

## GROWTH OF THE {100} FACES OF AMMONIUM DIHYDROGEN PHOSPHATE CRYSTALS IN THE PRESENCE OF IONIC SPECIES

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Received 18 June 1974

The kinetics of movement of elliptical growth layers on the {100} faces of ammonium dihydrogen phosphate crystals are reported for growth from aqueous solution at 19.3, 23.9 and 28.5 °C in the supersaturation range  $0.025 < \sigma < 0.08$ . The layers are shown to be step bunches and surface diffusion is considered to play the rate determining role in the growth process. The effects of trace amounts (up to 100 ppm) of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3$  and  $\text{AlCl}_3$  on the kinetics of movement of the growth layers were studied at 23.9 °C and  $\sigma = 0.052$ . The results are interpreted in terms of adsorption of the impurity species at kink, step or ledge sites.

### 1. Introduction

The {100} faces of ammonium dihydrogen phosphate (ADP) crystals (see fig. 1) grow extremely slowly compared with the {101} faces. It was not possible, therefore, to measure their growth rates by direct microscopic measurement by the flow cell technique used for the {101} faces<sup>1,2</sup>. However, distinct growth layers could be seen moving across growing {100} faces so it was decided to characterize the growth kinetics of these faces by measuring the layer velocities under well-defined conditions of supersaturation and temperature.

Observations of growth layers were made by the technique of reflection microscopy similar to that used by Albon and Dunning<sup>3</sup>) for studies with sucrose, and by Torgesen and Jackson<sup>4</sup>) with ADP.

The present work is concerned with the kinetics of movement of growth layers on the {100} faces of ADP crystals and the effect of certain trace impurities.

### 2. Experimental

Small crystals (~ 0.5 mm long) were nucleated and grown on the lower, non-reflecting surface of a small observation cell (fig. 2). The arrangement comprised a central portion, 20 mm diameter and 4 mm deep, in which the crystals were grown, enclosed in a water jacket which controlled the cell temperature to within  $\pm 0.05$  °C of any preset value.

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Crystals grew on the lower surface of the cell and the growth layers on the {100} faces were clearly visible when illuminated with a highly collimated, intense light beam from a 24 V, 150 W tungsten-

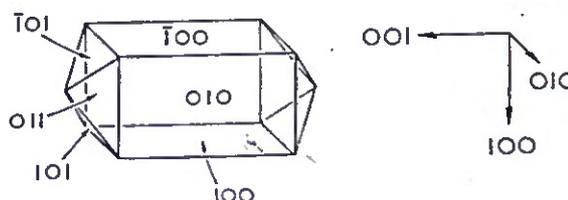


Fig. 1. The morphology of ADP.

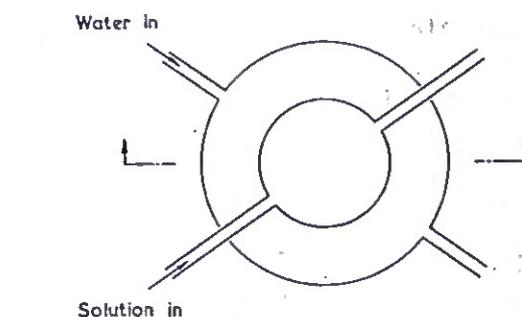
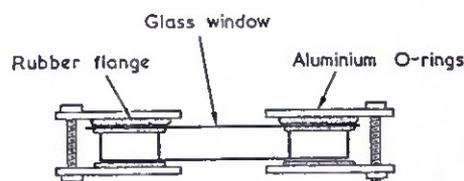


Fig. 2. The cell used for making growth layer observations by the technique of reflection microscopy.

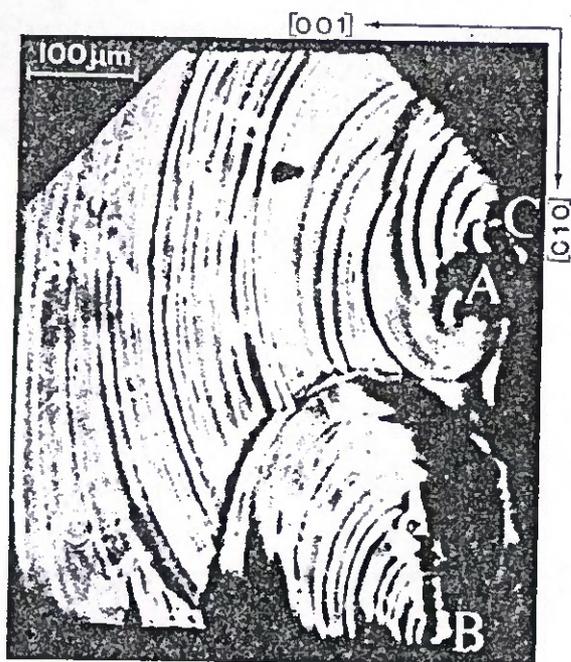


Fig. 3. Layers on a (100) face of an ADP crystal growing from pure solution.

halogen lamp. Angular adjustment of the cell in the horizontal and vertical planes allowed the light reflected from the crystal surfaces to be diverted into a microscope. The growth layer velocities were measured with a micrometer eyepiece. Aqueous solutions of ADP were circulated through the cell under controlled conditions of temperature, supersaturation, flow rate and purity. The solution velocity across the central portion of the cell was varied between about 1 and 18 mm/s.

### 3. Growth from pure solution

In the supersaturation range  $0.025 < \sigma < 0.08$  the growth of the {100} faces of ADP was characterised by elliptical layers moving outwards across the surfaces from well-defined growth centres situated at the apices of low-angle growth hills. The layers had a maximum velocity in [010] direction and a minimum in the [001]. Fig. 3 shows a typical surface in which three growth centres (A, B and C) may be seen, each giving rise to sequences of elliptical layers.

The distance between the layers on the {100} faces of ADP appeared to depend on temperature, time, supersaturation and the particular crystal surface under

TABLE 1  
Dependence of interlayer separation on supersaturation and temperature

Layer separation $Y (\pm 1)$ ( $\mu\text{m}$ )	Supersaturation $\sigma (\pm 0.05 \times 10^{-2})$	Temperature $T (\pm 0.05)$ ( $^{\circ}\text{C}$ )
47	$4.98 \times 10^{-2}$	19.63
21	$5.65 \times 10^{-2}$	19.36
17	$6.97 \times 10^{-2}$	19.36
18	$4.85 \times 10^{-2}$	23.96
25	$6.06 \times 10^{-2}$	23.96
15	$6.67 \times 10^{-2}$	23.96
25	$2.50 \times 10^{-2}$	28.54

investigation. In general, increases in both temperature and supersaturation decreased the layer separation (table 1). No quantitative study was made of the time-dependence.

Visual observations gave a clear indication that at any one time there existed a wide variation in the layer heights on any given crystal surface. Rough estimates ranged from about 0.5 to 3  $\mu\text{m}$ .

Layer velocities across the {100} faces were measured in both the [010] and [001] directions at three temperatures: 19.3<sub>6</sub>, 23.9<sub>6</sub> and 28.5<sub>4</sub>  $^{\circ}\text{C}$ . The measured relations between layer velocity and supersaturation (fig. 4) appear to be linear in the supersaturation range  $0.025 < \sigma < 0.080$ . Under given conditions of temperature and supersaturation, layer movement was found to be a steady-state process; all layer velocities were within  $\pm 10^{-8}$  m/s of the recorded values and were independent of the size of the crystal surface, layer height and solution velocity.

However, from fig. 4 it may be seen that two growth régimes were possible at 23.9<sub>6</sub>  $^{\circ}\text{C}$  where the layer velocity-supersaturation data obeyed one of two possible relationships (A and B). The actual régime encountered appeared to depend only on the surface under study: no interchange between the two régimes was recorded in the course of numerous observations.

#### 3.1. MECHANISM OF GROWTH AND NATURE OF THE GROWTH LAYERS

The growth layers on the {100} faces of ADP crystals are elliptical and their velocity is independent of the layer height. It may be concluded, therefore, that these

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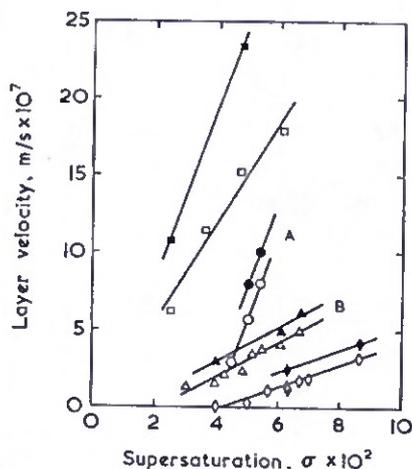


Fig. 4. The dependence of layer velocity on temperature and supersaturation (see key below). A and B denote high and low growth regimes observed at 23.9°C.

Symbol	Direction of layer movement	Temperature (°C)
◆	[010]	19.3 <sub>6</sub>
◇	[001]	19.3 <sub>6</sub>
▲	[010]	23.9 <sub>6</sub>
△	[001]	23.9 <sub>6</sub>
●	[010]	23.9 <sub>6</sub>
○	[001]	23.9 <sub>6</sub>
■	[010]	28.5 <sub>4</sub>
□	[001]	28.5 <sub>4</sub>

layers are bunches of small steps, perhaps even monolayers, rather than true macrosteps which should exhibit polygonal form and a height-dependent velocity<sup>5</sup>).

The creation of step bunches at well-defined growth centres on the crystal surface may then occur, as suggested by Dunning et al.<sup>6,7</sup>, if these centres are the points of emergence of groups of dislocations. Perturbations at the group centres during growth could then lead to bunching of steps.

The elliptical shape of the layers may be explained, as suggested by Bennema<sup>8</sup>, if the individual steps within the bunches are fed by a surface diffusional flux, since the {100} faces of ADP consist of alternate regions of  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  ions which makes surface diffusion easier in the [010] direction than in the [001]. The observation that layer velocities are independent of solution velocity is consistent with the importance of surface diffusion since it implies that the surface processes rather than the bulk volume processes are rate determining.

The activation energy for layer movement, estimated from an Arrhenius plot of  $\log(\text{layer velocity})$  versus  $T^{-1}$  at a supersaturation of  $\sigma = 0.05$ , is  $\sim 50$  kcal/mol. This value is considerably higher than the activation energies generally associated with crystal growth processes (5–15 kcal/mol) but this anomaly may be explained if the layers are step bunches. The velocity of a bunch depends on its slope<sup>5</sup>) and if the slopes of the bunches are temperature-dependent an Arrhenius-type correlation would be meaningless since a true comparison could only be made between the velocities of layers of equal slope. Such a dependence of bunch slope on temperature could also explain the existence of the two growth regimes observed at 23.9°C (fig. 4) if two slopes are possible at this temperature.

#### 4. Growth in the presence of impurities

The effect of trace quantities (0–100 ppm) of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3$  and  $\text{AlCl}_3$  on the velocity of growth layers on the {100} faces of ADP were investigated at 23.9°C under a supersaturation  $\sigma = 0.052$ . In pure solution, all surfaces studied grew in the high growth regime (fig. 4) with layer velocities  $V[001] = 5.8 \times 10^{-7}$  m/s and  $V[010] = 8.1 \times 10^{-7}$  m/s. In the presence of the above impurities layer movement was observed to be a steady-state process.

No polygonisation of growth layers was observed in these studies in which  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was added to the growth solution, contrary to the report by Torgesen

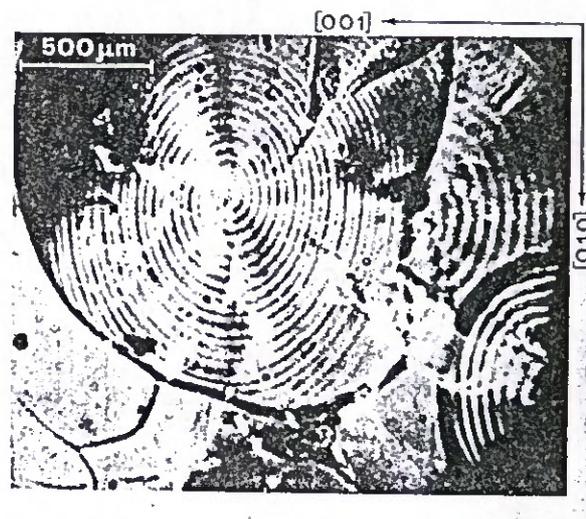


Fig. 5. Layers on a {100} face of an ADP crystal growing in the presence of 40 ppm  $\text{AlCl}_3$ .

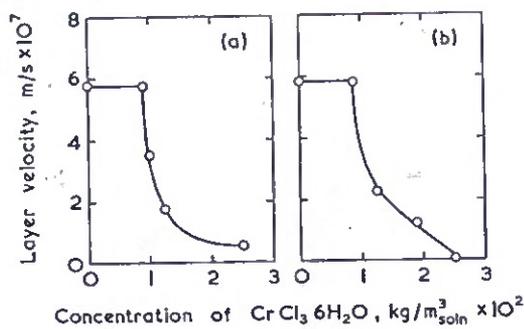


Fig. 6. The effect of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  on layer velocity in the [001] direction for two different crystals of ADP (a) and (b) growing at  $23.9^\circ\text{C}$  and  $\sigma = 0.052$ .

and Jackson<sup>4</sup>), despite several hundred experimental observations made over many months. In all cases, the layers were elliptical (see fig. 5). The ionic impurities reduced the layer velocities, but caused no change in layer shape.

#### 4.1. EFFECT OF $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

The quantitative effect of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  was found to depend on the particular surface under consideration. However, in all cases a critical concentration of  $\sim 8$  ppm of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  ( $1 \times 10^{-2}$  kg  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}/\text{m}^3$  solution) was required to cause any measurable retardation of the layer velocity, while 20 ppm reduced it to a minimum value. Fig. 6 shows two typical examples of this effect for layer movement in the [001] direction.

The dependence of the layer velocities,  $V_1$  in impure solution and  $V_0$  in pure solution, on the impurity concentration,  $c_1$ , was investigated by considering three possible relationships\*

$$V_0 - V_1 = A c_1^n, \quad (1)$$

$$V_1/V_0 = B c_1^n, \quad (2)$$

$$V_0 - V_1 = K_1 c_1 / (1 + K_2 c_1). \quad (3)$$

Eq. (2) gave the best fit (fig. 6) for layer velocities in the presence of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (fig. 7b) with  $n = -2.13$  and  $B = 3.6 \times 10^{-5}$ .

#### 4.2. EFFECT OF $\text{FeCl}_3$ AND $\text{AlCl}_3$

Layer velocities were measured for concentrations of up to 100 ppm of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  in solution. The quantitative effect of these impurities was well-defined,

\* See list of symbols, section 7.

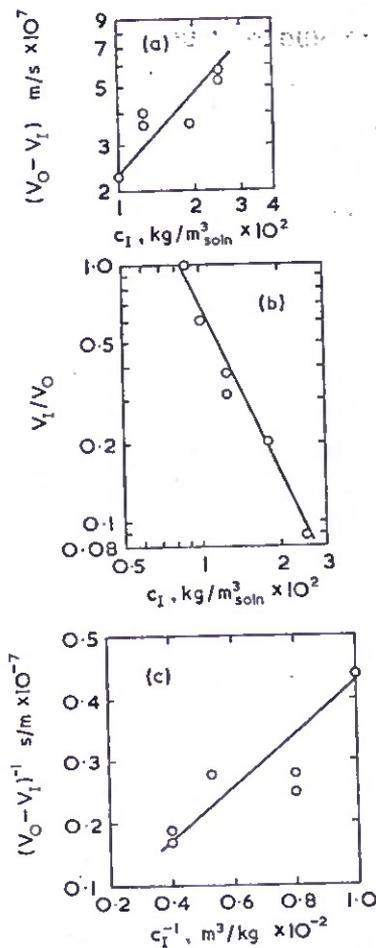


Fig. 7. Testing eqs. (2)–(4) to find the best relationship between  $V_0$ ,  $V_1$  and  $c_1$  for growth of ADP in the presence of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .

showing only a slight dependence on the crystal surface under observation. The measured dependence of  $V_1$  on  $c_1$  (fig. 8) is best correlated by eq. (3). Values of  $K_1$  and  $K_2$  are given in table 2.

#### 5. Mechanism of impurity action

Assuming, as discussed above, that the growth layers observed on the {100} faces of ADP are bunches of small or monolayer steps, three sites may be considered at which impurity species may become adsorbed and hence reduce the layer velocity, viz. at a kink, at a step or on a ledge between steps (see fig. 9).

Considering the theoretical implications of adsorption at each of these sites in relation to the experimental observations, it is possible to assess which of the adsorption sites are important in reducing layer velocities.

TABLE 2  
Values of  $K_1$  and  $K_2$  in eq. (3)

Impurity	Crystallographic direction	$K_1 (\pm 0.1 \times 10^{-5})$ ( $\text{m}^4/\text{kg s}$ )	$K_2 (\pm 0.1 \times 10^2)$ ( $\text{m}^3/\text{kg}$ )
$\text{FeCl}_3$	[001]	$4.0 \times 10^{-5}$	$0.7 \times 10^2$
$\text{FeCl}_3$	[010]	$5.5 \times 10^{-5}$	$0.7 \times 10^2$
$\text{AlCl}_3$	[001]	$2.9 \times 10^{-5}$	$0.5 \times 10^2$
$\text{AlCl}_3$	[010]	$6.3 \times 10^{-5}$	$0.8 \times 10^2$

### 5.1. ADSORPTION AT A KINK SITE

Adsorption at kinks would effectively reduce their number and, since they are the sites at which growth units are incorporated into the lattice, reduce the layer velocity. Further, an increase in the interkink distance would reduce the importance of surface diffusion in the growth process. As pointed out by Bennema<sup>8</sup>) and Larson and Mullin<sup>9</sup>), this would lead to a situation in which the rate of advance of the steps would depend on the density of kinks and result in polygonisation of the growth layers.

Since no polygonisation was observed, this mechanism is not considered to play an important role in the reduction of layer velocity in the present case.

### 5.2. ADSORPTION AT A STEP

Sears<sup>10</sup>) proposed that adsorption of impurities giving monolayer coverage at a step would reduce the number of sites available for growth at the step and hence reduce its velocity. However, for adsorption of impurities corresponding to less than monostep coverage, the advancing step could squeeze between the

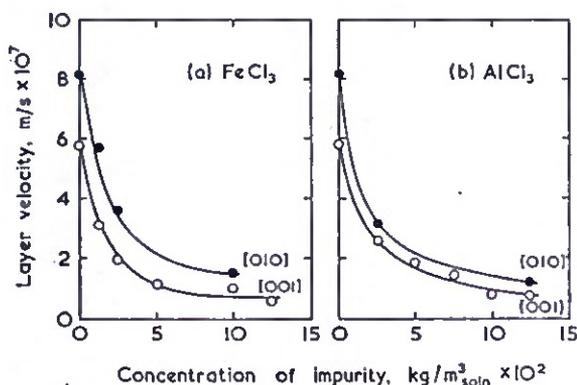


Fig. 8. The effect of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  on the layer velocity in the [001] and [010] directions for the {100} faces of ADP crystals growing at  $23.9^\circ\text{C}$  and  $\sigma = 0.052$ .

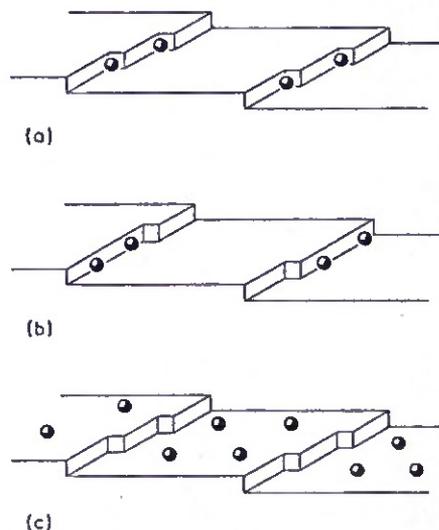


Fig. 9. Sites for impurity adsorption on a crystal surface (a) at a kink site, (b) at a step, and (c) on a ledge.

impurity species relatively unimpeded. This mechanism thus implies a critical concentration of impurity in solution, below which the layer velocity would be unaffected and above which it would rapidly decrease. This is consistent with the observations made for growth in the presence of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ : no change in layer velocity was observed below an impurity concentration of 8 ppm, whilst between 8 and 20 ppm a rapid decrease occurred (fig. 6). It is likely, therefore, that adsorption at the step is important for the reduction of layer velocity by  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ .

### 5.3. ADSORPTION ON A LEDGE

Adsorption of impurity on a ledge is applicable in cases where the surface processes, particularly surface diffusion, play an important role in the growth process<sup>11</sup>). The result would be to decrease the surface area and the surface flux of growth units to the step, and thus reduce the step velocity.

The flux of growth units to a single step in pure solution may be written

$$j_0 = (a/t_k)(n_s - n^*), \quad (4)$$

where  $a$  is the distance between neighbouring positions on the surface,  $t_k$  is the relaxation time for entering a kink,  $n_s$  is the number of adsorbed growth units per unit area of crystal surface, and  $n^*$  is the number adsorbed at equilibrium.

If the surface coverage of impurity is denoted by  $A$ ,

then the flux in impure solution is given by

$$j_1 = (a/t_k) (1 - A_1) (n_s - n^*) = j_0(1 - A_1) \quad (5)$$

Since the step velocity may be expressed by

$$v = 2jf, \quad (6)$$

where  $f$  is the area occupied by one growth unit, we may write

$$(v_0 - v_1)/v_0 = A_1, \quad (7)$$

where  $v_0$  and  $v_1$  are the step velocities in pure and impure solution respectively.

Considering the crystal surface as a matrix of adsorption sites, with no interaction occurring between adsorbed species on neighbouring sites, then if the rate of adsorption of impurity,  $q_{ads}$ , is linearly dependent on its concentration in solution and the area of free surface, we may write

$$q_{ads} = k_{ads} (1 - A_1) c_1 \quad (8)$$

The rate constant,  $k_{ads}$ , is defined by the Arrhenius expression

$$k_{ads} = S \exp(-\Delta E_{ads}/RT), \quad (9)$$

where  $\Delta E_{ads}$  is the activation energy for adsorption.

Similarly, if the rate of desorption,  $q_{des}$ , is dependent on the concentration of adsorbed impurity:

$$q_{des} = k_{des} A_1, \quad (10)$$

where

$$k_{des} = S \exp(-\Delta E_{des}/RT). \quad (11)$$

In the steady state,  $q_{des} = q_{ads}$  so that

$$A_1 = Kc_1/(1 + Kc_1), \quad (12)$$

where

$$K = (k_{ads}/k_{des}) = \exp(-\Delta G/RT), \quad (13)$$

and  $\Delta G$  is the free energy of adsorption of the impurity species.

Combination of eqs. (7) and (12) gives

$$(v_0 - v_1)/v_0 = Kc_1/(1 + Kc_1), \quad (14)$$

for the relation between step velocities in pure and impure solution and the concentration of impurity. Equating the step velocities  $v_0$  and  $v_1$  with the measured layer velocities  $V_0$  and  $V_1$  eq. (14) may be used as a

basis for comparing the theoretical prediction of the model with the experimentally measured dependence of the layer velocity on impurity concentration.

Assuming that the layers on the {100} faces of ADP are step bunches, the equality of the step and layer velocities is consistent with the steady-state nature of their progression across the crystal surface, as discussed elsewhere<sup>12</sup>. Further, the theoretical relationship [eq. (14)] is of precisely the same form as the experimental relationship [eq. (3)] which best correlates the data, suggesting that the mechanism of growth inhibition by adsorption of the impurity between steps on the crystal surface is a reasonable one in the present case.

From this equivalence of eqs. (3) and (14) it follows that  $K = K_2 = K_1/V_0$ , so that  $\Delta G$  may be estimated from the measured values of  $K_2$  using eq. (13). Table 3 gives values of  $\Delta G$  for adsorption in the [001] and [010] directions which are in good agreement with similar estimates made by Bliznakov<sup>13</sup> for the adsorption of phenol on KBr (5.10 kcal/mol), borax on  $MgSO_4 \cdot 7H_2O$  (4.18 kcal/mol) and Ponceau 3R on  $KClO_4$  (3.68 kcal/mol). The suggested mechanism of growth inhibition by the adsorption of impurity between steps thus appears reasonable for the case of  $FeCl_3$  and  $AlCl_3$ .

## 6. Conclusions

Observation and measurement of layer velocities on the {100} faces of ADP growing in pure and impure solutions lead to the conclusion that the layers are bunches of small steps and that reductions in layer velocity (and hence in crystal growth rate) are caused by adsorption of impurity species.

Growth rates measured in the presence of  $CrCl_3 \cdot 6H_2O$  are consistent with the view that the decreases in layer velocity are caused by adsorption at the steps. On the other hand, adsorption on the ledges between steps

TABLE 3

Free energies of adsorption of  $FeCl_3$  and  $AlCl_3$  on the {100} faces of ADP

Impurity	Crystallographic direction	$\Delta G (\pm 0.1)$ (kcal/mol)
$FeCl_3$	[001]	3.8
$FeCl_3$	[010]	3.9
$AlCl_3$	[001]	3.7
$AlCl_3$	[010]	4.0

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K

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m

is considered to be the important process for growth in the presence of  $\text{FeCl}_3$  and  $\text{AlCl}_3$ .

As discussed previously<sup>2</sup>) the impurity species most likely involved are  $\text{Cl}^-$  and  $\text{M}(\text{H}_2\text{O})_4(\text{OH})_2^+$  ions ( $\text{M} = \text{Cr, Fe or Al}$ ) which become adsorbed on the {100} faces of ADP by the formation of bonds with the  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  ions in the crystal surface. Since the {100} surfaces contain regions of both  $\text{NH}_4^+$  and  $\text{H}_2\text{PO}_4^-$  ions during growth, an adsorption equilibrium may be established, which would account for the observed steady-state growth. This is in contrast to the growth of the {101} faces of ADP in the presence of these impurities for which it was suggested<sup>2</sup>) that the alternating polarity of the {101} face during growth could be one of the factors responsible for their non-steady state growth.

#### 7. Symbols used

$a$	Distance between neighbouring equilibrium positions on crystal surface.
$A_1$	Fraction of crystal surface covered by impurity.
$c_1$	Concentration of impurity in solution.
$C$	Solution concentration.
$C^*$	Equilibrium concentration.
$\Delta C$	Concentration driving force ( $C - C^*$ ).
$f$	Area of a growth unit in a crystal lattice.
$\Delta G$	Free energy of adsorption of impurity species on the crystal surface.
$j_0$	Surface flux of growth units to a step in pure solution.
$j_1$	Surface flux of growth units to a step in impure solution.
$k_{\text{ads}}$	Rate constant for adsorption of impurity.
$k_{\text{des}}$	Rate constant for desorption of impurity.
$K$	Constant in the adsorption isotherm, eqs. (12) and (13).
$K_1, K_2$	Constants in eq. (3).
$n$	Exponent in eq. (1).

$n$	Exponent in eq. (2).
$n_{s,0}$	Number of adsorbed growth units per unit area of crystal surface at equilibrium.
$n_{s,\text{gcd}}$	Number of adsorbed growth units per unit area of crystal surface during growth.
$R$	Gas constant.
$S$	Constant in the Arrhenius relationship.
$t_k$	Relaxation time for entry into kink site.
$q_{\text{ads}}$	Rate of adsorption of impurity species.
$q_{\text{des}}$	Rate of desorption of impurity species.
$v_0$	Step velocity in pure solution.
$v_1$	Step velocity in impure solution.
$V_0$	Layer velocity in pure solution.
$V_1$	Layer velocity in impure solution.
$Y$	Layer separation.
$\Delta E_{\text{ads}}$	Activation energy for adsorption of impurity species.
$\Delta E_{\text{des}}$	Activation energy for desorption of impurity species.
$\sigma$	Relative supersaturation ( $\Delta C/C^*$ ), where concentrations are expressed as kg of ADP per $\text{m}^3$ of solution.

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