A. A. Chernov. *Elementary processes of crystal growth from solutions.*

1. Parameters of step crystallization. Crystals in solutions are usually edged and grow by deposition of atomic layers.[1,2] The faces of the layers—so-called steps—possess specific free energy α and kinetic coefficient β. This last coefficient refers to the ratio between step velocity and the supersaturation of the solution above the step; it characterizes the rate at which ions (molecules) are incorporated into the lattice. Despite their fundamental importance, parameters α and β have not been directly measured to date with the single exception of Ag electrocrystallization.[3] The role of surface diffusion and dislocation effects in solution remained unclear, and the theory of spiral-layer growth in solutions lacked any quantitative verification.

Our experiments involved the simultaneous measurement of step velocities $v(\sigma)$ and slopes $p(\sigma)$ of spiral-layer growth protrusions at various values of relative supersaturation σ (Fig. 1, a),[4] with the protrusions forming on the growing edge near dislocation exit points. The measurements were carried out using *in situ* laser interferometry (Fig. 1, b) and X-ray topographic imaging of dislocations and other defects (Fig. 1, c).[5] We studied ADP, KDP, and DKDP crystals grown in vigorously mixed aqueous solutions.[2,6]

We found that step velocity increased linearly with supersaturation σ (at $\sigma < 3\%$, see Fig. 2, a), even though the protrusion slopes, i.e., step densities, varied from $\sim 10^{-4}$ to $5 \cdot 10^{-3}$. Consequently, in this parameter range there is no competition for material between the steps and the effects of diffusion, be it surface or volume, are insignificant—the step processes dominate. Kinetic coefficients β for steps at the (110) bipyramidal edges of ADP turned out to be higher by 1.5–2 orders of magnitude than coefficients at the (001) prism edges: $\beta_{(110)} \approx 0.4$–$0.7$ cm/s, whereas $\beta_{(001)} \approx (3$–$6) \cdot 10^{-3}$ cm/s depending on step orientation. At the same time, the effective surface energies α of the faces proved to be quite similar ($\alpha_{(110)} \approx \alpha_{(001)} \approx 20$ erg/cm^2). Consequently the differences in edge velocities are due to step advance kinetics, i.e., desolvation of the surface and individual ions.

The growth rate of a given macroscopic edge in a given solution at a given supersaturation varied severalfold, depending on the total component of Burgers vector normal to the edge (up to 12 lattice constants) and the extent of the region (~ 0.3–1 μm) in which the dislocations exited to the surface, forming an extended source. Extended sources are the norm and therefore crystal growth rates may vary severalfold because of differences in internal structure (on < 1 μm scale) of layer growth sources at the edges.

2. Nonlinear step kinetics. Departures of $v(\sigma)$ from linearity were observed (Fig. 2, b) at the prism edges of ADP-KDP crystals, which are known for their sensitivity to impurities (especially Cr^{3+}, Fe^{3+}, Al^{3+}). As illustrated in Fig.

2, b, $v(\sigma)$ is made up of two linear regions occurring at $\sigma < \sigma_*$ and $\sigma > \sigma_*$, with $\sigma_* \sim 4\%$. In the latter region the kinetic coefficient is larger by a factor of ~ 7. Analogous results were obtained in the case of (001) ADP. Apparently impurities (with a finite lifetime on the edge) are adsorbed at and in front of slowly advancing steps at low supersaturation values, but have insufficient time to do so (and are more effectively captured by the crystal) at high supersaturation ($\sigma > \sigma_*$).

In the $\sigma \approx \sigma_*$ supersaturation region, where the step velocity increases sharply, the vicinal growth protrusion slope passes through a minimum, in contrast to the theoretically predicted linear increase of protrusion slope with supersaturation (see Fig. 2). This happens because in the immediate vicinity of a dislocation source (approximately within the critical two-dimensional recrystallization radius, ~ 200 Å from the peak of the growth protrusion) step motion is slowed by the Gibbs-Thomson effect; the step is consequently more contaminated with impurities there, than far away from a dislocation exit point. The newly formulated nonlinear theory described the observed nonmonotonic behavior of $p(\sigma)$ and the typical sharp increase in edge growth that occurs at some value of supersaturation $\sigma \approx \sigma_*$ that becomes a threshold condition for impurity effects.

Our research permitted an estimate of the greatest theoretically attainable growth rate. At $\sigma \approx 10\%$ in (100) KDP this maximum rate is ~ 5–10 mm/day (depending on the source intensity) and at $\sigma \approx 50\%$ it reaches 10 cm/day. Furthermore, should a supersaturation exceeding 50% be achieved, it will become possible to grow crystals completely free of dislocations at even greater rates. Current industrial growth rates are ~ 0.5–1 mm/day.

3. Surface instability and the appearance of dissipative structures. The original vicinal surface, which consists of a "ladder" of equidistant elementary steps, is spontaneously "wrinkled" and broken up into clusters of elementary steps known as macrosteps (Fig. 3). This instability develops gradually and thus becomes evident only at a certain distance from the peak of vicinal growth protrusion which emits the steps (marked with a black arrow in Fig. 3). We then found that step clusters appear only on those slopes of the protrusion where the direction of step motion coincides with the solution flux, marked with a white arrow in Fig. 3.[7] The edge growth rate is unaffected by the solution flow rate, however, i.e., the growth remains in the kinetic regime. The cause of this effect is illustrated by Fig. 4, wherein curve *a* traces the profile of a growth protrusion with random clusters and rarefactions of elementary steps. Figure 4, *b*, schematically plots the supersaturation above this surface in a stagnant solution: where the step density and, consequently, absorption of crystallizing material is lower the supersaturation is above average and *vice versa*. In Fig. 4, *c* the distribu-
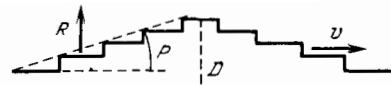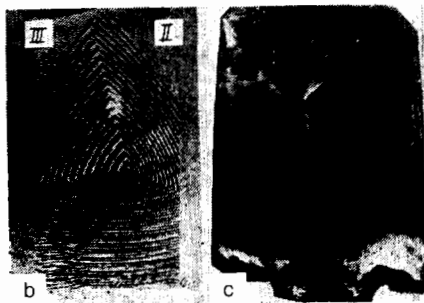
FIG. 1. a—Profile of a vicinal step-like growth protrusion formed on the growing crystal surface around a dislocation exit D. b—Laser interferometric image of a growth protrusion on the bipyramidal edge of the $NH_4H_2PO_4$ (ADP) cyrstal. c—Side view X-ray topogram of a dislocation cluster that appears at an inclusion in a crystal and produces an analogous growth protrusion.
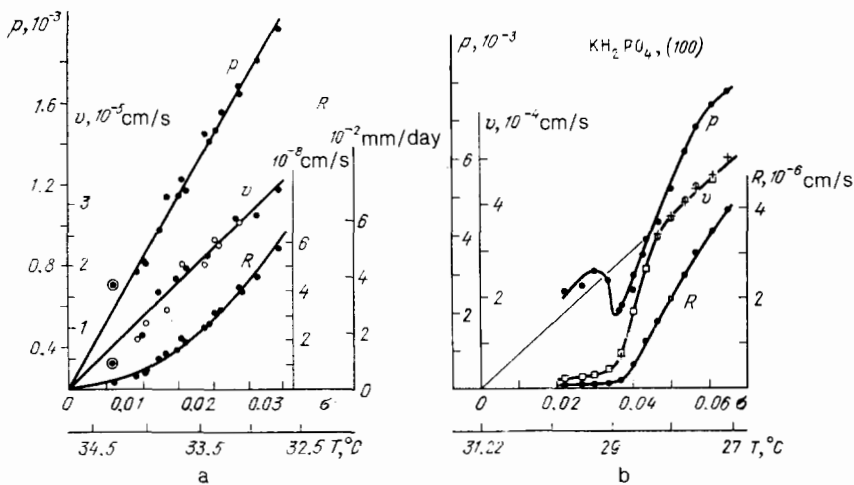
FIG. 2. Dependence of normal edge growth rate R, determined by the slope p of the dislocation growth protrusion and the effective velocity v of step motion, on relative supersaturation σ (see Fig. 1, a): a) along prism edges of ADP crystals, b) along prism edges of KDP (KH_2PO_4) crystals.
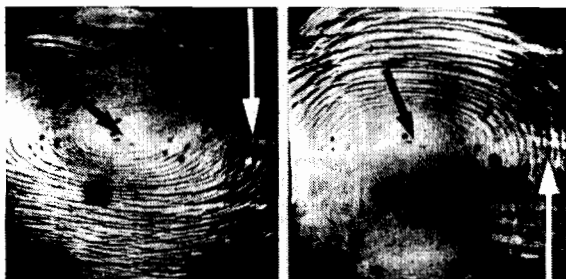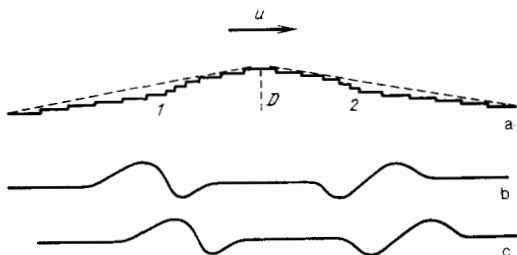

FIG. 3. Dissipative structures (macrosteps) on the slopes of a vicinal growth protrusion created by a dislocation source marked by the black arrow (the direction of solution flux is marked by the white arrow).

FIG. 4. Schematic appearance of a vicinal edge instability: a) edge profile near a dislocation source D; b) supersaturation distribution above the surface in stationary solution; c) the same supersaturation distribution in a solution flowing to the right.

1099   Sov. Phys. Usp. 30 (12), December 1987

Meetings and Conferences   1099

tion of Fig. 4, *b* is shifted to the right by the flowing solution. Because of this shift the trough 1 receives an relatively concentrated solution (maximum supersaturation) and should fill up. The trough 2, on the other hand, receives a impoverished solution that has passed over a step cluster—this trough will deepen and the protrusion slope on the right becomes unstable.

Macrosteps lead to inclusions and other crystal defects, which reduce laser optical strength and result in scattering and anomalous birefringence. By periodically varying the direction of solution flux macrosteps can be avoided even at high (~ 1 cm/day) growth rates.[8,9]

X-ray topographic studies of these crystals revealed the lattice constant to depend on the direction and rate of step growth at a given edge.[5]

[1] A. A. Chernov, Crystallization Processes (in Russian), Nauka, M., 1980 (Contemporary Crystallography, Vol. 3); Usp. Fiz. Nauk **73**, 277 (1961) [Sov. Phys. Usp. **4**, 116 (1961–62)].

[2] A. A. Chernov, L. N. Rashkovich, and A. A. Mkrtchan, J. Cryst. Growth **74**, 101 (1986).

[3] E. Budevski, V. Bostonov, and G. Staikov, Ann. Rev. Mater. Sci. **10**, 85 (1980).

[4] A. A. Chernov and E. D. Dukova, Kristallografiya **14**, 169 (1969) [Sov. Phys. Crystallogr. **14**, 150 (1969)].

[5] A. A. Chernov, L. N. Rashkovich, I. L. Smol'skiĭ *et al.*, Crystal Growth, Vol. 15 (in Russian), Nauka, M., 1986, p. 43.

[6] A. A. Chernov and L. N. Rashkovich, Kristallografiya **32**, 737 (1987) [Sov. Phys. Crystallogr. **32**, 432 (1987)].

[7] A. A. Chernov, Yu. G. Kuznetsov, I. L. Smol'skiĭ, and V. N. Rozhanskiĭ, Kristallografiya **31**, 1193 (1986) [Sov. Phys. Crystallogr. **31**, 705 (1986)].

[8] V. I. Bespalov, V. I. Bredikhin, V. P. Ershov *et al.*, Kvant. Elektron. **9**, 2343 (1982) [Sov. J. Quantum Electron. **12**, 1527 (1982)].

[9] L. N. Rashkovich, Vestnik Akad. Nauk SSSR No. 9, 15 (1984).