GROWTH RATE DISPERSION AMONG ADP-MICROCRYSTALS. TEMPERATURE INFLUENCE ON THE RELATIVE WIDTH OF GAMMA DISTRIBUTION

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Amonium dihydrogen phosphate, ADP, is aqueous solution growth crystal. At supersaturation less than $\sigma = 0{,}07$ crystals grow by completing the growth steps generated by screw dislocations /1/. According to the spiral growth theory, developed by Burton, Cabrera and Frank /2/, linear growth rate is:

$$R = \frac{C}{\sigma_1}\ \sigma^2 \tanh \frac{\sigma_1}{\sigma},$$

where the parameters C and σ_1 are given by:

$$C = \frac{kT}{h}\ \beta C_o \lambda N_o V_o\, e^{-\frac{\Delta G}{kT}}$$

$$\sigma_1 = \frac{9{,}5}{\epsilon}\quad \frac{\gamma}{kT}\ \frac{d}{X_s}$$

β, C_o – constants ≈ 1, λ – mean free path of growth units in the solution, N_o – the equilibrium value of the volume solute density, V_o – volume of growth units, ΔG – dehidratation energy, ϵ – activity of dominant dislocation group, d – lattice spacing, X_s – mean free surface diffusion distance, γ – the edge free energy of a growth unit in the step, T – absolute temperature, σ – the supersaturation, k – Boltzmann constant, h – Planck constant

This equation is obtained under assumption that growth steps are equidistant and monomolecular. This is valid for very low supersaturations.

There is experimental evidence that under the constant external conditions /σ and T/ different crystals of the same material grow at different rates. It was shown in paper /3/ that variations in growth rate at σ = 0,04 and T = 27,6°C can be represented by a gamma distribution:

$$\psi(R) = \frac{R^a e^{-\frac{aR}{b}}}{\Gamma(a+1)\left(\frac{b}{a}\right)^{a+1}},$$

where a is width parameter and b is size parameter.

Our previous measurements suggested that gamma distributions occured in the case of $\sigma < \sigma_1$, as well as in the case of $\sigma > \sigma_1$. When the supersaturation is low $\sigma < \sigma_1$, steps are monomolecular and the dispersion of growth rate could be related to different activities of dominant dislocation group /$\epsilon > 1$/ of the different crystals, as BCF equation suggests. When the supersaturation is high $\sigma > \sigma_1$, growth spirals do not cooperate any more and parameter ϵ /$\rightarrow 1$/ has no influence on the value of the growth rate. However, there is another reason for growth rate distribution. At such supersaturations growth steps become too close, so that they form macrosteps and kinematic waves with different hights and slopes and with different growth rates on the surface. Naturaly, in both cases, besides surface structure, the presence of impurities in the adsorption layer esentially affects the growth rate. It was observed that fluctuations of linear growth rate decrease as the supersaturation increase.

In this paper we intend to investigate the influence of temperature on the relative width of the growth rate distribution. The data were obtained from observations of a large number of crystals growing under the same supersaturation σ = 0,02 /$< \sigma_1$/ at several temperatures. The experimental distribution of growth rate for each temperature is represented by histogram with frequences normalized to the total number of observed crystals. Experimental results are best fitted by the gamma distribution. On the Fig. 1.

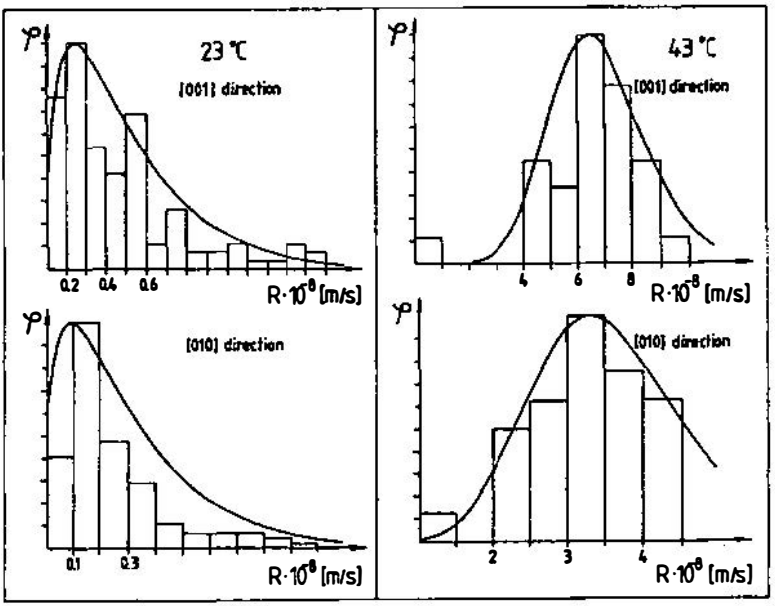

Fig. 1. Gamma distributions measured at 23 and 43°C

two distributions measured at 23°C and 43°C are presented as illustration. Parameters of all gamma distributions for different temperatures, as width parameter a, size parameter b, mean values of growth rate $\bar{R} = \frac{a+1}{a} b$, standard deviation σ and coefficient of variation c. v. $= \frac{\sigma}{R} = \frac{100}{\sqrt{a+1}}$ % are given in Table I.

Table I — Parameters of gamma distributions for different temperatures

†	[001] direction					[010] direction				
[°C]	a	b 10^{-8}m/s	$\bar{R}$ 10^{-8}m/s	σ 10^{-8}m/s	c.v.	a	b 10^{-8}m/s	$\bar{R}$ 10^{-8}m/s	σ 10^{-8}m/s	c.v.
23	0,55	0,25	0,70	0,56	80%	0,46	0,08	0,25	0,21	83%
33	6,00	1,25	1,46	0,35	38%	4,60	0,45	0,55	0,23	42%
43	20,80	6,25	6,55	1,40	21%	20,10	3,25	3,40	0,70	22%
53	80,00	12,00	12,15	1,35	11%	34,70	7,50	7,72	1,29	17%

On the basis of data given in Table I it is obvious that relative widths, i.e. coefficients of variation, decrease as the temperature increases for both crystallographic directions. This could be explained by attenuation of influence of the impurities present in the solution. It is well known that the concentration fluctuations in adsorption layer could affect the time dependence of linear growth rate /4/. It was observed that growth rates change their values oscilatorlly from maximal value which corresponds to growth without impurities to zero. Therefore mean values of growth rates could be very different depending on the time spent in fast or slow regime of growth. However, when the growth rates increase with the supersaturation or temperature increase, differences in the values of growth rate in superclean solution and in solution with impurities become smaller and smaller. Our results are presented graphically in the form of temperature dependence of width parameter $a^{1/3}$ of the gamma distribution, fig. 2. It is obvious that function $a^{1/3}$ (t) could be aproximated with straight line. That means that coefficient of variation changes as $(\text{temperature})^{-3/2}$ in temperature interval 23 — 53°C.

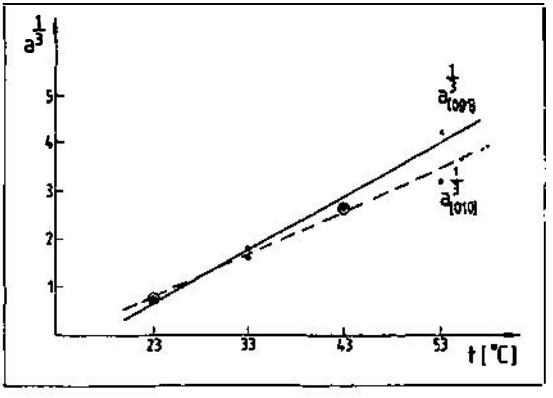

Fig. 2. Temperature dependence of the width parameter $a^{1/3}$

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