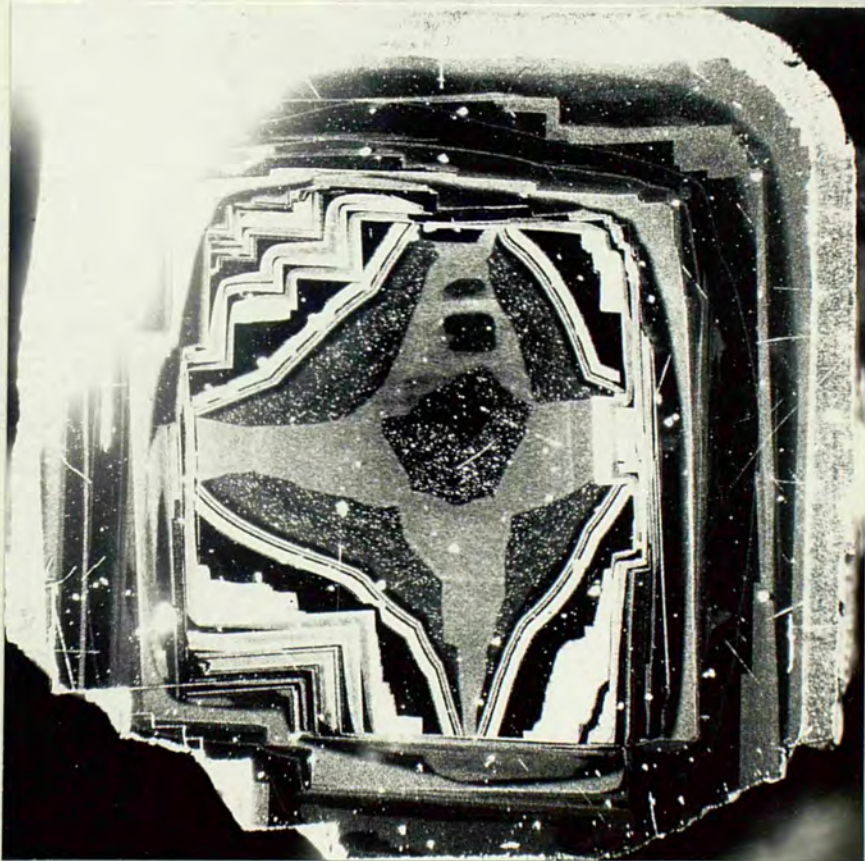


Figure 7.39. B, section 2. (x 20).

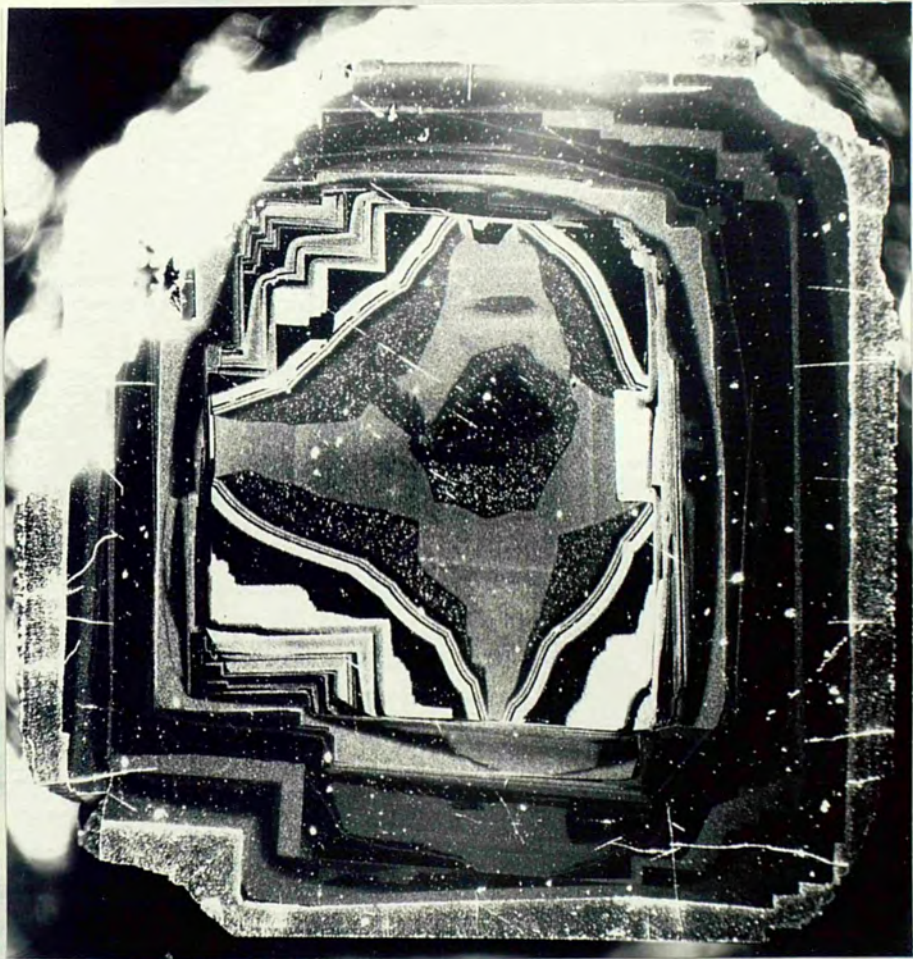


Figure 7.40. B, section 1. (x 20).

Figure 7.41. B, Section 2. x 35.

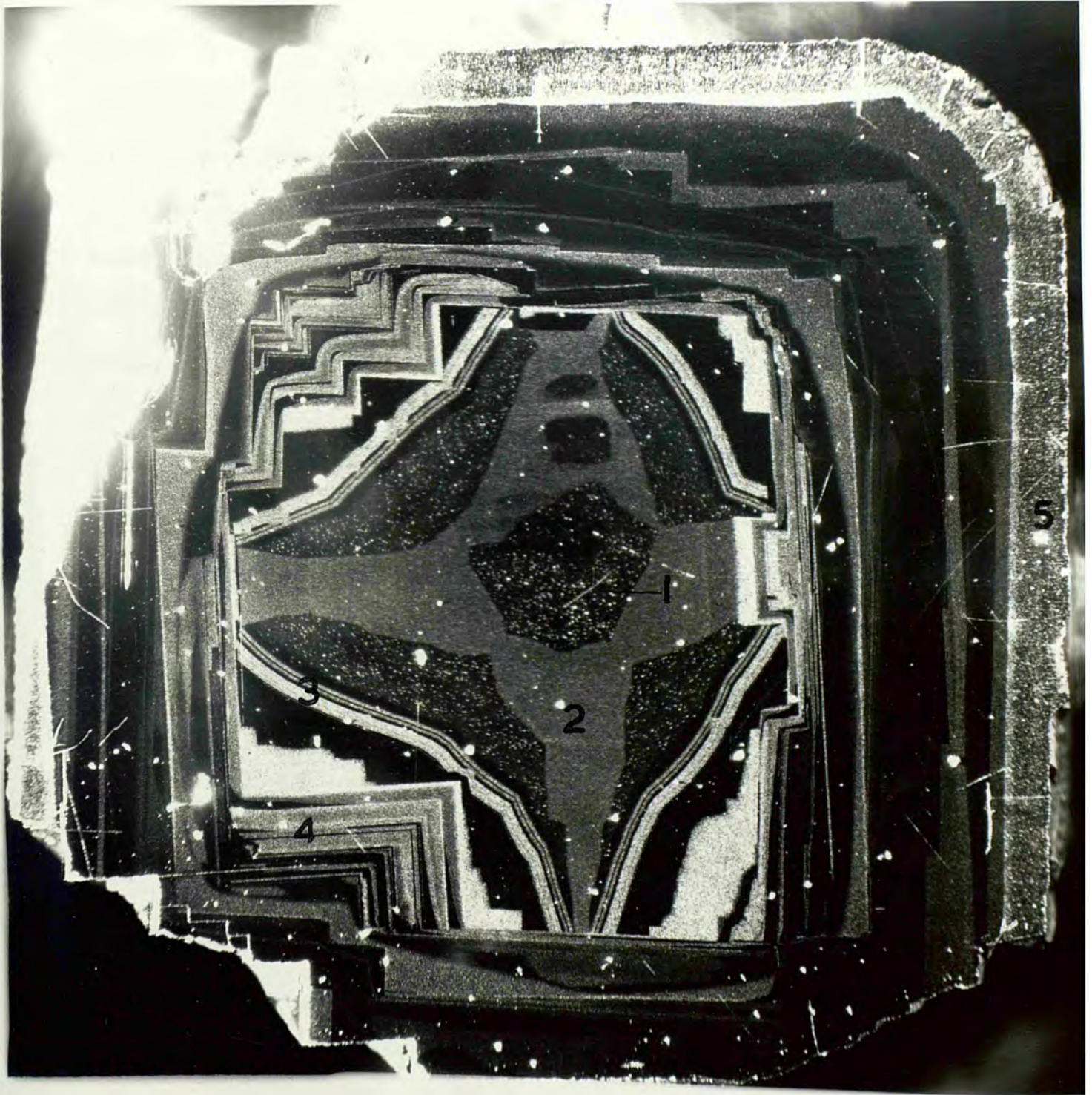


Figure 7.41. B, Section 2. x 35.

containing a greater concentration of etch pits. There are some light striations, one on each arm, running parallel to the edges of the crystal. That these occur "in depth" can be seen by reference to figures 7.37 to 7.40 inclusive. This region is bounded by a striking complex 3, which shows in the picture as several parallel bands, one broad and two narrow ones separated by dark bands and with dark ones on either side. High resolution photomicrographs shown below (figures 7.45 to 7.47) reveal a wealth of fine structure in this region. A remarkable feature of these bands is the way in which they maintain their uniformity of width despite their strongly undulating character, being at some points concave and at others convex. The pattern gives the impression that the diamond has been crumpled, undergoing plastic deformation. These bands are visible in sections H, J, 1 and 2 (figures 7.37 to 7.40) and what may be a new one has appeared in section G, figure 7.36. The "crumpling" is obviously three-dimensional. It would appear that the crystal has taken on a habit with faces which are far from flat and of perhaps cubic and dodecahedral character. It may be that the crystal has grown with plane faces and has been subjected to a crumpling force, the inner structure being due to subsequent anneal. The rectilinear lines in the cross mentioned above, however, are

difficult to explain unless the whole structure is considered as due to growth.

There appears to have been a lay down of relatively defect-free material around the banded region, 3 (figure 7.41), followed by rectangular banded areas, 4, in each corner. In the top *left* hand these bands have acquired a peculiar undulating effect. It is commonly observed that in diamonds of octahedral habit with well formed flat faces the edges are irregular and this is so far this diamond. The way in which they have developed is revealed in the photograph and will be discussed further below.

The diamond has then tended to acquire a square outline shape in section, and growth appears to have been by a mechanism similar to that by which diamonds A1, A2 and possibly A3 also have grown. But even in the outer regions diamond B has some bandings which are not rectilinear. These occur largely in the dark etch-free areas which would appear to be etch resisting, and are strongly suggestive of growth having been arrested and dissolution having taken place. Subsequent regrowth has tended to restore the octahedral habit.

The outermost layer, 5, of the diamond is coarsely etched, the character being different from the etch

anywhere else on the section. This is the coloured coating. Referring to the series of figures 7.30 to 7.40 it is apparent that this layer tends to be much thicker as the tip T is approached. It is commonly observed (e.g. Sutton, 1928) that coated diamonds tend to assume the cubic habit.

7.8. Examination of the Slab from Diamond B1.

The thin slab of diamond B1 remaining after sectioning was examined for ultra-violet absorption. As discussed in section 7.2 this diamond was found to have variable absorption of ultra-violet in the region about 3000\AA . Using the ultra-violet microscope shown diagrammatically in figure 7.7, the slab illuminated with light of wavelength about 2966\AA , was photographed in transmission. The resultant ultra-violet absorption micrograph is shown in figure 7.42 (x 20). Before taking the micrograph the diamond was lightly polished on both sectioned faces to remove the previously studied etch patterns. This pattern bears a striking resemblance to the etch patterns from the two sectioned faces J and 2 shown in figures 7.38 and 7.39, especially when it is remembered that the absorption micrograph is the result of an integrated effect over some $3/4$ mm, even some of the fine detail in the corners and in the

outer layers being resolved. There is an extremely close correlation with the shape of the core within the curved banded area, 3, of figure 7.41.

In interpreting this figure it should be remembered that this is a print of a transmission picture and the dark areas in fact represent the absorbing regions of the crystal and the clear ones the transmitting regions. The central area is clearly type 1 diamond absorbing ultra-violet of the wavelength used. The surrounding bright area transmitting ultra-violet is clearly type 11, while the outer layers alternate. The outer coating appears quite opaque but the effect in the microscope could be caused equally by light being reflected from the rough outer natural surface of the diamond and by this outer coating being type 1 material, as diamond coat is accepted to be. In the picture it can be seen that there is even a difference in the absorption of the central cross and the surrounding region.

The slab was now examined between crossed polars, the resulting micrograph being shown in figure 7.43 (x 20). Correspondence with the etch figures and with the ultra-violet micrograph is very striking. Considerable strain is shown to be present in the slab.



Figure 7.42. B, Slab, $00\bar{1}$ (x 20).

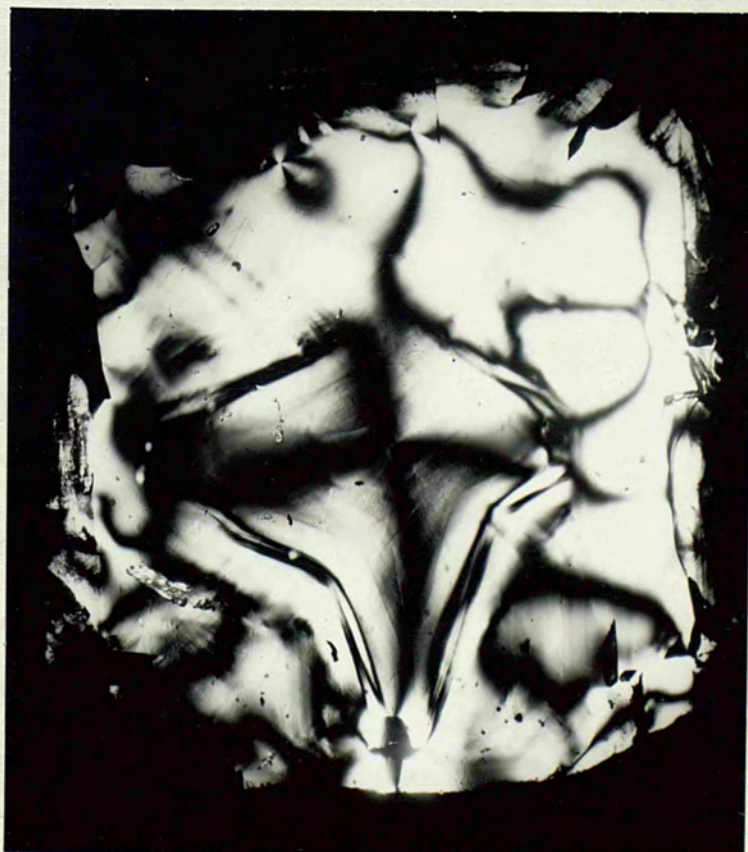


Figure 7.43. B, Slab $00\bar{1}$ (x 20).

The central core shows the crude crossed rectangular hyperbola indicating strain in this region, and moreover the shape of this area conforms with that to be seen in the etch and ultra-violet micrographs. More notable, however, are the interference fringes in the region surrounding the inner core, as many as three being close packed here. This suggests that a large strain exists at this junction of predominantly type 1 and type 11 materials, and is possibly due to a difference in elastic properties between the two types, the diamond now being at a vastly different temperature and pressure from when it was formed.

The areas in the outer regions of the crystal and particularly in the corners show stress patterns and these more strikingly match the etch figures when the polars are crossed at different angles. For example figure 7.44 (x 20) shows a micrograph with the polars crossed to best show up the regions in the bottom left corner.

7.9. Fine Structure in the Etch Pattern on Sections of Diamond B.

Although there is a wealth of information in the micrographs, e.g. figure 7.40, at magnification x 20, high resolution micrographs reveal much more detail. Parts of the inner core border as at 3 in figure 7.41

are shown in figures 7.45 and 7.46 (x 250) of adjacent regions of section 1, figure 7.40. The bands are shown to be made up in fact of a large number of finer bands, etch pits occurring in rows. Here the broad band consists of over fifty lines while in each of the narrow ones there are over a dozen. In some places the lines of etch pits are more widely spaced than in others and especially in these regions it would appear that there has been alternate laying down of type 1 and type 11 material.

The abrupt oblique cut-offs as at positions marked A in figures 7.45 and 7.46 cannot readily be explained unless it is assumed that dissolution has taken place forming what are in effect large etch pits. Subsequent laying down of growth sheets has tended to fill in these depressions. In the regions marked B the rate of growth has been faster within the pits, the spacing of the layers being greater there, so that finally by the time the black areas have been reached the kinks in the lines of micro etch pits have become much less pronounced.

It is not unlikely that similar effects have taken place in the dark unetched regions of type 11 material but here there are no etch pits to show up the growth layers. But evidence that dissolution and

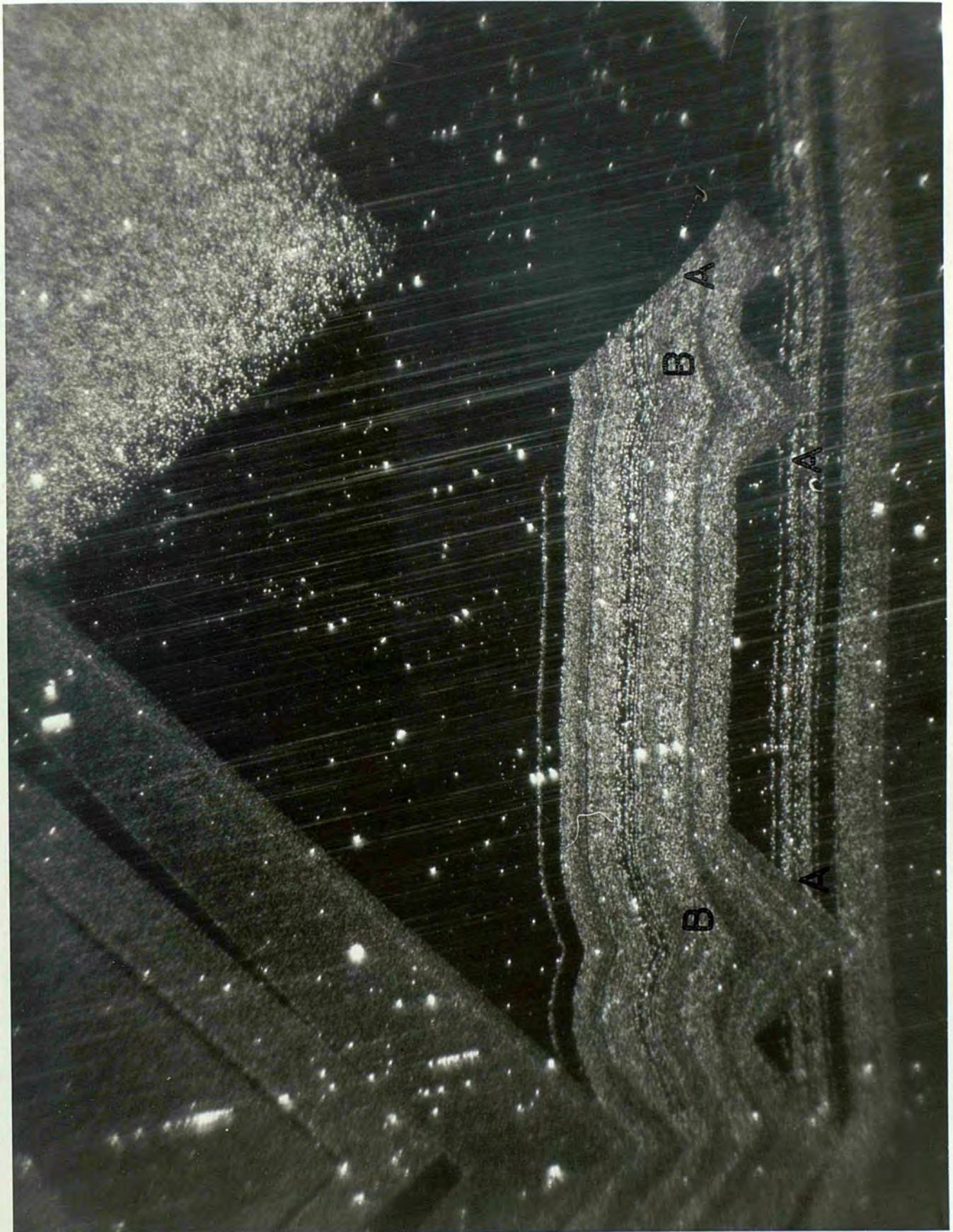


Figure 7.45. B, Section I. x 400.



Figure 7.46. B, Section I. x 400.

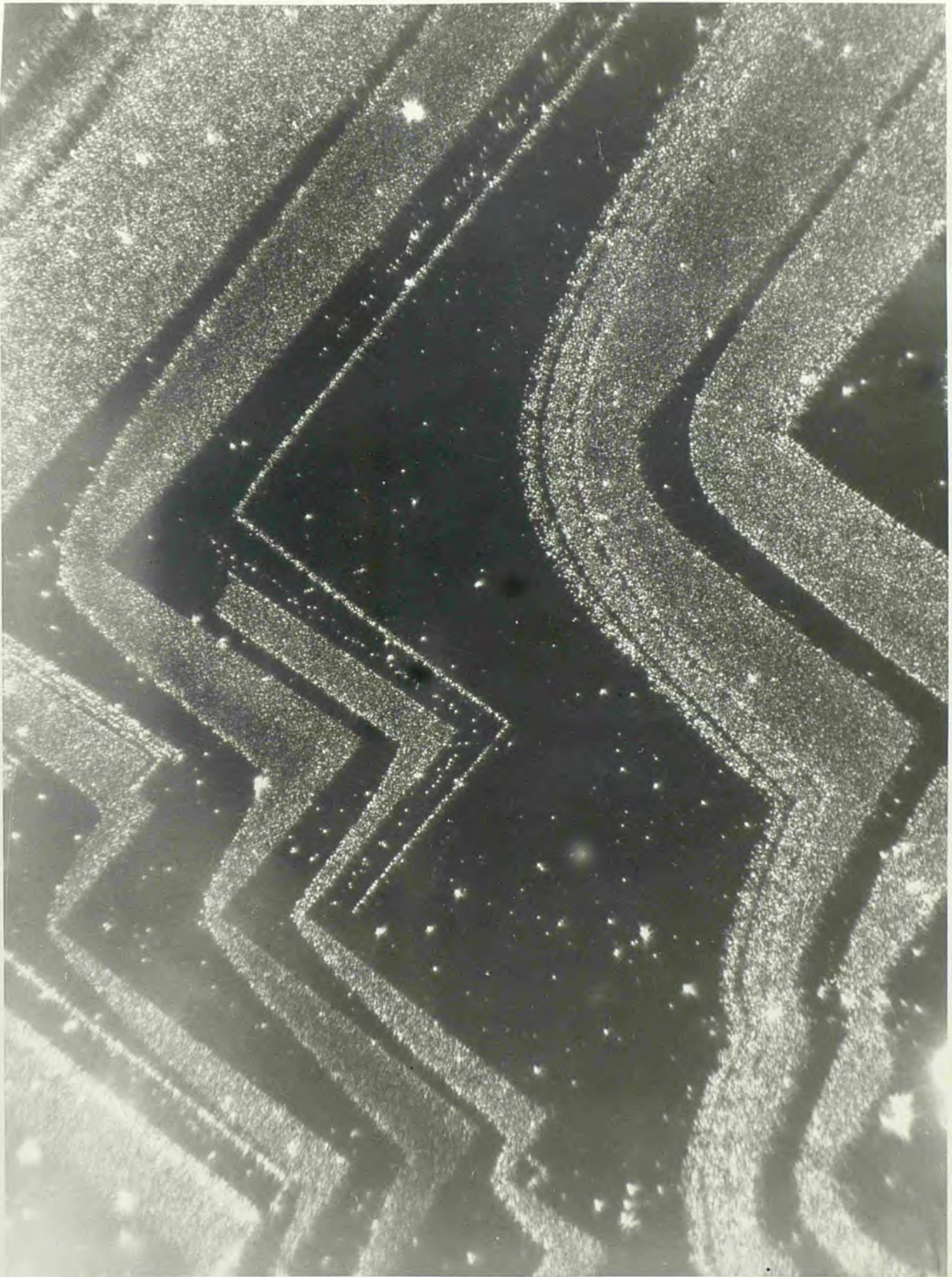


Figure 7.47. B, Section I, x400.

re-growth do occur in such regions is to be found, as mentioned above, in the outer regions of figure 7.41 for example where non rectilinear banding occurs in these type 11 regions.

Figure 7.47 (x 250) shows a high resolution photomicrograph of part of the top left corner of section 1 (figure 7.40). This complex pattern is strongly suggestive of dissolution having taken place and rounding originally sharp corners. Re-growth appears to have been by uniform lay-down of material over the surface. Where this has taken place with type 11 material, which is more resistant to dissolution than type 1 because of the lower density of defect sites at which etch would be initiated, the corners tend to be rebuilt. More sharp corners thus tend to be present in the outer (growing) surface of those regions which are of type 11 material.

It will be observed that the size of the etch pits seems to vary from region to region. One would expect that once etch was nucleated at the site of a lattice defect that the size of the etch pit would depend only on the etching time. By reference to figure 7.41 the etch pits in the small central inner core, 1, though not densely packed, nevertheless appear larger than in the surrounding cross-like feature 2, where

the density of etch pits is greater. The size of the etch pits in the region of the outer coating of the diamond is certainly greater than those in the area they surround. Etch pits of different size can be seen in the high resolution picture of figure 7.48 (x 250). To the left of the region at A, where the etch pits are very small, there is a region where the etch pits are relatively large. It is conjectured that the commencement of etch at a defect site may depend on the type of defect, but once etch has commenced the rate may be constant as expected provided etch is taking place on facets of the same index. We have seen in Chapter 6 how etch pits of different orientation do occur on the one face even under the same conditions of etch. Another explanation for the difference in size of the etch pits may thus be that etch is occurring on different types of crystallographic facets at different rates.

If it is assumed that etching commences to attack the surface at the defect sites, an estimate of the density of defects in the material can be made by counting the number of etch pits. We made such estimates from magnified prints such as the one shown in figure 7.49 (x 1200) and for this particular diamond we conclude that in the type 1 regions, which were heavily

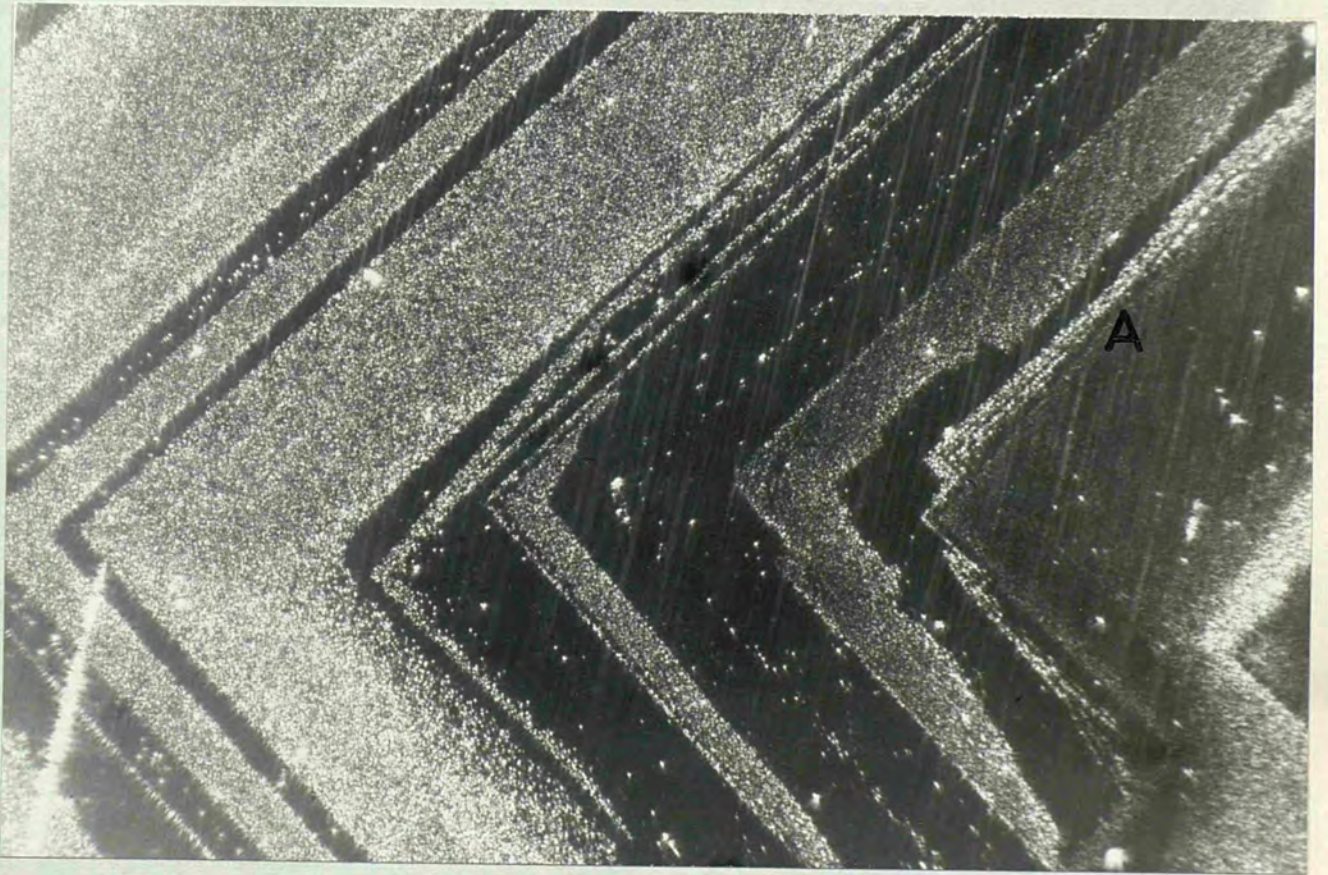


Figure 7.48. B, Section 1. (x 300).

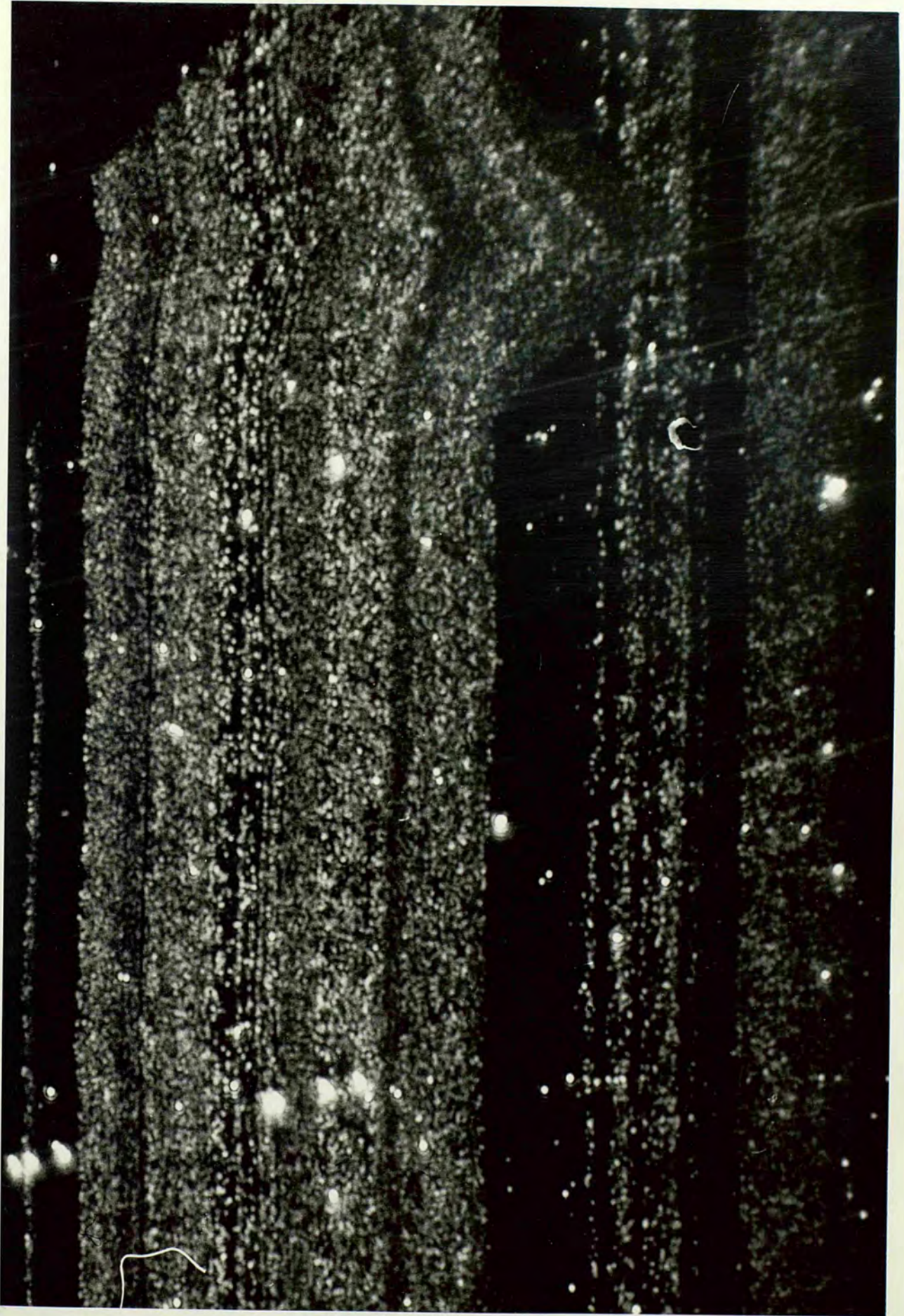


Figure 7.49. B, Section I x 1000.

etched, the density is greater than 5×10^5 per mm^2 on the surface, whereas in the type 11 regions, which were only lightly etched, the density is often less than 1.6×10^3 per mm^2 on the surface.

If it is assumed that the defects are point defects, and this is not an unreasonable assumption as there are no etch pits of large linear dimensions on the surface as compared with the size of an etch pit, the number of defects per cubic mm may be estimated. For type I material it is in excess of 4×10^8 per mm^3 and for type II material may be less than 6×10^4 per mm^3 .

CHAPTER 8.

SURFACE STUDIES ON SYNTHETIC DIAMONDS.

8.1. Introduction.

While cubic surfaces on natural diamonds are rare and are never well formed and flat, the proportion of cubic faces on synthetics is quite large. Of these many are quite flat and of good quality. A selection of synthetic diamonds from a sample of good quality large crystals made by de Beers about 1962 is shown in figure 8.1 (x 100). The diamonds have good faces of both cubic and octahedral character and may be considered as truncated octahedra or as cubes truncated at the corners by octahedral faces. On some crystals there are small but definite dodecahedral faces.

The actual temperatures and pressures at which synthetics were first formed is stated by Tolansky (1962a) to be around 3000°C and 100 000 atmospheres and it is understood that in present day practice temperatures and pressures a little below this are used. The diamonds formed in more recent production are certainly larger and of better crystal habit than the earlier ones, but this is probably due to better control of conditions. The time for which the conditions were maintained for the

original production is stated by Tolansky to be some hours. The announcement in the scientific press by Bundy et al (1955) of General Electric Corporation of the first successful production of synthetics simply stated that a pressure vessel, which was capable of maintaining pressures of at least $100\ 000\ \text{kg/cm}^2$ for hours of continuous operation, was available. They published a phase diagram for diamond (see figure 8.2) of which they claimed that only the boundary between graphite and its vapour at low pressures was accurately established experimentally.

Surface studies by Tolansky (1961,1962b) on some thousands of synthetic cubic diamonds made by G.E.C. and de Beers show on cubic faces growth hillocks, oriented dendritic-like overgrowths, and in a few cases spirals. These two latter features have not been observed on natural faces. On octahedral faces of these synthetics, trigons were rarely found. However on both cubic and octahedral faces, particularly on some batches of crystals, extensive etch figures were observed.

The study of surfaces of synthetic diamonds is restricted by the extreme difficulty of handling them because of their small size. Occasionally a synthetic with a linear dimension as large as 1mm is found but

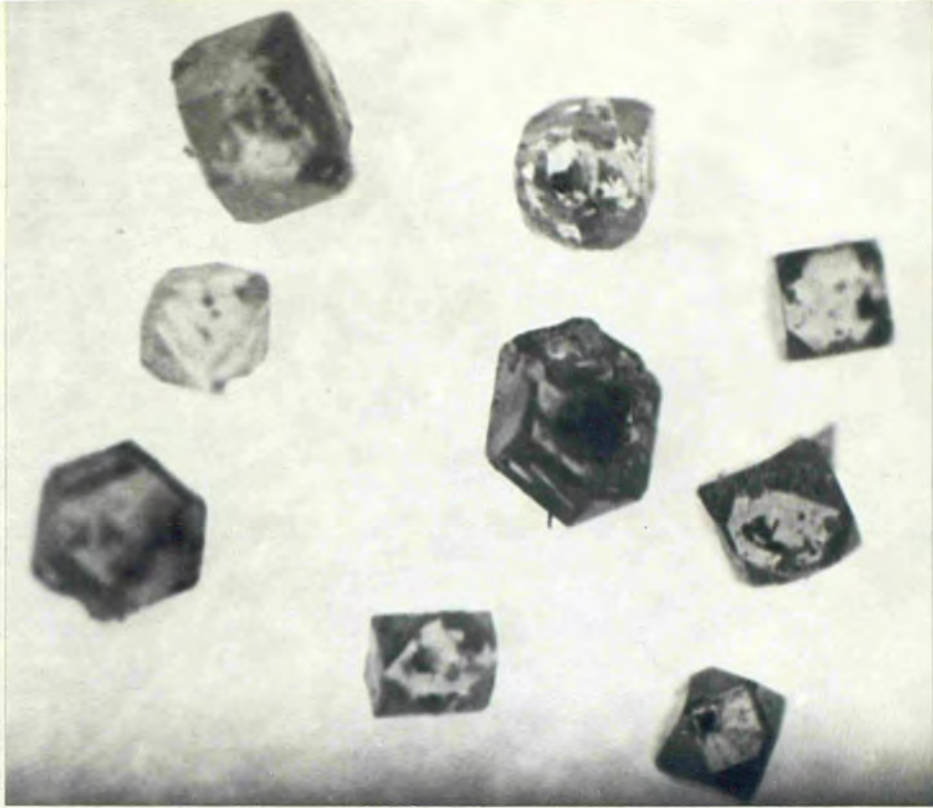


Figure 8.1. Synthetic Diamonds. (x 100).

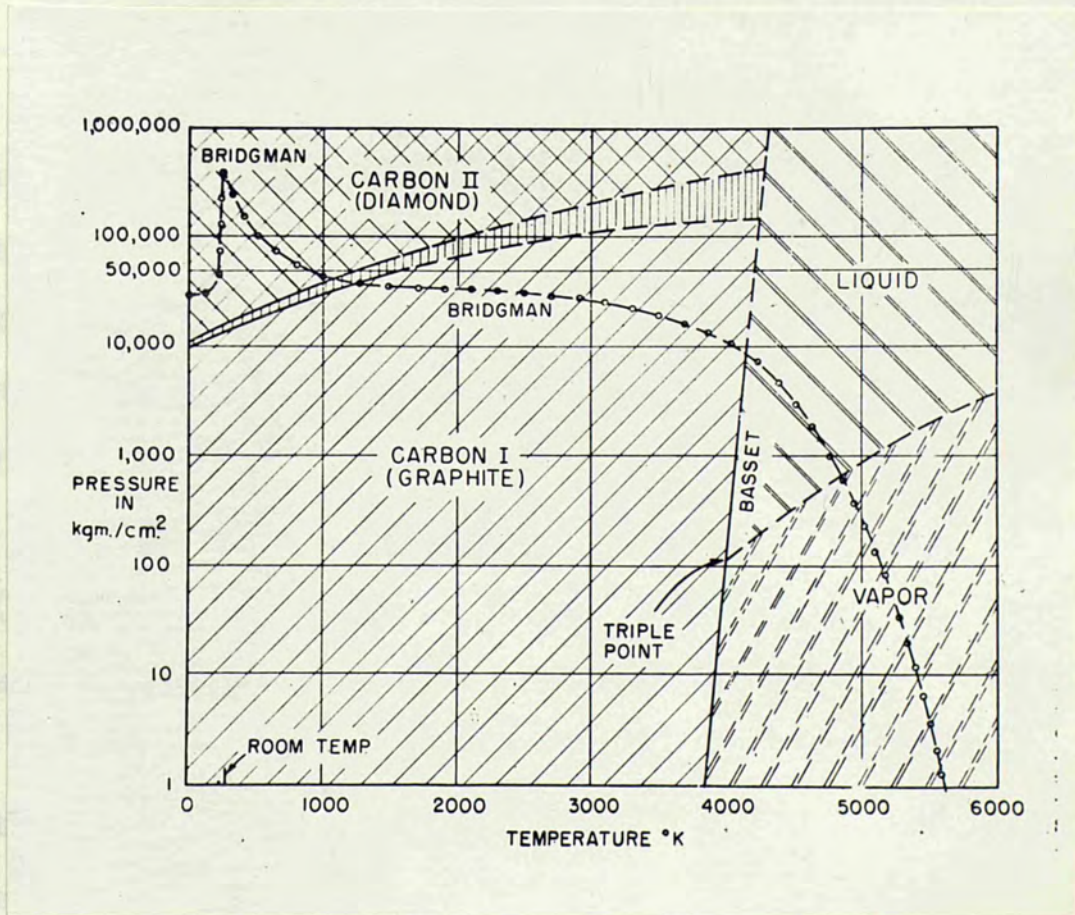


Figure 8.2. Phase diagram of carbon
(After Bundy et al, 1955).

this is very rare. Those described here had linear dimensions of the order of 0.1-0.2 mm and may be considered large for synthetics. Tolansky (1962b) has developed a simple system for quick examination of a number of surfaces using two-beam interferometry. The powder is spread out on a glass flat and by judicious tapping many of the faces can be made to contact it sufficiently closely and parallel so that when illuminated from below with monochromatic light two-beam fringes are formed. These may be viewed with a microscope.

8.2. Character of Synthetic Cubic Faces.

A typical good quality cubic face is shown in figure 8.3 (x 1000). This particular face is made up in fact of a number of facets, each making angles with the reference flat of 1 or 2 degrees. The junctions of these facets are quite well defined. The facets are not flat but have radii of curvature of the order of 2 mm.

Two photomicrographs are shown in figures 8.4 and 8.5 (x 500) of cubic (010) surfaces on which are a number of rectangular depressions presumed to be etch pits formed at some stage following the growth process. The two-beam fringes on the surfaces indicate that the faces are each made up of a single surface which is



Figure 8.3. Synthetic, 010 face. (x 1000).

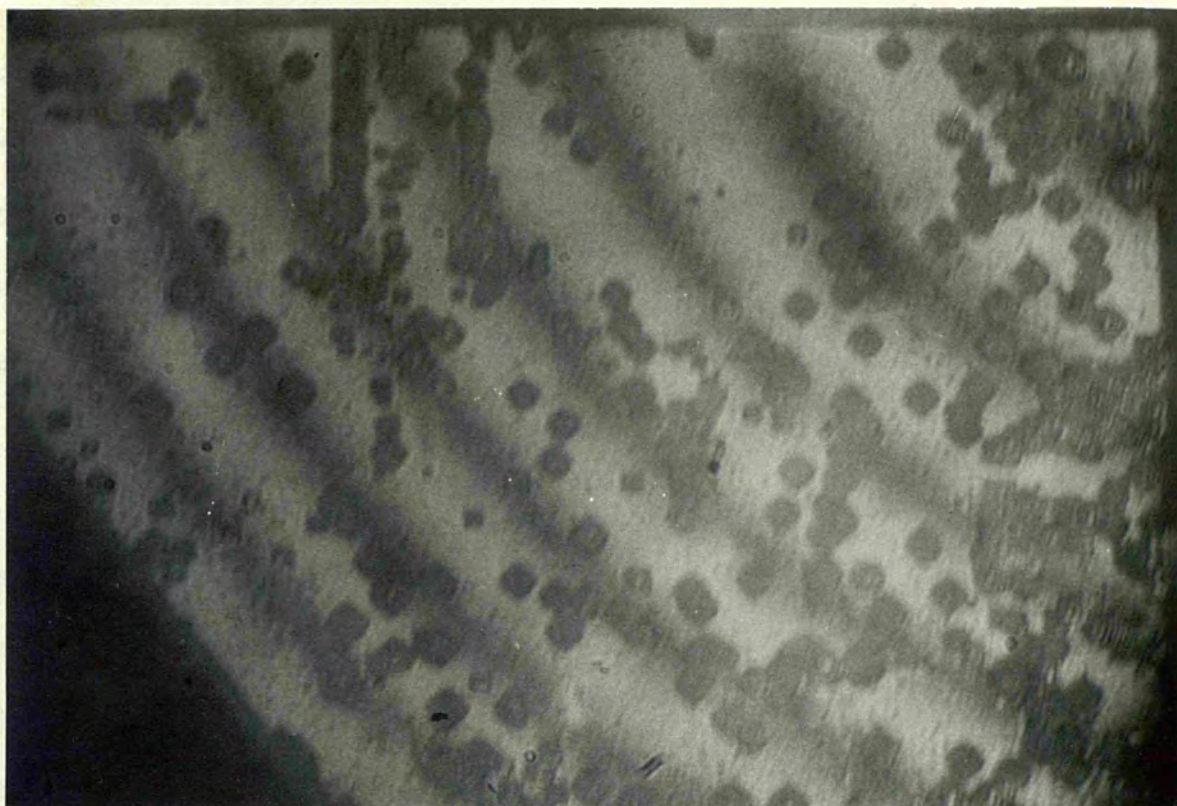


Figure 8.4. Synthetic, 010 face. (x 500).

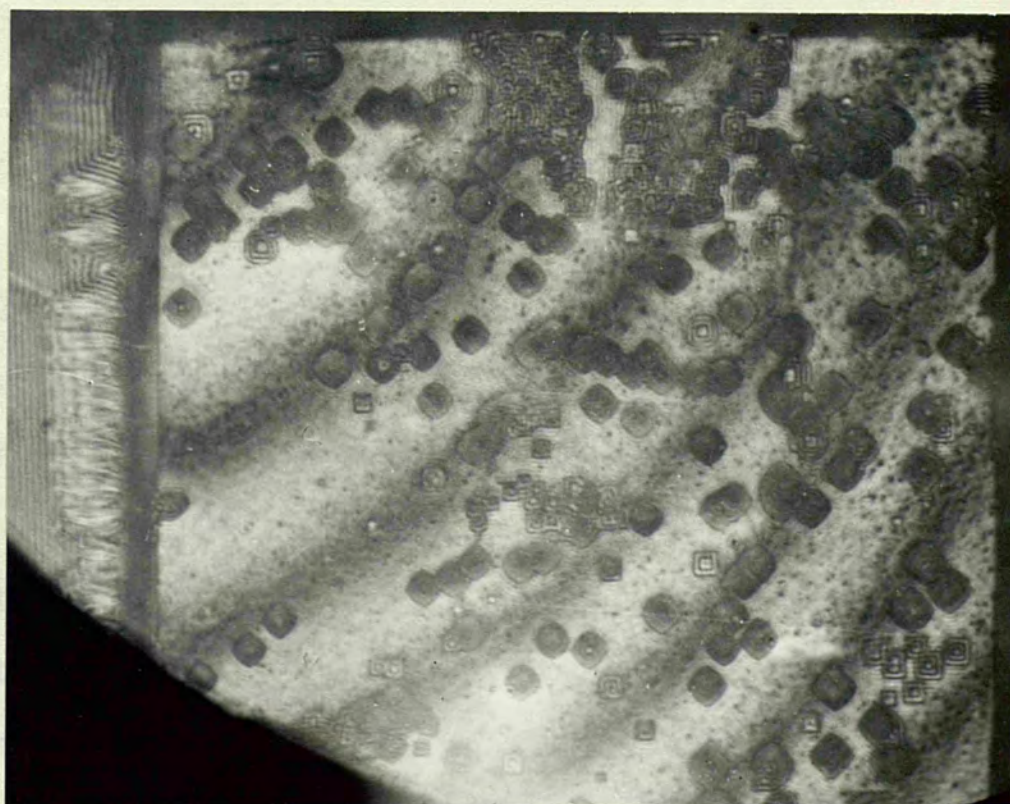


Figure 8.5. Synthetic, 010 face. (x 500).

curved, the radius of curvature being of the order of of 25mm. For the most part the pits are isolated but in figure 8.4 there are two lines of pits which have merged, and several other groups forming a line are to be seen.

The orientation of the pits is interesting. For the most part they are oriented so that one pair of edges is parallel to the $[100]$ direction, i.e. parallel to the cube direction. With these truncated crystals the edges shown in the picture may be the intersection with cubic or dodecahedral faces but no ambiguity arises if the crystals are illuminated with light from above, when their true orientation can be readily determined. As well as pits orientated with their edges parallel to the $[1 0 0]$ direction on each surface there are pits oriented with one pair of edges parallel to the $[1 0 1]$ direction. In figure 8.5 interference fringes can be seen in many cases running round the walls of the pits indicating sloping walls whereas the majority of the pits in the other orientation appear to be flat bottomed. Thus we have etch pits of the two orientations side by side on the one surface, the general character of those of each orientation being different.

8.3. Etching of Synthetic Cubic Faces in the Laboratory.

Two cubes were etched in fused potassium nitrate for six hours at 570°C . One surface is shown after etching in figure 8.6 (x 500), viewed by "prism illumination". A large part of this face was flat to within one fringe and on this part of the face there is very little evidence of etch as compared with the surfaces of natural crystals. In one corner (lower right) however the surface can be seen to be faceted. This corner is in fact low with respect to the rest of the face and the picture shows that the etching has taken place on the facets only, especially at the junction with the main flat part of the face. The photomicrograph in figure 8.7 (x 500) shows the same face viewed with dark field illumination and it can be seen that etching has taken place at what appears to be the edge of layers. The etch pits here and on the surface elsewhere are too small for the shape to be properly resolved.

Figure 8.8 (x 500) shows another face viewed with controlled oblique illumination. Etch pits are again small and occur in bands. Etching tends to be more severe once more at the edges of layers.

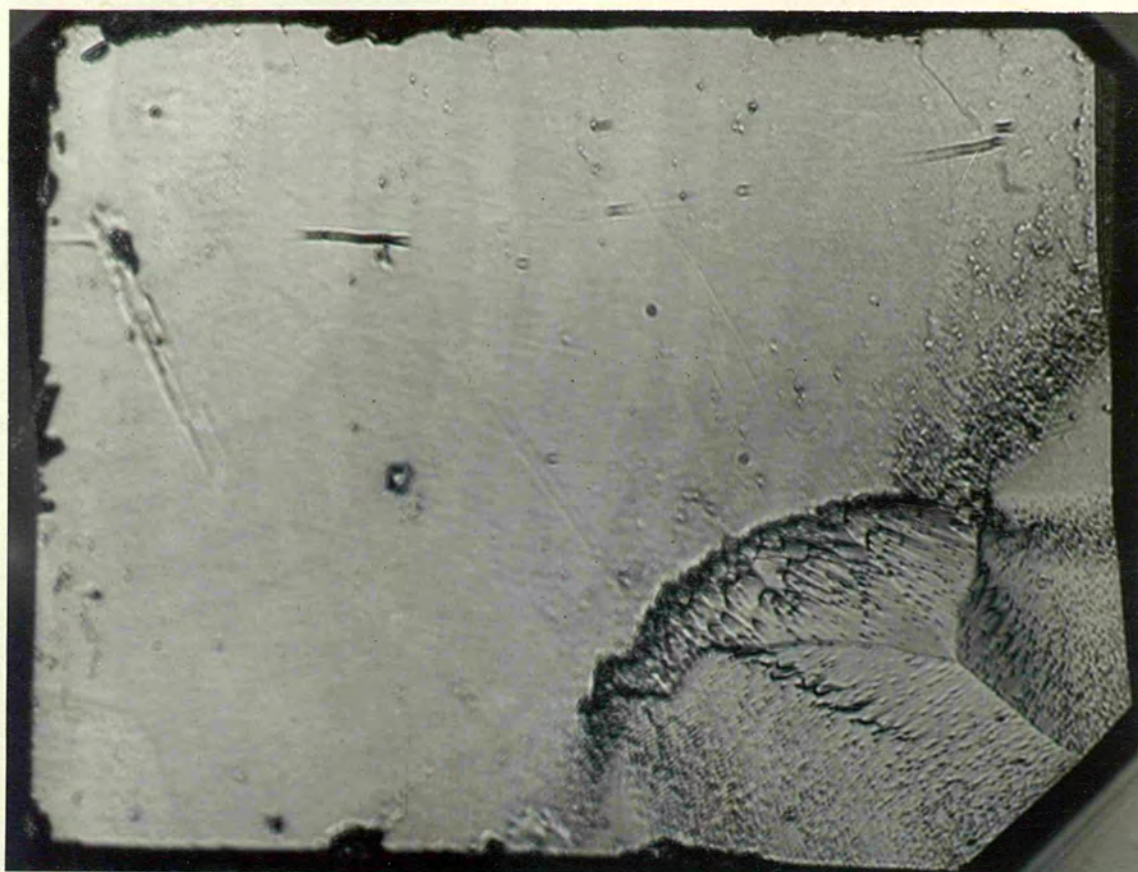


Figure 8.6. Synthetic, 010 face. (x 500).

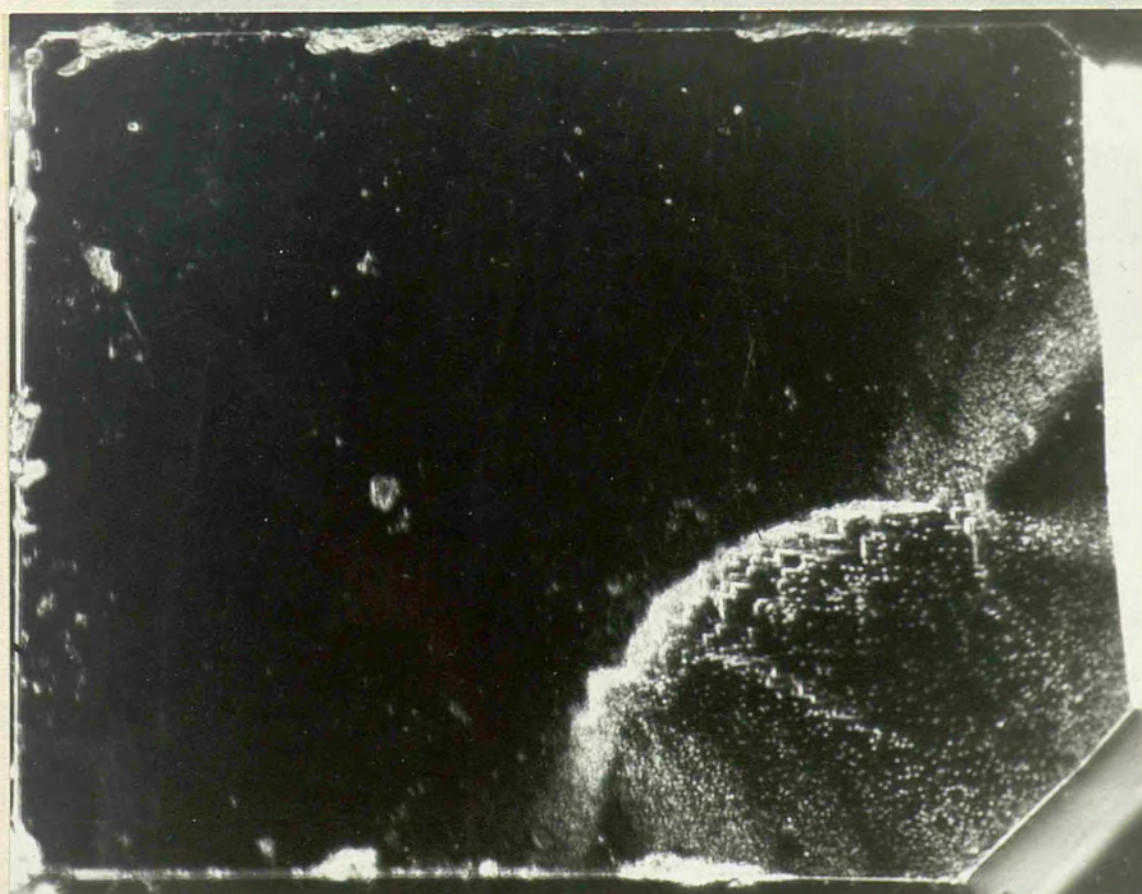


Figure 8.7. Synthetic, 010 face. (x 500).



Figure 8.8. Synthetic, 010 face. (x 500).

8.4. Discussion.

These observations on synthetic diamonds have been very cursory. The following facts however emerge:

1. Several cubic surfaces of synthetics were observed which were made up of a number of curved facets inclined to one another at angles of the order of several degrees, the radius of curvature being in one instance as small as 2mm.

2. Pits in both "growth" and "etch" orientation have been observed side by side on cubic faces of synthetics as received from the manufacturers. In the etching experiments carried out on the cubic faces of natural diamonds and described in chapter 6, pits in both orientations were observed on the same surface as a result of etch in the laboratory. It is believed that all the pits observed on the cubic surfaces of synthetics are due to etch.

3. Etching which occurred on the two cubic surfaces examined after etching in the laboratory was much less severe than on polished cubic surfaces of natural diamonds.

There has been some speculation in the literature about the origin of trigonal twinning which are growth by

CHAPTER 9.DISCUSSION OF RESULTS.9.1. Surface Topography of Cubic Diamonds.

The batch of 50 cubic diamonds examined originated in alluvial deposits in the Congo. When it is remembered that there is a large variation in the surface topography, colour and so on of octahedra and dodecahedra originating in different localities then any conclusions drawn here can only apply to those cubic diamonds of which those examined were a sample.

As the description in chapter 5 shows the faces of these crystals were all markedly faceted. On the cubic surfaces there are a multitude of tetragons, which are highly complex features made up of near-cubic facets and "octahedral-like" facets (i.e. ones having indices like $h\ 1\ 1$): there are many small facets of cubic or near-cubic orientation: and there are an appreciable number of "dodecahedral-like" facets (i.e. ones having indices like $h\ 1\ 0$). The dodecahedral faces are made up of octahedral-like facets. Octahedral faces evidently occur only rarely but on the one properly formed face studied a large number of trigons were present.

There has been much speculation in the literature about the origin of trigons: whether they are growth or

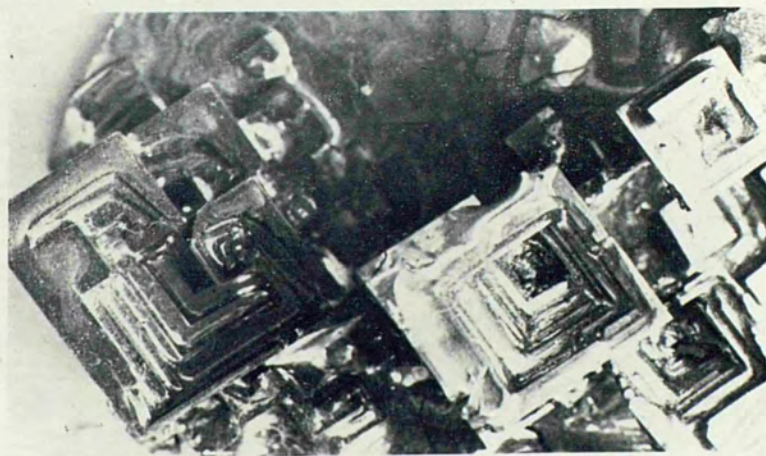
dissolution features. It appears not unlikely to us that whatever the origin of trigons, tetragons are likely to have formed in a similar way.

As in the case of trigons where one side (or perhaps two) projects beyond the trigon and is associated with an abrupt change in level of the surface, so in the case of tetragons a "tail" usually extends from one side and is also associated with a change in level of the surface. If the surface topography is due to a type of faceted growth then presumably the trigons on the octahedral faces may well also be a type of faceted growth.

There is some similarity in appearance between faceted features on some bismuth crystals grown from the melt by Hurle (1962) and shown in figure 9.1. Both the simple (a) and terraced (b) facets are $(1\ 0\ 0)$ type planes bounded by $\{1\ 0\ 0\}$ type edges. We do not know whether features made up of the terraced facets are depressions or hillocks. It is interesting to speculate if these cubic diamonds could in fact be melt-grown crystals. Faceted growth does not of course occur only in melt-grown crystals but also in solution-grown ones, e.g. (figure 9.2 (x 10) shows a faceted face of NaCl.



(a)



(b)

Figure 9.1. Facets on Bismuth crystals grown from the melt.

(a) Simple (b) Terraced. (Hurle, 1962).

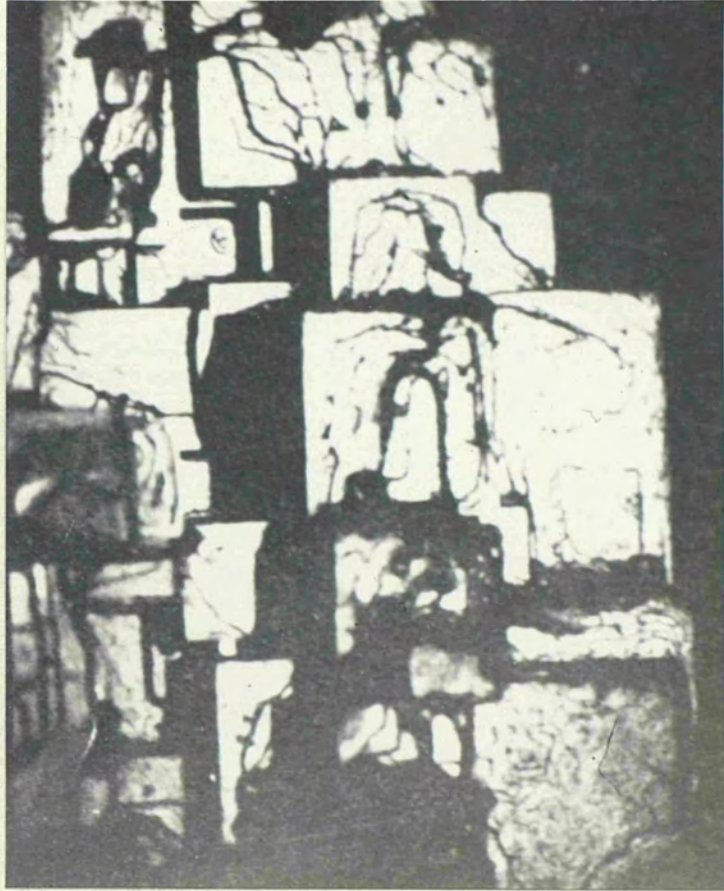


Figure 9.2. Faceted cube face of NaCl, (x 10).
(Buckley, 1951).

Raman is said to believe that Indian diamonds have grown from the melt from globules of molten carbon, (see section 9.6 below).

The other possibility is that the topography is due to dissolution or etch. However, as in the case of faces of octahedral and dodecahedral habits, the features are differently orientated from the majority of the similar ones formed by etch in the laboratory. Careful etch experiments at different temperatures and pressures are required to be carried out to determine if etch pits in tetragon orientation are possible. From the etch figures on cubic faces of octahedra described in section 7.7 there can be little doubt that dissolution, alternating with periods of growth, occurred in the history of diamond B.

If the topographical features on the surface are the result of a dissolution process we would expect that they originated at lattice defect sites and that further etch would continue at these same sites and no new etch pits would form. In fact new ones do appear. We have suggested that these are due to strain induced defects formed in the crystal subsequent to growth. Therefore the surface features are growth

phenomena or, if they are due to dissolution or etch, then they occurred in the original growth environment before the defects revealed by etch in the laboratory had been produced. This will be discussed further below in section 9.5.

It is frequently stated in the literature that coated diamonds tend to assume the cubic habit. Confirmatory evidence of this was shown in the studies on diamond B in which the coat can be seen in the sections (figures 7.30 to 7.40) to be thicker as the tip T (figure 7.29) of the diamond is approached.

9.2. Etch Figures on Polished Cube Faces.

When a crystal surface is etched preferential etching takes place at any cracks or scratches which might be present, but rather surprisingly there does not appear to be any etching along the polishing marks. For example in figure 7.46 which shows part of a polished cubic face at x250 magnification, the polishing marks are not visible although a scratch on the surface is shown to have etched up. (Controlled oblique illumination was used for this picture and the next one to be considered). In figure 7.45, which shows an adjacent part of the same surface the polish marks can be seen but if there are any etch pits present they are

very small indeed compared with the other etch pits. The difference in the ease of etching of scratches and polish marks indicates that there is a definite difference in the degree, and possibly the type, of damage to the crystal lattice in the two processes.

In section 6.2 above we showed that etch pits on a polished cube face were present in two orientations. The majority were four sided pyramidal depressions with their sides oriented at 45° to the cube edges but there are some shallow flat-bottomed pits in the tetragon orientation. Those along scratches were of this type but there were others too, both isolated and in linear arrays. The flat-bottomed pits showed up at a slightly later stage of etching. Etch pits of both types were also observed on two cubic surfaces of synthetic diamonds (figures 8.4 and 8.5). It seems likely that these two different types of pit originate from different types of lattice defect.

Shah (1962) observed triangular pits on pairs of etched cleavage faces of fluorite. There were two types of pit: pyramidal, and there was correspondance between pits of this type on both cleavage surfaces, and occasional flat-bottomed ones which appeared on one cleavage face and not on the other. He also induced

slip lines on a cleavage surface with a Vickers pyramidal indenter. These etched up with dense arrays of pyramidal pits. He concluded that the pyramidal ones arose from dislocations and the others at sites of local impurities.

The fact that we observed flat-bottomed pits on scratches suggests that the damage to the lattice caused by them is local and that etch proceeds along the edges of layers preferentially, the direction of attack being $[1\ 1\ 1]$, octahedral layers being removed. If indeed the pyramidal pits occur at dislocation sites then presumably the attack proceeds along the dislocation and lateral spread is by removal of dodecahedral layers. It is to be noted too that when natural tetragon vestiges were etched (see figures 6.18 to 6.20) etch took place at the corners giving octagonal pits. Presumably further etching would have completely changed the orientation. The question still remains as to the reason for the different lateral directions of attack for etch pits of the two types. The arrays of etch pits on the Congo cubes have been shown to be associated with strain and will be discussed further below in section 9.5. It is likely that lattice deformation has occurred subsequent to growth and that etch pits occur at sites of strain-induced dislocations.

The etch pits observed on cubic faces of octahedra were arranged in layer and block formations. These will now be discussed in section 9.3.

9.3. Layer Structure in Octahedral Diamond.

Etching of polished cubic faces of octahedral diamond reveals layer structure, the density of etch pits, and hence of lattice defects, varying from layer to layer. It is not known at this stage what defects are present but etch pits of different size (see figure 7.48) occur and it is suggested that they arise from different types of defect. The patterns themselves have been shown to be three dimensional. In some cases the layers are rectilinear and diamond A1 (figures 7.14 to 7.20) appears to have been built up by the deposition of successive octahedral shells one upon another. Diamond B (figures 7.30 to 7.40), on the other hand, appears to have a very complex structure and, although built up in layers, they are not crystallographic nor even rectilinear. The core border, shown at 3, figure 7.41, and parts of it at higher magnification in figures 7.45 and 7.46, is built up by parallel layers which are variously concave and convex. This has been considered fairly fully in section 7.7 but it is worth recapitulating here that the patterns in this

diamond strongly suggest that growth and dissolution have taken place alternately, the dissolution being very severe at times. The part played by dissolution in the formation of the striated or fluted edges which are found more often than not on octahedral diamonds, even those with good flat faces, is revealed by the etch patterns shown in figures 7.30 to 7.40.

An ultra-violet absorption picture of a slab from diamond B (figure 7.42) shows unmistakably that there is a correlation between the etch pit density and type of diamond. As a result it is certain that the octahedral diamonds studied (and probably most diamonds) are made up of layers of type 1 and type 11 material. A point which supports this is that 30% of a group of 175 small octahedral diamonds (1 to 3 mm edge) were reported by Grenville-Wells (1952) to be type 11. This is an abnormally high proportion and she suggested that this was possibly due to their small size and possibly the addition of further growth of type 1 material in larger diamonds would tend to render them opaque to ultra-violet and mask the presence of the type 11 material.

We have made an estimate of the number of lattice defects for some type 1 and type 11 regions of diamond B. For the type 1 regions there are in excess of 4×10^8 per mm^3

and for type 11 regions as low as 6×10^4 per mm^3 .

Champion (1953) has established that for a semi-conducting diamond to be a good counter it is required to have layers of good defect-free material $\sim 10\mu$ thick and separated by much thinner layers containing bunched defects. Fine layers do occur in the core border 3 (figure 7.41) but the separation is $\sim 1\mu$ and therefore they are probably too fine for this part of the diamond to be good counter material.

9.4. Diamond Cores.

At the centre of several of the diamonds studied, A1, A2 and B, (see figures 7.8, 7.9 and 7.12) there is a core which shows a different type of etch from that of the surrounding material. Studies of the slab from diamond B show the core to be unmistakably type 1 material and the remaining layers to be alternately type 1 and type 11 (see figure 7.42). Etch patterns suggest the core of A1 to be type 11 and the core of A2 to be made up of blocks of type 11. The number of crystals studied is too small to allow generalization but these observations raise the question : Is a core a feature of common occurrence in diamond? Several points tend to confirm that this is so.

1. Tolansky has told us verbally that sawers of diamond find that when a diamond is sawn into two

nearly equal parts (as is frequently done to yield two gem stones of reasonable size), the saw cut is usually not planar but one side of the cut is concave and the other convex. They attribute this to the property of the diamond rather than the conditions of sawing.

2. A central slice from a type 1 diamond of irregular habit, the cut faces being approximately cubic planes, was examined (Shah and Lang, 1963) by optical and X-ray techniques. It showed a central core when viewed between crossed polars and in an X-ray projection topograph (Lang, 1959). The region of the central core contained precipitates (of unidentified material) visible to the naked eye.

3. Grenville-Wells (1952), in connection with studies on the texture of diamond for counting α , and β -particles, observed that there was no correlation between type and the morphology of diamond. However in a batch of 175 octahedra of small size (1 to 3 mm) 30% were type 11. As suggested above the fact that this large percentage of type 11 crystals amongst small stones is not to be found amongst larger ones, indicates that layers of type 1 and type 11 material should be frequent in diamond. It suggests too that cores of type 11 material may be of frequent occurrence.

With regard to the core of A2 (see figure 7.27), there appears to be a number of small blocks of type 11 material suggestive of multiple seeding. It is known that small crystals will sometimes grow into parallel positions on a seed crystal especially at high supersaturations. For example, Sheftal (1956) reported an observation in which a number of small quartz crystals grew in parallel positions and a number of these grew into one crystal. He states that this was possible because originally they had a common orientation. It is tentatively suggested that some mechanism of this type might be responsible for the core structure of A2.

9.5. Internal Strain.

The arrays of etch pits obtained on sections from near the middle of the Congo cubes show very strong correlation with the strain patterns obtained between crossed polars. We have suggested in section 6.4 that the etch pits have originated from strain-induced dislocations. It is difficult to imagine how this strain might arise during growth but it could occur due to very sudden cooling. Sudden cooling might occur if the crystals were ejected in volcanic pipes from their growth medium at high temperatures and pressures deep within the earth to regions of vastly lower temperature (and pressure). Because of the low thermal expansion

and high thermal conductivity of diamond such a temperature change would have to be very great and occur very suddenly indeed. We conjecture that cooling of the outer layers might so cause them to contract that great stresses might cause strains beyond the elastic limit and give rise to lattice defects. This would also account for the cracks observed within the diamonds.

Strain of surely another origin was found in octahedral diamond B at the junction of type 1 and type 11 material at the core border 3 (figure 7.41) and the rest of the crystal (figure 7.43) and between alternating layers of type 1 and type 11 material (figure 7.44). These strains suggest that type 1 and type 11 diamond have slightly different elastic properties.

9.6. Inner Core Border of Diamond B.

It has been suggested in section 7.7 that plastic deformation may have caused crumpling of the inner section of diamond B but the rectilinear banding in the cross-like pattern 2 (figure 7.41) remains to be explained.

The curvature of the core border 3 (figure 7.41) is puzzling.

Curvature of a diamond face could well arise through operation of one or more of several mechanisms,

of which at least four might be considered. Thus (a) surfaces could become convex through successive layers diminishing slightly in extension, layer on layer becoming smaller (b) a crystal originally rectilinear in growth shape would tend to convexity if subject to solution processes, since solution attacks edges and corners in preference to face centres (c) a diamond under high temperature and pressure conditions might well be plastic enough to suffer plastic deformation through alteration of ambient conditions after a given period of regular growth (d) Raman has suggested in discussion that he conjectures there is a possibility that diamonds might crystallize from the melt, indeed from a globule of molten carbon, and as a consequence such diamonds will have marked rounded outline.

It is quite clear at the outset that solution mechanism will not account for the outline shape. For this has both concavity as well as convexity in outline and in any case solution would eat into the pattern and the shape would not be retained all round.

Here either growth sheets have been laid down persistently parallel in a complicated curved manner, or the crystal has suffered plastic deformation after reaching this stage of growth. The pattern is uniform

in thickness round regions which clearly differ markedly in crystal orientation and one might have expected variable thickness in the pattern if the mechanism is essentially one of growth in curvilinear fashion.

The evidence here tends to favour the occurrence in the past of some plastic deformation at this stage of growth.

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ACKNOWLEDGEMENTS.

We gratefully acknowledge the financial assistance of the Department of Supply, Australia, under whose patronage this work was carried out, and the guidance and encouragement of Professor S. Tolansky, F.R.S.