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A study of the growth and growth mechanism of potassium dihydrogen orthophosphate crystals from aqueous solution

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Observations made during the growth of potassium dihydrogen orthophosphate (KDP) crystals from aqueous solution are recorded. A model of the growth process is given which attempts to explain the origin of the features observed.

1. Introduction

Studies of the growth of potassium dihydrogen orthophosphate (KDP) crystals from aqueous solution have been made by several groups of workers [1–4]. In these studies small-volume crystallization equipment was used, and growth was induced at constant temperature by circulation of a saturated solution through the growth cell. Since KDP crystals are potentially useful in electro-optic electronic devices, such crystals were grown for testing these applications and the observations made during the course of this work are described below. In addition, the relationship to the growth mechanism is discussed.

2. Expermental procedure

The equipment used has been described previously [5]. The baths hold 4 l of solution and the temperature is controlled and varied by means of a motorized Beckmann thermometer. Cooling rates from 10° C per day to 0.2° C per day were available. Starting temperatures were between 38 and 42° C and growth experiments at constant temperature were performed at 39° C. The solutions were prepared from Analar grade potassium dihydrogen orthophosphate and were filtered, if required, using a heated filter funnel fitted with a glass frit filter pad. Seeds were either crystal plates cut at 90° to the z-axis of the crystals or the tetragonal pyramid caps of crystals. These were measured, weighed and mounted at one end of a rubber stopper in which a slot of the required size had been cut. The stoppers were supported by a thermometer which fitted into a hole drilled into the stopper at the end opposite to the seed. The solution was stirred by an independent paddle rotating at 700 rpm as measured and checked by a stroboscope. The seed mount could be rotated at 1 rpm with a change of direction every minute. The linear rate of growth of the crystal was monitored by means of a cathetometer and telescope focused on a selected point of the crystal. The range of experiments described below involved the use of two baths. The baths were not completely sealed and solvent loss by evaporation was experienced. This loss was measured by means of a graduated dipstick. The cooling rate used was obtained graphically by plotting temperature readings of the control and support thermometers against time. Readings of the position of the tip of the tetragonal pyramid and one horizontal edge of the pyramid were made. The axial growth rate was obtained graphically from plots of position against time. In addition, each crystal was weighed on completion of growth with all other crystals in the bath to give the total crystal weight formed during growth. The axial temperature gradient in the baths was measured. Crystals were grown with no stirring in the bath or no rotation of the crystal or both. The axial distance grown was either measured directly on removal from the bath or obtained from the cathetometer readings corrected for magnification by the liquid (1:1.184) and the crystals were measured along the remaining two directions at the pyramid end.

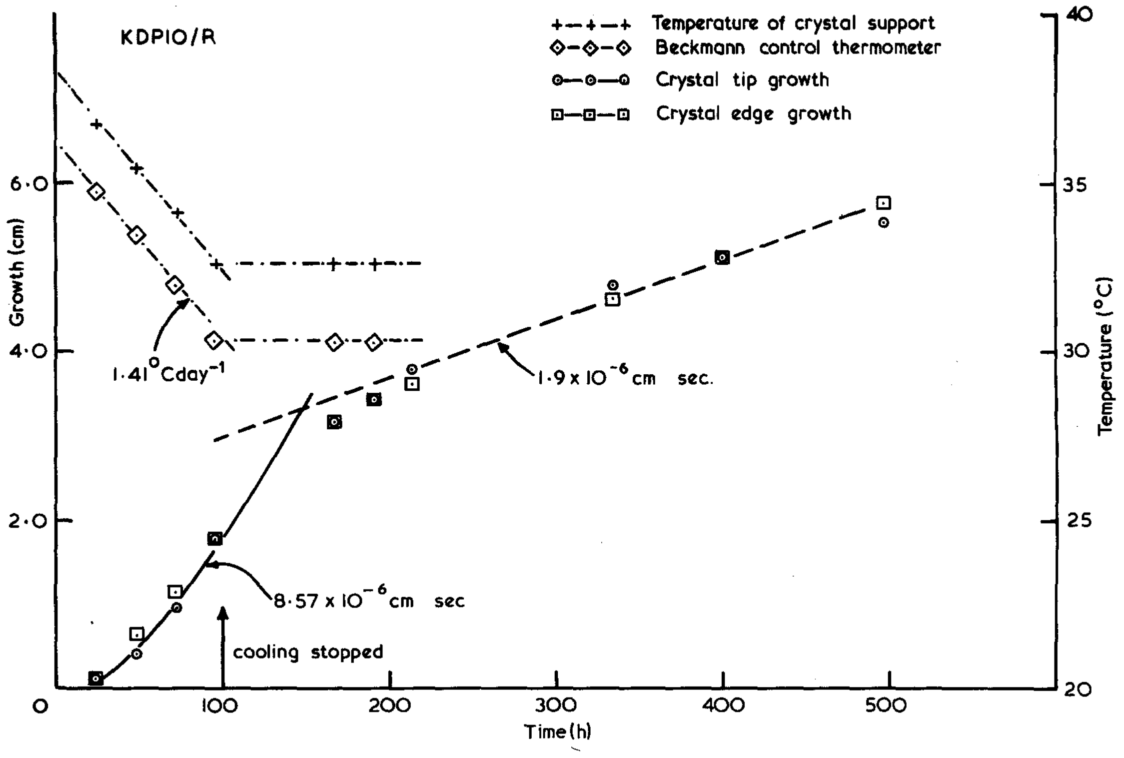

Figure 1 Axial growth rate and temperature change plot with time. Growth by cooling, showing effect of stopping cooling.

3. Results

Fig. 1 shows graphically the growth of potassium dihydrogen orthophosphate by cooling the solution. Similar plots were obtained from growth by evaporation of the solution. The plots were obtained by plotting the position of the tip and horizontal edge of the pyramid terminating the crystals against time. In each case a portion of the growth near the start of the growth period where the growth rate was slower than attained later. Fig. 2 is a plot showing the effect of ceasing stirring and crystal rotation and some after growth started by cooling. There is a short period of temperature change after movement was stopped, then growth continued. During the former period grooves appeared in the vertical faces of the crystal, as shown in Fig. 3. This latter effect also appeared in other crystals grown with no hydrodynamic fluid flow in the system. Careful examination of these plots showed they were curves. As a result, measurements of the growth rates were made on those portions of such curves where the growth rate was nearly linear. Fig. 1 also shows that when cooling has been deliberately stopped, growth continued by evaporation. It is also clear that the points at which measurements were taken advance at the same rate. Occasionally, a temperature difference was observed between the two thermometers, one at the centre and one at the edge of the bath separated by a distance of 45 mm. However, this temperature difference and cooling rate were not related. The temperature difference from surface to base of the baths was 0.1° C maximum. Using graphs like Fig. 1, the cooling rate and axial rate were obtained for several cooling rates. The results are recorded in Table I. These results show that at high cooling rates growth takes place on all faces of the crystal whereas at low cooling rates growth is mainly confined to the four facets of the tetragonal pyramid in which the crystals terminate. In addition, at high cooling rates the amount of crystalline material which formed in other parts of the bath was very much higher than at low cooling rates. Crystals grown at high cooling rates were very much more susceptible to cracking and the presence of inclusions and veils. At low cooling rates, growth by evaporation or growth without stirring usually produced tapering of the crystals, as the dimensions recorded in Table I indicate.

From the measured results for axial growth there does not appear to be a strong relationship

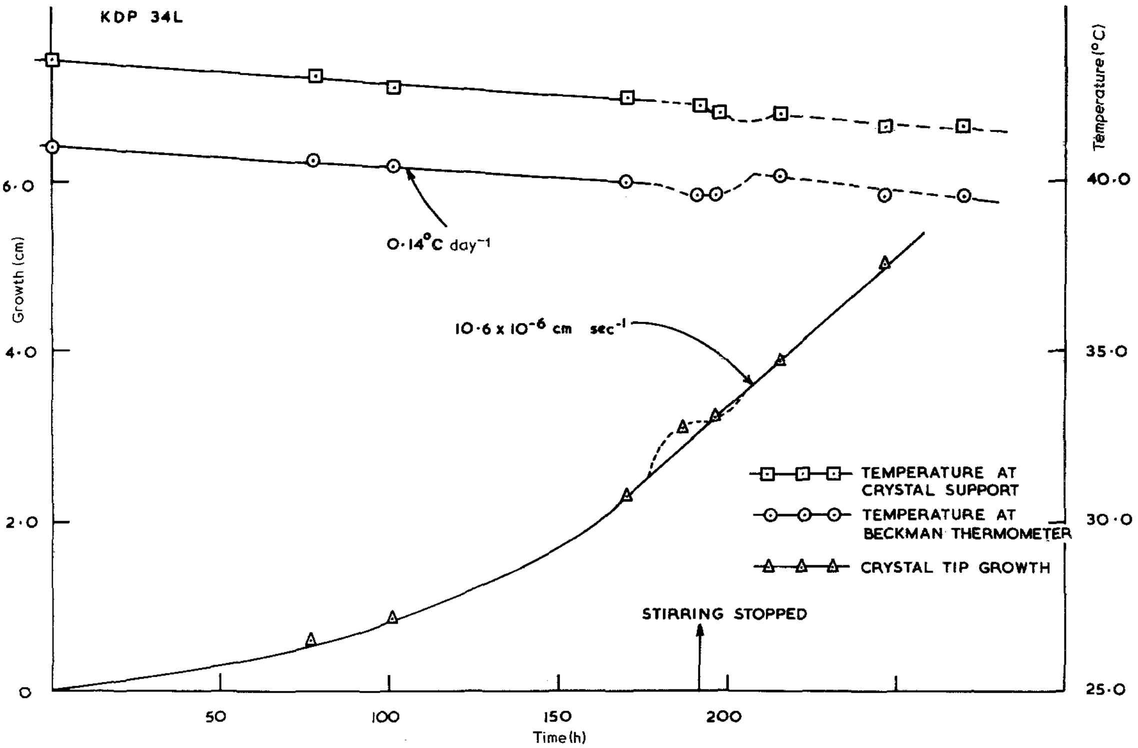

Figure 2 Axial growth rate and temperature change plot with time. Growth by cooling, showing effect of stopping fluid movement.

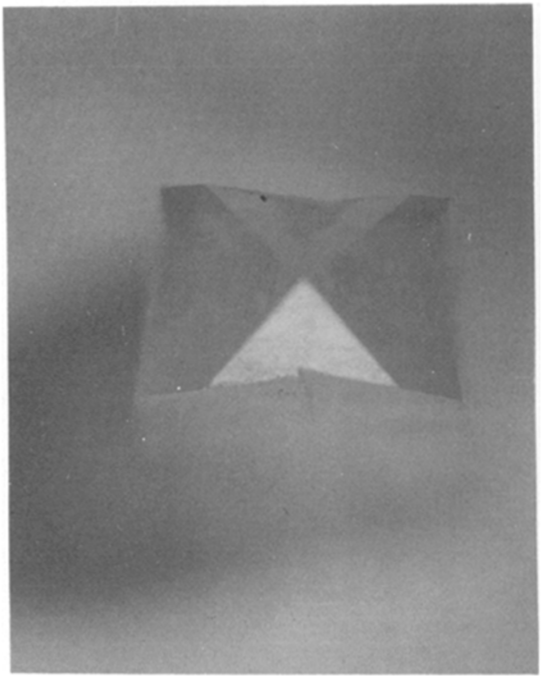

Figure 3 End on photograph of a KDP crystal showing development of grooves in vertical faces.

between this and the measured cooling rate. These results include some growth by evaporation but, as Table I shows, the volume reduction by evaporation was often the same and if correction is made for the amount grown by evaporation, using the measured growth rate by evaporation on Table I, the corrected results produce the same conclusion. The results given in Table I include measurements of growth rate for growth with stirring and crystal rotation, for growth with stirring only and growth without stirring or crystal rotation. The results for the latter indicate that the axial growth rate was similar to that measured with stirring present. However, the significant difference was the amount grown in other parts of the bath. This was very much greater than with stirring and indicates that whatever effect stirring has on crystal growth it also reduces the degree of random crystal growth by homogenizing the solution.

4. Discussion

The results given above demonstrate that during growth of crystals of KDP the growth rate during a given experiment is not a linear function of time

TABLE I

Crystal code	Seed type	Seed dimensions (mm) x y z	Seed weight (g)	Crystal dimensions (mm) x y z	Crystal weight (g)	Total weight (g)	Starting temperature (° C)	Growth period (*d*)	Cooling range (° C)	Measured cooling rate (× 10^5 ° C sec^{-1})	Measured axial growth rate (× 10^6 cm sec^{-1})	Volume reduction of solution (cm^3)
KDP26/R	Cap	18 × 21 × 12	5.7	30 × 32 × 34	51.2	227.7	42.5	2.25	16.1	7.9	17.3	133
KDP28/R	Cap	19 × 23 × 13	7.0	24 × 35 × 30	45.5	244.9	41.7	2.25	15.2	7.7	12.6	155
KDP27/L*	Cap	20 × 22 × 16	7.0	24 × 36 × 34	56.3	141.5	38.3	2.25	10.5	6.4	14.3	148
KDP25/L*	Cap	18 × 25 × 12	8.0	28 × 31 × 35	70.6	262.0	39.4	3.2	15.4	5.4	20.0	150
KDP16/L	Cap	21 × 23 × 14	8.0	46 × 46 × 38	111.4	317.2	39.7	3.9	17.9	5.3	11.1	155
KDP15/R	Cap	16 × 25 × 12	5.1	20 × 36 × 36	77.0	257.7	39.8	4.3	15.4	4.2	9.4	140
KDP18/R	Plate	17 × 25 × 4	4.1	25 × 39 × 40	78.6	306	41.5	5.8	14.9	3.0	5.6	200
KDP19/R	Cap	17 × 22 × 12	4.8	24 × 34 × 37	65.8	209.2	42.6	4.6	10.2	2.6	6.9	156
KDP12/L	Cap	17 × 20 × 15	9.2	31 × 34 × 43	79.5	154.3	39.8	6.4	9.9	1.8	6.6	100
KDP17/L*	Plate	16 × 24 × 6	4.5	14 × 26 × 38	55.0	180.6	39.9	5.8	8.6	1.7	7.7	90
KDP20/L*	Cap	20 × 26 × 15	8.8	21 × 28 × 42	59.0	139.2	39.2	6.1	8.6	1.6	6.9	78
KDP30/R	Cap	18 × 20 × 11	3.6	18 × 19 × 50	35.3	35.3	40.0	7.0	5.6	0.8	7.6	100
KDP22/R	Cap	18 × 24 × 12	6.4	18 × 27 × 52	56.7	77.1	41.5	9.6	6.9	0.8	6.8	150
KDP31/R†	Cap	17 × 17 × 10	3.1	15 × 16 × 27	14.8	176.1	40.3	9.6	6.6	0.9	5.2	163
KDP21/L*	Cap	20 × 34 × 18	16.6	18 × 30 × 56	74.4	75.0	36.7	11.8	5.3	0.6	8.3	100
KDP29/L	Cap	15 × 21 × 10	3.7	14 × 18 × 47	32.3	37.7	39.1	7.7	3.7	0.6	10.4	90
KDP32/L†	Plate	18 × 25 × 3	2.9	15 × 22 × 33	24.8	214.5	39.1	9.0	3.8	0.6	3.6	446
KDP35R†	Plate	21 × 29 × 4	5.5	15 × 23 × 34	33.7	112.3	39.1	17.0	2.4	0.25	2.7	124
KDP23/L*	Cap	18 × 30 × 10	6.7	10 × 23 × 32	27.4	29.6	38.5	19.0	Constant	None	0.8	200
KDP24/L	Cap	18 × 27 × 11	5.8	10 × 22 × 42	29.3	31.1	39.3	19.0	Constant	None	3.4	200

* Crystal *not* rotated.

† Crystal *not* rotated, paddle *not* rotated.

either during growth by cooling or evaporation of the solution. The growth rate by cooling, measured as described, was within a factor of two of that previously measured [1]. The period of slower growth was longer for growth by evaporation and the growth rate was slower by evaporation in the same temperature region as used for cooling. When the growth process was changed from that by cooling to that by evaporation a smooth change of growth rate was observed. When cooling rate was increased the habit of the crystal adjusted and growth commenced on the four vertical faces of the crystal which normally grow very slowly. With respect to the axial growth rate, there is no simple relationship between this parameter and cooling rate. The existence of temperature gradients horizontally and vertically in the sytem could not be definitely established and if present are less than $0.1^\circ \mathrm{C\,cm^{-1}}$. Crystals grown without hydrodynamic fluid movement in the system gave similar results, and tapering of the crystals under these conditions was more often observed.

Earlier studies of the growth of KDP [1] have shown that the growth rate is a function of supersaturation, that initial growth rate is higher if plate seeds were used, that the final growth rate was attained when cap formation was complete and that interface break-down never occurred after the cap was formed, even at growth rates much higher than those attained in this work. These workers also noted changes in growth in the x- and y-directions and that hydrodynamic flow did not greatly affect the growth rate. Growth rate was also shown not to be a linear funcition of concentration and at low concentrations tapering of the crystals was noted. Thus some of the results in the above work confirm previous observations. In addition, this work has shown that there is no simple relationship between cooling rate and axial growth rate and that both high cooling rates and low cooling rates lead to morphology changes.

All of the above observations and those of previous workers are related to the manner in which these crystals grow. Theories of nucleation of the crystallizing phase on a crystal surface propose that nucleation takes place at steps, kinks and dislocations on the surface [6–8]. Faces with a large number of such defects are considered to grow more rapidly than those with a low number of such defects and the final morphology is a result of an arrangement of faces with a low number of defects. The removal of any non-crystallizing phase, such as water in the case of KDP crystals, is postulated to take place by rejection into a boundary layer in contact with the interface [9]. This boundary layer is then treated as a diffusion dominated region in which the non-crystallizing phase leaves the region near the interface by diffusion under the influence of concentration gradients set up in the boundary layer. There is evidence that concentration variations exist near the interface of crystals growing from solution but the evidence is in dispute as to whether the concentration increases or decreases as the interface is approached [10–13].

The evidence presented above, along with that of previous workers, demonstrates several facts. KDP crystals always form a pyramid cap initially from a plate seed and this cap is full of defects. Alternatively, flawless quality can be obtained more readily by using caps as seeds. The rate of advance of the crystal tip (axial growth rate) is not related to the rate of cooling of the solution in a simple manner. Changes in the rate of cooling cause changes in morphology; as do changes in fluid flow. Neither, however, materially affect the axial growth rate. In order to relate these observations to a growth mechanism the following model is proposed.

It is assumed that growth always starts where there is a high density of sites and these regions can be taken as the junctions between crystallographic planes. This is not unreasonable since Fig. 4 clearly shows the presence of junctions between planes on slices of crystal obtained during this work. These are seen by optical transmission through polished slices cut at 90° to the z-axis and they are known as growth sector boundaries. They

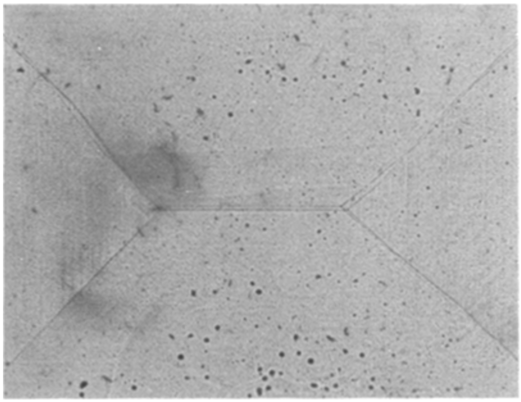

Figure 4 Growth sector boundaries in a KDP crystal.

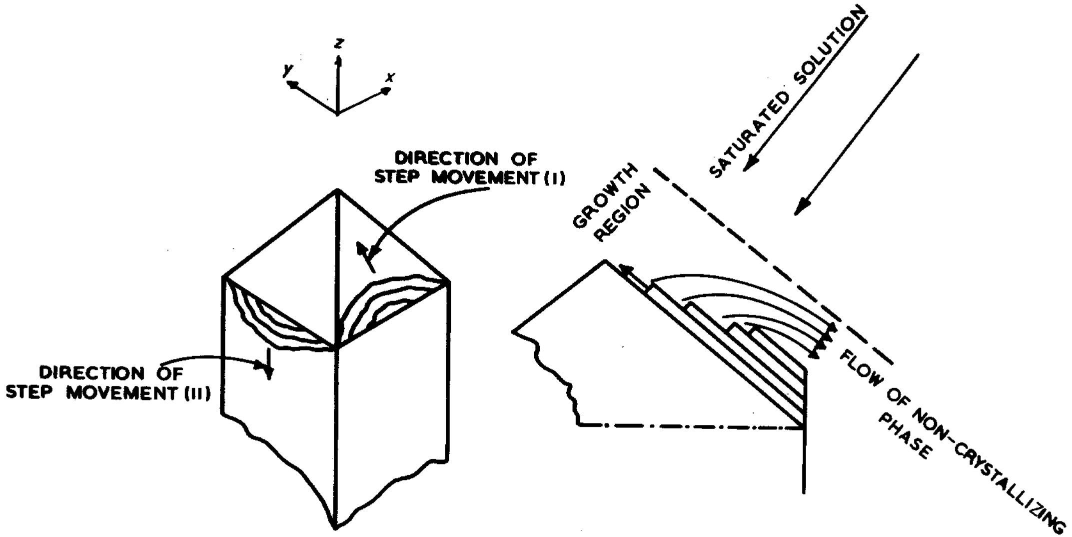

Figure 5 Proposed origin of growth and growth induced fluid flow.

are made visible by the presence of strain or high defect concentration. The work of Bunn [12] (Experiment 3) showed that growth took place preferentially at points with a large number of defects, in this case a broken corner. On this basis Fig. 5 illustrates the origin and advance growth (growth starting at the four junctions at the base of the pyramid which terminates the crystals). The growth fronts then advance up the angled faces.

The evidence of this work indicates that growth on the pyramid is normal. As a crystal grows it is moving through the fluid and Wilcox [14] has considered the effect of this movement on the distribution of any non-crystallizing phase at the interface. The treatment however was based on the presence of a static region ahead of the interface. This movement, however slow, would tend to direct fluid from the tip down over the pyramid faces. In addition to this the crystallizing fronts advancing up the pyramid faces mean that there is in fact physical movement at the interface. This advance is rejecting non-crystallizing phase (water) which means that there is also movement in the fluid. It is considered that the combination of these effects leads to a stream of fluid passing over the crystal faces and Fig. 5 illustrates the concept. Since this flow is very close to the interface it is unlikely to be disturbed by fluid flows in the bulk of the liquid. Removal of the non-crystallizing phase is by this flow and hence the presence of a diffusion region is not invoked.

This postulation infers that hydrodynamic, thermal or density fluid flows do not take part in the removal of non-crystallizing phases. This is supported by the observation that growth proceeds in the absence of hydrodynamic fluid flow. Random density and thermal fluid flows would not result in the changing of only specific regions of a KDP crystal, as shown in Fig. 3.

The crystallizing phase is thus deposited from a stream of fluid passing over the surface generated by growth.

Wagner [15] derived an expression for the decrease in the concentration of depositing species in a gas stream as it passes along a surface. The derivation assumes that the rate of transfer of the species from the fluid to the surface is very high and is hence not a rate limiting step. In addition, it is assumed that a quasi-stationary state exists in the fluid allowing diffusion in the fluid to be neglected and also that any concentration gradients perpendicular to the surface over which the fluid stream is passing are neglected. The form of the expression is as follows

$$\frac{C}{C_0}(x, t) = 1 - \frac{2kDx}{(\pi)^{1/2} hv2(Dt)^{1/2}}, \qquad (1)$$

where C_0 is the initial concentration in the stream, C is the concentration in the stream at point x along the surface, v is the velocity of the stream, k is the distribution coefficient of the depositing species in solid and fluid phases and h is the height of the fluid stream. This expression leads to the conclusion that the concentration of the depositing species decreases as the fluid traverses the surface, that is, concentration gradients exist parallel to the interface and the concentration is highest where the fluid first reaches the surface, or in this case the point at which flow commences. In applying the expression to the deposition of crystallizing species from solution onto the surface of a crystal, the first two assumptions used in its derivation are reasonable. The experimental evidence [11, 12] shows that the concentration of crystallizing species is lower at the centre of a given face. It has also been shown that concentration gradients form where growth is proceeding and disappear when growth ceases [12]. Thus, since the observed concentration gradients parallel to the interface are the most prominent, those perpendicular to the interface can be neglected. The form of the concentration gradients observed experimentally from the edge to the centre of a face [12] often approached that predicted by the Wagner expression. In Equation 1 the diffusion parameter, D, would be substituted by D_S the surface diffusion parameter of nucleation theory [8]. The parameter v becomes the interface fluid velocity induced by crystallization as previously postulated. The fluid velocity has some value at the interface directly related to the rate of advance of the crystallization front over the face involved and falls in value as distance from the interface increases. At some point in the liquid it will become equal to the thermal or hydrodynamic fluid flows in the bulk of the liquid. This distance then defines in the height, h, of the fluid stream in the Wagner expression. On this basis hydrodynamic fluid flow changes, induced by stirring changes in the baths, should have minimal effect on growth since hydrodynamic flow falls to zero at a liquid–solid interface. During this and other work [1] such a minimal effect is observed.

Equation 1 indicates that changes in the concentration gradient are to be expected with time since in the particular case studied [15] diffusion of the depositing species onto the surface would be different when there were no species present on the surface (at $t = 0$) and at some later time ($t = t_1$) when deposition had been proceeding for a period. In applying this expression to crystal growth the analogous situation is related to the concentration of suitable sites (defects). Changes in concentration in fluid would be experienced if the number of sites changed. Thus, concentration distribution would be different at the beginning of growth from a plate of crystal with an enormous number of defects induced during fabrication and later, when these defects were reduced by growth. This again has been recorded [12] where it was observed that the concentration at a given point often decreased as growth proceeded. Thus the Wagner expression when modified as described is a reasonable description of the origin of observations recorded.

In applying this expression to growth, the magnitude of the parameter k is the driving force for crystallization. This is defined as a lower ratio of concentration of crystallizing species on the surface (C_s) to that in the liquid (C_L) than would be expected from the solubility curve (equilibrium liquidus curve) at the temperature of the interface, that is, C_L has been increased by cooling the solution or evaporating the solvent.

Since the value of k is related at any given time to the solubility of the crystallizing phase at the particular temperature of the interface then it is to be expected that growth rate with time will be related to the solubility curve. Fig. 6 [16, 17] shows logarithmic plots of the growth–time curves and the solubility–temperature curve. It can be seen that their similarity supports the above postulation. Only during growth at high cooling rates and growth by evaporation do deviations occur and in these instances changes in morphology were noted.

The magnitude of k decides whether or not impoverishment of the stream takes place and impoverishment is avoided and deposition encouraged by small values of k. In addition, since the concentration of deposited species affects the concentration distribution in the fluid stream, the value of k alters with time.

The experimental results show that decreasing k progressively by more rapid cooling does not lead to an unlimited, progressive increase in the axial growth rate. This means that concentration of the species on the surface must approach some limiting value decided by either surface diffusion D_S or defect concentration. In approaching this limit changes in the concentration distribution in the fluid stream will take place and the concentration over the surface would tend to uniformity. As higher and higher cooling rates are used k will become smaller and the tendency towards deposition increased. Since deposition is now limited on a given face it will commence on other faces. Thus, at high cooling rates the effect is to produce a high enough concentration of species reaching the vertical faces of KDP crystals to allow growth on these faces as shown in Fig. 5.

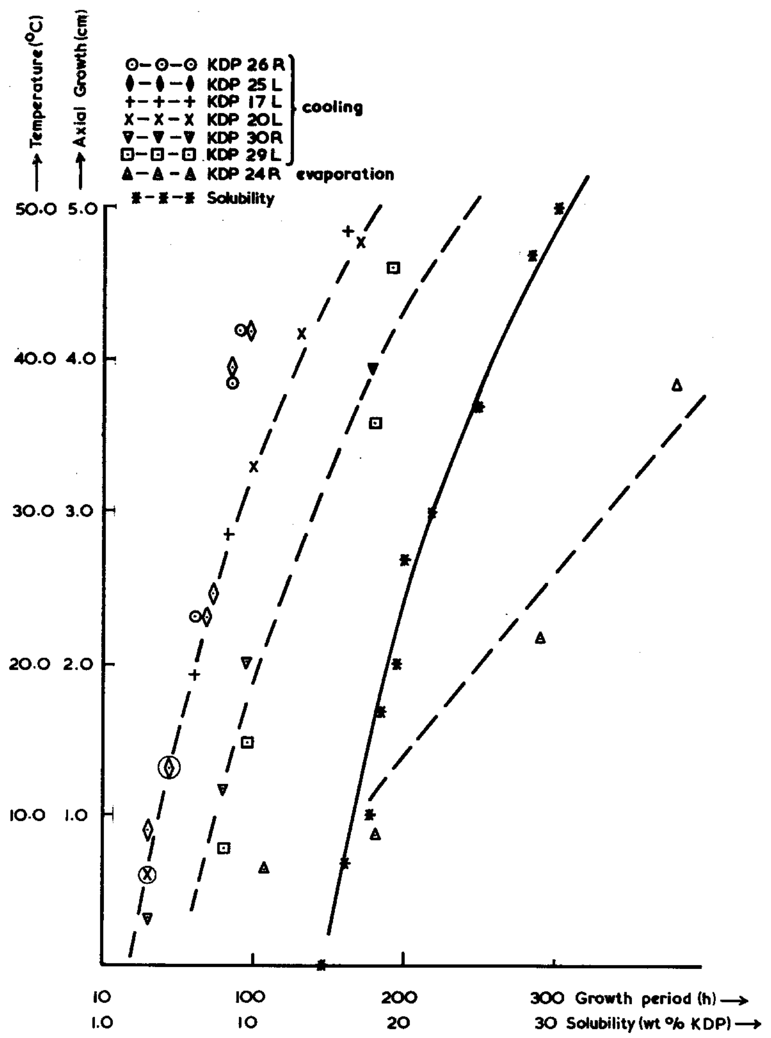

Figure 6 Logarithmic plots of axial growth rate and solubility. Solubility values taken from [16, 17].

Alternatively, if the limiting value of the concentration on the surface is not reached and *k* increases in value, impoverishment is more likely and the concentration of depositing species reaching the vertical face is insufficient to maintain growth, and tapering results. This then is the reason for the morphology changes observed and the reason why progressively higher cooling rates do not lead to progressively higher axial growth rates, and why tapering is observed during growth by evaporation or slow cooling. The latter two processes are taking place under impoverished conditions. Support of the existence of the growth induced flow postulated and the effect of growth under impoverished conditions is given by the development of curvature in the vertical faces shown in Fig. 3. Such an effect arises from the flow impoverished by deposition on the pyramid faces actually dissolving the vertical faces.

The two visible defects observed in crystals of the KDP-type are firstly poor crystal quality formed as a plate grows to a cap and secondly "veils" are produced as follows. The latter are regions of defects which originate at either the centre of the pyramid faces or at the point of the pyramid [18] but only very rarely at the base of the pyramid. Observations of the former shows that capping proceeds by the angled faces forming at the edge of the plate and growing faster than the central regions. As this continues a distinct depression forms in the plate centre and this is ultimately closed over.

On the basis of the above model, where a growth-induced surface fluid flow which removes rejected water can form, growth is normal i.e. at the plate edges, but in the regions where it is disturbed or restricted impoverishment of the stream ensues and growth is inhibited. The case of veil formation also results from impoverishment of the fluid stream but in this case it is impoverishment of the stream reaching the crystal. The origin of the veils at the pyramid tip or face centre supports the postulation that growth originates at the junctions of the pyramid base and moves up the pyramid face since if it originated at the tip and moved down the veils, on the above model, it would appear at the pyramid base.

In conclusion, the postulation of the existence of a growth-induced surface fluid flow during growth of KDP from solution, in combination with an expression describing the deposition of species from such a stream, allows a qualitative description of effects observed during the growth of such crystals.

Acknowledgement

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