

A CONTRIBUTION TO THE INVESTIGATION OF THE AMMONIUM
DIHYDROGEN PHOSPHATE (ADP) CRYSTAL GROWTH PROCESS

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ADP crystals are antiferroelectrics with the Curie temperature of about 148 K. In technology they are used as piezoelectrics. Due to their good transparency and suitability for crystallization they are used in the investigation of crystal growth processes.

Several authors⁽¹⁻³⁾ have already investigated the crystal growth process on ADP crystals. The aim of the present experiment was to investigate the interaction of growth spirals of ADP crystal as well as their influence on the growth rate in the direction $|010|$, on the basis of the experimental curve of growth rate R as a function of supersaturation σ .

ADP crystal seed of $0.5 \times 1 \times 0.5 \text{ mm}^3$ was placed on the bottom of a crystallization cell in which the constant temperature ($23.00 \pm 0.02^\circ\text{C}$) as well as the constant solution supersaturation was maintained. The dimension of the crystals in the direction $|010|$ was measured by means of an optical microscope ocular scale with the magnification of 180x. After the measurements were accomplished the crystal was coated by a thin layer of paraffin oil so that the crystal face relief could be preserved. The palladium-gold-carbon replicas were taken from some of the samples and were afterwards scanned by the electronic microscope.

The dependance $R=f(\sigma)$ in the supersaturation range $0.06 < \sigma < 0.10$ is presented on diagram 1, and in Figs. 1-3 the characteristic relief of the face (100) is shown (the magnification is 11500x). The BCF⁽⁴⁾ dislocation theory of crystal growth in the case of surface diffusion

mechanism gives, for medium values of supersaturations, the dependance $R=b+k\sigma/\sigma_1$, where $\sigma_1=A/\epsilon$ (A and b are the constants for certain crystallization conditions, and ϵ - is the activity of a group of dislocations which characterizes the crystal growth rate); for high supersaturations $R=C\sigma$, where C is a constant.

The experimental results $R=f/\sigma$, shown on the graph have considerable scatter, and at first glance it seems as if they could not be explained by the approximations of the ECF⁴⁾ theory. However, the groups of growth spirals of different activities are formed on the crystal surface, provided the interaction of growth spirals with the centres at a distance less than $9.5 \rho_c$ ⁴⁾ (ρ_c in the spiral critical radius) occurs. Values corresponding to $\epsilon=3;4$ and 5 are calculated using $\sigma_1=0.024$ for $\epsilon=2$, which has been determined in (1). For σ_1 estimated in that way the lines $R=f/\sigma$ are drawn (graph) in the interval of the experimental values of σ . From the graph it can be seen that in the supersaturation range from 0.06 to 0.07 the experimental points follow only the line with $\sigma_1 = 0.024$ ($\epsilon=2$) so that it could be concluded that the crystal growth in that range of supersaturation takes place according to the surface diffusion mechanism. For supersaturations from 0.07 to 0.085, the experimental points follow the line with $\sigma_1=0.015$ ($\epsilon=3$) so that in this supersaturation range the spiral growth, with possible interactions of spirals, takes place. For supersaturations $\sigma > 0.085$ the dislocational mechanism of growth decreases and a new one appears - the mechanism of surface nucleation. The relief of the crystals that have grown under various supersaturations confirm these conclusions. Fig. 1 shows the layer growth of ADP crystal from a dislocational centre of small activity ($\epsilon=2$) for supersaturation $\sigma=0.082$. Fig. 2 shows the layer crystal growth from a dislocational centre of greater activity at $\sigma=0.097$. The boundaries of the crystal growth layers are meandering but still dis-

cernable. Fig. 3 shows the crystal growth at $\sigma=0.102$. The beginnings of surface nucleation appear on the rough layers, and that indicate the complexity of the mechanism of crystal growth in this range of supersaturation.

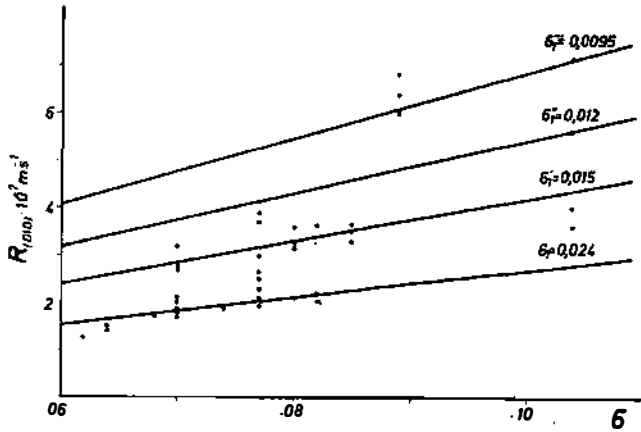


Fig. 1.

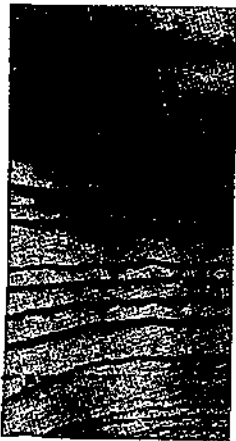


Fig. 2.

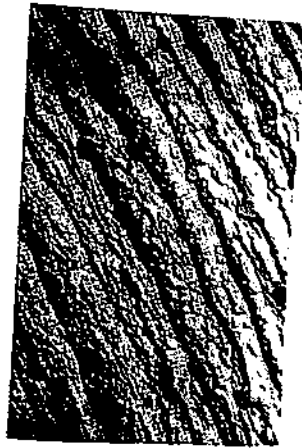


Fig. 3.

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