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Some Physical-chemical Processes Involved in the Generation of Vacancies During Crystal Growth

By *J. L. Leray* (Paris)*)

With 7 figures on a plate

Summary. Review of some physical and chemical processes contributing to formation of vacancies during crystal-growth as observed on dihydrated copper chloride: diffusion of solute and impurities; absorption of additives in the course of regular growth; oriented dendritic growth in heterogeneous solutions; spherulithic growth.

The observation of crystal growth from an aqueous solution through an interference microscope leads one to identify and to follow up several physical and chemical processes which often initiate the building of vacancies within single crystals or polycrystalline clusters. In the course of our work on dihydrated copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$)¹), we had the opportunity to take a photographic record of some of those processes, which might be of some interest to the petrographer (DEICHA, 1964).

Copper chloride crystallizes in the orthorhombic system, generally in the form of long prismatic needles parallel to the c-axis, the (001) bases growing much faster than the (110) elongated faces (BECKMANN, 1959).

Fig. 1 shows such a growing monocrystalline seed with the (001) face perpendicular to plane of picture and an isoconcentration curve around one $\langle 110 \rangle$ edge. The widely different growth rates along $\langle 001 \rangle$ and $\langle 110 \rangle$ directions produce there a higher saturation at the corners and edges of this (001) base than in its central part. As a result, diffusion currents which set up along the orthogonal trajectories of the isoconcentration curves will accumulate on the corners and edges of the (001) face. The spatial distribution of both parameters in the solution, namely higher concentration and diffusion on the outer parts, leads to higher growth rates and initiate the birth of local dendrites in this area during quasi-regular growth, that is in the transition stage between regular and dendritic growth. It becomes evident that the further extension of such

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dendrites from the edges of the growing face will contribute to the formation of a vacancy in the middle zone.

Variations of the growth rate, however, might be produced, not by anisotropy of the crystalline structure of the solid phase, but by heterogeneity of the surrounding fluid in which the seed develops. As an example, fig. 2 shows how a gas bubble sticking to the growing face will be simultaneously repulsed and swallowed by the crystal in due course. Focussing on the lower part of this inclusion reveals a secondary recrystallisation of the wall inside the cavity. The whole process may be compared with the „spraying“ of quartz crystals in alpine splits.

The aforementioned effects take place in pure aqueous solutions, however they may be either enhanced or hindered with suitable „impurities“ in the mother liquor. It has been shown elsewhere (LERAY, 1968) that an additive like glycine which raises the solubility of copper chloride in water will eventually produce sharp extrema of supersaturation respectively at the middle and outer parts of the growing face. The growth which is already slowed down overall by physical or chemical absorption of the impurity on the crystalline surface, will be practically blocked in the central part and regular in the outer part. It will generate a central vacancy, the size of which depends upon the value and extent of the supersaturation minimum as shown on fig. 3: the large base of vacancy is produced immediately after a sharp decrease of temperature, the „width“ of this inclusion decreases simultaneously with overall concentration of the solution as the crystal grows at constant temperature in a closed cell. This width vanishes eventually at the pointed tip of the cavity, when growth becomes regular again over the whole face.

The role of an additive such as gelatin which lowers the solubility of CuCl_2 , is illustrated on fig. 4. In this reverse case supersaturation maximum is located in the central portion of the growing face and produces eventually a precipitation in the immediate vicinity of the face. The precipitates – or perhaps coprecipitates – may be later swallowed as inclusions by the growing crystal.

When specific absorption on the growing face prevails over diffusion, the absorbed layer along preferred orientations reveals a set of growing islands im-

Legend Plate

Left side: From up to bottom

Fig. 1: Nascent dendrite on a (001) face, X 150

Fig. 2: Gas bubble inclusion, X 120

Fig. 3: Liquid inclusion, X 120

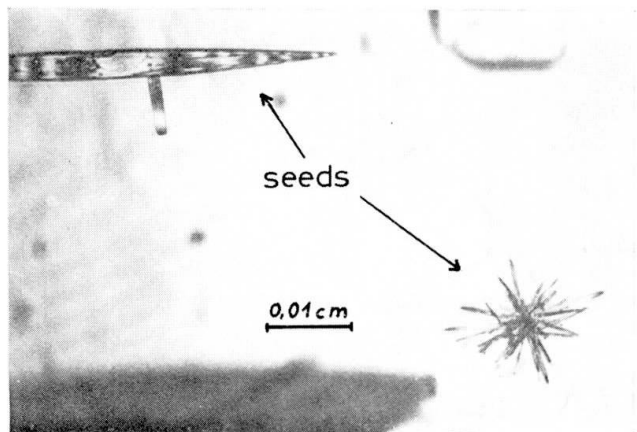
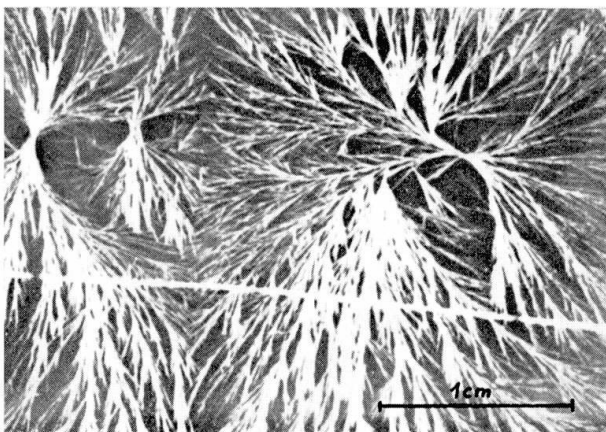
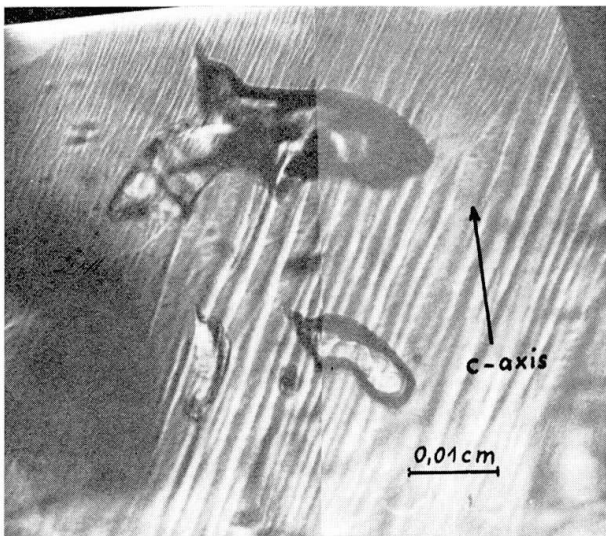
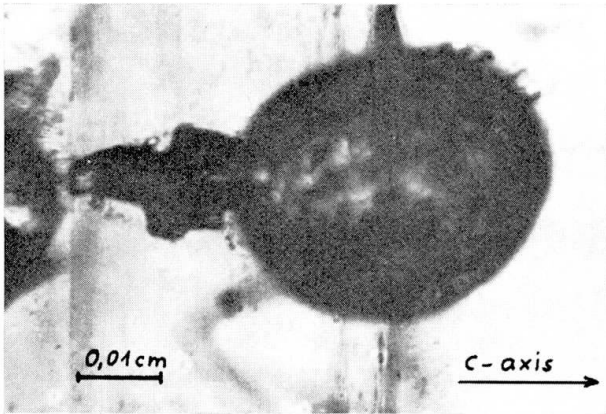
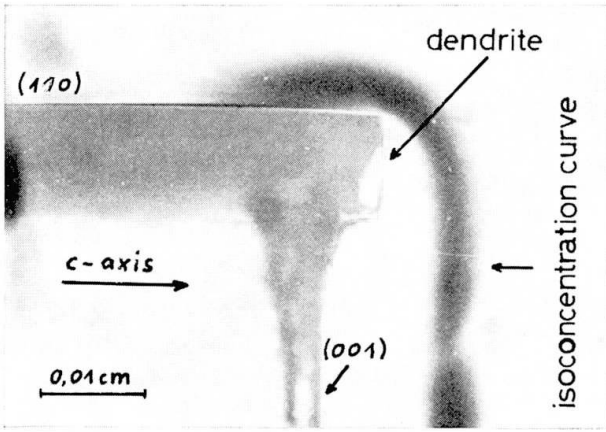
Fig. 7: Dendritic pattern with „leave-like“ vacancies, X 2.7

Right side: From up to bottom

Fig. 4: Precipitation in front of face growing in aqueous solution containing 1% gelatin, X 120

Fig. 5: (001)-growing face in solution containing 1% mandelic acid, X 120

Fig. 6: Spherulitic and twinned seeds, X 120



bedded in a network of blocked grooves. Fig. 5 shows the (001) growing surface in the presence of mandelic acid which seems to display the mosaic structure of the seed. This configuration of grooves may be compared to the filamentary one present inside some gemstones.

The events associated with rapid or dendritic growth may be related not directly to proper fluid inclusions within single crystals, but to spaces left out by polycrystalline clusters, which have not yet been extensively studied by petrographers.

Fig. 6 shows the precipitation of mono and polycrystalline seeds triggered by sharp undercooling of 15° C about. Subsequent growth is no longer controlled by diffusion of the solute; it will proceed preferentially towards the regions of highest supersaturation: the dendrites tend to lie along the orthogonal trajectories of the isoconcentration curves.

Here the heterogeneity of the solution is not produced initially by the crystallisation process, but by external factors acting upon the fluid phase (evaporation, fluid flow, thermal gradient, etc...). The two dimensional vacancies of the pattern on fig. 7 were obtained by V. HAHN (1962) among others, who let evaporate slowly a thin layer of a diluted solution containing additives of biological origin.

On this picture, the „two buds” pattern is similar to the “zweiblatt” studied by POPOFF (1934) who interpreted it as the meeting curve of dendrites belonging to the alternate forms of a polymorphic substance crystallizing at slightly different speeds. The assembly of sections of logarithmic spirals builds up the pattern, in the same way as the process suggested by LEONHARDT (1953).

Thus the various modes of “spherulithic growth” (RÖSCH, 1967) lead to similar vacancy patterns, hence requiring extreme caution when one attempts to assign a formative process to a completed configuration.

BIBLIOGRAPHIE

- BECKMANN, H. (1959): Über Keimbildung, Einkristallwachstum und Auffächerungswachstum von $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in rein-wässrigen und eiweisshaltigen Lösungen. Diss., Bonn.
- DEICHA, G. (1964): L'expansion actuelle des recherches sur les inclusions fluides des minéraux et des roches. *Annales Soc. Géol. du Nord*, 84, p. 83.
- HAHN, F. V. (1962): Thesigraphie – Untersuchungsmethode an biologischen Objekten, insbesondere Nahrungsmitteln. F. Steiner Verlag, Wiesbaden.
- LEONHARDT, J. (1953): Zum Keimbildungsproblem bei Strahlungskristallisaten und gerillten Kristallen. *Tscherm. mineral. petrogr. Mitt.* 4, S. 382–385.
- LERAY, J. L. (1968): Growth Kinetics of hydrated cupric chloride. *J. of crystal growth*, 3/4, p. 344.
- POPOFF, B. (1934): Spherolithenbau und Strahlungskristallisation. *Latv. farm. Zurn.*, Riga.
- RÖSCH, S. (1967): Beobachtungen und Gedanken über das Sphäritenwachstum der Kristalle. *Tscherm. mineral. petrogr. Mitt.* 12, S. 290–298.