

Crystal Growth from High-Temperature Solutions

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The term *growth from non-stoichiometric melts* is sometimes used to include all cases where crystals are grown from a liquid containing only the crystal constituents but of a composition which differs from that of the crystal. The scope of this book includes this technique along with "flux growth" and also growth from metallic solvents.

Liquid phase epitaxy (LPE) is a technologically important process in which a thin layer of crystalline material is deposited from solution onto a substrate of similar composition or surface structure.

The literature of high-temperature solution growth, as for all aspects of crystal growth, is very widespread. In addition to the more specialized journals such as the *Journal of Crystal Growth*, *Materials Research Bulletin*, *Journal of Materials Science*, and *Kristall und Technik*, a very large number of journals on crystallography, physics, chemistry, metallurgy, ceramics, mineralogy and electronic technology may contain articles dealing partly or wholly with HTS growth.

Although this book is the first on the subject an extensive number of review articles have appeared over the last ten years. Reference is made to Laudise (1963), White (1965), Schroeder and Linares (1966), Cobb and Wallis (1967), Roy and White (1968), Luzhnaya (1968), Laurent (1969), Elwell and Neate (1971), Chase (1971), Nielsen (1972), Brice (1973), Elwell (1975) and Vanklyn (1975). Although review articles have been used in the compilation of this book, the subject matter has been synthesized from the original articles and any interpretation of theory and of observations is our own or that of the original authors.

The terms "high temperature" and "solution" are not exactly defined in the context of this book. The experiments described are normally in the range from 300°-1800°C and the solute concentration is usually between 1% and 30% in terms of either molar or weight fraction. Some examples will, however, be discussed where the solute concentration is as high as 80% or 90%. Crystals grown from HTS are normally faceted, but again exceptions will be occasionally encountered in the text. Clearly the boundaries between HTS and other growth methods may be only roughly specified; the principal alternative growth methods are described briefly in the next section.

The boundary between solution growth and growth from a doped melt is particularly difficult to define. The distinction which will be made here is that in the latter case the dopant is added in order to change some property of the crystal by virtue of its presence in the lattice. In solution growth the "dopant" is added to the melt in order to lower the crystallization temperature and is rejected by the growing crystal under ideal conditions. The most popular materials grown from high-temperature solution are oxides crystallized from molten salts and this emphasis is reflected in the

of materials which cannot be crystallized from their pure melts for the reasons outlined in the previous section. Even when melt growth is possible, as in the case of alumina Al_2O_3 and spinel $MgAl_2O_4$, a solution method may be preferred on the grounds of crystal quality. Growth from the melt is the subject of a book by Brice (1965, 1973).

3. *Growth from the vapour.* A wide variety of materials may be grown from the vapour phase and the reaction equilibria are now well understood for many systems. With certain materials growth may occur using a single component system, by sublimation-condensation or sputtering. Molecular beam techniques have also been applied recently to crystal growth problems.

The most frequently used method for the growth of bulk crystals utilizes *chemical transport reactions* in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. The book by Schäfer (1962, 1964) and the review of Nitsche (1967) are strongly recommended as an introduction to this subject, and Kaldis (1974) discusses the principles of crystal growth from the vapour phase.

The limitations of chemical transport are partly of chemical origin, especially the problem of finding a suitable transporting agent, and formidable difficulties arise if it is necessary to produce uniformly doped materials or solid solutions. In addition, it is rarely possible to grow large crystals because of multinucleation, although exceptions such as Al_2O_3 , CdS , $ZnSe$, GaP , $GaAs$ and Cd_3GeS_6 are known. The commercial importance of vapour growth is in the production of thin layers by *chemical vapour deposition* (CVD) where usually irreversible reactions (e.g. decomposition of silicon halides or of organic compounds) are used to deposit material epitaxially on a substrate. CVD may often be used as an alternative to liquid phase epitaxy.

4. *Growth from aqueous solution.* The simplest and oldest method of crystal growth is that from aqueous solutions. Enormous quantities of materials such as sugar, salt and of inorganic and organic chemicals are crystallized from solution in water, and excellent quality crystals of such ferroelectric and piezoelectric materials as ammonium dihydrogen phosphate ADP, potassium dihydrogen phosphate KDP and triglycine sulphate TGS are commercially grown for use in electronic devices. Chemical instability or the requirement of an appreciable solubility in water excludes a number of classes of materials from being crystallized from aqueous solutions, a low solubility arising either from a different type of bonding (metals, semiconductors, covalent compounds) or from a high lattice energy (many metal oxides).

Substances with a low solubility in water can be grown by the *gel*

I. INTRODUCTION TO HIGH-TEMPERATURE SOLUTION GROWTH 9

- a. The universality, that is the number of materials to which the method may be applied.
- b. The size and quality of the crystals grown.
- c. The requirements on apparatus and chemicals.
- d. The requirements on experience, theory and time.
- e. Particularly in industrial applications, the crucial factor is the cost per acceptable crystal or layer.

The greatest general advantage of HTS growth is its wide applicability. Except for those organics, hydrates and similar compounds which decompose at relatively low temperatures, there seems to be no limitation to the type of crystal which can be grown from high-temperature solution. In most cases a practical solvent can be found and also growth from non-stoichiometric melts is often possible. The use of HTS growth for the crystallization of oxides is well known but it may not be widely appreciated that such materials as nitrides, borides and carbides may often best be grown from solution.

Until comparatively recently, nucleation was a major problem and the majority of crystals grown from HTS were rather small. This problem has now been largely solved by general advances in techniques and by greater understanding of the growth mechanisms. Large crystals, weighing in some cases over 200 g, have now been produced of a variety of materials ranging from yttrium iron garnet ($Y_3Fe_5O_{12}$), lithium ferrite ($LiFe_5O_8$), gadolinium aluminate ($GdAlO_3$) and barium titanate ($BaTiO_3$) to $Ba_2MgGe_2O_7$, ruby and emerald (see Chapter 10).

The quality of HTS-grown crystals may vary considerably but generally it is a function of the effort (experience, cost, time) devoted to the growth of high-quality crystals. Normally the crystals will contain a higher concentration of impurities than crystals grown from the melt, but will have a lower concentration of equilibrium defects such as vacancies and frequently a lower dislocation density. As an example, the dislocation density of Al_2O_3 crystals grown by a variety of crystal growth techniques is shown in Table 1.1. In this comparison, which looks very favourable for HTS growth, it should be remembered that a number of defects do not depend only on the growth technique but originate from the cooling procedure of the crystal after growth and from any mechanical cutting, grinding and polishing processes. Evidence for the high quality which may be achieved in HTS growth is provided by the observation by Nelson and Remelka (1964) of laser action in an as-grown crystal of ruby a few mm in length, which was silver plated on its natural growth faces.

Apart from the problem of chemical contamination by substitution and

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certain and any model of atomistic behaviour in the neighbourhood of a crystal-solution interface is therefore highly speculative. It may be expected that the recent advances in understanding of the liquid state will lead to new experimental and theoretical studies on solutions, and there is considerable scope for original work. The content of this chapter is limited to an explanation of existing theories in order to formulate the most complete model of crystal growth from solution which can be given at present.

4.2. Nucleation

The initial stage of crystallization in a supercooled liquid is the formation of nuclei of the crystalline phase. Crystal growth, as distinct from nucleation, is the process by which these nuclei attain macroscopic dimensions. The most important early study of nucleation was that of Tammann (1925), who determined the rate of nucleation of complex organic materials. The form of the curve he obtained is shown in Fig. 4.1. On cooling below

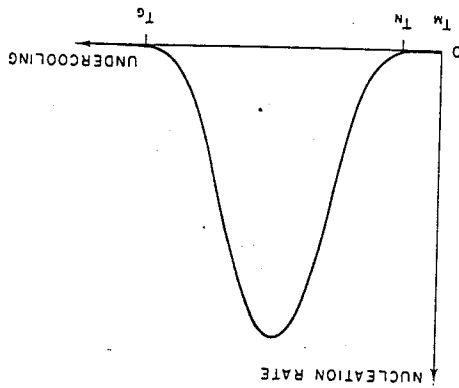


FIG. 4.1. Temperature dependence of nucleation rate (after Tammann, 1925).

the melting point T_m , the nucleation rate is low until some temperature T_y is reached at which the nucleation rate increases very rapidly. The metastable region $T_m \rightarrow T_y$ will depend on such factors as the purity of the melt and the presence of dust or other particles which may act as centres for nucleation. The maximum in the nucleation-temperature curve is due to a slowing down in the kinetics as the temperature is decreased. The fall in the nucleation rate is particularly marked in viscous melts, and will become essentially zero at some temperature T_g . If the melt is cooled to T_g without any crystallization, a glass will be formed. A similar curve to Fig. 4.1 will apply to solutions and it is possible to cool very viscous solutions to a temperature at which nucleation does not occur.

molar volume. The relative supersaturation for small values of ΔT is

$$\sigma = \frac{\Delta n}{n_0} = \frac{\phi \Delta T}{RT_0} \quad (4.4)$$

so that

$$\Delta G^v = \frac{\phi^v \Delta T}{T} = \frac{\phi \Delta T}{RT_0} = \frac{V_M L}{V_M} \quad (4.5)$$

Substitution for ΔG^v in Eqn (4.2) gives the value of the critical radius as

$$r^* = \frac{2\gamma V_M}{RT_0} \quad (4.6)$$

so that an increase in supersaturation will decrease r^* and will therefore favour nucleation.

The value of ΔG in Eqn (4.1) for a nucleus of critical size is

$$\Delta G^* = \frac{16\pi\gamma^2}{16\pi\gamma^2} = \frac{3\Delta G^v}{3RT_0} = \frac{3RT_0}{16\pi\gamma^2} \quad (4.7)$$

and, if there are n molecules per unit volume, the concentration of nuclei of critical size is

$$n^* = n \exp(-\Delta G^*/kT). \quad (4.8)$$

The nucleation rate I , being defined as the number of critical nuclei generated in unit volume per second, is given by the product of the concentration of nuclei of critical size and the rate at which molecules join such nuclei as

$$I = n^* z^* A^* = 4\pi n^* z^* r^{*2}. \quad (4.9)$$

Here z^* is the frequency of attachment of single molecules to unit area of nuclei and A^* is the area of a critical nucleus. Substitution for r^* and n^* in Eqn (4.9) gives

$$I = \frac{16\pi z^* \gamma^2 n^2 V_M^2}{R^2 T_0^2} \exp\left(-\frac{16\gamma^2 V_M^2}{3kR^2 T_0^2}\right) \quad (4.10)$$

from which it is apparent that I will vary rapidly with the supersaturation σ , mainly through the exponential term.

The above treatment follows that given by Volmer and Weber (1926) who assumed that the probability of growth of the nuclei undergoes a sharp discontinuity at the critical radius r^* . Actually embryos of sub-critical size will have a finite probability of growing and those of super-critical size may shrink. A correction for such behaviour was applied by Becker and Döring (1935), but the resulting expression for I still varies

10% and so will not interfere to any appreciable extent with growth on established crystals in well-stirred solutions at supersaturations much below this value. The form of the $I(\sigma)$ curve is in quite good agreement with that of Eqn (4.10) and, in the region of supersaturation above 10%, the nucleation rate can be approximated by a power law $\sim \sigma^n$.

In the presence of a solid surface or other favourable centre, the nucleation rate increases because of a reduction in the interfacial free energy. An expression for the rate of heterogeneous nucleation may be obtained by replacing ΔG^* by some lower value, depending on the nature of the surface and the shape of the embryos. Foreign particles are well known to provide nucleation centres and the problem of achieving a really clean system makes truly homogeneous nucleation difficult to achieve experimentally.

When the conditions for nucleation are first created in a solution, a finite period is required before the steady nucleation rate is established. The rate at which the nucleation rate approaches the steady value I_0 can be described (Dunning, 1955) by a relation

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right)$$

The time constant τ can be written as

$$\tau = \frac{N_c^2 h}{N_s^* k T} \exp\left(\frac{k T}{11 d}\right) \quad (4.11)$$

where N_c is the number of molecules in the critical nucleus and N_s^* the number of solute molecules in the layer of solution adjacent to this nucleus. Cobb and Wallis (1967) have estimated that, in the growth of Al_2O_3 from high-temperature solution, τ can have values from about 0.4 μs to 40 μs for undercoolings between 1°C and 10°C. Under normal growth conditions, therefore, this time dependence should have little effect since undercoolings are expected to be less than 10°C. Long induction periods prior to nucleation may, however, be possible in highly viscous solutions.

4.3. Rough and Smooth Interfaces

Once a crystal has nucleated in a solution, the growth process involves the transport of solute molecules from the solution to some point on the crystal surface where they become part of that surface. Of critical importance is the nature of the crystal-solution interface and we consider first the atomic models of the surfaces of crystals.

To the unaided eye, many crystals grown from solution have perfectly flat faces. The important question which will determine the growth kinetics of the crystal is whether this flatness persists down to the atomic

the rate-limiting step will be the addition of a new atom or group of atoms on that surface, since this group will form a layer with a "rough" edge at which atoms can be integrated relatively easily until the layer covers the whole crystal face and the surface is again smooth.

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4.4. Models of Surface Roughness

Several calculations have been performed of the degree of roughness of a crystal surface and its variation with temperature. Burton and Cabrera (1949) used the Onsager (1944) solution of the Ising model to treat the behaviour of an array of atoms on the surface of the crystal. If U is the surface potential energy per atom of the actual surface and U_0 that of a perfectly flat surface, the surface roughness is defined as $S_r = (U - U_0)/U_0$. The parameter S_r will clearly be zero for a perfectly flat surface and so a non-zero value of S_r is a measure of the degree of roughness. A simple cubic array (such as that of Fig. 4.3) is treated and is assumed to be perfectly flat at absolute zero.

The energy required to remove an atom from the perfectly flat surface and to place it on a site in the next layer (previously empty) is $2W_B$ since four bonds must be broken. For temperatures well below a critical value T_c , $S_r = 4 \exp(-2W_B/kT)$ in which the factor $\exp(-2W_B/kT)$ is the probability of excitation of a single atom from a full to an empty layer on the surface. The variation of this function with temperature is shown in Fig. 4.4(a). It will be seen that the surface may be assumed flat provided that T is much less than $0.1 W_B/k$. More recent treatments have predicted

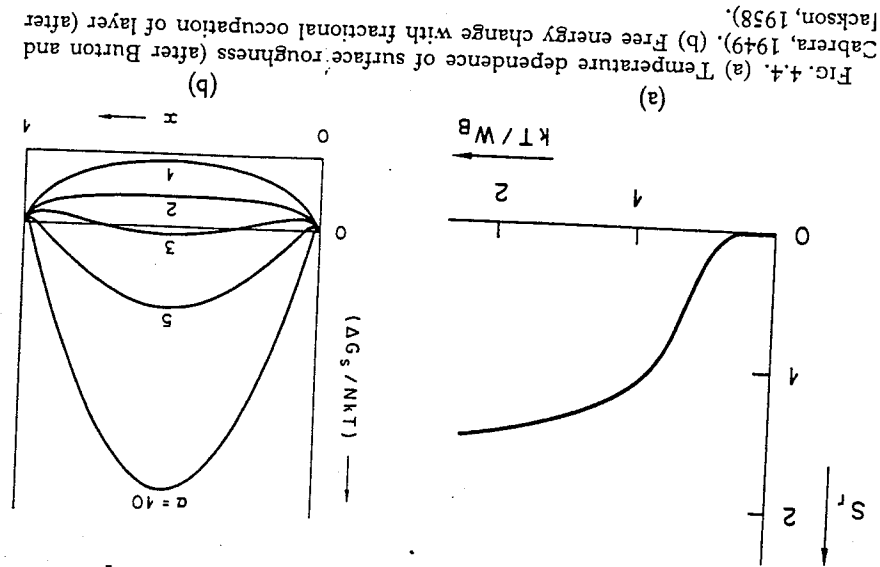


FIG. 4.4. (a) Temperature dependence of surface roughness (after Burton and Cabrera, 1949). (b) Free energy change of surface roughness (after Burton and Jackson, 1958).

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in certain directions which contain the strongest chemical bonds. The flat (F) crystal faces are those which are parallel to at least two of these chains. Stepped or S faces are those parallel to one PBC and rough or kinked (K) faces are not parallel to any PBC. This theory gives good qualitative results for the crystal morphology of several materials but it cannot be used for quantitative work such as calculations of surface energy.

The observation of smooth, highly reflecting facets on most crystals grown from solutions suggests that these are the F faces. If a small crystal is nucleated with an approximately spherical shape in a supersaturated solution, the rough faces will have more sites available for the attachment of solute molecules and will therefore grow more rapidly. As growth proceeds, these rapidly growing faces tend to disappear and the crystal will eventually be bounded by the relatively slow-growing "habit" faces.

The sequence of formation of the habit faces is illustrated in Fig. 4.5. These slow-growing faces, which form the boundaries of crystals grown under stable conditions, are of course not perfectly flat on the atomic scale. They contain vacancies and adatoms (note that the minima in Fig. 4.4(b) for $\alpha > 2$ do not occur exactly at $x = 0$ or 1), but their important property is that growth can only occur at certain sites where a new layer is nucleated.

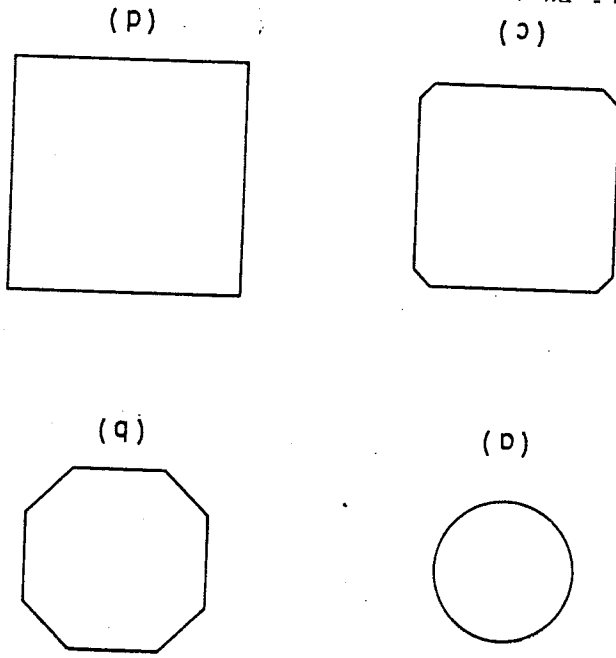


Fig. 4.5. Elimination of more rapidly growing faces during growth.

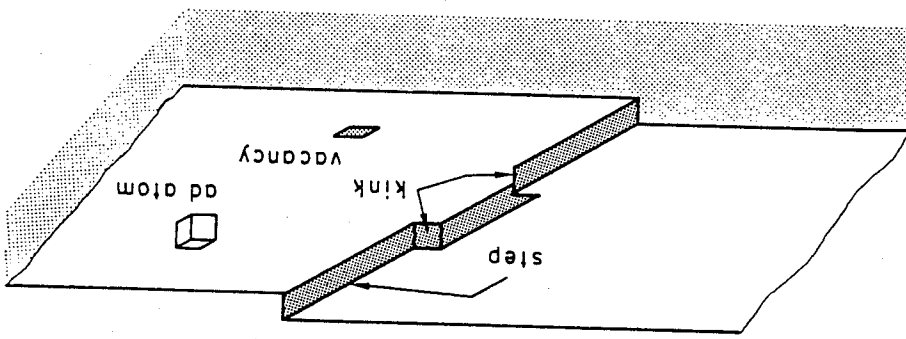


FIG. 4.6. Idealized model of "flat" crystal surface.

If a crystal which has a stepped interface is in contact with a super-saturated solution, the process of growth can be considered to occur in the following stages:

- (i) Transport of solute to the neighbourhood of the crystal surface.
- (ii) Diffusion through a boundary layer, adjacent to the surface, in which a gradient in the solute concentration exists because of depletion of material at the crystal-solution interface.
- (iii) Adsorption on the crystal surface.
- (iv) Diffusion over the surface.
- (v) Attachment to a step.
- (vi) Diffusion along the step.
- (vii) Integration into the crystal at a kink.

The sequence (i)-(vii) is illustrated in Fig. 4.7(a). The detailed nature of the solute particles is not known but it is likely that ions of opposite sign will tend to diffuse together because of their electrostatic attraction. It is certain that some interaction between solute and solvent particles exists in the solution. Such interactions are described by the term *solvation* which is used here to include all forms of interaction. For simplicity the solute particles of Fig. 4.7(a) have been shown to be surrounded in the solution by six particles of the solvent forming a regular octahedron. Solvation may reduce the tendency of solute particles to form clusters near the crystal surface, but the importance of clustering in vapour growth has been demonstrated by Lydtin (1970) and there is a need for experiments aimed at understanding the nature of the solute particles near the crystal interface.

Stages (iii), (v) and (vii) are accompanied by partial desolvation and there will be a new flow of solvent away from the growing crystal. The solute particles may become desorbed at any stage after (iii) and the desorption process has been represented on the diagram by (iv)*. The solute does not

It should be noted that some of the processes (i)-(vii) occur in series but that some occur in parallel so that not all the stages are necessarily involved in the growth of a chosen material. For example, solute particles may diffuse directly to a kink site by surface migration and so eliminate the necessity for (v) and (vi). Some of the processes will normally occur so quickly (in series) and some so slowly (in parallel) that they may be neglected in comparison with the other stages. In practical crystal growth it is most important to know which process determines the rate of growth and we shall be particularly concerned in this Chapter and in Chapter 6 with the problem of deciding which step is likely to be rate-determining.

In order to discuss the growth process in more detail, it is convenient to take stages (iii)-(vii) together as the interfacial kinetic stage. It is also necessary to consider the origin of the steps, which has been neglected in the previous discussion. The transport process (stage (i)) by which solute is transferred to the crystal is crucial to the growth of good quality crystals but we defer discussion of this process until Chapter 6, in which the use of the theory in the design of crystal-growth experiments is considered. Stage (ii), diffusion through the boundary layer, is first considered separately for the case in which the interfacial kinetics are not rate determining. The interfacial kinetic stage (iii)-(vii) is considered separately and the general case where stages (ii) and (iii)-(iv) are combined is also treated.

4.6. The Boundary Layer

The concept of a boundary or "unstirred" layer was introduced by Noyes and Whitney (1897) and its importance in crystal growth from solution was stressed by Nernst (1904). There is often confusion between the solute diffusion boundary layer, which was introduced in the previous section, and the "hydrodynamic" boundary layer. The latter is a layer of solution while the remainder of the solution is flowing past this surface (see Wilcox, 1969). A simple relation exists between the two layer thicknesses, and the layer referred to in the remainder of the book will be the solute diffusion boundary layer.

A boundary layer, whether diffusion or hydrodynamic, is a simplified concept in any system fluctuating with time. Its use in diffusion-limited growth can be illustrated with reference to a plane crystal surface growing uniformly in a supersaturated solution. The rate of transport of solute per unit area in the z direction, normal to this surface, is given by Fick's law

$$\frac{dm}{dt} = -D \frac{\partial c}{\partial z} \quad (+12)$$

as

The fact that crystals normally grow uniformly in spite of this variation in supersaturation has been explained by Frank (1958a), who supposed that the rate of growth of any face is determined by the local value of the supersaturation at one point at which the dominant growth centre for the whole face is located. However, if solute is deposited too rapidly from the solution, it may be expected that faster growth will occur at the corners or edges of the crystal where the supersaturation is highest, and this is confirmed by experiment (Chernov, 1963; Lefever and Chace, 1962). The face of the crystal confirms the approximate nature of equations such as (4.14). The variation of the solute concentration normal to a crystal surface in aqueous solution has been measured by Goldsztaub, Irti and Mussard (1970) and their result is shown in Fig. 4.9. The equation of solute flow in one dimension is normally written in the form

$$D \frac{\partial^2 n}{\partial z^2} + u_s \frac{\partial n}{\partial z} = \frac{\partial n}{\partial t} \quad (4.15)$$

The first term represents the diffusional flow, the second growth-induced convection (Willcox, 1972) and the third takes into account the time dependence of the solute concentration. In the steady state, $\partial n / \partial t = 0$ and so, if u is negligible,

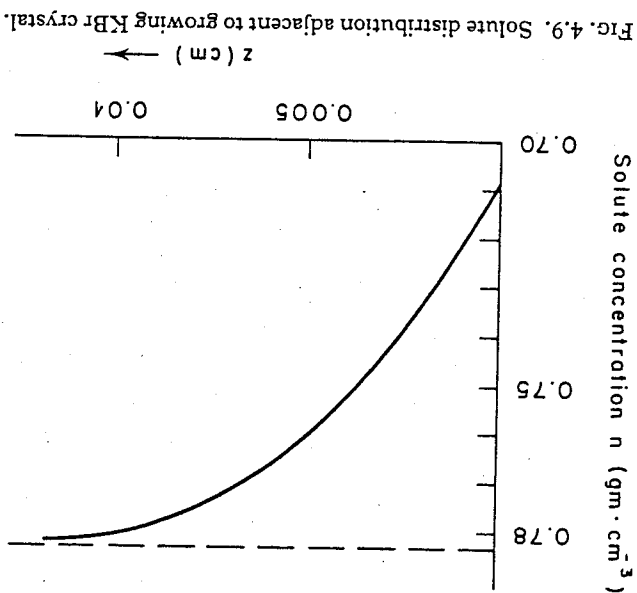
$$\frac{\partial^2 n}{\partial z^2} = 0 \quad \text{i.e.} \quad \frac{\partial n}{\partial z} = \text{const} = \frac{s}{n_{sn} - n_s}$$


FIG. 4.9. Solute distribution adjacent to growing KBr crystal.

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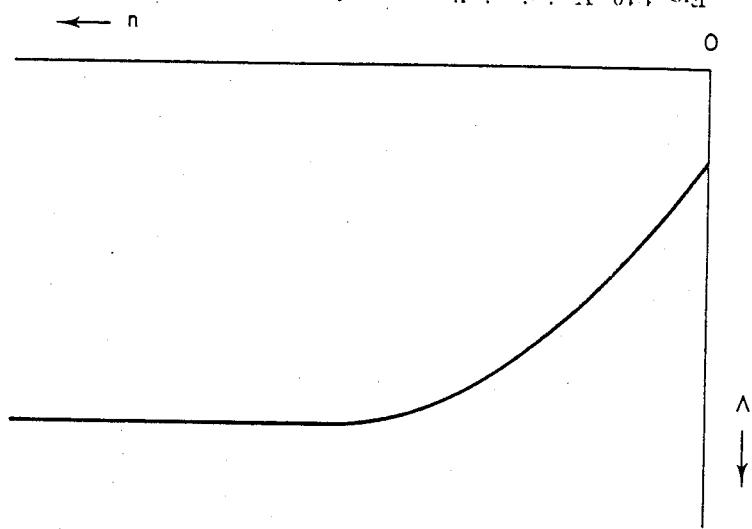


FIG. 4.10. Variation in linear growth rate with solution flow rate.

rotated in solution. The boundary-layer thickness in this case is given by Burton, Prim and Slichter (1953) as

$$\delta \approx 2^{2/3} D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (4.18)$$

where ω is the angular velocity of rotation of the crystal and ν the kinematic viscosity of the solution. A linear dependence of the growth rate τ on $\omega^{1/2}$ is found for the growth of sodium thiosulphate using the data of Coulson and Richardson (1956), for low values of ω . Laudise, Linares and Dearborn (1962) measured the variation of the growth rate of yttrium iron garnet from solution in $\text{BaO}-\text{B}_2\text{O}_3$ with crystal rotation rate. They found an increase in τ for values of ω up to about 50 r.p.m., beyond which the growth rate was independent of the rotation rate. The data are insufficient to confirm an $\omega^{1/2}$ dependence at low rotation rates.

In general the observed rate of growth of a crystal will depend partly on boundary-layer diffusion and partly on the interface kinetics. Brice (1967a) has shown how the role of the boundary layer may be taken into account in order to deduce the form of the interface kinetic law. His approach is based on that of Berthoud (1912) and Valetton (1924). The solute concentration at the interface is taken as n_i and the kinetic law is assumed to have the form

$$v = A(n_i - n_e)^m \quad (4.19)$$

where A and m are independent of the solute concentration. The growth law may also be expressed in terms of the diffusional flow by a modification of Eqn (4.14). In this case

$$\Delta G \approx \frac{4}{3}\pi r^3 \gamma_m - \pi r^2 a \Delta G^v \quad (4.23)$$

and differentiation gives the radius of the critical nucleus as

$$r_s = \frac{a^2 \Delta G^v}{\gamma_m} \quad (4.24a)$$

and the corresponding value of ΔG is

$$\Delta G^* = \frac{4}{3}\pi \gamma_m \frac{a^3}{3} \Delta G^v \quad (4.24b)$$

Substitution for ΔG^v from Eqn (4.5) gives

$$r_s^* = \frac{a^2 R T \sigma}{\gamma_m V_M}.$$

A more familiar form of this equation is obtained by putting $V_M = N_A a^3$, where N_A is Avogadro's number and the molecule is assumed to be a cube of side a . This gives

$$r_s^* = \frac{\gamma_m a}{k T \sigma} \quad (4.25a)$$

and correspondingly

$$\Delta G^* = \pi \gamma_m \frac{a^2}{k T \sigma} \quad (4.25b)$$

The number i^* of molecules in a critical nucleus is

$$i^* = \frac{\pi r_s^{*2}}{\gamma_m} = \left(\frac{k T \sigma}{\gamma_m} \right)^2. \quad (4.25c)$$

The rate of surface nucleation, and hence of crystal growth, depends by analogy with Eqn (4.8) on $\exp(-\Delta G^*/kT)$, and it is instructive to estimate the order of magnitude of this factor as a function of the supersaturation. The energy γ_m is of the order of the binding energy W_B , introduced in Section 4.3, that is $\gamma_m \approx \phi_m/6$, where W_B is the binding energy, ϕ_m is the heat of solution per molecule. (Strictly, the value of γ_m will be higher on low energy planes.) Using a value for $\phi = 72$ kJ mole⁻¹ as found for nickel ferrite in barium borate (Elwell, Neate and Smith, 1969) so that $\phi_m \sim 2 \times 10^{-20}$ J molecule⁻¹, then, with $T = 1500$ K, $\gamma_m/kT \approx 1$ so that $\Delta G^* \approx \pi/\sigma$. The term $\exp(-G^*/kT)$ varies from 3×10^{-3} for $\sigma = 0.5$ and $\sim 10^{-13}$ for $\sigma = 0.1$ to $\sim 10^{-130}$ for $\sigma = 0.01$. Growth by two-dimensional nucleation therefore has a high probability except at very low supersaturation values. In the system referred to above, growth was observed experimentally at relative supersaturations down to about 1%.

Fig. 4.12. Growth spiral on a rare-earth orthoferrite crystal (after Tolkssdorf and Welz, 1972).



91
w
e
t
J
t
c
s
h
f
a

1
1
1

f
f
B
S
2

U
O
B
3
O
H
T

and this value will be used in the subsequent development. The second part of the BCF theory is concerned with the transport of molecules from the bulk of the solution to kinks in the steps of the spiral. It is assumed that the surface-diffusion coefficient is independent of the local concentration and this, together with the neglect of surface vacancies, is the main assumption of the theory. As mentioned earlier, the nature of

$$y_0 \approx 19r_s^* = \frac{19\gamma_m a}{kT\sigma}$$

(4.27)

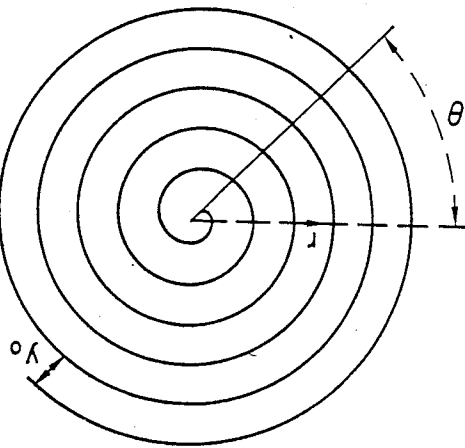


FIG. 4.13. Growth spiral.

solute particles on the crystal surface is not known but, if local electrical neutrality is assumed, it is possible to define a single relaxation time for each stage of the surface transport process in the same way that an effective volume-diffusion coefficient can be specified for the flow of ions of opposite charge. The steps in the spiral are assumed to move negligibly slowly compared with the rate of migration of molecules on the surface. This assumption is justified since the rate at which the step moves is governed by the rate of arrival of diffusing molecules. For simplicity, the distance from the spiral centre is taken to be so large that curvature of the steps may be neglected. The net flux of particles into a strip of width Δy on the surface in the region of a step will depend upon the flux j_s from the solution to the surface and on the flux j_s across the surface into the step due to the concentration gradient created by integration of molecules into the surface at the step.

$$j^s = \frac{n_s^{\text{Tdeads}} - n_s}{n_s^{\text{Tdeads}}(\sigma - \sigma_s)} = \frac{n_s^{\text{Tdeads}}}{n_s^{\text{Tdeads}}} \quad (4.32)$$

On substitution of Eqns (4.31) and (4.32) into Eqn (4.28), the differential equation of solute transport becomes

$$D_s \tau_{\text{deads}} \frac{d^2 \psi}{dy^2} = \psi$$

or

$$y^s \frac{d^2 \psi}{dy^2} = \psi \quad (4.33)$$

where $y^s = \sqrt{D_s \tau_{\text{deads}}}$ is the mean distance travelled by solute molecules on the surface. Equation (4.33) has a general solution

$$\psi = A \exp(y/y^s) + B \exp(-y/y^s) \quad (4.34)$$

and it is necessary to introduce boundary conditions to obtain values for A and B . The most probable situation is that $y^s \gg x_0$, where x_0 is the average distance between kinks in a step. For a set of equidistant steps of separation y_0 and with the origin of y chosen to be mid-way between the steps, the boundary condition may be expressed by putting the value of ψ at a step as $\psi = \beta\sigma$, so that $\psi = \beta\sigma$ when $y = \frac{1}{2}y_0$. Then, from Eqn (4.34), for $y = +\frac{1}{2}y_0$, $\psi = \beta\sigma = A \exp(y_0/2y^s) + B \exp(-y_0/2y^s)$ and for $y = -\frac{1}{2}y_0$, $\psi = \beta\sigma = A \exp(-y_0/2y^s) + B \exp(y_0/2y^s)$ from which $A = B$, and substitution in terms of $\beta\sigma$ in Eqn (4.34) gives

$$\psi = \beta\sigma \cosh(y/y^s) \quad (4.35)$$

If $x_0 \gg y_0$, it is necessary to introduce an extra factor c_0 into Eqn (4.35) to take into account the non-planar diffusion fields around the kinks. From Eqn (4.31), the flux of particles towards a step may now be written as

$$j^s = D_s n_s^{\text{sc}} \frac{d\psi}{dy} = \frac{D_s n_s^{\text{sc}} \beta\sigma}{y^s} \frac{\sinh(y/y^s)}{\cosh(y_0/2y^s)} \quad (4.36)$$

If n_s^{sc} is measured in g cm^{-2} , j^s represents the flux in $\text{g cm}^{-1} \text{s}^{-1}$ towards a step either of monomolecular or larger height. The linear rate of advance of the step v_s^{sc} is obtained by multiplying j^s by the area l/da per unit mass of the crystal so that, for a step of monatomic height,

$$v_s^{\text{sc}} = 2l j^s = 2l \frac{D_s n_s^{\text{sc}} \beta\sigma}{y^s} \tanh \frac{y_0}{2y^s} \quad (4.37)$$

The factor 2 is introduced since molecules enter the step from two sides.

Cabrera and Coleman (1963) have pointed out that at higher supersaturations, the surface supersaturation near the centre of the spiral may be lower than σ because of the depletion caused by surface diffusion to that portion of the spiral where the step spacing y_0 is small. The result is that y_0 decreases more slowly with σ than predicted by Eqn (4.27). This "back stress" effect makes the transition from a quadratic to a linear law occur at higher values of σ than predicted by Eqn (4.42) and a perfectly linear law is unlikely over any wide range of supersaturation values.

If a number of screw dislocations emerge at the growth centre the form of the spiral will be more complex than that shown in Fig. 4.13. In order to take into account the effect of cooperation between a number of interacting spirals, BCF introduced a factor ϵ such that

$$y_0 = \frac{\epsilon}{19\gamma_s^*} = \frac{\epsilon kT\sigma}{19\gamma_m a} \quad (4.43)$$

Equation (4.41) then becomes

$$v = \frac{C\epsilon\sigma^2}{\sigma_1} \tanh \frac{\sigma_1}{\sigma} \quad (4.44)$$

The factor ϵ can be quite complex and some examples of cooperating dislocations will be discussed in Section 4.12.

BCF Theory of Solution Growth

As mentioned earlier, the BCF theory was derived for growth from the vapour. In the case of solution growth, the molecules were assumed to enter the kinks directly rather than by entering an adsorption layer and undergoing surface diffusion. The justification for this assumption was that the coefficient of volume diffusion ($\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) is normally much higher than the coefficient of surface diffusion ($\sim 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) for molecules in solution so that any diffusion in a direction parallel to the crystal surface might be expected to occur in the boundary layer. If the rate of flow of solute molecules to the kinks is governed by diffusion through the boundary layer, the net flux reaching the steps, which governs their rate of advance v_{st} , will be proportional to the supersaturation σ . With $1/y_0 x \sigma$ according to Eqn (4.27), the growth rate v will again vary as σ^2 since $v = v_{st} a/y_0$ [Eqn (4.38)]. BCF considered solute flow towards a kink in a hemispherical diffusion field and obtained an expression for the

$$v_{st} = \frac{Dn_s 2\pi\sigma}{px_0} \left[1 + \frac{x_0 y_0}{2\pi a(\delta - y_0)} + \frac{x_0}{2a} \ln \left(\frac{x_0}{y_0} \right) \right]^{-1} \quad (4.45)$$

For low supersaturations y_0 is large and the third term in the bracket is the

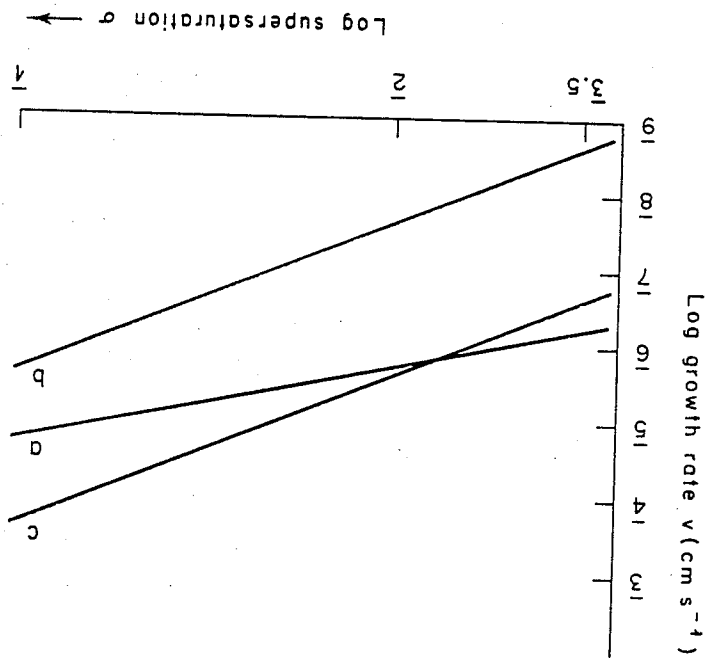


FIG. 4.15. Growth rate for BCF volume and surface-diffusion theories: (a) volume diffusion, (b) surface diffusion, $\beta = 10^{-2}$; (c) surface diffusion, $\beta = 1$.

(Bennema, 1965). The latter value gives $\sigma_1 \approx 0.4$ which is within the range of supersaturation values considered. The value of the growth rate for the surface-diffusion model depends critically on the parameter β of Eqn (4.35). A value $\beta \approx 1$ would indicate that the surface supersaturation has its maximum value and so corresponds to a maximum growth rate. Bennema's estimates of the relevant activation energies suggest a value of $\beta \sim 10^{-2}$ and the usual values are probably somewhere between these limits. There is no reason in principle why a factor β should not be included in Eqn (4.45) also. Figure 4.15 shows that v varies as σ^2 in the supersaturation range shown.

It should be emphasized that the data of Fig. 4.15 represent typical values and do not indicate the effect of surface diffusion on the system considered. Surface diffusion will always increase the growth rate, if its effect is not negligible, by increasing the probability that a solute molecule will find a kink site. Chernov (1961) also proposed a theory of crystal growth from solution based on calculation of the flow to a system of parallel steps, assuming no surface or edge diffusion. The concentration n is assumed to be described by an equation

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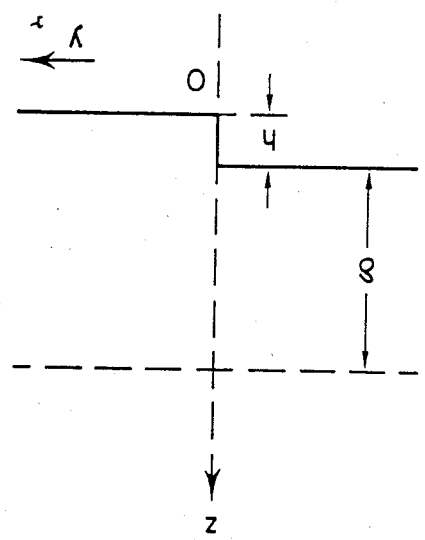


FIG. 4.17. Step at $y=0$.

process as affected by the volume to surface flow is described by the equation

$$D_s \frac{\partial^2 n_s}{\partial y^2} + D \left(\frac{\partial n}{\partial z} \right)_{z=0} = 0 \tag{4.49b}$$

where n_s in this case is the surface concentration of solute per unit area. Finally, the exchange of solute between surface and volume is given by

$$D \left(\frac{\partial n}{\partial z} \right)_{z=0} = \frac{V}{Dn} - \frac{V}{n_s} \tau_{\text{deads}} \tag{4.49c}$$

The factor D/V represents a "drift velocity" of solute molecules entering the adsorption layer from the adjacent volume such that $V = \lambda \tau_{\text{desolv}} / \tau_{\text{diff}}$ where λ is the mean free path in the solution and the τ 's are relaxation times for desolvation and volume diffusion.

The net exchange of solute at a kink is given by the net flux from neighbouring sites as

$$j = D \left(\frac{\partial n}{\partial y} \right)_{y=0} = \frac{V}{D} \left[(n_s)_{y=0} - n_s \right] \tag{4.50}$$

where $V_s = \lambda \tau_{\text{kink}} / \tau_{\text{diff}}$ is the quantity analogous to V for surface diffusion. In the solution to these equations, the critical parameter is found to be $b = \gamma_s / V$ where γ_s is, as before, the mean distance travelled by an adsorbed molecule on the crystal surface. The growth rate in the limit $b=0$ is given by

of relatively insoluble salts and also stressed the importance of an adsorption layer. In experiments where ions of one constituent were added in excess of the stoichiometric ratio, the rate of precipitation was found to be substantially unchanged on adding more of the excess ions. This result is best explained by assuming the existence of an adsorption layer which is "saturated" by the excess ions since the growth rate then depends only on the minority ion concentration. Doremus extended the concept of surface reaction-controlled growth, considering both the formation of molecules on the surface prior to diffusion to a kink and the separate surface diffusion of oppositely charged ions which are integrated alternately into the crystal at the kink sites. In the first case, the precipitation rate was calculated to be proportional to $(n_{s1} - n_1)^2$ for a "one-one" electrolyte AB and to $(n_{s2} - n_2)^4$ for a "two-one" electrolyte A_2B . These dependences became $(n_{s1} - n_1)^2$ and $(n_{s2} - n_2)^2$ respectively for the latter model. Several examples of a cubic growth law were quoted.

Reich and Kahlweit (1968) proposed a theory which is related to the BCF volume diffusion theory but which should be applicable to those cases where desolvation at the kinks is the rate limiting kinetic process. According to their treatment, the rate of advance of steps is governed by the flux of desolvated ions to the kinks. The step velocity is given by

$$v_{st} = \frac{31^m v^2}{\tau_{des} x_0} (n_{s1} - n_1) \exp(H_{des}/kT) \quad (4.52)$$

where τ_{des} is the relaxation time for desolvation at a kink and W_{des} the potential barrier for desolvation. At low supersaturations $v_{st} \propto \sigma$ through the term $(n_{s1} - n_1)$ and a parabolic $v(\sigma)$ law is expected since $y_0 \propto 1/\sigma$ as in the BCF theory. At high supersaturations volume diffusion will become the rate-limiting step as predicted in all treatments of solution growth.

4.11. Comparison of Solution Growth Theory with Experiment

One spectacular success of the BCF theory is that it successfully predicted the occurrence on crystal surfaces of growth spirals, which have now been observed on a wide variety of crystals. In this section we examine the ability of this theory and its various extensions to account for experimental determinations of the variation with supersaturation of the growth rate of crystals from solution.

In interpreting experimental data, difficulty is frequently encountered in distinguishing between boundary-layer and interface-kinetic effects. Two methods are available for obtaining the form of the $v(\sigma)$ relationship for the kinetic process by experiment. The first is to measure the variation of growth rate with solution flow rate or crystal rotation rate and to extract

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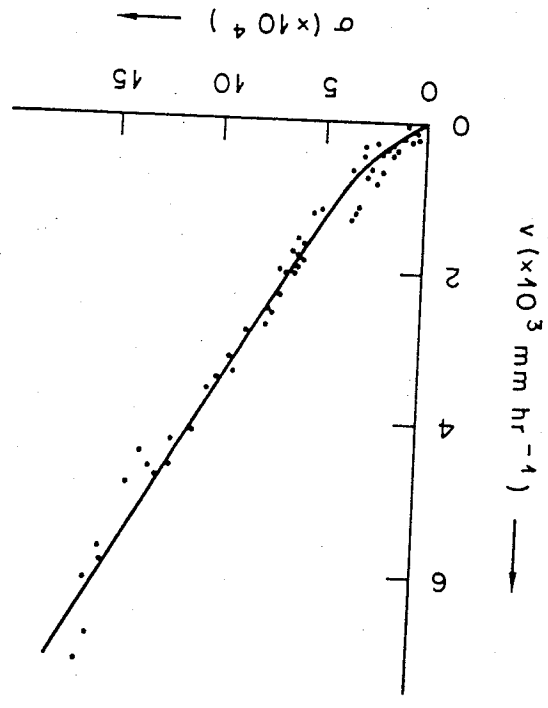


FIG. 4.18. Growth rate of sodium chlorate (after Bennema, 1967).

Garbedian and Strickland-Constable (1970), who reported a variation of the form $v \propto \sigma^{1.73}$ for the growth of sodium chlorate. Bennema (1967) used his own results on sodium chlorate to support his case for the inclusion of surface diffusion in crystal growth from solution. The experimental data are shown in Fig. 4.18 together with a curve plotted using the BCF surface-diffusion formula, Eqn (4.41). A similar curve would be predicted by the BCF volume-diffusion theory but in that case the linear region would be controlled by boundary-layer diffusion. Bennema found, however, that changing the stirring rate had no effect on the crystal growth rate and was therefore confident that the measured growth rate was determined by the interface kinetics. The slope in the linear region is roughly one tenth that expected for volume-diffusion control (Eqn 4.14). This discrepancy was given an alternative explanation by Gilmer *et al.* (1971) by the inclusion of the parameter λ which appears in Eqn (4.51). Then, in the linear region,

$$\frac{dv}{d\sigma} = \frac{Dn_s}{\rho(\delta + \lambda)}$$

(4.53)

of the quadratic law to supersaturations of up to 10%. A critical supersaturation σ_1 of 10% is two orders of magnitude greater than the highest value reported by Bennema (1967) for crystal growth from aqueous solution although Bennema *et al.* (1972) recently revised their estimate of σ_1 to $\sim 10^{-1}$. According to Eqn (4.40), σ_1 is given by $9.5\gamma_m a/kTY_s$, so that a high value of σ_1 requires either a high value of γ_m or a low value of γ_s . Both low γ_s and high γ_m will favour deadorption of surface molecules rather than integration into the kinks, and it is found experimentally that $\text{Ba}_0.5\text{Sr}_{0.5}\text{Nb}_2\text{O}_8$ is a difficult material to crystallize from borate solvents. The quadratic law may also be due to a surface reaction between, say, BaNb_2O_8 and SrNb_2O_8 units, as suggested by Tiller (1971), but current knowledge of the ionic species present in the solution is insufficient to allow any firm conclusion. A quadratic $v(\sigma)$ variation was found to explain the growth-rate measurements of NaNbO_3 from a NaNbO_3 flux (Dawson *et al.*, 1974) and of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ from a K_2CO_3 flux (Whiffin and Brice 1974). Newkirk and Smith (1965) observed a linear variation in the growth of BeO from a number of $\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ solvents. The growth rates for this

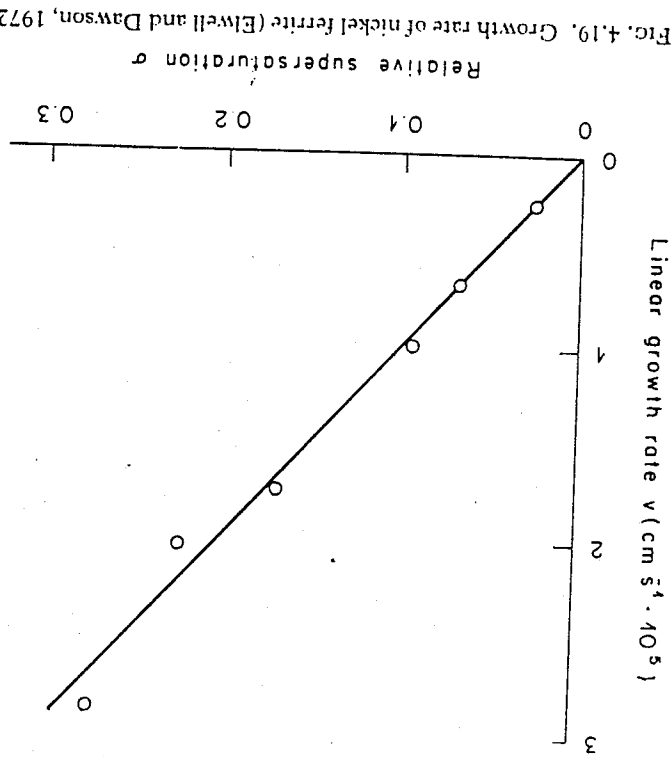


FIG. 4.19. Growth rate of nickel ferrite (Elwell and Dawson, 1972).

normally have more complex shapes, and the growth mechanism may differ from the simpler case considered in Section 4.7.

If the growth centre is a pair of dislocations of like sign, separated by a distance greater than $2\pi r_s^*$, the shape of the resulting spiral will have the form shown in Fig. 4.21. If the crystal face is divided as shown by the heavy

dashed line, which will be slightly curved, the two sections will be fed with steps from the two centres, respectively. The activity is approximately the

same as that of a single spiral. When the centres are separated by less than $2\pi r_s^*$, the arms of both spirals reach the whole area; if the separation is

much less than r_s^* , the centre effectively generates two spirals, each with the same step velocity, and so the activity of the centre will be twice that of

a single dislocation.

When a pair of dislocations of opposite sign are separated by a distance greater than $2\pi r_s^*$, the steps join up to form closed loops, as shown

in Fig. 4.22. This type of cooperation in which a screw-dislocation source generates a series of continuous layers has been observed by Forty

(1951) and Griffin (1951), along with many other examples of spirals due to

interacting dislocations.

If there are two similar pairs of dislocations separated by a distance large compared with the separation in each pair, the steps will combine on

meeting and the number of steps passing any point on the surface will be the same as if only one pair existed. Generalizing from this statement, the

growth rate of a face containing several pairs of dislocations of opposite sign will be the same as that of a face having only one such pair as the

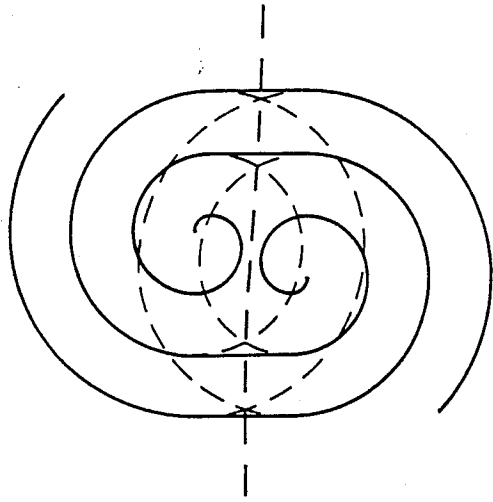


FIG. 4.21. Growth spiral due to pair of dislocations of like sign.

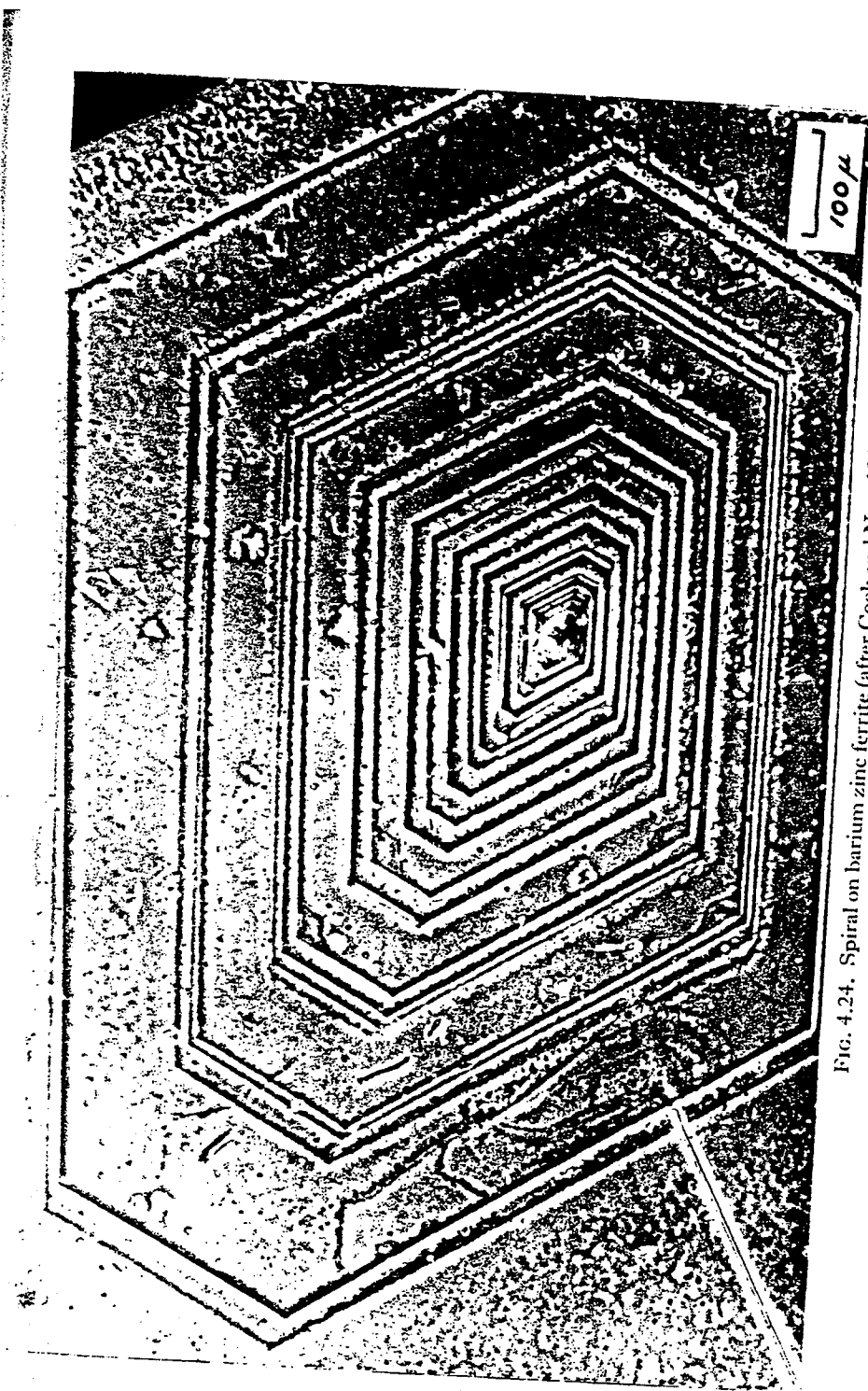


FIG. 4.24. Spiral on barium zinc ferrite (after Cook and Nye, 1967).

was explained by Amelinckx, Bontinck and Deysser (1957) as being due to a "wobbling" of the centre of the spiral at a helicoidal screw dislocation. Fig. 4.25, in which the regular fluctuation in the pitch of the spiral may be seen to give the impression of a spiral of greater pitch. The periodic perturbation can be included in the theory by replacing the factor ϵ in Eqn (4.44) by $\epsilon_0 \sin \omega t$, so that

$$r(t) = \frac{C \epsilon_0 \sin \omega t \sigma^2}{\sigma_1} \tanh \frac{\sigma_1}{\epsilon_0 \sin \omega t \sigma}$$

and the appearance of a macrospiral will be governed by the relative magnitudes of the frequency ω of the perturbation and the frequency of rotation of the spiral. Bennema and van Rosmalen (1972) have shown that fluctuations will always reduce the flow of steps and therefore the rate of growth.

Bennema (1969) has argued that polygonization of the macrospiral is explained more readily if surface diffusion of solute occurs than if solute enters the kink sites directly. He considered in particular the observations of Torgeson and Jackson (1965) of the macrospiral shapes on ADP crystals grown from aqueous solution. When the crystals are grown in a pure solution, the macrospiral on (100) faces are elliptical with a shorter axis in the [001] direction as shown in Fig. 4.26(a). When Cr^{3+} ions are added to the solution, the spirals become polygonized along [010] and [001] directions as shown in Fig. 4.26(b).

According to the PBC description of Hartman (1956), the {100} surfaces

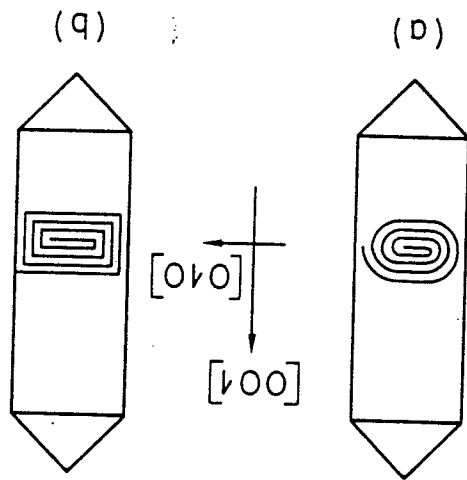


Fig. 4.26. Macrospiral on ADP, schematic (after Torgeson and Jackson, 1965).

treatment of the "bunching" of steps has been given by Cabrera and Vermilyea (1958) and by Frank (1958b) based on the kinematic wave theory of Lighthill and Whitam (1955). The formation of large steps by bunching is governed by kinetics rather than by thermodynamics. The velocity of any step depends on the proximity of other steps, which will remove some of the solute. The rate of flow of steps will therefore depend on the average separation between steps and the kinematic wave theory describes the motion of macrosteps of constant separation at some rate v_2 which is less than the velocity v_1 of a single step. Bunching will be particularly likely to occur if the velocity v_2 is increasing as crystal growth continues, since in this case newly formed steps will tend to overtake those already present on the surface. Bunching is also more probable in impure solutions, since impurity molecules which are rejected by the crystal interface tend to impede the motion of steps; highly immobile impurities may become incorporated into the crystal at the resulting macrosteps. Also the solution flow rate might have an effect on the average step height.

4.13. Surface Morphology of Flux-grown Crystals

Reference has been made above to the observation of growth spirals on the surfaces of orthoferrite crystals by Tolksdorf and Welz (1972) and of polygonized spirals on hexagonal ferrites by Cook and Nye (1967). These observations and the earlier ones of Sunagawa (1967) and others support the validity of Frank's screw-dislocation model. In this section we consider other observations of surface features of crystals grown from high-temperature solutions and the relation between these features and the mode of growth. A more extensive discussion of this topic has been given by Chase (1971).

When crystals nucleate in solution, the supersaturation is normally much higher than that at which the subsequent growth occurs. As a result the initial growth of spontaneously nucleated crystals tends to be highly dendritic. The dendrites grow along fast growth directions and this rapid growth reduces the supersaturation. Subsequent growth occurs more slowly but the ends of the dendrites will be located in regions of higher supersaturation than the central region, and solvent inclusions are trapped near the growth centre as the dendrite arms close. An initial dendritic growth stage has been described by several authors, for example Letever and Chase (1962), White (1965), Chase (1968) and Scheel and Schulz-Dubois (1971). Figure 4.28(a) shows a large crystal of $GdAlO_3$ in which the central dendritic region may be clearly seen, and Fig. 4.28(b) shows the same crystal in reflected light with the large concentration of growth hillocks in the region above the dendritic core. As growth proceeds on the stepped edges of the

dendrite arms provide sites for the integration of solute and a terraced structure is produced. If growth is terminated at this stage the crystals are found to exhibit a "hopper" morphology as illustrated in Fig. 4.29. The mechanism of hopper formation was discussed by Lefever and Giess (1963), who pointed out that hopper crystals will be more likely if the initial dendrites attain large dimensions and so incorporate a large fraction of the available solute.

According to Scheel and Elwell (1973a) hopper growth is assumed to be an effect of unstable growth. By increasing the supersaturation gradient, increasingly unstable growth in the following sequence will occur: flat faces → formation of inclusions → edge nucleation → hopper growth → dendritic growth.

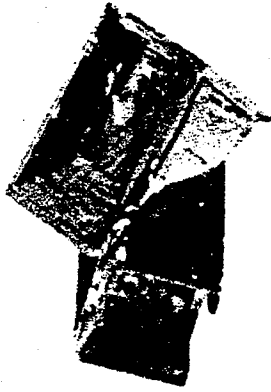


Fig. 4.29. Hopper crystal of hematite (courtesy Mrs. B. M. Wanklyn).

An alternative mechanism of hopper formation was proposed by Amelinckx (1953). The crystals in this case were considered to grow while floating on the solution so that the centre of the face is not in contact with the supersaturated solution. Since contact with the solution occurs only at the edge, growth occurs only where a step in the growth spiral meets an edge and a narrow strip of material is deposited. This strip continues to grow along the edge of the crystal and a vertical hollow box would tend to develop except that the crystal simultaneously grows laterally. Each turn therefore appears at a greater lateral distance from the centre than the previous one and the characteristic terraced depression develops. In the extreme case of growth at the edges of a crystal, the resulting shape will be a hollow rectangular tube.

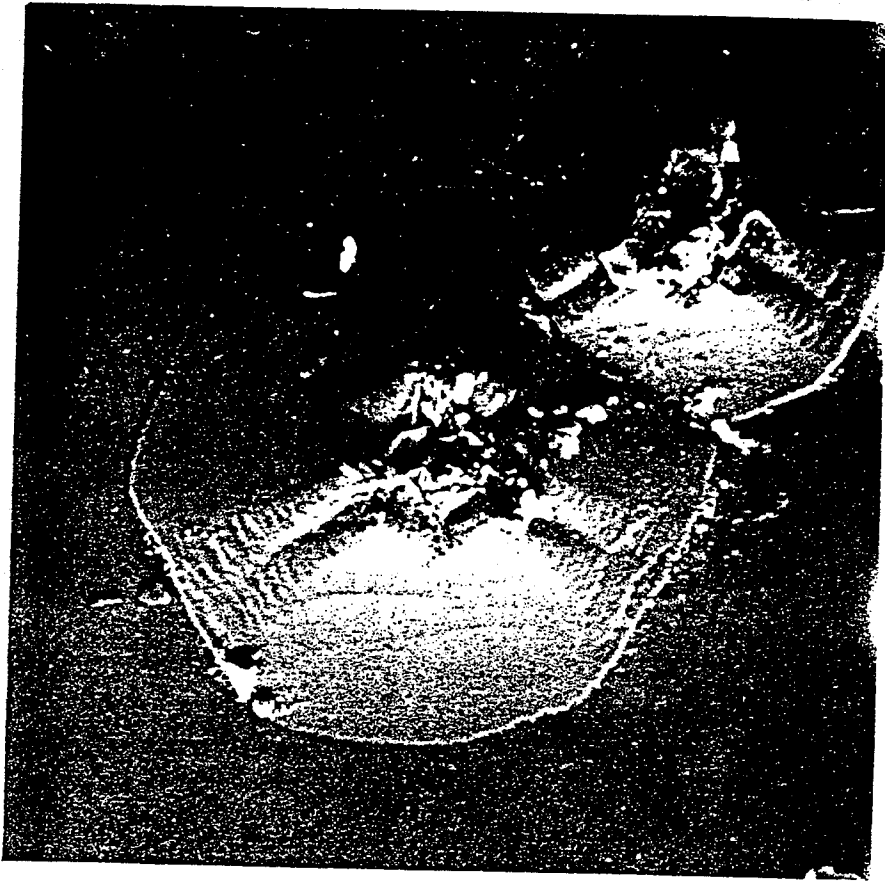


FIG. 4.31. Growth hillocks on nickel ferrite (Elwell and Neate, 1971).

If all the crystal faces remain in contact with the solution, continued growth will eventually result in the establishment of the habit faces. (Growth at relatively high temperatures (and presumably at rather high supersaturation) was found by Lefever and Chase (1962) to proceed by nucleation of layers at corners or edges of the garnet crystals studied. The layers in this case were normally curved in a direction concave from the point of origin, as shown in Fig. 4.31(a). This curvature arises because of the higher supersaturation at corners and edges which can lead to an increase of growth rate with distance from the centre of the face. Similar layers were observed by Chase (1968) on In_2O_3 crystals and by Quon and Sadler (1967) on yttrium iron garnet. In the latter case a similar structure made up of much finer layers was also observed. An example of edge

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investigated a large number of flux grown crystals and has observed spirals of monomolecular step height on magnetoplumbite, $PbFe_{12}O_{19}$, on ferric oxide, alumina and yttrium iron garnet. Pyramidal layers were observed on spinel, $MgAl_2O_4$. The number of features seen on a given face appears to depend on the supersaturation and a single feature often dominates a whole face when growth occurs at low supersaturation. This decrease in the number of active centres as growth proceeds may have an influence on the maximum rate of stable growth, as is discussed in Chapter 6.

Triangular growth layers were observed by Elwell and Neate (1971) on ferrite crystals, an example being shown in Fig. 4.32. This feature appeared to be the only active growth centre on that particular face, and the layer height ($\sim 10^{-3}$ cm) is clearly determined by some bunching effect. A mechanism of crystal growth by the spreading of layers of similar height was reported by Bunn and Emmett (1949) who studied the growth of lead nitrate from aqueous solution.

As discussed earlier in the chapter, layers, hillocks and macrospirals may all have their origin in screw dislocations. Confirmation of the dislocated nature of hillock centres was reported by Lefever and Chase (1962), who found on etching the crystal surfaces that an oriented etch pit was formed at the centre of each hillock. The most likely conclusion to be drawn from these surface studies is that growth on habit faces at low supersaturation frequently occurs by the Frank screw-dislocation mechanism but that edge nucleation may be dominant at higher supersaturations.

4.14. Alternative Growth Mechanisms

Although the mechanism by which crystals grow from fluxed melts is often not rare (Scheel and Elwell, 1973b), the BCF screw-dislocation mechanism, alternative growth mechanisms

Nucleation of surface layers at corners or edges of a crystal may be by 2-D nucleation rather than at screw dislocations. The relative ease of nucleation at corners or edges was first proposed from binding energy considerations by Stranski (1928). Corner and edge nucleation will clearly be favoured because of the relatively high concentration of solute in these regions, even if growth occurs by the screw-dislocation mechanism. Figure 4.33 shows an optical reflection micrograph of a $GdAlO_3$ crystal in which the concentration of hillocks is higher at the crystal edges due to the higher local supersaturation. As growth continues at a stable rate, the concentration of hillocks near the edges decreases and so edge growth becomes less important. The tendency of crystals to grow with raised edges is, however, favoured if growth becomes unstable, as will be discussed in Chapter 6.

FIG. 4.33. Layer spreading influenced by interdomain twinning of NdAlO_3 (Scheel and Eivell, 1973b).

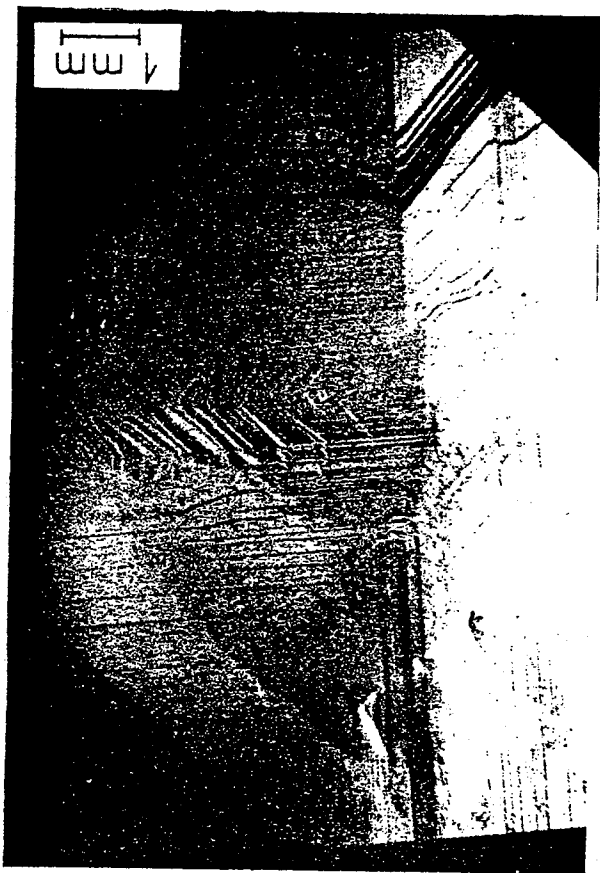
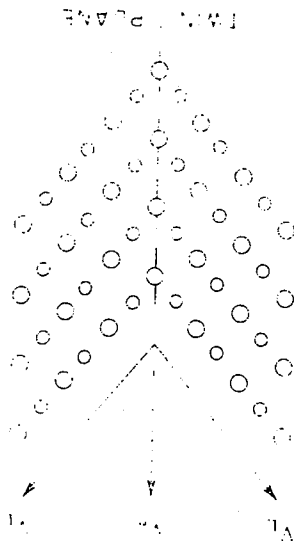


FIG. 4.34. Twin-plane re-entrant edge growth mechanism.



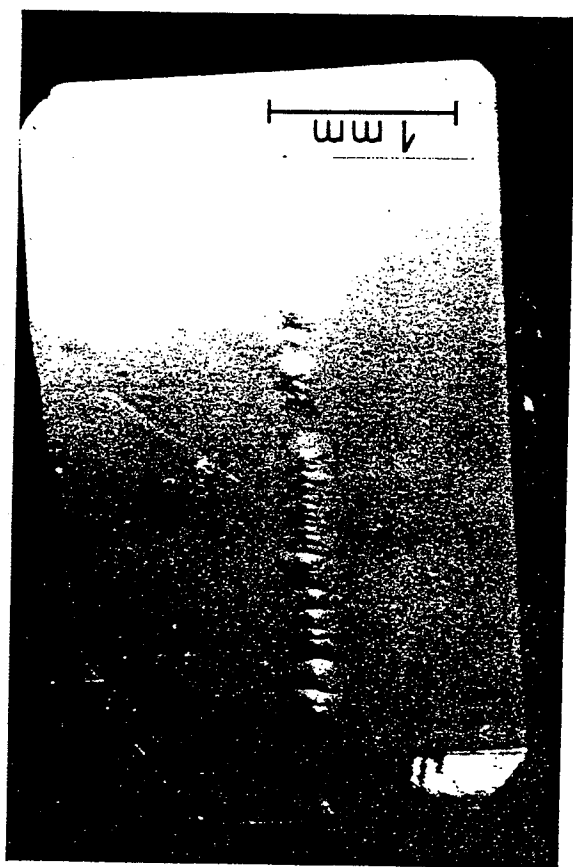


Fig. 4.37. (growth hillocks along a twin plane of GdAlO₃ (Scheel and Eiwell, 1973b).

It is not clear whether twin boundaries at very low angles act by domains are formed at temperatures well below the growth temperature. layers and domains is not observed in crystals such as BaTiO₃ in which the less than 1° (Geller and Bala, 1956). This interrelation between growth closely related to the domain structure, although the twinning angle is surface of neodymium-aluminate crystals. The pattern of layers is very twins is very small. Figures 4.35 and 4.36 show growth layers on the affect the growth mechanism even when the angular deviation between Twin domains formed due to a phase transition during growth may be discussed in the next Chapter.

BaTiO₃ is controlled by the relative importance of this mechanism as will conductors grown by this mechanism. The habit of Al₂O₃, BeO and

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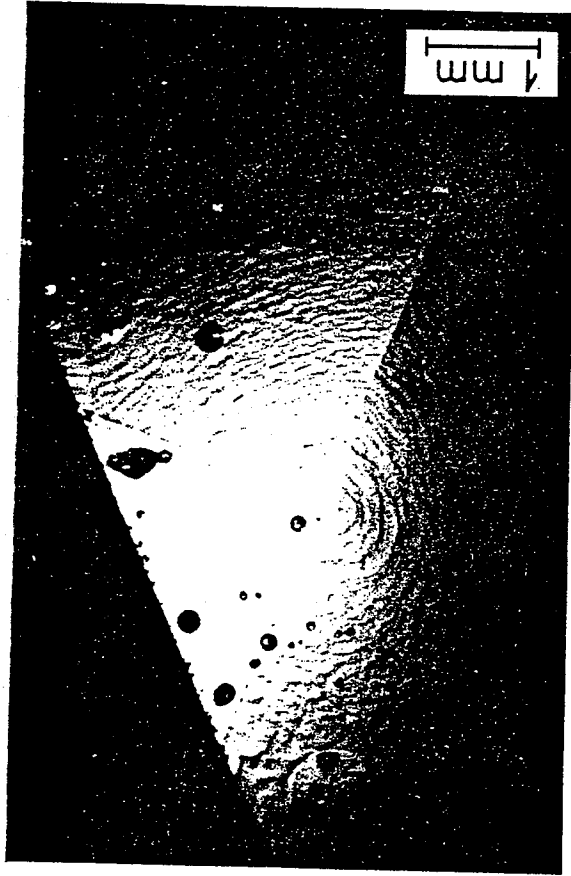


Fig. 4.39. Dominating growth centre near a twin plane of CrAlO_3 (Scheel and Elwell, 1973b).

$$d = \frac{a}{2} \operatorname{cosec} \phi$$

where a is the interatomic separation and ϕ the angle between the adjacent grains. Using the criterion of BCF for the cooperation between screw dislocations of like sign, that $d < 2\pi r^*$, the minimum angle for preferential growth at screw dislocations is given by

$$\sin \phi > \frac{2\pi r^*}{a}$$

Thus for $r^* \sim 20a$, (see Eqn (+25a) with $\gamma = K\Gamma > 1$ and $\alpha = 0.05$), ϕ must be of the order of $1/2$, which is typical of the values at which a twin plane acts as the dominant growth centre.

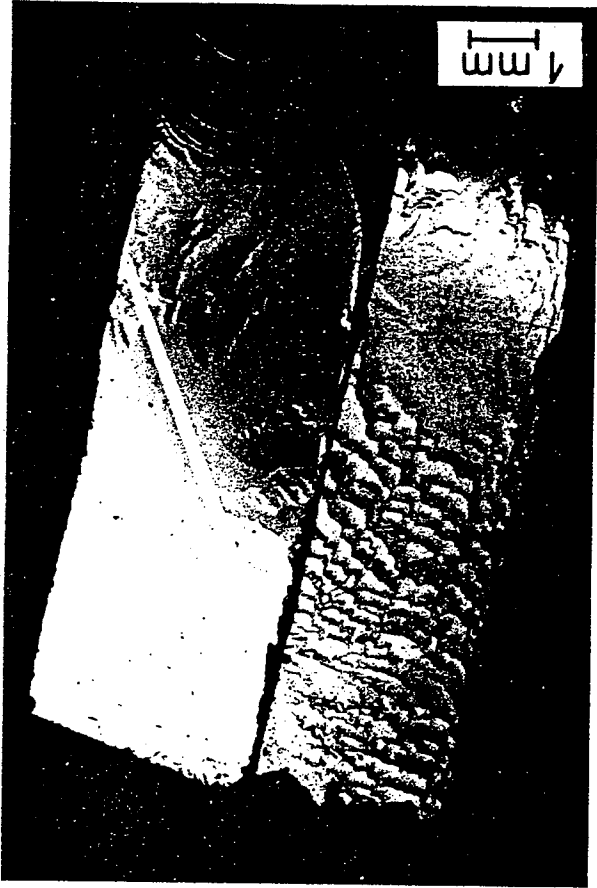
Cracks which develop in any crystal due to severe strain during growth

(i) The rate of nucleation of crystals varies rapidly with supersaturation once a critical value, of the order of 10^{-3} , is exceeded and is very low at lower supersaturations.

4.15. Summary

and indicate that generalizations on growth mechanisms should be expressed with care. active growth centres, with adjacent faces showing hardly any features, suggesting that the latter faces grew by edge nucleation from the more active face. Such observations are contrary to the PBC concept, which treats all $\{100\}$ faces of a pseudocubic perovskite as essentially equivalent,

FIG. 4.11. Two adjacent faces (at nearly 90°) of $GdAlO_3$ (Scheel and Eiwel, 1973b).



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