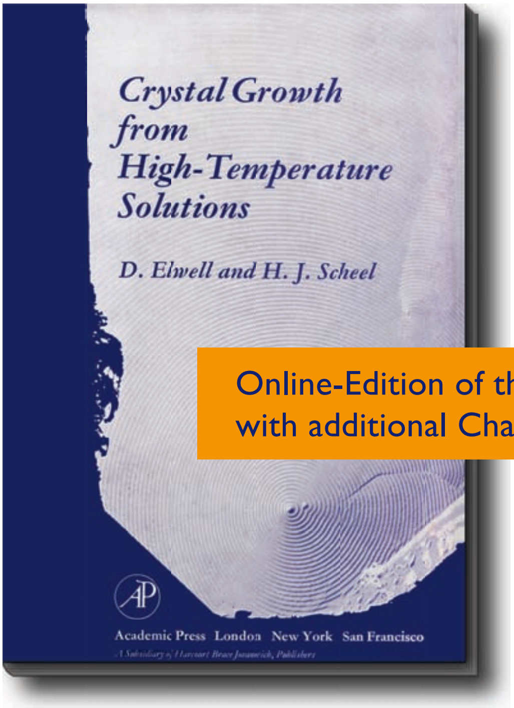

Crystal Growth from High-Temperature Solutions

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Part 009

6. Conditions for Stable Growth

6.1. Stability of Growth

The aim of most crystal-growth experiments is to produce crystals which are sufficiently large and perfect for some measurement or application. The crystal grower is therefore particularly concerned to establish, either by trial and error or by the application of theoretical principles, the conditions under which such large and relatively perfect crystals may be produced.

Stable growth of a crystal from solution may be defined as growth without the entrapment at any stage of solvent inclusions. Alternative definitions of stability are possible and growth-rate fluctuations will always occur on some scale. Large fluctuations may facilitate inclusion formation or compositional variations and are likely to have an adverse effect on the crystal quality.

The problem which is normally considered in a theoretical approach to the calculation of conditions for stable growth is that of morphological stability, or whether a specified shape is stable against small perturbations. This problem differs from the related question of whether a given shape or habit is preserved as the crystal grows. Both aspects are of importance and will be discussed in this chapter. Reviews on morphological stability have recently been published by Parker (1970) and by Chernov (1972).

Perturbation analyses and related studies are concerned with simple shapes but have given a number of results which are of great relevance in the design of experiments. The most important conclusions are that the stability tends to decrease as the crystal increases in size, and the concept of *constitutional supercooling*. Both these results of stability theory have been appreciated for some years but their relation to experiments on high-temperature solution has received comparatively little attention and will be stressed where possible.

Particular importance is attached in this chapter to the concept of a maximum stable growth rate and its dependence on the growth conditions. Practical considerations for the attainment of stable growth will be discussed in the later sections of the chapter.

6.1.1. Stability of the sphere and cylinder

Mullins and Sekerka (1963) used the perturbation method to examine the stability of a spherical crystal with isotropic surface kinetics growing in a supersaturated medium. They concluded that the sphere is stable against perturbations only if its radius is less than a value of $7r^*$, where r^* is the radius of the critical nucleus. For a supersaturation of 10%, the maximum stable radius was calculated to be of the order of 0.1 μm. Nichols and Mullins (1965) and Coriell and Parker (1966) studied the effect of surface diffusion on the stability of a spherical crystal and found that the maximum stable radius is increased by a large factor. In the example considered by Nichols and Mullins, this factor was of the order of 100 so that spheres were estimated to be stable to a radius of about 10^{-3} cm.

Cahn (1967) included the effect of interface kinetics and of an anisotropic surface tension. He found that the latter has no stabilizing effect but this result is not surprising for a sphere since the anisotropy is not shape preserving as it would be for a polyhedral crystal, and its main effect will be to cause an anisotropy in the instability. The inclusion of interface kinetics leads to an expression for the rate of increase of radius of the sphere given by

$$\frac{\mathrm{d}R}{\mathrm{d}t}=\frac{F(n_{sn}-n_e)}{1+F\rho R/D} \tag{6.1}$$

where F is a kinetic coefficient such that the linear growth rate $v=F(n_i-n_e)$ and the other symbols have been defined previously.

For small crystals the term $F\rho R/D$ may be neglected and the growth rate becomes $F(n_{sn}-n_e)$. Since the diffusion coefficient D does not appear in the expression for $\mathrm{d}R/\mathrm{d}t$, growth is said to be interface controlled. The interface concentration in this case is approximately the same as in the bulk solution and growth should be stable since the concentration gradient in the solution is approximately zero. At high values of R the increase of radius is given by

$$\frac{\mathrm{d}R}{\mathrm{d}t}=\frac{D}{\rho R}(n_{sn}-n_e)$$

and the sphere becomes unstable as shown by Mullins and Sekerka (1963).

This treatment therefore leads to the conclusion that the sphere will be stable only up to a radius such that $K\rho R/D \sim 1$. For $D = 10^{-5}$ cm^2 s^{-1}, $\rho = 5$ g cm^{-3} and $F = 10^{-4}$ cm^{-2} s^{-1} g^{-1}, the maximum stable radius is only of the order of 0.02 cm. Coriell and Parker (1967) performed a similar but more quantitative calculation for both linear and quadratic interface kinetics. In the example they quoted, of salol growing from aqueous solution, kinetic control increases the maximum size for stable growth by a factor 3000, to a value of 0.5 cm.

The stability of a cylindrical crystal has been studied by Coriell and Parker (1966) and is found to exhibit approximately the same behaviour as that predicted for the sphere. Surface diffusion was estimated to increase the maximum stable radius by a factor of about 40. Kotler and Tiller (1966) included interface kinetics and found that the maximum radius is strongly dependent on the undercooling and the kinetic coefficient.

The main conclusion to be drawn from these studies is that instability tends to occur when the crystal reaches a critical size, which will be increased by surface diffusion of solute and by interface kinetics. These predictions must, however, be treated with great caution in their application to solution growth because of the strong tendency of crystals to develop habit faces. As a result of this tendency, it has not been found possible to study the stability of spherical or cylindrical crystals in solution, as for ice crystals in water (Hardy and Coriell, 1968). Greater significance must therefore be attached to studies of polyhedral crystals and of a single plane interface, which is treated in greater detail in the following section.

6.1.2. Stability of a plane interface

A. *Constitutional supercooling/supersaturation gradient.* Perturbation treatments of the stability of a planar crystal surface growing in a doped melt were first given by Mullins and Sekerka (1964), Sekerka (1965) and Voronkov (1965). When conduction of heat through the crystal is included, the condition for stability may be written as

$$\frac{mn(1-k)v}{kD} < \frac{K_c}{K_c + K_l}\left(\frac{\mathrm{d}T}{\mathrm{d}z}\right)_c + \frac{K_l}{K_c + K_l}\left(\frac{\mathrm{d}T}{\mathrm{d}z}\right)_l. \qquad (6.2)$$

Here m is the slope of the liquidus curve, n the concentration of the impurity in the bulk liquid, K the thermal conductivity and $\mathrm{d}T/\mathrm{d}z$ the temperature gradient normal to the interface, with the suffices c and l referring to the crystal and liquid, respectively. k is the partition coefficient which is defined as the ratio n_c/n_l of the impurity concentration in the crystal to that in the liquid, and which is normally less than unity. Equation (6.2) could be extended to growth from very concentrated solutions where

n_c and n_l would be the solvent concentrations in the crystal and solution, respectively.

The condition expressed by Eqn (6.2) is closely related to the *constitutional supercooling criterion*, introduced by Ivantsov (1951, 1952) as "diffusional undercooling", by Rutter and Chalmers (1953) and quantitatively by Tiller *et al.* (1953). As the crystal grows, impurities are rejected at the crystal surface and so the impurity concentration in the liquid immediately ahead of the interface becomes appreciably higher than that in the bulk of the liquid (Fig. 6.1a). This accumulation of impurities results in a depression of the equilibrium liquidus temperature T_L (according to the phase diagram) as illustrated in Fig. 6.1(b). The actual temperature distribution in the melt is as shown in the dashed line (i) of Fig. 6.1(b) and any protuberance on the interface will tend to grow (relative to the interface) since it will experience a higher supercooling.

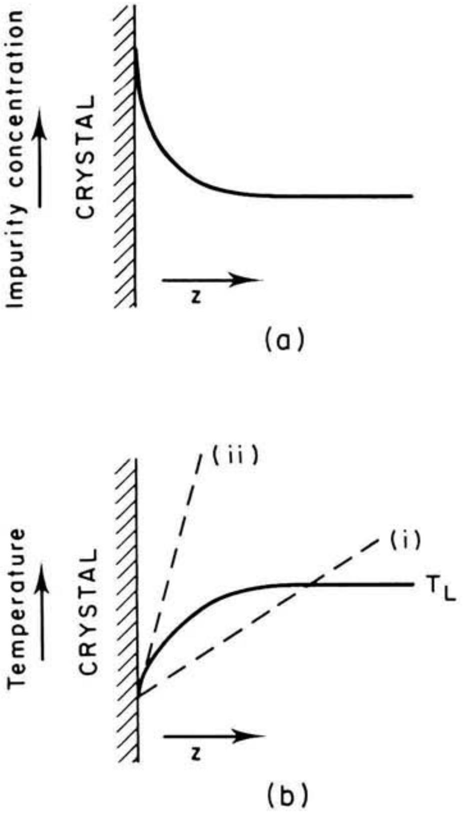

FIG. 6.1. (a) Impurity distribution and (b) equilibrium liquidus temperature T_L ahead of an advancing interface in a doped melt.

The region ahead of the interface is then unstable. Stable growth can occur if the temperature gradient at the interface is increased as in (ii) of Fig. 6.1(b), in which case the actual temperature ahead of the interface is higher than the liquidus.

The condition for constitutional supercooling may be readily derived as

$$\frac{mn(1-k)v}{kD} > \frac{\mathrm{d}T}{\mathrm{d}z} \tag{6.3}$$

which is identical with Eqn (6.2) if $K_c = 0$, or if $K_c = K_L$ and the latent heat is zero. Lucid reviews of constitutional supercooling and of the modes of unstable growth which can result have been given by Tiller (1963, 1970). Experimental confirmation of the validity of the constitutional supercooling criterion for melt growth has been provided by Walton *et al.* (1955) and Bardsley *et al.* (1961).

The similarity between growth from a doped melt and growth from solution has been pointed out by White (1965). In the latter case solvent is rejected by the growing crystal and there will inevitably be a gradient of solute ahead of the interface due to local depletion by the crystal. Tiller (1968) has proposed the application of the constitutional supercooling criterion to growth from solution by a modification of Eqn (6.3). Since the solution normally contains a number (j) of solute constituents, the condition for instability may be expressed by writing for the growth rate:

$$v > D_0 \frac{\mathrm{d}T}{\mathrm{d}z} \Big/ \sum_{i=1}^{j} \left\{ \frac{m_i(k_i^* - 1)n_i}{D_i/D_0} \right\} \tag{6.4}$$

where D_0 is the diffusion coefficient of the solvent and m_i, k_i^*, n_i and D_i refer to the solute constituent i. The effective partition coefficient is defined by

$$k_i^* = \left(\frac{n_c^{\,i}}{n_{sn}^{i}} \right)_{z=0}$$

where $n_c^{\,i}$ and n_{sn}^{i} are the concentration of i in the crystal and solution, respectively. Tiller has calculated the ratio of the maximum stable growth rate $v_{\max}$ to the gradient $(\mathrm{d}T/\mathrm{d}z)$ as a function of temperature for various compound semiconductors and his results are shown in Fig. 6.2.

An alternative and much simpler calculation of the criterion for stable growth in solution under diffusion-limited conditions may be obtained by considering the condition for the appearance of a supersaturation gradient —an increase in supersaturation ahead of the interface which may be a consequence of solute diffusion (Elwell and Neate, 1971; Scheel and Elwell, 1973a). The condition for instability is that a protuberance will encounter a higher supersaturation as it advances so that at the interface,

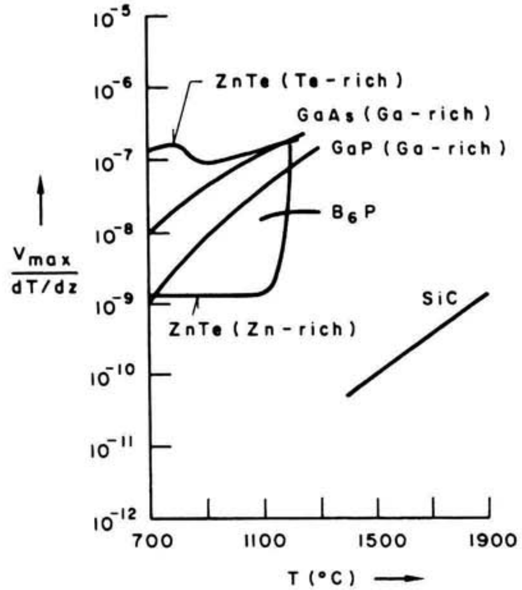

FIG. 6.2. Ratio of maximum stable growth rate to temperature gradient for solution growth of some compound semiconductors (Tiller, 1968).

$$\frac{\mathrm{d}n}{\mathrm{d}z} > \frac{\mathrm{d}n_e}{\mathrm{d}z}\,. \tag{6.5}$$

Now $\mathrm{d}n/\mathrm{d}z$ is related to the linear growth rate v by Eqn (4.13)

$$v \simeq \frac{D}{\rho}\left(\frac{\mathrm{d}n}{\mathrm{d}z}\right)_{z=0}$$

and, for an ideal solution with $n_e = \text{const} \exp(-\phi/RT)$,

$$\frac{\mathrm{d}n_e}{\mathrm{d}z} = \frac{\phi n_e}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}z}\,.$$

Substitution into Eqn (6.5) gives the condition for instability as

$$v > \frac{D\phi n_e}{\rho RT^2}\frac{\mathrm{d}T}{\mathrm{d}z} \tag{6.6}$$

which is substantially the same result as Eqn (6.4) for a single component.

Using typical values of $D = 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$, $n_e = 1\ \text{g cm}^{-3}$, $\rho = 5\ \text{g cm}^{-3}$, $\phi = 70\ \text{kJ mole}^{-1}$ and $T = 1500°\text{K}$, the maximum stable growth rate according to Eqn (6.6) will be $v_{\max} \sim 10^{-8}\ \text{cm s}^{-1}$ for $\mathrm{d}T/\mathrm{d}z = 10\ \text{deg cm}^{-1}$ or $v_{\max} \sim 10^{-9}\ \text{cm s}^{-1}$ for $\mathrm{d}T/\mathrm{d}z = 1\ \text{deg cm}^{-1}$. The value of $v_{\max}/(\mathrm{d}T/\mathrm{d}z) \sim 10^{-9}\ \text{s}^{-1}\ \text{deg}^{-1}$ is typical of the values quoted by Tiller (Fig. 6.2).

In practice crystals are grown at stable rates of the order of 10^{-6} cm s^{-1} in temperature gradients of the order of 1 deg cm^{-1}. It is therefore clear that *crystal growth from high-temperature solution normally occurs in a destabilizing supersaturation gradient.*

For stable growth to occur at rates much greater than those given by Eqn (6.6), it must be assumed that the supersaturation gradient must be insufficient for a perturbation to nucleate (Wagner, 1954; Tiller and Kang, 1968; O'Hara *et al.*, 1968). The crystals may therefore be said to grow in a *metastable region of the supersaturation (or supercooling) gradient* as discussed by Scheel and Elwell (1973a). This region is analogous to the normal metastable or Ostwald-Miers region and is illustrated in Fig. 6.3.† In Fig. 6.3(a) is shown the actual solute concentration n_{sn} in front of the

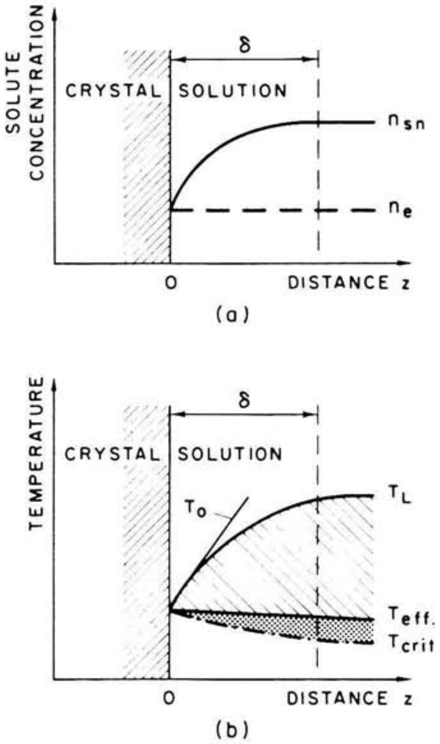

FIG. 6.3. (a) Solute concentration ahead of crystal growing in solution. (b) Metastable region of supersaturation gradient. (T_o corresponds to ii of Fig. 6.1.) (Scheel and Elwell, 1973a.)

† The width of the boundary layer is denoted approximately in the diagrams. The exact definition of δ is that of Eqn (4.14).

growing crystal for diffusion-controlled growth and the corresponding liquidus temperature T_L is shown in Fig. 6.3(b). The significance of this metastable region between T_L and T_{crit} is that a perturbation will not nucleate (or will develop at a negligibly slow rate) so long as the temperature T_{eff} ahead of the crystal exceeds the limiting value. In the example shown, growth will occur in the metastable region even if the temperature gradient at the interface is zero. If, however, the requirement of conduction of the heat of crystallization through the solution leads to a temperature distribution below that of the dashed line T_{crit} in Fig. 6.3(b), growth will be unstable and the crystal will contain an appreciable concentration of solvent inclusions.

By analogy with observations on the Ostwald-Miers region, it may be expected that the width of the metastable supersaturation (supercooling) gradient region will depend on such factors as the crystal-growth rate and the degree of disturbance, particularly thermal or mechanical shock, to which the solution is subjected.

An important question concerns the origin of the metastability and we now consider in some detail the relative importance of the various stabilizing factors which were not taken into account in the derivation of Eqns (6.4) or (6.6). We consider first the results of a perturbation approach.

B. *Perturbation analysis.* In view of the importance of the perturbation method of stability analysis, a summary is given here of a simplified treatment of the stability of a plane interface growing in solution, due to Shewmon (1965).

Consider a plane crystal surface growing in a supersaturated solution in the volume diffusion-controlled regime. Any protuberance on this surface may be analysed into a number of sine waves of different wavelength and it is convenient to discuss the stability condition in terms of such sine waves. A protuberance of the interface such as that shown in Fig. 6.4 will have components of the form

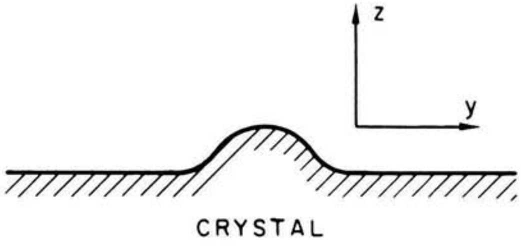

FIG. 6.4. Proturberance on plane crystal-solution interface.

$$z = \epsilon(t) \sin \omega y \tag{6.7}$$

where ϵ is the time-dependent amplitude of the perturbation and the wavelength is specified by ω. The perturbation causes local changes in the solute concentration at the surface, which is given by the Gibbs-Thomson equation. The local curvature is assumed to be d^2z/dy^2 so that the equilibrium concentration is specified by

$$n_s = n_{se}(1 + \Gamma\epsilon(t)\omega^2 \sin \omega y) \tag{6.8}$$

where n_{se} is the equilibrium concentration per unit volume for a flat surface, and Γ is the capillary constant $\gamma V_M/RT$. (As in Chapter 4, V_M is the molar volume of the solute and γ the surface energy per unit area.)

An approximate solution may be obtained by assuming that the interface is static, in which case the solute distribution obeys Laplace's equation $\nabla^2 n = 0$. The general solution to the latter equation for a sinusoidal interface and a static solute gradient $G = (dn/dz)_{\epsilon=0}$ is

$$n(z, y) = A + B \exp(-\omega z)\epsilon \sin \omega y + Gz. \tag{6.9}$$

The constants A and B are chosen to make Eqn (6.9) identical with Eqn (6.8) at the interface, that is by equating coefficients with $z = \epsilon \sin \omega y$. This gives $A = n_{se}$ and $B = (n_{se}\Gamma\omega^2 - G)$, so that

$$n(z, y) = n_{se} + (n_{se}\Gamma\omega^2 - G) \exp(-\omega z)\epsilon \sin \omega y + Gz. \tag{6.10}$$

The linear growth rate is then given by Eqn (4.13) as

$$v \simeq \frac{D}{\rho}\left(\frac{dn}{dz}\right)_{z=0} = \frac{D}{\rho}[G + (G - n_{se}\Gamma\omega^2)\omega\epsilon \sin \omega y]. \tag{6.11}$$

The first term in Eqn (6.11) represents the growth rate v_o in the absence of any perturbation, and so the development of any perturbation relative to the mean position of the surface is given by the second term as

$$\dot{\epsilon} = \frac{D}{\rho}(G - n_{se}\Gamma\omega^2)\omega\epsilon \sin \omega y \tag{6.12}$$

so that

$$\frac{\dot{\epsilon}}{\epsilon} = (1 - n_{se}\Gamma\omega^2/G)\omega v_o. \tag{6.13}$$

The first term on the right-hand side of Eqn (6.13) may be interpreted physically as being due to an increase in the concentration gradient in front of the "hills" on the perturbed "valleys". The second term is due to the concentration gradients along the surface which cause solute transport and so tend to smooth out the sinusoidal disturbance. The two effects balance at a critical value of ω, denoted ω_o, such that

$$\omega_o = (G/n_{se}\Gamma)^{1/2}. \tag{6.14}$$

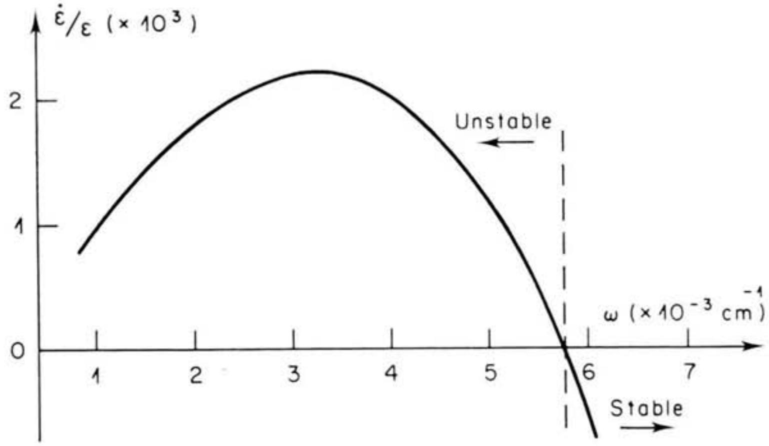

FIG. 6.5. Rate of development of instability for various values of ω ($= 2\pi/\lambda$).

Taking typical values of $G/n_{se} = 1$ cm^{-1} (1% supersaturation and $\delta = 10^{-2}$ cm) and $\Gamma = 3 \times 10^{-8}$ cm ($V_M = 40$ cm^3 mole^{-1}, $\gamma = 10^{-5}$ J cm^{-2} and $T = 1500$°K) gives a value of $\omega_o \simeq 6 \times 10^3$ cm^{-1}. A plot in Fig. 6.5 of $\dot{\epsilon}/\epsilon$ for various values of ω using the same parameters with $v_o = 10^{-6}$ cm s^{-1} shows that a particular wavelength will tend to become dominant if growth occurs under unstable conditions. In the example chosen, the maximum value of ω is about 3×10^3 cm^{-1} so that the corresponding wavelength is in the region of 20 μm. Some confirmation of this prediction is provided by the surface structure of a $GdAlO_3$ crystal shown in Fig. 6.6. The surface shows

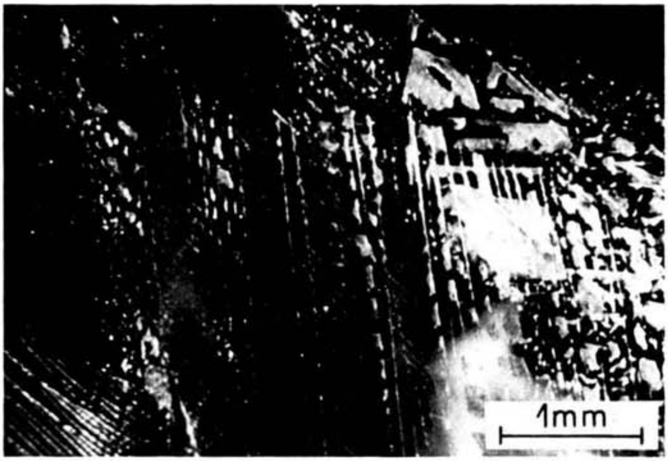

FIG. 6.6. Periodic solvent inclusions on surface of $GdAlO_3$ due to interruption of stirring at the end of growth experiment (Scheel and Elwell, 1973a).

an inclusion structure which exhibits a fine periodicity of approximately 30 μm. A transient instability in this case resulted from the cessation of stirring at the termination of growth prior to removal of the excess solution.

For values of ω greater than ω_o, $\dot{\epsilon}/\epsilon$ is negative and so the perturbation tends to decay; the interface is therefore unstable against perturbations of relatively long wavelength. The stability range is increased if the solute gradient G is small and if the capillary constant Γ is large. Absolute stability, for all values of ω, requires that $G=0$ which is incompatible with volume diffusion (and would also require $v_o=0$ under the conditions assumed!).

Additional stability is obtained if surface diffusion of the solute is included since this will tend to smooth out any disturbance by transporting solute from the "hills" to the "valleys". The inclusion of surface diffusion introduces an additional term so that Eqn (6.12) becomes

$$\dot{\epsilon}/\epsilon = \frac{D}{\rho}\left(G - n_{se}\Gamma\omega^2 - \frac{\Gamma D_s \Lambda \omega^3}{D}\right)\omega \sin \omega y \tag{6.15}$$

where D_s is the surface-diffusion coefficient and Λ the thickness of the adsorption layer in which this diffusion occurs.

In the general case, the growth rate is determined partly by interface kinetics and Eqn (6.10) will no longer be valid. If the linear growth rate is specified in terms of the kinetic coefficient F such that $v = F(n_i - n_e)$, as in Section 6.2, an extension of the analysis outlined above leads to an expression for the growth of the protuberance

$$\dot{\epsilon} = \frac{(1 - \Gamma n_{se}\omega^2 G)\omega\epsilon v_o}{(1 + D\omega/F)} \tag{6.16}$$

in which surface diffusion has been neglected. This equation reduces to Eqn (6.13) in the volume-diffusion regime where $D\omega/F < 1$.

It is seen that, according to this treatment, the condition for stability is the same as in the diffusion-controlled case since the boundary between $\dot{\epsilon} < 0$ and $\dot{\epsilon} > 0$ is still given by Eqn (6.14). As $D\omega/F$ increases, so $\dot{\epsilon}/\epsilon v_o$ will decrease and the principal effect of kinetic control will be to reduce the rate of development of the instability.

According to the above model, the instability condition applies to all values of ω below ω_o and therefore to all wavelengths above the corresponding value $\lambda_o = 2\pi/\omega_o$. However, the model must break down at long wavelengths since it requires redistribution of solute due to a perturbation of wavelength λ over a distance of the order of λ. This redistribution must occur by volume diffusion and so the model breaks down when $\lambda \gtrsim (D\tau)^{1/2}$, where $(D\tau)^{1/2}$ is the mean displacement due to diffusion. At higher values of λ, stabilization will be present because of surface tension but there will be no enhancement of the solute gradient to give instability. Since $(D\tau)^{1/2} \sim \delta$, the wavelength region over which growth is unstable will be given by

$$\delta \gtrsim \lambda 2 \gtrsim \pi \left(\frac{n_{se} \Gamma}{G} \right)^{1/2} . \tag{6.17a}$$

Since $G \simeq (\sigma n_e / \delta) \simeq (\sigma n_{se} / \delta)$, this condition may alternatively be expressed as

$$\delta \gtrsim \lambda \gtrsim 2\pi \left(\frac{\Gamma \delta}{\sigma} \right)^{1/2} . \tag{6.17b}$$

An alternative stability condition is therefore that $2\pi(\Gamma\delta/\sigma)^{1/2} > \delta$ or, as is equivalent,

$$\sigma < \frac{4\pi^2 \Gamma}{\delta} \tag{6.18}$$

The maximum supersaturation required by this condition is, however, unreasonably low. If $\Gamma \simeq 3 \times 10^{-8}$ cm and $\delta \simeq 10^{-2}$ cm as in the example above, Eqn (6.18) requires that $\sigma < 1 \times 10^{-4}$ which would correspond to an extremely slow growth rate.

In summary, Shewmon's treatment predicts that a planar crystal surface is unstable towards perturbations above some critical value of the order of 10 μm. Stability is enhanced by surface diffusion but not by surface kinetics, although the latter retards the development of the instability. The main success of this approach is in the prediction of a periodic structure of wavelength about 20 μm when growth is unstable, but it does not yield a criterion for stable growth which may be used in practice.

The effect of interface kinetics on the stability of a plane interface was considered by Tarshis and Tiller (1967). They concluded that kinetics will stabilize the interface, but only under source-limited growth conditions.

C. *Stabilization due to facetting*. The most important factor which has been neglected in the above treatment is the normal tendency of solution-grown crystals to develop habit faces. Such faces have a characteristically low energy and it may be expected that the development of a perturbation on such faces will be more difficult than on non-habit faces since protuberances will involve the formation of surfaces of relatively high energy.

The stability of habit faces has been discussed qualitatively by O'Hara *et al.* (1968), who consider both kinetic and capillarity effects. If growth on a particular facet is controlled by a single active centre which generates a growth spiral, then a perturbation which tends to increase the small angle between the resulting vicinal face and the crystallographic habit face will also increase the number of layer edges per unit area. The lateral motion of these edges will cause the surface to revert back towards the original geometry with the separation between adjacent spiral arms given by $19r^*$ according to the BCF theory (see Chapter 4). Capillarity tends to stabilize a facet when the growth is strongly anisotropic, particularly when the energy minimum in the Wulff plot is very sharp. This effect can be enhanced by non-isotropic adsorption of impurities, which could explain why the addition of impurities may sometimes result in improvement in crystal quality.

The stability of polyhedral crystals has been considered in more detail by Chernov (1972) in a review of morphological stability. Chernov explains the stability of facetted crystals in terms of the anisotropy of the surface processes. A ridge or hollow produced by some fluctuation on an anisotropic surface has along its edges much higher kinetic coefficients than at the vertex, so that it expands tangentially at a rapid rate relative to the normal growth direction. This anisotropy invalidates the use of a perturbation approach.

Of particular importance when polyhedral crystals (as distinct from a plane surface of unspecified extent) are considered is the difference in supersaturation between the corners and face centres. The variation in supersaturation across a crystal face was measured, for example, by Bunn (1949) (see Chapter 4) and was found to be about 25% in the case of sodium chlorate. According to Chernov, this supersaturation inhomogeneity is compensated by the development of vicinal faces as indicated in Fig. 6.7. The slope at the centre of the face to the crystallographic habit face must differ from that at the corners by about 2° if the increased kinetic coefficient at the centre is to balance the lower supersaturation. The supersaturation inhomogeneity increases as the crystal grows and the curvature

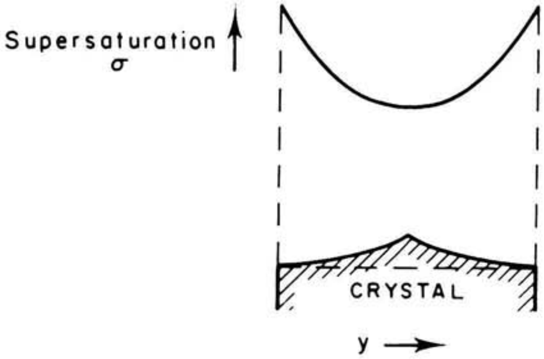

FIG. 6.7. Supersaturation inhomogeneity and compensating curvature for a crystal face (Chernov, 1972).

of the crystal must also increase if the face is to remain stable. Chernov's condition for instability is that the face centre attains some maximum deviation from the simple crystallographic orientation such that the kinetic coefficient becomes very large. This approach gives the maximum length l of a crystal having N faces as

$$l = \frac{D(p_o - p_i)\tan(\pi/N)}{2F_i\epsilon\theta f(\theta)} \tag{6.19}$$

where p_o and p_i are the slope of the crystal face to the crystallographic habit plane at the centre and edge, respectively. F is the kinetic coefficient, ϵ a measure of the difference in solute concentration between the edges and the face centre and θ represents the anisotropy in the growth kinetics. The complex function $f(\theta)$ depends on the anisotropy and also on the limiting value of $(p_o - p_i)$. Using typical values of the various parameters, Chernov estimates $l \sim 10^{-2}$ cm for $\theta = 2$ (a minimum value for a regular polyhedron), and $l = 10^{-1}$ cm for $\theta = 40$. These values are clearly at variance with experiment by one or two orders of magnitude.

A factor not considered by Chernov which could increase the maximum size for stable growth is the tendency for dislocations to propagate in bundles radiating either from a seed crystal or from the nucleation centre towards the centre of the crystal faces rather than towards the corners. This tendency is illustrated in Figs 4.28(a) and (b) which show the surface of a large $GdAlO_3$ crystal grown by spontaneous nucleation (Scheel and Elwell, 1973b). The high concentration of defects at the centre of the face is clearly correlated in extent with the dendritic core of the crystal, while the outer regions of the face are relatively free from defects.

The main technique which has been used to demonstrate this tendency of dislocation propagation towards face centres is that of X-ray topography, which will be discussed in detail in Chapter 9. In the topograph shown in Fig. 6.8, which is fairly typical, the dislocation bundles are revealed as white streaks and the preferential propagation towards the face centres is clearly noticeable.

If the crystal does contain a higher concentration of active sites near the face centres, an enhanced departure from the habit plane will be unnecessary and crystals will be able to grow to greater size than that predicted by Chernov without the development of excessive curvature. However, the tendency illustrated in Figs. 4.28 and 6.8 is by no means universal and alternative sources of stabilization must be considered.

Cahn (1967) also treated the stability of a habit face with growth by layer propagation but took as his stability condition the requirement that the supersaturation must not fall to zero at the face centre. By assuming that the solute is transported over the surface only by volume diffusion,

FIG. 6.8. X-ray topograph of triglycine sulphate crystal showing bundles of dislocations radiating from the seed (Vergnoux *et al.*, 1971).

Cahn arrived at an expression for the maximum size of a crystal for stable growth

$$l = \frac{D(n_{sn} - n_e)}{v\rho}\,. \tag{6.20}$$

With $D = 10^{-5}\ \mathrm{cm^2\,s^{-1}}$, $n_{sn} - n_e = 5 \times 10^{-2}\ \mathrm{g\,cm^{-3}}$, $v = 10^{-5}\ \mathrm{cm\,s^{-1}}$ and $\rho = 5\ \mathrm{gm\,cm^{-3}}$, Eqn (6.20) gives $l = 2 \times 10^{-3}$ cm which is again much too small in relation to experiment.

The most likely cause of the large discrepancy between Chernov's or Cahn's treatment and experiment is in the assumption that the flow of solvent between the edges and centre of the crystal faces occurs only by volume diffusion. The principle that the difference in supersaturation between the edges and centre of a face leads to instability is likely to be correct, but convective flow must be taken into account in any realistic estimate of the maximum stable size. The importance of solution flow will be considered in the next section.

D. *Velocity gradient*. An alternative and attractively simple method of treating the effect of surface kinetics on stability was proposed by Brice (1969). If a crystal is growing in the z direction at a stable rate v, the condition for stability proposed by Brice is that a projection will grow less rapidly and a depression more rapidly than the rest of the surface. This requires that the *velocity gradient* should be negative, that is that

$$\frac{\mathrm{d}v}{\mathrm{d}z} < 0. \tag{6.21}$$

If it is assumed that the crystal is growing at a rate determined by the BCF formula [Eqn (4.42a)] written in the form

$$v = A\left(\frac{n_{sn} - n_e}{n_e}\right)^2 T^2 \exp\left(-B/RT\right),$$

then differentiation and substitution into Eqn (6.21) gives

$$v\left[\left(\frac{2}{T} + \frac{B}{RT^2}\right)\frac{\mathrm{d}T}{\mathrm{d}z} + \frac{2}{(n_{sn} - n_e)}\frac{\mathrm{d}n}{\mathrm{d}z} - \frac{2n\phi}{(n_{sn} - n_e)}\frac{\mathrm{d}T}{\mathrm{d}z}\right] < 0.$$

With $\rho v/D$ substituted for $\mathrm{d}n/\mathrm{d}z$ from Eqn (4.13), the stability condition becomes

$$v < \frac{D}{\rho}\frac{\mathrm{d}T}{\mathrm{d}z}\left[\frac{n_{sn}\phi}{RT^2} - (n_{sn} - n_e)\left(\frac{1}{T} + \frac{B}{RT^2}\right)\right] \tag{6.22}$$

which is the same as Eqn (6.6) except for the second term in the square bracket. This term in fact reduces the maximum stable growth rate by about 35% if B is taken to have a value of 20 kJ/mole. It would be of interest to extend this model to treat the stability of a rectangular protuberance considering both its movement along and normal to the crystal surface, and the results of the above one-dimensional approach must be treated with caution. The various treatments of the effect of interface kinetics are seen to be somewhat conflicting.

6.2. Solution Flow and Stability

An increase in the rate of flow of solution past a crystal surface has two main effects. It will even out the distribution of solute over the surface and will reduce the thickness of the boundary layer. The first effect, as argued in the previous section, will lead to enhanced stability for a polyhedral crystal, but the beneficial effect of the reduced boundary-layer thickness is not so obvious and will be discussed first.

According to the concept of a metastable region of supersaturation gradient, stirring may lead to an enhancement of stability even of an infinite plane surface. The distribution of solute and the temperature

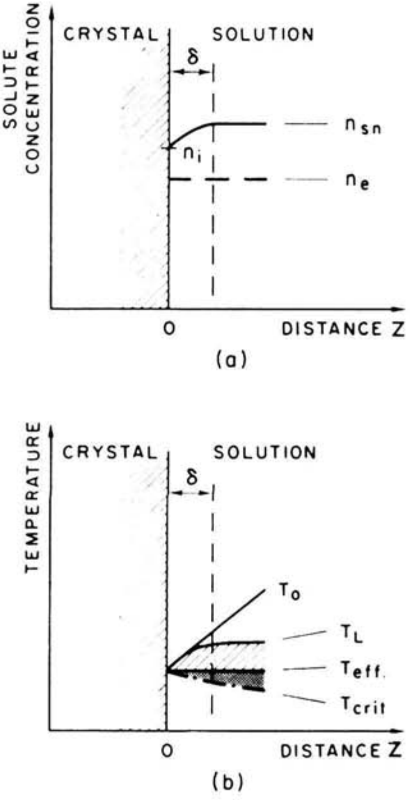

FIG. 6.9. (a) Solute concentration ahead of crystal growing in stirred solution (b) Metastable region of supersaturation gradient in stirred solution (compare Figs 6.3(a) and (b)) (Scheel and Elwell, 1973a).

relationships ahead of the interface are shown in Figs 6.9(a) and (b), which may be compared with the corresponding diagrams for an unstirred solution shown in Figs 6.3(a) and (b). The interface concentration n_i will exceed the equilibrium value as interface-kinetic control becomes dominant and the solute gradient will depend, to a good approximation, on $(n_{sn} - n_i)/\delta$. Thus, although δ decreases with stirring, there is a corresponding decrease in the width of δ_T of the thermal boundary layer. So if the temperatures of the crystal surface and the bulk solution remain constant, stabilization results since the temperarute gradient is steepened by stirring to a greater extent than the solute gradient. This additional stabilization is a result of the enhanced degree of interface control, which determines the growth rate v (see Eqn. 6.3).

Tiller (1968) reached the opposite conclusion, namely that stirring leads to reduced stability in the case of an infinite plane surface. This conclusion will apply to cases where the temperature control is such that the increase in solute gradient is not compensated by an increased temperature gradient. Hurle (1961) examined the conditions for stable growth in the case of a rotating crystal and concluded that the supersaturation gradient is independent of the crystal rotation rate.

The theory of interface stability during growth from stirred melts was also considered by Delves (1968) and by Hurle (1969), who used a perturbation analysis. Delves concluded that the interface may be stabilized by fast stirring if the liquid is slightly supercooled. Under conditions near to instability, a self-excited oscillatory motion of the interface was predicted, with a wavelength of 30 μm in the example quoted. This result is very similar to that of Shewmon which was discussed in Section 6.1.2. Hurle also concluded that the effect of stirring on the stability of a plane interface is small, and found that there is no condition of absolute stability in a stirred solution.

When crystals of finite size are considered, the important condition is that growth should be uniform over the whole surface. As discussed in the previous section, instability will result if the supersaturation falls to zero at the centre of a face, and the probability that this will occur is clearly much reduced in a flowing solution. The problem of the maximum size of a crystal face for stable growth has been considered by Carlson (1958) who assumed a region of laminar flow between the surface and the bulk solution. For the crystal to grow at a uniform rate, the concentration was assumed to vary with the distance y from the leading edge according to

$$n = n_{sn} - b y^{1/2} \tag{6.23}$$

where b is independent of n or y. The maximum length l of the face for stable growth is then determined by the condition that the surface concentration should not fall below the equilibrium value. This gives for the limiting value

$$l = 0.214\, Du/\mathrm{Sc}^{1/3}[v\rho/(n_{sn} - n_e)]^2 \tag{6.24}$$

where Sc is the Schmidt number $\eta/\rho_{sn} D$, u the solution flow rate and v the linear growth rate. With this equation, and assuming similar values for D, v, $n_{sn} - n_e$, etc., to those in the previous examples, values of l some two orders of magnitude higher than those given by the theory of Chernov [Eqn (6.19)] or Cahn [Eqn (6.20)] are predicted. Equation (6.24) therefore appears to provide a stability criterion which may be used as a basis for practical procedures for crystal growth under stable conditions, as will be discussed further in Section 6.6.

6.3. Ultimate Limit of Stable Growth

A prediction of the constitutional-supercooling or supersaturation-gradient approach is that the maximum stable growth rate may be increased as the temperature gradient at the interface is increased. However, experimental evidence indicates that there exists for any material an ultimate rate of stable growth which cannot be exceeded even with a steep temperature gradient and a high degree of stirring.

Data for the stable growth rates from a number of typical HTS and LPE growth experiments have been listed in Table 6.1 and in no case was this rate found to exceed significantly 5×10^{-6} cm s^{-1}, or about 4 mm per day. It is probable that a limiting growth rate of this order is imposed by surface-kinetic processes such as desolvation, integration at kinks and removal of solvent molecules from the surface. In several cases spontaneous nucleation of further crystals might limit the maximum feasible growth rate.

However, faster growth rates are possible in crystal growth from the melt and it is clear that the transition from a dilute solution to a pure melt is gradual. This implies that higher stable growth rates may be achieved in solution growth if the solute concentration is relatively high. This conclusion is confirmed by the work of Belruss *et al.* (1971), who reported stable growth rates of 10^{-5} cm s^{-1} in top seeding experiments using a 70–90% solute concentration. At high values of the growth rate, the removal of the heat of crystallization cannot be neglected as a rate determining factor.

Wilcox (1970) has discussed the influence of a temperature gradient on crystal facetting. In high temperature gradients, crystals tend to grow without facets and it is possible that, in certain systems, even higher growth rates than those of Belruss *et al.* (1971) could be achieved with non-facetted crystals.†

If crystals are to remain facetted, the only possibility of faster stable growth than by the usual layer mechanism would appear to be by encouraging a high activity of hillock sources on highly dislocated faces. Figure 6.10 shows the large activity of growth hillocks on an yttrium iron garnet crystal compared with the layer mechanism. The photograph shows a surface which normally grows by spreading of layers from relatively few centres. The surface has two raised circular areas due to solution droplets which have remained after removal of the bulk of the solution by hot pouring. During cooling to room temperature, rapid growth continued on these areas and the remaining flux was subsequently removed by dissolution. One droplet shows continued layer growth with a raised rim due

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† This conclusion is confirmed by results reported by Mrs. V. A. Timofeeva at ICCG 4, Tokyo, 1974.

TABLE 6.1. Experimentally Observed Growth Rates in Crystal Growth from HTS

Crystal	Solvent	Linear growth rate Å · s^{-1}	Remarks	Reference
$Ba_2Zn_2Fe_{12}O_{22}$	$BaO—B_2O_3$	200	Pulling from solution	AuCoin *et al.* (1966)
$GdAlO_3$	$PbO—PbF_2—B_2O_3$	~200	Accelerated crucible rotation technique	Scheel (1972)
$NiFe_2O_4$	$NaFeO_2$	200	Pulling from solution	Kunnmann *et al.* (1963)
$NiFe_2O_4$	$BaO—B_2O_3$	~500	Pulling from solution	Smith and Elwell (1968)
$NiFe_2O_4$	$PbO—PbF_2$	~260	Seeded growth from solution	Kvapil *et al.* (1969)
$Y_3Fe_5O_{12}$	$BaO—B_2O_3$	120	Seed crystal on stirrer	Laudise *et al.* (1962)
$Y_3Fe_5O_{12}$	$BaO—B_2O_3$	150	Pulling from solution	Linares (1964)
$Y_3Fe_5O_{12}$	$BaO—B_2O_3$	~150	Pulling from solution	Kestigian (1967)
Growth by liquid phase epitaxy				
$Al_xGa_{1-x}As$	Ga	22	LPE, slow cooling	Blum and Shih (1971)
GaAs	Ga	~140	LPE, fast cooling	Kang and Greene (1967)
GaAs	Ga	~170	LPE, slow cooling	Kinoshita *et al.* (1968)
$Ga_{1-x}Al_xAs$	Ga	~10	LPE, slow cooling	Woodall (1972)
$InAs_{1-x}Sb$	In	250	LPE, gradient transport	Stringfellow and Greene (1971)
$InAs_{1-x}Sb$	In	170	LPE, gradient transport	Stringfellow and Greene (1971)
$Eu_1Er_2Fe_{4.3}Ga_{0.7}O_{12}$	$PbO—B_2O_3$ $Bi_2O_3—V_2O_5$	660	LPE, 30° supercooling	Levinstein *et al.* (1971)
$Eu_{0.6}Y_{2.4}Fe_{3.9}Ga_{1.1}O_{12}$	$PbO—B_2O_3$	340	LPE, slow cooling	Giess *et al.* (1972)
$Y_3Fe_5O_{12}$	$BaO—B_2O_3$	260	LPE, gradient transport	Linares *et al.* (1965)
$Y_3Fe_5O_{12}$	$BaO—B_2O_3$	8	LPE, slow cooling	Brochier *et al.* (1972)
$RFeO_3$	$PbO—B_2O_3$	11	LPE, slow cooling	Shick and Nielsen (1971)

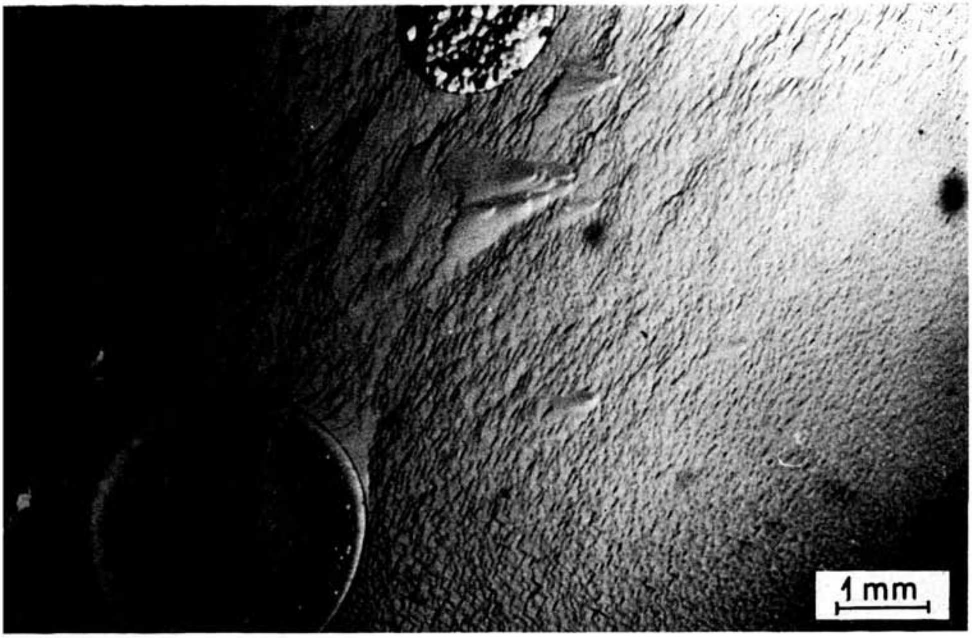


FIG. 6.10. Surface of a garnet crystal showing growth layers and two solidified solution droplets from which the solvent was dissolved. The large droplet shows continued layer growth during cooling, the smaller one the "nucleation" of growth hillocks (Scheel and Elwell, 1973b).

to faster cooling and crystallization in that region. On the other droplet many hillocks have been nucleated and the resulting region appears to be inclusion-free in spite of the rapid growth. An increase in growth rate of bulk crystals by this mechanism would clearly be at the expense of crystal quality, as measured by the dislocation density and impurity incorporation.

A method of achieving fast growth rates which has been little explored is the use of a very thin zone of solvent over the whole crystal surface, with solute supplied from the vapour phase. The advantage of a very thin zone is that supersaturation gradients would be avoided, and the use of an "ultra-thin" alloy zone for the growth of silicon has been proposed by Hurle *et al.* (1964, 1967) and by Filby and Nielsen (1966).

In view of the severe limitation imposed by the normally slow growth rates used in solution growth, any method which could permit an increase in the maximum stable growth rate by a substantial factor is worthy of investigation. The most significant contribution to fast stable growth rates is given, assuming an optimum choice of solvent and growth technique, by an adequate temperature gradient and sufficient solution flow rates at the growing crystal faces.

6.4. Experiments on Growth Stability

Several experiments have been performed, particularly with aqueous solutions, with the aim of determining the conditions for stable growth and in order to observe the effects of instability.

The existence of a maximum rate of stable growth and its dependence on crystal size was demonstrated as long ago as 1939 by Yamamoto. He measured the critical growth rate of alkali halide crystals of various sizes growing in aqueous solution. The incidence of inclusions at the higher growth rates was found by microscopic observation to depend upon the spreading of layers across the crystal face. Under stable conditions, only one layer could be seen to be advancing across a given face at any time. Unstable conditions leading to inclusion formation could be correlated with the formation of successive layers before a previous layer had reached the edge of the crystal. Yamamoto's observations led him to propose that the maximum rate of stable growth decreases in proportion to the area of the crystal face.

The decrease in the maximum stable growth rate with crystal size was also stressed by Egli and Zerfoss (1949) and by Egli (1958), although quantitative data were not given.

Detailed studies were made by Denbigh and White (1966) of the growth stability of hexamethylenetetramine. They found no inclusions in the central 65 μm of crystals and concluded that this represents a critical size below which inclusions are not formed, irrespective of the growth conditions. The incidence of inclusions in larger crystals confirmed the validity of a critical growth rate, which has a value of about 2×10^{-5} cm s^{-1} for this material. The critical growth rate was substantially independent of the stirring rate for the small crystals grown ($\sim 10^{-2}$ cm), but inclusions were not observed when the stirring rate was very high. In the batch system used, however, the main effect of stirring was to increase the nucleation rate and hence to reduce the crystal size. A quantitative investigation was also made by Alexandru (1972) of the stability of Rochelle salt. The crystals used in this case were large, up to 600 g in weight, in contrast to the relatively small crystals studied by Yamamoto (1939) and Denbigh and White (1966). The measurements were made under conditions of fairly rapid solution flow. Alexandru found that the maximum stable growth rate varies in inverse proportion to the length of the crystal face. As with Yamamoto's observations, stability was believed to be correlated with the rate of movement of layers across the crystals and was influenced by the presence of impurities in the solution. The stability condition could also be expressed in terms of a maximum supersaturation $\sigma_{\max}$, which was related to the face length by an expression of the form

$$\sigma_{\max}=a+\frac{b}{x}. \tag{6.25a}$$

When a seed crystal of length x_o was used, a modified relation

$$\sigma_{\max}=a+\frac{b}{x-x_o} \tag{6.25b}$$

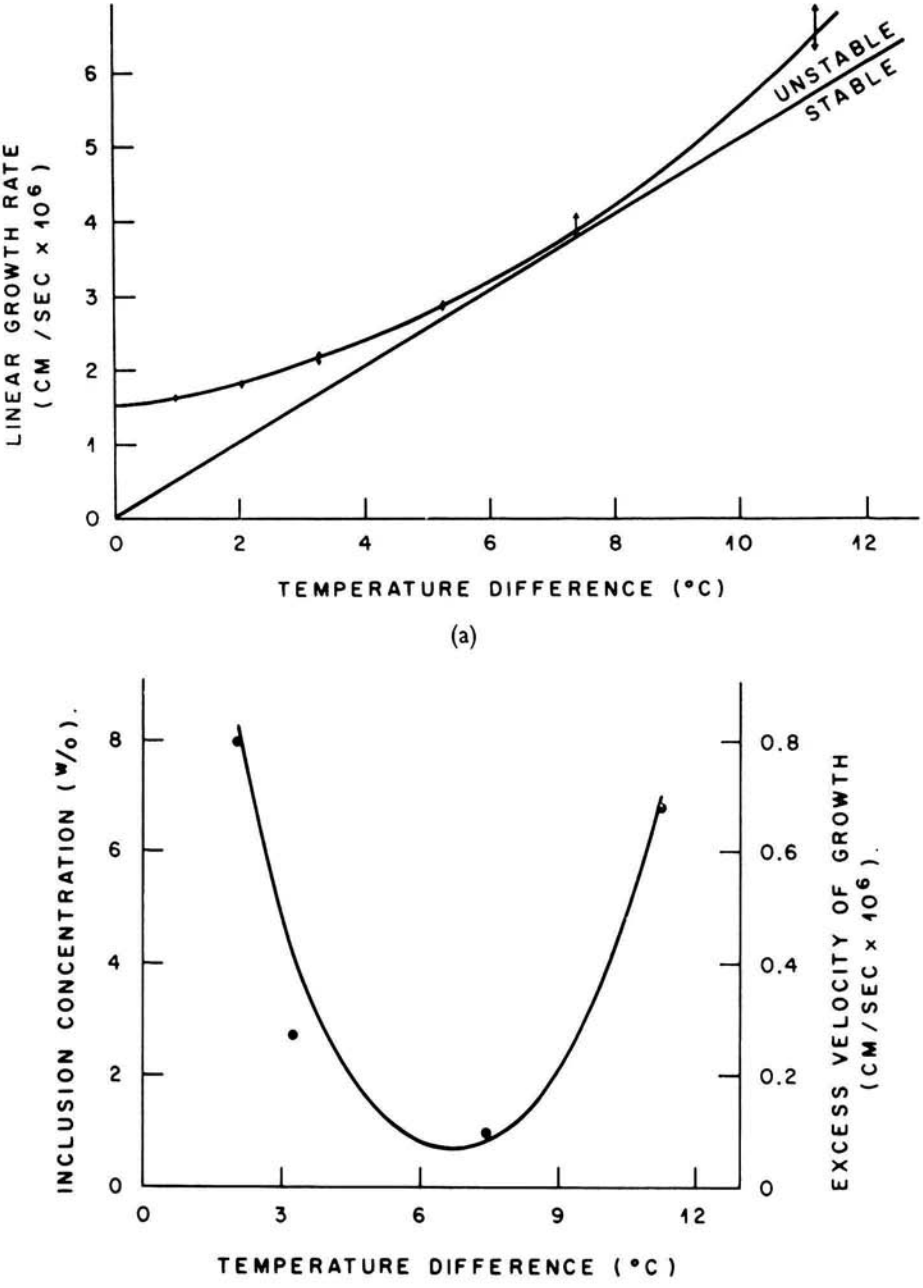
was found to fit the data. It is perhaps surprising that the maximum supersaturation for a given crystal size should depend on the previous history of the crystal, and these observations indicate the importance of the distribution of dislocations in the crystal.

Relatively few measurements have been made of maximum stable growth rates in high-temperature solution but Wentorf (1971) reached the same conclusion for the growth of diamond as did Alexandru for Rochelle salt, namely that the stable growth rate should decrease inversely as the diameter of the crystal. For a 1 mm crystal, the maximum growth rate was found to be about 0.2 mm hr^{-1}, decreasing to 0.04 mm hr^{-1} when the crystal reached its maximum size of 5 mm.

Bruton (1971) studied the stability of growth of lead tantalate, $PbTa_2O_6$, by top seeding from a $Pb_2V_2O_7$ flux under conditions which were believed to be turbulent. According to Carlson's criterion [Eqn(6.24)] the maximum size of crystal for stable growth was calculated to be 1.2 cm. In practice inclusion-free crystals rarely grew larger than $4\times2\times1$ mm, and larger crystals usually contained many inclusions.

Dawson *et al.* (1974) measured the growth rate and inclusion concentration of $NaNbO_3$ grown on a rotating seed in $NaBO_2$ as a function of the temperature difference across the melt. The results are shown in Fig. 6.11. The growth rate varies approximately as ΔT^2 and extrapolates to rather a large value at $\Delta T=0$ because of solvent evaporation. Also shown in Fig. 6.11(a) is the line which is believed to denote the boundary between stable and unstable growth. The justification for this particular choice of stability condition is that the variation with ΔT of the inclusion concentration is very similar to a plot of the difference between the actual growth rate and the value given by this boundary line, as may be seen from Fig. 6.11(b).

The stability condition represented by the boundary in Fig. 6.11(a) is in good agreement with the supersaturation-gradient concept, if it is assumed that the temperature gradient at the crystal surface varies directly as ΔT. From Eqn (6.6), $(v/\Delta T)>(D\phi n_e/\rho RT^2\Delta z)$ for instability, where Δz is the length over which the temperature drop occurs. If Δz is taken to be the depth of the melt (2.3 cm) with $D=4\times10^{-5}\ \mathrm{cm^2\,s^{-1}}$, $\phi=59$ kJ mole^{-1}, $\rho=4.44\ \mathrm{g\,cm^{-3}}$, $n_e=1.77\ \mathrm{g\,cm^{-3}}$, $T=1378$ K (all measured experimental values), the value predicted for $v/\Delta T$ is $12\times10^{-9}\ \mathrm{cm\,s^{-1}\,K^{-1}}$.



(a)

(b)

FIG. 6.11. (a) Growth rate of $NaNbO_3$ on a rotating seed in $NaBO_2$ solution, with estimated limit of stable growth. (b) Solvent inclusions concentration and excess growth rate above estimated limit for $NaNbO_3$ (Dawson *et al.*, 1974).

This is much lower than the experimental value of 5.3×10^{-7} cm s^{-1} K^{-1}. However, if the temperature is assumed, due to stirring in the bulk solution, to be dropped over a thermal boundary layer of width $\delta(\mathrm{Sc}/\mathrm{Pr})^{1/2}$, where Sc is the Schmidt number and Pr the Prandtl number, a value in the region of 5×10^{-7} cm s^{-1} K^{-1} for $v/\Delta T$ is predicted by the supersaturation-gradient model. Unfortunately a direct measurement of the temperature gradient at the interface was not possible, but these results strongly support the validity of the supersaturation-gradient approach.

6.5. Results of Unstable Growth

Since stable growth has been defined in the present context as growth without solvent inclusions, it is clear that instability will result in inclusions. What is interesting is to consider the extent to which the quantative and qualitative models discussed above can account for the observed features which result from the onset of instability.

The development of a periodic disturbance has already been discussed in Section 6.1.2 and examples of theoretical treatments which predict this periodicity have been mentioned. Another observation of a crystal with periodic inclusions is illustrated in Fig. 6.12, which shows a section parallel to the growth direction of a $NaNbO_3$ crystal grown by top seeding (Dawson *et al.*, 1974). As in Fig. 6.6, the instability has occurred at the termination

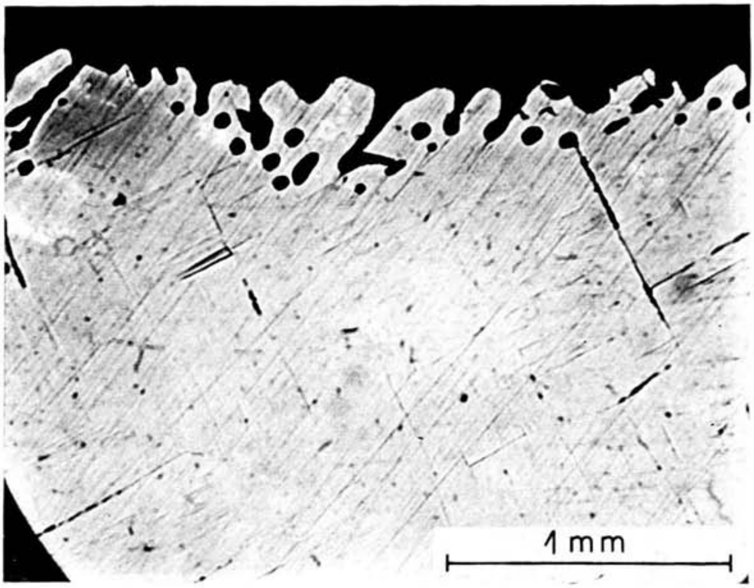


FIG. 6.12. Section through $NaNbO_3$ showing periodic inclusion structure (Dawson *et al.*, 1974).

of growth, possibly following removal from the solution. The period in this case is about 80 μm.

A cellular interface similar in appearance to that observed on melt-grown crystals under unstable conditions was reported by Hurle *et al.* (1962) on crystals of InSb grown from solution in a supersaturation gradient and recently by Schieber and Eidelberg (1973) on crystals of $BaFe_{12}O_{19}$. The cells in the latter case were believed to be due to platinum segregation.

Another example of a crystal with periodic inclusions, in this case $DyVO_4$ grown by slow cooling by Garton and Wanklyn (1969), is shown in Fig. 6.13. It is by no means certain that the periodicity in this case is due to excitation of the longer face since the periodicity may well be *in* the growth direction. Landau (1958) has predicted that, under constitutionally supercooled conditions, the growth rate may vary periodically, resulting in a periodic distribution of impurities. The periodicity is caused by the lowering of the degree of constitutional supercooling by an interval of unstable growth with inclusion formation, so that an interval of stable growth follows during which the instability builds up to some critical value and the cycle is re-initiated. This model could account for some of the striations and bands of inclusions which are observed in HTS-grown crystals (see Chapter 9) but has not found wide acceptance.

Particularly under diffusion-limited conditions, the higher supersatura-

FIG. 6.13. $DyVO_4$ crystal with periodic inclusions (Garton and Wanklyn, 1969).

tion at the corners and edges of a crystal will lead to an onset of more rapid growth in these regions as the degree of constitutional supersaturation is increased. A progressive increase in the supersaturation gradient leads first to the formation of raised edges, then to the development of terraces or "hopper" crystals and finally to dendrite formation with projections in the directions of rapid growth. This sequence is illustrated in Fig. 6.14 which is taken from the paper of Fredriksson (1971), who discusses the morphology of metal crystals as a function of the growth conditions.

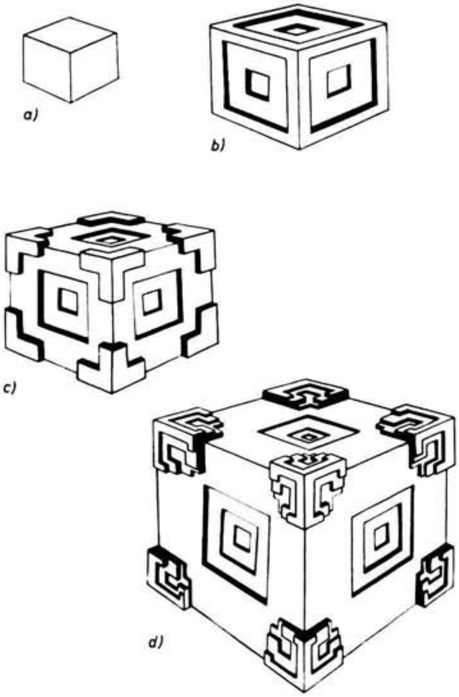


FIG. 6.14. (a)—(d) Progressive changes in shape of an ideally cubic crystal with increasing degree of supersaturation gradient (Fredriksson, 1971).

If growth occurs by a mechanism of layer spreading from corners and edges, it is very probable that the inclusions will be formed at the face centres of the crystal where the supersaturation is low. This has been confirmed by several observations by the authors, by the work of Carlson (1958) on aqueous solution growth and, for example, by Lefever and Chase (1962) on yttrium iron garnet. A more detailed description of the types of inclusion found in crystals grown from HTS will be given in

Chapter 9. Many examples of the transition from the normal habit form to skeletal and similar crystal shapes are quoted in the review by Chernov (1972).

6.6. Experimental Conditions for Stable Growth

6.6.1. Optimum programming for stable growth

The essential criterion for stable growth is that the growth rate should always lie below the maximum stable value, with a "safety margin" to allow for temperature fluctuations due to imperfect regulation or to convection overstability in the solution.

Scheel and Elwell (1972) and Pohl and Scheel (1975) presented a temperature programme for the growth of crystals by slow cooling, with the stable growth rate estimated according to Carlson's criterion which was discussed in Section 6.5. Rearrangement of Eqn (6.24) gives the maximum stable growth rate $v_{\max} = \mathrm{d}l/2\mathrm{d}t$ for a crystal of side l as

$$v_{\max} = Bn_e/\sqrt{l} \tag{6.26}$$

with

$$B = (0.214\, Du\sigma^2\, \mathrm{Sc}^{1/3}\rho^2)^{1/2}. \tag{6.27}$$

Here n_e is the solubility at temperature T, and σ is the relative supersaturation $(n_{sn} - n_e)/n_e$ which is assumed to remain constant throughout the crystallization process. The crystal volume is

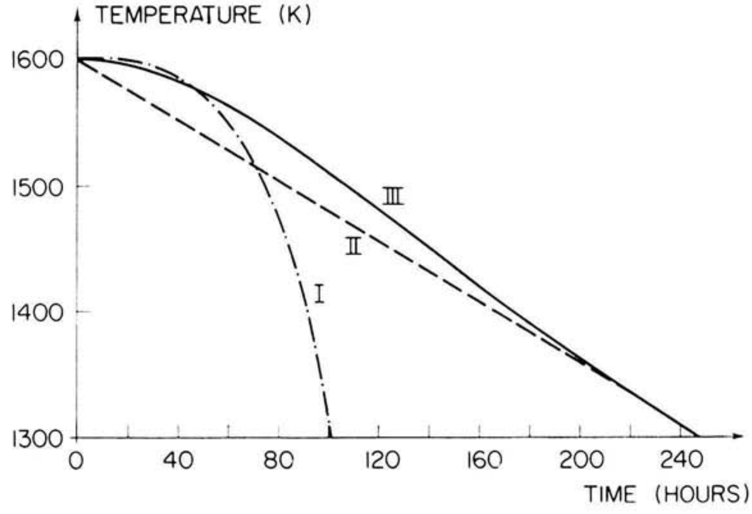
$$l^3 = (n_0 - n_e)V/\rho, \tag{6.28}$$

where n_0 is the initial solubility at time $t = 0$ and V the volume of the solution. Combination of (6.26) and (6.27) yields after integration

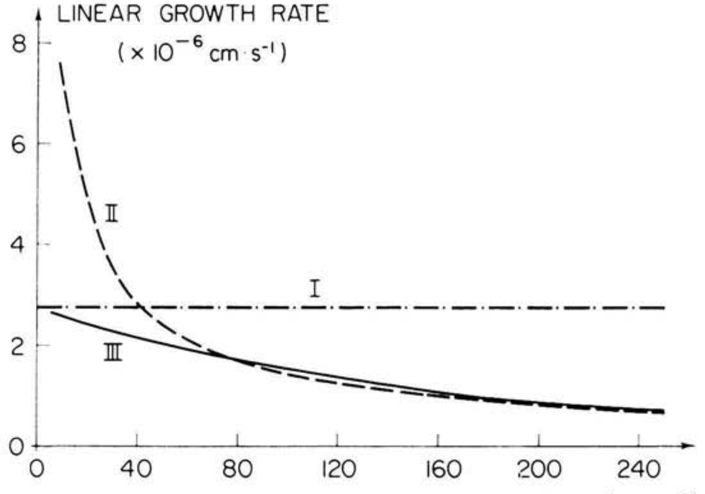
$$n_e(T) = n_0 \cosh^2[B(n_0\rho/V)^{1/2}t]. \tag{6.29}$$

This equation defines the temperature T as a function of the time t if the solubility curve is known and the supersaturation is given a value below some critical limit.

An example of a cooling programme based on Eqn (6.29) is shown as curve III in Fig. 6.15(a). The parameters assumed are: solution volume $V = 80$ cm^3, $\rho = \rho_{sn} = 5$ g cm^{-3}, $n = 15\%$ at 1600 K and 5% at 1300 K, $D = 10^{-5}$ cm^2 s^{-1}, $\sigma = 10^{-2}$, Sc $= 420$ and $u = 10$ cm s^{-1}. It may be seen that the deviation of the calculated programme from a constant cooling rate [II of Fig. 6.15(a)] is relatively slight except at the early stage where the crystal is very small. The corresponding growth rates are shown in Fig. 6.15(b)



(a)



(b)

FIG. 6.15. (a) Temperature programmes for HTS growth by slow cooling. I constant linear growth rate; II constant cooling rate; III for maximum stable growth rate according to Eqn (6.29). (b) Linear growth rate for programmes I—III (Scheel and Elwell, 1972).

from which it is clear that the initial growth rate in case II is much higher than the limiting value, which explains the frequent observation of a dendritic core in large crystals grown by spontaneous nucleation.

Curve I of Fig. 6.15(a) is based on the assumption of a constant linear growth rate, in which case the temperature change from the initial value will vary as t^3. Several proposals for temperature programmes (Neuhaus and Liebertz, 1962; Koldobskaya and Gavrilova, 1962; Sasaki and Matsuo, 1963; Bibr and Kvapil, 1964; Kvapil, 1966; Cobb and Wallis, 1967; Kvapil *et al.*, 1969; Fletcher and Small, 1972; Wood and White, 1972) have been based on the use of a constant linear growth rate, but it is clear from Fig. 6.15(b) that the growth rate may exceed the maximum stable value during the later stages of growth unless the constant value is initially well below the stable limit.

Figure 6.16 shows the effect of viscosity, solution flow rate and crucible size on the temperature programme calculated using Eqn (6.29) with otherwise the same parameters as in the previous example. A total duration of 10^3 hours (about 6 weeks) is considered acceptable but twice this value would probably be prohibitive. A rapid solution flow rate can be seen to be essential if one large crystal is to be grown. Large crucibles are unlikely to result in one crystal per run but stable growth is possible if multinucleation is taken into account. The effect of flux viscosity is seen to be relatively

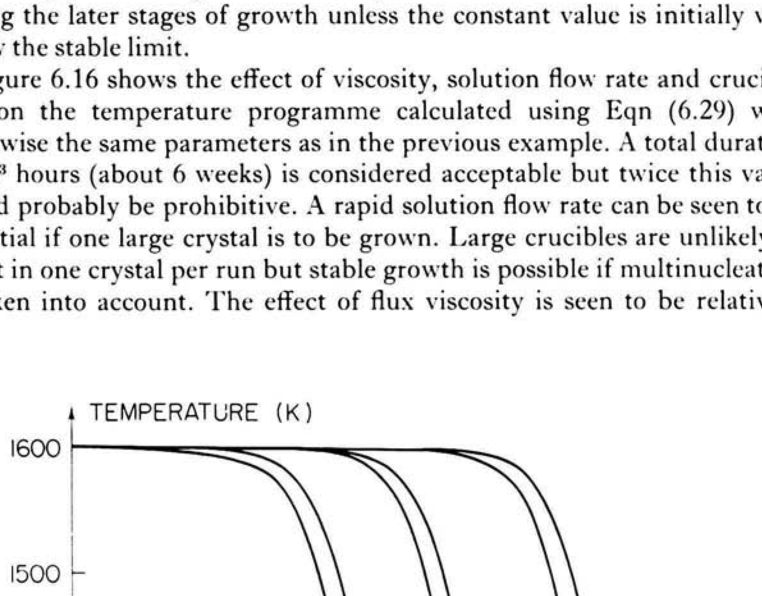


FIG. 6.16. Temperature programmes according to Eqn (6.29) for various values of solution flow rate u, viscosity η and solution volume V (Scheel and Elwell, 1972).

minor, but it is unlikely that high values of solution flow rate will be possible in viscous solvents.

The slowest cooling rates must be used in the early stage following nucleation and a considerable saving in time without the onset of unstable growth can be achieved by the use of seed crystals. The initial cooling rate with a seed crystal will be chosen to correspond to the maximum stable growth rate for the particular size of seed chosen.

The programme specified by Eqn (6.29) was calculated on the basis that the growth rate should at all times have its maximum stable value. In practice it is desirable to use a growth rate which is less than the maximum value by a sufficient margin to allow for minor temperature fluctuations within the solution. The best temperature regulation which can be obtained with commercial controllers is about ± 0.1°C and, in the example considered above, a sudden drop of 0.1°C would result in the deposition of about 13 mg of solute. If this drop were to occur in 10 s on a crystal of area 1 cm^2, the resulting growth rate would be 3×10^{-4} cm s^{-1}, which is two orders higher than the maximum stable value! In practice the supersaturation is created throughout the melt and the effect of the temperature drop is much less drastic, but sudden temperature drops of 2°C may occur when cooling is effected by a motor-driven helipot or similar mechanical means. This shows that excellent temperature control and programming are necessary when large inclusion-free crystals are to be grown.

Curve I of Fig. 6.17 shows the cooling rate according to the programme of Fig. 6.15 (curve III) and a less idealized practical procedure is indicated by the dotted line II. The actual values of the cooling rate proposed in this example are: 0.2°C hr^{-1} for the first 48 hr, 0.5°C hr^{-1} for the next 24 hr and 1.2°C hr^{-1} for the remainder of the growth period, about 220 hr. Those values are chosen to give a reasonable safety margin, except for the initial value which is selected on the basis that it is pointless to use a cooling rate which is not at least comparable with the random fluctuations (Laudise, 1963). The increase in time required by the proposed procedure is about 75 hr or 25%.

Also shown in Fig. 6.17 as curve III is the cooling rate required by the programme of Eqn (6.29) for the same conditions as for curve I but with $u = 0.1$ cm s^{-1}, a value typical of stirring by natural convection. The maximum stable value in this case is only 0.175°C hr^{-1} and the total time required by the programme is about 100 days. Since such a period would be unacceptable to most crystal growers we propose the use of a constant cooling rate of 0.2 or 0.3°C hr^{-1} for experiments using unstirred melts. Such a cooling rate will probably result in more than one crystal but should yield only a few crystals with substantial inclusion-free regions.

Temperature programming for the growth of crystals in industrial crystallizers has been discussed by Mullin and Nyvlt (1971), and Wood and White (1968) advocated the use of programming in crystal growth by flux evaporation in order to achieve a constant linear growth rate. However, the linear growth rate has to decrease according to Scheel and Elwell (1972), and the flux evaporation rate should be programmed according to the maximum stable growth rate. In certain cases a constant linear growth rate might be necessary, for instance for homogeneous doping. Constant growth conditions necessitate, according to the Burton-Prim-Slichter equation for the effective distribution coefficient, a nonvarying boundary-layer thickness and therefore a nonvarying area of the growing crystal face. These conditions are only fulfilled in liquid phase epitaxy and in such cases where the application of large seed plates is possible and crystal growth occurs mainly in the direction normal to the seed plate by proper choice of the seed orientation. In any case a value of a constant linear growth rate has to be chosen which is equal to or lower than the maximum stable growth rate for the final crystal size. From this discussion it follows that it is difficult to obtain the quasi-steady-state conditions necessary for the growth of large crystals of homogeneous dopant concentration or of homogeneous solid solutions, and the experimental conditions required are discussed in the next chapter.

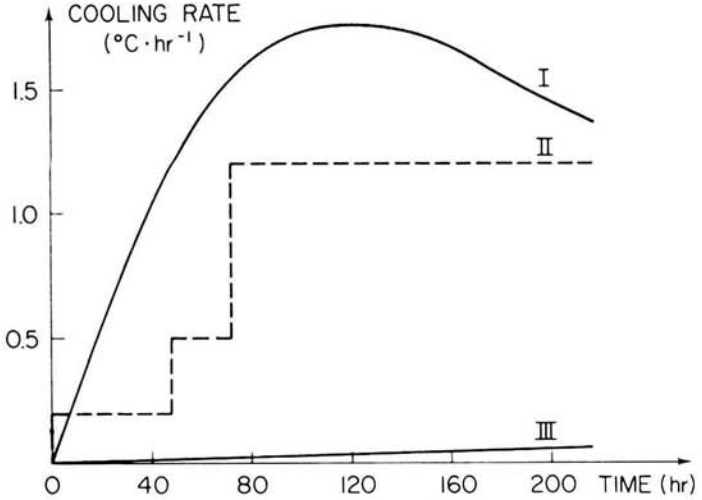


FIG. 6.17. Cooling rates for stable growth. I as for programme III of Fig. 6.16(a); II suggested practical procedure; III for an unstirred solution (Scheel and Elwell, 1972).

6.6.2. Stirring in flux growth

The desirability of stirring for the achievement of stable growth at relatively rapid rates has been mentioned in the discussion of the examples in Section 6.4, and stirring techniques are discussed in the next chapter. In the great majority of experiments, some stirring action is achieved by natural convection. The role of natural convection in crystal growth has been reviewed by Cobb and Wallis (1967), Parker (1970), Wilcox (1971), and Schulz-Dubois (1972).

The onset of convection is normally specified (Chandrasekhar, 1961) by the value of the dimensionless Rayleigh number

$$R=\frac{g\alpha L^3\Delta T}{K\nu} \tag{6.30a}$$

where α is the volume expansion coefficient, L the depth, K the thermal diffusivity and ν the kinematic viscosity of the liquid, with ΔT the temperature difference across it. Some critical value of R, depending on an idealized geometry, must be exceeded for convection while higher values of R may lead to temperature oscillations, or to turbulence at even higher values. However, in real crystal-growth systems some convection will occur below the critical R values due to some inevitable asymmetric or reverse temperature gradients due to buoyancy.

In solutions it is also necessary to consider thermosolutal convection due to density differences between the solute and solvent. The onset of solutal convection may be specified by defining a solutal Rayleigh number R_s as

$$R_s=\frac{g\beta L^3\Delta n}{K_s\nu} \tag{6.30b}$$

where β is the rate of change of density with concentration, Δn the solute concentration difference across the liquid and K_s the diffusivity of the solute. Since K_s is normally lower than the thermal diffusivity K by some orders of magnitude, convection is highly probable in solutions even if the temperature gradient is in the "wrong" direction. Oscillations are particularly likely in solution due, for example, to "overstability" which can occur when a destabilizing temperature gradient is opposed by a solute gradient (Jakeman and Hurle, 1972).

Even for pure melts, it is difficult to obtain a reliable expression for the rate of convective flow of the liquid. Cobb and Wallis (1967) derived a simple expression for the flow rate of a liquid, unbounded in the horizontal direction, between horizontal plates differing in temperature by ΔT. The average flow rate u was estimated as

$$u = \frac{K}{\rho_{sn} L C_P} \left[0.208(R)^{1/4} - 1\right] \tag{6.31}$$

where C_P is the specific heat of the liquid and R the Rayleigh number. Figure 6.18(a) shows the value of u as a function of the liquid depth L for various values of the convection parameter $a = R/L^3$ and for a fixed value of $\Delta T = 10$°C. Except for very low values of L, where u increases very rapidly, the solution flow rate is seen to remain between roughly 0.01 and 0.04 cm s^{-1}. Figure 6.18(b) shows the convection flow rate versus temperature difference ΔT for a typical value of $a = 1500$. The latter is limited in a crystal-growth experiment because of nucleation at high values of ΔT, and therefore this possibility of increasing u is also limited. Maximum rates of thermal convection flow in high-temperature ionic solutions will be of the order of 0.1 cm s^{-1} and in metallic solutions one order of magnitude faster.

From the examples illustrated in Fig. 6.16, it is clear that such values of the flow rate are too low for stable growth of a few large crystals per crucible, and so forced convection by stirring is desirable where possible. Stirring may be achieved by rotating a seed crystal as in the *top-seeded solution-growth* (TSSG) technique and the resulting flow patterns have been studied by Robertson (1966) and Carruthers and Nassau (1968) using an aqueous analogue. Stirring may be enhanced by occasional reversal of the seed rotation (Miller, 1958; Senhouse *et al.*, 1966) or of the crucible rotation direction (Nassau, 1964; Bonner *et al.*, 1965; Schroeder and Linares, 1966). This TSSG technique is restricted to solvents of low volatility and is therefore not applicable to PbO/PbF_2 and many other widely used solvents.

The problem of stirring a corrosive liquid at high temperatures is by no means simple. Serious problems are associated with sealing the crucible and stirring the solution in a sealed crucible at high temperatures or with the corrosive solvent vapours. The only really effective method proposed to date is the *accelerated crucible rotation technique* (Scheel and Schulz-DuBois, 1971; Scheel, 1972) in which the rate (and frequently also the sense) of crucible rotation is varied continuously (but not abruptly as in the crucible reversal mentioned above) and the inertia of the liquid used to promote mixing. Experience from aqueous solution growth indicates that flow rates of 10–50 cm s^{-1} are desirable and the practical realization of such conditions will be discussed in the next chapter.

An alternative approach to the problem of non-uniform solute flow has been proposed by Tiller (1968) and is illustrated in Fig. 6.19. He suggested the use of a convection-free cell with a seed crystal located inside a platinum tube inserted into a well-mixed solution. Convection is prevented by

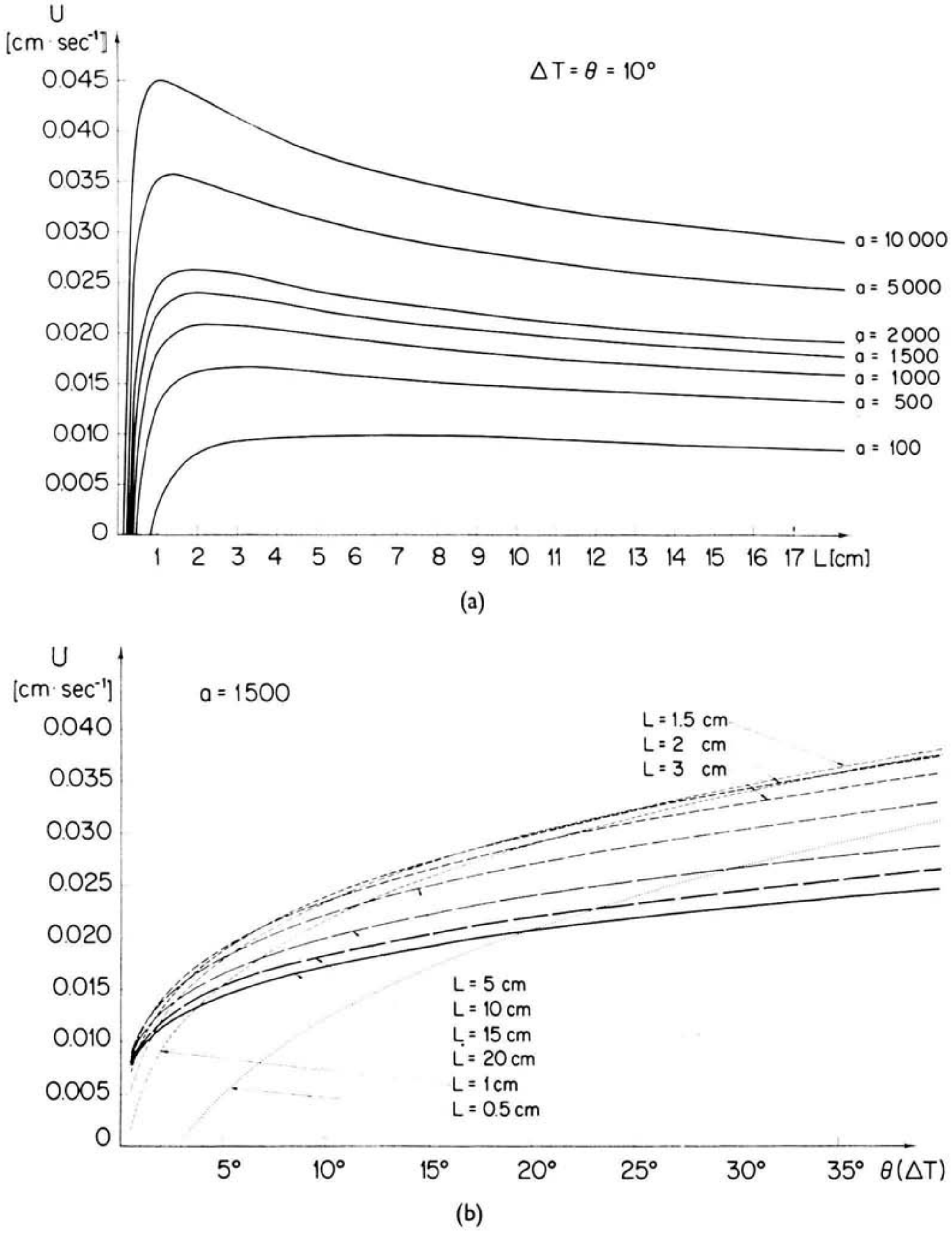


FIG. 6.18 (a) Solution flow rate by natural convection for various convection parameters a ($= R/L^3$) and temperature difference of 10°C versus liquid layer height L. (b) Solution flow rate by natural convection versus temperature difference ΔT for various liquid layer heights and a constant convection parameter $a = 1500$. (Scheel and Elwell, 1973a.)

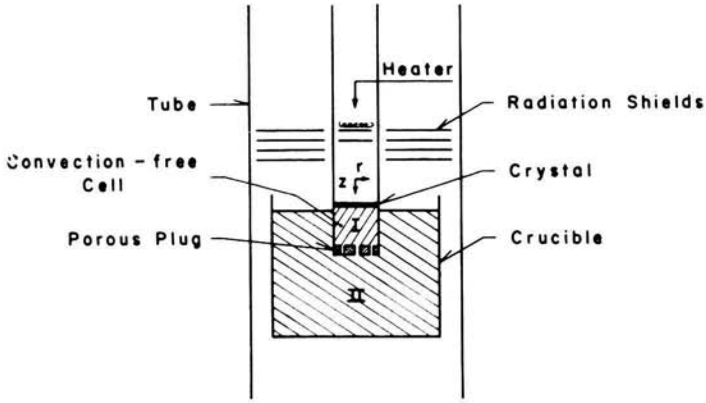


FIG. 6.19. Convection-free cell (I) in a stirred solution (II) (Tiller, 1968).

baffles across the end of the tube and a uniform flow of solute to the seed by diffusion may be realized. This method does not yet appear to have been tested in practice on Earth but could give stable growth if technical problems and problems associated with heat conduction through the platinum tube (and nucleation on the tube) could be solved. The growth rate would, however, be appreciably lower than in a stirred solution. Interesting results on convection-free growth may be expected from the Skylab experiments where convection does not occur due to the near zero gravity in space.

6.6.3. Temperature control and distribution

The importance has been stressed of using the best possible controller to regulate the temperature of the furnace. Commercial controllers using saturable core reactors or thyristors can give regulation to ±0.1°C and their ready availability has greatly contributed to a continuing improvement in crystal size and quality. However a high degree of control is pointless if temperature oscillations due to convection overstability are present in an unstirred solution. Smith and Elwell (1968) measured oscillations of amplitude 0.5°C in a solution of $NiFe_2O_4$ in $BaO.0.62B_2O_3$ at 1200°C with a melt depth of about 3 cm. The amplitude of these oscillations was reduced to some extent by rotating the crucible (see Section 9.2.4).

By effective stirring such temperature oscillations could be prevented so that exact temperature regulation becomes meaningful. It is technically difficult to measure small temperature fluctuations in stirred high-temperature solutions but estimates of Schulz-DuBois (1972) and Scheel (1972) indicate a high degree of temperature homogenization, for instance by the accelerated crucible rotation technique, and this applies also to other stirring techniques which dominate the hydrodynamics in the high-temperature solutions.

From the discussion of the supersaturation-gradient criterion it is evident that the temperature gradient at the crystal surface is of major importance in determining the crystal quality. In theory a very large temperature gradient is desirable so that stable growth will be possible at high growth rates but in practice a compromise is always used because of an adverse effect on the crystal quality. A large gradient will result in a high degree of strain and so more dislocations will be produced in the crystal. In top-seeded growth where the temperature gradient at the crystal can be varied by changing the depth of the crystallizing interface below the liquid level and by altering the degree of coolant flow through the seed holder, a high cooling rate is often found to result in nucleation at the edges of the crystal and it is important to ensure that the radial temperature gradient across the surface of the solution is not too great.

Similar considerations apply to growth by spontaneous nucleation where localized cooling is used. Measurements of the optimum temperature distribution for the growth of garnet crystals at the base of a crucible have been reported by Tolksdorf and Welz (1972).

6.6.4. Mechanical disturbances

The concept of a metastable region of supersaturation gradient suggests that instability will be favoured if the growing crystal is subjected to mechanical shock, which will tend to nucleate any instability. This view is supported by the experience of the authors with both growth by spontaneous nucleation and by top seeding. In the former case the size of inclusion-free regions was found to be increased by a factor greater than two when the furnaces were mounted on antivibration supports inside closed metal cabinets. In top-seeded growth, a gradual deterioration in crystal quality and an increase in the nucleation of secondary crystals on the edge of a seed have been noted as the seed rotation mechanism became worn.

The practical aspects mentioned above will be discussed more fully in the next chapter.

6.7. Summary

Theoretical treatments of the growth of spherical and cylindrical crystals indicate that these will be stable only up to a critical radius, which will be increased by interface kinetics and surface diffusion.

In the case of a plane crystal surface growing in solution, unstable growth may result if there exists a supersaturation gradient ahead of the interface. A solute gradient associated with the volume-diffusion process will inevitably be present and a supersaturation gradient may be avoided only by the application of a sufficiently large temperature gradient. The experimental observation of inclusion-free growth in very small or negative temperature gradients may be explained by the assumption of a metastable region of supersaturation gradient. Stabilization is believed to result primarily from the kinetic mechanisms on the low-energy habit faces normally exhibited by solution-grown crystals.

An important factor when polyhedral crystals are considered is the difference in supersaturation between the edges and centre of any face. This supersaturation inhomogeneity may be offset by a higher kinetic coefficient at the face centres due to curvature of the vicinal face or to a higher concentration of active growth centres. Stirring the solution is desirable in order to minimize the supersaturation inhomogeneity. Even in well-stirred solutions with a large stabilizing temperature gradient, it is likely that there will exist for any material an ultimate rate of stable growth.

For the experimental attainment of stable growth, precise temperature regulation is required and mechanical shocks should be prevented. The maximum growth rate may be increased by the application of a sufficiently large temperature gradient and by stirring the solution.

A considerable body of evidence has been presented to demonstrate that the maximum stable growth rate decreases with increase in crystal size. Temperature programmes for crystal growth by slow cooling have been presented which are based on the requirement that the growth rate should never exceed its maximum stable value.

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lowed by several others but serve to illustrate a need for intensive development so that this important technology of LPE can achieve its true potential. This requires the education of crystal/epitaxy technologists (Scheel 2003&2004).

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