Morphological instability of steps during crystal growth from solution flow∗

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(12-06-95)

Abstract

It is shown that step moving to meet solution flow can be unstable against lateral perturbations. The instability of long-wavelength perturbations occurs at values of the solution flow intensity less than some critical value depending on the step velocity. At given intensity of the solution flow, the instability comes at the step velocity exceeding a critical velocity. Decay of short-wavelength fluctuations is conditioned by the line tension of the step. The step moving along the solution flow is laterally stable at all values of the step velocity and the intensity of the solution flow. The overlapping diffusion field of the neighbour steps suppresses the lateral instability but it gives an instability of the step train against doubling of the period, i.e. neighbouring steps are attracted. The equidistant train moving to meet the solution flow is stable against the period variations.

∗will be appeared in Journal of Crystal Growth
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I. INTRODUCTION

The appearance of numerous investigations of step dynamics on the surface of growing crystals both experimental and theoretical is evidently stimulated by two factors. Firstly, development of technologies to obtain high quality crystal structures requires deep understanding of elemental surface processes during the crystal growth. The control of the step dynamics plays a key role to provide the stable laminar growth, that gives high quality crystals. The experimental results had been mainly obtained by ex situ observations and by in situ very sensitive optical phase contrast or differential interference contrast microscopy. For the growth from solutions, observations of “live” mono-molecular steps on growing crystal were performed with the novel in situ optical technique [1]. Secondly, the advent of scanning tunneling and atomic force microscopy has open the door to investigate atomic scale structure of the crystal surfaces. In this measurements, the nanometer-scale precision can be achieved not only in the perpendicular to the surface direction as for the optical observations, but also along the surface. The direct observation during crystal growth from solution has been realized [2].

Most studies have been devoted to the growth from vapour phases. Barton, Cabrera and Frank (BCF) in their seminal paper [3] who considered a step flow model, outlined this case. A vicinal surface consists of broad terraces separated by monoatomic steps. The transfer of the crystallizing matter includes adsorption upon the solid, diffusing across the terraces during some lifetime and further desorption back into the vapour phase or attachment to a step. BCF considered the steps as a perfect sink, when the attachment kinetics was neglected and the surface concentration of the substance had a local equilibrium value, taking into account the curvature correction via the Gibbs-Thomson effect. Taking into account of the kinetics of the adatoms attachment introduces, in general, two kinetic coefficients corresponding to adatom attachment from the lower and upper terraces [4,5].

\[\text{One dimensional diffusion along the step is also possible while the adatoms build into the solid}\]
A linear stability analysis within quasi-static approximation \[6\] predicted that the step can undergo a morphological instability at a step velocity of more than a critical value, only if the attachment rate from lower terrace exceeds the upper one. The instability mechanism is an analog of the Mullins-Sekerka instability \[7\]. More general studies of the stability both the lateral and the longitudinal has been recently performed \[8–10\] without using a quasi-static approximation. It was shown that the lateral instability can still take place for symmetric step kinetics because of an asymmetry in forward and backward direction of the step since it is in motion.

The papers cited above are devoted to the linear stability analysis against small fluctuations. Scenario of further evolution of the step pattern was studied in Ref. \[11\]. This is evidence of presence of the spatiotemporal chaos in the step dynamics of the BCF model at the asymmetrical attachment kinetics. A competition between the thermal noise and the determinism was addressed in Ref. \[12\].

Step bunching can be induced by an electromigration force during sublimation of vicinal surfaces, when the heating source is an electric current \[13–15\]. Adatoms on the surface are assumed to carry electric charges and therefore their Brownian motion is modified by the electric field. The diffusion equation for adatom concentration \(c\) contains the term proportional \(F \nabla c\), where \(F\) is the electric force. The presence of the step bunching depends both on the temperature and on the direction of the heating current. In particular, reversing the current direction transforms a stable temperature region into an unstable one and vice versa.

In contrast with the growth from gas phase, there are no convicting evidences on the mechanism of the substance transfer during growth from solutions. At the solution growth, the solute concentration is closer than the vapour density to the crystal density and the solution diffusivity is scarcely less than the surface diffusivity. Therefore, the volume diffusion in the solution with a direct incorporation into the step can be basic process transferring the crystallizing units \[16\]. On the other hand, the direct incorporation can be suppressed by an interaction of the units with the solution and there is a possibility of the competition
between the volume diffusion and the surface diffusion. In Ref. [17], in situ observation of the dynamics of monomolecular growth step on the (10\text{I}4) cleavage surface of calcite was presented and it was concluded that the surface diffusion does not control the calcite growth. However, the kinetic coefficient of these steps is very small $\sim 2 \times 10^{-7}$ cm/c, and the step motion is not controlled by any diffusion. The only attachment kinetics determines the step velocity. At the same time, there are reasons for the surface diffusion at growth of the KDP crystals [18,19]. We believe that investigations of step dynamics peculiarities at the volume diffusion can throw a light on this question.

A formation of step bunches or a longitudinal instability forced by the influence of solution flow within the diffusion boundary layer was observed in Ref. [20] and has been considered theoretically in Ref. [21]. The stepped vicinal was described as a continuous surface with kinematic waves of the step density. It was found that the step bunching depends on the angle of the riser and way of the heat transfer in the case of the melt growth. It can be developed only at the parallel motion of the straight steps and the solution. In Ref. [22], the kinetics of the rectilinear macrosteps under diffusion or thermal interactions in stagnant media has been studied when the velocities of the steps are controlled by the supersaturation at the feet of the steps. The stability of the macrostep train depends on the angle of the step risers and way of the heat transfer in the case of the melt growth.

The present study addresses the zig-zag instability of steps and the instability of the step train against doubling of the period during the crystal growth in the solution flow.

II. GREEN’S FUNCTION FOR CONVECTIVE DIFFUSION

Let us consider the diffusion nearby the vicinal crystal face being in a steady solution flow. We suppose that the height of the step shown in Fig. 1 is small in compare with the thickness of the diffusion layer and the characteristic curvature radius of the step, so the steps can be considered as a linear sinks for the diffusion field on the flat crystal surface. At large values of the Prandtl number $Pr = \nu/D \gg 1$, where $\nu$ is the kinematic viscosity and
$D$ stands for diffusivity, the thickness of the diffusion layer is much less than the thickness of the hydrodynamic boundary layer. The solution velocity can be developed in a series in perpendicular to the surface direction $y$. The solution velocity at the crystal surface vanishes and the velocity component parallel to the surface in the first order is

$$v_z = B(z)y. \quad (1)$$

The perpendicular component $v_y$, being determined by equation of continuity

$$\frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0, \quad (2)$$

has the form

$$v_y = -\frac{y^2}{2} \frac{dB}{dz}. \quad (3)$$

The component $v_y$ is in inverse proportion to a characteristic length of variation of the solution flow along the surface $L_{flow}$, i.e. in fact the size of the crystal face. Since the diffusion fields, varying in sufficient less scales, are of our interest, so the terms with $v_y$ can be omitted in diffusion equation and the parameter of the solution intensity $B$ can be taken independent on $z$ within the given part of the crystal surface. Then the diffusion equation for the solute concentration $C$ takes the form

$$\frac{\partial C}{\partial t} + By \frac{\partial C}{\partial z} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) - j(x, z)\delta(y), \quad (4)$$

where $j(x, z)$ is the substance flux crystallized in this point of the surface. Let the solution velocity $v_z > 0$ and so $B > 0$, whereas the step velocity can be both positive and negative. After the Fourier transformation from $t, x$ and $z$ to $\omega, p_x$ and $p_z$ we obtain the equation and the boundary condition

$$\frac{d^2 C}{d\xi^2} - (\xi_0 + \xi)C = 0; \quad \left. \frac{dC}{d\xi} \right|_{\xi=0} = (BD^2 ip_z)^{-1/3}j, \quad (5)$$

where $\xi = (ip_z \Lambda^{-2})^{1/3}y$ and $\xi_0 = (ip_z \Lambda^{-2})^{-2/3}(i\omega/D + p_x^2 + p_z^2)$, $\Lambda^2 = D/B$. The solution of Eq. (5) is expressed through the Airy function vanished at $y \rightarrow \infty$:
\[ C = j(BD^2ip_z)^{-1/3}\text{Ai}(\xi + \zeta_0)/\text{Ai}'(\xi_0). \] (6)

Here at \( p_z > 0 \), in order to satisfy the boundary condition at infinity we have to suppose \( ip_z = p_z \exp(i\pi/2) \) and at \( p_z < 0 \): \( ip_z = |p_z| \exp(-i\pi/2) \). Taking these conditions into account, we obtain the Green’s function of Eq. (4) in the form

\[
G(x, y, z, t) = \frac{2}{(2\pi)^3} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dp_x \int_0^\infty dp_z \, e^{i\omega t + ip_x x} \Re \left\{ \frac{\text{Ai}'[(ip_z\Lambda^{-2})^{1/3} y + (ip_z\Lambda^{-2})^{-2/3}(i\omega D^{-1} + p_x^2 + p_z^2)]}{\text{Ai}[(ip_z\Lambda^{-2})^{1/3} y + (ip_z\Lambda^{-2})^{-2/3}(i\omega D^{-1} + p_x^2 + p_z^2)]} \right\} \times \frac{1}{\text{Ai}'[(ip_z\Lambda^{-2})^{1/3} y + (ip_z\Lambda^{-2})^{-2/3}(p_x^2 + VD^{-1}ip_z)]}.
\] (7)

Consider the diffusion field formed by the rectilinear steps moving as \( z = \sqrt{y^2 + z^2}; \quad \zeta = z - Vt \). The main contribution in the integral (8) goes from the large values of \( s = \Lambda p_z \), when the ratio of the Airy function to its derivative tends as

\[
F(s) = \frac{\text{Ai}[(is)^{1/3} y/\Lambda + (is)^{-2/3}(s^2 - \Lambda^2VD^{-1}is)]}{\text{Ai}'[(is)^{-2/3}(s^2 - \Lambda^2VD^{-1}is)]} \rightarrow -s^{-2/3} e^{i\pi/6 - sy/\Lambda}.
\] (9)

To use this asymptote as an approximation we have to correct the factor before exponent to provide the right value at \( s = 0 \): \( F_0 = F(0) = -3^{-1/3}\Gamma(1/3)/\Gamma(2/3) \), where \( \Gamma(z) \) is the gamma function. \( F(s) \) can be approximated by the function

\[
F(s) = -(s + s_0)^{-2/3} e^{i\pi/6 - sy/\Lambda}, \quad s_0 = e^{i\pi/4}|F_0|^{-3/2},
\] (10)

for which integrating in (8) gives

\[
C_0 - C = \frac{j}{\pi D} \Gamma(2/3) \Re \left\{ \Psi \left[2/3, 1; s_0\Lambda^{-1}(y - i\zeta) \right] \right\}.
\] (11)
Here $\Psi(a, b; z)$ is the confluent hypergeometric function \[23\]. In the limit $r \to 0$, we have

$$C_0 - C(r) = \frac{j}{\pi D} \ln \frac{\alpha_0 \Lambda}{r}, \quad \alpha_0 = 3^{-1/2} \left[ \frac{\Gamma(1/3)}{\Gamma(2/3)} \right]^{3/2} e^{2\psi(1) - \psi(2/3)} \approx 1.90,$$

(12)

where $\psi(z) = \Gamma'(z)/\Gamma(z)$ is the digamma function. The numerical integration gives $\alpha_0 \approx 2.81$.

If the step height is small, $h \ll \Lambda$, then the step velocity is controlled by the concentration (12), where one has to put $r \approx h$. For the linear step kinetics,

$$V = \beta \left[ C_e - C(h) \right] / C_e,$$

(13)

where $\beta$ is the kinetic coefficient and $C_e$ is the concentration of the saturated solution, taking into account $j = \rho h V$, we obtain

$$V = \frac{\beta \sigma_b}{1 + \rho \beta h (\pi D C_e)^{-1} \ln(\alpha_0 \Lambda / h)}.$$

(14)

Here $\sigma_b = (C_0 - C_e)/C_e$ is the bulk supersaturation and $\rho$ is the crystal density.

Let us investigate the asymptotes of the concentration field far from the step within quasi-static approximation. At $y = 0$ and $\zeta > 0$ in the limit $\zeta \to \infty$, the expression (11) is exact because, in this case, the main contribution of the integral (8) goes from the small values of $p_z$, where the approximation (10) is exact. At $\zeta \gg \Lambda$, using asymptotic development of the confluent hypergeometric function \[23\] we arrive to the expression for the surface concentration

$$C_0 - C(\zeta) = j \frac{3^{1/6} \Gamma(1/3)}{2\pi D} \left( \frac{\Lambda}{\zeta} \right)^{2/3}, \quad \zeta > 0.$$

(15)

To find the surface concentration at the side of flow incoming in the limit $\zeta \to -\infty$, we change the integration variable in (8) to $\tau = ip_z \Lambda$:

$$C_0 - C(\zeta) = \frac{j}{\pi D} \text{Im} \int_0^{i\infty} d\tau \tau^{-1/3} e^{\xi \tau/\Lambda} \frac{\text{Ai}(-\tau^{4/3})}{\text{Ai}'(-\tau^{4/3})}. $$

(16)

At $\zeta < 0$, the path of the integration in the $\tau$-plain shown in Fig. 2 can be reduced to the positive part of the real axis. The integrable function has poles only on this new path, where
the function is real. So the imaginary part of the integral is the half-sum of residuals in
the poles. If \(|\zeta| \gg \Lambda\), the main contribution goes from the closest to zero pole \(\tau = (a'_1)^{3/4}\),
where \(a'_1 \approx 1.01879\) is the least root of the equation \(\text{Ai}'(-a') = 0\). The result is
\[
C_0 - C(\zeta) = \frac{3j}{4D(a'_1)^{-3/2}} \exp \left[-(a'_1)^{3/4} \left|\frac{\zeta}{\Lambda}\right|\right], \quad \zeta < 0. \tag{17}
\]
The concentration field relaxes slow along the solution flow and fast in the opposite direc-
tion. Analogous calculation for the concentration far from the crystal surface leads to the
expression
\[
C_0 - C(y) = \frac{3j}{8\pi^{1/2}D (a'_1)^{25/16} \text{Ai}(-a'_1)} \left(\frac{y}{\Lambda}\right)^{9/4} \exp \left[-\frac{2}{3}(a'_1)^{3/8} \left(\frac{y}{\Lambda}\right)^{3/2}\right]. \tag{18}
\]
Note that the quantity \(\Lambda\) can be interpreted as an effective thickness of the diffusion layer
in this case.

At the large step velocities, \(V \sim D\Lambda^{-4/3}\zeta^{1/3}\), the quasi-static approach is not correct. In
the limits \(V \gg D\Lambda^{-4/3}\zeta^{1/3}\) and \(|\zeta| \to \infty\), the diffusion field reads as
\[
C_0 - C(\zeta) = j \times \begin{cases} 
(\pi V D \zeta)^{-1/2}, & \zeta > 0 \\
3D^{-1} \exp \left[-(a'_1)^{1/3} w^{-3} \Lambda^{-1} |\zeta|\right], & \zeta < 0
\end{cases} \tag{19}
\]
where \(w = V\Lambda/D\) characterizes the degree of the quasi-stationarity of the diffusion. Like
the quasi-static case, the zone impoverished by the step sink is drifted by the solution flow.
The results obtained in this Section will be used for analysis of the step train stability.

III. STABILITY OF ONE ISOLATED STEP

A step can be treated as isolated if the diffusion length \(\Lambda\) is small in compare with the
step spacing. Certainly, the isolated step can contain several elementary crystal layers. We
shall assume that scale of internal structure, such as height and width of this composite step
is the least of sufficient length parameters. For the isolated step, the scale plays a role of
effective step height \(h\) which determines the concentration controlled the step motion.

Near by the crystal surface, the concentration up the solution stream is higher than the
concentration down the stream. The isolines of the concentration field are schematically
shown in Fig. 3. It is clear that a negative local deviation of the step from a straight, \(\delta z(x) < 0\), being directed upstream, finds the more concentrated solute and the opposite deviation meets the impoverished solution. Further evolution of the perturbation depends on the relation between directions of the step motion and the solution flow. For the step moving along the flow, being at the less concentration the leading part of the step becomes slower. At that time, finding the larger concentration the dropping behind part overtakes the rest step. Therefore, the lateral perturbations of the step moving along the flow always decay. At the case of the opposite motion, the velocity increment of the perturbed part is having the same sign with the variation of the \(z\)-coordinate of the step. The presence of this positive back-coupling can produce a spontaneous growth of the perturbation, i.e. to the instability of the straight step shape. The line strain of the step and forcing the solution flow stabilize the straight shape.

Thus, the flow of the solution gives rise an analogous effect to the Schwoebel’s barrier \([4]\) at the surface diffusion transport. In the case of the volume diffusion, the substance flux is larger from the side of the solution incoming than from the opposite side. At the surface diffusion, the fluxes arriving from the opposite terraces are differ due to a difference of the energy barrier of the adatom attachment from the upper and the lower terraces. The feature of the volume diffusion is in a possibility to govern the quantity of the attachment asymmetry by the direction and the intensity of the solution flow.

Consider the kinetics of small fluctuations, \(z = Vt + \delta z(x, t)\), from the straight step. The unperturbed step velocity \(V\) is determined by (13). Taking into account the Gibbs-Thomson effect, the kinematics equation takes the form

\[
\dot{z} = \pm \beta \sigma(z, t) + \beta \lambda z'' \left[ 1 + (z')^2 \right]^{-3/2},
\]  

(20)

where \(\rho_c(\sigma) = \lambda / \sigma\) is the critical nucleus radius on the crystal surface at the supersaturation \(\sigma\) near by the given point of the surface and \(\lambda\) is the capillary length. The upper sign (20) corresponds to the parallel motion of the step and the flow and the lower sign corresponds to the opposite motion. Assuming \(\delta z(x, t) = \epsilon(t) \cos(qx)\), let us calculate the concentration
near by the step at $\epsilon q \ll 1$. The substance flux per the unit length is $j = \rho h [V + \dot{\epsilon}(qx)]$.

Using the Green’s function (7), we obtain

$$
\tilde{\sigma}(x,t) = \sigma_0 - (\pi U)^{-1} V \ln(\alpha_0/H) - \left[ \dot{\epsilon} I_0(H,Q) + \epsilon V \Lambda^{-1} I(Q) \right] U^{-1} \cos(qx),
$$

where

$$
I_0(H,Q) = -\frac{1}{\pi} \text{Re} \int_0^\infty \frac{d\tau}{(i\tau)^{1/3}} \frac{\text{Ai}[H(i\tau)^{1/3}] + (i\tau)^{-2/3}(\tau^2 + Q^2)}{\text{Ai}'[(i\tau)^{-2/3}(\tau^2 + Q^2)]},
$$

and

$$
I(Q) = \frac{1}{\pi} \text{Re} \int_0^\infty d\tau (i\tau)^{2/3} \frac{\text{Ai}[-(i\tau)^{4/3}]}{\text{Ai}'[-(i\tau)^{4/3}]} - \frac{\text{Ai}[-(i\tau)^{-2/3}(\tau^2 + Q^2)]}{\text{Ai}'[(i\tau)^{-2/3}(\tau^2 + Q^2)]},
$$

where $U = DC_{\epsilon}/(\rho h)$, $H = h/\Lambda$ and $Q = q\Lambda$. Taking into account (21) reduces the kinematic equation (20) to

$$
\dot{\epsilon} = \nu^\pm \epsilon, \quad \nu^\pm = \frac{\beta}{\Lambda} \cdot \frac{\mp VU^{-1} I - \lambda \Lambda^{-1} Q^2}{1 + \beta U^{-1} I_0},
$$

where $\nu^\pm$ are the amplification rates for the parallel and the opposite motion respectively. At positive $\nu$, the perturbation amplitude $\epsilon$ is exponential growing in time and negative values imply decaying. The function $I_0(H,Q)$ and $I(Q)$ are always nonnegative. The dependences $I_0$ on $H$ at several values $Q$ are shown in Fig. 4. At $H \ll 1$, they can be written as

$$
I_0(H,Q) = \pi^{-1} \ln \left[ \alpha(Q)/H \right].
$$

The dependence $\alpha^{-1}(Q)$ is shown in Fig. 5, where $\alpha(0) = \alpha_0$, $\alpha(\infty) = 2 \exp(-\gamma)$ and $\gamma \approx 0.5772$ is the Euler number. The dependence $I(Q)$ are shown in Fig. 6. At $Q \ll 1$, we have $I(Q) \approx 0.19Q^2$ and $I(\infty) \approx 0.128$. With a relative error below 1% the functions $I_0$ and $I$ can be approximated by the expressions

$$
I_0(H,Q) = (2\pi)^{-1} \ln \left[ (0.77 + 0.12Q^2)/H \right],
$$

$$
I(Q) = 0.19Q^2/(1 + 1.58Q^2).
$$

The expression (24) shows that the step moving along the stream is stable for the lateral disturbances at all wavelengths. At the opposite motion, if $I''(0) > U\Lambda/(V\Lambda)$, then the step
is unstable for the long wave disturbances with \( q < q_{cr} \), where \( q_{cr} \approx \Lambda^{-1}[0.12\Lambda V/(\lambda U) - 0.63]^{1/2} \). The instability condition is given by

\[
\frac{B^{1/2}}{Vh} < \frac{0.19\rho}{C_e\Lambda D^{1/2}}.
\] (28)

Thus, the lateral instability occurs at low intensity of the solution flow or/and at sufficient high values of the step velocity and the step height. The instability zone, \( 0 < q < q_{cr} \), of the disturbance wave vectors is shown by shading in Fig. 7. The thick line, \( q_{cr} \), starts at origin because the step is stable without flow in the frame of quasi-statics. The minimal wavelength of the unstable disturbances \( l_{min} = 82.7(U/V)\lambda \) is determined by the capillary length times the ratio of the parameter of the diffusion velocity to the step velocity. Remember that the quasi-static approximation is correct at \( V\Lambda/D \ll 1 \).

At low intensities of the solution flow, \( B \to 0 \), the characteristic size of the impoverished zone \( \Lambda \to \infty \), therefore the instability vanishes in this limit. At high flow intensities, the concentration near by the step is close to the bulk concentration at all points of the step that explains for the stability at large \( B \). Thus the instability vanishes at \( q = 0 \) and \( q = q_{cr} \) and the amplification rate of the instability has a maximum within the interval \( 0 < q < q_{cr} \).

If at least one of the inequalities \( q_0\Lambda \ll 1 \) and \( \beta/(2\pi U) \ll 1 \) is fulfilled then

\[
q_0\Lambda = 0.80 \left[ \left( \frac{0.19AV}{\lambda U} \right)^{1/2} - 1 \right]^{1/2}, \quad \nu_{max} = \frac{0.12\beta V}{\Lambda U} \left[ \left( \frac{\lambda U}{0.19AV} \right)^{1/2} - 1 \right]^2.
\] (29)

The instability requires the step track length \( L = V/\nu_{max} \) to manifest itself.

The single step approximation addressed in this Section becomes inapplicable when the step spacing \( d \) is comparable to the diffusion length \( \Lambda \). If a screw dislocation, having the net number \( m \) of unit steps in the normal component of the Burgers vector, generates a step train, each step consisting of \( n \) of unit steps, then

\[
d \approx 20n\rho_c/m.
\] (30)

At \( d < \Lambda \), the single step instability can be realized by a sharp dropping of the solution temperature from a value at which \( d^* \gg \Lambda \) in the steady state. The spacing \( d^* \) will have been conserved while new generated steps have not arrived.
IV. LATERAL STABILITY OF VICINAL FACE

To understand the influence of the diffusion interaction of neighbour steps it is appropriate to consider the inverse limit to the single step case. At $d \ll \Lambda$, the crystal relief is described by a height function $h(x, z)$. Volume conservation implies that a continuity equation satisfies:

$$\frac{\partial P}{\partial t} + \nabla (PV) = 0, \quad P = \nabla h, \quad \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial z} \right),$$

(31)

where $|P|$ is the surface slope to a singular face and the direction $P$ is parallel to the step velocity $V$. The normal growth rate of the crystal face $R = PV$ and the flux per unit area is $J = \rho R$. Using the Green’s function (7), for the small fluctuations from the plain $P_0 = (0, P_0)$ of the form

$$P = P_0 + \tilde{P} \exp(i\omega t + iqx + \kappa z)$$

(32)

$$R = R_0 + \tilde{R} \exp(i\omega t + iqx + \kappa z), \quad R_0 = P_0 V_0,$$

(33)

where $R_0$ and $V_0 = (0, V_0)$ are unperturbed normal growth rate and step velocity, we obtain the surface concentration in the form

$$C = C_0 - \rho\Lambda D^{-1}T(\omega, q, \kappa) \tilde{R} \exp(i\omega t + iqx + \kappa z),$$

(34)

$$T(\omega, q, \kappa) = (\Lambda \kappa)^{-1/3} \frac{\text{Ai} \left[ (\Lambda^{-2} \kappa)^{-2/3} (i\omega D^{-1} q^2 - \kappa^2) \right]}{\text{Ai}' \left[ (\Lambda^{-2} \kappa)^{-2/3} (i\omega D^{-1} q^2 - \kappa^2) \right]}.$$  

(35)

These perturbations are the quite lateral only at $\kappa = 0$. The stability against the quite longitudinal perturbations, $q = 0$, has been considered in Ref. [21]. Using the kinematic equation (31), we obtain the linear stability equation

$$i\omega + V_0 \kappa + \rho_c R_0 q^2 - iT(\omega, q, \kappa) \omega \rho P_0 \beta \Lambda (DC_e)^{-1} = 0.$$  

(36)

In the limit $\kappa'' \ll \kappa'$, where $\kappa'$ and $\kappa''$ are the real and imaginary parts of $\kappa = \kappa' + i\kappa''$, the linear dispersion relations are given by
\[ \kappa'' = -\omega/V_0 \equiv \Lambda^{-1} \theta, \quad \kappa' = P_0 \rho C_e^{-1} \beta \theta \text{Im}(T) - P_0 \rho \varrho q^2. \] (37)

The amplification or decay lengths for the step motion up and down the solution flow (upper and lower sign respectively) are given by

\[ \left( L^\pm \right)^{-1} = \pm \left| P_0 \right| \rho \beta C_e D \theta^{2/3} \text{Im} \left\{ i^{-1/3} \left[ \frac{\text{Ai} \left[ (i\theta)^{-2/3} (Q^2 + \theta^2 \mp iw\theta) \right]}{\text{Ai}' \left[ (i\theta)^{-2/3} (Q^2 + \theta^2 \mp iw\theta) \right]} \right] \right\} - \frac{|P_0| \rho \varrho Q^2}{\Lambda^2}, \] (38)

where \( w = |V_0| \Lambda/D \) takes into account the influence of the step motion on the diffusion field. Positive and negative signs of \( L \) imply the instability and the stability respectively. For quite longitudinal displacements of steps from steady state positions, \( Q = 0 \), the expression (38) is a particular case of the results of Ref. [21].

Quite lateral fluctuations, \( \theta = 0 \), are always decay, \( L^\pm = -|P_0| \rho \varrho q^2 < 0 \), the decay rate being determined only the step line tension. The explanation lies in the variation of the concentration along curved step being compensated with the diffusion influence of neighbour steps.

It can be numerically shown that at the opposite motion of the steps and the solution flow, at all values of the parameters, the length \( L^- < 0 \), hence the strong diffusion interaction completely suppresses the lateral instability. In the case of parallel motion, there is bunching with simultaneous amplification of the perturbation along the steps for only sufficient long-wave perturbations: \( \theta < \theta_{cr}(w, Q) \). The presence of the lateral perturbation, \( Q \neq 0 \), decreases the instability of the density waves of steps i.e. straight steps are more unstable. Note that the diffusion nonstationarity has a stabilizing character: the instability drops with increasing \( w \).

Thus, the diffusion interaction suppresses the lateral instability at \( \Lambda > A d \), where \( A \sim 1 \). For the dislocation steady growth (30), it confines the unstable zone of supersaturation from above. As a whole, the unstable zone reads as

\[ \frac{5.3 \lambda U_0}{\beta n} \left( \frac{B}{D} \right)^{1/2} < \sigma < \frac{20 \lambda \Lambda n}{m} \left( \frac{B}{D} \right)^{1/2}, \] (39)

where \( U_0 = DC_e/(\rho h_0) \) and \( h_0 \) is the height of unit step. This zone exists only at \( n^2/m > 0.26 U_0/(A \beta) \).
For an example, evaluate the instability of step on the (101) face of the KDP crystal. The value of the solution flow intensity is given by
\[ B = \frac{\partial^2 \psi}{\partial y^2} \bigg|_{y=0}, \] (40)
where \( \psi \) is the stream function. \( B \) can approximately be evaluated as \( B \sim \frac{U_{\text{sol}}}{\delta} \), where \( U_{\text{sol}} \) characterizes the flow velocity far from the surface and \( \delta \) is the thickness of the hydrodynamic boundary layer at this point. For concreteness, let us take a tangential flow of solution. Other useful plane mass transfer models have been described in Ref. [24]. For the flow around a semi-infinite plate [23], \( z > 0 \), at an incoming velocity \( U_{\text{sol}} \), we have \( B = 0.33\left(\frac{U_{\text{sol}}^3}{\nu z}\right)^{1/2} \). For \( U_{\text{sol}} = 10 \text{ cm/c} \) and \( z = 1 \text{ cm} \) we obtain \( B = 100 \text{ c}^{-1} \), and the instability zone is given by \( 0.3/n < \sigma < 0.003n/m \), it existing if \( n^2/m > 100 \). Taking into account an anisotropy of the step kinetic coefficient and the isotropy of the critical nucleus [19] weakens this restriction, because the step spacing in the direction of the largest kinetic coefficient exceeds \( 20\rho_c \) [20]. At the case of \( m = 1 \), the unit steps are stable against the lateral fluctuation but the steps containing ten or more units are unstable. At \( \sigma = 0.05 \), for the step of 20 unit layers, the amplification length \( L^{-} \approx 0.15 \text{ cm} \) that can be observed.

V. INSTABILITY OF STEP TRAIN AT WEAK INTERACTION

The diffusion interaction between steps of a train is weak when the step spacing is considerably greater than the diffusion length: \( d \gg \Lambda \). If the steps are moving to meet the solution flow then the condition of the lateral instability is given by (28) with a weak stabilizing influence of the interaction. A sufficient effect of the weak coupling occurs at the parallel motion of the step and the solution. In this case, the lateral instability does not develop, so we will assume that the steps are straights with the coordinates \( z_n \). Since the diffusion field going from a step to meet the solution flow decays faster than along the flow, we will take into account only influence of the closest step from the side of solution incoming. The velocity of \( n \)th step is given by
\[ V_n = V - \frac{3^{1/6} \Gamma(1/3) \beta}{2\pi DC_e} \left( \frac{\Lambda}{z_n - z_{n-1}} \right)^{2/3} j_{n-1}, \]  

(41)

where the unperturbed step velocity \( V \) is determined by (14). The perturbation doubling the train period, \( z_n = nd + (-1)^n \bar{\epsilon} \exp(\nu t) \), has a maximal amplification rate. The amplification length for parallel motion and the decay length for antiparallel are respectively given by

\[ L^\pm = \pm \frac{3^{5/6} \pi Ud}{2\Gamma(1/3)\beta} \left( 1 + \frac{\beta}{\pi U} \ln \frac{\alpha_0}{H} \right) \left( \frac{d}{\Lambda} \right)^{2/3}. \]  

(42)

The magnitude of \( \chi = (\beta/\pi U) \ln(\alpha_0/H) \) is a criterion of the regime of the step motion. In the limit of the small values, the step velocity is controlled by the crystallization kinetics, i.e. the kinetic regime takes place, and at the limit \( \chi \gg 1 \) the diffusion regime occurs. Note that even near by the kinetic regime, when the step velocity practically does not depend on the flow velocity, the instability nevertheless exists though the amplification rate is small with respect to this parameter.

The reason of the instability of the train period at parallel motion with respect to the flow is quite clear because if a step displaces forward then the step velocity takes an increment due to weakening the diffusion overlap of the previous step, and at the same time, the next step becomes slowing down, hence the perturbation will grow. This effect is an analogous to the current-induced step bunching during sublimation [13–15] for the step up direction of the force if the surface diffusion length \( \lambda_{2d} \) is small compared to the step spacing \( d \). In this case, the induced migration is directed along the step motion. However, the migration force can also induce the bunching for the step down direction if there is the opposite correlation between the surface diffusion length and the step spacing. This correlation depends on the temperature. Increasing the temperature, the surface diffusion length decreases exponentially and may become smaller then \( d \). At the volume diffusion growth and dissolution, the bunching can takes place only for the parallel motion of the steps and the solution flow at any relation between the diffusion length \( \Lambda \) and \( d \). At the surface diffusion, if the \( d \) is small compared to \( \lambda_{2d} \), the most adatoms departed from a step reach the adjacent step to which the migration is directed. The adatom concentration grows along the force because they can
only incorporate into the step or evaporate. It is precisely this fact that gives the instability for the opposite direction of the step motion and the adatom migration. On the contrary, at the volume diffusion, the solute reached the following step can move further with the flow and the opposite motion is always stable.

At large step velocities laying out of the frame of the quasi-static approximation, the diffusion field of step has the power-type asymptotic along the solution flow and the exponential decay in the opposite direction \(^{(19)}\). Hence in this case, the step train is also stable against the doubling of the period during motion in the opposite direction with the flow and it is unstable during the parallel motion.

**VI. RESULTS AND CONCLUSIONS**

The linear stability analysis has shown that, at the opposite motion of step and solution flow, the lateral instability is possible, and, at the parallel motion, the instability against perturbation in the distances between steps can occur. The overlap of the step diffusion fields suppresses the lateral instability and gives rise the longitudinal instability of step train. Intensification of the solution flow and decrease of the step height stabilize the equidistant train of straight steps. Though the instability has a diffusion nature, it can be even noticeable near by the kinetic regime of the step motion. While the quasi-static approximation is correct, the lateral instability becomes stronger with an increase in the step velocity. Out of the quasi-static frame, the effect of step motion plays a stabilizing role.

The evaluations have shown that the instability considered here can be observed under the real conditions of solution growth of crystals like KDP. As a rule at solution growth, meandering unit steps and presence of the straight macrosteps allow to grow high quality crystals. A danger of defect formation like solution inclusions does go from the presence of meandered macrosteps. The concave segments of such steps further a development of overhanging upper step layers, and then the formed cavity can capture solution into the crystal. During the high-rate growth of large KDP crystals, the crystal surface with macrosteps is
commonplace, so providing with uniformity of the diffusion layer thickness does not guarantee a stable growth without the inclusion formation. Increasing the convection until the kinetic growth regime can be also insufficient condition to obtain high quality crystals. It is important to note that fast reversal of the flow direction can eliminate the instability both lateral and longitudinal. If the interruption time between equal intervals of the opposite solution flow is small in compare with the time of the instability development \(1/\nu\), then we find from (24) that the lateral shape perturbations decays with the average decay constant

\[
\tau = -\beta \lambda q^2 (1 + \beta U^{-1} I_0)^{-1}.
\]  

(43)

A model of the diffusion layer relaxation when varying the flow velocity was considered in Ref. [24].

One of the goals for this study is the search of phenomena of the step dynamics in order that the mechanism of the crystallizing matter transfer should be determined. The distinct qualitative difference takes place for step bunching. At the surface diffusion in the presence of the heating current, step bunching appears both for step up and down direction of the current, whereas at the volume diffusion in the solution flow, the only steps moving parallel to the flow can be unstable.

The lateral instability considered here occurs both at the surface diffusion due to the Schwoebel’s effect and at the volume diffusion due to the drift of the diffusion field by the solution flow. However, in the case of the volume diffusion, the instability is controlled by the intensity of the solution flow and the flow direction with respect to the step motion. While interpreting experimental results, one should bear in mind the possibility that a lateral instability can be excited by the solution flow at the surface diffusion, because the delivery of the crystallizing units to the crystal surface goes through the moving solution at any rate. In the presence of the surface diffusion with the diffusion length \(\lambda_{2d} = (D_2 \tau_s)^{1/2}\), where \(D_2\) is the surface diffusivity and \(\tau_s\) is the characteristic time of the desorption of the units back into the solution, the whole path of the units includes diffusing in the solution to
a sink strip with the width of order of $\lambda_{2d}$ and then diffusing on the crystal surface within this strip to the step. The drift of the volume diffusion layer by the solution flow leads to a nonuniformity of the supersaturation along the disturbed step, so the lateral instability is possible. In this case, only long wave perturbations, $q < \tilde{A}/\lambda_{2d}$, where $\tilde{A} \sim 1$, can be unstable, corresponding critical wavelength depending on neither the flow intensity nor the step velocity. Thus, these differences of the step dynamics may be the criterion determining the delivery mechanism.

At the same time with the diffusion processes, the morphological instability can be conditioned by an impurity effect. The processes resulting in the loss of vicinal-surface stability of the prismatic faces of ADP and KDP under the action of the supersaturation nonuniformity and the presence of growth-decelerating impurities had been observed by in situ laser interferometry [29]. It had been established that the instability are most pronounced in the supersaturation range corresponding to the maximum partial derivatives of the step velocity with respect to the supersaturation and the impurity concentration. As it was found in Ref. [30], an impurity influence can lead to the S-shape dependence of the step velocity on the supersaturation and on the step curvature too. At the supersaturation near by this hysteretic range, the step is unstable against the lateral perturbations. A model of instability of the step spacings owing to impurity effect was considered in Ref. [31]. These instabilities conditioned by the impurities can be separated through the dependence on the impurity concentration.

ACKNOWLEDGMENTS

The author expresses his gratitude to Professor V.I.Bespalov for useful discussion. The research described in this publication was made possible in part by Grant 95-02-03773-a from the Russian Foundation for Fundamental Research and Grant JEM100 from the International Science Foundation and Russian Goverment.
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Fig. 1. Scheme of singular crystal surface with single step.

Fig. 2. Integration path in expression (17).

Fig. 3. Scheme of the concentration isoline near by rectilinear step in the solution flow.

Fig. 4. Dependence of $I_0$ on dimensionless step height $H = h/\Lambda$.

Fig. 5. Dependence of $\alpha(Q)$.

Fig. 6. Dependence of $I$ on dimensionless wave vector of lateral perturbation $Q = q\Lambda$.

Fig. 7. Shaded zone corresponds to unstable lateral perturbation during contrary motion of step and solution flow.