CRYSTALLOGRAPHY

A. A. CHERNOV

1960

SovietRxiv

Fig. 1. Scheme of the boundary between the crystal and the solution. The boundary coincides with the x-axis. The solution occupies the half-plane $y > 0$. Sinks are located at the points $x = 0, \pm\lambda, \pm 2\lambda \ldots$. The fluxes of matter through AB and CD are equal to zero.

Figure 1: Fig. 1. Scheme of the boundary between the crystal and the solution. The boundary coincides with the x-axis. The solution occupies the half-plane $y > 0$. Sinks are located at the points $x = 0, \pm\lambda, \pm 2\lambda \ldots$. The fluxes of matter through AB and CD are equal to zero.

Abstract

Full Text

CRYSTALLOGRAPHY

A. A. CHERNOV

THE RATE OF LAYER-SPIRAL GROWTH OF CRYSTALS FROM SOLUTION AND MELT

(Presented by Academician A. V. Shubnikov, 9 IV 1960)

Let us consider the growth of a stepped surface of a crystal whose orientation differs little from that of close packing. We shall assume, as usual, that the transition of matter into the crystalline phase occurs only at the edges of the steps, each of which thus becomes a linear sink of matter (in growth from solution) or a linear source of heat (in growth from the melt). We neglect diffusion of adsorbed particles over the crystal surface ([1]).

We shall first dwell on growth from solution. When the mother liquor is stirred, the transport of matter to the crystal is accomplished in a purely diffusive manner only in the thin boundary layer of unstirred solution adjacent to the crystal, of thickness δ. It is this transport that will be considered.

Let there be on the surface of the crystal a train of parallel steps, each of height a, where a is a lattice parameter. We shall denote the distance between steps by λ ($\lambda \gg a$), the equilibrium concentration of the solution above the crystal by c_e, and the concentration at the edge of the boundary layer by c_δ.

Fig. 1. Scheme of the boundary between the crystal and the solution. The boundary coincides with the x-axis. The solution occupies the half-plane $y > 0$. Sinks are located at the points $x = 0, \pm\lambda, \pm 2\lambda \ldots$. The fluxes of matter through AB and CD are equal to zero.

Let us align the z-axis of a rectangular coordinate system with one of the steps and orient the (x, y) plane so that it cuts the crystal surface along the x-axis

(Fig. 1). The concentration of the solution $c(x, y)$ obeys Laplace' s equation $\Delta c = 0$ everywhere in the boundary layer and the condition

$$D\frac{\partial c}{\partial r} = \beta(c - c_e), \quad r = a, \tag{1}$$

at the step, to which we assign the shape of a semicylinder of radius a; D is the diffusion coefficient, and β characterizes the rate of exchange of particles between the step and the solution. As the number of kinks on the step decreases, β decreases ([1]).

By virtue of the translational symmetry of the problem, and also because crystallization proceeds only at the edges of the steps, everywhere on the contour $ABOCD$, except for the sink at the point O, we shall have $\partial c/\partial n = 0$. In addition, $c(0, \delta) = c_\delta$. The two-dimensional problem thus posed for $c(x, y)$ in the strip $-\lambda/2 \leq \operatorname{Re} z \leq \lambda/2$ of the complex plane $z = x + iy$ is readily solved after conformally mapping this strip onto the upper half-plane $\operatorname{Im} \zeta > 0$ of the complex plane ζ.

The solution has the form

$$c(x, y) = A \ln |\zeta| + B = A \ln \sqrt{\sin^2 \frac{\pi}{\lambda} x + \operatorname{sh}^2 \frac{\pi}{\lambda} y} + B, \tag{2}$$

$$\zeta = \sin \frac{\pi}{\lambda} z,$$

where A and B are constants. The solution (2), as it should, near the step ($\sqrt{x^2 + y^2} \ll \lambda$) has a logarithmic singularity, while far from the crystal surface it has the form it would have if crystallization proceeded continuously over the entire surface. From the boundary conditions we have:

$$A = \frac{\beta a (c - c_e)}{D + \beta a \ln \frac{\lambda}{\pi a} \operatorname{sh} \frac{\pi}{\lambda} \delta}, \qquad B = c_\delta - A \ln \operatorname{sh} \frac{\pi}{\lambda} \delta. \tag{3}$$

Hence the velocity of displacement of the elementary steps in an echelon is

$$v = \pi \Omega \beta (c - c_e) = \frac{\pi \Omega \beta c_e \sigma}{1 + \frac{\beta a}{D} \ln \frac{\lambda}{\pi a} \operatorname{sh} \frac{\pi}{\lambda} \delta}, \tag{4}$$

where the supersaturation is

$$\sigma \equiv \frac{c_\delta - c_e}{c_e},$$

and Ω is the specific volume of a molecule (atom) in the crystal. The dependence of this velocity on the distance λ between steps in the echelon, which is a consequence of the overlap of the diffusion fields of the individual steps, is here considerably weaker than in growth from vapor.

The distance between steps is determined by the strength of the source of these steps. If a screw dislocation serves as the source, the steps will be not straight but spiral. Far from the center of the spiral, when the radius of curvature of the steps $R \gg \lambda$, the step displacement velocity is given by formula (4), while near the center it must be somewhat smaller. Let us assume, however, that the spiral is Archimedean and that $\lambda = 4\pi\rho_c$, $\rho_c = \Omega a(kT\sigma)^{-1}$, where ρ_c is the radius of the two-dimensional critical nucleus, and a is the specific surface energy between the end face of the step and the solution. Hence the normal growth rate of a face, determined by a single screw dislocation, is equal to

$$V_n = \frac{a}{\lambda}v = \frac{D\beta akTc_e}{4a}\,\frac{\sigma^2}{D + \beta a \ln\frac{\delta}{a} + \beta a \ln\frac{\sigma_c}{\sigma}\,\mathrm{sh}\,\frac{\sigma}{\sigma_c}}, \tag{5}$$

where

$$\sigma_c = 4\Omega a(kT\delta)^{-1}.$$

The product βa represents the coefficient of "diffusion" of particles of the crystal substance across the crystal-solution phase boundary. As a rough approximation one may take $\beta a \sim D$ (in reality this quantity will evidently be smaller).

Taking, for a qualitative estimate, $\Omega = 3 \cdot 10^{-23}$ cm^3, $a = 3 \cdot 10^2$ erg/cm^2, $kT = 5 \cdot 10^{-14}$ erg, $\delta = 7 \cdot 10^{-5}$ cm, $D = 10^{-5}$ cm^2/sec, $c_e = 10^{21}$ cm^{-3}, we obtain $\sigma_c = 10^{-2}$, $\beta akTc_e/4a = 0.4$ cm/sec. A graph of the function

$$\frac{4a}{\beta akTc_e}V_n(\sigma)$$

for $\delta = 3.5 \cdot 10^{-5}$ cm ($\sigma_c = 2 \cdot 10^{-2}$) and $\delta = 7 \cdot 10^{-5}$ cm ($\sigma_c = 10^{-2}$) is shown in Fig. 2.

At very small supersaturations $\sigma \ll \sigma_c$, $V_n \sim \sigma^2$. In this case the steps forming the spiral are far apart, their concentration fields do not overlap ($\lambda \lesssim \delta$), and they do not interfere with one another' s feeding. With increasing σ and the approach of the turns of the spiral, $V_n(\sigma)$ becomes almost

linear:

$$V_n = \frac{D\Omega c_e\sigma}{\delta} - \left(1 + \frac{\beta a}{D}\ln\frac{\sigma_c\delta}{\sigma a}\right)\frac{D^2\Omega c_e\sigma_c}{\beta a\delta}. \tag{6}$$

Fig. 2

Figure 2: Fig. 2

This straight line does not pass through the origin, but is shifted downward and intersects the σ-axis at

$$\sigma = \left(\frac{D}{\beta a} + \ln\frac{\sigma_c\delta}{\sigma a}\right)\sigma_c.$$

By direct calculation it is easy to verify that the function $\frac{4a}{\beta akTc_e}V_n(\sigma)$ for $\delta = 3.5\cdot 10^{-5}$ cm, $\sigma_c' = 2\cdot 10^{-2}$, i.e. curve 1 in Fig. 2, can be approximated, to an accuracy of $\sim 3\%$ in the interval $0.01 \lesssim \sigma \lesssim 0.2$, by the expression $400\sigma^{1.65}$. For other numerical values of σ_c and δ in (5), an analogous approximation is possible with somewhat different coefficients. The exponent of σ increases with increasing σ_c and decreasing δ: the more intense the stirring of the solution, the larger the region of the quadratic dependence $V_n(\sigma)$.

Fig. 2. Dependence of the normal growth rate of a face on supersaturation. 1 –for $\delta = 3.5\cdot 10^{-5}$ cm, $\sigma_c = 2\cdot 10^{-2}$; 2–for $\delta = 7\cdot 10^{-5}$ cm, $\sigma_c = 10^{-2}$.

Layer-spiral growth from the melt can be considered in an analogous manner. In this case the heat-conduction problem inside the crystal must be solved. Boundary condition (1) should be replaced by

$$-\frac{\varkappa}{q}\frac{\partial T}{\partial r} = \beta_T(T_0 - T), \qquad r = a;$$

where T is the temperature of the melt at the crystallization front, T_0 is the melting temperature, $\varkappa$ is the coefficient of thermal conductivity, and q is the latent heat of crystallization. Expressions (4), (5), and (6) will give the corresponding growth rates if the ratio β/D is replaced by $\beta_{Tq}/\varkappa$, the concentration difference $c_\delta - c_e$ by the difference between the melting temperature and the temperature of the cooler, and δ is understood as the characteristic distance determining the temperature gradient in the crystal. For example, in the case of a plate-like crystal lying on a cooler, δ is equal to the thickness of the crystal; in growth in a capillary it is the radius of the capillary, etc. Consequently, at sufficiently large values of $\beta_{Taq}/\varkappa$, the normal growth rate increases almost linearly with the undercooling $\Delta T/T$, while at smaller values of this parameter the dependence of the normal growth rate of a close-packed face should be determined by curves of the type shown in Fig. 2 (formula (5)).

Experimental data on growth from the melt, according to Hillig and Turnbull ([2,3]), give $V_n \sim (\Delta T)^{1.75}$. The authors ([2]) also relate this effect to dislocation growth.

A nonlinear dependence $V_n(\sigma)$ in growth from solution apparently occurred in the experiments of M. I. Kozlovskii ([4]). He measured the angular rate of "rotation" of a spiral on a β-methylnaphthalene crystal growing from an alcohol solution flowing over it. After processing these data, we obtained the dependence $V_n \sim \sigma^{1.8}$. According to a kind communication from G. Bliznakov, a dependence of the type shown in Fig. 2 was also observed by him for growth from solution. The data of Dunning and Elbaum ([5]) also do not contradict such a dependence.

An impurity contained in the mother medium affects the dependence $V_n(\sigma)$ through the quantities β and a. Both are reduced by a surface-active impurity, but, generally speaking, not in the same way. If the impurity is not captured by the crystal (i.e. its action is reduced mainly to poisoning of

fractures ([6,7]), then, in its motion, the step "scrapes off" the impurity adsorbed on the close-packed regions and therefore becomes a linear impurity source, which diffuses into the mother solution through an immobile boundary layer of thickness δ. The strength of each step as an impurity source is proportional to its velocity.

Let us denote the impurity concentration by $c_i(x, y)$, $c_i(0, \delta) = c_{i\delta}$, and specify the dependence of the absorption coefficient of the dissolved substance by the step on the impurity concentration c_s on it in the form ([6]) $\beta(c_s) = \beta_\infty + \beta_0(1 + \chi c_s)^{-1}$. Then the calculation of the impurity diffusion field, analogous to the preceding one, gives for the velocity of motion of elementary steps in an echelon (to accuracy up to terms $\sim \sigma^2$)

$$v = v(c_{i\delta}) - \frac{D\beta_0\chi c_{i\delta} g}{\beta(c_{i\delta})(1 + \chi c_{i\delta})^2 \left[D + a\beta(c_{i\delta}) \ln \frac{\lambda}{\pi a} \operatorname{sh} \frac{\pi}{\lambda}\delta\right]} v^2(c_{i\delta}), \qquad (7)$$

where

$$g = \frac{a}{D} \exp\left(\frac{u_s}{kT}\right) \ln \frac{\lambda}{\pi a} \operatorname{sh} \frac{\pi}{\lambda}\delta,$$

and the velocity $v(c_{i\delta})$ is obtained from (4) by replacing β by $\beta(c_{i\delta})$. For an impurity adsorption energy $u_s \sim 6$ kcal/mole, $\delta \sim 10^{-4}$ cm, $\sigma \sim 0.1$, $\chi c_{i\delta} \sim 5$, $\beta_0/\beta_\infty \sim 5$, the coefficient at $v^2(c_{i\delta})$ in the second term of (7) is ~ 30 sec/cm. Thus, if α is regarded as constant, the impurity at small supersaturations should decrease β, broaden the nonlinear region $V_n(\sigma)$, and weaken the dependence of the growth rate on supersaturation.

Using the results of ([8,9]) and of the present work, one may obtain the following expression for the velocity of motion of an echelon of rectilinear macroscopic steps of height h, separated from one another by distances λ:

$$V = \frac{\Omega\beta(c_\delta - c_e)}{\sin\varphi_0 \left[1 + \frac{\beta h}{D\pi \sin\varphi_0} \ln \frac{2\varphi_0\lambda}{\pi h} \operatorname{sh} \frac{\pi}{\lambda}\delta + \frac{\beta h}{4D\pi\varphi_0^2} K(\varphi_0)\right]},$$

where φ_0 is the angle of inclination of the end surface of the macrostep at equilibrium between the crystal and the solution, and $K(\varphi_0)$ is a constant depending only on this angle.

Institute of Crystallography
Academy of Sciences of the USSR

Received
5 IV 1960

REFERENCES

1. W. K. Burton, N. Cabrera, F. C. Frank, Phil. Trans., A243, 299 (1951).
2. W. B. Hillig, D. Turnbull, J. Chem. Phys., 24, 914 (1956); *Collection: Elementary Processes of Crystal Growth*, IIL, 1959.
3. W. B. Hillig, in *Growth and Perfection of Crystals*, N. Y., 1958.
4. M. I. Kozlovskii, *Experimental Investigation of the Growth of Crystals from Solutions in the Light of Dislocation Theory*, Dissertation, Inst. of Crystallography, Acad. Sci. USSR, Moscow, 1957.
5. W. J. Dunning, N. Albon, in *Growth and Perfection of Crystals*, N. Y., 1958.
6. G. Bliznakov, E. Kirkova, Zs. f. phys. Chem., 206, H. 3/4, 271 (1957).
7. G. Sears, in *Growth and Perfection of Crystals*, N. Y., 1958.
8. A. Seeger, Phil. Mag., 44, No. 348, 1 (1953).
9. I. M. Lifshits, A. A. Chernov, Kristallografiya, 4, issue 5, 788 (1959).

Note: Figure translations are in progress. See original paper for figures.