Abstract.

A very simple microscopic technique has been developed for the observation of uni-molecular steps. This technique utilises the diffraction effect at the edge of such steps, and steps of 4.6 Å and 7.9 Å have been observed on beryl crystals. This effect is discussed and a theoretical account given of methods of microscopic examination likely to result in the greatest sensitivity. It is concluded that steps of 1 Å, or less, should be visible when reflexion phase contrast equipment is used.

A review is given of past work on crystal growth in which it is shown that only the dislocation theory of growth is capable of satisfactorily explaining much of the experimental data.

The microscopic diffraction technique and multiple beam interferometric techniques are applied to the study of the topography of faces of beryl and quartz crystals. As the microscopic technique enables one to observe dislocations directly, experimental proof is given that these crystals have grown by a dislocation mechanism, and that the dislocation theory of growth must therefore be generally applicable. This theory is shown to be correct in its many detailed predictions and quantitative information is obtained about the conditions in which some of these crystals have grown. The activity of dislocation groups, the cross-linking of layers, the "bunching" of layers, and "rod-formation" on beryl, are discussed.

The treatment by the dislocation theory of dissolution as the simple reverse of the growth process is shown to be correct. Information is obtained on the density of dislocations and they are shown to occur frequently on transition surfaces and
limited slip-zones. Direct visual proof is given that the
dislocation theory of slip is correct.

The topography of a cleavage face of topaz is briefly
discussed.
INTERFEROMETRIC STUDIES

OF

FACES OF BERYL, QUARTZ, AND TOPAZ CRYSTALS

by

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CHAPTER I.

Historical Review of Work on Crystal Growth

The extent of published literature on crystal growth has reached such proportions that a review of all work published, even within the last few years, would run to excessive length. It has, therefore, been necessary to restrict this review to the experimental and theoretical work which has been of prime importance in moulding the main approaches to the problem of crystal growth, and to that work which bears closely upon the experimental results which are to be described later.

One of the earliest points to excite theoretical speculation was the way in which crystals retain their typical polyhedral form under a wide range of growth conditions. An analogy was drawn by Curie between the equilibrium of a fluid surface and its environment, and the equilibrium between a crystal and its environment. (Curie, 1885). A crystal thus tends to a shape corresponding to a minimum free energy, and Curie attempted to forecast this shape. The free energy comprises two sorts of terms - one set proportional to the masses present, the other proportional to the surface areas separating the two media, the coefficients of the latter being the capillary constants of the system. Due to the anisotropy of the capillary constants the crystal will limit itself by plane surfaces.

It can easily be seen from a mathematical statement of Curie's theory that not only is the equilibrium form of the crystal defined, but also its absolute dimensions, so that only
one unique solution is possible - an obvious absurdity. In actual practice, however, the dimensions of the crystal are only important when the theory is applied to very small crystalline nuclei.

For a crystal of non-equilibrium form placed in a saturated solution, it is necessary, if the crystal is to tend toward the state of minimum free energy, that there should be a change in shape of the crystal. This can only happen if the crystal dissolves in certain directions and grows in others; therefore the solubilities of the faces must differ.

A logical extension of the Curie theory was made by Wulff (Wulff, 1901), who enunciated the rule sometimes called Wulff's law, that "the rate of normal growth of the faces is proportional to the capillary constants." This rule reveals a self-contradiction inherent in the Curie theory, for it defines all the capillary constants as being of the same sign, a state incompatible with simultaneous growth and solution.

At the basis of the Curie theory, is the view that all points on a crystal face are equivalent, all molecules entering or leaving the crystal doing so with equal facility from any point on any face.

For a considerable period the influence of the Curie theory was such that it was generally accepted that the faces of a crystal were not equally soluble, and it was claimed that experimental results supported this view. Berthoud refuted those results, claiming considerable differences in solubility, and was able to show, both from observation and independent calculation, that any difference in solubility must, for macroscopic crystals, be very small (Berthoud, 1912). The
claim that infinitely large faces of the same crystal have different solubilities was shown to be necessarily contrary to the Second law of Thermodynamics. No such positive statement is possible for the general case, as the relationship between the faces of the same crystal is a complex one, depending on several factors.

In slightly supersaturated solutions, when any slight differences in solubility must be most effective, the rates of growth are likely to be most unequal, and a crystal should therefore limit itself by comparatively simple forms. With increasing supersaturation, the effect of differing solubilities will wane and the rates of growth should be nearer equality, more complex forms resulting. In general, the converse of this behaviour results.

It was therefore pointed out by Berthoud, that surface energy is not as important in the development of crystals as Curie's treatment would make it, and the formation of plane faces must be due to other causes. It was at this point that Berthoud made a significant break with the thermodynamical reasoning of the Curie type. It is, he said, improbable that the growth of a crystal is independent of the nature of the faces, their reticular density, and the orientation of the molecules with respect to the surface. By this means, one could explain the general behaviour as due to a specific action of the faces on the ease with which the molecules add themselves on.

In general, the faces with greatest packing density develop during growth. Bravais supposed these to be the faces
which most oppose external influences (thus forging a strong link with the Curie theory), but this was refuted by the evidence, previously used against the Curie theory, that the differences in free energy between two crystal forms, and therefore the work necessary for transformation, are too small to influence the existing form. Hence, the form of a crystal is determined not only by its internal structure, but also by the degree of supersaturation, concentration currents, viscosity, etc., which, while influencing the stability of the face but little, can influence the rate of growth. (It is striking to see the same type of arguments used here as were to be used, some thirty years later, to criticise the Donnay-Harker hypothesis).

The Curie theory never recovered from the arguments advanced by Berthoud. It was not only the refutation of the theory that was important, but also the move away from the thermodynamical type of reasoning to one which considered the interaction between the crystal face and each molecule, and the happenings in the external medium. The way now lay open to the kinetic treatments which were subsequently to develop from the standpoint that, in general, addition of a molecule to a crystal face could only take place at one point at any given time, the converse of the Curie type of viewpoint.

An approach similar in many ways to that of Berthoud, but even more far-sighted, had been developed many years previously by J. Willard Gibbs (J. Gibbs, 1906). Unfortunately this work, although published eight years earlier than the Curie theory, and avoiding many of the latter's faults, was overlooked for
many years, although within it lay the germs of the theories to be developed some fifty years later.

Gibbs deduced that a crystal in equilibrium with its surroundings will possess a minimum 'total free energy' for a given volume. Unlike Curie however, he did not consider all points on a crystal face to be equivalent, and he said, with striking insight, "we cannot imagine a body of the internal structure and external form of a crystal to grow or dissolve by an entirely continuous process, or by a process in the same sense continuous as condensation or evaporation between a liquid and a gas, or the corresponding process between an amorphous solid and a fluid. The process is rather to be considered as periodic."

With great physical insight Gibbs perceived some of the decisive points of crystal growth. "A continual growth on any side of a crystal is impossible unless new layers can be formed .... Since the difficulty in the formation of a new layer is at, or near, the commencement of the formation, the necessary values of the Potential may be independent of the area of the side, except when the side is very small. The value of the Potential which is necessary for the growth of the crystal will, however, be different for different kinds of surfaces, and probably will generally be greatest for the surface for which the surface tension is the least."

The precise application of the free energy condition was taken to apply only to very minute crystals, the deposition of matter on the faces of larger crystals being determined more by the nature of the face. Thus large crystals will generally be
bounded by those surfaces on which the deposition of new matter
takes place least readily, with small, perhaps insensible
truncations. If a closed figure cannot be formed by one 'kind
of surface' satisfying this condition, then two or three 'kinds
of surface', determined by the same condition, may be present.
Although these surfaces will probably be those for which the
surface tension is least, their relative development will not
be such as to make the free energy a minimum.

The equilibrium between a crystal face and its environment
was pictured as essentially a statistical one. Since the
molecules at the edges and corners of the face are less firmly
bound than those in the centre of the face, then when a crystal
is in equilibrium several of the outermost layers will be in­
complete towards the edges, the boundary of their layers con­
stantly fluctuating. Seventy years were to pass before Frenkel
applied arguments of this nature, and began the swing away from
long established theories to a new and completely novel theory.

When one considers the state of physical knowledge at the
time of Gibbs' writings, then his reasoning and physical insight
are amazing.

Throughout the whole of the published work on crystal
growth there is an unfortunate lack of experimental work
directly concerned with the nature and behaviour of crystal
faces. Some of the earliest work following a direct approach
was carried out by Miers (Miers, 1903) on the variation of
angles observed on crystals due to the presence of vicinal faces.

A goniometric study of crystals of certain substances was
carried out while they were growing from aqueous solution.
Observations on crystals of potassium alum and ammonium alum established that the images from the various faces continually altered their positions, the angle between adjacent faces never being the theoretical angle. Moreover, the faces usually yielded multiple images very close together, which were shown to be due to the theoretically plane surface actually consisting of a number of reflecting surfaces. During growth it was found that one set of vicinal faces was continually being replaced by another along certain zones. The change was not gradual, sharply defined images succeeding each other, sometimes after an interim period of multiple and confused signals.

Extension of the experiments to other crystals showed that in all cases the vicinal development was in accordance with the symmetry of the crystal. This study led Miers to enunciate the rule that "the faces which actually occur upon a crystal are, in general, not those with simple rational indices, but are vicinal faces."

In order to explain the presence of these vicinal faces, it was shown that if successive plane layers of material were to be laid down on the theoretical crystal face of very high packing density, then a very considerable discontinuity existed between the packing of the solute in the solution and in the crystal. The vicinal planes are, however, much less densely packed than the theoretical face, since they make a slight angle with a plane of greatest packing density. Therefore, if the face is to grow as a succession of vicinal faces, this very abrupt change in packing is much decreased. A regular arrangement of the solute, corresponding to a lattice structure,
immediately before deposition on the actual crystal occurs, would reduce the disproportion in packing even more. Such a regular structure should result in the solution in this region exhibiting double refraction, but Miers was unable to detect any such effect experimentally.

It was during the course of this work that the following observation was made: "Sometimes the growing crystal (of alum) had its octahedron face covered with flat triangular plates whose outline is parallel to that of the octahedron face; when the solution is diluted these have their corners rounded and become converted into hexagonal plates, then disappear and become replaced by inscribed, circular, pits." This is possibly the first experimental observation of layer growth and dissolution, the importance of which will be seen later.

It was some fifteen years later that a posthumous publication of Marcelin's discussed the first detailed observations on the growth of crystals by layer deposition (Marcelin, 1918). The growth of paratoluidine crystals from alcoholic solution was observed, these crystals being in the form of very thin plates which exhibited Newton's colours in reflection. These colours provided a record of growth in thickness while microscopic observation allowed of simultaneous study of growth in surface area. Once a crystal was formed at the surface of the solution it emitted a projection of precise geometric limits, which grew at a regular speed. This was followed by the appearance of another coloured band at the base of the projection, soon followed by others, until all the colours of the scale were shown. All these bands ran parallel, one behind the other.
and at the same speed, with the colour of each band remaining constant.

The observed steps were found to be, in some cases, only five and three molecules thick. It was found possible to keep crystals indefinitely after growth had stopped without alteration in colour or size, such stable crystals usually showing a perfectly uniform tint. Solution of the crystals originated from a single point, the bands spreading out in the form of concentric irregular figures, sometimes partially bounded by straight lines. Each band again retained a constant colour, and steps corresponding to a thickness of four molecules were observed. Thus, Marcelin established that para-toluidine crystals grew and dissolved by the deposition or removal respectively, of successive layers of material, these layers approaching molecular dimensions.

By observing the growth of mercury crystals from super-cooled vapour, Volmer and Estermann studied the condensation coefficient of solid mercury (Volmer and Estermann, 1921). The mercury vapour impinged on a cooled surface and formed very thin crystal plates standing out from the surface. By definition, the condensation coefficient cannot be greater than unity, yet the experimental results gave the condensation coefficient of one face as approximately 1,000. There are only two possible causes of this discrepancy. Either gas kinetic theory is grossly in error, or the classical hypothesis of incorporation of molecules on a crystal surface is incorrect. A great deal of evidence establishes the validity of gas kinetic theory and Volmer was, therefore, led to the conclusion that it
is not correct that, as had always been supposed previously, a molecule either incorporates on the crystal surface where it strikes, or else rebounds. He was thus led to postulate a mechanism, whereby molecules can move from one face to another remaining partially bound to the surface but with lateral mobility (Volmer, 1921, 1922). The only alternative is that molecules can penetrate into the crystal surface and so force it out laterally, a phenomenon not in accordance with observation.

From the crystal surface a field of force projects, varying in a direction parallel to the surface according to the nature of the surface. Thus, densely packed surfaces will possess a field of force with only shallow potential 'troughs', adsorbed molecules being able to move about fairly easily, the chance of formation of nuclei being small, and the surface, therefore, growing slowly; on the other hand, less densely packed surfaces will show greater variations in the field of force and much deeper potential 'troughs', so that these surfaces will grow more rapidly, particularly as the densely packed surfaces will, in addition, supply molecules which wander over the boundary and become bound to the less densely packed face.

In growth from the vapour, a new stage in the growth process had been introduced. This process will obviously permit of a much greater supply of material to the growing layers which exist on a face.

A theory, taking into account some of the experimental observations of growth by layer deposition, was developed by Brandes (Brandes, 1927). An analogy was drawn with the case of elementary fluid drops which have to achieve a critical size,
with sufficiently reduced vapour pressure, before they can persist. Similarly, two-dimensional crystal nuclei must achieve a critical size before they can overcome the tendency to redissolve under the influence of their boundary energy, and the different rates of growth of faces were therefore taken as being due to the different chances of formation of nuclei of critical size, all points on a face being taken as equivalent. The boundary energy of the nucleus was calculated, assuming nearest-neighbour interactions between the perimeter ions (for sodium chloride) and the two-dimensional lattice.

The rate of extension of the nucleus, once past the critical size, was assumed to be much greater than the rate of formation of nuclei, so that any one layer would be complete before the next nucleus passed the critical size. The work of formation of (100), (110), and (111) type nuclei was calculated and in the case of the first two the numerical values agreed, generally speaking, with the observed growth rates. In the case of (111) nuclei, the work of formation was found to be negative for similar values of supersaturation. Substitution in the growth rate formula indicates a much higher rate of growth, but the physical significance of this negative value would seem to be that no nucleation is necessary on this face.

In this treatment, one sees an attempt to make the theory fit the experimental facts. This attempt is, in some ways, novel and of considerable value, but it neglected the fact, already indicated by Marcelin, and later to prove very significant, that initiation of layers takes place at one, or few, points on the surface, these points remaining fixed, and not
undergoing random movements with time. The incorporation of such preferred growing points in a thermodynamical treatment is necessarily very difficult, and it is significant that, from this time, one finds a marked trend towards a kinetic, rather than a thermodynamic treatment. Yet nine years were to pass, and several attempts at refinement of the above treatment were to be made, before the theory of two-dimensional nucleation was to be deduced from purely kinetic arguments by Becker and Döring.

The approach in subsequent treatments was to start with a complete crystal plane and to build up a complete new plane by addition of one molecule at a time. For each possible position of a new molecule, the binding energy was calculated, the positions of greatest binding energy being the most stable. In such a position it is most probable that a molecule will remain long enough to be joined by others, and therefore reach a point when it is unlikely to be completely removed. A complete plane will therefore eventually spread from it. In the positions of least binding energy, however, molecules are less likely to be able to form a stable nucleus before being ejected. Should there be but one, or few, positions of greatest binding energy, then the addition of molecules will tend to be strictly ordered, but if many positions, and many points of subsequent addition of molecules, do not differ significantly in binding energy, then the addition of molecules will tend to be of a random nature.

The first attempt to apply a treatment of this type was made by Stranski. He calculated the work needed to remove to
infinity a molecule from various points on the face of a sodium chloride cube, making the simplifying assumptions that the rest position of each molecule is its lattice position, and also that any external forces (such as solvent forces) could be ignored (Stranski, 1928). The forces between ions will decrease very rapidly with distance, and therefore, the nearest-neighbour interaction only was considered at first. The chief positions considered were those of a single molecule resting on the corners, edges, and centre of a complete plane and, in the case of incomplete planes, a molecule added to the centre or the end of a complete row, and also the 'half-crystal' position, or 'repeatable step', in which the molecule is added to the incomplete end of a partially completed row.

Calculation for the (100) sodium chloride cube showed that, in conditions not far removed from saturation, new planes will start from the corners or edges of the cube, but not from the centres of the cube faces. Once a plane is initiated, the position at the end of a partially completed row has the greatest work of separation and the plane will, therefore, spread row by row. When rows are complete then it is more likely that another row will start on the partially formed plane, rather than that another plane should start at a corner.

It is the 'repeatable step' which, after the commencement of any plane, governs its subsequent behaviour. If the outer medium is supersaturated with respect to the 'repeatable-step', then any partially completed row will fill up. A chance fluctuation in the local concentration is then necessary before a new row can be started, which will soon fill up, and there will
be another pause before the next row is started. In the same way, a chance fluctuation in concentration might strip down a row.

The rate of growth of a plane is thus governed mainly by the rate of formation of new planes, the rate of extension of a plane being governed by the probability of occurrence of the chance fluctuation necessary to start a new row.

A very similar method of approach was used by Kossel, who showed that this type of theory could, for the first time, satisfactorily account for the inhibiting action of small amounts of impurity (Kossel, 1930). Should this impurity be selectively adsorbed on to the corners and edges, then growth will be impossible, unless the supersaturation is sufficient to start a new plane on the centre of the face, the most difficult position of all.

For the case of non-ionic crystals, it was shown that the position of greatest binding energy is the centre of a plane or face (Stranski, 1931). New planes will, therefore, start from the centre of a face, and, if the surface is in equilibrium with its environment, the outer layers at the corners and edges will tend to partially strip down. When growth is possible, these stripped-down positions are grown out before commencement of a new plane.

This type of approach was later used, largely by Stranski and his school, to determine the equilibrium form of various types of crystals (Stranski, 1949). The accuracy of the method was improved by considering not only the nearest-neighbour interactions, but nearest-neighbour but two interactions. By
this method very satisfactory agreement was obtained in some cases between the theoretical equilibrium form and that experimentally observed, but, as the method is of limited application, it will not be considered at length. It need only be said that this work supports the Kossel-Stranski type of approach.

The study of vicinal faces inaugurated by Miers was carried on by Kalb, who, in a series of papers (Kalb, 1927, 1930, 1932, 1933), applied Miers' findings to natural crystals and minerals, being mainly concerned with the question of form development and the discovery of general laws governing vicinal development. These 'general laws' were not satisfactory, as is hardly surprising.

The main trend of both experimental and theoretical work was now in harmony in stating that the growth of a crystal took place by extension of layers lying parallel to the true crystal face. If vicinal faces were to be considered as fundamental, then another complication was added which must be explained by any satisfactory theory of crystal growth. A simple extension of the existing state of knowledge could satisfactorily explain vicinal faces as consisting of very thin stepped layers, which would result in a face which, on a macroscopic scale, would make a small angle with the plane of the layers. Kalb apparently never considered this possibility, for his views on the growth of crystal faces were nothing more than a vague restatement of Miers' theory (Kalb, 1934). The main additional argument used by Kalb to support this theory was that vicinal faces approach more nearly to the basic (i.e., true) faces, the less the degree of supersaturation of the medium, thus tending, as
far as possible, to decrease the disparities in packing between
the crystal and the solution. This behaviour could be more
satisfactorily explained as being due to the decrease in the
number of layers growing on the face at any one time as the
supersaturation decreased.

The growth of magnesium crystals from vapour was studied
by Straumanis. By microscopic examination he showed that at the
commencement of growth, and particularly when the supersatura-
tion is high, crystal nuclei without exterior faces were formed
(Straumanis, 1934). As the size of the nucleus increased, the
rate of growth decreased, and vicinal faces appeared, to be
superceded by faces of the equilibrium form. The vicinal faces
are then non-equilibrium forms which only occur when the crystal
grows quickly. By applying the Stranski theory, it was found
possible to predict the equilibrium form of magnesium crystals.

Further work was done on the growth of paratoluidine cry-
stals on this occasion from vapour (Kowarski, 1934). The growth
in surface area and thickness was studied in the same way as
Marcelin, by observing the interference colours. Two apparently
different types of crystal were found to form. At the moment
of birth of any constituent crystal of the first of these, the
'curved system', the crystal possessed a definite colour which
was uniform over its surface. While the crystal grew in surface
area, this tint did not change for some time, until suddenly,
and always at an edge (usually at the point of intersection of
the edge with another crystal) a coloured spot was seen to form.
At first, this spot was bounded by the arc of a circle, with
the source as centre, but as it spread over the face the contour
became deformed, successive spots surging out from the source so that the successive layers formed a scale of colours. Very often the succession of layers was so rapid that the colour gradation appeared continuous, but on occasion a difference in tint could be observed, corresponding to the dimension of the unit cell. Successive layers were propagated at different speeds, slow layers being sometimes overtaken by rapid layers which followed, resulting in a distinct discontinuity in thickness. In general, it was found that the thinnest layers propagated most quickly. It was invariably found however, that a coloured layer, no matter how slow its speed of propagation, did not stop before covering the whole of the surface of the crystal. Also the contour of each layer always remained entirely curvilinear.

The other system observed, "the oriented system", was such that individual crystals were difficult to observe. The crystals of this system needed no external cause or accident to start growth in thickness, the surface being divided into several bands of different colour. The frontiers between these bands were rigorously rectilinear, and rigorously perpendicular, to the principal edges of the face, a pronounced discontinuity in thickness occurring between the bands. The bands receded from the base until, finally, the white tint of the support covered the whole crystal. The different frontiers could, again, advance at different rates, but the process could stop en route before covering the whole surface, and then start again some time later.

Growth by layers was occasionally found to occur with
crystals of this system when two individuals touched and set off an 'accident'. In exceptional cases a frontier became the seat of two or several sources. The band below this frontier then became covered with layers of circular contour succeeding one another until the two bands were of the same thickness, the layers propagating much more quickly than the bands.

Liquid drops of paratoluidine were found to form on the crystals under certain circumstances. Under the experimental conditions, this liquid could not have been in contact with the crystal surface or it would have crystallised immediately. An adsorbed film, of the Volmer type, must exist on the surface, and the liquid drops must rest on this film.

Kowarski showed that for very dissimilar types of crystals of the curved system, the curves of surface area against time were always very similar, consisting of first, a parabolic section, then a rectilinear section, and finally a section tending toward an asymptotic limit. He was able to explain this behaviour in terms of the properties of the molecules in the adsorbed film, assuming that, at first, the adsorbed molecules could wander over all the crystal surface, but that after a time their mobility decreased, and movement over one face only was possible. The first part of the curve corresponds to free movement of the molecules, the second part to the period when a considerable number of the molecules are limited to one particular face, so that all the 'free places' are soon occupied, while the third section corresponds to the period when practically all the free places are occupied and very little growth can occur.

It was shown that the adsorbed film possessed a regular
molecular structure, although differing from that of the solid. An ordering process must therefore take place in this film, before incorporation of the molecules into the crystal.

It should be noted that molecules of paratoluidine are of a long asymmetrical type and one must, therefore, be cautious in assuming all the observations and conclusions to be generally valid. However, this work provided direct evidence for the presence of an adsorbed film of the type postulated by Volmer, and the theories of Kossel and Stranski received further valuable support, for not only was layer growth again shown to take place, but also the probability of nucleation of new layers was shown to be much less than the probability of extension of an existing layer.

In general, the main theories of the time appeared to be soundly established. Yet one serious difficulty lay in their path, although apparently tacitly avoided—namely, the frequent occurrence of vicinal faces. The choice lay between consideration of vicinal faces as fundamental phenomena, or merely as manifestations of the mechanism of layer growth. Either way presents difficulties in the path of theory. If vicinal faces are of fundamental nature, then an attempt must be made to account for their presence and growth. In fact, no serious attempt to do so had been made since Miers' work. If vicinal faces consist of stepped layers, then the prediction made by Stranski that, in general, one layer will be completed before the nucleation of the next layer, is very far from correct, and constitutes a serious deviation from theoretical predictions. Worse is to follow, for vicinal faces often meet at
some point on a face. On the layer viewpoint this junction must correspond to a growing point. This introduces no further difficulty for non-ionic crystals, but in the case of ionic crystals this is far from the case, for it means that in very many cases the layers spread from those sites predicted by theory as being least probable. Thus, grave difficulties lie in the way of the Straniski-Kossel type of theory, if one accepts vicinal faces as being composed of stepped layers, yet no statement of these obvious problems has been found in the literature.

One of the most important aspects of crystal growth, the nucleation of new phases (three-dimensional nucleation) and the nucleation of new layers (two-dimensional nucleation), was given a rigorous theoretical treatment by Becker and Doring, who rejected the thermodynamical type of argument which had previously been used, and derived their theory on purely kinetic grounds. (Becker and Doring, 1935). This treatment is lengthy and difficult to summarise, but a short account which serves to show the essentials of the treatment is given below, in a form due to Frenkel (Frenkel, 1946). The general case of three-dimensional nucleation will be considered later, as a special case.

The fundamental hypothesis of the theory is that changes of the nucleus $\mu$ are due to condensation or evaporation of single molecules, and clusters of molecules are not considered. The theory is therefore only strictly valid for low concentrations. Let the probability per unit time for a nucleus of $\mu$ molecules to transform by evaporation to $\mu-1$ molecules be $q(\mu)$. Similarly, let the probability per unit time for transformation to a nucleus of $\mu+1$ molecules by condensation be $a(\mu)$. 
Then \[ q(\mu) = s(\mu) \nu e^{-W(\mu)/kT} \]
and \[ a(\mu) = s(\mu) \nu \alpha e^{-W/\nu^T} \]
where \( W(\mu) \) = energy of evaporation
\( W = \) lattice energy
\( \alpha = \frac{\beta}{\nu} \) \( \beta = \text{constant} \) \( e^{-W/\nu^T} \)
\( \nu = \) frequency factor

Let \( Z(\mu) \) represent the number of nuclei containing \( \mu \) molecules in the phase. The chances per unit time for a nucleus of \( \mu-1 \) molecules to increase to \( \mu \) molecules is \( Z(\mu-1)a(\mu-1) \)
The chances of the reverse process are similarly \( Z(\mu)q(\mu) \)
Then the number of nuclei \( \mu \) formed per unit time per \( cm^3 \) is \( I(\mu) \)
is \( I(\mu) = Z(\mu-1)a(\mu-1)-Z(\mu)q(\mu) \) \hspace{1cm} (1)
The rate of change of nuclei \( \mu \) per \( cm^3 \) per second is:
\[ \frac{dZ(\mu)}{dt} = I(\mu) - I(\mu+1) \] \hspace{1cm} (2)

Let us consider a fictitious distribution of nuclei corresponding to an equilibrium distribution. Then the number of nuclei transforming to \( \mu \) are equal to those transforming to \( \mu-1 \) from \( \mu \).

Writing \( N(\nu) \) for the number of nuclei of size \( \nu \) then
\[ N(\nu-1)a(\nu-1) = N(\nu)q(\nu) \]
and \[ N(\nu-2)a(\nu-2) = N(\nu-1)q(\nu-1) \] etc., etc.

It is easy to show that
\[ N(\nu)a(\nu) = N(1)a(1) \sum_{i=2}^{\nu} \frac{a(i)}{q(i)} \]
It follows from (1) and (2) that
\[ I(\mu) = -N(\mu)a(\mu)\frac{\partial}{\partial \mu} \frac{Z(\mu)}{N(\mu)} \] \hspace{1cm} (3)
\[ \frac{dZ(\mu)}{dt} = -\frac{dI(\mu)}{d\mu} \] \hspace{1cm} (4)
If we assume a steady state
\[ \frac{dZ(\mu)}{dt} = - \frac{dI(\mu)}{d\mu} = 0 \]
A steady state (although not an equilibrium state) is attained if all nuclei bigger than a maximum size \( M \) are replaced by \( M \) single molecules. The rate of formation of nuclei is independent of \( \mu \). We can write
\[
\int_{I(\mu)}^{M} \frac{I}{N(\mu) \alpha(\mu)} \, d\mu = - \int_{I(\mu)}^{M} \frac{dZ(\mu)}{d\mu} \frac{1}{N(\mu)} \, d\mu
\]
as in the steady state \( I(\mu) \) becomes \( I \).

Now
\[
- \int_{I(\mu)}^{M} \frac{dZ(\mu)}{d\mu} \frac{1}{N(\mu)} \, d\mu = - \left[ \frac{2(\mu)}{N(\mu)} \right]^{M}_{I(\mu)}
\]
\( Z(i) \) and \( N(i) \) refer to single molecules and, by definition
\[ Z(M) = 0 \]
\[ - \int_{I(\mu)}^{M} \frac{dZ(\mu)}{d\mu} \frac{1}{N(\mu)} \, d\mu = 1 \]

\[ I = \int_{I(\mu)}^{M} \frac{1}{N(\mu) \alpha(\mu)} \, d\mu \]

This is the general formula for the rate of formation of nuclei.

For vapour
\[ I = \frac{C e^{y/kT}}{\int_{I(\mu)}^{M} e^{F(\mu)c} \, d\mu} \]
where \( C \) = number of collisions per cm\(^2\) per sec.
\( \gamma \) = surface energy per molecule

The function to be integrated rises to a very steep maximum value and it is possible to write
\[ I = C e^{y/kT} e^{-F(\mu)c/kT} \]
where \( F(\mu) \) represents the maximum of the free energy curve.
Taking \( C \sim 10^{24} \, \text{cm}^3/\text{sec} \) at saturation pressure of 1 mm.

Then we can write (Cabrera, unpublished)

\[
I \sim 10^{24} \exp \left\{ -\frac{4}{27} \left( \frac{Y}{kT} \right)^2 \left( \frac{L_{\infty}}{kT} \right)^2 \right\} \, \text{cm}^3/\text{sec}.
\]

For \( I \sim 1 \), taking \( Y/kT \sim 10 \) then

\[ \alpha \sim 5 \]

For nucleation of water drops from the vapour, Volmer and Flood found the experimental value of the supersaturation to be 4.21, compared to a theoretical value of 4.16 (Volmer and Flood, 1934). The agreement is thus excellent.

For the case of three-dimensional nucleation from solution it was found that agreement between the theoretical and experimental values of the supersaturation was only satisfactory if an unreasonably low value of the surface energy of the nucleus was assumed. It is possible however, that in solution the fundamental hypotheses are no longer justified.

In the case of two-dimensional nucleation, the arguments are precisely similar and we can arrive at a final expression

\[
I = C \exp \left\{ -\frac{U}{kT} \right\} \exp \left\{ -\frac{A}{kT} \right\}
\]

where the free energy terms comprise edge energy factors instead of surface energy factors.

\[
C \exp \left\{ \frac{U}{kT} \right\} = \frac{1}{a^2} \exp \left\{ -\frac{2A}{kT} \right\} \exp \left\{ -\frac{U}{kT} \right\} \exp \left\{ -\frac{\gamma}{kT} \right\}
\]

where \( U \) = activation energy

\( A \) = energy of evaporation

Then

\[
C \exp \left\{ \frac{U}{kT} \right\} \sim 10^{22} \, \text{cm}^{-2}/\text{sec}^{-1}
\]

\[
I = 10^{22} \exp \left\{ \left( \frac{Y}{2kT} \right)^2 \left( \frac{L_{\infty}}{kT} \right)^2 \right\} \, \text{cm}^3/\text{sec} \]
Thus, for a supersaturation of less than two, no two-dimensional nucleation should take place on a crystal surface. For growth of iodine from the vapour, a supersaturation of about 1.01 was observed, which was claimed to agree satisfactorily with the theory (Volmer and Schultze, 1931). Growth of sodium chloride crystals from aqueous solution was shown to take place at a supersaturation of about 1.045, and this was accepted as being in general accord with theory. We shall see later that this was by no means true. It was at this point that work on crystal growth, both theoretical and experimental, achieved a striking unanimity. The Becker-Doring nucleation theory was generally accepted as forming a firm foundation stone to the subject, the general pictures of layer growth appeared to be in almost complete accord with experiment, and it seemed that the main aspects of the subject had been mapped out. Yet this accord was eventually to wane, until, some fifteen years later, an almost completely new theory of crystal growth was evolved.

An intensive investigation of the growth of sodium chloride crystals from aqueous solution was made, first by Bunn, then by Berg, and subsequently by Humphries-Owen (Bunn, 1949, Berg, 1938, Humphries-Owen, 1949 a,b). An interferometric technique was used to measure the refractive index of the solution around a growing crystal, and from this the concentrations and gradients of concentration contiguous to the crystal could be measured. It was found that the concentration of the solution was not uniform along a face, but lowest at the centre, rising on each side to the corners. Faces of the same crystal, though
all the same type and initially in contact with solution of the same concentration, usually grew at different rates and sometimes ceased growing altogether, the slower growing faces being, in general, in contact with solution of higher concentration. The component of the concentration gradient normal to the surface, which is a measure of the exit of solute per unit area, was found to be highest at the centre of a face, decreasing toward the corners. As the faces remain plane, despite such apparent differences in supply of material, Berg postulated that an intermediate layer, possibly of the Volmer type, must exist to transport material along the face. Humphries-Owen was led to the same conclusion. Such a behaviour is unexpected for an ionic crystal of this type must have considerable, and very sudden, variations in the field of force along its surface, and one would expect the mobility of any adsorbed ions to be strictly limited. Humphries-Owen has suggested that the presence of the solvent might modify the field of force in such a way as to allow of lateral mobility.

This work presented many puzzling aspects. Although the complete stoppage of growth of faces which was occasionally observed could easily be explained as being due to the inhibiting action of impurities, this explanation cannot be so easily applied to the common cases when growth of a face took place very slowly and for a considerable period. It would seem rather that, in this latter case, some specific and lasting change occurred in the nucleation characteristics of the face.

The postulation of an adsorbed layer of the Volmer type has been criticised by Frank, who claims that convection could
invalidate the assumption that the flux of solute is simply proportional to the concentration gradient, and that until the effects of convection can be eliminated from these experiments no definite statement can be made about the existence of an adsorbed layer (Frank, 1949 b). Moreover, Frank is able to provide an explanation of the behaviour of slow growing faces in terms of his theory, which will be discussed later.

A highly significant fact, which has received little attention, is that the rate at which growth from solution can proceed to form a good transparent crystal, decreases with increase of the surface considered (Yamamoto, 1939). The only theory which can even attempt to explain this behaviour is that advanced by Frank. Yamamoto also showed that large transparent crystals of some substance could only be obtained when grown from a solution containing certain metallic cations. He pointed out that when any orientation defect occurs in the lattice of a growing crystal surface, then the field of force is weakened, and other defects are induced to appear, until at last, numerous microscopic hollows are produced. The metallic cations are, however, capable of occupying the lattice point of the crystals and occupying the point of structural defect as it appears, thus preventing the first major weakening of the field of force, the addition of solute molecules therefore proceeding smoothly.

The first serious difficulty in the way of the theories of Kossel and Stranski, as yet scarcely unchallenged, was provided by a considerable body of evidence on layer formation on crystals faces (Bunn and Emmett, 1946, 1949). A drop of warm saturated solution was placed on a warm microscope slide,
covered with a cover slip and observed under high magnification while cooling on the microscope stage. This was done for a considerable number of substances. This simple and direct approach, a type of approach unfortunately lacking in much of the work on crystal growth, revealed much novel information.

Using dark ground illumination, layers were seen to spread across the faces of crystals of many substances. Such layers were found to be at least several hundred angstrom units thick. On some crystals the layers were so thick that they were observed by transmitted light, or, for birefringent crystals, between crossed nicols.

Under experimental conditions, layers were seen only on crystals of ionic or polar substances, and were not observed on crystals of non-polar substances. These layers, in general, started from the centres of the faces, spreading outward towards the edges, and not from the edges or corners of crystals as predicted by theory.

The boundaries of the layers were often irregular, especially when growth was rapid. As growth slowed down, there was a tendency to regularity of shape, this shape conforming to the symmetry of the crystal face.

On many crystals it was found that the layers increased in thickness as they approached the edge of the face. In some cases this was seen to be due to thinner, barely visible, layers spreading more rapidly than the thicker layers and adding on to these layers when they overtook them. It was assumed that such behaviour by layers too thin to be visible, was the general cause of the increase in thickness of the layers.
Dissolved impurities were found to influence strongly the thickness and the shape of the layers, the effect being highly specific.

In the case of some typical experiments on sodium chloride, the layer thickness was found to be some 300-700 unit cells. Usually only one system of layers was seen on any one face, but occasionally two systems were seen to spread from different points. Pits were occasionally formed by the encirclement of a small area by a layer growing all round it, the layer subsequently spreading in to fill up the pit.

In order to explain the formation of thick layers, the explanation was advanced that the surface energy per unit height of low steps was greater than that at a high step. At the basis of this reasoning, was the assumption that a series of stepped uni-molecular layers form a high index surface, while, for a thick layer, the upper surface is of low index, thus forming a predominantly low index surface. On the molecular scale, which is surely the point of view to be considered, this appears to be dubious reasoning.

As the edge of a layer, several hundred atoms high, is quite a large face on the atomic scale, the manner of deposition on such edges was considered. It was concluded that such edges are usually high index surfaces for which evidence exists that normal two-dimensional nucleation is not necessary, but that growth takes place in a more indiscriminate way. Such surfaces must tend to become of low index as growth slows down, and it was taken that, in these circumstances, growth will be much inhibited, for each new layer on the step edge would require
fresh nucleation. The primary necessity for rapid growth was therefore taken to be the existence of step edges of high index.

Not only did layers usually start from the centres of faces, but also such initiating centres usually remained almost stationary during the period of observation. Such behaviour is of course, directly contrary to the theoretical predictions, and the extent of the evidence for this behaviour makes it a formidable obstacle to the Stranski type of theory. Moreover, the work of Bunn, Berg, and Humphries-Owen, shows that in experimental conditions very similar to those under consideration, the supersaturation is greater at the edges of a face than at the centre, which should favour nucleation at the edges and corners (Bunn, 1949, Berg, 1938, Humphries-Owen, 1949 a,b,). (It is possible that the concentration gradients in the solution might neutralise this latter effect, but until the effect of convection has been determined nothing definite can be claimed).

The only other possible cause which could mask the predicted type of behaviour, would be the presence of surface imperfections in the centres of the crystals faces. Yet no convincing reason can be advanced as to why ordinary surface imperfections should be situated at the centre of face rather than elsewhere. The conclusion to be drawn is that either Stranski's theory has overlooked some important energy term, or else some other factor, of a type quite different from those considered by Stranski, is responsible.

A novel viewpoint was adopted by Frenkel, in a paper which at first aroused little attention, but which later was to have considerable influence on later work (Frenkel, 1945). From the
principles of statistical mechanism, Frenkel concluded that the surface of a crystal, in a state of equilibrium, must consist, not only of basic faces, but also of vicinal faces, formed by steps arising spontaneously from thermal fluctuations. With an increase of temperature these steps were shown to increase considerably in number.

On the flat portions of each step adsorbed atoms exist behaving as a 'plane' gas for a three-dimensional crystal (or a 'linear' gas for a two-dimensional model). A continuous exchange takes place between each 'plane' phase and the next higher step, which acts as the 'condensed' phase, leading to a lengthening or shortening of the various steps.

Applying similar considerations to the case of a two-dimensional crystal allows one to determine the shape of the steps limiting the terraces on a three-dimensional crystal. The energy of such a step is dependent on its orientation with respect to the crystallographic axes, and when in statistical equilibrium it will be fluctuating about a set of crystallographic directions corresponding to low energy per unit length. As well as the two-dimensional gas on the surface of each terrace there will be a one-dimensional gas on each step edge, formed by the atoms adsorbed there. Such atoms will move about until they either 'build on' to a kink or a hole, or revert to the plane gas phase.

The mode of addition of material to the crystal consists of, firstly, random deposition on the surface from the external phase. Thus, in general, atoms are deposited on to the flat positions of the terraces to form a two-dimensional plane gas.
Then random attachments take place of some of the atoms on the vertical step, such atoms forming a linear gas and moving along the step until, finally, they build on at a kink or a hole or evaporate.

Evaporation, dissolution, or melting takes place in the reverse order, starting with linear evaporation, passing through plane evaporation and ending with space evaporation.

A significant difference exists between these ideas and those of Kossel and Stranski, for the latter's theories consider addition or removal of material to occur at one place only on each layer, the 'repeatable step'. On Frenkel's theory there will be many such points for any one step, the number depending on the temperature. Contrasting pictures then exist of an irregular statistical advance of a step and a regular ordered advance. Moreover, on Kossel's theory addition or removal of atoms takes place directly between the external phase and the repeatable step, as compared with the three stage process envisaged by Frenkel. The physical basis of Frenkel's theory appears to be more satisfactory, so that another weakness has been exposed in the Kossel-Stranski theory.

The final expression of the Becker-Doring theory for the rate of two-dimensional nucleation was examined in the form shown in equation 6 by Burton, Cabrera, and Frank. They observed that the value of $I$ was very sensitive to the value of the exponential term, and particularly to the $h_x$ term. Substitution of the experimental values of $\alpha$ obtained by Volmer and Schultze revealed that, far from the agreement which had been claimed, the theoretical value of the nucleation rate
was incorrect by a factor of the order of $e^{-3,400}$ (Burton, Cabrera, and Frank, 1949). Burton and Cabrera, therefore, carefully re-examined the bases of the Becker-Doring two-dimensional nucleation theory. In the original theory the critical nucleus was assumed to have a circular shape. This is not likely to be correct as the symmetry of the crystal face must influence the shape of the critical nucleus, but it was found that more refined calculations, taking into account various possible shapes, only resulted in a reduction of the index of the exponential term by a factor of 0.86.

The whole problem was, therefore, approached again, the first step being to divide all crystal surfaces into two types (Burton and Cabrera, 1949). The first type, 'close-packed surfaces,' is defined as consisting of those surfaces which, when as flat as possible, have all the surface molecules at the same distance from a plane parallel to the surface. All other surfaces will present a stepped appearance, and it can be shown that the position between the steps will consist of close-packed surfaces. Deposition on a close-packed surface can only take place by a surface nucleation process, whereas deposition on the edge of a step can take place without a linear nucleation process. Hence, the growth problem for a stepped surface is solved once the corresponding problem for the steps is solved.

Easy growth of the steps is assured provided that kinks are present in the step at equilibrium. In order to approach this problem, kinks of the type discussed by Frenkel were considered. The number of such kinks in a step is dependent upon
the temperature and it was shown that for $T \sim 600\,^\circ K$
there is a kink every ten molecules along the step, and a mole-
cule is adsorbed on to the step, or there is a 'hole' in the
step, every hundred molecules. Thus, a stepped surface is
always capable of easy growth.

In the case of close-packed surfaces, it is necessary to
determine whether differences in level can occur spontaneously;
that is whether 'jumps' can occur in the surface, these 'jumps'
being quite distinct from the presence of adsorbed molecules
and holes. Should such jumps be present, then the problem of
two-dimensional nucleation would probably be solved. By means
of a difficult mathematical treatment, it was shown that there
is a critical temperature at which the surface steps can
appear, this temperature depending, upon other things, on the
type of lattice considered. Substituting reasonable numerical
values in the equations, the following values for the critical
temperature were obtained.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Surface</th>
<th>$T_c(\degree C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple</td>
<td>(100)</td>
<td>1,000</td>
</tr>
<tr>
<td>cubic</td>
<td>(110)</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>-30</td>
</tr>
<tr>
<td>Face-centred cubic</td>
<td>(111)</td>
<td>1,700</td>
</tr>
</tbody>
</table>

Thus, close-packed (habit) faces will not grow at low super-
saturations because surface nucleation is necessary except
above a certain critical temperature, normally very high, when
these surfaces become equivalent to stepped surfaces.
An attempt was made to estimate the effect of diffusion on the condensation currents around the nuclei (Cabrera and Burton, 1949). This problem proved very difficult to treat, and only a semi-quantitative estimate could be made of this effect, which, although it differed from that given by the single nucleation theory, did not agree with experimental observations.

The main problem thus remained obdurate. Although the Becker-Doring theory agreed very well with experiment in the case of molecules coming together to form a three-dimensional nucleus, yet once the individual faces of the crystal so formed are to be considered, a gross discrepancy between theory and experiment is apparent. Just such a discrepancy in the siting of the nucleation points had also been observed by Bunn and Emmett. Either some gross errors existed in the theories, although careful scrutiny had failed to reveal this, or some factor of prime importance had yet to be recognised.

It was suggested by Frank that the difficulty would be resolved if, instead of the implicitly assumed perfect lattice, account was taken of the presence of dislocations, which the study of the mechanical properties would suggest are in every crystal (Frank, 1949a). The form of the cube face of a simple cubic crystal when a 'screw dislocation' emerges normally at the face, is shown in Fig. 1 as a continuous deformation of a plane and on Fig. 2, as a block model. The presence of such dislocations would provide a constant molecular terrace, which growth could not eliminate, and the need for two-dimensional nucleation would never arise. Much of the theory which follows, due to Frank, is as yet unpublished.
If a single dislocation emerges on a cube face, the associated ledge will run across to the edge of the face. If the vapour pressure is near the equilibrium value, the ledge will round off near the edge of the face if the crystal is homopolar, or possibly remain quite sharp if the crystal is ionic. The step will show a certain number of Frenkel kinks and when in contact with its vapour will constantly receive and lose molecules. Under conditions of supersaturation, an excess of molecules will be received by the edge, which will consequently advance. There are two cases to be considered:

(a) When the Frenkel kinks are close together and the distance moved by an adsorbed molecule is large.

The molecules will then have a high probability of reaching the step before evaporating. Such conditions are only likely to occur in growth from the vapour.

(b) When the kinks are few, or the distance moved by an adsorbed molecule is small, compared to the distance between steps. This is most likely to apply to growth from solution. When these conditions apply to growth from the vapour, a circular type of diffusion problem exists - in the case of solution this has to be extended to a hemispherical diffusion problem.

The rate of advance of a straight step was shown to be

\[ v_\infty = \sigma \chi_s \nu e^{-V/kT} \]

where

\[ \sigma = \lambda - 1 = \frac{\rho}{\rho_0} - 1 \]

\[ \chi_s = \text{characteristic distance diffused by a molecule before evaporation.} \]
In general, the edge running from a dislocation will be curved, the rate of evaporation of molecules being, therefore, increased, and the normal rate of advance will be

\[ v_p = v_\infty \left(1 - \frac{\rho^2}{\rho_c^2}\right) \]

where \( \rho_c \) = radius of curvature of the critical nucleus

\( \rho = \) " " " " " " edge.

For \( \rho_c > \rho \), \( v_p \) is negative and no growth occurs.

For \( \rho_c = \rho \), \( v_p = 0 \), the equilibrium position.

For \( \rho_c < \rho \), \( v_p \) is positive and the edge advances.

For a circular nucleus \( \rho_c \) is the radius, but we shall consider the critical nucleus to be a square of side \( l_0 \); we shall take \( \rho_c = \frac{l_0}{2} \) (i.e., the radius of the inscribed circle).

Then

\[ \rho_c = \frac{a \sqrt{y}}{h \ln a} \]

or, for low supersaturations

\[ \rho_c = \frac{a \sqrt{y}}{h \sigma} \]

where \( a \) = inter-atomic spacing

When the step moves forward, the section near the dislocation can only rotate, growth only occurring if the critical nucleus will pass between the dislocation and the boundary. This results in the step taking a spiral form as it advances (Fig. 3), the rate of advance of the edge being constant when the curvature is large compared to the critical nucleus.

For growth from the vapour this edge can be considered as forming a simple spiral, because it is only when a factor dependent on the number of kinks in the edge enters into the growth rate formula that \( v_p \) depends to any extent on the crystallographic direction. The simple spiral can be repre-
sented by the Archimedian spiral
\[ r = 2\rho_c \theta > 0 \]
for which the spacing between turns
\[ s = 4 \pi \rho_c \]
An equation found to fit the behaviour more exactly is
\[ \Theta = \frac{\sqrt{3}}{2(1+\sqrt{3})} \left[ \frac{r}{\rho_c} + \ln \left( 1 + \frac{r}{\sqrt{3} \rho_c} \right) \right] \]
The conditions of application of this theory were defined as being for any homopolar crystal at a temperature of about half the boiling point.

For two screw dislocations of opposite sign, the step runs from one to the other, following the outline of a section of the critical nucleus. If the critical nucleus can pass between the dislocations, then the edge grows in the way shown in Fig. 4. Growth fronts always annihilate when they meet and the dislocation pair, therefore, produce a series of closed loops which extend outwards. Hence, the number of growth fronts passing any point on the face is the same as if either dislocation alone was active.

In the same way, a group of dislocations is as active as its most active member and the growth rate of the whole face is determined by its most active dislocation group, all the other groups merely passing on the growth fronts received from the active group with a slight delay and in a slightly modified form. If two dislocations of opposite sign are further apart than \( \frac{4\pi \rho_c}{9} \), then they act independently, both producing their own spiral.

Consider a step following some arbitrary curve. Then if
one section of the step follows a close-packed direction only thermal (i.e., Frenkel) kinks will be present in this section. All those sections of the step not parallel to the close-packed direction can be considered, as previously in the three-dimensional case, to consist of short sections parallel to the directions of close-packing, joined by steps perpendicular to this direction. Such sections, therefore, show both thermal kinks and 'directional' kinks, the density of the latter being
\[ n = n_+ + n_- \]
where the signs allow for the direction of inclination to the close-packed direction.

We may take
\[ n_+ n_- = e^{-\gamma/kT} \]

The angle of inclination, \( \theta \), between the direction of any section of the step and the direction of close-packing is given by
\[ \theta = n_+ - n_- \]
\[ n_+ \theta^2 = 4 e^{-\gamma/kT} \]

When the number of kinks per unit length enter into the growth rate, conditions expected to apply to growth from solution, then
\[ v \propto \sqrt{4 e^{-\gamma/kT} + \psi^2} \]

Or when \( \psi \) is small
\[ v = v_0 (1 + \beta \psi^2) \]

where \( v_0 \) = rate of growth for \( \psi = 0 \)
\[ \beta = \frac{e^{\gamma/kT}}{\psi} \]

Thus, the rate of growth increases with the angle of inclination to a close-packed direction. After time \( \delta t \) the distance of advance of a section of the step is
\[ s_n = v \cdot \delta t = v_0 (1 + \beta \psi^2) \delta t \]
By the forward movement of the step each element of arc suffers a rotation
\[ \delta \psi = \frac{\delta}{\delta s} (\delta \kappa) = v_0 \delta t \cdot 2B \psi \frac{\delta \psi}{\delta s} \]
\[ = -s \rho \cdot 2B \psi \]

Where \( s \rho = v_0 \delta t \equiv \text{advance of close-packed section} \)
\( \rho = \text{radius of curvature of step} \)

The total increase in curvature
\[ \delta \left( \frac{1}{\rho} \right) = -\left( \frac{1}{\rho^2} \right) s \rho - \frac{\delta}{\delta s} (\delta \psi) \]
\[ = -\frac{1}{\rho^2} s \rho - 2B \left( \frac{1}{\rho^2} \right) s \rho \]
\[ \frac{d \rho}{d s} = 1 + 2B \]

\[ \rho = \left( 1 + 2B \right) \rho + \rho_0 \]

where \( \rho_0 \) radius of curvature of original arc

When \( \rho_0 \) is very small
\[ \frac{\rho}{\rho_0} = 1 + 2B \]

i.e., the ratio of the radius of curvature to the distance from the centre is constant.

The dependence of growth rate on orientation should allow a polar diagram to be drawn which relates these two quantities, a straight edge corresponding to a sharp minimum (i.e., a direction of close-packing). Thus, a step, originally of any arbitrary form, should, after growth from solution, take an outline corresponding to the symmetry of the face, and should form a figure whose dimensions will governed by the polar.
This very brief account shows the predictions of the theory to be precise, and, therefore, capable of definite experimental verification. Moreover, the growth rates predicted by the theory appear to be in general agreement with experimental evidence (Cabrera and Burton, 1949). Thus, when the supersaturation first reaches the appropriate, very small, value growth will suddenly start and proceed at a rate proportional to the square of the supersaturation. As the supersaturation increases, a linear law of proportionality will then hold. This agrees with the experiments of Volmer and Schultze on iodine.

The sitting of the growth centres in the centres of faces of small crystals as observed by Bunn and Emmett is precisely what one would expect on the dislocation theory. Due to their very high energy per unit length, dislocations are effectively under tension and would usually emerge more or less normally at a crystal face, in order to keep themselves as short as possible. Those of early origin should lie near the foot of the normal to the crystal face from the original seed, and, therefore, for regularly developed crystals, near the centre of the face.

The dislocation theory is also capable of explaining the sudden stoppages or onset of growth, observed in the Bunn, Berg, Humphries-Owen series of experiments, as due to the movement and generation of dislocations. The main difficulty confronting the dislocation theory of growth is not the formidable amount of experimental evidence to be satisfactorily
explained, for in this it is very much more fruitful than any other type of theory, but rather the explanation of the origin of the dislocations. This will be dealt with in the next chapter.

Having now traced the evolution of the main theories of crystal growth and given an account of the most important experimental work by which these theories should be tested, it can be seen that only the dislocation theory is capable of overcoming some of the formidable difficulties. Moreover, it appears to be in accord with almost all the experimental evidence. This theory has also the incidental, but considerable advantage of linking together two sections of physical phenomena - the growth of crystals and their mechanical properties. If correct, this theory then marks a considerable advance, not only in the theory of crystal growth, but also in the theory of the solid state. The experimental evidence to be presented later is in such exact accord with the predictions of this theory that there appears to be no alternative conclusion to be drawn other than that beryl crystals do grow by growth fronts spreading from dislocations. Taking into account the very serious shortcomings of all the other theories, this would seem to establish the general validity of the dislocation theory of crystal growth.
CHAPTER II

Theory of Dislocations

The object of this chapter is to provide a brief general account of some of the more important properties of dislocations, in order that the dislocation theory of crystal growth, and the experimental results to be observed later, will be more readily understood. No attempt is made to give a critical review of the subject; for an excellent review see Cottrell (Cottrell, 1949).

The concept of a dislocation, as developed by Volterra in the theory of continuum elasticity, was introduced into the theory of real crystalline solids in order to account for the observed phenomena of plastic deformation.

In strained metals it was observed that slip lines marked important crystal planes, and it was shown that the plastic strains could be resolved into simple shears along these planes, these shear stresses determining the plastic flow. Thus, plastic flow must take place by the sliding of certain atomic planes over each other, the glide taking place in the direction of closest atomic packing of the planes, and not in the direction of maximum resolved shear stress, so that the structure in the glide plane must remain crystalline. Atoms in a crystal are not rigidly bound to any one point and thermal vibrations and local irregularities must make the forces acting over glide planes non-uniform. If we consider an upper plane as sliding over a lower plane it can be seen that, at any instant, different portions of the upper plane will have slipped by different amounts. The boundaries
between these regions of different degrees of slip are defined as dislocations.

As the glide plane possesses a discrete atomic structure the differences in amounts of slip between neighbouring regions are limited to the value of the atomic spacing, or possibly a small multiple or fraction of this spacing. The differences in the amount of slip across a boundary defines the strength of the dislocation.

A necessary consequence of the discrete atomic structure is that all dislocations must be made up of a few standard types. The first type is the Taylor, or edge dislocation, which was first considered by Taylor simultaneously with Orowan and Polanyi (Taylor, 1934). In Fig. 5a the region ABED has slipped over the glide plane ABCD in the direction A'B', while the region FEDC has not slipped. The dislocation line EF divides the slipped and unslipped regions. For a dislocation of this type the slip direction is perpendicular to the dislocation line. A section normal to EF will have the atomic structure shown in Fig. 5b. The atoms in the upper half-crystal are compressed along the slip direction, while those in the lower half are extended.

The second type of dislocation is the screw dislocation (Burgers, 1939, 1940). A part ABED of the slip plane (see Fig. 6a) has slipped in the direction EF, while the remainder has not slipped, the boundary EF being a screw dislocation. It will be seen that in this case the line of the screw dislocation is parallel to the slip direction and not perpendicular to it, as was the case for an edge dislocation. Fig. 6b shows the atomic
arrangement of a screw dislocation. This is a plan in which the full lines and circles represent the atoms if the upper plane and the others are the lower plane.

In the case of both edge and screw dislocations, dislocations of opposite sign can exist, two similar dislocations of opposite sign being capable of self-annihilation. In the case of screw dislocations the terms right-handed and left-handed are usually applied.

Both edge and screw dislocations constitute linear discontinuities but dislocations of any arbitrary non-linear form can be made by joining together segments of edge and screw dislocations, and in actual crystals it is probable that dislocations are of this compound type and rarely of a simple type.

An important property of any type of dislocation line is that it can never end at a point in the interior of a crystal (Burgers, 1939, 1940). Either closed chains of compound type must be formed, or the dislocation must terminate at the crystal surface. This can be seen if the edge dislocation of Fig. 5a is assumed to stop at F'. This defines the slipped region as ABEF' and therefore the line A'F' is a screw dislocation. Similar reasoning can be applied to a screw dislocation.

It will now be readily appreciated that a screw dislocation emerging at a crystal face must have a molecular terrace associated with it, but it should be noticed that any dislocation will so behave which has a component of its displacement vector normal to the surface. For simplicity, such dislocations are usually termed screw dislocations in the dislocation theory of
crystal growth.

It can be seen from consideration of Fig. 6a that if a screw dislocation of opposite hand was produced in a precisely similar manner then, denoting the latter case by by dashed letters, one could join the section AB to A'B'. The surface containing DFAA'T'D would then display a short slipped section FAA'T', and if this surface be considered as a crystal face then this slipped section will consist of a short area of exposed lattice limited at either end by a screw dislocation. We shall return to this point during the discussion of experimental work.

One of the primary properties of a dislocation is its high mobility along a glide plane, a simplified treatment of such movement giving the external forces necessary as being, to a first approximation, vanishingly small. To a better degree of approximation a finite, but small, force is necessary. Such mobility probably provided the answer to the sudden commencement, and stoppage, of growth often observed in the experiments of Bunn, Berg, and Humphries-Owen.

Transition surfaces in a crystal, such as surfaces between mosaic blocks, or crystallites inclined at a small angle to each other, can be treated as assemblies of dislocations. It is geometrically possible to join two crystals in arbitrary orientation to each other by means of a complex transition surface composed of sets of edge and screw dislocations, and it can be shown that, despite the force of repulsion which normally exists between them, dislocations of the same sign will tend to assemble at such surfaces. As crystals are normally imperfect on quite a
large scale, one would expect to find groups, or irregular lines of dislocations on a surface due to the presence of lineage boundaries and the like.

Although dislocation theory was applied to the study of the mechanical strength of solids with considerable success, the question of the origin of dislocations was a major problem for which no satisfactory solution had been found. Although it is generally agreed that applied stress can multiply the number of dislocations present in a crystalline body, yet the energy of dislocations, of the order of one electron volt per atom plane, is so high that there can be little chance of the initial dislocation in a perfect body being formed by thermal fluctuations, even if the body is highly stressed.

This difficulty appears to be momentarily solved if one considers the dislocation theory of crystal growth as valid, for then only crystals containing dislocations can grow from the original crystalline germ. However, this is only the translation of the problem into other terms, for one must then explain how the dislocations came to be formed in the crystal \textit{ab initio}.

A number of possible causes have been suggested (Frank, 1949 a). Once the initial (three-dimensional) nucleation of a crystal takes place the supersaturation is very high, much higher than is necessary even for Becker-Doring conditions for two-dimensional nucleation. It is possible, therefore, that layers are nucleated in improper (e.g. twin) positions and
proper positions simultaneously on the same face. Where the layers meet a dislocation will exist.

It is also possible to have one-dimensional dislocations in the edge row of a growing terrace (Frank and Van der Merwe, 1949). These dislocations have an energy similar to the latent heat of evaporation of a molecule, and can exist in thermal equilibrium, unlike a normal type of dislocation. These dislocations, trapped in the edge row at the very high supersaturations subsequent to the original nucleation, develop into two-dimensional and subsequently three-dimensional dislocations.

The addition of a foreign molecule to a lattice will result in the development of curvature in the lattice. This will result in stress in the surface, which can produce surface faults which become true dislocations when buried under additional layers. Such a mode of generation of dislocations will be considered later in more detail in relation to the experimental results.

Once systems of dislocations are present, it is probable that the stress they cause in a perfect crystal compels the formation of further members of the system in growth. Thus, sub-grain boundaries are propagated in lineage structure. Also once dislocations are present, any mechanical stress producing plastic yield is likely to result in the formation of new dislocations.
Multiple Beam Interferometry

Section 1. Theory

Multiple beam interferometry is now a well established technique and no attempt will be made to give a general discussion of the theory. A full general treatment of multiple beam interferometry has been given by Tolansky (Tolansky, 1948) and various treatments of specific sections are available (Tolansky, 1944a, 1944b, 1946a, Tolansky and Wilcock, 1947, Brosset, 1947a, b, Holden, 1949). Only the most important aspects of the theory and those which are of particular importance in the study of surface topography will be considered briefly here.

General considerations

The types of fringes used in this work consisted of fringes of equal thickness, usually called Fizeau fringes, and fringes of equal chromatic order. Both types of fringes were used in transmission and reflection. It has been shown by N. Barakat of this Department, in unpublished work, that the basic law of interference

\[ n \lambda = 2\mu t \cos \theta \]

should be modified by adding an additional term to the right hand side to allow for the phase change on reflection. When working with a very low order of interference this term produces an uncertainty in the assignment of the current order to any fringe, but this is not normally of importance in topographical
In order that sharp fringes should be obtained in the interference system produced by two highly reflecting surfaces inclined at a small angle to each other, it is necessary that the Airy summation should apply. The path difference between successive reflected beams is not constant, but alters progressively with the order of reflection. Thus, if we consider a number of beams interfering at a point in space, it can be seen that the phases of beams of higher order gradually get out of step with the first beam. Consequently, instead of assisting the Airy summation series, these beams will begin to oppose it, and ultimately, when the retardation of a beam is $\frac{\lambda}{2}$, the conditions for the formation of sharp fringes will tend to be destroyed.

The path difference between the first and $n$th beams is $2nt - \frac{n}{2} \Delta \theta t$. Hence, the term $\frac{n}{2} \Delta \theta t$ should be restricted to a maximum value of $\frac{\lambda}{2}$. Examination of this term immediately shows that in order to retain very sharp fringes $t$ must be reduced to a certain critical value. This is the factor which is of paramount importance. The value of $t$ is dependent on the value of the dispersion (i.e., the number of fringes per cm.) which it is necessary to use. Some values are tabulated below.

<table>
<thead>
<tr>
<th>Number of fringes per cm.</th>
<th>1</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical $t$, mm.</td>
<td>1.26</td>
<td>0.12</td>
<td>0.0001</td>
</tr>
</tbody>
</table>
| $d_{60}$, mm.             | 0.25| 0.025| 0.0025 | Table I
It is thus possible to retain very sharp fringes, provided that the value of $t$ is below the critical value, and utilise up to 90 multiple reflexions within the wedge.

The fringe half width $S$ is determined by the reflectivity $R$, according to the relation

$$S = \frac{1-R}{\sqrt{R}}$$

It is possible to use reflectivities of up to 94%, thereby producing fringes whose half width is only one fiftieth of the distance between successive orders.

The linear displacement of successive beams along the surface is obviously of importance when the surface under examination has a complex topography. The beams must have scanned as small an area as possible if confusion is not to occur, due to beams from different topographical features meeting at arbitrary points. The third row in the table above gives some values of this linear displacement between the first and sixtieth beams.

It can be seen that the wedge thickness $t$ should again be reduced to very small values in order to minimise this effect, and, even so, small scale detail in the fringes should always be interpreted with caution.

If a deviation exists from perfect parallelism in the incident beam, a broadening of the fringe will occur. Assuming that the maximum permissible increase of fringe width is one fifth of the half width, then in typical conditions the following table gives the maximum permissible angular deviation from perfect parallelism.
The third row represents the maximum permissible source size when a collimating lens of 10 cm focal length is used. It can be seen that these conditions can be quite easily satisfied.

The increase in fringe width due to non-parallel light takes place on the side of greater gap. This is important in surface topography as an increase in source size often enables one to differentiate directly between hills and valleys.

The line width of the source (δλ) must also be kept below a certain value dependent upon the wedge thickness. The fourth row in Table II gives the permissible values for various values of the wedge thickness. If a high pressure mercury arc is used which is slightly under-run, these conditions can normally be satisfied. Some specimens, however, possess features of such a height that it is necessary to seriously under-run a high pressure mercury arc if considerable fringe broadening is to be avoided.

It can be seen that, in the case of all the factors discussed, a wedge thickness of the order of 0.001 mms. will ensure very good fringe definition, while allowing considerable latitude in several other factors. Hence, it must always be the aim in topographical studies to reduce the wedge thickness to this value, or as near to this value as the topography of the specimen will permit.

<table>
<thead>
<tr>
<th>λ (mm)</th>
<th>1</th>
<th>0.1</th>
<th>0.01</th>
<th>0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ (°)</td>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.001</td>
</tr>
<tr>
<td>d (mm)</td>
<td>0.2</td>
<td>0.02</td>
<td>0.0002</td>
<td>0.00002</td>
</tr>
<tr>
<td>δλ (Å)</td>
<td>0.6</td>
<td>0.06</td>
<td>0.0006</td>
<td>0.000006</td>
</tr>
</tbody>
</table>

Table II
Choice of objective.

The value of the aperture of the microscope objective used to observe Fizeau fringes is important. Should it be insufficient, then the objective acts as a mask. Consequently, all the beams are not collected, the fringe image is broadened and secondary maxima may appear. It has been shown that at least 40 beams should be collected by the objective.

The angle between the first and \( n^{th} \) beam is \( 2n \) times the wedge angle and it can easily be shown that an objective of N.A. 0.3 will, under normal conditions, collect a sufficient number of beams. Indeed for the low magnifications which, as will be seen later, are particularly advantageous in the study of surface topography, an objective of N.A. 0.1 is frequently adequate and a numerical aperture of 0.15 is almost always adequate.

Ghost systems

Theoretically, every glass surface in the optical train is capable of producing ghost sources with their own fringe systems. In practice the only important ghost system in the study of crystals of high refractive index is normally that produced by a face making a slight angle with the actual face under examination. This ghost system cannot be eliminated but seldom constitutes a serious nuisance.

It was also found that when working in reflexion the 45° reflector of a metallurgical microscope produced a parasitic fringe system which was very difficult to eliminate.
Localisation of the fringes

The interference system is localised on a surface (the Feussner surface of zero order (Feussner, 1927)) lying along the wedge. (There are an infinite number of other planes of localisation which are of no practical importance). The Feussner surface is of practical importance in topographical studies in as much as the matching of a complex area against an optical flat may result in a surface of localisation in which the gradients are steeper than those on the specimen. Consequently, different areas of the surface in the field of view may not lie in the focal plane of the objective simultaneously and the appearance of the fringes in these different areas is therefore dependent upon the focal setting.

Multiple beam Fizeau fringes in the reflected system

The reflected system can be used when the crystal under examination is opaque, of such a habit to render the obtaining of a normally incident beam very difficult, or when an otherwise satisfactory specimen contains internal scattering planes which partially ruin the collimation of the incident beam, causing a blurring and a broadening of the fringes.

Although fringes of the reflected system are inherently sharper than the corresponding transmitted system they have the disadvantage that the intensity distribution of the fringes, as obtained on a photographic plate, is critically dependent on focus. Consequently great care must be taken that the objective is focused exactly on the Feussner surface, not always easy, or
even possible experimentally, if quantitative deductions are to be made.

The theory of the reflected system has been treated by Hamy (1906) and Holden (1949). It need only be mentioned that the considerations discussed above can be taken to apply generally to the reflected system.

Points of difference are (a) the effect of increase in line width of the source, which tends to make the maxima extend into the region of the minima (i.e., the fringes) thus producing an apparent sharpening, (b) the visibility of the reflected system. The visibility is always less than unity due to the absorption of the silver films and also decreases very rapidly with increase in the number of incident wavelengths. Monochromatic light only, therefore, can be used.

Resolution using Fizeau fringes. When an objective is used to view Fizeau fringes, it is collecting almost plane waves. This corresponds to the worst possible working conditions for lateral resolutions of the true details of the surface, and in fact, the resolving power of the objective is approximately half its nominal value.

This limitation is not as harmful as might at first appear, for a high lateral resolving power is seldom necessary in topographical studies, particularly in the case of crystals.

The resolution parallel to the axis of objects introducing a phase difference is, of course, enormous, and comparable to that of the electron microscope in the other two dimensions.
fringes of equal chromatic order

These fringes provide a true line section of the surface, without the need to adjust the wedge angle to make fringes run across the area being examined. It should be stressed, however, that a true line section is obtained only as far as the slit of the spectrograph. The shape of the fringes seen in the eyepiece, or on a photographic plate, has been shown by N. Barakat to be dependent on the dispersion of the instrument. If it is only required to learn the general nature of the topography of a surface, and not, for example, the types of the curvature displayed, then these deviations from true correspondence may be ignored.

The effect of diffraction.

Diffraction of the incident plane waves must take place at surface steps. Even at uni-molecular steps, as will be seen later, the effect of diffraction is quite considerable. It is therefore necessary to consider the effect of diffraction on multiple beam fringes.

That this effect does exist can be seen on many interferograms in which the fringes are running across sharp steps, or, particularly, narrow grooves. In the latter case a portion of the fringes appears to run along the edge of the groove in both directions. Diffraction effects of this type are always particularly noticeable in the reflected system.

The obvious way in which to minimise the effects of diffraction at a step is to run the fringes across the surface so that they are perpendicular to the edge of the step. Even so the
the behaviour of the fringes near the step edge must always be suspect, and in the case of measurement of step height portions of the fringes should be used which are from the immediate vicinity of the step. In the case of fringes running almost parallel to a step edge, a serious disturbance may result, particularly in the case of steps of several hundred Å or more, in height. The effect of diffraction may then result in a displacement of the fringe so that the basic law of interference, \( k\lambda = 2n\pi \), is no longer applicable to the system.

In the case of very narrow grooves or flat-bottomed channels the effect of diffraction is such that the fringe no longer delineates the true contour. A groove some 0.003 mms. in width and 200 Å in depth was found to produce a very marked diffraction wing, covering most of the area of the groove for some distance from the fringe. It would certainly be unjustifiable to draw any conclusions from the fringe patterns of the shape of features of this size. In general, definition of small features improves by working with a very low order of interference. This must also reduce the linear displacement of the beams to a very small value, hence aiding good definition. For features less than 0.01 mms. in width, the effect of diffraction is probably always sufficient to require extreme caution in deductions of the shape of the feature.
Section II. Experimental techniques.

The following experimental conditions must be satisfied if the full power of multiple beam fringes are to be utilised.

(a) The surfaces must be coated with a highly reflecting layer.
(b) This layer must contour the surface exactly.
(c) The surfaces should, preferably, not be further apart than a few wavelengths of light.
(d) The incident light should be normal.
(e) A parallel beam should be used (with a 1° - 3° tolerance)

It is the satisfaction of condition (c) which must be the main experimental aim, for once this is satisfied, the tolerances for conditions (d) and (e) are comparatively easy to attain. Unfortunately, it is not always possible to achieve this in the study of the topography of crystal surfaces, for the surface under examination very often possesses sharp local protuberances several wavelengths in height, and frequently much higher than this.

Moreover, many crystals, and all the crystals studied in this work, are considerably harder than glass, so that great care must be taken to see that these protuberances do not mark the optical flat. It is possible to avoid this danger and also to arrive at an accurate estimate of the spacing of the main portions of the wedge by utilising both the green (5,461 Å) and the yellow doublet (5,770 Å and 5,791 Å) lines from a high pressure mercury arc.

It can be shown that the thickness of the wedge

\[ t = \frac{1}{2} \frac{\lambda}{d\lambda} \frac{d\lambda}{\Delta \lambda} \leq 0.6 \frac{\lambda}{\Delta \lambda} \text{ mms.} \]
where \( \frac{d_x}{\Delta x} \) spacing of doublet as a fraction of an order.

Hence, by noting the spacing of the doublet over the whole of the surface both the general spacing and any local variations are immediately obvious. The surfaces are therefore comparatively easily adjusted to the minimum permissable spacing.

The way in which the flat and the specimen were mounted was as follows. The flat fitted snugly into a turned brass base, designed to mount on a microscope stage, so that the flat was always perpendicular to the optic axis. From this brass base 3 threaded rods (of 8 B.A. thread) projected, these rods being spaced at equal intervals around the flat. Around each rod was a light spring, being wound so that ample clearance space existed between the rod and the spring. A flat brass ring, which carried the specimen had 3 clearance holes drilled in it, so that the ring dropped down the rods on to the top of the springs. Small nuts were then screwed down the rods to press on the flat ring, so that the crystal surface approached the flat. After the preliminary adjustments, a "tommy bar", some 6 inches in length, was used to adjust the position of the specimen. This "tommy bar" fitted into holes in the nuts and adjustments of the position could be made to about \( \frac{1}{200} \) turn of the thread, the springs on which the brass ring pressed ensuring that there was no appreciable backlash.

This mount was used on a Vickers projection microscope on which a short optical bench replaced the usual condensing system, so that a parallel beam of light could be produced. This collimator arm could run down a mechanical way so that the interfer-
ence system could be viewed at will in either transmission or reflexion with a minimum of trouble. The two sources, a high pressure mercury arc and a clockwork fed carbon arc, could be used in the normal way as either a transmission or metallurgical microscope.

Multiple beam interference systems are extremely sensitive to vibration or mechanical shock. This type of microscope is almost completely free from vibration and this property, and its extreme flexibility, make it an ideal instrument for work of this type.

A Hilger constant deviation spectrograph could be coupled with this microscope when fringes of equal chromatic order were used. Unfortunately, it was necessary to use a spectrograph of so low a dispersion, and of such limited focussing properties, that the great power of fringes of this type was partially masked.

The high pressure mercury arc on this microscope was run in series with a rheostat. Adjustment of the rheostat enabled the source line width to be reduced very considerably. This proved to be very useful when the topography of the surface made it necessary to work with a comparatively widely spaced wedge.

In all topographical work it was found very advantageous to work at high dispersion. This has the advantages of:-

(a) resulting in great sensitivity of the fringes to changes in height.

(b) allowing a comparatively low magnification to be used, while still ensuring that a sufficient number of beams are collected. This means that the topography of crystal faces can be sur-
veyed comparatively rapidly and that the relationship between widely spaced areas of the same face can be immediately seen. (c) greatly simplifying the interpretation of the fringe patterns. At high dispersions the reference plane (i.e., the optical flat) makes only a very slight angle with the surface, so that the fringes approximate to geographical contours. At low dispersions this is often very far from the case.

There is one apparent disadvantage of working at high dispersion - the considerable spacing between fringes, which if only one wavelength was used would necessitate inspection of the surface at many wedge angles in order to ensure that any small feature was not missed. In fact, by using the mercury green and yellow doublet lines this difficulty is avoided, for the presence of three wavelengths is roughly equivalent to simultaneous inspection at three wedge angles using one wavelength. There are also other advantages to be gained from using these three wavelengths, as has been explained above.

The main advantage of fringes of equal chromatic order in topographical work is that, within the limitations previously discussed, these fringes provide a true section along any line on the surface. Fizeau fringes are therefore used for the general survey and fringes of equal chromatic order for the investigation of particular features.

The intensity of the fringes is normally rather low. In order to keep the exposure time down to a few minutes (sometimes less) the general practice is to use either Kodak P1200 or
Ilford HP3 plates, both of which are panchromatic and fast. In the case of Fizeau fringes in the reflected system the intensity is often sufficiently high to make it both possible and advisable to use a slower plate.
Section III. The Silvering Technique

The immediate aim of coating a surface with a film of silver is to achieve a high reflectivity, but the achievement of low absorptions in such films is of equal importance in interferometry. For a given reflectivity the necessary consequence of high absorption is low transmission, the latter producing a low intensity in the transmitted system, while high absorption results in very low visibility in the reflected system. High absorption thus results in

(a) excessive exposure times for the transmitted system
(b) considerable difficulty in focussing either the transmitted or reflected systems on a screen. Consequently, the interferograms are liable to be slightly out of focus, a considerable increase in fringe width being thereby produced. Equivalent results could therefore be obtained by using a film of much lower reflectivity and greater transmission.

One of the main requirements is therefore that the silver films should have low absorption. This requirement is satisfied by thorough cleaning of the surface and by deposition of the silver film by thermal evaporation in high vacuum. For general treatments of the technique of evaporation of silver films in vacuo see Strong (1940), Olsen, Smith and Crittenden (1945) and Tolansky (1946, 1948).

Surface cleaning.

The surfaces to be silvered are, if necessary, first washed with soap and water to remove gross amounts of grease contamination. Optical flats are then cleaned by rubbing...
the surface gently with cotton wool damped with concentrated hydrogen peroxide. The latter substance removes many organic materials and is also very effective in removing silver from a surface which has to be re-coated. The surface is then polished with successive pieces of clean cotton wool and the state of cleanliness of the surface can be tested by means of "breath figures." This is done by breathing gently on the surface, the moisture condensing into a film of minute droplets which persist on imperfectly cleaned areas. On a very clean surface either an invisible film is formed or the opaque "figure" disappears almost immediately.

In the case of crystals highly resistant to chemical attack concentrated acids can be used for cleaning. It is advisable to wash off such acid with distilled water rather than merely polishing the specimen until it is quite dry, as the acid tends to persist in surface cracks even in a high vacuum, and will attack the silver film after it has been deposited.

All specimens are subject to a final cleaning by means of a glow discharge in vacuo.

The evaporation equipment.

The great majority of work was carried out using a commercial type of evaporation plant, an Edwards E.3 coating unit. In this equipment a 6 inch rotary pump of speed 10 litres per second, backed a type 9/0/3 oil diffusion pump which had a speed of 1,000 litres per second at a pressure of 2 $10^{-4}$ mms. of mercury.

The high vacuum chamber was made of pyrex having a diameter
of 18 inches and a height of 30 inches, and was sealed to a machined base plate by an "L" section rubber gasket. The chamber could be isolated from the diffusion pump by a high vacuum valve. A three way valve in the backing line enabled the rotary pump either to back the diffusion pump, or to evacuate the chamber while the diffusion pump was isolated, or to open the rotary pump to the atmosphere.

A molybdenum filament was always used for the evaporation of silver. The silver was placed in a depression in the filament, a Variac control enabling a current of 0-120 amps to be passed through the filament. A shutter was placed above the filament so that the silver could be fused and impurities burned off, before the specimens were exposed to the material evaporating from the filament.

Ring electrodes were fitted within the chamber. The power for the glow discharge was supplied by an H.T. transformer rated at 3.3 kV, 500mA. A Variac control allowed of control of the primary current between 0-10 amps.

The work table stood 50cms above the filament and the variation in the thickness of silver deposited per unit area across this table was calculated to be not more than 1%. The work table and all specimen supports were made of aluminium in order to restrict to a minimum any sputtering caused by the glow discharge.

The pressure in the chamber was indicated by a cold cathode Philips ionisation gauge of range 0.1 to 5 microns. In the backing line a Pirani gauge indicated the pressure.
Cycle of operation.

The cleaned specimens were placed face downward on the work table and the chamber sealed to the base plate. With the diffusion pump running, but isolated from the chamber, the rotary pump evacuated the chamber down to a pressure of about 0.2 mms of mercury. Ionic bombardment by glow discharge was then started and continued for some 4 minutes. Because of the possible local heating effects on crystals of the full voltage of the glow discharge, the current in the primary was regulated so that the output of the secondary of the transformer was only some 60mA.

With the discharge still running the three way valve was altered so that the rotary pump backed the diffusion pump and the high vacuum valve was then slowly opened. The pressure was soon reduced to a value such that the discharge blacked out. From the time that the high vacuum valve was fully open it was possible to reduce the pressure in the chamber to approximately $10^{-5}$ mms in some 10-20 minutes.

When the silver had been fused and was evaporating readily, the shutter was moved and the filament viewed, looking downward through one of the specimens. A visual estimate was made of the reflectivity of the silver by the intensity and colour of the transmitted light; the necessary values having been learned by experience.

Contouring of the silver films.

All the evidence from multiple beam interferometric work supports the view that silver films
contour the surface of the substrate to within very close limits (Tolansky 1948). Further valuable support is given this view by measurements by an optical method of the height of cleavage steps on unsilvered mica surfaces (Bond, 1933), which agree very well with those determined by interferometry using a silvered surface.

Evidence will be presented later which very strongly supports the observation of a step step 4.6 Å high when viewed at high magnification with a metallurgical microscope, with a silver film of some 400 Å thickness deposited on the substrate. The step is made visible by a diffraction effect, so that not only must the silver contour the surface, but it can also only "smooth out" the steep edge of the step to a very limited degree.

This is supported by electron microscope studies which show that the distance of migration of silver atoms on the substrate when deposited under normal conditions is not more than 500 Å (Picard and Duffendack, 1943). The mobility time of such atoms has also been shown to be very small (Levinstein, 1949). From a study of the growth of thin metallic films, Levinstein has suggested that by using a high rate of evaporation the mean distance of migration of the molecules may be considerably reduced, consequently resulting in better contouring of the surface. It would therefore seem desirable to evaporate the silver while using the maximum permissible filament current.
CHAPTER IV

The Observation of uni-molecular steps

Section 1. Experimental application of an edge diffraction effect.

Nature of effect.

During the course of interferometric investigations of the topography of prism faces of beryl crystals it was found that interpretation of the interferograms was much simplified if these were compared with a photomicrograph of similar magnification. This was most clearly demonstrated by Figs 7 and 8. Comparing the two figures it will be seen that the lines on the photomicrograph correspond to surface steps which follow the contours of the crystal face. In areas where no steps, or but few, can be seen in Fig 8, plane areas are seen in Fig 7, these plane areas being parallel to within very close limits.

More detailed investigation proved these step free areas to be perfectly plane and very closely parallel, the apparent curvature and varying orientation in Fig. 7 being due to a fine scale step structure either not resolved, or not clearly shown, in Fig. 8. The crystal is then built up of plane parallel surfaces separated by steps of varying height.

Investigation under the microscope at high magnification revealed a great number of lines showing the same type of intensity distribution and focal behaviour as the surface steps, and all following, as far as could be determined, contour lines
of the surface. Hence, lines of this type on faces of beryl must always represent surface steps.

**Effect of silvering the crystal surface.**

The surface steps were at first observed on the crystal face in its natural untouched state, and it was found that photomicrographs, using plates of very high contrast (Kodak, B20) were capable of revealing more than could be seen by eye. The technique used at this stage consisted in observing the crystal surface in reflexion, using a metallurgical microscope. Observation in reflexion was used in order to increase the optical height of the steps (their apparent height being 2t instead of (μ -1)t as in transmission) and also to obviate the effect of any opacity or inclusions in the body of the crystal.

An attempt was made to use medium and high magnifications while employing this method of observation, but this was found to be unsatisfactory. A crystal face was therefore silvered in the usual way and both visual and photographic comparisons were made of silvered and unsilvered parts of the same step. Even at low magnification the silvered portion of the step was found to have a much higher visibility than the unsilvered portion, this difference being much more marked at high magnifications. The nature of the intensity distribution in the line denoting the step did not appear to alter on the silvered portion. This is what one would expect from the evidence of multiple interferometry that such silver films, when properly deposited, contour the surface to within very close limits.
Effect of step height and nature.

The intensity distribution delineating a step edge is, of course, a diffraction effect. A marked distinction was found to exist between this effect, on beryl crystals, for steps of considerable height (i.e., not less than several hundred Å in height) and lesser steps. This distinction can be immediately explained by reference to Figs. 7 and 8 for it can be seen that all the very high steps are composed of steep slopes of finite extension, while the lesser steps fall very sharply and appear to be of the discontinuous type.

It will be shown later that these "lesser" steps are normally uni-molecular, and the step edge must therefore be of a truly discontinuous nature, a factor which must influence any diffraction phenomena.

Experimental technique.

The experimental technique which was developed for step observation is extremely simple. The specimen to be examined is first silvered under conditions usual for multiple beam interferometry, the reflectivity of the reflected silver layer not being critical, a value of 85%-94% being convenient. The surface is then examined in reflection by a normal type of metallurgical microscope, using bright field illumination with the field iris stopped down to give a fairly narrow illuminating beam, the steps being visible immediately the surface comes in focus.
The angular aperture of the illuminating beam can be varied a little depending upon the height of the step under observation. The optimum value for the field iris can easily be determined by closing it down to its lowest limit and then slowly opening it. A point will soon be reached when the visibility of the edges decreases very rapidly and one should keep the field iris stopped down well below this value. (A convenient value of the angular aperture of the illuminating train for uni-molecular steps is about 4.5°).

The diffraction effect is actually an in-focus effect for, as will be shown below, the intensity distribution is simplest in nature, shows the maximum peak intensities, and is of least lateral extension, when the focal plane of the objective is coincident with the plane of the crystal surface. Under these circumstances the edge is seen as a luminous line, with a narrow minimum on the side corresponding to an increase in height. These luminous lines are superimposed on a bright field.

If, however, one goes slightly off focus the minimum becomes broader and more obvious, the maximum decreasing in peak density. It is then much easier to see the dark line of the minimum superimposed on the bright field and this method has been found more convenient, both for visual observation and for focusing on a screen for photography. The diffraction effect is, therefore, used as an out of focus effect although, of course, there is no particular merit in this except on the grounds of convenience and personal preference.
Investigation of the diffraction effect in relation to the focal setting

(a) Bright field.

In order to investigate the nature of the diffraction effect, a series of observations were made on a step on a prism face of a beryl crystal. Evidence will be presented below to show that this step is 7.9 Å in height. Preliminary observations showed the diffraction effect was visible over a considerable focal range and a series of observations was therefore made at intervals of one micron traverse of the objective, as read from the fine focus scale.

The objective used was of normal metallurgical type, of focal length 4 mm. and N.A. 0.95. (It was later found that this objective was slightly off centre with respect to the microscope. This does not effect the findings if the same small portion of the field of view is always considered). Considering the full aperture to be used, the depth of focus of the objective is 0.14 microns and this can be neglected in comparison to the distance of one micron between successive positions of the objective. However, a narrow illuminating pencil was used, and although the diffracted waves would be theoretically expected to fill the whole of the aperture, evidence exists to suggest that an objective of N.A. 0.45 is sufficient to collect most of the diffracted wavefronts. A numerical aperture of this value corresponds to a depth of focus of approximately 0.6 microns. This should be borne in mind.

A total traverse of 10 microns was made, the position of the objective being originally drawn back from focus, proceeding...
through focus to beyond-focus positions. Positions 3-10 of this traverse are shown in Figs. 9-16. (The peak intensities of the diffraction maximum and minimum were so small in some of the positions that it was necessary to print out the original plates on contrasty paper. The original relationship of the intensities was therefore sacrificed in order that the nature of the intensity distributions should be clearly shown).

The plates taken at positions 1 and 2 were too faint to print satisfactorily, but were similar to the intensity distribution in position 3 (Fig. 9). At position 1 a central broad maximum is symmetrical between two slightly broader minima, the whole distribution being diffuse in nature.

The intensity distribution is a little more clearly defined at position 2. The pattern is precisely similar to that of position 1, except for a possible slight asymmetry of the minima.

The intensity distribution sharpens a little at position 3 (Fig. 9). In this case the asymmetry of the minima is more apparent and an additional low narrow maxima has appeared on the upper side. (In all cases in these Figs. the straight section of the diffraction pattern running from the triangular area is considered).

By position 4 (Fig. 10) the total width of the pattern has decreased. The form of the intensity distribution is much the same as for position 3, with more marked maxima and minima.

An obvious change has occurred by position 5 (Fig. 11), the peak intensities of both maxima and minima being greater. The maximum on the upper side is also now quite obvious and the
central maximum shows a definite asymmetry.

Position 6 (Fig. 12) shows a sudden sharpening of the whole pattern with a marked increase in the peak intensities. The asymmetry of the central maximum seems to have almost disappeared and it appears to be situated symmetrically between two outer maxima, one beyond each minimum, although the lower maximum is less marked.

A sharp change takes place by position 7 (Fig. 13) and the pattern is now almost perfectly symmetrical. The central maximum has disappeared and the pattern, now very narrow, consists of a central minimum between two almost equal maxima. (The occasional faint dotting on the minimum is probably due, not to faint traces of a maximum, but to entraneous influences to be discussed later.)

By position 8 (Fig. 14) the pattern is again broadening with decreasing peak intensities. The lower maximum is now split into two parts by a very narrow minimum. A very faint central maximum is possibly appearing again.

After this point the peak intensities decrease rapidly and the pattern broadens for position 9 (Fig. 15). A definite, but still rather faint, central maximum can now be seen to exist, while both outer maxima are single.

The pattern seen at position 10 (Fig. 16) is still broader and fainter. The central part of the pattern is quite symmetrical, consisting of a central, narrow, deep minimum, on either side of which are faint maxima, in turn bounded by minima. Beyond these two minima are two broad maxima, the lower one of which
shows a tendency to split into two components.

The intensity distribution is very diffuse at position II. Here the two outer maxima have split into 2 approximately equal components. The central portion of the pattern seen in Fig. 16 is further complicated by the appearance of a faint maximum which splits the central minimum into 2 parts.

The above estimates of the intensity distribution are merely visual and no attempt is made at any accurate estimate of the relative peak intensities. The general irregular mottling is such as to make it necessary to take several microphotometer traces of the same general section of the edge before any claim for accurate representation can be made. This has been done in some cases and the results found to confirm the visual estimates.

Some examples are shown in Figs. 17-20. These figures are drawn with an arbitrary intensity scale corresponding directly to the deflection of the microphotometer. Consequently, a maximum in the figures corresponds to a minimum in the diffraction pattern, etc. These curves were not taken from the plates discussed above, but still, of course, apply to them.

Figs. 17 and 18 show the intensity distribution for a pattern very similar to that observed at position 7. The shapes of the maxima and minima are very symmetrical, particularly in the case of Fig. 18.

Fig. 19 shows a common type of pattern, which occurs for focal positions not far removed from position 7 but which was not observed in any of the Figs. described above. (This suggests the focal depth of the objective to be small compared to the
distance between successive positions). The pattern shown in Fig. 19 corresponds to a central maximum dividing 2 minima. It appears possible that this division can be almost perfectly symmetrical but that the focal setting in this case is in the direction of increasing asymmetry.

Fig. 20 demonstrates the considerable regularity and symmetry of the diffraction pattern which still exists for positions of the objective well beyond true focus.

Evidence will be advanced later in this chapter to prove that the edges producing the diffraction patterns shown in Figs. 9-20 are only 7.9 Å high. Some specimens of beryl showed multimolecular steps, probable at least 50 Å high, which produced very similar diffraction patterns to those just discussed. In the case of these multiple edges for focal settings roughly corresponding to position 7, a narrow steep maximum was visible lying some distance from the main pattern. It therefore appears probable that a similar effect takes place with uni-molecular steps, although lost against the general background.

In Figs 9-16 it is very difficult to know when the crystal surface is sharply in focus and an estimate could hardly hope to be within less than 1-2 microns of the true focal position. Careful visual observations also failed to give any definite indication of the precise in-focus position.

Therefore, the surface of a freshly deposited silver film which covered the area shown in Figs. 9-16, was scratched with a pin. This film was some 350 Å thick (estimating from the reflectivity) and therefore considerably less than the depth of
focus of the 4 mm objective which was used to observe it. Previous work on specimens with scratched silverings had shown that the edges of the silver film produced no marked diffraction effect. Two methods of investigation were therefore used.

Firstly, a series of plates were taken at 1 micron intervals exactly as before, the field of view covering an edge which ran up to a scratch on the silver film. Then, independently, and before the series of plates were examined, a single plate was taken, for which the microscope was focussed very carefully on the edge of the scratched silver film alone.

The latter plate was found to correspond exactly with one taken in the through-focus series. On these 2 plates the edge of the silver film showed no trace of a diffraction effect (see lower edge of Fig. 21), while all other plates of the series did. It therefore seems that these plates must represent the in-focus position. For this position the diffraction pattern caused by the 7.9 A step took its simplest form, consisting of a minimum with a narrow outer maximum.

The main deduction to be drawn from the experimental investigations are:—
1) that the diffraction phenomenon is an "in-focus" effect. This seems a fair deduction to make, as we know that in the "in-focus" position the diffraction pattern takes its simplest form, has the least lateral extension and the maximum peak intensities — the criterion usually applied to judge whether an image is "in" or "out of" focus.

2) that the intensity distributions are not complementary about
the in-focus position.

By analogy with the usual method for observing small path differences in a transparent body with a transmission microscope, the converse would be expected.

3) that, due to this non-complementary intensity distribution, one can determine the direction of the step by simple inspection of the diffraction pattern, having once determined the nature of the pattern for a step of known direction.

Reasons will be advanced later to show that in Figs. 9-16 the area bounded by the edge is higher than the remaining area. Hence, one can always predict the step direction in subsequent observations.

4) that the relation between the phase and amplitude of the direct and the diffracted waves is a complex one and varies with the focal setting. A comparatively simple relationship appears to exist in the "in-focus" position.

Unfortunately little can be learned of the nature of the diffracted wave fronts because of the variation in phase and amplitude of the direct beam as the focal setting is altered. This variation is considerable and possibly partially masks alterations in the behaviour of the diffracted wave fronts. It would therefore seem that considerably more could be learned from the focal traverse method if a central dark field objective was used, as an objective of this type completely eliminates the direct beam. An objective of this type unfortunately could not be obtained. A further attempt was therefore made to obtain more information by using oblique dark field illumination.
Uni-molecular steps of 7.9 Å height are also visible in dark field when the surface is silvered. An investigation precisely similar to that described above was therefore carried out. Not only does the step edge scatter light into the objective however, but also any other feature protruding above the general surface level. The general mottling seen in Figs. 9-16 is typical of one type of random marking caused by foreign material deposited on the crystal surface, after the crystal itself had ceased to grow. Marking due to such causes was almost universal on the prism faces of the beryl crystals which were studied. Although a comparatively free area was chosen for the dark field investigation, it was found that these surface foreign bodies scattered so much light as to mask all but the main effects due to the uni-molecular step.

A series of plates for different focal settings was taken as before. The central maximum was found to vary in intensity and lateral extension with setting, and also to lie between other fainter maxima, the number of which varied with the setting.

Little can be said, with certainty, of the number, position, and relative intensities of these maxima. It appears probable, as indeed one would expect, that the dark field phenomenon is again an in-focus effect.

Effect of the observing numerical aperture.

The effect of the observing numerical aperture on the diffraction pattern could probable only be accurately determined by taking microphotometer
curves of the patterns given by the same step for different numerical apertures of the objective. However, it is hoped that the main factors have been determined by visual observation.

A complicating factor to be considered first is that the objective acts as both condenser and observing objective. As the angular aperture of the illuminating beam is small (e.g. of the order of 4.5° in the illuminating train) this joint function can be neglected for medium to large numerical apertures of the objective. In the case of very small observing numerical apertures, an external reflector was used so that the aperture of the illuminating beam should not be limited.

A step of 7.9 Å was observed using numerical apertures ranging from 1.3 to 0.08. It may immediately be deduced that the angular divergence of a significant part of the diffracted wave fronts must be very small.

Visual estimates of relative intensities are notoriously inaccurate, and in this case a change of N.A. normally necessitated a change in focal length of the objective, so that a relationship existed between the lateral extent of the diffraction pattern and the value of the N.A. Consequently, the pattern presumably tended to decrease in visibility with increase in N.A. Against this one must balance the tendency of the eye to prefer an easily resolved pattern. These limitations must result in an estimate of the optimum observing N.A. of a very tentative nature. Recognising these limitations an N.A. lying between 0.45 and 0.15 may be claimed as the optimum value for observation of steps 7.9 Å high.
We already know that an angular spread of 9'10' contains a significant part of the diffracted wave fronts, and it can now be stated that almost the whole of the diffracted wave fronts are probably contained in a total angular spread of 17°-53°.

On the terminal (0001) faces of beryl a uni-molecular step is 4.6 Å high. The visibility of the diffraction effect produced by such steps is less than for steps 7.9 Å high, and two additional factors should be considered.

1) As the visibility has decreased the eye may be able to estimate more easily the onset of "empty magnification" due to the use of an objective of unnecessarily high N.A.

2) The angular spread of the diffracted wavefronts may be dependent upon the height of the step. The difference between two steps of this order is not, however, to be great.

In the case of 4.5 Å steps, an observing N.A. of 0.28 definitely gave better results than N.A.'s of 0.45 greater. The experimental conditions did not permit of the determination of a lower limit to the observing N.A. The upper limit of the angular spread of the diffracted wavefronts can, therefore, be tentatively claimed as 32° in this case.

The general conclusion to be drawn is that the angular spread of the diffracted wave fronts is small and that, other things being equal, greater visibility will be obtained by the use of an objective of medium or low N.A. and corresponding focal length. In practice it is often necessary to choose the objective primarily for satisfactory lateral resolution of the
different diffraction patterns.

Determination of the sensitivity of the effect.

Three measures of the sensitivity of the effect have obtained, all on prism faces of beryl crystals.

The first measure covers a large body of observations for, on many areas of several crystals, no kink has been observed in fringes crossing the known positions of steps. One may therefore infer that such steps cannot exceed 20 Å in height. Accepting the dimensions of the unit cell determined by X-ray diffraction methods (Bragg and West, 1926) a uni-molecular step on these faces will be 7.9 Å high. One may then additionally infer that the steps must not be more than 2 molecules high (i.e., 15.8 Å).

Another estimate can be made from Fig. 22. The system of steps seen in the centre of the Fig. was encompassed within one order when the surface was examined by Fizeau fringes. The whole system must therefore correspond to a change of height of less than one order. A single gradient leading up to a feature of, say, half a wavelength in height, may be compensated by the setting of the reference plane so that this feature is not seen. In this case 3 gradients exist, making marked angles with each other and though the wedge angle may be such as to compensate one gradient it must, therefore, "steepen" at least one of the other gradients, resulting in a decrease in the change of height due to the feature necessary to produce another fringe.
Fig. 22
x 250 (N.A. 0.45)

Fig. 23
x 250 (N.A. 0.45)
Thus, the system must have a total height of less than half a wavelength. Since the amount by which the feature falls below this height cannot be estimated, it will be neglected. Repeated countings by two observers gave the number of steps in (a) the upper rectilinear section, (b) the curved termination and (c) the lower rectilinear section, as 80, 76, and 76 respectively. Thus, averaging over all the steps we have:

- the total step height for 80 steps < 2,730 Å
- average step height at one step edge < 34 Å

Thus, the average height cannot be greater than 4 molecules.

The last and most accurate estimate was made by means of fringes of equal chromatic order. In principle, any area of a face which showed one section containing very few steps, and an adjacent section with a considerable number of steps, could be used to determine the height of the steps by determining the angle between the two sections. Such areas were normally of a kind such that very high magnification would have to be used, with its attendant serious experimental difficulties.

The only area observed which lent itself to avoidance of these considerable difficulties is shown in Fig. 23. In this case a large number of edges suddenly turn through a sharp angle, and it is possible to project an image of the interference system covering this area so that the slit is roughly perpendicular to the horizontal edges. This was done in Fig. 24, in which the left hand part shows the relative gradients of the 2 areas in which the slit is roughly parallel, and roughly perpendicular respectively, to the 2 directions of this system of
steps. The angle measurement was made by a method using both Fizeau fringes and fringes of equal chromatic order (Barakat, 1949). The number of edges which turn through this angle was determined, using a 2 mm. objective (N.A. 1.32), and came to approximately 150.

The slit of the spectrograph was known to cut the central edge system of Fig.23 at some point, but it is immediately obvious from this figure that the exact position of this point of intersection is very important. In order to assign this position we shall first assume that the slit was parallel to the c-axis (i.e., roughly parallel to the vertical edges of Fig.23). Attainment of such parallelism was one of the experimental aims and it was probably attained within a tolerance of some degrees. From the lateral extent of the gradient in Fig.24, it is possible to deduce that the slit lay some 0.02 mms. to the right of the tip of the coarse structure.

Some 110 edges were therefore cut by the slit approximately in the direction of maximum gradient. One must allow for the fact that over an equivalent distance a high magnification photomicrograph showed that some 40 edges must be crossed by the slit. The difference in angle between these two sections is \( \tan^{-1} 0.57 \times 10^{-3} \), which for the equivalent of 70 steps gives an average step height of 8.5 A. This agrees very well with the height of 7.9 A for a unimolecular step.

It therefore seems quite definite that the diffraction effect is capable of revealing unimolecular steps 7.9 A high. This conclusion is also strongly supported by the behaviour of
the steps at obstacles as observed on face 2 of specimen A. This behaviour is discussed with the experimental results.

On terminal (0001) faces of beryl crystals edges were observed running from dislocations. In view of the measurements discussed above, there appears to be no reason to doubt that these steps are also uni-molecular. The value of the step height must then be half that of the X-ray unit cell, namely 4.6 Å.

Estimate of the ultimate sensitivity of the effect.

A relation exists between the height of a step and the visibility of its diffraction effect, the nature of the relationship being unknown. Theoretically, the nature of the relationship could be determined by plotting the relative peak intensities against step height for a number of steps of known height, but in actual practice, there are normally very considerable variations in visibility of steps nominally of the same height. This variation is due primarily to crystallographic reasons rather than to optical reasons, and will not be discussed here.

(a) Bright field.

Steps of 4.6 Å have been observed using dry objectives, and there can be little doubt that a step of 4.0 Å would also be visible. A tentative estimate of the ultimate sensitivity in bright field may be cited as a step of 3.6 Å. (This estimate applies to visual observation; photographic processing is probably capable of reducing the limit below this value.)
It is of some importance that the optical height of a step by this method is $2\mu \text{t}$. Consequently, by the application of immersion fluid to a surface, the optical height is easily increased. Immersion fluid can be used with dry objectives if a thin film is applied to the surface and backed with a cover glass. The paramount requirement is the observation of very small steps and some loss of definition in the image can therefore be tolerated under such conditions. Observation in such conditions has revealed no serious impairment of the definition however.

Thus, by using immersion fluids of refractive index 1.5 and 1.8, the limit of sensitivity can be reduced to 2.4 Å and 2.0 Å respectively.

(b) Central dark field.

The sensitivity should be capable of further improvement if a central dark field objective is used, for by this means the troublesome effects of the direct beam are eliminated, and the visibility of the diffraction effect should increase considerably. A fuller discussion of central dark field will be given in the theoretical discussion below, but some estimates will be made at this point of its possible effect.

A ruled diffraction grating has been observed with normal bright field and central dark field objectives, and comparative pictures published (Seifriz, 1936). A diffraction grating should behave in a similar way to the small steps considered here, and it is of interest that the difference in contrast for the published pictures was, at a purely visual estimate, a factor of 10. Allowing for any photographic increase in contrast
and the approximate nature of the visual estimate, one may make the very conservative estimate that a central dark field objective may increase the visibility of the diffraction effect by a factor of 3.

Estimates of the limits of sensitivity using a central dark field objective may be made as follows:-
1) Assuming a linear, or near-linear, relationship between visibility and step height, a metrical height of 1.2 Å should be observable. With immersion fluids of refractive index 1.5 and 1.8 this corresponds to the observation of steps of metrical heights 0.8 and 0.66 Å. For steps of this height it is, however, probable that the structure of the silver film would play an important part.
2) Assuming a non-linear relationship to hold, than the visibility is likely to decrease rapidly with decrease of step heights for very small steps. One may then estimate the limiting step height as 2.5 Å, which could be reduced to 1.7 Å and 1.4 Å by the use of immersion fluids.

Thus, accepting the most conservative estimates, it appears that a step of optical height 2.5 Å should be visible with a central dark field objective.

(c) Oblique dark field illumination.

In general, it was found easier to observe a uni-molecular step with bright field illumination rather than oblique dark field illumination. This discrepancy in ease of observation was further increased by the general haze produced by the light scattered from foreign material deposited on the surface. Consequently, on all the crystals
observed, the contrast in bright field was always greater than in dark field.

However, if a perfect crystal surface is considered the conditions are significantly different. In this case the dark field image is superimposed on an almost perfectly black field, and even for very slight scattering from the edge, the contrast must, by definition, approach unity. Theoretically therefore, there should be no limit to the step height observable in dark field.

In practice, with a crystal surface free of all deposited matter, the maximum sensitivity would be attained by using a very high intensity source (a carbon arc), and a silver film with a reflectivity of about 94%. A recently deposited film should be used to minimize scattering from "pin-holes." 

Comparison with other techniques.

It is interesting to compare this method of observing small surface steps with other techniques which could be applied.

The electron microscope has a theoretical resolving power of 5 Å, but in practice the resolving power is seldom better than 20 Å. This, of course, is the lateral resolving power and it is difficult to know what the resolution in depth would be, but it appears probable that it will be of the same order. If a diffraction technique could be developed in electron microscopy which was analogous to that used in this work, the sensitivity would be very great indeed.

Multiple beam interferometry is capable of detecting a 10 Å
step under very special conditions, and in very exceptional conditions perhaps even lower steps. The need for a surface of very high quality and the very serious experimental difficulties incidental to work at very high magnifications strictly limit possible applications.

Surface steps of $10^4 \AA$ have been detected by an X-ray reflexion technique (Ehrenberg, 1949). This method appears to be of very limited application however.

Phase contrast microscopy has detected path differences of $10 \AA$ in transmission. This latter value corresponds to a path difference of $5 \AA$ in reflexion, and it appears possible that even small path differences will be ultimately detected.

A phase contrast method has also been used for the study of defects of polish and homogeneity of lenses. A stereoscopic pair of pictures was taken, and with a phase plate of density $3 (N/1000)$ defects of $2 \AA$ depth were quoted as producing a contrast of 0.1 (Loret and Francon, 1948). This is the smallest path difference ever observed by optical methods.

Thus, microscopic techniques, which are of extreme simplicity and very wide application, appear to be the most sensitive method for the observation of very small steps.
Section 11. Theory

General.

At first sight it would seem that the present method of observation is very similar to the long-known method of observing differences in refractive index in transparent bodies, which consists in using a narrow illuminating pencil and going slightly off focus. The similarity lies in the technique of observation rather than in the types of diffraction mechanisms utilised. In the transmission method the image disappears in the in-focus position, and the images are complementary on opposite sides of the true focus.

The use of oblique dark field illumination to reveal surface steps is by no means novel. It has long been maintained (Beck; 1925) that the use of a sufficiently intense source should reveal very small surface steps, and the present technique of coating the surface with a silver film of very high reflectivity is equivalent to the use of just such a source.

No technique comparable to that described here appears to have been developed for the observation of surface features. Surface steps of some 100 Å in height have been observed using light incident at a near glancing-angle to the surface (Tolansky 1945), but in this case the effect was very critically dependent on the angle of illumination, a condition which certainly does not apply to the present technique.

The theoretical considerations are divided into two parts kept artificially apart. In part (a) the luminous amplitude in the image of an object introducing phase variations is considered for different methods of observation. The effect
of diffraction at sharp edges is almost entirely ignored in this section, but this is justified by deduction of the general ways of increasing the sensitivity.

In part (b) the phenomenon of diffraction at an edge is discussed in the light of previous work and the means of deriving a solution of the present problem considered.

(a) Calculation of the luminous amplitude in the image of an object introducing phase-variations.

Let p (Fig. 25) be a transparent object with only local variations in thickness. The point source S illuminates this object with monochromatic light, the source being taken at infinity on the axis of the system. The object lies in a plane normal to the axis and is near an objective 0', which forms an image S' of the point source S in its focal plane. A second objective 0, lies in the plane of S' and forms an image of the object P at P'. Both of these objectives are taken to be thin lenses.

The object P is illuminated by coherent light if the apparent diameter of the source S is small enough for all optical paths to be of equal length which connect points of the source to corresponding points of the image.

Let us take as origin of the co-ordinate system, the optical centre of 0'. We can now proceed using throughout a method due to Francon. (1946)

At a point N (x, y) of the object the phase and amplitude of the vibration can be represented by the complex function

\[ f(x, y) = A(x, y) e^{i\phi(x, y)} \]
(Throughout this calculation the factor representing the undulatory nature of light will be neglected. Consistently during this calculation constant factors will also be neglected, as they do not influence the form of the result.)

\[ |A| = \text{amplitude} \]
\[ \phi = \text{phase} \]

As the object is perfectly transparent \( A(x, y) \) is constant for all points of the pupil situated inside the circumference \( D \) which limits \( O \), and at all exterior points \( A(x, y) = 0 \). The object \( P \) produces variations in the phase \( \phi(x, y) \), due to variations in thickness. Then for an optical path \( S \)

\[ \Delta S = (\kappa - 1) c \]

where \( \kappa \) = refractive index of object
\( c = \text{thickness} \)

Let \( S' \) be the path difference at any point \( C \) in the focal plane, between vibrations diffracted at \( M \) and \( O \). Let \( \xi, \eta, \zeta \) be the co-ordinates of \( C \), and take

\[ u = \frac{\xi}{\xi}, \quad v = \frac{\eta}{\eta}, \quad \kappa = \frac{2\pi}{\lambda} \]

Then

\[ S' = (w_x + w_y) \]

The amplitude \( g(u, v) \) at the point \( C \) is given by

\[ g(u, v) = \int \int_{D_1} f(x, y) e^{i\kappa S' dx dy} \]

or

\[ g(u, v) = A \int \int_{D_1} (\cos \phi + i \sin \phi) \cos \kappa S' dx dy \ldots \ldots \ldots \ldots (1) \]

Let us take as our origin of phase the mean phase for which

\[ \int \int_{D_1} \sin \phi \ dx \ dy = 0 \quad \text{and let } m \text{ be the new value of } \cos \phi \]

in the interior of the pupil.
Then equation (1) can be written
\[ g(u,v) = m \iint_{D_1} e^{ikS'} dx dy + \iint_{D_1} \left[ (\omega \phi - m) + i \omega \phi \right] e^{ikS'} dx dy. \]  

The first term on the R.H.S. represents the diffraction of a "perfect" wave limited by D. The second term represents the diffracted light produced by phase variations in the object.

At \( O_2 \), \( S' = 0 \) and \( \iint_{D_1} (\omega \phi - m) dx dy = 0 \).

The second term is therefore zero at this point. Thus the light diffracted because of phase variations must spread around the central diffraction spot due to the "perfect" wave. As the path differences decrease, so the diffracted light will be spread over a larger area.

Fourier's transformation allows one, being given a pupil, to calculate the corresponding diffraction figure, or vice versa (Duffieux, Tirouflet, Guenoche, Lansraux, 1944). Due to the limited aperture of \( O_2 \), only a part, \( g'(u,v) \), of the amplitude \( g(u,v) \) is used to form the image \( P' \). Thus, the pupil \( f'(\xi,\eta) \) corresponding to \( g'(u,v) \) is given by
\[ f'(\xi,\eta) = \iint_{D_1} g'(u,v) e^{ikS'} du dv. \]

The coordinates of the image plane \( P' \) are related to those of the object plane by the point transformation object-image, and the function \( f'(\xi,\eta) \) therefore represents the distribution of phase and amplitude in the image.

If the objective \( O_2 \) has an infinite aperture
\[ f'(\xi,\eta) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g(u,v) e^{ikS'} du dv = f(\xi,\eta). \]
and the image is identical with the object. The amplitude at any point of the image is given by

\[ f(x,y) = m + \sum (\cos \phi - m) + \sin \phi \cdot \ldots \ldots \ldots (3) \]

where \( m \) is the term due to the "perfect" wave and the second term on the R.H.S. represents the wave diffracted by the object. If the differences in thickness are very small, then the factor \( \cos \phi - m \), being of the second order with respect to \( \phi \), can be neglected. Then for the focal plane of \( O_1 \), we may write, from equation (2)

\[ g(x,y) = \int \int e^{ik\delta} \, dx \, dy + i \int \int e^{ik\delta'} \, dx \, dy \ldots \ldots \ldots (4) \]

For an infinite aperture of \( O_2 \) the complex amplitude in any point of the image can be written, from equation (3),

\[ f(x,y) = 1 + i \phi \ldots \ldots \ldots (5) \]

Neglecting \( \phi^2 \) the sum of the squares of the real and complex parts is constant, hence the image is of uniform intensity and the variations of phase are not visible.

Consider an object symmetrical about \( O, y \) (see Fig. 26). The phase is constant except in the neighbourhood of the axis \( O, y \), where there is a narrow strip of width \( a \) and thickness \( e \). The phase difference introduced by this step is

\[ \phi = \phi_1 + \phi_2 = k(a-1)e \]

We shall take \( O \), as being limited by a rectangular aperture \( D_1 \), which is symmetrical about \( O, y \) and of the same height as the strip. As before defining the origin of phase by

\[ \int_{-\frac{D_1}{2}}^{+\frac{D_1}{2}} \phi \cdot dx = 0 \]
Fig. 26

Fig. 27

Fig. 28
then for all points of the pupil outside the band the phase
\[ \phi_1 = \frac{a}{D_1} \phi \]
and for all points within the band \( \phi_2 = (1 - \frac{a}{D_1}) \phi \).

Putting \( a = \rho \), then equation (4) becomes
\[
g(n) = \int_{-\frac{D_1}{2}}^{\frac{D_1}{2}} e^{-ikux} \, dx + i \rho \phi \left[ \int_{-\frac{a}{2}}^{\frac{a}{2}} e^{-ikux} \, dx - \int_{-\frac{D_1}{2}}^{\frac{D_1}{2}} e^{-ikux} \, dx \right] + i \left( 1 - \rho \right) \phi \int_{-\frac{a}{2}}^{\frac{a}{2}} e^{ikux} \, dx.
\]

Then, neglecting as usual a constant factor,
\[
g(n) = \frac{\sin \frac{kud_1}{2}}{\frac{kud_1}{2}} + i \rho \phi \left[ \frac{\sin \frac{kux}{2}}{\frac{kux}{2}} - \frac{\sin \frac{kud_1}{2}}{\frac{kud_1}{2}} \right] \cdots \cdots (6)
\]

The first term on the R.H.S. represents the diffraction pattern of the rectangular diaphragm \( D_1 \), and the second term is due to the presence of the central strip. As in equation (2) this latter term is zero at \( O_x \) and is spread around the central image. Let us consider the first term. The amplitude in the image due to this term is
\[
A_1 = \int_{-\infty}^{+\infty} \frac{\sin \frac{kud_1}{2}}{\frac{kud_1}{2}} \cdot e^{-ik\phi} \, dx.
\]

For \( x < D_1 \), the amplitude \( A_1 \) is almost constant and equal to the amplitude at the centre \( (\phi' = 0) \). Thus,
\[
A_1 \div \frac{2}{kD_1} \int_{-\infty}^{+\infty} \frac{\sin \frac{kud_1}{2}}{\frac{kud_1}{2}} \cdot d \left( \frac{kud_1}{2} \right) = \frac{2\pi}{kD_1}
\]
The amplitude due to the first term within the brackets in equation (6) is
\[
A_2 = \frac{2}{k\rho} \int_{-\infty}^{+\infty} \frac{\sin \frac{kux}{2}}{\frac{kux}{2}} \cdot e^{-ik\phi} \cdot d \left( \frac{kux}{2} \right)
\]
Then in the central region

\[ A_2 = \frac{2\pi}{ka} \]

Therefore, in the interior of the strips \((x < \frac{a}{2})\), neglecting a constant factor \(\frac{2\pi}{kD_1}\), the amplitude of the image is given by

\[ f(x) = 1 + i\left(1 + \frac{a}{x}\right) \phi \]

and outside the strip \((\frac{a}{2} < x < \frac{D}{2})\) by

\[ f(x) = 1 - i\frac{a}{x} \phi \]

The form of \(f(x)\) is shown in Fig.27. The image can be considered as the resultant of two waves in quadrature. The wave due to the direct image has a constant amplitude equal to that in the pupil \(D_1\), supposed "perfect" and without phase variations. The other wave is due to the variations of phase produced by the object.

In practice the discontinuities shown in Fig.27 are modified by the effects of diffraction so that the increase in amplitude is less rapid, and maxima and minima, which as we have seen may be of considerable amplitude, exist around the points \(-\frac{a}{2}, +\frac{a}{2}\).

It can be seen immediately from Fig.27 that the visibility of the central strip would be much greater if the "perfect" wave was eliminated. This corresponds to the use of central dark field and we will consider this point in more detail.

**Central dark field.**

If the objective \(O_2\) receives all the light diffracted by the object, then at any point of the image the complex amplitude is given by equation(3)

\[ f(x, y) = m + \sum \left[ \cos \phi + i \sin \phi \right] \]
The term in brackets is of zero amplitude at 0, and one can therefore place a small opaque screen at 0, which will block the diffraction pattern of the whole aperture (i.e., the direct beam) with very little modification of the diffraction pattern caused by the phase variations in the object. Then at any point of the image the amplitude will be

$$f(x, y) = \cos \phi - \sin \phi$$

If \( \phi \) is small then \( m = 1 \) and

$$f(x, y) = \cos \phi$$

Therefore the intensity at any point of the image is

$$I = \phi^2(x, y)$$

The intensity is thus zero at all points where the phase is equal to the mean phase on the pupil. Hence, if the local variations in phase affect only a small part of the pupil, then the mean phase of the pupil is almost zero, and the intensity in the image is proportional to the square of the phase difference introduced by the element under consideration.

Defining the contrast \( \gamma \) by the usual relation

$$\gamma = \frac{I_1 - I_2}{I_1}$$

the maximum visibility corresponds to a contrast of one. As in our case the intensity of the general field is almost zero, then the contrast will be unity. Although the visibility is a maximum the intensity of the image of the strip will be small.

Central dark field observation of a narrow strip.

Returning to consider the case of the image of a phase strip, we can write, from equation (6)

$$q(u) = \int \phi \left[ \frac{\sin \frac{k u q}{2}}{\frac{k u q}{2}} - \frac{\sin \frac{k u D_1}{2}}{\frac{k u D_1}{2}} \right]$$

...... (8)
the first term being eliminated because of the presence of the screen. Then in a similar way to that described above it can be shown that the amplitude inside the strip is

$$f(n) = (1 - p) \phi$$

and that outside the strip ($\frac{a}{2} < n < \frac{D}{2}$) it is

$$f(n) = -p \phi$$

Thus, the intensities in the image are given by the squares of the ordinates of the lower wave in Fig. 27 resulting in an image of the type shown in Fig. 28.

The contrast

$$\gamma = \frac{(1 - p^2)\phi^2 - p^2 \phi^2}{(1 - p^2)\phi^2}$$

As $p$ is small then

$$\gamma \approx 1$$

The above treatment is oversimplified since all the direct image can never be blocked by the screen and a small part of it must be spread over the image. This parasitic illumination is, however, of very low intensity, since almost all the direct beam which is not blocked lies round the edges of the image (Banerji, 1919).

If the phase strip is very narrow then, allowing for the presence of the parasitic light, the intensity within the strip has been shown to (Francon, 1950)

$$I_1 = \left[ 1 - \frac{2}{n} \sum i \frac{u_i e D_i}{\lambda} \right]^2 + \phi^2$$

where $u_e = \frac{1}{2}$ half the width of screen

Similarly, outside the strip the intensity is approximately

$$I_2 = \left[ 1 - \frac{2}{n} \sum m \frac{u_m e D_m}{\lambda} \right]^2$$
Hence the contrast 

\[ \gamma = \frac{\phi^2}{\left[1 - \frac{2}{\pi} \frac{S_i \pi u e D_1}{\lambda}\right]^2 + \phi^2} \]

When only the central image is masked 

\[ \frac{\pi u e D_1}{\lambda} = \pi \]

and then 

\[ \left[1 - \frac{2}{\pi} \frac{S_i \pi u e D_1}{\lambda}\right]^2 = 0.032 \]

Let us consider the case when the central image only is masked and a step of 8 A is observed in reflection.

Then 

\[ \gamma = \frac{(0.02)^2}{0.03 + (0.02)^2} \]

\[ = \frac{1}{80} \]

This is very near to the limit of contrast observable by the eye. We have already seen that in ordinary bright field illumination the contrast for such a path difference is much higher than this value. Yet in the above calculation the effect of the direct beam has been largely eliminated and this should considerably increase the contrast. This would seem to indicate that the size of the screen must be extremely critical, but this does not correspond to practical experience.

Thus, a considerable discrepancy exists between the theory outlined above and experimental observation. Consideration of the treatment will show that the method of calculation is apparently not at fault, so the difficulty must be caused by one of the basic assumptions of the calculation. It has in fact been shown (Francon, 1950) that the difficulty is resolved when the finite source used in practice is considered in relation to the size of the opaque screen, instead of the theoretical
point source.

At the edges of the geometric image of the source the presence of a finite source does not alter the conditions with respect to the blocking action of the screen. For points within the geometric image of the source the result is equivalent to an increase in size of the screen, the parasitic light within the image of the strip becoming less important. The parasitic intensity in these circumstances was shown to decrease rapidly with the true size of the screen. Thus, for a source of angular size 1' by 8', and D, a square of 4 cms. side, Francon showed that a screen of angular size 1' 20" gave a value of the parasitic intensity within the image of $10^{-4}$ of the intensity with the screen absent. Then for the 8 A step considered above, the contrast will be much greater, in fact approaching unity.

Thus, in the case of a very narrow strip which introduces a very small phase difference one can always achieve high contrast by increasing the angular size of the screen to reduce the parasitic intensity to a very low level, this being possible without serious impairment of the image of the strip.

This case of a very narrow strip corresponds to 2 steps facing each other at a small distance apart. Although of interest, this is a special case and we shall now consider two steps which are comparatively widely spaced, thus forming a "phase band" which may extend over an important part of the pupil.

Observation of a wide band.

In this case only the light diffracted to the outer part of $0_2$ can be used to form the image and as
a result only phase discontinuities will be seen.

Let us take $0_2$ to be of infinite aperture and integrate equation (8) over the part not covered by the opaque screen,

$$f(u) = \left[ \int_{-\infty}^{+\infty} \frac{\sin \frac{k u}{2}}{k u} e^{-i k s'} \, du - \int_{u_1}^{u_2} \frac{\sin \frac{k u}{2}}{k u} e^{-i k s'} \, du \right. $$

$$ - \left. \int_{-\infty}^{+\infty} \frac{\sin \frac{k u D_1}{2}}{k u D_1} e^{-i k s'} \, du + \int_{u_1}^{u_2} \frac{\sin \frac{k u D_1}{2}}{k u D_1} e^{-i k s'} \, du \right]$$

Then, to a constant factor and taking $t = \frac{2\pi}{D_1}$, the intensity is given by

$$f(u) = \left[ 2\pi - 2S_i(p - t)\alpha_e - 2S_i[p - t]\alpha_e \right.$$  

$$- p \left[ 2\pi - 2S_i[1 + t]\alpha_e - 2S_i[1 - t]\alpha_e \right] \right]$$

where $2\alpha_e = \frac{\pi u D_1}{\lambda}$

For $t > \frac{p}{2}$

$$f(u) = \left[ 2S_i[1 - t]\alpha_e - 2S_i(p + t)\alpha_e \right.$$  

$$- p \left[ 2\pi - 2S_i(1 + t)\alpha_e - 2S_i[1 - t]\alpha_e \right] \right]$$

The intensity is then given by

$$I(u) = \frac{f^2(u)}{4\pi u^2}$$

if the intensity is taken as unity in the absence of the screen. The parasitic intensity has not been allowed for here; it can always be calculated in the same way as before.

Taking $a = \frac{D}{2}$ and $\alpha_e = 5\pi$, then the intensities in the image are shown in Fig. 29. The strip itself is no longer visible, but only the edges where the phase is varying very rapidly, the contrast of the edges approaching unity. These
conditions are therefore approaching those of oblique dark field, but the peak intensities are greater.

In both of the cases considered \( \mathcal{I} \propto \phi^2 \). Taking \( h \) as the metrical height of a step, then in reflection \( \mathcal{I} \propto 4n^2 h^2 \). An estimate of the limit of observation in bright field has been given as 3.6 Å. A step of this height should certainly be visible in central dark field and therefore, for the same intensity we can write

\[ h_1 h_2 = h_1 h_2 \]

or for \( h_1 = 1 \)

\[ h_2 = \frac{h_1}{n} \]

Thus, by using immersion fluid of refractive index 1.8, a step of 2.0 Å should give the same peak intensity as a step of 3.6 Å in air, with a contrast approaching unity.

As the contrast normally approaches unity, the estimate given above of 1.2 Å as the limit of observation would appear to be justified if 2 conditions are satisfied, namely

1) that the intensity is great enough. As a 7.8 Å step is easily visible with oblique dark field illumination, it appears possible that this should be so.

2) that, in practice, the deposited impurity on the crystal surface does not, as in the case of oblique dark field, result in a marked decrease in contrast. This effect should be less serious in central dark field as only foreign bodies with steep edges should produce any marked effect. It is, however, likely to be the main factor limiting the sensitivity in many cases.
Phase-contrast.

The optical technique of phase-contrast (Zernicke, 1942) is already an important and widely used technique and it is likely to become even more important in the future. This method is capable of greater sensitivity than any other, while at the same time giving an image which corresponds very closely to the object. The use of phase-contrast in the observation of small steps has a surprising effect, as we shall see later. First, a very brief account of the general method will be given.

We have already seen that when a transparent object introduces small variations of phase we can write

\[ f(x, \gamma) \equiv 1 + i \phi \]

This equation shows that we can transform phase variations into amplitude variations by changing the phase of the "perfect" wave by \( \frac{\pi}{2} \) with respect to the diffracted wave. This is equivalent to multiplying the last term by \(-i\) when we have

\[ f(x, \gamma) \equiv 1 + \phi \]

Then the intensity, within the limits of the approximations made is

\[ I = f^*(x, \gamma) \equiv 1 + 2\phi \]

The contrast between a region corresponding to a phase difference \( \phi \) and a region corresponding to the general level is

\[ \gamma = \frac{2\phi}{1+2\phi} \equiv 2\phi \]

Thus, a total path difference of 50 A corresponds, on this simple theory, to a contrast of about 0.1.

A further considerable increase in sensitivity is possible if the intensity of the direct light is decreased by a factor of \( \frac{1}{n} \).
Then we have
\[ I_1 = \left( \frac{1}{N} + \phi^2 \right) = \frac{1}{N} \left( 1 + 2\phi \sqrt{N} \right) \]
and for the general level \( I_2 = \frac{1}{N} \)

\[ \gamma = \frac{2\phi \sqrt{N}}{1 + 2\phi \sqrt{N}} = 2\phi \sqrt{N} \]

This formula gives a total path of difference of 1\( \lambda \), when observed with a phase plate of \( N = 2500 \), as producing a contrast of 0.1. This method is thus of great sensitivity.

Observation of a small phase strip.

In the plane conjugate with the source we can apply equation (4):

\[ g(u) = \frac{\sin k_w D_1}{k_w D_1} + \frac{1}{2} \left( \frac{k_w q}{k_w D_1} - \frac{k_w q}{k_w D_1} \right) \]

Due to the introduction of a phase difference of \( \frac{\pi}{2} \) between the direct and diffracted waves (positive phase-contrast) the factor \( i \) disappears and

\[ g(u) = \frac{\sin k_w D_1}{k_w D_1} + \frac{1}{2} \left( \frac{k_w q}{k_w D_1} - \frac{k_w q}{k_w D_1} \right) \] 

Then using our previous notation, the image \( f(x) \) is given by

\[ f(x) = \frac{A_1 + 1 - \phi}{1 + \phi} \]

Within the image of the strip \( x < \frac{a}{2} \), and omitting a constant factor

\[ f(x) = 1 + (1 - \phi) \frac{A_2 - A_1}{A_1} \] 

Outside the image \( \frac{a}{2} < x < \frac{D_1}{2} \)

\[ f(x) = 1 - \phi \frac{A_1}{A_1} \]
Thus, the profile of the intensity distribution in the image corresponds exactly to the phase profile in the object. Hence, for the first time for any of the methods of observation discussed, a point to point correspondence exists between object and image. Of course, a more rigorous theory would result in modification of this exact correspondence, but it is still true to say that the object-image correspondence is very much better than for any other method of observation.

For an absorbing phase plate, the relative intensity of the image of the phase strip will be increased in precisely the same way as we have mentioned above, the contrast thus increasing.

In the above calculation it has been assumed that a phase difference of $\frac{\pi}{2}$ has been introduced between the whole of the direct and diffracted waves. In practice, this can never take place for some part of the direct wave must pass outside the phase plate. For a transparent phase plate this only results in a negligible lowering of the contrast. This is not the case with an absorbing phase plate. When such a phase plate just covers the central spot and has for example $N = 100$ then the contrast is only one quarter of the value given by the simple theory (Francon, 1950).

The value of the contrast can be increased by increasing the size of the phase plate. By this method a contrast almost equal to the theoretical value can be attained, but this must result in a modification of the structure of the diffracted light and consequently in a modification of the image. The
effect is similar to that produced in central dark field by the use of a large screen, in the case of a strongly absorbing phase plate. The result will be the same if a narrow phase plate is used to observe features covering an important part of the pupil. In both cases only regions corresponding to phase discontinuities will be seen.

It appears that this effect may be operative in the example shown in Fig. 30. Before this figure is discussed some information is necessary about the conditions under which it was taken.

This picture was obtained using an 8 mm. focal length (N.A. 0.45) phase contrast objective made by Cooke, Troughton and Sims, and designed to work in reflection. No information is available about the characteristics of the phase plates, but they did not appear to be very highly absorbing, and were of the normal annular type. The area shown is part of a prism face of a beryl crystal, with the surface silvered, and a solid film of cedar wood oil over the silver. (The specimen had to be used in this condition as the phase contrast equipment only became available after all experimental work had been concluded.)

The general variations of intensity in this Fig. were produced by the varying thickness of solid cedar wood oil on the surface, and more especially by the interference colours produced between the upper surface of the "oil" and the silver film. The conditions were thus by no means propitious to crisp definition yet the upper definition is, in fact, surprisingly good.

The lines seen in Fig. 30 correspond to steps 7.9 Å high.
Each step is defined by a narrow minimum of surprisingly low intensity. No appreciable difference in intensity appears to exist between successive planes between the steps, which is to be expected unless highly absorbing phase plates were used. The intensity of the minima is so low that it appears possible that some other factor may be operative in addition to that already discussed.

Quite apart from the theoretical implications of this type of behaviour, the practical consequences are of considerable importance. It had never before been possible to observe steps in the area shown in Fig. 30 and although the optical path difference was considerably increased by the presence of the cedar wood "oil", only some of the edges were visible in bright field and these so faint that it was impossible to focus satisfactorily on a screen in order to get a comparative picture.

Moreover, the edge shown in Figs. 9-16 was observed using phase contrast when the surface was silvered and the contrast obtained was, at a visual estimate, quite as high as that obtained with the surface silvered in bright field. Compared with the very poor contrast obtained with an unsilvered surface and bright field illumination the increase of contrast obtained by the use of phase contrast was approximately a factor of 2.5 or possibly more. If the same relation between the contrasts holds for a silvered surface, then the limiting observable step height should be very small indeed.

Comparing phase contrast with central dark field, the former method would appear to be more sensitive. Thus, the 2
limitations, applicable in the latter case, of low intensity and loss of contrast due to the presence of foreign material, do not apply to the use of phase contrast. In the case of phase contrast, the presence of the minima on a bright field ensure high contrast without the need to consider the effect of foreign bodies, or the limiting of the eye.

It should be noted that the two specific results cited above were of general application. All the edges observed showed greatly increased contrast. Another, and considerable, advantage of the use of phase contrast is the narrowness of the minima which mark the edges. These minima are much narrower than the diffraction patterns produced in bright field and the resolution of closely spaced edges is considerably improved.

To sum up, it may be said that the advantages consequent upon the use of phase contrast are much greater than for any other method, and that the sensitivity promises to be quite as great, in practice, as any other method.

It should also be mentioned that by the use of phase plates which can produce continuous variations in phase and amplitude, true imaging of the object can be restored while the sensitivity is still very high. Probably the best of these methods is that due to Kastler and Montarnal in which polarised light is used, the amplitude being controlled by a half-wave plate and the phase by a quarter-wave plate. (Kastler and Montarnal, 1948, Montarnal, 1948). Path differences of 10 Å have been observed using this method (in transmission). Another advantage of this method which is of some importance is that the optical height of features can be measured and Montarnal
quotes path differences of 10-1,000 Å as being determined to a fair degree of accuracy. It should thus be possible to measure a step height of 2.5 Å in reflection. It is also possible that for step heights which are too small for any observable differences in intensity by this method the step edge may perhaps be visible.

(b) Diffraction at an edge.

The rigorous treatment of diffraction problems involves considerable analytical difficulties and in only one case has a truly rigorous solution been possible (Sommerfeld, 1896). This difficulty is usually overcome by applying approximate treatments which give satisfactory agreement with experiment when the angles of diffraction are small and the region in the immediate vicinity of the edge of geometric shadow is neglected. In the present case the angles of diffraction are comparatively large and it is the equivalent of the edge of the geometric shadow (i.e., the uni-molecular step edge) which is of particular interest. Also the problem is further complicated by the need to consider the effect of the mode of image formation of the microscope. The problem is thus a difficult one but previous work, and in particular one very recent publication, points the way to a possible approximate solution.

The luminous line which is apparently centred on the edge of a diffracting screen, when seen from a viewpoint within the shadow, has long aroused attention and was first fully explained by Rubinowicz (1917). Starting with the ordinary Kirchhoff
diffraction integral, he first transformed it into two distinct surface integrals, one of which was equivalent to the amplitude produced if the direct light was strictly limited by rectilinear propagation from the source. A geometric method was used to transform the other surface integral into a line integral along the diffracting edge. By this means he arrived at an equation for the amplitude of

\[ u = u_\xi + u_\delta \]

\[ = u_\xi + \frac{1}{4\pi} \int_{\partial D} \frac{e^{ik\beta}}{\rho_3} \cdot \frac{e^{ikr_3}}{r_3} \cdot \frac{\cos (\kappa_1 r_3)}{1 + \cos (\kappa_1 \rho_3)} \cdot \sin (\rho_3, ds) ds \]  

(11)

where \( u_\xi \) is the "direct" amplitude

\( u_\delta \) the amplitude of the diffracted light.

and the symbols refer to Fig. 30A. Subsequently, general methods for transformation of the type, using purely analytical arguments, have been evolved which confirm this result (Baker and Copson, 1939). It is also of interest to note that the way in which the amplitude is split into two parts is analogous to the results obtained in the previous section.

The diffracted light consists of the superposition of spherical waves

\[ d u_\delta = \frac{1}{4\pi} \cdot \frac{e^{ik\beta}}{\rho_3} \cdot \frac{e^{ikr_3}}{r_3} \cdot \frac{\cos (\kappa_1 r_3)}{1 + \cos (\kappa_1 \rho_3)} \cdot \sin (\rho_3, ds) ds \]

in which the factor

\[ \frac{1}{4\pi} \cdot \frac{e^{ik\beta}}{\rho_3} \cdot \sin (\rho_3, ds) ds \]

determines the amount of light scattered by the edge element \( ds \);

\( e^{ikr_3/r_3} \) determines the nature of the wave (i.e., that it is spherical); and the direction factor \( \cos (\kappa_1 r_3) \) describes
The unsymmetrical nature of the spherical waves. With the exception of ds and of the edge of the shadow, \( du_b \) is regular in all space.

The above considerations only apply to the solution of the Kirchhoff diffraction problem on the dark side of the screen, where it is identical with the function defined by the Kirchhoff integral. This latter function will now be termed \( \psi_{\text{Kirch}} \). On the bright side of the screen \( \psi_{\text{Kirch}} \) does not describe the diffraction process, but the "physical part" of the function \( U \), which describes the entire physical process (here denoted as \( U_{\text{phys}} \)), is obtained by regular continuation of the function:

\[
U_{\text{phys}} = \psi_{\text{Kirch}} = U_E + U_B
\]

from the dark side of the screen, through the surface \( F \), on to the bright side of \( S \). (This is an extension of the function beyond the limited region in which it was originally defined and the process of analytical continuation is therefore necessary). \( U_B \) is then determined in the whole of space by equation (11) and \( U_E \) is equal to \( \frac{1}{r} e^{ik\rho} \) in all regions outside the geometric shadow.

By continuously circling round the diffracting edge \( B \), all branches of the function \( U \) can be obtained and the final expression is

\[
u = u_{\text{phys}} + ne^{ik\rho} = u_B + u_E + ne^{ik\rho}
\]

where \( \rho = 0, \pm 1, \pm 2, \ldots \).

Thus, if \( U \) is to be single valued it must be defined in the range of a Riemannian surface \( R_\infty \), consisting of similar
sheets and which occupies the diffracting edge B to the individual line branching (the analogy of point-branching in the function theory).

It should be noted that this Riemannian space is constructed from an infinite number of superimposed ordinary three-dimensional spaces. The sheets of this space are joined together along the boundary of the geometrical shadow so that by crossing the shadow one passes from one sheet to another. Physical space near the screen does not all belong to the same sheet of the Riemannian space, since it is only possible to get from one side of the screen to the other by crossing the boundary of the shadow. Consequently, the light incident on the screen leaves physical space and enters non-physical space and can only be observed when it crosses the screen into physical space.

Rubinowicz continues to show that the function $U$ contains another branch ($U^\text{phys}$), which can also be considered as a solution of the Kirchhoff diffraction problem. The three branches $U^\text{phys}$, $U^\text{Kirch}$, and $U^\text{phys}'$ are next to one another in the Riemannian space $R^\kappa$ and are contained in the three sheets $\kappa = 0$, $\kappa = \pm 1$.

The expression for $U^\text{phys}$ on the bright side of the screen contains no term which can be interpreted as the reflected light and the Kirchhoff screen must, therefore, be truly black. For the case of a reflecting screen, a similar method to that outlined above was used to show that a regular solution of the vibration equation

$$u = u_E + u_D + (-u_R + u_D')$$

can be obtained in the whole of physical space except at
on the screen. $U_B'$ corresponds to the value of $U_B$ at the reflected position in the screen of a point $P$. $U_R$ denotes the reflected wave which is equal to $e^{i k \rho'}$ in the space between the diffracting aperture and the reflected position of the geometric shadow, and is zero elsewhere.

On the dark side of the screen, the above equation fulfills, according to the sign, the normal boundary conditions $\frac{\partial u}{\partial z} = 0$ or $u = 0$. On the bright side of the screen, neither of these conditions is satisfied, for while the diffracted waves can satisfy one boundary value, the incident and reflected waves satisfy the other, inapplicable, boundary value. Consequently, the screen is reflecting on both sides, but only perfectly reflecting on the dark side.

This treatment is subject to precisely the same limitations as the normal Kirchhoff treatment. The boundary values accepted by Kirchhoff have, in fact, been shown to be incompatible (Baker and Copson, 1939), but the treatment is nevertheless justified by the good degree of agreement it maintains with experimental observation. The extensions made by Rubinowicz are valuable in that they show diffraction by a screen to be entirely an edge effect. It can again be seen that elimination of the direct wave, $U_D$, should greatly increase the visibility of the edge waves.

The method of application to the present problem is not obvious. We are concerned with observation on the source side of the screen, but it is difficult to know what will happen to the "transmitted light." Thus, in the ideal case we can
consider the upper plane of a step as representing a diffracting screen. Diffraction will take place at the step edge in the way considered above, but the main problem consists in determining the part played by the lower plane lying behind the diffracting edge. If diffraction could be described by the process of ray-tracing from a point, then one could consider the dark-side phenomena as undergoing reflection at the lower plane, and consequent superposition on the bright side phenomena. In fact, the distance between the two planes may be 5 Å, or less, the all important part of space is non-physical space, and, to complicate matters still further, with a silvered surface the edge is no longer perfectly sharp but may extend up to 500 Å in length.

This last point may, perhaps, be settled by taking a drop of 5 Å in a length of 500 Å as constituting a perfectly sharp edge as compared to the wavelength of light. This is not invalidated by the observation of diffraction at a step of 5 Å, which on the same line of argument could be considered as a negligible height, for it is primarily the edge effect which is important in this case, rather than the height of the step. From the standpoint of the edge effect, therefore, if the diffraction pattern from a 5Å step is visible there is no reason why the pattern from an 0.5 Å step should not also be visible, other things being equal.

Quite independently of Rubinowicz, Banerji (1919) raised the question of the possible representation of the Kirchhoff surface integral as a line integral along the diffracting screen.
He was prompted in this by his experimental observations on diffracting screens, in which varying amounts of the direct and diffracted light were cut out. In particular, when the light was blocked he observed the edge of the diffracting aperture as a very fine black line with luminous bands on either side. This work led him to propose that two sets of waves must propagate from the diffracting edge in a direction roughly parallel to the wave normal and with a difference in phase of $\pi$.

The concept of the edge, or boundary, waves introduced by Rubinowicz was applied by Martin (1943) to consider the theory of image formation when dark field illumination is used. In a very recent paper (Martin, 1949), this has been extended to the study of image formation in bright-field, dark-field and phase contrast conditions, when a restricted illuminating aperture is used. The findings thus apply in a general way to the present case.

As well as providing a very elegant theory of image formation in the microscope, this method of approach has the additional virtue that the diffraction and image formation problems are considered together.

Numerical integration of the term $U_\phi$, as defined by equation (11), was carried out and found to lead to results similar to those obtained from the usual Fresnel integrals and the Cornu spiral. The discussion was therefore confined to the two-dimensional case and the Fresnel integrals used.

Sharp edges are taken as diffracting a pair of boundary waves into the objective. The amplitude due to these waves
alone will be symmetrical about the point corresponding to the edge and zero at this point (compare with Banerji). The direct light may be considered as giving a uniform amplitude in addition to this, and it is stated that it will not normally be possible to predict its relative phase, since this will depend on the integration of all the contributions derived from the object plane.

These considerations all apply to the case of transmission. Although it has not been possible to attempt to apply this method to the present problem, it would seem advisable to attempt to calculate the pattern to be expected in transmission first. If this does not agree at all with the experimental observations then it will be necessary to make various assumptions about the light diffracted past the screen.
CHAPTER V

Topographical Studies on Beryl Crystals

Introduction:

Beryl is a beryllium alumino-silicate of formula $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. It belongs to the symmetry class $6/mmm$ (hexagonal holosymmetric class) possessing a hexad axis at the intersection of 2 sets of 3 vertical planes of symmetry, 2 sets of 3 diad axes normal to these planes, a plane of symmetry normal to the hexad axis and a centre. The special forms of this class consist of a basal pinacoid $\{0001\}$, hexagonal prisms $\{10\overline{1}0\}$ and $\{1\overline{1}0\}$, dihexagonal prisms $\{h\ k\ i\ 0\}$ and hexagonal bipyramids $\{h\ 0\ h\ 1\}$ and $\{h\ h\ 2h\ 1\}$. The general form is a dihexagonal bipyramid $\{h\ k\ i\ 1\}$.

The pale green varieties of beryl are known as aquamarine, and the dark green variety known as emerald is a familiar precious stone. Beryl is typically of prismatic habit, the basal pinacoid usually directly terminating the hexagonal prism $\{10\overline{1}0\}$ for emerald crystals, without any intervening forms. Aquamarine crystals usually show, in addition, hexagonal and dihexagonal bipyramidal forms.

Most text books describe the prism faces as being normally vertically striated.

The atomic structure of beryl was determined by Bragg and West (1926). The binding is ionic in nature, beryl providing an example of what are sometimes called ionic mesodesmic structures (Evans, 1938). This means that the strongest binding has
an electrostatic valency of one half the charge on the anion, which, in this case, is $\text{O}^-$ of course. The silicon-oxygen structure consists of hexagonal rings of six $\text{SiO}_4^-$ tetrahedra. These rings lie with the silicon and shared oxygen atoms on the reflexion planes of the unit cell, the latter being parallel to the base and heights $0, \frac{c}{2}, c$. The aluminium and beryllium atoms lie on sheets at heights $3c/4, c/4$, half-way between the reflexion planes, each atom lying between 6 different rings, and being octahedrally co-ordinated by the oxygen, while each Be atom is similarly tetrahedrally surrounded by 4 oxygen ions belonging to 4 different rings. Thus, the oxygen-cation bonds bind together the rings both laterally and vertically. Wide, empty tunnels parallel to the C-axis pass through the centre of the $\text{Si}_6\text{O}_{18}$ rings. It is thought that the helium, often found physically occluded in beryl, must be accommodated in these channels.

The dimensions of the unit cell are $a = 9.21\, \text{Å}$ and $c = 9.17\, \text{Å}$. This corresponds to a spacing of $7.9\, \text{Å}$ on the $\{10\overline{1}0\}$ prism faces. There are 2 molecules in the unit cell, the alternate $\text{Si}_6\text{O}_{18}$ rings differing in orientation along the hexad axis by $25^\circ$. Consequently, the building unit on $(0001)$ faces will be a molecule $4.6\, \text{Å}$ high.

The various specimens examined in the course of the experimental work came from widely different localities. Thus, specimen A came from California, specimen B from Columbia, specimen C from the Urals, and specimen D from Colorado.
Preliminary Experimental Work

Specimen A - prism face number one.

This specimen was of typical aquamarine type and of long prismatic habit, and face number one was 4.6 cms. long and 1.0 cms. wide. An investigation of the topography of the face, using Fizeau fringes, showed that this face could be divided into (a) the main face, (b) a large vicinal area and (c) an area of complex topography, probably due to growth.

Interferograms of the latter area showed that the structure possessed two distinctive properties, typified in Fig.31, resulting in a distinct tendency of the fringes to follow a rectilinear 'preferred direction' and then ending suddenly in a smooth curve. This can only mean that on this part of the face are a number of plane areas of very similar orientation which terminate abruptly in a characteristic manner.

Two parts of this area were found to show these characteristics very clearly. The first of these (Fig.32) had 3 main plateaus separated from each other by the steep gradients AA, EE, XX. A series of partial terminations along the lines BB and CC show the curved contours marking the transverse gradients at the ends of the plateaux. The 'wing' on the fringes, due partly to the large gap which it was necessary to use and partly to scattering within the crystal, marks the direction of increasing gap, and it can be seen that only the highest plateau shows 2 distinct longitudinal terminations, the second of these being faintly visible along FF. The plateaux are slightly curved and
adjustment of the wedge angle so that the fringes on the plateaux were perpendicular to their direction in Fig. 32 showed that they are very closely parallel.

The second area (Fig. 33) shows near-plane, parallel sections again, the main plateau lying well above the surrounding level. It is terminated, as before, by a steep gradient along its length and a curved transverse gradient. The plateau is also split into three different levels by two very sharp drops running parallel to the rectilinear gradient.

In both Figs. 32 and 33 the direction of the longitudinal gradient is approximately parallel to the hexad axis. The main plateau of Fig. 32 conforms in shape to the elements of symmetry of the face. The inference to be drawn seemed to be that this area of the face, at least, grew by a succession of approximately plane layers of molecules, the outline of the layers roughly conforming to the symmetry of the face; comparatively few points appeared to be the centres of this growth.

Any one crystal of unknown antecedents may have grown under very unusual or exceptional circumstances, and it therefore seemed necessary at this stage to attempt to discover whether behaviour of this type was of general application.

**Examination of specimen B.**

In an attempt to obtain confirmatory evidence of this behaviour, the prism faces were studied on the only other beryl crystal at that time available.

These faces were found to be comparatively rough, causing a good deal of fringe broadening. The better of these faces
appeared to be built up of a number of roughly equally spaced uni-directional steps, these steps showing a slight curvature. The edge of the step was always curved and showed a definite tendency to follow an arc of a circle. Although the specimen thus afforded no very definite confirmatory evidence the general nature of the surface structure appeared to be the same and, considering the comparatively rough and irregular nature of the surfaces, the presence of the curved steps is not likely to be entirely accidental. In the main, then, this evidence lent a certain degree of weight to the growth mechanism invoked for specimen A.

Further examination of prism face number 1 of specimen A.

Thus, it appeared that more detailed investigations of the growth area would be worthwhile and sections were taken across the areas shown in Figs. 32 and 33 by means of fringes of equal chromatic order.

The section taken along I of Fig. 33 confirmed the previous findings that the "plateau" of this feature consists of 3 plane parallel areas separated by sudden changes in height. The section along II is shown in Fig. 34. The length AB corresponds to the main plateau and the topography from left to right is seen to consist of a plane section showing a sudden upward curvature to a sharp peak, followed by another curved section which sweeps up very rapidly to the main plateau, which descends in four steep runs to as many short steps, followed again by a short plane area closely parallel to the main plateau.

The section along III showed a structure very similar to
that shown by section II. The same sharp rise to the plateau took place, but in this case, when about halfway across the plateau, after a sudden short rise followed by a slightly greater drop, the plateau took a more irregular formation, showing two other sharp short drops. The plateau dropped in three step sections between short steps to a stepped section parallel to the main plateau. There is thus a strong similarity between the two sections.

Fig. 35 shows the section taken along I in Fig. 32, A'B' corresponding to the main plateau. The surface on the left rises by an intermediate parallel step before the very rapid and considerable rise to the main plateau, which, after descending very rapidly for a considerable height, shows a series of three steps approximately parallel to the main plateau. A very rapid fall and rise then leads to another plateau.

A section taken along II, the first plateau following the main plateau showed a striking similarity with section I, the only points of difference being that the distance of the rise to the main plateau was less great and that the descent takes place in 2 instead of 3 steps. In all other features they were exactly alike.

The close similarity between all these features thus very strongly supports the action of a common growth mechanism.

It is only when the whole of the area is studied simultaneously (Fig. 7) that a good deal of unifying detail is immediately apparent. Thus, the areas previously discussed, (12, 11) (12, 4), are only part of the main complex, the whole of this
area being characterised by comparatively plane areas separated by steep longitudinal gradients (i.e., gradients parallel to the hexad axis) and smooth transverse curves.

There are two obvious similarities of orientation. The first is that of the "plateaux" over the whole of the growth region and the second is the similarity between these latter and the main (i.e., basic) face, seen in the top left hand corner of Fig. 7. This can be compared with the dissimilarity of orientation between the plateaux and the vicinal area (seen in the lower half of the Fig.). One is thus led to the conclusion that the growth areas represent regions in which approximately plane layers of molecules have been deposited, the plane of the layers approximating to the lattice plane corresponding to the face.

The recurrent phenomenon observed in the f.e.c.o. pictures of parallel sections separated by steep gradients, can thus be readily explained as being due to the stacking up of many growth layers.

The most obvious objection to the main conclusion can be stated thus. Why, if these layers are the fundamental building units of the face, are they not truly plane? Fig. 8 helps to provide the answer that the layers are true planes, the apparent curvature in Fig. 7 and any apparent deviations from parallelism being in fact due to a stepping of the very thin layers which is not resolved in the interferogram. Moreover, microscopic examination of the surface revealed the presence of many unimolecular layers which are not seen in Fig. 8 and which cause
the slight deviations from parallelism of the plateaux. Thus, the evidence points to the layers being truly plane and parallel.

Comparing Figs. 7 and 8, it can be seen that the area lying between the irregular hole at (8, 10) and the tip of the ragged pear-shaped region at (8, 7½) consists of a small part of the main face, making an obvious junction with an area of the vicinal face. Fig. 8 shows that a stepped layer structure covers the vicinal area, while no such structure is seen in the region corresponding to the main face. This is direct evidence that the vicinal face consists of a series of stepped layers, a conclusion supported by all more detailed and subsequent investigation.

(The main face shows a definite curvature in Fig. 8. Microscopic investigation at high powers showed that this was due to the stepping of a comparatively small number of layers, so that this area is theoretically a vicinal face also. In normal crystallographic practice the distinction between a basic and a vicinal face must always be one of degree, depending as it does on the accuracy of measurement of an optical goniometer. This limit of accuracy defines, in this case, the basic face as one with less than about 70 uni-molecular steps per mm.)

Comparison of various regions of Figs. 7 and 8 shows that the orientation exemplifying the vicinal face always corresponds to the presence of stepped layers. The region from (6,5) to (8, 7) appears at first sight to contradict this finding, but it does in fact show a number of very faint layer edges. This may be inferred from the fact that the edges to the right of this area display no apparent termination. Observation at
higher magnifications confirmed this view.

It will be noticed that the layer edges running parallel to the hexad axis are, in the main growth region, usually rectilinear. These edges showed no fine structure even at high magnifications while, in contrast, the curved edges in this area display a marked structure in the majority of cases. On this face the structure was invariably irregular, consisting of short straight sections, parallel to the hexad axis, joined by ragged transverse sections. The question of this ragged structure and the shape of the layer edges will be dealt with fully later,

Prism face number two.

Following the examination of face 1, a careful examination was made of all the other prism faces of this specimen, and this face was found to display another growth nucleus with typical rectilinear edges parallel to the hexad axis and terminated as before by an arc of a circle (Fig. 36). The gradient from the curved edge also showed the same type of ragged structure.

Due to the presence of sharp protuberances, some 1-2 mms. in height, very close to this nucleus, a detailed interferometric investigation would have presented many experimental difficulties. It was, however, possible to obtain Fizeau fringes in reflection across this feature and the structure was found to be of precisely the same type as was observed on face 1.

Specimen C

This specimen showed a typical emerald habit, in
contrast to the aquamarine type of habit displayed by specimens A and B.

Prism face number 1.

On one side of this face was a projection (Fig. 37), the termination of which showed the characteristic smooth curve, although distorted from a simple arc of a circle. The upper surface of the projection lies at a considerable height above the main face, sloping down in a concave curve longitudinally and in a convex curve transversely. The longitudinal edges of the projection are very nearly rectilinear. Perpendicular to these edges is a fault which runs right across the face.

A small typical area of the downward slope from the curved termination is shown in Fig. 38. The whole of this slope is quite steep and as the objective used had a very small depth of focus, only a small section of this Fig. is sharply in focus. What appears in Fig. 37 to be the normal ragged structure is, in fact, quite regular, the straight sections all running parallel to the hexad axis. The outline of these small features is very similar to that of the layer structure discussed above. Very few of these features are doubly terminated, but they all terminate on the end facing down the slope. They thus behave as if protruding from the steep downward slope. Several of the features here are only some 4 $10^{-4}$ cms, in height.

At first glance the structure might be thought to be dendritic, but the small area shown in Fig. 38 is quite typical of the uniformity in size of the structure. In particular no
Fig. 37
x44  (N.A. 0.28)

Fig. 38
x1250  (N.A. 0.95)
very long features were observed of the type expected of dendrite formation. Considering their size these features are remarkably uniform in outline.

A typical part of the plateau of the projection is shown in Fig. 39. The 'plateau' is, in fact, composed of a considerable number of stepped layers, the spacing between curved edges being quite large (over the area shown about 0.05 mm.), the straight edges being packed much more closely. The variation in curvature and geometric form of the curved edges seen, is typical of the whole of the plateau.

Examination of the whole of the plateau showed that many of the layers were doubly terminated, but owing to the poor visibility of the edges it did not prove possible to trace the centre of their origin.

The very marked mottled structure which tends to mask the layer edges in Fig. 39 covered almost the whole of the face, only a small area near the base of the crystal being clear (Fig. 22). This latter area is very much smoother and a sharp line of demarcation existed between the two areas, as seen in the figure, so that it would seem that some foreign material has been deposited on the main part of the face. The presence of such foreign material has been found to be almost invariable on all the specimens examined.

A striking example of variation in curvature and geometric form of the edges is shown in Fig. 40. Here the two well marked terminations on the right are followed by a most unusual sickle-shaped form. The left hand edge of the sickle follows a
Fig. 39
x 250 (N.A. 0.45)

Fig. 40
x 500 (N.A. 0.95)
circular curvature and is set slightly skew in relation to the neighbouring edge on the right. It is particularly noticeable that no trace of the usual straight edge can be seen, either on the feature itself, or leading towards or away from it. Moreover, after the faint, but normal termination to the left of the "sickle" another, very faint, sickle-shape appears to be present.

Again, Fig. 41, corresponding to an area lying immediately to the right of Fig. 40, shows a number of unusual features forming closed loops on the right. The straight edges also, for the first time, show what appear to be random irregularities.

In addition to the projection, the whole of the main face displayed a closely packed stepped layer structure. A typical area is shown in Fig. 42. The spacing of the curved edges increased along the length of the face, the total number of layers on the face being some 1,500. Growth over the whole of the face appeared to be almost entirely uni-directional, originating from the fractured end of the crystal (corresponding to the right hand end of all the figures).

In most of the figures a striking regularity of spacing of the straight edges of the layers can be seen. Over considerable areas of the face this spacing was so periodic as to cause the surface to act, when silvered, as a diffractive grating producing marked spectral effects.

Examination of this face by Fizeau fringes, showed that, as was to be expected, the irregular mottled structure was such as to cause considerable fringe broadening, thus preventing any
Fig. 41
x 500  (N.A. 0.95)

Fig. 42
x 250  (N.A. 0.45)
direct measurement of the step height at the edges of the layers. The fault seen in Fig. 37 was found to have been accompanied by some degree of tilting (Fig. 43), this fault being a very narrow valley of approximate depth $\frac{A}{4} - \frac{2A}{5}$.

Another fault was also observed running across the face near its upper termination. The breadth of the fault was much greater in this case, the fault line not being rectilinear but curving a little. The difference of orientation on the two sides was less than in the previous case, the depth of the fault being about $\frac{A}{2}$. A short perpendicular fault also existed running parallel to the hexad axis, the tilting in this case being much more marked. In the larger of these two faults some deposition had taken place after its formation.

Both of these major faults could be traced across the adjacent faces, the difference of orientation on opposite sides of the faults varying from face to face. One of the faults stopped part way across a face, and both faults could be traced down into the body of the crystal as the fault planes were marked by a slight opacity. It would thus seem that the faults were not formed by any form of translation gliding, but rather by simple cracking.

**Prism face number 2.**

This adjacent face although showing areas with a coarse structure, also had areas covered by a large number of stepped layers. The outline and spacing of these layers was very similar to those seen on face 1.
Terminal faces.

As it seemed that the growth layers on beryl tended to conform to the symmetry of the face, it appeared that in the case of the terminal (0001) faces, which are perpendicular to the hexad axis, the layers should take the form of a regular hexagon. A search was therefore made through the specimens available at the British Museum, and three examples were selected which showed the predicted hexagonal structure. Low power photomicrographs of the unsilvered faces of two of these specimens are shown in Figs. 44 and 45.

General discussion.

At this point it may be of value to summarise the main conclusions to be drawn from the experimental work described above.

At the time when this work had been completed the theories of Kossel and Stranski were generally accepted as being broadly correct, and this work appeared to support that conclusion. Definite evidence had been obtained that prism faces of beryl crystals grew by the deposition of layers of molecules, the shape of these layers tending to conform to the symmetry of the face. It therefore appeared that growth layers on all faces of beryl should so behave and evidence in support of this had been obtained from terminal faces.

It had always been necessary, if the Kossel-Stranski type of approach was correct, that vicinal faces should be formed of stepped layers. On the other hand some workers were still of the opinion that vicinal faces were fundamental phenomena.
of a nature distinct from the basic faces. The above experimental work provided what was probably the first direct experimental evidence that vicinal faces do, in fact, consist of stepped layers.

This allows of some clarification of previous work. Thus, both Marcelin and Kowarski showed that, in the case of paratoluidine crystals, a stable crystal showed a uniform tint over the whole of a face (i.e., it was covered by a single layer). The theory developed by Stranski for conditions not far removed from equilibrium, also stressed the probability of the completion of any one layer before the next layer was nucleated. It is thus obvious why Stranski should find that the vicinal faces of magnesium crystals correspond to non-equilibrium forms, for a series of stepped layers should, both from theory and experiment, correspond to a non-equilibrium state.

The growth of crystal faces by the formation of successive vicinal faces, as first proposed by Miers and later restated by Kalb, can be seen to rest on a misconception. Kalb accepted as proof of this mechanism the widely observed phenomenon of the approach of a vicinal face more nearly to the true face as the supersaturation of the solution decreased. In these conditions the crystal is approaching the equilibrium state, the number of growth layers on the surface at any one time decreasing, thus causing the vicinal faces to approach the true face (i.e. in the ideal case, a single layer).

The experimental evidence thus seemed to lend support to the, then, current theories. The frequent occurrence of vicinal faces, even at low supersaturations, would appear, as has been
indicated in Chapter I, to cast doubt on the theoretical assumptions of the probability of nucleation of new layers. If, however, the theory is taken to be limited to conditions only very near to equilibrium, then at least part of this discrepancy may be explained.

A more serious objection is that of the siting of the growing points. Beryl is predominantly ionic in behaviour and the theory predicts that the growing points should be situated on corners and edges. Specimen A showed growing points situated in all cases well away from corners or edges, and Fig. 44 also gave some evidence of this type of behaviour. In the case of specimen C, growth appeared to have taken place entirely from the fractured end, but this fractured end might not correspond to the original termination of the crystal. Such evidence is too fragmentary to provide a very serious objection, but it was known that extensive work carried out by I.C.I., at that time unpublished, also showed that the great majority of a large number of ionic crystals had growing points situated away from corners and edges. As it was pointed out in Chapter I, this may be deduced in many cases from the position of vicinal faces on ionic crystals.

When one comes to attempt to explain the unusual forms seen in Figs. 40 and 41, a stubborn difficulty has to be faced. Let us consider the sickle shape first and let us consider it to be a closed figure. This would appear to be an eminently reasonable assumption, as the apparently blank section of the edge could well be caused by some overlapping impurity, as often happens on
this face. Moreover, no case of the sudden termination of an edge had on any other occasion been observed.

One may consider the edge as

(a) enclosing a hole which is below the general level, or

(b) enclosing a layer above the general level.

Subdividing the first possibility, this feature may have been caused by

(1) incomplete filling in of a layer, as observed by Bunn and Emmett, or

(2) by localised dissolution,

If this feature was caused by incomplete filling in of a layer, one must remember that the curved edges are always convex in the direction of growth and that the rate of growth, on this face, is at least twice as great in the direction of the hexad axis, as in the perpendicular direction. No matter what assumptions are made of the mode of "filling-in", the shape of this feature can only be satisfactorily explained if it is assumed that the left hand edge of the sickle is composed of a large number of short straight sections linked by short curved sections which are convex towards the right. This is an unsatisfactory explanation.

If the possibility of local dissolution is considered, the dissolution must have started from a point within the sickle and none of the usual dissolution phenomena observed on beryl are in accordance with this shape.

Should the area within the sickle be taken as standing above the general level then the area might be due to
(a) nucleation
(b) dissolution which cut off an area of a large layer.

Once more, the shape of the sickle is entirely incompatible with the observed nucleation characteristics. If the area is considered as cut off from the layer to the right by dissolution one still has to account for the rapid rate of dissolution perpendicular to the hexad axis, a type of behaviour contrary to observation.

The closed shapes seen in Fig. 42 raise much the same problems, although in some cases accentuated because of the close proximity of these areas.

The only good general conclusion to be drawn is that this type of behaviour may possibly be due to dissolution, although this decision can only be arrived at on the grounds of the possibility of the existance of an unknown type of behaviour, and not on the grounds of the known behaviour during dissolution.

General Conclusions.

In the main, the layer-by-layer growth picture provided by the current theory appeared to agree with the experimental results. The siting of the growth nuclei appeared to differ from that predicted by theory, but the observations were much too limited for any claim that this was the general type of behaviour on beryl.

Although no very satisfactory explanation could be advanced for the areas shown in Figs. 40 and 41, it did not appear that this constituted any serious difficulty to the theories of growth.
CHAPTER VI

Further microscopic examination of Specimen A - Face 1.

Introduction.

The work described in the previous chapter had been concluded when the first paper was published by Frank on the influence of dislocations on crystal growth. Such ideas, although very novel, had, if correct, the great advantage of accounting for the grave deficiencies in two-dimensional nucleation theory. On the other hand, the Stranski type of mechanism seemed to be in accordance with the experimental results.

By this time it was known that steps only some 2 or 3 molecules high could be observed. It therefore seemed worthwhile to carry out an extensive search for layers which had the spiral form predicted by Frank, and it was during the course of this work that it proved possible to show that the majority of the steps observed were uni-molecular.

Over a period of several months devoted to the inspection of the prism faces of this specimen at high magnification, a very small number of layers were observed to have a spiral form, these spirals showing only a few turns. In addition to the rarely observed spirals the layers were found in many cases to behave in a way incompatible with growth from two-dimensional nuclei and it was only when a fuller account of the dislocation theory of crystal growth was available that it was seen that the behaviour in many such cases had been predicted entirely in terms of dislocations and that in all cases the behaviour was explicable in terms of this theory.
The account that follows in this and subsequent chapters is therefore only roughly chronological in terms of the order of work. The evidence presented will, for simplicity, be considered in terms of the full development of the dislocation theory, rather than from the viewpoint necessary at the time.

Due to the considerable volume of evidence obtained, only the major points which arose will be considered.

This face is of considerable size and, for convenience, it will be considered in two parts, devoted to the crystal growth region, and the area beyond this up to the termination of the face. This latter area will be called the "upper region" of the face.

The upper region of the face.

Behaviour at surface obstacles.

A typical example of the behaviour of the layers at surface obstacles is shown in Fig.46. In this case a system of layers of considerable extent has met with a surface obstacle, probably a crystal inclusion. This obstacle is roughly pentagonal in shape, and the upper half can be seen in the figure. The layers are forced to split into two parts by the obstacle and as they advance towards the top of the fig., it is necessary for them to attempt to 'fill in' by outward growth of the straight edges once the obstacle begins to decrease in extent. Due to the fact that growth is much more rapid parallel to the c-axis (i.e., the hexad axis) than perpendicular to it, the two sections of the system only unite at some distance beyond the obstacle.
Fig. 46
\( \times 800 \)
(N.A. 0.95)

Fig. 47
\( \times 500 \)
(N.A. 0.95)
The points to be noted are:-

(a) the rapid elimination of the re-entrant angle at the junction. As the re-entrant angle is parallel to the direction of rapid growth, this would be expected on almost any theory of growth.

(b) the relative rates of growth parallel, and perpendicular, to the c-axis. In this case the ratios, for the two parts of the system, are 1.7 and 2.1. The ratio of the rates of growth varies with the local conditions being, for another similar case, 2.9 and 2.76.

(c) each edge is equivalent to a contour of vertical integral 7.9 A. The obstacle thus results in a triangular V-shaped valley, with a maximum depth of 38 molecules (300 A).

Surface features.

Not far from the termination of this face, a number of features were seen, often roughly pentagonal in shape, which appeared to correspond to a depression in the surface. An example is shown in the lower left hand corner of Fig. 47. Sides of such features which were not too far removed from parallelism with the c-axis often showed signs of a layer structure, as in Fig. 47.

The cause of such features is not obvious. On the dislocation theory, solution takes place by a reversal of the rates of growth of the layers. In this case the behaviour is much more irregular and evidence will be presented later that edges do, in fact, retreat in a regular way during dissolution. It may be then, that these areas result from mechanical damage to
the crystal. Later growth or dissolution might produce the common pentagonal shape and growth would certainly tend to produce edges linked to the existing layer edges.

The triangular area seen in Fig. 46, together with the attached area on the right, appears more likely to be an overgrowth of foreign material, particularly as the greater part of this crystal was found to be covered with an irregular small scale deposition of foreign material, together with occasional larger areas. The trace of structure in the area on the right of Fig. 46 suggests that the deposit on this area must be thin. The presence of a ragged edge structure close to the left hand edge of the triangular area throws doubt upon the complete adequacy of a simple overgrowth explanation.

A similar problem is met with in the diagonal area crossing Fig. 47. This area has well defined edges and the unimolecular layers stop abruptly on meeting these edges. However, the area itself shows a faint curving edge structure and the question of the origin of this feature must again be posed. Any conclusions must be of an even more tentative nature in this case, and it is safer to leave the question open.

Ragged edge structure.

A very ragged edge structure was rare on this crystal, but some specimens showed little else. In the case of Fig. 48, it appears that this behaviour may be related to the problems discussed immediately above. The edges on Fig. 48 suddenly cut back in the direction of increasing height, the edges with the small kinks remaining fairly regular, but the
outline of the layers becoming progressively more ragged towards the bottom of the figure.

In this case, slight surface abrasion would appear to be the cause. If slight local abrasion took place over these areas then, recalling that these steps are uni-molecular, the resulting appearance would be that the abraded area showed very irregular edges with a number of deep re-entrant scratches. Should a slight amount of growth then follow, the deposition would first tend to eliminate the re-entrant scratches, and then roughly equal deposits per unit length of edge would take place.

The whole of the behaviour in this area is thus consistent with an almost tangential approach of an abrading surface to the lower areas (i.e., the upper parts of the figure). This surface would then tear more deeply into the surface as it advanced, while slight subsequent growth could smooth out the grosser irregularities, in particular those of the less severely abraded areas.

**Visibility of the layer edges.**

Over most of this general region of the face, the visibility of the edges was normally very low, but by no means uniform over the whole region, or even always uniform over very small areas.

The two general trends of the visibility were

(a) a decrease to an extremely low visibility as the end of the face was approached, and

(b) a sudden increase in visibility around surface features or obstacles.
As the edges are almost invariably uni-molecular, a change in the nature of the edges can hardly be responsible for the variations in visibility and some other variation in surface structure must be the cause. Such a variation could only be due to material deposited on the surface of the crystal so that variations in the silver film might be responsible, or alternatively foreign material might be present which was deposited on the surface after the crystal had ceased to grow. All the evidence is in favour of uniformity of behaviour of the silver film, so that the presence of foreign material must be responsible.

This conclusion is supported by Fig. 49. The edges in this case are of fairly low visibility, and go out of focus rather rapidly, but over one well defined small area the visibility of the edges is very high. This area is of triangular shape and one can only conclude that deposition of material has taken place within this area in such a way as to enhance the original step height. A similar type of behaviour can be seen to the left of the figure also.

There appears to be no reason to believe that dissolution can have enhanced the step heights in these areas. An enhanced visibility, as in this case, is comparatively rare. More usually small areas are observed within which the edges are only faintly visible or quite invisible.

Any satisfactory explanation must account for the uniform low visibility which exists over considerable areas, with local areas having edges with a "normal" visibility. This is achieved if we consider very thin uniform layers of water, silica, or
other substances of small molecular dimensions bound to the surface in the low visibility areas, but absent in the "normal" areas. Such layers would probably not contour the step edges well and would result in a diminution of the effective step height of the layers and a consequent decrease in visibility.

A good deal of chemical evidence exists to suggest that a uni-molecular layer of water is almost invariably bound to a surface in such a way that it no longer displays the normal properties of water. The difficulty in this case lies less in explaining the presence of such a layer than its postulated absence over some areas.

The presence of silica on the surface could be explained in terms of its presence in the original geode, for after the crystal had ceased to grow and the temperature/pressure decreased it would probably tend to deposit on all available surfaces.

**Bunching of layers.**

Very occasionally layers were observed to bunch and form multiple layers. One would expect such behaviour to take place occasionally and the main interest lies in the increase in visibility of the multi-molecular steps. Even in the case of the combination of 4 single layers to form a multiple layer, the increase in visibility was very much less than in the triangular area of Fig. 49. One can estimate that in this latter case the effective step height must be at least 100 Å.

**Dislocation structure (i)**

The first evidence obtained of the existence of a dislocation structure is shown in Fig. 50. In this case
Fig. 50
x500  (N.A. 0.95)

Fig. 51
x800  (N.A. 0.95)
the form of the layers starting from the dislocations, is very
different from the spiral type of structure obtained when the
dislocation layer is very active.

Near the bottom right hand corner of Fig. 50 two black dots,
quite closely spaced, mark the point of divergence of two edges
from a single edge. This divergence is much too steep to be
due to the splitting up of a "bunched" step and, in fact, the
dot marks the point of termination of these edges. As the
layers are uni-molecular then the dot, by definition, marks the
point of emergence of a dislocation with a screw component
normal to the surface. In this case there must be an unresolved
pair of dislocations at each dot. These pairs of dislocations
are of opposite hand, and form a limited slip zone of the type
mentioned in Chapter II.

In the case seen here, the two pairs of dislocations appear
to be playing a fairly passive role and merely pass on the
edges after slight modification of their outline. Such a
behaviour was forecast by the theory in terms of "dominant"
group of dislocations, from which layers spread outwards. When
these layers reach the inactive dislocations, the dominant
system of layers suffers only a slight check and then passes on
with slightly modified outline. In this case, the 2 pairs of
dislocations are behaving in just this way.

The general behaviour shown in this Fig. is complex. One
opposite sides of the central strip are very different numbers
of edges and it is probable that many of those on the left arise
from dislocations. In particular, some of the black dots near
the top of this region probably mark dislocations, for edges
appear to terminate on them.

The behaviour in an area lying to the right of the centre of the figure is of a type which will be considered later. **Dislocation area [iii].**

In this case the dislocation structure consists of 2 roughly parallel lines of eight dislocations each (Fig.51). From each dislocation of the inner line, a spiral edge starts, the straight edges from these dislocations being so closely packed that they are not properly resolved. Using a high power eyepiece, visual observation showed these straight edges to be distinct, but the edges from the outer line of dislocations could still not be resolved.

The second straight edge of the spiral is not parallel to the original direction, an unusual feature. These edges end in an irregular boundary formed by the maingrowth region. The area blocking out part of the spiral is probably due to some overlying foreign material.

From the position and behaviour of the series of edges to the left of the dislocation system, it appears probable that these may have been part of the spiral structure. **General discussion.**

There is no need to attempt an elaborate proof that the dots which have been mentioned are dislocations. If a unimolecular step terminates on a surface, then it is possible to proceed from the lower side of the step to the upper side of the step, thus rising in height by one molecule, without at any point crossing a discontinuity in height. The
point of termination of the step then, by definition, must mark
the point of emergence of a dislocation with a screw component
normal to the surface.

When one considers that the dislocation density for a
perfect metal crystal is usually given as $10^6$ dislocations per
sq.cm. then it is striking that the dislocations seen on the
area shown above, some 3 sq.cms., were confined to the two
areas shown above and another example not shown. It is possible
however, that there were many more dislocations present than
this. Over a considerable area of the face the visibility was
so poor that the presence of inactive dislocations could have
been missed. It was also observed that many layer systems
appeared to start from surface features, either depressions or
elevations, and although no dislocation structure was observed
it may have existed.

Another point to be noted is that subsequent experience
showed that the very irregular type of structure seen around
the edges of the 'obstacle' in Fig.46 might well consist of a
large number of dislocations with short connecting edges. The
possibility of other similar areas showing the same type of
structure should also be taken into account.

Even if a factor of 100 is allowed for the dislocations
not observed the number must still fall far short of the number
ascribed to a metal crystal. In particular, comparatively large
areas existed on this face where any dislocation structure would
probably have been observed had it existed.

The two lines of dislocations seen in Fig.51 correspond
to the boundaries between sections of the crystal inclined at a small angle to each other. The reciprocal angle of rotation in the two cases is much the same, being approximately $10^{-4}$ radians.

The irregular boundary corresponding to the main growth system, which has built well up above the level of the dislocation system in Fig. 51 strongly suggests that it is the dislocation layer system which is preventing further extension of the main system. Such an obstruction could be totally impassable to other layers below a certain critical supersaturation.

In the case of the interaction of an inactive dislocation with a layer system originating from a dominant group, it is interesting to note the behaviour predicted by theory. The successive stages are shown in Fig. 52. The layers are advancing from right to left and in (A) one layer has just passed on. In (B) the layer originating from the inactive dislocation has grown in the normal way, while the layer advancing from the right is now quite close to it. The kink in the edge on the left is being eliminated as the layer extends. In (C) the incident layer is being held up at the dislocation, as this layer is now very close to the region of deformed crystal structure around the dislocation and an effective small repulsion also exists between the two layers. By stage (D) sufficient molecules have built on to the requisite section of the incident layer, probably because of a statistical fluctuation, to enable the layer to link across with the layer running from the dislocation.
The dislocation is consequently attached to the shorter edge, which was originally part of the incident layer. Meanwhile, the kink in the left hand edge has been almost eliminated. This type of behaviour can be repeated indefinitely.

In Fig. 50 each pair of dislocations is encountered almost simultaneously so that the incident layer must link across twice in succession and so takes the profile of the outer edge. A marked re-entrant is therefore formed after both pairs of dislocations have been passed.

(b) Central growth region.

As this region had dominated the growth of the face it appeared probable that several examples of dislocation structure would be found. In fact, this was not the case. Both of the main plateaux in this region, which have been discussed above, were carefully examined and although both showed traces of an edge structure of very poor visibility, in neither case could the centre of the system be traced.

One of the very few examples of dislocation structure seen in this region is shown in Fig. 53. In this case the edge joining 2 dislocations of opposite hand lies in the centre. The theory predicted that the inner loop should extend to form a series of closed loops, exemplified by the outer loop in Fig. 53. One need only compare the theoretical predictions as shown in Fig. 4 with Fig. 53 to see the very close correspondence between theory and experiment. (The triangular area obliterating part of the edge of the closed loop is probably some foreign crystalline...
In this case the dislocation pair appears to have been operating unhampered by the disturbing presence of other dislocation systems and in consequence the outer loop took a near-ideal form. The general small scale mottling seen in this fig. extended over the whole of the surrounding area and is probably due to small scale deposits of foreign material.

**Structure of the sides of the plateaux.**

We have already seen that all the plateaux in this area had structureless straight edges, but an irregular ragged structure on their curved edges. Examination at medium magnification cast a good deal of light on the nature of the plateaux. Some of the plateaux which run from the right hand end of the main plateau, as shown in Fig.8, are shown in Fig.23. The most immediately striking point is that the "plateaux" are composed of a large number of closely packed layer edges. When a gap exists in the ragged structure these edges "pour" out to form a section of the vicinal face.

Also examination of the "ragged" structure showed that it is not entirely irregular, but possesses a definite surface structure (Fig.54). The steep slopes are composed of a large number of rod-like features, lying parallel to the c-axis and all pointing down the slope. In the centre of this figure three well defined rods project on to the "plateau" from the first steep slope. The surfaces of these rods stand above the general level of the "plateau", and each rod shows a marked tendency to take the growth shape typical of this crystal. This growth
shape, the best example of which is provided by the outer loop of Fig. 53, is similar to a razor-blade shape and will, for convenience, be so-called in future.

Comparison of the three isolated rods with the structure on the steep slopes shows that the general tendency is toward rods of this general shape, although normally with a greater ratio of length to breadth. A good example of the general behaviour is shown on the right hand of the 3 rods, where a thinner rod has grown along the parent rod.

A clue to the general behaviour of these rods is provided by Fig. 55. In this case isolated rods projecting from the base of a steep slope have grown right across a small plateau to meet the rod structure on its far edge. The plateau is thus split into several parts and if growth had continued the rods would presumably have extended and multiplied to cover all trace of the original plateau.

Thus it seems probable that the structure of the end slopes of the plateaux originally consisted of closely packed layer edges only. The steep gradient parallel to the c-axis which is formed by such close packing is, for some reason, conducive to rod formation. Having once formed, the rods begin to spread until an intermediate stage is reached, represented by Fig. 55. A subsequent slow advance of the rods will ensue, probably often as individuals, until the gradient is split into several portions and eventually entirely covered by the rod structure. A merging of the individual rods is then likely to take place, so that they lose their identity and are replaced by a smaller scale and more
irregular rod structure with occasional marked differences in level, as on the left of Fig. 54.

General discussion.

It has already been shown in Chapter I that the theory predicts that, for directions not far removed from a direction of close-packing, the edge will have a radius of curvature \((1 + 2B)\) times its distance from the center of origin. A close-packed direction corresponds to a minimum growth rate and will manifest itself as a straight edge. The "straight" edges in Fig. 53 must then correspond to a minimum growth rate.

In fact the radius of curvature of these almost straight edges is 100 times the distance from the center, although this curvature may be partially due to aberration in the objective. The presence of aberrations thus limits the accuracy of this and subsequent factors. Accepting the lower value of 100 and remembering that \(B = e^{\phi / kT / \Omega} \), then \(\phi / kT\) is 6 or more.

By applying the theory it is also possible to measure the size of the critical nucleus from Fig. 53. This is found to be about 1 micron. Equating this value with the term defining the size of the critical nucleus, \((a \Phi)^\frac{1}{\Omega}\), and using the estimate of \(\phi / kT\) obtained above, it can be deduced that the degree of supersaturation at which growth took place was about 0.5%.

It should be noted that this value of the supersaturation corresponds to the actual surface of the crystal and not to the value existing in the solution beyond the diffusion barrier. Thus it may well be the first measurement of the supersaturation at a crystal surface for growth from solution.
As the theory predicts a dependence of the growth rate on the crystallographic orientation of the surface, it is possible to construct a polar diagram of the two-dimensional growth rate. The curved edges in Fig. 53 are very nearly arcs of the same circle, so that the growth rate is practically independent of orientation for the range covered by these edges (±30° measured from the centre). The "straight" edges must correspond to a steep, but not discontinuous minimum, and it is therefore possible to construct a polar diagram of the type shown in Fig. 56.

In the case of orientations not seen in Fig. 53 the polar diagram must be approximate, as one can only say that such orientations must correspond to a section of the diagram lying outside the dotted circle.

There are several questions to be posed about the rod type of structure, most of these questions probably being interrelated.

1) Why should a slope parallel to the c-axis be favourable to rod formation?
2) Why are rods not observed on the steep slopes perpendicular to the c-axis?
3) Why do these features take a rod-like form?
4) Why should they appear to follow a different mode of growth from that of the normal layers?
5) Why are the constituent edges of the rods irregular?

The third, fourth, and fifth questions may be linked together if one assumes a dislocation structure to be responsible
Fig. 56

Fig. 57

x 800  (N.A. 1:32)
for the behaviour. Thus, the advance of the numerous edges running from closely spaced dislocations may possibly be held up for some reason. The arrival of other layer edges would result in a piling up above the delayed or stationary edge, so that a steep gradient would be formed which might correspond to some comparatively stable orientation. Thus, at first, the rods would be very short, but would subsequently increase slowly in length, while the rod width would still be governed by the distance between the original groups of dislocations. A long thin rod shape would be expected in this case, of the type seen in the main rod areas. The stability of the features should be assured if the shape of the edges corresponds to a stable orientation, and growth should be slow because of the considerable height of the edges. These features would then be largely equivalent to small "seed" crystals projecting above the mother surface.

The main objection to this line of reasoning would appear to be the absence of dislocations in this area. A very high power objective was not available when this work was being carried out, but subsequently a 2 mm. metallurgical objective (N.A.1·32) was used to examine the area. The enhanced resolving power enabled one to see that many of the edges did not run to the straight sides of the rods, but stopped short at a little distance away at what appeared to be dislocations. This supports an argument of the type outlined above. Moreover, as we shall see, in many other cases rods were associated with the presence of dislocations.

No very satisfactory answer can be provided for questions
1) and 2), and this matter will be left open. It is interesting to note the analogy between the rod and layer structure observed here and the oriented and curved systems observed by Kowarski on paratoluidine crystals.
CHAPTER VII

Microscopic examination of specimen A - prism face number 1.

The main plateau.

The discovery of the main growth plateau shown in Fig. 36 has already been mentioned. Near the point of termination of the feature propagating on to the plateau is the spiral shown in Fig. 57. In this instance we see the simplest possible case, that of growth from a single screw dislocation. The kink in the right hand edge is not due to any break in the edge, but presumably to some disturbing influence, such as the presence of impurity.

The variation in visibility of the edge is almost entirely due to the focal behaviour of the objective. This was a 2mm. objective (NA. 1.32) which was designed only for use as a transmission objective and consequently a considerable variation in the intensity of illumination takes place across the field of view.

On either side of this spiral were a number of edges, limited on one side by the gross feature, and of approximately equal spacing. It appears possible that these edges may originally have formed part of the spiral seen in Fig. 57.

Immediately to the right of Fig. 57 another very faint spiral existed, in this case of opposite hand (Fig. 58). This considerable difference in visibility typifies the variations which can exist over a small area. The number of turns of this spiral are too many for the whole of it to be seen in the figure; it showed $2\frac{1}{2}$ turns as compared with the $1\frac{3}{4}$ turns of Fig. 57. The
plateau as a whole showed a fairly regular edge structure which probably originated from the general area containing Figs. 57 and 58.

**Behaviour at obstacles.**

This face showed one particularly interesting case of the behaviour of the layers at obstacles (Fig. 59). The layers advancing from the right are split into those sections by a succession of 3 crystal inclusions, which act as obstacles. Of the 3 sections the central and lower sections first combine again to form a single section. Counting from the last edge before diversion commences on the right, there are 37 edges in both the central and lower sections before a junction occurs again. Similarly, considering the junction beyond the third obstacle, there are 57 edges in both the upper and lower sections between the first division of the edge and the first complete edge.

It must, therefore, be that in general each step is a similar unit step. For a step one molecule high this type of behaviour is immediately understandable and in fact necessary, but for steps 2 or more molecules high it would appear very probable that in these circumstances the steps would either split into smaller units, or combine to form multiple steps. This evidence thus strongly supports the conclusion that the steps are one molecule high.

The slow closing in of the edges beyond any inclusion, and the rapid elimination of the re-entrant angle formed at the junctions of the different sections, is typical.
Surface depressions.

The question of the origin of many surface depressions, which was raised during the discussion of face 1, is again posed on this face, and in particular by Fig. 60. This shows a feature of well defined limits, undoubtedly below the general level of the surface, and displaying some kind of edge structure. Two points to note about this feature are that the main part of its upper limit is rectilinear and parallel to the c-axis, a most improbable chance occurrence, and also that the row of rods on its left hand edge points as usual down the slope. Some edges within the feature end abruptly, but this may be of no particular significance. The origin of such a feature must again remain obscure.

Another, even more puzzling example, shown in Fig. 61, is very similar in type to an area of Fig. 50. In this case the central area has 3 well defined sides, quite distinct from the main layer system. Over part of the upper edge, however, there is no obvious line of demarcation and, in fact, some 25 layers from the main system appear to run down into the feature and terminate on its lower limit, which is well below the general surface level. This behaviour is probably only apparent, for it will be noticed that at the point where the layers "enter" the limits of the feature they become suddenly more visible. Thus, it may be that the edges within the feature correspond to a greater step height, but there is no denying the continuity of the edges. Moreover, the presence of this feature appears to have little effect on the shape of the edges of the
main system, as they pass by and leave it behind. It will also be noticed that some of the edges appear to extend into the extreme right hand section of this feature.

Behaviour of this kind appears quite inexplicable in terms of the processes which might ordinarily produce surface depressions.

The behaviour of the layer system in the upper part of Fig. 60 is unusual in some ways. A single edge of rather irregular outline loops from the upper rectilinear boundary of the depression. The first 2 edges of the main system lying beyond this are much more widely spaced than the rest of the system. It seems that this could be caused by a junction with an active system (which in this case would have to be the irregular edge), or by a sudden decrease in the supersaturation over this area.

The depression in this figure has split the main layer system into two parts which are about to recombine on the left of the figure. A number of rods again line the gradient due to the upper system.

Position of the dominant growth centres.

This face could be conveniently divided into 3 parts. The first part runs from the fractured end of the crystal to the intermediate region and showed the usual type of layer structure, and some dislocation structure of no especial interest.

The intermediate region was of very coarse, irregular structure, and stretched from one side of the face to the other,
thus dividing off the third part.

The third region, several areas of which have already been discussed above, had a dominant growth centre which lay a centi-metre further up the face than these areas. From this centre layers spread over the whole of this third region. Over much the greater part of this region the edges were of very poor visibility, but the edges were traced back until the centre was found. This consisted of a number of surface features of the slip-zone type, from which a considerable number of layers spiralled. It proved impossible to obtain a satisfactory picture of this area, but several very similar examples will be shown later.

Central region.

Almost the whole of this central region of the face had a very coarse structure and nothing of interest could be seen. At one point where this coarse area met with the boundary of the upper region, there were several small blocks which showed a rather irregular edge structure which appeared to be caused almost entirely by dislocations. A typical area is shown in Fig. 62. All these blocks appeared to be tilted slightly with respect to the main face so that they went rapidly out of focus across the field of view.

The most clearly defined edge in this figure lies in the centre, and joins two dislocations. The left hand position of the edge shows a point of inflexion, as though the dislocation had switched suddenly from one hand to the other. Several other edges in this area displayed a similar type of behaviour.
General discussion.

Deductions from the theory.

The spirals shown in Figs. 57 and 58 correspond precisely to the growth spirals predicted by theory when the two-dimensional growth rate depends on the orientation of the step line. Just as in the case of Fig. 53, a number of deductions can be made from these figures.

It is not possible to arrive at any reliable estimate of the constant $B$ from measurements of the curvature of the 'straight' edges of the spirals in Figs. 57 and 58. The third and fourth straight edges of Fig. 57 are definitely concave, due to the imaging of the objective, and although the second edge is convex any measurement of the curvature must be of a very approximate nature. Similarly, the third straight edge of the spiral in Fig. 58 has a very slight convex curvature, but the fourth and fifth straight edges appear to be almost perfectly rectilinear.

Three estimates of the size of the critical nucleus can be obtained, one of which is rather approximate. The loop of Fig. 62 gives a reliable estimate of the maximum size of the critical nucleus. A direct estimate of the size can also be deduced from the spacing of a number of edges, lying just off the area shown in Fig. 57, and probably originally part of the spiral. Finally, a measurement of the radius of curvature of the first curved edge of this spiral provides another estimate which is necessarily only approximate. The values so obtained are
These values can be compared with the value of 1 micron for face number 1. Using the estimate of $\phi / k$ obtained on face 1, the above values correspond to a supersaturation of about 0.25%.

The spirals in Figs. 57 and 58 are very similar. The spacing of successive turns, reduced to units of the first turn of each spiral, is:

<table>
<thead>
<tr>
<th>Fig. 57</th>
<th>1</th>
<th>4.2</th>
<th>8.4</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 58</td>
<td>1</td>
<td>4.3</td>
<td>8.2</td>
<td>11.2</td>
</tr>
</tbody>
</table>

It would appear from these figures that the spirals have not developed sufficiently to settle down to a constant spacing between successive corresponding edges. This is supported by estimates of the size of the critical nucleus obtained from measurements of the spacing of the outer edges of Figs. 57 and 58. The values obtained were 2.8 microns and 2.5 microns for Figs. 57 and 58 respectively.

**Behaviour at obstacles.**

The behaviour of the layers at the 3 obstacles seen in Fig. 59 is strongly in favour of these steps being uni-molecular. The situation here also allows a closer investigation of the additional curvature of the edges which always takes place near an obstacle. Such curvature is equiva-
lent to the presence of a "virtual source", being analogous to the passage of light waves through a refracting medium. Normally such behaviour is complicated by the fact that only a small section of the edge is subject to such behaviour, for it is necessary for the whole of the edge to be affected before it is possible to determine whether the effect is really regular.

The central portion of the edge system shown in Fig. 59 provides just such a system and it can be immediately seen that it behaves as if a "virtual source" were present near the marrow neck between the 2 obstacles. (The analogy could be extended by considering the system to be brought to a focus and then diverging again, the focus being caused by successive compressions of the growth fronts by the obstacles. Such an analogy must be superficial and it would be dangerous to press it too far).

The approximate position of the "source" can be found by producing back the lines joining the points of junction of the curved and straight edges; it lies off the upper edge of the narrow neck. The ratio of the radius of curvature of the curved edges of this small system to their distance from the "source" is constant and equal to unity. This relation still holds for those sections corresponding to the central system of the first 4 edges of the joint lower system. The system diverging from the "virtual source" thus behaves in precisely the same way as the closed loop of Fig. 53.

Effects of dissolution.

The point of inflexion of the left hand edge of the loop in the centre of Fig. 62 would at first seem to
be at variance with the simple spiralling predicted by theory. As this behaviour is not explicable in terms of growth let us consider what happens when an edge is subject to dissolution.

The theory predicts that during dissolution the edges will reverse their direction of movement, but retain the same relative "growth" rates. Fig. 63 A shows 4 successive positions of a spiral during dissolution. The right hand edge marks the original position of the spiral. The next edge to the left shows that dissolution is perfectly regular in nature except for sections of the edge very close to the dislocation.

The 2 edges further left again show successive positions of the edge, the final position corresponding to the case seen in Fig. 62. Thus, over the area shown in Fig. 62 a small amount of dissolution must have occurred after growth had ceased.

Consideration of Fig. 63 A will show that the shape of the edge resulting from dissolution is very much dependent on the original shape of the spiral and, particularly, on the position of the dislocation on the original spiral. Fig. 63 B shows a spiral similar to that shown in (A) except that the straight edge running from the dislocation is shorter. Successive positions of the edge during dissolution are shown, moving from right to left. Although the behaviour of the spiral is essentially the same as that in (A), because of the different position of the dislocation a good deal of difference appears to exist between the shapes of the edges in the 2 cases. Thus, the most obvious point of inflexion seen in (A) occurs much closer to the dislocation in (B), and the shape of the edge therefore appears to be quite different. In particular, for spirals of
type B the shape corresponding to the left hand edge should be reached quite quickly.

There are several other cases which could be considered; one of particular interest is shown in Fig. 63 C. The spiral in this case is drawn to be of typical dimensions. These dimensions are such that in an early stage of dissolution, the 2 curved edges moving in from the left and right must approach each other. As they become very close a slight deviation from the normal dissolution rate should take place, to produce a hook-shaped edge. Further, slight retraction from the final position marked in (C) would make the hook much narrower and at a further stage it is probable that the edges would meet near the dislocation and leave behind a small closed loop. Such a closed loop should disappear rapidly.

It appears that dissolution of the nature predicted by theory is capable of producing an edge of the type seen in Fig. 62. Figs. 63 B and C have been drawn merely assuming typical shapes of the spirals and a regular retraction of the edges, drawn roughly to scale. Consequently, if the other edges are observed which have an outline not explicable in terms of growth, but which correspond to one of the stages in 63 B or C, it may be considered proved that this crystal conforms with the predictions of theory during dissolution. Such evidence will be considered in the next chapter.
CHAPTER VIII

Microscopic examination of prism face number 3 of specimen A.

This face was contiguous to face 2 and was similar to it in that a region of coarse structure effectively divided the face into 2 main regions. In this case the coarse structure did not quite reach the edge of the face, so that the 2 areas were not completely independent. The discussion will be divided into two parts, the first dealing with the region of the face lying between the fractured end of the crystal and the central coarse region, the second with the region stretching from the coarse structure to the terminated end of the crystal.

(a) Lower region of the face.

A layer system of considerable extent spread from the fractured end of the crystal. On the upper part of this system and no far from the fractured end, an area was seen which considerably modified the behaviour of the layers in its vicinity. Part of this area is shown in Fig. 64. The layer edges running from the fractured end are on the left.

In the centre of this figure are some 40 closely packed dislocations, apparently all of the same hand, which spiral round to terminate on two surface steps on the right. Below this central area a strip with well defined edges runs downwards both edges of this strip being bounded by "rods" which point away from it. This can only mean that this strip lies above the general level and that its edges mark a sudden fall in height. This strip also shows a layer structure, which on its lower left
hand edge appears to originate entirely from dislocations.

This strip continued downwards beyond the point shown, decreasing in width as it went. As in the case of the majority of the edges within the strip which are seen in Fig. 64, it was difficult to determine whether these edges terminated on dislocations. A clue was provided by the fact that one side of the step apparently sank below the general surface level, while the other side remained above it. Thus, in Fig. 65 shows the continuation of the strip. In the upper part of the figure there is a large rod structure on the right of the strip, with a smaller rod structure on the left. The rods on the left decrease in length as one travels down the strip, until, after a short blank length of the edge, they are seen pointing into the strip, while the rods on the right still point to the right. This must mean that the strip has some form of complex twist in relation to the surrounding area.

The rods on the right tend to decrease in size toward the lower part of the figure, which may correspond to a decrease in the fall in height at the edge of the strip, although such a relation between step height and rod size is possibly of doubtful validity, even although it appears to hold in the other section of the figure. However, beyond the lower part of Fig. 65 the rods on the left continued to increase in size until they covered the entire width of the strip, while the rods on the right entirely dissappeared although a well defined boundary still remained.

The final merging of the strip into the surface was marked
by the sudden decrease in size of the rods running from the left hand boundary, followed by the abrupt disappearance of this boundary. At the point of the right hand boundary which corresponded to the point of disappearance of the other edge, a line of rods suddenly appeared again, although for some distance above this point the edge had been bare of rods. These rods were of a rather irregular outline and were succeeded by a line of dislocations before the strip finally lost its identity.

This strip may have been subject to some complex deforming process and it seems probable that its boundaries mark some kind of transition surfaces. These transition surfaces possibly consist of a close line of dislocations. Also, all those edges in Fig. 64 which apparently terminate on dislocations in the strip appear to be of the same hand. Consequently, if such behaviour is taken to be general the traces on the face of the transition surfaces must be defined by two long lines of dislocations, the great majority of dislocations in any one surface being of the same sign, but the two main lines being of opposite hand.

All the rods showed the usual type of surface structure. In Fig. 64, it is particularly noticeable that there is a high concentration of dots along the bases of many of the rods. These dots appear to be very similar to some examples which are shown below, in which a single dot apparently corresponds to a number of unresolved dislocations.

Altogether there are some dislocations in the centre of Fig. 64 which cause the local modification of shape of the dominant layer system. If the edges within the strip are attributed to
dislocations, and this seems a reasonable assumption, then the "linear" density of dislocations along short sections of the boundary corresponds to values as high as 18,700 per cm., but a more typical value is some 7,100 per cm.

Another region of part of the same main system which lies near the lower edge of the face is shown in Fig. 66. The main system is again advancing from the left when, along a line perpendicular to the hexad axis, disturbing influences cause a rapid change in the shape of the edges. These "disturbing influences", which are shown below to be dislocations, result in a subsidiary system being formed. This subsidiary system makes a junction with the section of the main system seen on the lower part of this figure, and from this junction a slightly curving edge results, running at a slight angle to the c-axis and continually encroaching on the curved edges of the other system. This encroachment continued until these slightly curved edges spread across to make a junction with the straight edges and so completely eliminated the curved edges of the other system. At this point the edges were slightly concave in curvature and made an angle of approximately 25° with the c-axis. This junction was followed for some 5 mms. (i.e., some 1,000 edges) and the edges gradually became straighter and progressively less inclined to the c-axis. A locally dominant system then altered the conditions and these edges were replaced by the normal type of curved edges. The general conclusion to be drawn from this behaviour appears to be that edges inclined at small angles to the c-axis can grow more rapidly than the normal curved edges.

Returning again to Fig. 66 a sudden increase in the spacing
of the edges can be seen to take place in the upper central part of the figure. This is caused by several edges running between, or from, the dislocations. The main layer system must propagate across this line of dislocations, yet the edges show very little variation in outline compared to those on the left. This is because this group of dislocations is comparatively inactive, and is behaving in just the way shown in Fig. 52.

Examination at higher magnification of the area shown in Fig. 66 reveals a good deal of information (Fig. 67). Before the layer system reaches the main line of dislocations, a number of single dislocations, and closely packed groups, are encountered, which make no major change in the shape of the edges. Close examination of the "disturbing influences" in the upper central part of this figure shows that these consist of a large number of closely spaced dislocation, all of which are of the same hand. If these dislocations were at all active they would form a barrier which would be very difficult to overcome, but in fact they appear to be even less active than the dislocation represented in Fig. 52 and the incident edges undergo very little modification.

It would seem from Figs. 66 and 67 that the lower line of dislocations is of opposite hand to that discussed immediately above. This agrees with the presence of a rod structure only in the centre, for if this line marks a slip-zone (see Chapter II) then the centre must be at the maximum height above the general level. In this case it is difficult to estimate this difference in height, but from the number of dislocations above the centre it must be some 70 atomic spacings. The rods again show quite
a number of dots, which probably represent dislocations, near their bases.

The long rod which projects farthest right shows one very obvious dislocation near its tip, while other dislocations appear to be present on its surface. Some of the other rods also show several dislocations on their upper surfaces. This is a point of some significance.

Particularly noticeable is the speed of elimination of the re-entrant between the upper and lower sections of the edge system. A very sharp re-entrant is formed by the first joint edge which almost touches the rod projecting furthest right. Yet by the fourth joint edge this re-entrant is almost entirely eliminated, due to this being the direction of rapid growth.

Immediately below the tip of the re-entrant first joint edge, is an edge joining 2 dislocations. There is a point of inflexion of this edge near the lower dislocation; comparison with Fig. 63 shows that this has presumably been caused by slight retraction of the straight edge due to dissolution.

The other main system on this region of the face, also originated at some point beyond the fractured end of the crystal. The curvature of the edges at this end was considerable and it seems probable that the original source may have been near this point.

Not far removed from the edge was a long line of dislocations roughly perpendicular to the c-axis, which was sufficiently active to modify the form of the main system. The lower end of this line is shown in Fig. 68. The main system is again advancing from the left, passing various single inactive
dislocations, which only very slightly modify the edges. Near
the main dislocation system these odd dislocations increase in
number. Two groups in the centre of the figure are sufficiently
active to form small layer systems which soon unite.

It should be noted that in the central area of the figure
rods only appear on the steep downward slopes of the various
systems and not on the plateaux. This supports the proposal
that a steep gradient or a sudden difference in height is
necessary for their production. There are also a considerable
number of dots running along the base of these rods; these dots
almost certainly indicate the presence of dislocations in the
great majority of cases.

The slight spiralling of the edges in the upper part of
the figure indicates that these edges are running from a closely
spaced line of dislocations. Thus, toward the centre of the
main rod system in the upper part of the figure the rods are
marking a difference in height of about 80 molecules.

The upper limit of this system is shown in Figs. 69 and 70,
which overlap slightly with each other. Fig. 69 also overlaps
slightly with Fig. 68, so that the whole of the system is shown.

Inspection of Fig. 69 shows that the majority of the edges
to the right of the rod system run from dislocations, and in
fact it is probable that every edge is so generated. The large
rods near the top of Fig. 69 must then project over a drop in
height of some 170 molecules.

Fig. 69 also shows the relation existing between the rods
and the presence of dislocations, in a particularly striking
manner. There are 2 main rows of rods and it can hardly be a
Fig. 70
x 500  (N.A. 0.95)

Fig. 71
x 500  (N.A. 0.95)
coincidence that the bases of these two rows are marked by two rows of closely spaced dislocations. Some of the dots in these rows may merely mark the sharp termination of a steep edge of a rod, but in the majority of cases, they appear to denote the presence of dislocations. The linear density of these dislocations is very high, being roughly 8,500 per cm. over very short distances.

In Fig. 70 the rods tail away toward the centre of the figure as the level approaches that of the main layer system. The upper limit of the dislocation system is marked by a line of dislocations which is much more widely spaced. This line is spread quite regularly and has little effect on the dominant system, showing all the stages sketched in Fig. 52, including a kinking of the incident edge as it approaches very close to the dislocation.

For a considerable distance beyond the area just discussed, the system behaved fairly regularly, except for occasional kinking of the edges along lines perpendicular to the c-axis, presumably caused by rows of inactive dislocations. Some hundreds of layers further up the face was the area shown in Fig. 71. In this case a small group of more active dislocations form a layer system which results in an increased curvature of the main system. This group consisted of two main branches of dislocations of opposite hand. Some of the more obvious dots in Fig. 71 must correspond to a number of unresolved dislocations, or a multiple dislocation, for several edges run from these dots.

On this part of the face, and more frequently on the upper part of the face, edges were often found to run from surface
steps not perpendicular to the c-axis. One exceptional case is shown in Fig. 72. In this area the straight edges are so closely packed that they are not resolved at this magnification and yet every edge on the upper two-thirds of this figure starts from one of the surface steps seen in the centre. The density of dislocations along these steps must be extremely high in some cases.

The very obvious step in the lower part of the figure must correspond to a very considerable drop in height. Below this step the edges show a curious type of behaviour typical of several areas on the lower part of the face. Multiple edges form at fairly regular intervals and all the edges display a quasi-regular kinking which leaves small areas devoid of edges.

The right hand extremity of one of the main systems is shown in Fig. 73. The coarse structure which marks the commencement of the central region lies on the right of this figure. The main system is incident on a local slip-zone which has a main series of dislocations of opposite hand on either side of the centre. This line of dislocations is sufficiently active, and sufficiently close-packed, in the lower part particularly, to have what would have been at least a local effect on the main system.

As usual there are a few scattered dislocations before the main group is reached, but these former are inactive and merely behave in the way previously discussed. There are indications that the edges continue, or had previously continued, on to the coarse structure on the right.

On the upper part of the figure a number of very small rods
project from a drop of some 13-20 molecules, the only steep
gradient. Along the base of these rods are 6 dots which probably
mark dislocations. The largest rod also appears to have 2 other
dislocations on its upper surface.

In the lower group of dislocations is one very obvious dot,
from which 8 edges run in 2 groups of four. From the form of
the edges it appears that this dot marks the presence of 2
unresolved sets of 4 dislocations of opposite hand (or alterna-
tively, 2 multiple dislocations of opposite hand).

General Discussion.
The density of dislocations.

From the examples already given it is
obvious that the density of dislocations is greater in this region
than on the faces previously discussed. The figures shown by
no means represent the total of dislocations seen in this region,
but are presented either as typical cases, or as examples which
show some effect particularly well. Even although the dislocation
density is much greater in this region, the general density by
no means agrees with the figure usually quoted for "perfect"
crystals. Thus, during growth this must have been a very perfect
crystal, judging from the standpoint of the density of imper-
fections; there is, of course, no clue to the increase in the
number of dislocations since growth ceased.

It is, however, of interest of compare the greatest observed
dislocation density with the values quoted for metal crystals.
In Fig. 64 the greatest observed value was a "linear" density of
about 18,700 per cm., which agrees very well with the figure of
10,000 per cm. often attributed to annealed metal crystals. This
close correspondence is of some significance, particularly as the density for the beryl crystal applies to what appears to be a transition surface. Moreover, the correspondence is quite as close for the more typical value of about 7,000 per cm. for the 'linear' density of dislocations along this 'transition surface'.

A similarly close-packed line of dislocations occurs in parts of Fig. 68. For example, one short section of 0.04 mms. shows 50 dislocations, corresponding to a linear density of some 12,500 per cm. Another example which might be cited, is the line of dislocations along the base of the second row of rods in Fig. 69, which corresponds to a density of 10,000 per cm. Other areas in the same region give a linear dislocation density of about $10^4$ per cm., and the conclusion to be drawn is that the most imperfect areas of this crystal, and in particular slip-zones and transition surfaces, have a linear dislocation density equal to that of an annealed metal crystal.

As this surface only shows the intersections with the face of comparatively widely spaced dislocation surfaces the area density never reaches $10^8$ per sq. cm. Some small areas with two closely spaced dislocation lines have a density of about $10^7$ per sq. cm., the more normal value being $10^6$ per sq. cm. or less. The surface density is thus less than the value quoted for annealed metal crystals.

Structure of slip-zones.

One point brought out particularly clearly in this region is the frequent occurrence of lines of dislocations perpendicular to the c-axis, which must represent slip-
zones of the type mentioned in Chapter II. This agrees with
the general finding that crystals of this type of symmetry
frequently slip along a (00\cdot1) plane (Buerger, 1930), which is
parallel to the basal pinacoid and perpendicular to the hexad
axis. The presence of such a slip plane would also be expected
from the nature of the atomic structure of beryl.

As these steep cliffs marked by lines of dislocations do
not appear to be explicable in terms of either growth or disso-
lution, and as all the evidence points to these cliffs marking
the line of a slip plane, there appears to be no other conclusion
than that these cliffs resulted from local plastic deformation.
Moreover, the distribution of dislocations is precisely that
predicted by the theory for a limited slip-zone. The experi-
mental observations thus provide direct proof that the mechanism
evisaged by dislocation theory for simple slip is correct.

Areas such as those shown in Fig.68 cannot be attributed to
a single slip-zone, but may be caused by a number of closely
spaced slip-zones.

In the case of Figs.64 and 65 some kind of complex deforma-
tion may have taken place. This area was the only one of its
kind observed on this crystal.

Rod structure.

The experimental results in this section provide
some interesting information about the rod type of structure.
Figs.64, 66, and 67, and especially fig.69 show that dislocations
very often exist at the base of the rods. In this region of the
face this behaviour is so common that it lends a good deal of
weight to the argument that the presence of dislocations is a
necessary condition for the formation of rods. Although many rods have been observed which are apparently not associated with dislocations, it should be noted that several examples are shown above in which a dislocation structure can be seen on the main body of the rods. Examination at high magnification of apparently dislocation-free rods on face 1 showed that, in fact, there were a considerable number of dislocation on their surfaces. There can be little doubt that a close connection exists between the presence of rods and the existence of dislocations; it may well be that the presence of dislocations is a necessary condition for rod formation.

Rate of growth of layers.

In the area near Fig. 66 edges making an angle with the c-axis of $4°-25°$, grew sufficiently quickly to eliminate the curved edge of one system and continued unchanged for some 1,000 edges. Within these limits, these edges must grow more quickly than the curved edges. The same kind of behaviour was shown at the junction of two of the systems seen in Fig. 68, when the straight edges of the larger system took on an inclination of approximately $15°$ to the c-axis after the junction.

In this latter case the rate of normal advance of the inclined edges is approximately 4 times as great as that of the curved edges of the first system, and slightly greater than the rate of growth of the curved edges of the same system. The presence of a re-entrant is probably sufficient to enhance the rate of growth of the inclined edges with respect to the curved edges of the smaller system, but even without the added help of a re-entrant angle they grow sufficiently quickly to be...
eliminated by the curved edges.

The formation of inclined edges of this kind is quite common when two systems join, and normally as above, their rate of growth is sufficient for them to eliminate the curved edges of one system, while the geometry of the system and the slower growth rate of their corresponding curved edges results in their eventual elimination. It is therefore possible to make an addition to the polar diagram of the kind shown in Fig. 74.

Delaying action of closely spaced dislocations.

Any line of dislocations must delay the incident layers, but in the case of some of the very closely packed lines of dislocations which have been discussed the effect must be equivalent to an impassable barrier. This barrier could be overcome when the supersaturation passes a certain critical value, but in some of these cases the necessary value of the supersaturation must be much higher than any that is ordinarily attained.

(b) Examination of the upper region of the face.

The central region of a dominant group of dislocations is shown in Fig. 75. To the right of centre two rows of rods face each other across a depression. The upper section of the right hand line of rods shows a notable number of dislocations running along the bases. There are at least 18 dislocations in a length of 0.015 mms. and it is quite possible that some of these dots may mark multiple, or unresolved dislocations. There are also a number of dislocations on other parts of the rod system.
Around these rod systems, and indeed in the whole of the lower two-thirds of the figure, every edge appears to run from a dislocation or between a pair of dislocations. In the central area there are some 100 screw dislocations in an area of $7.6 \times 10^{-3}$ sq. mms., corresponding to a surface density of approximately $10^6$ dislocations per sq. cm.

At the top of Fig. 75 part of a large layer system can be seen. It is obvious that the system starting from the central dislocation group is travelling very much faster than this larger system; the first two edges of this active system are spaced 10 times further apart than the last two edges of the upper system.

The first edge of the system starting from the dislocation group has an unusual hook shape near its parent dislocation. This is immediately reminiscent of the type of dissolution effect predicted in Fig. 63 C and could hardly be a growth effect. The edge immediately underneath this hook also shows a curious kink which looks at first as if it might have been caused by cross linking with the edge above. However, the lower edge can be traced across a small light patch (it is very faint here), to a sudden upward kink and termination on a dislocation. This kink near the dislocation suggests the action of dissolution and if this edge is compared with the extreme left hand edge shown in Fig. 63 B, the similarity is obvious. The edge under consideration shows a more advanced form of dissolution than that in Fig. 63 B. Such a form would appear much more rapidly if the dislocation was originally very near to, or, alternatively, on the commencement of, the original curved edge., for in this case a straight edge would be left behind almost immediately.
Inspection of Fig. 75 shows that the original curved edge could not have lain far from its parent dislocation, because of the presence of other edges, and presumably other dislocations. The observed behaviour thus agrees with the behaviour predicted by theory.

The form of the main kink in this edge is rather surprising but this provides no argument against the above evidence. As the hook shape can also be satisfactorily explained in terms of dissolution there is no need to assume that cross-linking of the edges has taken place.

Some of the edges lying immediately to the right of those two edges just discussed also have outlines which suggest that a slight degree of dissolution has taken place.

An area adjacent to Fig. 75 is shown in Fig. 76. The rod structure lies on the extreme right of this figure and the edge of the face runs along the bottom of the figure. At about 4 o'clock from the centre of the figure is what appears to be a twin-armed spiral. The lower arm actually terminates on another dislocation, but it is obvious that two dislocations of the same hand must lie within the dot.

To the left of this spiral is a well defined loop running between two dislocations. Another edge runs very near to the left hand dislocation of this pair and from the rather irregular shape of the edge it appears the presence of the dislocation has resulted in some kind of interaction between the two edges.

To the right of the twin-armed spiral is a kinked edge of the type drawn in Fig. 63 A, so that this edge has probably been subject to dissolution also.
Immediately to the right again are edges arising from dislocations, which run off to the edge of the face with no apparent attempt at spiralling.

This figure shows how the layer system is building up in a regular way on the left, although the parent dislocations are randomly distributed. The spacing of the curved edges of the system is considerable, but by no means as great as between the first two edges. A general view of the dislocation group and the system spreading from it (Fig. 77) shows how much more rapidly than the upper system this system is growing. This upper system is dominated by the lower system, which rapidly encroaches on the curved edges, so that they are soon eliminated.

Immediately to the left of the area shown in Fig. 77 and slightly overlapping with its left hand edge is the area shown in Fig. 78. The system advancing from the right meets a group of dislocations which are only sufficiently active to cause local variations in the outline of the advancing layers of the dominant system.

The lower part of this area is shown in greater detail in Fig. 79. The central group is divided on either side of the centre into two groups of opposite hand, the line of dislocations in this case lying along, rather than perpendicular to, the c-axis. Almost all the edges in the lower central part of this figure run between pairs of dislocations. The lowest right hand loop of this group is of an unusual form, but it appears probable that in the course of the growth of the layer immediately to the right, contact must occasionally occur with the loop. Cross-linking of the edges would then occur and a complicated form of
Fig. 78
x312  (N.A.0.45)
loop could result. If a loop of this latter type was subject to dissolution a loop of the same might result.

To the immediate left of this loop is another loop with a hook-shaped lower section of the type previously predicted for some cases of dissolution. The form of this loop thus adds some weight to the explanation given in the preceding paragraph.

Immediately above these loops there appears to be a completely closed figure. However the right hand edge of this figure runs from what appears to be two barely resolved dislocations of the same hand. If the two left hand edges do actually run from a single point then this must represent a pair of dislocations. From the shape of the inner left hand edge it appears possible that this effect may be spurious and caused by a thread of foreign material running across the two edges. If the effect is not spurious it would mean that during growth a double loop must have expanded from these 2 pairs of dislocations. Such an expansion of the loops is likely to take a very complicated form, for, due to the presence of a number of dislocations in the immediate vicinity, a good deal of cross-linking must occur with the parent dislocations.

On the left hand side of the central dislocation group two of the loops show a reversed curvature of the types shown in Figs. 63 A and B. Immediately to the left of these edges is another very pronounced hook shape which can only be ascribed to dissolution of a type C spiral. The obvious kink above the main hook is probably due to growth rather than dissolution, for growth of the layers on the right would result in a switching across of the edges and produce just such a kink.
Six layers to the left of the large hook shaped edge there is another typical type C hook shape.

The propagation of layers across areas with such closely spaced dislocations must result in some complicated happenings. As an example of what happens in the less simple cases, although by no means equivalent to the most complicated cases, the propagation of the layers in the upper part of Fig. 79 is dealt with later in the general discussion.

In both figures 78 and 79 there are instances of edges taking a reversed 'S' shape. Such behaviour is not contrary to the theory, but merely due to the dominant characteristics of the incident system. Thus a very acute elbow runs from a single dislocation in the upper central part of Fig. 78. (The dotting in the elbow is spurious and is not due to dislocations). It is evident that this edge, which originally curved downward, must form a re-entrant of this type on junction with the incident layers. Moreover, this re-entrant cannot be rapidly eliminated as it lies in the direction corresponding to a minimum growth rate.

The area to the left of the main dislocation group (Fig. 80) also shows examples of the complications introduced during propagation of layers past a number of dislocations. The two hook shapes discussed for Fig. 79 lie in the lower central region of this figure. In the left central region the incident edges undergo such local distortion that it is difficult to assign an edge to its appropriate dislocation, or dislocation pair.

In one case a section of two edges is coincident, and it is probable that this corresponds to the moment of cross-linking
of the dislocation to the right hand edge. An alternative explanation of slight dissolution after growth had ceased, which could explain the kink in the left hand edge, appears to be of doubtful validity, for the shape of none of the other edges, including the right hand edge of the overlapping pair, supports this view.

A curious incident near two single dislocations on the edge marked in Fig. 81. A linking across of the edges has apparently just occurred and it appears that the local kink in the incident edge must have been quite marked (see Fig. 52 C), for the dislocations are now both attached to kinked edges which are concave in the direction of growth. This would seem to indicate that the concave loop has either been unusually deep, or asymmetrical about the dislocation, and the agreement with the theory would be satisfactory was it not that the edges which have just passed these dislocations show the normal type of kink, but rather far removed from the dislocations.

Another group of dislocations lying in the path of the main system is shown in Fig. 82, the central area of which is shown at a higher magnification in Fig. 83. The group consists of some 23 dislocations which run in a straight line almost to the edge of the face, and are all of the same hand. Fig. 82 shows that the closely spaced edges of the main system suddenly alter in behaviour as they pass this dislocation group. The group itself does not appear to be particularly active, yet the curved edges of the main layer system are much more widely spaced after passing through the group and show an increased curvature denoting a "virtual source". Hence, either the group must be
Fig. 81  
\[ x \times 500 \]  
(N.A. 0.95)

Fig. 82  
\[ x \times 250 \]  
(N.A. 0.45)
sufficiently active to stimulate the propagation of the layers, or else a local variation in concentration must be responsible for the increase in spacing.

The main layer system, areas of which have been discussed above, extended across the face to become of considerable width, and also extended along the face to the central coarse region, a distance of several millimetres. At the point of maximum lateral extension of the system the layers suddenly reversed the direction of their longitudinal edges (Fig. 84). This reversed edge then continually encroached on the curved edges of the main system, until the termination on the coarse structure was reached.

Such behaviour could only be due to the formation of a junction with another system, commencing in the area shown in Fig. 84. No edges of such a system can be seen, but it is not unusual to have systems with straight edges so closely packed that their edge diffraction pattern cannot be resolved. These "reversed" edges are then the inclined edges which have been discussed in the previous section. On this occasion they encroached upon the curved edges but did not finally eliminate them.

Other instances of the formation of behaviour of inclined edges were also observed in this region. They normally behaved in the way which has already been discussed.

Above the dominant dislocation group of Fig. 75 was a layer system, a general view of which is shown in Fig. 85. A large number of edges start from dislocations and surface imperfections in the centre, many of the edges terminating on other dislocations.
Fig. 85
x250 (N.A. 0.45)

Fig. 86
x625 (N.A. 0.95)
The coarse structure on the right of the figure becomes increasingly frequent as one moves right, toward the terminated end of the crystal. Not far to the right from Fig. 85 this coarse structure became so dense that all traces of edge structure were lost except for occasional small clear areas.

The upper part of Fig. 85 is shown at higher magnification in Fig. 86. The visibility over this area was extremely low. In the upper right hand part of this figure there is an obvious surface step, from which a large number of edges of the same hand run on the right, while a number of edges of opposite hand run from the left. This must be, then, a slip -zone which differs from those previously shown in that it runs parallel to the c-axis. This slip-zone appears to show some signs of a structure, but this is probably caused by the edges running from it being slightly out of focus.

On the left of this figure the edges can run mainly from single dislocations, as far as can be determined, except for one surface step, probably a slip-zone, from which a number of edges run.

Running down the centre of the figure is a line of rods which presumably mark a steep gradient. There are some 22 dislocations spaced along the base of these rods. Above the main line of rods is a series of very faint closed figures, also showing a number of dots along the base, usually at the point of junction of the edge which marks the base and a side of one of the figures. It appears probable that this is a line of rods in the process of formation. The outline of these figures is less visible than that of the main rod system and is
almost of identical visibility with a normal single edge, from which it may be assumed that these rods are, as yet, projecting very little above the surface. Consequently, this supports the conclusion that these rods are just forming.

Part of the lower area of Fig. 85 is shown in Fig. 87. On the left of this figure a system spreads from a number of twin-dislocation loops and Fig. 85 shows this area to be the centre of the main layer system formed on the left. Comparing the regular ordering and spacing of this central area with the closely packed tangle of edges on the right of Fig. 87, it is not surprising that no active system spreads from the latter area. Many of the edges are so closely packed that a good deal of competition must have existed during growth for the material adsorbed on the surface, the progress of any individual edge thus being hindered. Moreover, the close-packed edges themselves must present an obstacle to rapid growth.

The majority of edges in this area are so closely packed and of such poor visibility that it is difficult to determine the point of origin. Observation at very high magnification showed that in every case these edges appeared to terminate on a dislocation. Many of the edges did not take their characteristic spiral outline, but instead had an irregular or roughly circular shape. This can be attributed to a competition between edges which was sufficiently strong to mask the dependence of growth rate on crystallographic orientation.

Fig. 85 shows that this central close-packed mass of layers plays little part in the formation of the system which spreads from the right. This system is formed by edges linking
Fig. 87
x500 (N.A. 0.95)

Fig. 88
x500 (N.A. 0.95)
dislocations in the right hand part of Fig. 86 with other dislocations seen in the lower right hand part of Fig. 87. It is doubtful if the edges of the right hand system originally linked across in this way for this would imply that this group was more active than in fact it appears to be.

In the lower part of the left hand system of Fig. 87 is an edge outlining a very acute angle, the sides of which appear to be almost rectilinear up to the point of contact. This must either represent the actual moment of junction of 2 edges, before the re-entrant could be at all smoothed out, or else it is a spurious effect due to a thread of impurity.

The main system meets a small group of dislocations in the lower right hand corner of Fig. 85. This group, together with another group a little lower down, forms a system which rapidly extends across the curved edges of the large system, in just the same way as the layers from the dominant group of Fig. 75 rapidly spread across the curved edges at the other end of this system.

In the small dislocation group in the lower right hand corner of Fig. 85 is a double armed spiral of the type previously seen, except that in this case both areas are full single spirals.

The results so far quoted for this region all refer to areas of the lower third of the region. The remainder of the face was characterised by the comparatively frequent occurrence of steps running parallel to the c-axis, of the type previously mentioned for Figs. 72 and 85.

An example is shown in Fig. 88. In this case some 50 edges start from the main surface step, while another group of edges
starts from another step a little lower and to the right. The step again appears to show a structure which is probably only apparent and caused by the termination of the edges. On the right hand side of the system resulting from these steps, an isolated rod has formed. The edge structure on the surface of the rod and near its base is co-linear with the edges running immediately below it, so that in this case the layers must travel along the surface of the rod until they are halted at the edge and so pile up in the way postulated in Chapter V.

It might be argued that features of the kind shown here do not consist of a line of dislocations, but that the layers merely curve round in this way because of the presence of a surface step. In many cases, however, the edges running from these features consist of two groups of opposite hand, whose behaviour could hardly be explained on these lines. Moreover, features of the type shown in Fig. 89 were not uncommon. In this case the surface step runs from one side of the figure to the other, although barely visible on the left hand side. There are 2 groups of dislocations of opposite hand in the left hand half of the feature and even should the first section of this step correspond to a separate step the same behaviour still holds for the central part of the step. There can be little doubt that such cases as these are precisely analogous to the lines of dislocations marking slip-zones which were discussed for the lower section of the face, the only difference being that in this case the slip-zone is either parallel to the c-axis, or almost so.

On no slip-zone or surface step of this latter kind were any rod structures ever observed, although the necessary steep
Fig. 89
x500  (N.A. 0.95)

Fig. 90
x250  (N.A. 0.45)
The central group of five edges running from the step in Fig. 89 show a point of inflexion near the step. This behaviour is typical of slight dissolution. The way in which these systems spread raises some interesting points which will be considered in the general discussion.

An area which is in many ways typical of large areas of this part of the face is shown in Fig. 90. The edges here are of typically low visibility, largely due to the high density of foreign material which has been deposited, causing irregular speckling and marking. There are also large deposits which either wipe out the original edge structure or reduce its visibility. Consequently, such areas have not been generally shown and instead areas have been chosen in which the visibility of the edges is higher, or the behaviour of the edges is more obvious.

In the centre of Fig. 90 is a surface step lying parallel to the c-axis, from which many edges commence to spiral. The poor visibility of the edges in this figure obscures any isolated points of origin except for one well defined edge running from a dislocation in the upper left hand "semi-opaque" area.

An area in which all the edges run from dislocations is shown in Fig. 91. On the upper right hand side a single dislocation is sufficiently active to start a full spiral before it meets with the main system, the joint edge continuing down to the bottom of the figure. The majority of the edges in this group, as far as one can determine, run between pairs of dislocations. One edge running between a pair of dislocations is
visible as it runs across the light region on the left. This edge has a most unusual shape which could not be caused by either normal growth or normal dislocation. It may be that other edges, obscured by the light patch, resulted in a cross-linking which would give the observed edge this temporary shape, but even so the shape of the edge near the lower dislocation would still have to be explained.

An area of a type unique on this crystal, and indeed on any of the crystals observed, is shown in Figs. 92 and 93. The layer system on the right of Fig. 92 arises entirely from dislocations situated off the figure to the right. At the left hand extremity of this system a line of rods marks the commencement of a layer system of unusual shape. The rod system lies only on the central and lower parts of the right hand system, which suggests that the drop in height is either greater or steeper than in the upper part of the system.

Now if the left hand system were of a normal type, the configuration of the edges would mean that the rods were growing where the drop in height was almost negligible, while avoiding a considerable drop on the boundary higher up the figure. Examination of the closed figures formed by the edges shows that the usual polar diagram of growth is not applicable in this case and any attempt to construct such a diagram would result in a very unusual and asymmetrical figure. The only conclusion to be drawn is that, in this case the asymmetrical layer system is marking a hole, the deepest part of which is marked by the area enclosed by the short central edge running from the rods.

This supported by the behaviour of the edges shown in
Fig. 93
x500 (N.A. 0.95)
Fig. 92. In the upper part of this figure the 'hole' sheet system is joining with the normal system seen on the right. The junction between the edges is very acute and remained so as the edges continued above the area shown in the figure. This acute angled junction was traced until it reached the centre of the extreme left hand curved edge of the normal system. Another series of acute angled junctions (i.e., a sharp V-valley) was also found on the other side of the normal system. The left hand edges of this latter junction ran off to the edge of the face.

General discussion.

The figures shown above have all been chosen for some special reason, and by no means represent the total number of dislocations in this region. The density of dislocations in this region was much the greatest observed on this, or any other crystal. Unfortunately, at least half of this region showed a coarse structure of unknown cause which obscured almost every trace of the original layer structure.

The linear density of lines of dislocations in this region is much the same as in the lower part of the face. Thus, along the surface steps in Figs. 86 and 88 the linear density was very close to $0.5 \times 10^4$ per cm., while both higher and lower densities existed on different areas.

The surface density of dislocations in the two most imperfect areas observed on this part of the face is much the highest observed on any area of any crystal. There are some 100 dislocations in an area of $7.6 \times 10^{-3}$ sq. mms. of the dominant
dislocation group of Fig. 75. In the most closely packed area of the system shown in Fig. 85 there are $84 \pm 10$ dislocations in an area of $0.64 \times 10^{-3}$ sq. mms. (the uncertainty is caused by the low visibility of the edges and their very close packing). These values correspond to surface densities of $1.3 \times 10^6$ per cm. and $1.4 \times 10^7$ per cm. respectively, the latter density being of the same order as that attributed to annealed metal crystals. Thus the most imperfect areas of this crystal during growth had a density of dislocations equivalent to the value for an annealed metal crystal.

The mechanism of dissolution.

There are many examples shown above which correspond so closely to the types of edge shape shown in Fig. 63 A, B, C, that there appears to be no doubt that these edges have undergone varying degrees of dissolution. It is thus proved that the process of dissolution is the reverse of the process of growth, a statement which does not infer, as we have already seen, that the typical shapes of edges produced in the two cases are at all similar.

Activity of dislocation groups.

Various examples have been given of dominant and inactive dislocation groups. The dislocation group of Fig. 75 provides a very good example of a dominant group. In this case many of the dislocations are widely spaced and they appear to work together in a co-operative manner which can be contrasted with the behaviour shown in Figs. 85, 86 and 87. The irregular form of many of the edges in this latter group has already been mentioned and it is very probable that competition
took place between densely packed edges for the available material. Competition may have taken place between other groups of edges in this system, although not in this case sufficient to entirely mask the effect of crystallographic orientation.

Quite apart from possible competition it is hardly to be expected that a considerable number of closely spaced dislocations (probably several hundred or more) would combine in a cooperative way, for any layer attempting to expand through some of the less densely packed parts of this group is likely to suffer many hold-ups and delays, while in the really densely packed region a critical supersaturation would have to be reached before such passage was possible. As the evidence points to the presence of competition between the edges the value of the supersaturation was probably well below this critical value and such areas would provide an impassable barrier.

Several other systems which expanded to become of considerable extent were observed to start from comparatively few, and usually well spaced, dislocations. The conclusion to be drawn is that when the number of dislocations within a group is too great, and in particular when such a group is closely packed, then the growth of the resulting layer system will be hindered and will almost certainly be dominated by a system originating from a small number of well spaced dislocations, assuming equivalent conditions to hold.

For small or medium sized groups of dislocations the values of the supersaturation at different points on the face must decide which is to be the dominant group.
Cross-linking of edges.

Many examples of cross-linking of edges have already been given, particularly for the passage of a dominant system past widely spaced inactive dislocations. Examples showing all the types of behaviour portrayed in Fig. 52 have been cited, even to the actual moment of cross-linking.

One rather unusual example of this type of behaviour (Fig. 81) demands further consideration. Neither the shape of the kinked edges, or of the edges running from the dislocations, is what one expect from slight dissolution. The location of these kinks can thus be attributed to:

(i) some unusual departure from normal growth conditions due to unknown causes, or
(ii) the movement of the 2 dislocations just before cross-linking of the edges occurred.

It is reasonable to assume from the position of the large kinks that the dislocations may originally have been nearer the upper limit of the bulge of the incident edge, rather than near the lower limit. The dislocations could then, because of some internal, or applied, stress, have moved down in the direction of the trace of the glide plane and consequently have arrived at the other side of the bulge of the incident edge just before cross-linking occurred. This would result in the type of edge shape observed.

This second possibility offers a reasonable explanation in terms of known behaviour, for dislocations are known to move under small applied stresses, and it is very probable that they do so during the growth of the crystal. This may be an instance
when such behaviour can be detected, due to chance circumstances.

The propagation of layers past a group of dislocations must at times result in some very complicated forms of cross-linking. As an example of the type of behaviour which occurs, we will consider the way in which the layers in the upper part of Fig.79 would propagate if growth were to start again. The behaviour is shown in diagrammatic form in Fig.94.

In this figure a part of Fig.79 has been isolated and the edges are drawn in full line in (i). It is necessary to consider a limited area only, in order to simplify the actual behaviour. Thus, the curved edges running down on the left of all the diagrams terminate on a group of dislocations all of the same hand. These terminations have not been shown because (a) it would involve a considerable increase in the size of the diagrams, and (b) as all the dislocations are of the same hand only a simple type of cross-linking will result, of a type to be seen in the area studied. Hence, over the area shown in the figure, these curved edges can be considered to propagate fairly regularly, without any considerable deviation from the true conditions.

In these diagrams the propagation of the edges has not been drawn exactly to scale, but only approximately so. This means that deviations from the actual order of events probably occur in these diagrams, but the aim is to show the general way in which propagation by cross-linking takes place, rather than to predict the actual order of events.

In (i), (ii), and (iii) five successive positions of the edges are shown, commencing from their position as in Fig.79.
The advance of the edges from their original position in any of these diagrams is shown by a dotted line, and the position of edge I, for example, after an advance will be referred to as dotted I.

The original position of the edges in (i) is such that a slight advance will result in no immediate change except for edges A and B. Let us consider the advanced positions working up the diagram. Dotted I and dotted H show little significant change. Dotted G is now held up at the parent dislocation of dotted F and cross-linking will soon take place. Dotted E is similarly held up at the dislocation of dotted D. Dotted C shows no important change. The advance of edge B however, has caused cross-linking between the dotted A edge and the right hand part of dotted B. The edge dotted A, B results, and a new dislocation loop has formed on the left hand side of dotted B.

A further stage of advance of these edges is shown in full line in (ii). The lowest edge has now advanced until it is held up by the dislocation of edge Q (formerly H). The linking between dotted G and dotted F which was imminent in (i) has now taken place, resulting in the linking of the dislocation to the lower edge P, and the continuation of edge O with a considerable kink. The linking between dotted D and dotted E also imminent in (i) has occurred, leaving the dislocation joined to N, while the edge M passes on with a very marked kink. Advance of dotted C has also resulted in cross-linking with the dislocation loop which was formed at the first advance. Dotted C has linked on to the right hand dislocation, forming K, while the left hand dislocation of the loop has joined with the parent dislocation.
of dotted C, to form the loop L. The joint edge A, B continues to advance and is shown as J.

Further advance immediately causes R to cross-link with Q so that dotted R is now attached to a dislocation, while dotted Q (composed of sections of Q and R) passes on, on the right, with a marked re-entrant. On the left dotted Q is held up at the dislocation of dotted P, where another cross-linking is imminent. Dotted O is drawing close to the dislocation attached to dotted H, which is advancing normally. Dotted M has advanced almost to the right hand dislocation of the loop dotted L, and cross-linking will soon occur. Dotted K and dotted J have advanced normally.

The position after a further advance is shown in (iii). Dotted R has advanced to the position A. (By this time another edge would have advanced from below and would be held up at the dislocation). Dotted Q and dotted P have linked across in the usual way, the dislocation attaching to Z, while the edge Y passes on with the usual kinked outline. Linking has taken place between dotted O and dotted N in much the same way, resulting in X and W. The loop dotted L and dotted M have linked, the right hand dislocation attaching itself to part of dotted M to form V, the other dislocation of the loop being attached to U. Dotted K and dotted J have linked so that the loop T has formed and the edge S passes on with a very kinked outline, and is now beyond the influence of this group of dislocations. S is then the first edge to pass through the group.
This group of dislocations which has been studied is both small and comparatively widely spaced. In the case of many of the larger, closely packed groups, it is obvious that the general outline of the edges will be complicated and varying very rapidly, so that any one edge in its passage through the group must very soon lose any semblance of composition from its original layer, and will undergo a great many changes in outline.

It can be seen from (i) and (iii) that the original and final positions of the edges are very similar. A certain periodicity is bound to occur of course, if the conditions remain uniform, and if the incident edges advance in a regular way a cycle of events of quite short period should result. Normally, the conditions probably fluctuate sufficiently to prevent the establishment of such a cycle, although a semi-periodic behaviour may result.

The diagrams show that when dislocations, whatever their hand, are spaced with one or more edges between them, only a considerable kinking of the edges is likely to result. A very good example is shown in Fig. 82 of the kinking resulting from growth past a line of dislocations of the same hand. However, when successive edges run from dislocations of opposite hand, then a succession of double-dislocation loops and single dislocation edges must occur very rapidly. If a considerable number of such dislocations of opposite hand lie together, then a complicated pattern of looping and linking must ensue as any one edge progresses through the system.

There are of course, many other figures whose behaviour could be studied in detail. Few general principles are likely
to emerge from such study which have not already been noted above. One case of especial interest, however, is shown in Fig. 89.

In the centre of this figure the loops on the left must expand and meet the layers expanding from the right. Junction will then occur and the lower joint edge will propagate normally in the way seen in the figure. At the point of junction the upper joint edge formed will enclose a hollow. The sharp point of this hollow will fill in very rapidly to form a figure of the type seen faintly between the two extreme edges of the two systems in Fig. 89.

As this hollow continues to fill in, a position of some constraint must arise, for both dislocations will be linked to edges which show the opposite type of curvature to that appropriate in each case. Thus, it is probable that a critical value of the supersaturation must exist below which the hole will never be entirely eliminated. As systems of this type are not very uncommon this type of behaviour must occur quite frequently.

The systems in Figs. 92 and 93 show this type of behaviour on a larger scale. This situation can be explained if the following behaviour is assumed. The system in the right hand top corner of Fig. 93 rises to a considerable height above the smaller system which lies on the right of Fig. 92. This may be due to the latter system being of comparatively recent creation or because this was not an active dislocation group. From the left a large dominant system is advancing rapidly. Consequently its layers join with the upper system of Fig. 93, the junction remaining at an acute angle as it lies along the direction of
minimum growth rate. In the area lying below that shown in Fig. 92 this dominant system met with no hindrance and therefore advanced rapidly.

The two systems on the right are linked together by joint layers. On the lower system the rod structure marks a line of dislocations on which several of the edges can be seen to terminate; it is probable that many of the other edges also terminate in this way.

Thus, considering the outline of any one edge, a sharp angle is formed by the junction on Fig. 93. Successive edges advance toward each other, partially eliminating the re-entrant until the lower corner of the right hand system is reached. The section of the edge originating from this system joins with an edge from the lower system, and after the resulting layer has extended a little cross-linking occurs with one of the rows of dislocations near the rod structure.

The position then corresponds to one of the upper edges of Fig. 92. Following the path of such an edge from the dislocation it first spirals round in a rather irregular way, before running down as a constituent part of the main system. Further advance of this edge soon results in its lower part meeting the left hand corner of the small system. Junction then occurs, and also possibly linking of the edge to another dislocation, so that an almost closed figure results. Edges of this type thus enclose a hollow which will tend to fill in.

The shape of the upper part of the edges defining the hollow and the way in which they crowd together in the upper right hand section, suggest that some kind of constraint must exist against
further advanced of these edges. Such a constraint is likely to be due to the edges following the opposite curvature to that appropriate to the dislocations to which they are linked, just as in the previous case. It appears that such a constraint might become considerable as the radius of curvature of the edges decreased and that, again, a critical value of the supersaturation would have to be attained before the hole was finally filled in. The filling in, and shape, of these edges might be affected by the presence of a diffusion gradient but as the gradients of the sides of the hole are so slight except on the right hand side this appears to be improbable.

It is not easy to forecast the behaviour of the dislocations in either of the two above cases when the hole has been filled in. In the case of Fig. 89, assuming the supersaturation to be sufficient for the holes to fill up, another edge enclosing a hole would form by the time that the first hole has been filled. Consequently, although the two "free" dislocations might start a spiral, cross-linking would occur so that they were again attached to edges with the "wrong" type of curvature. Meanwhile, the outer pair of dislocations would, if there was room, attach an edge running out of the area, or if a closed figure had again been formed by the expanding systems before this could happen, cross-linking of the edges would again take place, and so on. Similar considerations also apply to Fig. 92.

General deductions from the theory.

One should be able to estimate the size of the critical nucleus (ρ) by measurement of the distance between any 2 dislocations of opposite hand which are
linked by an edge. If such an edge is expanding outwards the theory gives the distance between the dislocations as being greater than $4\pi \rho_\alpha$. The account of the theory which is available to the writer, however, makes no prediction of the behaviour of such an edge when the dislocations are a distance of $2\pi \rho_\alpha$ apart. In these circumstances it appears that the edge should persist, but possibly not expand.

It has therefore been thought advisable to estimate the value of $\rho_\alpha$ only for those loops which appeared to have been expanding. Moreover, if any accurate estimate of $\rho_\alpha$ is to be obtained, only these expanding loops with the most closely spaced dislocations should be considered. A table for several different areas of this region of the face is below.

<table>
<thead>
<tr>
<th>Area</th>
<th>$\rho_\alpha$ microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dominant group (Fig. 75)</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>0.35*</td>
</tr>
<tr>
<td>Fig. 79</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>0.41*</td>
</tr>
<tr>
<td>Area not shown above</td>
<td>0.46</td>
</tr>
<tr>
<td>Centre of inactive group of Fig. 85</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>0.29*</td>
</tr>
<tr>
<td>Area not shown above</td>
<td>0.75</td>
</tr>
</tbody>
</table>

* denotes that some doubt existed whether the edge had really been expanding, or whether its form was due to cross-linking. From the above table it would seem that the loop giving a value of 0.29 microns had not been expanding. The same may apply to
one of the loops of Fig. 75. Neglecting these 2 values and the rather high final value in the table the average value of \( \rho \) over this region of the face was probably quite close to 0.49 microns. Taking \( \phi/kT = 6 \) this is equivalent to an average super-saturation over this part of the face of about 1.4.

It should be possible to deduce the variations in concentration on a face from a table of the above type, but in actual practice it is the chance occurrence of pairs of dislocations at a distance apart of almost exactly \( 4\pi \) which governs the actual accuracy obtainable.
CHAPTER IX

Examination of other prism faces of beryl and also of synthetic emerald.

Remaining prism faces of specimen A.

On all three of the remaining prism faces of this specimen a layer structure was observed. On two of the faces the edges were of extremely poor visibility and nothing of particular interest was observed. The other face was covered with coarse markings similar to those occurring on face 3. On the comparatively clear areas, edges were also observed which showed a great many small scale irregularities.

Prism faces of other crystals.

It was hoped that the dislocation theory of growth could be put to a kinetic test. In the case of beryl further growth is not easily obtainable, but by dissolution experiments one should be able to trace the successive steps of retraction of the edge. As dissolution experiments could not be carried out on any of the specimens so far described, a search was made of the prism faces of five crystals of rather inferior quality, in the hope that a suitable dislocation structure might be observed.

None of these crystals showed much a structure, any edge structure which they showed invariably being of an irregular and coarse appearance, the layers apparently being multi-molecular. One of these crystals showed a typical growth plateau, though not in a very well developed form, so that
some points of resemblance existed. Some of these crystals appeared to have large thick deposits of foreign material on their surfaces and others showed surface markings which could have been caused by severe localised etching.

**Synthetic emerald.**

Two synthetic emeralds were examined and gave evidence of growth behaviour very similar to specimen A. These emeralds were grown by Nacken by a hydrothermal process (Van Praagh, 1948), the details of which have not been revealed. Synthetic emeralds have also been grown by C.F. Chatham by a secret process which is presumably hydrothermal synthesis. It is therefore interesting to record that emeralds produced by Chatham when analysed were found to contain silica, alumina, beryllia, some chromium oxide, and small amounts of alkalies and other constituents. Both types of synthetic emerald are of typical emerald habit and colour.

**Specimen 1.**

The faces of this crystal were rough and a regular structure could only be detected on two of the faces. A part of one of these faces under oblique illumination is shown in Fig. 95. Almost every hill on this face had a structure of the type seen here. All the edges appear to be multî-molecular and the hills build up to a definite point, unlike the plateau which is usual on natural crystals. The inference here is that one central dislocation group has been responsible for the growth of each hill.

Another very obvious difference from the natural crystals is that the longitudinal edges of the layers are no longer
Fig. 95
x120 (N.A.0.28)

Fig. 96
x120 (N.A.0.28)
almost straight, but instead have a very definite curvature. This is very clearly shown in Fig. 96. Every case of layer formation on this crystal showed curved edges of this type.

On the one prism face which showed this structure clearly, which was about 4 mms by 1.5 mms in size, there were some 40 features of this type, presumably marking some 40 groups of dislocations.

**Specimen 2.**

This crystal showed a similar type of structure on one prism face (Fig. 97). This face, some 3 mms by 2 mms, showed approximately 25 features of this type. In no case on these two crystals was it possible to observe a dislocation, because of the rough surface structure.

**Discussion.**

The behaviour of these two crystals so closely resembles that of the natural crystals that there can be little doubt that these crystals grew by a dislocation mechanism. The terminal (0001) faces of both of these crystals were very rough and unsuitable for examination, but a photograph of such a face of one of the Chatham synthetic emeralds showed a hexagonal layer structure (Rogers and Spérisan, 1942).

From measurements of the curvature of the longitudinal edges it is possible to arrive at the following estimates:

<table>
<thead>
<tr>
<th></th>
<th>$b$</th>
<th>$\phi/kT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen 1</td>
<td>3.83</td>
<td>3.42</td>
</tr>
<tr>
<td>Specimen 2</td>
<td>3.71</td>
<td>3.38</td>
</tr>
</tbody>
</table>

These values are very similar, and it seems probable that both specimens have been grown in almost identical conditions.
The transverse edges on both specimens were nearly arcs of the same circle, as for natural crystals. Assuming that the natural and synthetic crystals grew from similar media, comparison of the respective values of $\phi/kT$ enables the ratio of the temperatures of growth to be determined directly. It can be seen that the natural crystals must have grown at an absolute temperature of almost half of Nacken's working temperature. Although the latter temperature is not known, the natural crystal must obviously have grown at quite a moderate temperature. Once the value of Nacken's working temperature is known it should be possible to deduce, with a fair degree of accuracy, the temperature at which growth of different natural beryl crystals took place. This may possibly be of some value to the geologist.

Specimen C.

Before closing the description of microscopic observations on prism faces, a brief mention will be made of the 'sickle' shape of Fig. 41 which proved very difficult to explain on the layer by layer growth theory. The sickle is not, in fact, a closed figure and the two parent dislocations can be seen. Some dissolution would appear to have taken place, judging from the shape of the figure. One or two other odd dislocations can be seen on this face.

It is possible to estimate the size of the critical nucleus from Fig. 41. This proves to be 1 micron and assuming a value of $\phi/kT=6$ one may deduce that this crystal grew at a supersaturation of about 0.5%.
Examination of terminal face of specimen D.

This was one of the five crystals which showed only a coarse surface structure on the prism faces. Although of typical emerald habit it had a pale green colour of the aquamarine type.

The basal face of this crystal showed a hexagonal structure to the eye at glancing incidence. Some typical features of this structure are shown in Fig. 98, the ideal shape of the layers being a regular hexagon. Many of the edges in this figure are of high visibility while there is a minority of very faint edges. The high visibility edges are multi-molecular while the majority of the low visibility edges are probably uni-molecular.

The main layer system spreads from the left, but the actual point of origin is masked by a hole, which must have developed since growth ceased. The origins of systems in the upper and lower left hand corners are similarly masked. As we shall see, the presence of holes at what must have been the origin of systems or of layers, is typical of this face.

On the extreme right of the figure is a small irregular area enclosed within a perimeter of dark lines. Within this area 2 distinct systems start, each apparently from the perimeter, while immediately above a multiple layer appears to start from another dark patch. The upper half of the right hand area when observed at higher magnification (Fig. 99) shows that the edges of the small systems do quite definitely end on the dark perimeter. Moreover, the outline of the multiple edge
Fig. 99
x300
(N.A.065)

Fig. 100
x300
(N.A.065)
in the lower part of the enclosed area is such that the dark patches above it could not have been present during growth. If they had, they must inevitably have formed some kind of obstacle to growth, which would have been quite inconsistent with the shape of the edge. Also this edge kinks near the right hand dark patch and is then co-linear with an edge which appears to be of the same height, running above the dark patch. The general configuration of the whole of this edge is such that it could either have spread from the central system on the left, or, alternatively, commenced from a point on its left hand extremity. In neither case does it appear that the lower dark patches, and therefore presumably all the dark patches, were present during growth. The sudden termination of some of the edges outside this area on the dark perimeter also support this view.

One of the edges inside the central system appears to terminate on the familiar type of dark spot, which may mark a dislocation.

The upper multiple edge, although of general hexagonal outline has a good many small scale irregularities, as do some of the other multiple edges in this figure. This type of small scale irregularity is very common on this face.

If all the areas around the points of emergence of dislocations were obscured it might be argued that some other mechanism was responsible for the growth of this face. However, in a small number of cases edges were observed running from dislocations which were still visible.

In fig. 100 an edge spirals in the form of a hexagon away from a dislocation. Although the edge runs close to an obstacle
the spacing is sufficiently great to make it obvious that an edge of this form would not result from expansion of a layer round the obstacle. A very faint dot appears at the point of termination of the edge. A very faint edge running between the longest edge of the dislocation spiral and the multiple edge above it also terminates suddenly on a definite dot. This must represent another dislocation - in this case inactive. In the area below the spiral there are other very faint edges which appear to terminate suddenly, but as the visibility of these edges is poor it is not justifiable to claim that these points mark dislocations.

There is a small group of dislocations near the centre of Fig. 101. Multiple edges appear to form near the dislocations, but this may only be due to lack of resolution of the individual edges. It is only possible to estimate the number of dislocations in this group by following the edges until they split into a number of constituent, and apparently uni-molecular, edges. Thus, 3 main multiple edges run to the left from this group. Where the first edge turns downward it splits into 3 edges. The second edge runs away without splitting, but as the visibility of these first two multi-molecular edges appears to be very similar, we may arbitrarily allot 3 uni-molecular edges to this second edge. The third edge runs very close to the main multiple edge and it is consequently very difficult to distinguish it from the latter. Just after the second edge turns downward, a uni-molecular edge leaves the third edge, and there are indications that part of this edge continues to run parallel to the main edge. Some distance to the left another edge turns downwards, but this is certainly multi-molecular and may be caused by the third edge and
of the main edge branching off simultaneously. The most probable estimate appears to be that the third edge was built up of two uni-molecular edges. Thus there are probably some 8 dislocations of the same hand on the left of the group.

On the right of the group two very faint edges suddenly increases very considerably in visibility and these joint edges run up to join the main edge on the right. It is thus difficult to arrive at a reliable estimate of the number of dislocations of this hand. However, the multiple edge which is formed is of much higher visibility than any of the 3 multiple edges formed by the other member of the group. Moreover, the main dislocation group appears to be divided into two sets of dislocations of opposite hand, in the manner found for slip-zones on the prism faces. The most probable estimate is therefore that 2 sets of 8 dislocations each are present in this group.

The edges of the left hand set of dislocations appear comparatively free to expand. The rate of expansion of these spirals is surprising, and very much greater than the example seen in Fig.100).

Another example which in this case is not altogether conclusive, is shown in Fig.102. The layer systems appear to be spreading past an obstacle, near the lower left hand boundary of which an edge suddenly starts. In this figure there appears to be a gap of 1 mm. between the point of termination of this edge and the nearest limit of the obstacle. However, this edge may be multi-molecular, although not likely to be more than two molecules high, and the point of termination may only be apparent. A layer expanding round the lower limit of the obstacle in the normal way would not produce an edge of
the length and position of the upper horizontal edge of this spiral, so that the balance of the evidence is in favour of this spiral developing from a single dislocation.

An area which throws considerable light on the nature of the features which obscure the position of origin of edges is shown in Fig.103. A fissure of considerable width and depth divides the lower left hand area of this figure from its neighbouring area further to the left. A system is spreading from this part of the figure and near the obvious black hexagon it makes a junction with another system spreading to the left. (The direction of propagation of the latter system can most easily be determined by observing that the small irregularities in the multiple edges cut back to the right. These irregularities invariably cut back into the higher position of each edge and therefore the system must be spreading to the left). From the general configuration of the edges this small system must have been centred at some point within the black hexagon, which is in fact a hole.

In the central right hand region of this figure are a considerable number of edges, most of them multi-molecular, every one of which appears to terminate on a black hexagonal shape. The larger hexagonal shapes are certainly holes so that there is little doubt that all such shapes represent a hole. These holes must lie on what were the points of emergence of dislocations for if it assumed that this is not so then, even after making a number of improbable assumptions, the most probable behaviour that could result would be that these edges outline a number of closed figures consisting of long thin hexagonal shaped peninsulars extending round the crystal face,
No dislocation mechanism would produce such figures and as some dislocations are known to occur on this face no other growth mechanism is likely to be operative.

Thus, a group of at least 50 dislocations must have existed along the lower, and right hand lines of holes. The general configuration of the edges also indicates that a line of dislocations of opposite hand to the previous group was present along the upper line of holes. The great majority of these holes approach surprisingly closely to a regular hexagon and none of them show any trace of specular reflexion.

Some other areas of the face which showed this hexagonal hole structure also showed traces of structure within the hole. These holes usually showed a central dot around which were traces of a concentric type of structure, which on occasion even showed a spiral form. It would be dangerous to attach too much weight to observations of this type, but the facts are recorded for what they are worth.

Some areas consisted of two approximately equal groups of dislocations of opposite hand, each group being composed of some 20-30 dislocations, spaced along a line parallel to one edge of the face (Fig.104). (The same type of argument could be used to show that these edges must terminate on dislocations but there is no need to repeat it). This area is of the familiar slip-zone type.

After layers from the two groups join on the right of this figure a very irregular layer structure is formed, the upper part of which is shown in Fig.105. (The general spotting in this figure is due to dust on the surfaces of the optical
Fig. 105
x150
(N.A. 0.45)

Fig. 106
x90
(N.A. 0.28)
system). Practically all the edges show a marked stepped effect and there is also a tendency for the multiple steps to break up into sub-multiples which are probably uni-molecular. Several areas on this face behaved in this way.

Another example is shown in Fig. 106 of the behaviour of systems at the minor fissures which branch off from the main fissures on the left of the face. The fissure in this case runs diagonally upwards to the left from the central hole and it appears that this fissure may have been formed by the merging of a number of small individual hexagonal holes. This is in accordance with the presence of two apparently independent systems on either side of it, the edges of these systems disappearing after entering the fissure. The main multiple edge at the commencement of the right hand system stops abruptly before reaching the fissure; it may be that this edge originates from a closely packed group of dislocations of the same hand.

Although the great majority of the small re-entrants in the multiple layers were entirely irregular a few instances were observed when the re-entrant took a roughly hexagonal form. The best example of such behaviour is shown in Fig. 107, on the second layer from the right. An example nearer to the normal state is shown a little higher by the right hand edge. In the former case there seems to be little probability of this re-entrant being either spurious or due to chance causes. The normal type of re-entrant as seen for example in this figure, is entirely irregular and could hardly be caused by flow round a small obstacle, is too irregularly spaced and of too short
extension to be due to abrasion, and is not what one would expect from steady dissolution.

General discussion.

Localised dissolution.

There are 3 phenomena observed on this face which may be related - namely the formation of hexagonal holes on the original sites of dislocations, the occasional hexagonal shaped re-entrant at a multiple edge, and the irregular re-entrant structure of multiple edges.

If a small amount of dissolution were general over the whole surface it would not in general be detectable unless an edge near a dislocation could be observed. In those few cases when dislocations were observed on this face no signs of any such general dissolution could be seen. Let us consider, therefore, a distribution of drops of solvent on the otherwise bare surface of the crystal.

Such a drop spread over a multi-molecular step would dissolve this step backwards almost to the limits of the drop, in the form of a hexagon. This could continue until the resulting solution was either in equilibrium with the crystal or, if the solution was still undersaturated, the layer might be dissolved to the limits of the drop, which should still give a roughly hexagonal shape, or alternatively, if the liquid was sufficiently undersaturated the edge would be eaten back to the limits of the drop and the liquid would then attack the underlying layer. (As the underlying layer is unlikely to show any kinks which will provide points for attack, a critical
under-saturation will be necessary, as this process is the converse of two-dimensional nucleation).

The presence of the hexagonal holes on the sites of dislocations can also be explained on the drop theory, for in such a case the portion of the spiral near the dislocation will "go into reverse" and rapidly burrow down into the surface, winding a spiral edge behind it.

The difficulties in the way of this drop theory are:

1) to explain why a drop should cover almost every dislocation on this face, and
2) why in some cases the holes did not appear to lie on the previous sites of dislocations.

These two difficulties can be overcome if it is assumed that the crystal was surrounded, for some time, by a supersaturated chemically active vapour. Drops would then condense on to the surface, forming particularly on any local protuberance, and therefore on the points of emergence of dislocations. Drops will also form elsewhere on the surface, but in smaller numbers, and these drops will also cause local solution within their boundaries provided that they are sufficiently undersaturated with respect to the crystal to remove the first molecules from close-packed surfaces. If the solvent is chemically active these conditions are likely to hold and a series of holes will result.

The small scale irregularities in the edges can be attributed to attack by the vapour, but the shape of these small re-entrants is rather unexpected, as one would expect them to have a greater ratio of breadth to length.

The presence of a slightly supersaturated, chemically
active vapour is thus sufficient to explain two of these phenomena, and possibly the third.

Areas of stepped edges.

The stepping of the edges which occurs in some areas (an example of which is shown in Fig. 105) is also accompanied by the splitting of multi-molecular edges into what are probably their constituent units. This can be due to one obvious cause, namely the passage of the multiple edges past a number of single dislocations.

When a multiple step approaches a dislocation this step presumably retains its identity until immediately before the first cross-linking occurs. As cross-linking can only take place between 2 single steps the lowest unit of the multiple layer must break away and link across with the dislocation step. This will be the more easily accomplished as this lowest unit will be unable to fluctuate back from the dislocation and consequently no kinking around the dislocation can take place.

After cross linking the section of the step which previously ran from the dislocation is quite separate from the multiple step and will propagate quite independently. The other section of the unit step may also propagate independently of the multiple step, or remain attached to it, or a sub-multiple step of it. Both cases seem to occur.

Multiple layers.

There are various ways in which "bunching" of umi-molecular steps might occur. A sudden uniform deposit of impurity on a face will result in the formation of multi-molecular steps at some distance from the growth centre, just as observed by Bunn and Emmett. Other mechanisms are also
possible, but although all such arguments appear to fit the facts, at least superficially, none appears to be conclusively correct.

It is possibly misleading that all the three examples of terminal faces cited show a multiple layer structure. These specimens were, in fact, chosen because they showed a hexagonal layer structure when observed visually at glancing incidence and the presence of multi-molecular layer structure was therefore a necessary corollary of the method of selection.

It is possible that the persistence of any multiple step is due to the step edge corresponding to a stable crystallographic orientation. In this context it is of interest to note that on the basal pinacoid the edges could have an orientation corresponding to two stable forms, while on prism faces the straight edges could correspond to two other stable forms, but that the curved edges could only possess a stable orientation over very short lengths. This may be one of the factors responsible for the very small number of multiple layers seen on prism faces.

Assuming multiple layers to be of frequent occurrence on the basal pinacoid, it can be seen from the normal habit of beryl crystals that they must spread quickly. If the edges have a mean orientation corresponding to a stable form, this raises the question of the transition between this mean orientation, for which every unit step apparently retains its individual kinks, and the true orientation, for which the step must become slow growing, as it will then represent a close-packed (habit) face.
From the experiments of Bunn and Emmett it would appear that the transformation only takes place for steps of several hundred molecules or more. Thus, there must be a critical size factor. In our case the steps correspond to directions of minimum growth rate, so that, to a good approximation, the edges will show only thermal kinks. The problem then can be posed in this form - what determines the continued existence of thermal kinks in the individual units of a multiple step?

The existence of a critical size factor suggests that an analogy may exist with the process of two-dimensional nucleation. Consequently, the transformation process may be visualised as follows. Each individual step will have kinks fluctuating in size and position. Moreover, the movement of the kinks, and of the unit layer as a whole, is subject to an additional constraint as no lower layer can fluctuate back beyond a higher layer. There is a certain probability that at any one moment sections of neighbouring edges will free of kinks, and co-planar, so that an area of close-packed surface is formed. This probability will increase with the total area of the step, and a critical height factor is therefore likely to exist. It also appears that this height factor may be related to the probability of the persistence of a small close-packed surface, once formed. As some properties of crystals vary as the size of the crystal becomes very small this appears to be reasonable. Moreover, in the investigations of Burton and Cabrera into the 'roughness' of a close-packed surface, a semi-infinite lattice was assumed. If the critical size of the close-packed surface is taken as being of the order of 200
molecules across, then it may be that the arguments developed for a semi-infinite lattice are inapplicable, and that below this critical size the temperature for transition from a close-packed to a stepped surface is very low, and the area would spontaneously revert to its former condition.

Deductions from the theory.

Unfortunately, as the great majority of dislocations which were active on this face are not visible, no reliable quantitative information can be obtained. The edges are too irregular for one to determine the constant $B$, but it is probably quite large. Also an upper limit of 5.5 microns can be fixed for the value of $\rho_c$.

From the observations the polar diagram must show six equally spaced minima, the scale of the diagram being greater than in the case of the prism faces.
CHAPTER XI

Interferometric examination of prism faces of quartz.

Introduction.

The compound $\text{SiO}_2$ can exist in several different forms. In this work only low-quartz was studied. Low quartz belongs to the symmetry class 32 (trigonal trapezohedral) and faces were studied of the hexagonal prism $\{10\overline{1}0\}$ and the major and minor rhombohedra $\{10\overline{1}1\}$ and $\{01\overline{1}1\}$.

The prism faces of quartz are almost invariable horizontally striated, and from these striations it is often possible to determine the direction of the optic axis (the $z$-axis) to within a degree or so. These striations are generally attributed to variations between prism and rhombohedral forms.

There are 3 molecules in the unit cell, the three tetrahedral groups lying on three layers at different heights. These tetrahedral groups form spirals, resulting in right handed or left handed quartz. The dimensions of the unit cell are $a = 4.9$ A.U. and $c = 5.39$ A.U. (Bragg, 1927).

The information obtained from a survey of the topography of crystal faces by means of interferometric methods is necessarily indirect so far as the fundamental growth mechanism is concerned. Such information will therefore be only briefly summarised in this and the following chapter.

Five of the six prism faces of one crystal were examined in detail, the other face being unsuitable for study. This
crystal was water-clear, of long prismatic habit, and originated from the Rhone Glacier.

Face 1.

One area of this face was very carefully investigated with both Fizeau fringes and fringes of equal chromatic order, and displayed some very regular features which are undoubtedly due to the process of growth.

When the flat was set nearly parallel to the face the central portion of this area was as shown in Fig. 108. The parallelism of the flat and the face was in this case close and the geographical representation is therefore approached. The central feature is roughly tetrahedral in appearance, one of the gradients showing considerable curvature along its length. This tetrahedron runs lengthwise across the face, with the apex in approximately the centre of the face. (The convention adopted in all the Fizeau pictures of prism faces is that the z-axis is horizontal). To the left a smaller tetrahedron can be seen, while to the right are two intergrown features, which further investigation proved to have the same type of structure. The regularity of the structure is striking.

Many of the steps (or striations) seen in this figure are much too small to be seen by the eye, the declivities probably corresponding to the type of striation usually seen. An unresolved structure prevents resolution of the yellow doublet.

The main step structure, which is particularly marked on the steeper gradient, also shows a secondary, and much smaller step structure. The diffraction 'tails' along these small steps are quite well shown, and it is in conditions such as this in which quantitative deductions are of doubtful validity.
The larger steps vary in height from some 60 A.U. to over 1,000 A.U.

The effect of the unresolved structure is shown more clearly in Fig. 109, in which the wedge angle has been adjusted to attain a higher dispersion over half of the area. The main tetrahedral feature corresponds to that seen in the previous figure, the individuality of the two features on the right being more clearly shown in this case. The step structure of this area, and indeed of the whole of this face, is extensive, but the characteristics of this structure will be considered later with respect to other faces which display the various aspects more clearly.

The whole of the area shown in Fig. 109 was investigated further by means of fringes of equal chromatic order. Fig. 110 shows a typical section taken parallel to the optic axis. The main feature is the well-developed tetrahedral feature of Fig. 108. The section was taken almost along the summits of the features, while Fig. 111 shows a section displaced from the summits, but cutting across several of the same features. These two Figs. typify the most striking general features of all the sections taken parallel to the optic axis which were

(a) the general regularity of behaviour
(b) the very close degree of parallelism between the steeper gradients of the features and the fairly close parallelism between the less steep gradients, increasing in the latter case as the features become more regular as the edges of the face are approached.

A section along the length of the main features (Fig. 112)
is also very regular, as was the case for all the features. The analogy with the fringe of equal chromatic order sections on beryl is evident.

Face 2.

The main features of this face were a large number of steps and a comparatively flat (although curved) area.

These steps in many cases showed no faint continuation, or "flick", between fringes. That is, the change of level was very rapid and almost discontinuous. Other steps showed a "flick" and others an effect which at first glance could be taken as focal. This was a step formation of the type shown in fig.113. Careful focusing and inspection showed that this was not a spurious effect.

The very abrupt steps were in some cases of height greater than one order, although the majority were only a fraction of an order. The difficulty of allocating the yellow doublets to equivalent orders on this face made pronouncements difficult on heights of greater than one order.

A large number of the steps varied along their length as follows. After running nearly plane for some distance, one edge of the step began to rear up while the other lagged behind, the step reaching a maximum "buckle" and then returning to its original direction. This buckle (which varied along the length of the step) ran across the step to a considerable degree. Over considerable areas large numbers of steps displayed approximately the same degree of buckling.

A considerable curvature also existed along the length of the steps. This was an extended phenomenon and some relation
Fig. 113
x44

Fig. 114 x 80
seemed to exist between the buckle of the steps and the overall curvature.

The steps also varied in height along their length with respect to one another.

A fine structure was found to be due to very small steps of the type seen in Fig. 113, superimposed on a larger structure, often producing a puckered appearance. It was noticeable that many of the step plateaux, both on this and other faces, were themselves striated, although the striations were not clearly resolved.

In the step areas subsidiary small features could be seen, the fringes on these features being very fine and faint due to a rapid change in level, the outline of the features being of general tetrahedral character.

F.e.c'o sections confirmed the general finding that the steps corresponded, with occasional exceptions, to a steady decrease in height towards the termination of the crystal.

**Face 3.**

On the main face was a small vicinal face of size approximately 1 mm. by 2 mm. This was made up of a large number of steps of very small height. The highest step was of about 350 A.U., while a step of about 55 A.U. could be seen and even smaller steps probably existed. The main steps crossing this face carried on across the main face without the slightest deviation, despite the different nature of the two faces, remaining strictly rectilinear and perpendicular to the optic axis.

Examination at high dispersion showed that these steps
were built up with a slight overall curvature resulting in a main hill with a number of slim and very distorted tetrahedra to one side. The general tendency of the whole formation seems to be towards the type of structure shown by face 1, which at certain wedge angles displayed a similar type of appearance.

The main face could be divided into two regions:—
(1) consisting of a very large number of steps, again showing a variation in orientation along their length,
(2) a comparatively plane area, also built up of steps, but in this case only about 1/20 order or less in height.

At high dispersion (Fig.114) more regularly developed features were evident, being of the familiar overlapping type. The features again run across the face and although not approaching the regularity of outline of the tetrahedral features on face 1, yet a general similarity exists, both in appearance and behaviour.

Face 5.

The topography of the face followed the now familiar pattern of large stepped areas displaying quite considerable curvature and more regular areas displaying tetrahedral features. A typical area is shown in Fig.115. The steps vary from plane, to buckled, and to those of such curvature as to subtend an angle of 180°. The steps again varied in height along their length.

It should be noted that the curvature usually displayed by the stepped areas very often signified the presence of a tetrahedral type of feature at appropriate adjustment of the wedge angle. The topography of the faces was often so uneven
Fig. 115  x22

Fig. 116  x22
and coarse (small areas of the surface sometimes showing projections of anything up to 2 mm. in height) that it was impossible to obtain such a wedge angle.

**Face 6.**

This face exemplified the complex topography which can be encountered (Fig. 116). The familiar phenomena can be seen—sharply curved steps and elongated intergrown features distorted from any regular tetrahedral form.

It can be seen that the step structure is intersecting one side of the outline of the features in preference to the other. Inspection at many wedge angles showed that this must be due to the steps running approximately parallel to the well defined curved edges seen in the above figure.

**General discussion.**

Only a very brief account has been given of the considerable amount of data which was obtained. This work was completed before any serious doubts had been cast upon the validity of the picture of growth occurring by the spreading of layers from two dimensional nuclei. The whole of the data was therefore carefully examined in this light, but it proved to be impossible to evolve a satisfactory explanation along these lines.

On the other hand the situation is considerably simplified if the results are interpreted in terms of the dislocation theory of growth. The tetrahedral features mark the sites of active dislocation groups, while the comparatively plane, or merely stepped areas correspond to the presence of few or inactive dislocations. Moreover, the varying types of step structure, which previously could not be satisfactorily
explained, are now readily understandable.

The main point of interest in the step structure is the great degree of 'bunching' which takes place. In this context it should be noted that form-variation steps must appear as the discontinuous type of step. Such steps are by no means in the majority, which implies that other factors may be responsible for the persistence of a 'bunch' as well as the assumption by the step of a stable crystallographic orientation.

Although no definite proof can be obtained it seems probable that form-variation steps are present. It is probably these steps which cut across vicinal faces with no apparent change in direction or nature. This again raises the question of the nature of the transformation of the bunch, each unit of which is kinked, into a close-packed surface.

The general topography of these faces is such that the dominant dislocation groups were probably situated towards the fractured end of the crystal.

The steepest gradient of the tetrahedral features must approach most nearly to a close-packed direction. From angle measurements of the fringes of equal chromatic order of the most regularly developed feature on face 1, and assuming a value for $\phi/k\tau$ of 5, it is possible to deduce that this crystal grew at a supersaturation of about 1.2. This value is very high and this estimate appears to be of the order of magnitude only. This is really to be expected as in this case a great deal of 'bunching' has taken place and the conditions are very different from those operative when a system of unimolecular layers spreads regularly from a very small group of dislocations. As a consequence of bunching the ideal gradient
will be steepened, so that the actual gradient will be equivalent to the ideal gradient produced for a higher supersaturation than that actually present. In this case the ideal gradient has probably been steepened by a factor of 5 to 10.

Mention has already been made of the small features which stood isolated on the prism faces, the sides of these features being very steep. What may be a particularly well developed example of this structure is shown in Fig. 117. Such an obvious and well defined structure must be very uncommon, for only one example was seen in the several hundred crystals which were handled and examined. A general similarity of outline exists between these features and the tetrahedral features seen on the right. The sides of these 'fish-tail' features are very steep, while the upper surface is almost plane; they appear to be the counterparts of the main plateaux seen on the beryl crystal, specimen A. It appears that these 'fish-tail' features and the similar small features observed, must result from an excessive degree of 'bunching' of the layers. The reason for this bunching must remain obscure.
Fig. 117  x12
Examination of rhombohedral faces of quartz

A) Interferometric examination.

Major rhombohedral face number 1.

This crystal originated from Madagascar and this face showed a slight rippled appearance of a type common for quartz crystals when examined visually at glancing incidence. Microscopic examination showed clearly defined boundaries between the different areas which caused the rippled appearance.

Fizeau fringes of a typical area of this face are shown in Fig. 118. (The mercury green wavelength only is used here). The face is composed of a very large number of approximately conical features, with gradients so steep that a change in the wedge angle made little difference to the apparent topography. That these features are invariably hills was shown by the use of fringes of equal chromatic order. The hills tended to flatten at the top and were separated by steep V-valleys. Even the dots seen on the Fizeau pictures were found to correspond to spot heights, or small hillocks. (An unresolved structure caused considerable broadening of both types of fringes).

The lack of any orientation is a notable feature shown by the hillocks over the whole of this face. A small number of larger features approached a tetrahedral shape, but there was no similarity of orientation between such features and it appears probable that they were formed by the intergrowth of a number of small hillocks.
Major rhombohedral face number 2.

This crystal originated from Brazil and this face was selected because it showed the same type of rippled appearance to the eye as the previous specimen. An area near the tip of the face, as observed under oblique illumination, is shown in Fig.119. The conical hills in this case show a certain amount of orientation. Many of the hills show signs of a multiple edge structure which becomes much more marked very near to the summits. In many cases the multiple edges follow a spiral form near the summits. This was confirmed by observation at higher magnifications, but the edges were irregular and there was so much foreign material on the surface that little additional information was revealed. However, there appears to be no reason to doubt that these edges originated from a dislocation or dislocations.

Surrounding this area of hills is a flat, semi-matt plateau which drops steeply to the level of the plain from which the hills emerge. This steep slope appears to have a definite structure, but it is difficult to determine just what this structure is. The plateau itself, which was quite featureless, extended for some distance and then dropped down steeply to another, and possibly the same level which again covered with many conical hills (Figs.120 and 121, mercury green wavelengths only). This face differs from the previous example both in the degree of orientation of the hills and in the smaller number of the latter. Figs.120 and 121 show that the hills emerge from a comparatively flat surface, the latter having a very similar orientation to, and showing the same type of topography as, the main plateau. From Fig.120 in particular
it appears that the plateau may have been advancing slowly and covering over the conical hills.

**Major rhombohedral face number 3.**

This face was examined in reflexion, and a general view of the greater part of the face is shown in Fig.122. This region consists of a number of vicinal faces with, in the left hand lower corner, a sharp drop to an area which slopes down from the rest of the face. One, in particular, of the vicinal areas exhibits what appears to be an extensive step structure. In fact, the step structure exists on both sides of the obvious junction, the direction of the steps making a marked angle with each other on opposite sides of the junction. It can be seen that either considerable areas of the face do not display this type of structure, or the structure is too small to be resolved in depth or extension.

The step structure is shown more clearly in Fig.123, which shows that the step height is much the same for a large number of steps covering a considerable area. Moreover, the steps show only slight variations in height along their length and display a close degree of parallelism over considerable areas.

The steps are not of the discontinuous type, one order being well defined along its length. Along the length of the step edge diffraction lines can be seen to continue the direction of the fringe. The steps in Fig.123 again make an approximately constant angle with each other, but the upper plane portions of the step retain the same orientation for both step systems. This is true for the whole of this general region, being particularly well shown in Fig.123 where single short sections of a fringe run between steps of the two
different systems.

The appearance of the stepped areas in transmission, and at high dispersion, is shown in Figs. 124 and 125, both of which demonstrate the striking effect of one order splitting into as many as 35 distinct, parallel sections. Although careful visual observation showed no connection between these sections they are certainly not a distinct subsidiary fringe system, for no trace of any but the one wavelength could be detected in these orders. This was not, as the two figures show, a localised phenomenon, but could take place in any part of the stepped areas when

(a) the fringes were running roughly parallel to the steps, and
(b) the dispersion was high.

Further information was gained by microscopical study of the surface, which immediately confirmed many of the findings (Fig. 126). The markings follow the vicinal development, making junctions at the junction of the different vicinal faces. Over the lower half of the face the markings are fairly regular, but at the junction in the top right hand corner of the figure the behaviour is much more irregular, subsidiary lines crossing between the main markings and kinking of the markings causing a furrowed appearance. The two obvious black lines in the lower half of the figure are scratch marks caused by abrasive during the grinding of the rear face of the specimen. The same scratch marks are shown very faintly in Fig. 122 and help to identify the common areas. Careful examination of these areas brings to light a significant fact - that the fringes marking the drop at the edges run slightly across the markings.
In other words, it seems that these sudden changes in level are by no means discontinuities. This is borne out by the appearance of the markings and the variations of their appearance with change of focus. In both cases these were quite different from the behaviour of the diffraction patterns produced by the true discontinuities at the step edges of beryl.

The main part of the evidence obtained is thus in favour of this being a true step structure, but such a finding would seem to be in variance with the behaviour shown in Figs. 124 and 125. These figures are, however, in a sense misleading. The situation in these two cases can be considered as follows. One fringe may, within its width, cover a change of height of say, $\frac{A}{80}$ or about 70 A.U. Normally, this latitude in wedge thickness is taken up by the slope of a surface of slowly varying topography, so that one fringe marks one order of interference. Let us consider, however, a stepped surface, for which the steps are about 200 A.U. in height and the step edges form quite a shallow slope running down from the plateau. We have already seen that the plateaux of the steps appear to be very nearly plane; consequently, the plane joining the junctions of the plateaux and the risers of any two steps is likely to pass through, or close to, such junctions of many other steps. If this plane is almost parallel to the plane of the optical flat, then when the wedge thickness is such as to produce one order of interference on this plane, this one order will no longer be marked by one fringe only. This is obviously due to the fact that though the upper part of any one step plateau, say, may correspond to the wedge thickness equivalent to this
order of interference, the result of the stepped surface lying at such an angle will be that a large number of neighbouring areas correspond to the same wedge thickness and it would be theoretically possible for an infinite number of fringes to mark the same order of interference. The areas of the step risers which correspond to the appropriate wedge thickness might also be expected to produce very faint, sharp fringes and this does, in fact, appear to take place. Figs. 124 and 125 thus confirm that this is an extensive step structure.

These steps remained almost rectilinear up to the point of junction (Fig. 127), as distinct from the type of behaviour seen on beryl.

The other part of the face which has not yet been discussed is shown in Fig. 128. The shelving valley in the bottom right hand corner is that shown in the bottom left hand corner of Fig. 122, and this feature helps to identify the relative position of the two areas. No trace of a bunched step structure was found on this area, the area being as shown in the figure built up of three intergrown tetrahedra, orientated with one side approximately parallel to the edge of the face. Traces of the formation of another tetrahedron can be seen on the slope down to the right. The two smaller tetrahedra show a greater degree of mutual intergrowth than they do with the longer tetrahedra, all three tetrahedra showing however, a much more regular form than any observed previously. The junction of the shortest side with the two other sides is, for all three of the features, quite distinct, although the longer sides show a sudden increase in curvature immediately before the junction.
Inspection at higher dispersion (Fig.129) shows more clearly the intergrown nature of two of the tetrahedra. (The sections of each order running along these tetrahedra diagonally upwards to the left are much fainter, due to the steeper nature of the gradient. Although the plate was, in fact, overexposed to help bring up these sections, they are only faintly shown in the print).

In the bottom left hand corner evidence is seen of the presence of some complicating structure at a very high dispersion (Fig.130); this is seen to be due to a convex feature in the area of the right hand tetrahedron, the feature extending to both left and right. In particular this figure, which is at a setting of extremely high sensitivity, shows no traces of a step structure on this area of the face.

**Minor rhombohedral face number 1.**

This crystal was cut primarily in order that a major rhombohedral face, adjacent to the present minor face, could be examined. This resulted in only a portion of the latter face being available for examination. Reflection Fizeau fringes over this area are shown in Fig.131. Two tetrahedral features are oriented along approximately the same axis, in both cases the junction of two of the sides being sharp and showing no signs of curvature, while the other junction takes place as a gradual curve. The curvature of the sides of the main tetrahedron is obvious. Fringes of equal chromatic order running across the two features showed that they met in a flat bottomed valley, with a groove running the side of the smaller feature. The smaller pyramid is also flatter than the other.
The major rhombohedral face which was adjacent to this face, showed only a very shallow vicinal development and little else of interest.

(B) Microscopic examination.

After it was established that dislocations could be observed on beryl crystals, an attempt was made to observe them on quartz crystals. This attempt met with only limited success for it was found that layers on quartz were very apt to 'bunch', and although many edges were found to stop abruptly, it appeared that these were probably multiple edges sub-dividing, and that no dislocations existed at the point of termination.

Two typical intergrowing tetrahedra are shown in Fig. 132. The layer structure is easily seen but, quite typically, it was not possible to trace the point of origin of the layers.

In only one case was a layer structure observed which could be unequivocally attributed to a dislocation origin (Fig. 133). A concentric multiple layer structure appears to originate from an area near the centre of the figure. In this area a surface step runs diagonally upwards from left to right and from the lower part of this step a multiple edge spirals out, showing 4 sides before it disappears. It appears probable that edges originate in the same way from the upper part of this step, but this area is largely masked by markings caused by mechanical damage of the face.
Fig. 132  x13

Fig. 133  (N.A.O·28)  x44
General discussion.

The surface step and the edges originating from it are very similar to the several parallel cases observed on beryl. Moreover, the multiple edge shows a pronounced curvature of the first side of the spiral, just as the theory predicts, and in general there appears to be no reason to doubt that this edge originated from a number of dislocations.

A dominant dislocation system is obviously situated near the surface step and it is probable that the dislocations along the step play an important part in this system. From the behaviour of the edges it would seem that this step may be produced by the familiar type of distribution of two groups of dislocations of opposite hand.

The multiple layers originating from the highest points of many of the conical hills on the major rhombohedral face number 2 also, almost certainly, arise from dislocations. A point of some interest is that these spirals should approximate to a circular form and show no dependence of growth rate upon orientation. This must be due to the spacing of the kinks along any uni-molecular step being less than the characteristic distance diffused by a molecule adsorbed on the surface. This will normally be true of growth from the vapour, but it is doubtful if this crystal has grown this way. Alternatively, growth at a high temperature from solution would result in a much closer spacing of the kinks, but would also alter the characteristic distance of diffusion. Without a detailed investigation it is difficult to determine whether an increase in kink density might not be compensated by a decrease in the
characteristic distance. It appears reasonable to assume that this might not be so and the form of the spirals could then be accounted for by growth from solution at a high temperature.

These observations and the behaviour seen in Fig.133 are sufficient to establish the general case for the growth of quartz crystals from dislocations.

On all the rhombohedral faces observed, the layers showed a marked tendency to bunch and the observations on major rhombohedral face number 3 enable one to derive more information about the nature of the bunched edges. Although diffraction may affect the fringes one can arrive at an approximate measurement of the angle between the plateaux and the edges of the steps. This proves to be about 0.5°, which explains why, on this face, steps some 200 A.U. in height produce a diffraction pattern of low visibility compared to steps of similar height on beryl.

Moreover, this angle of inclination of the edges appears to be almost constant, suggesting that this may be a general type of behaviour. This agrees with the low visibility of multiple steps on all the faces examined, and is of some importance in-as-much as it does not appear probable that such a small angle of inclination to a close-packed surface can correspond to a stable crystallographic orientation. Consequently, this casts a serious doubt on the general assumption that bunched edges may assume a stable crystallographic orientation.

This same face also raises once more the question why the edges over the whole of one part of a face should be bunched, on this occasion in a very regular way, while the remainder of
the face shows no signs of bunched edges.

The relationship between the plateaux and the hills on face number 2 is such that this face may have grown in one of two ways. Either

(a) the dislocation groups were formed at a late stage in the growth of the crystal, and were active at a high supersaturation, or

(b) the crystal originally grew at a low supersaturation, so that the closely packed dislocation groups were inactive and a flat face was formed. A sudden change in the surrounding medium so that it was considerably supersaturated would then result in the upper groups becoming active and forming conical hills standing out above the general level.

On either picture the different levels of the plateaux can not be explained very satisfactorily, except perhaps as an unusually large 'bunching' phenomena. As faces of quartz which have a rippled appearance to the eye are quite common, it is possible that closely spaced dislocation groups are a general feature of quartz crystals.
Conclusions

The observations on beryl crystals, and in particular those on specimen A, prove conclusively that these crystals grew by a dislocation mechanism. The observations of active dislocations on quartz are also sufficient, when one considers the grave deficiencies of two-dimensional nucleation theory, to prove that the same mechanism must be operative generally for quartz crystals. As all crystals appear to be imperfect it may therefore be claimed that the great majority of crystals must grow by a dislocation mechanism of this kind.

The observations on beryl show that not only is the dislocation theory of growth correct in principle, but also in detail. This is the more surprising when it is recalled that this theory was derived primarily for homopolar crystals formed from spherical or cubic molecules, with growth occurring from the vapour phase on faces of high symmetry. In the cases studied here the crystals are ionic, are of comparatively low symmetry, have comparatively complex molecules, and have grown from solution. As the theory applies so closely to the latter circumstances it must apply at least as closely to the conditions for which it was derived.

The advances possible because of this theory are many and important. Thus, for the first time it provides a quantitative account of crystal growth, and it is possible to learn a good deal about the conditions under which any crystal has grown from simple measurements on the faces. Such quantitative
knowledge may not only be of value in fields directly concerned with crystal growth, but also in such allied fields as geology.

The dislocation theory of growth makes a great step forward in the unification of growth phenomena and the general theory of the solid state, two fields which had previously been largely divorced. The theory also makes a direct advance of some importance in the theory of the solid state, and of the mechanical properties of metals in particular. The origin of dislocations in metal crystals has long been a matter of dispute and is of great importance to general dislocation theory. Until recently it was generally accepted that no satisfactory explanation of the origin of dislocations had been advanced, but the dislocation theory of growth solved the problem by showing that a perfect crystal could never be produced.

If we are to consider some of the more detailed conclusions it should be noted that the dislocation theory of dissolution, which is treated as a special case of growth, has also been shown to be correct in the case of beryl and we may, therefore, conclude that it is generally applicable. The phenomena of dissolution have been approached somewhat warily in the past, and kept rather distinct from the study of growth phenomena, so that the dislocation theory further unifies this field. In almost all the examples shown, the amount of dissolution has been slight and only noticeable very close to the dislocations. In the case of a crystal subject to prolonged dissolution the edges of the faces would provide a perpetual source of new steps and the part played by dislocations would be less
important. Prolonged dissolution of faces on which the edges played no important part for some reason, should result in the dislocations producing hollows of the same shape as the typical growth features. Examples of this behaviour have been given for specimen D. Also the prism faces on one beryl crystal in the British Museum show a large number of hollows of the typical razor-blade shape, probably caused by dissolution (Glaringbull, 1949).

The propagation of layers past dislocations, or dislocation groups, by means of cross-linking, can play an important part in the growth of a face. Cross-linking can produce complicated forms of layers, or, in the simple cases and for inactive dislocations, almost no change in the incident layers. Very closely spaced dislocation groups can constitute a serious obstacle which must often be impassable below a certain critical supersaturation.

The activity of dislocation groups appears to be primarily governed by the number and spacing of the constituent dislocations. Small or medium numbers of dislocations which were quite widely spaced appeared to function in a co-operative manner, when such a group was active, while the very large closely spaced groups did not function in a co-operative way. The latter type of group was invariably dominated, either directly or indirectly, by other systems. For the former type of co-operative group the variations of supersaturation on the face probably decided which were to be the dominant groups.

The bunching of layers, which was particularly common on quartz, is puzzling in several ways. There are several ways in which such bunching could arise. None of these ways appears
to be exclusively correct, and it may be that several of them are operative. The persistence of these bunches could be satisfactorily explained on the assumption that the edges take up a stable crystallographic orientation. In the case of quartz this is not correct and this throws doubt on whether it is so for beryl. As no constituent unit of a bunch can fluctuate back underneath its immediate upper neighbour, it might be thought that for very closely spaced unit edges this constraint would tend to maintain the bunch. In the case of one rhombohedral face of quartz at least, and possibly in general for such faces, the bunches produce a gradient of about 1 in 180. This should allow a good deal of fluctuation of the individual edges and yet these bunches persist, and, moreover, maintain much the same gradient. The whole question of bunching must therefore be left open. The transition from a normal bunch to a small close-packed surface presents an interesting theoretical problem.

The rod features on prism faces of beryl may be closely related to the general phenomenon of bunching. In this case a steep gradient parallel to the c-axis is necessary for the production of rods, and the presence of dislocations at the base or on the upper surface of such rods is very common and possibly necessary for rod formation. Although it would be possible for the straight edges of the rods to take up a stable orientation, this does not appear to be possible for the curved edges. In the cases when rods project from a steep drop, there appears to be a relation between the height of the drop and the size of the rods. In general, the main questions posed by the
phenomenon of rod formation appear to be very similar to those posed by the presence of bunching. In neither case can a satisfactory explanation be given.

In the case of beryl, various surface depressions were observed which cannot be explained on normal lines. More information is necessary to show whether these depressions were produced by similar, or differing, causes.

The quantitative measurements showed that specimens A and C had grown at a supersaturation of about 1%. The value of the supersaturation varied slightly for the Z faces of specimen A, this variation probably being genuine. Comparative measurements on synthetic emerald and natural beryl crystals have shown that the natural crystals have probably grown at about half the temperature at which the synthetic crystals were grown. From details of Macken's work on the growth of synthetic quartz (Van Praagh, 1949) it may therefore be estimated that the natural crystals grew at a temperature of less than 300°C, and probably in the region of 150-200°C. Once the value of T is known, the value of the edge energy can be deduced directly, the measurements of n and t for any crystal providing a direct method for the determination of the edge energy.

The observation of dislocations, or more correctly the observation of the diffraction spots due to the presence of dislocations, is of some importance in itself as it provides the first direct evidence of the existence of dislocations. General dislocation theory has proved to be highly successful in explaining the mechanical properties of metals, and although a good deal of experimental evidence supports the theory, the
very fact that this evidence is indirect has weighed against the theory in the past.

It is of interest to examine the nature of the proof, provided by the present work, of the correctness of the dislocation theory of slip. At first the evidence appears to be overwhelmingly in favour of the correctness of the theory, but when the structure of beryl is considered the matter is not quite so simple. The propagation of dislocations can only take place by the transference of bonds. This is a difficult process to visualise for beryl, but it appears that the Si₆O₁₈ rings will tend to retain their individuality under almost any conditions of applied stress.

A very high applied stress is probably necessary to produce slip in beryl, and on current theories one would expect the first small amount of slip to be followed by very rapid work hardening and subsequent fracture. It is thus necessary to decide whether

(a) the limited "slip-zones" are formed by slight amounts of slip, and the observed distribution of dislocations therefore proves the dislocation theory of slip, or

(b) the slip-zone type of structure is caused by the presence, on the same plane, of two equal groups of dislocations of opposite hand.

In the case of alternative (b) an argument of rather a negative type is outlined above. However, it is necessary to go further and attempt to explain why a distribution of dislocations of this kind, which takes place only along certain directions, should be so common. No satisfactory explanation can be given.
In support of (a) we have
(i) that the slip-zones run in only 2 directions on the prism faces, one of these directions corresponding to the trace on the face of a plane known to be a glide plane for crystals of this class of symmetry,
(ii) the evidence provided by Fig. 81, that movements of dislocations do occur, and
(iii) the prediction of just such a distribution of dislocations by the theory.

Thus, the evidence definitely supports the conclusion that the observed surface steps, along which were two equal groups of dislocations of opposite hand, correspond to limited slip-zones and that the dislocation theory of slip is correct.

In addition to the lines of dislocations along slip-zones, there were many other lines marking transition surfaces between parts of the crystal inclined at a small angle to each other. The majority of such surfaces ran parallel to the c-axis, as did many slip-zones. Such features have been ascribed to the stress resulting from inhomogeneity of ionic replacement in the crystal (Frank, 1950). As the crystals are coloured, ionic replacement must take place and this is very likely to lead to lattice curvature. Growth of such a crystal will, according to Frank, result in oscillations in the lattice spacing and the production of considerable stresses. The surface stress in new growing layers can produce surface faults which will eventually develop into true dislocations.

The density of dislocations on any area, or face, varied widely for the crystals studied. On face 3 of specimen A,
small areas existed with a dislocation density of about $10^7$ per sq. cm., while an area of a square centimetre or more on face 1 of the same crystal showed no signs of dislocations. The linear density of transition surfaces and slip-zones approached most nearly to a typical value of $10^4$ per cm. There appeared to be no approach to a typical value of the surface density for the most imperfect areas, possibly because comparatively few areas showed closely packed randomly spaced dislocations. The highest density observed for any such area was $1.4 \times 10^7$ per sq. cm. The many transition surfaces and slip-zones which intersected the surface were usually comparatively widely spaced so that the surface density for any area containing sections of two or more such features was only occasionally as high as $10^7$ per sq. cm. and usually $10^6$ per sq. cm., or less.

The use of phase contrast equipment should enable one to observe steps of 1 Å, and possibly still smaller steps. Consequently, it should be possible to observe uni-molecular steps on a great number of crystals and so study their growth behaviour and dislocation structure. The study of metal crystals should provide direct confirmation of several aspects of general dislocation theory and possibly information on the dynamical properties of dislocations.

Investigation of parts of a crystal which had very closely packed dislocations in one area, and no dislocations in another area, while growth took place, may enable an experimental determination to be made of the effect of screw dislocations on X-ray and electron diffraction.
APPENDIX

Interferometric examination of a (001) cleavage face of topaz.

This work does not bear directly on the problem of growth and it has therefore been kept distinct from the main body of work.

This cleavage face, of size 3.0 cms. by 2.5 cms. was examined entirely in reflection. A characteristic feature of this specimen was the smooth continuity of the fringes. An example of this is shown in Fig.134. This region consists of plane areas separated by sudden cleavage steps, with more complex areas to the left and right. The steps vary in breadth along their length, are plane, or very nearly so, and in general slope at a slight angle to other steps. The more complex areas probably result from local irregularities in the structure or composition of the crystal.

The plane areas, which were very common, show that this is a surface of perfect cleavage. The smooth, continuous nature of the fringes also shows that no micro-cleavage structure exists.

Although the great majority of cleavage step edges were straight, or only slightly curved as in Fig.134, some were very curved, although in a fairly regular way.

Local deviations from an entirely plane surface also existed, as in Fig.135. This figure also shows an the upper left section of the series of cleavage steps, the commencement of a new cleavage step. At first barely resolved, it increases in size as it progresses towards the top of the figure. Also
instances were observed of steps, the upper surface of which were very curved, breaking into a number of very small, shallow steps.

In general, the entire face was very plane and showed very few topographical features, apart from a large number of cleavage strips. From the two figures shown it can be seen that any attempt to establish a technique for the regular examination of fractured surfaces (Zapffe and Worden, 1949) would benefit considerably from the application of interferometric methods, even if only a two-beam method were used, as otherwise no information about relative orientation or any quantitative information can be obtained.
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