

## EQUILIBRIUM AND GROWTH KINETICS OF POLAR CRYSTALS

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Several papers by Kern and Monier<sup>1)–3)</sup> and Cadoret and Monier,<sup>4),5)</sup> showed the fundamentals of equilibrium properties and growth kinetics of the complementary forms  $\{hkl\}$  and  $\{\bar{h}\bar{k}\bar{l}\}$  belonging to polar crystals.

From growth experiments on sphalerite, wurtzite, chalcopyrite, Nisulphite hexahydrate, GaAs and other structurally analogue compounds, these authors inferred that the more developed between two complementary forms, is the one showing on the outermost layer the most polarizable atoms.

The role of the solvent moreover is such that it can invert the ratio of the growth rate  $R(hkl)/R(\bar{h}\bar{k}\bar{l})$ . It is a complex phenomenon depending on if the face is a perfect or imperfect one, and if it is growing at very low or at very high supersaturation.

To check the theory of polar crystal growth from solution we performed systematic experiments on two types of crystals, sucrose ( $C_{12}H_{22}O_{11}$ ) and epsomite ( $MgSO_4 \cdot 7H_2O$ ), the structure of which may be described in terms of dispersion forces + hydrogen bonding and Coulomb forces + hydrogen bonding respectively.

For both compounds growth isotherms ( $R, \sigma$ ) were obtained from pure and impure aqueous solutions. Growth rates were measured in a large supersaturation range and at low crystallization temperature ( $25 \leq T_c \leq 40^\circ C$ ), where the surface diffusion was known to be the rate determining step.

Our experimental method<sup>6)</sup> allowed us to measure the face-by-face growth kinetics “simultaneously” either on a large population of single crystals free falling in the growth solution, or on a single crystal subjected to a rotatory-translatory motion.

For both sucrose and epsomite crystals the character of each crystallographic form was determined<sup>7),8)</sup> by applying the Hartman and Perdok method in a first step; secondly, for the corresponding surface profiles, we calculated both surface and attachment energies and constructed the Wulff’s  $\gamma$ -plot and the growth form of the crystal in a steady state. A comparison is

made between theoretical growth morphology and “morphodromes” deduced from experiments.<sup>9)</sup>

### 1. *Growth Kinetics in Pure Solutions*

The difference in the growth rates of the complementary forms  $\{111\}$  and  $\{\bar{1}\bar{1}\bar{1}\}$  of epsomite crystals is independent on the supersaturation over a wide range of  $\sigma$  values, but is markedly affected by the crystallization temperature. On the contrary the difference in the growth rate of the complementary forms  $\{110\}$  and  $\{\bar{1}\bar{1}0\}$  of sucrose crystals strongly depends on the supersaturation, as it ensues from  $(R, \sigma)$  “stepped” curves, over the whole range of temperature.

This “stepped behaviour” of the growth isotherms is particularly shown by the complementary polar forms, but other non polar  $\{h01\}$  forms as well, exhibit the same trend. The general look agrees with the sequence of mechanisms theoretically proposed by Christoffersen and Nielsen:

— at low  $\sigma$  values the spiral growth is faster than the parallel two-dimensional nucleation between spiral steps. The two-dimensional nucleation reduces the actual equidistance between steps, anticipating towards lower values the transition from a parabolic to a linear kinetic relationship. A second jump appears on the isotherms at a  $\sigma$  value which is twice the  $\sigma$  value of the first jump (nucleation of double height embryos?).

Such complex isotherms are noticed, in our knowledge, for the first time.

### 2. *Growth from Impure Aqueous Solutions*

The growth habit is strongly affected by small amounts of suitable impurities. Two main effects of different nature occur:

— the complementary forms  $\{110\}$  and  $\{\bar{1}\bar{1}0\}$  of sucrose crystals behave, on adsorption of raffinose, differently. This is a stereochemical effect: the possible conformations of the kinks are such that the probability that the raffinose can form bonds with its fructose unit is higher at the right pole  $\{110\}$ .

— the second kind of poisoning concerns the surface between steps rather than the kinks. We observe that impurities as KCl and/or NaBr (sucrose solutions) and Glauber’s salt and/or Borax (epsomite solutions) dramatically affect the growth rates of several faces. In particular, in the case of epsomite, these impurities stop the growth of  $\{111\}$  faces, while their complementary ones continue growing: so the different surface structure of the two forms is nicely evidenced. This phenomenon can be understood considering a 2D-epitaxy between low index faces of Borax (or Glauber’s salt) and  $(111)$  surface of epsomite. The conditions to be met for a 2D-epitaxy can happen are: reticular coincidence and crystal-chemistry consistency.

It is the last the rule selectioning between complementary surfaces. Reticular coincidence calculations and systematic observations of inhibition

of the growth of (001) and (101) faces of sucrose, allow to infer that crystal chemistry conditions are also fulfilled and a 2D-epitaxy of the above mentioned impurities occurs on these faces.

#### REFERENCES

- 1) KERN, R. and MONIER, J. C. (1955): *Bull. Soc. Franç. Minéral. Crist.*, **78**, 585.
- 2) MONIER, J. C. and KERN, R. (1955): *Compt. Rend.*, **240**, 2338.
- 3) KERN, R. and MONIER, J. C. (1955): *Compt. Rend.*, **240**, 2430.
- 4) CADORET, R. and MONIER, J. C. (1960): *Compt. Rend.*, **250**, 3680.
- 5) CADORET, R. and MONIER, J. C. (1965): Adsorption et Croissance Cristalline-152° Colloque international du CNRS.
- 6) MANTOVANI, G., VACCARI, G., ACCORSI, C. A., AQUILANO, D. and RUBBO, M. (1983): *J. Crystal Growth*, **62**, 595.
- 7) AQUILANO, D., FRANCHINI ANGELA, M., RUBBO, M., MANTOVANI, G., and VACCARI, G. (1983): *J. Crystal Growth*, **61**, 369.
- 8) RUBBO, M., AQUILANO, D., FRANCHINI ANGELA, M. and SGUALDINO, G. (1985): *J. Crystal Growth*, **71**, 470.
- 9) AQUILANO, D., RUBBO, M., VACCARI, G., MANTOVANI, G. and SGUALDINO, G. (1984): in *Industrial Crystallization 84*, Ed. S. J. Jancic and E. J. de Jong, pp. 91.

#### DISCUSSION

Rodriguez

As the attachment energy in opposite faces of a polar crystal is the same, I wonder if the difference in crystal growth rates are due only to the different polarization of the adsorption layer on the surfaces. Perhaps this kind of studies could provide a method of clarifying the structural and kinetic influence of the adsorption layer.

- A: The concept of  $E_{att}$  does not work well to distinguish the polar complementary forms. In solution growth we need a model of the adsorbed layer from which we can calculate the differences between the opposite faces.

Tsukamoto

How did you measure the velocity of the solution? The velocity of the solution seems not be proportional to the velocity of the small particle which you put in the solution.

- A: I agree with you, but I am interested in the relative motion of the crystal with respect to the solution and we measured the relative motion of the particle with respect to the seed.

Chernov

1. How do you explain the jump on the  $R(\sigma)$  curves?
2. Did you work in kinetic regime? What is the origin of various levels of

plateau at different thickness of crystals?

- A: 1. I can only formulate one hypothesis: if the surface diffusion is the rate determining step, the jumps occurrence can be due to a 2D-nucleation in between the steps. This sudden increase of  $R$  changes over to a linear law because of the overlapping of the diffusion fields around the spiral steps and the steps of the nuclei. The second jump ( $\sigma \approx 8\%$ ) is surprising too. But if a 2D-nucleation (of 2h-nuclei) can occur this also can be explained. The relative values of  $\Delta G_{2D}^{2h}$  out  $\Delta G_{2D}^h$  agree with the corresponding supersaturation values.

But all that must be proved. No interpretation at the moment.

2. As concerning the kinetic regime, I suppose that 1.5–2 cm/sec are not sufficient to work in kinetic regime. An interesting experiment (Aquilano and Boistelle, 1975) was done on (110) faces of different size  $L$  (paraffin crystals) exposed to the solution flow ( $u$ ) perpendicular to the faces. At given  $T_c$ ,  $\sigma$  and  $u$  values,  $R_{110}$  strongly decreases when the size  $L$  of the face increases; the kinetic regime, for a given  $L$  size, is reached only when  $u \geq 4.0$  cm/sec. We didn't publish these results because we have not a quantitative interpretation. Now I think that this is not depending on the dislocation lines but do the change of the diffusion field thickness around the face. When  $L$  is not  $\infty$  the profile and  $\delta$  (thickness of the diffusion field) should vary, but I do not know how.

Schneer

1. What was the shape of the seed? Were they cut or growth faces?
2. In answer to the previous question, I believe that Wulff about 1901 measured what is called the capillary constant of distinct faces by their growth rates in solution—so we are proceeding in circles until we know the structure.

- A: The seed were as grown faces.

Van der Eerden

Is it possible to give, in the classical thermodynamical sense an independent definition of  $\gamma(hkl)$  and  $\gamma(\bar{h}\bar{k}\bar{l})$  of a polar crystal? Or is it really necessary to have knowledge about the relaxation and adsorption processes after cleaving a crystal.?

- A: According to our discussion it may be possible, cutting a polar crystal (it must be sufficiently thick in order to avoid the curvature due to the surface tension on  $hkl$ ) and putting  $(\bar{h}\bar{k}\bar{l})$  in contact with a non polar crystal surface; waiting for reaching the equilibrium and measuring the contact angle—the same must be done for the complementary  $(hkl)$ .