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On the Variation of Ice Crystal Habit with Temperature*

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Abstract

The variation of ice crystal habit with temperature was explained by Mason *et al.* and by Hobbs *et al.* in different manners, though both explanations are based on the idea that the relative rates of surface diffusion of water molecules on the basal and prism faces of ice crystal are responsible for determining the habit.

The surface migration of water molecules on the basal faces of ice crystal was studied experimentally by Mason *et al.* and by Hallett, but some important difference were noted between their results. Mason's explanation can be adopted if their own experimental data are valid, while Hobbs' explanation can be adopted if Hallett's data are valid.

For the purpose of checking their explanations a similar experiment was carried out by this writer. The results are in good agreement with those of Mason's experiment, which may suggest that Hobbs' idea is less valid to explain the habit change of ice.

I. Introduction

The growth of snow crystals from vapour has been studied by Nakaya (1954), Hallett and Mason (1958) and Kobayashi (1957, 1961). The results of all laboratory experiments on the variation of snow crystal habit with temperature and supersaturation or excess vapour density were consolidated by Kobayashi (1961) as shown in Figs. 1 and 2.

It is clear that the *basic* habit of ice crystals as determined by the relative growth rate along *c*- and *a*- axes is principally governed by temperature. Ice crystals distinctly change their habit at three points of temperature, *i. e.* -4 , -10 and around -22°C , in the sequence of plates—prisms—plates—prisms as the temperature is lowered. Recently, observation of ice crystal growth has been extended to lower temperatures, but no essential change in the basic habit has been found in the range between -22 and -90°C (Kobayashi, 1965 a).

The variations of ice crystal habit with temperature, as suggested by Mason (1963), are likely to be attributed to the surface diffusion of water molecules on the growing crystal faces. The studies concerning the epitaxial growth of ice crystals on the basal, cleavage surface of covellite, natural cupric sulfide, made by Bryant, Hallett and Mason (1959) have thrown a strong light on the study of surface diffusion on ice crystal.

Experimental evidences to show the temperature dependence of the surface migration of water molecules on the basal surface of ice have been obtained independently

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by Hallett (1961) and by Mason, Bryant and Van den Heuvel (1963), but an important discrepancy was noted between their results.

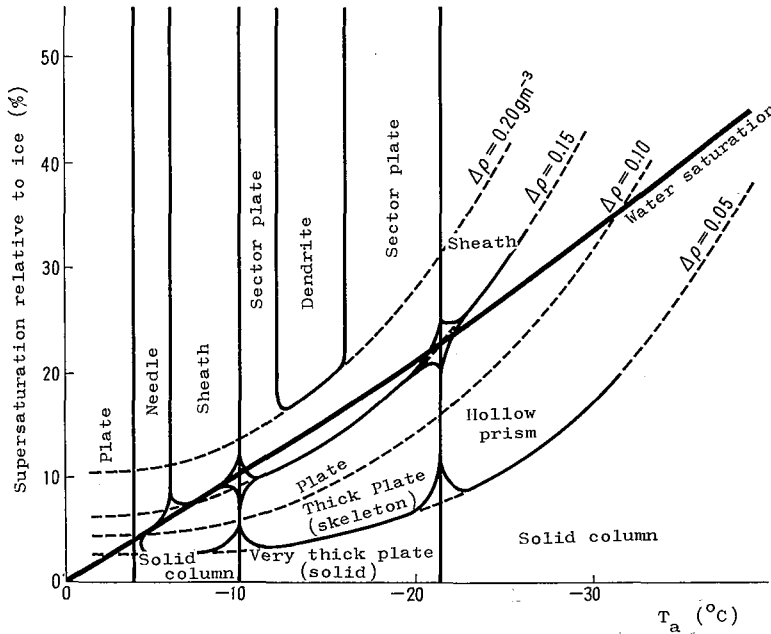


Fig. 1. The variation of ice crystal habit with temperature and supersaturation

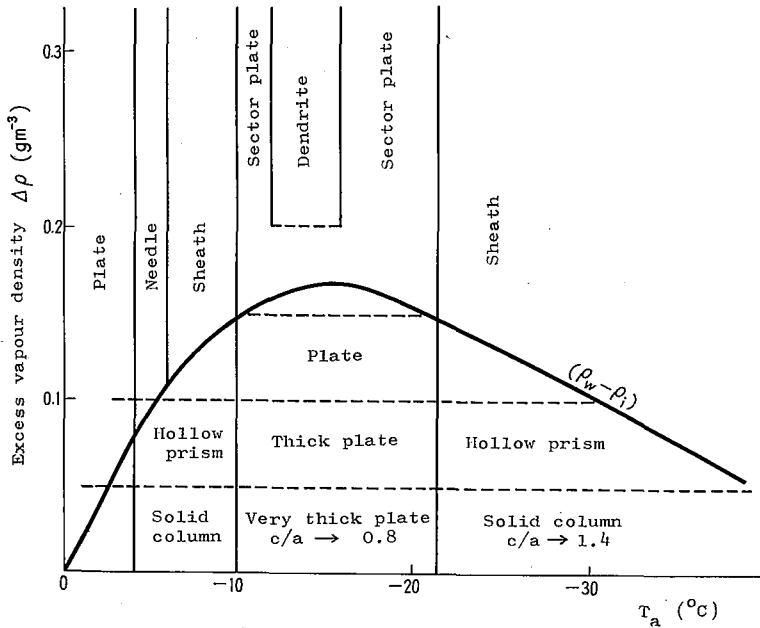


Fig. 2. The variation of ice crystal habit with temperature and excess vapour density

The epitaxial growth of ice crystal on covellite and lead iodide surfaces was carefully studied by the author (1965 b) to determine whether some fundamental difference of the epitaxy exists between both the substrates. The growth processes of ice crystals on covellite were recorded on 16 mm ciné-colour film* and were analyzed for the purpose of checking the validity of either Hallett's data and Mason *et al.*'s experimental results.

This paper will give some results of the film analysis.

II. Experimental Evidences for the Surface Migration of Water Molecules on Ice as a Function of Temperature

The ice crystals growing on fresh (0001) covellite cleavage surfaces are often so thin that they exhibit brilliant interference colours when viewed in reflected white light. The colours give the measure of the crystal thickness. Bryant *et al.* found that under low supersaturation, some crystals grew laterally to 200 μ in diameter without discernible change in colour (that is to say in thickness). This suggests that water molecules arriving on the upper basal surface of growing ice are not being assimilated by the surface but migrate for a considerable distance over the surface and are built into the prism faces.

It is frequently observed when a thin ice crystal contacts a thicker crystal or an obstacle, that the colour change starts from the contact point and spreads over the ice plate in a successive manner (Fig. 3). This may be considered to be evidence of lateral growth of a new layer on the surface of the ice crystal. Hallett (1961) showed experimentally that at constant temperature and supersaturation the layers travel with uniform velocity inversely proportional to their thickness.

He considered the case of a straight step of height h growing parallel to the basal plane by collecting material directly from the vapour phase and by surface diffusion. The mean collection distance over which a step may collect water molecules by surface diffusion is taken by Hallett to be equal to the mean displacement of adsorbed molecules, x_s , *i. e.* the mean distance travelled between landing on, and evaporating from, the surface. The velocity, v , of the step is then

$$v = (h + 2x_s) \frac{A}{h\rho_i}, \quad (1)$$

where ρ_i is the crystal density and A is the net mass flux of vapour to a unit surface area. If $x_s \gg h$, the step will grow largely by surface diffusion with $v \propto 1/h$.

Thus Hallett's finding, in itself, may suggest that the layers advance by surface diffusion and not by direct diffusion of water molecules from the air.

Hallett measured the velocity, v , of step-propagation as a function of temperature for definite values of A and h and obtained the results shown in Fig. 4. In his plot, the velocity of a layer of 250 Å thickness was deduced from that of any layers of thickness between 200 and 1000 Å. The result shows an unexpectedly remarkable variation with the temperature for the velocity of the step. He inferred that x_s would

* The film was presented at the International Conference on Low Temperature Science, 1966. Copies are available from the Institute.

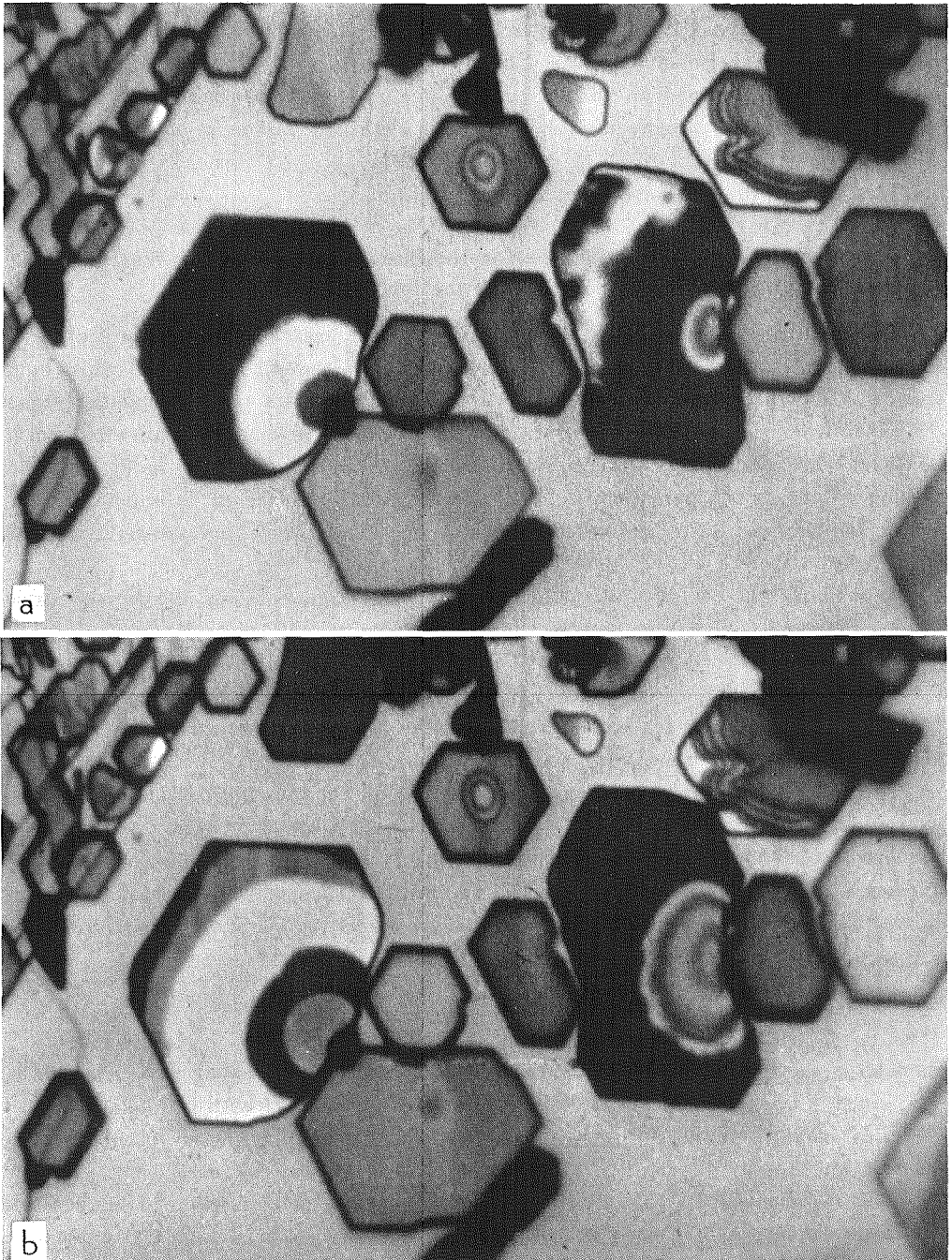


Fig. 3. a: Epitaxial deposit of ice crystals on a cleavage surface of covellite and successive stages of the spreading of growth layers across the basal face of ice crystals, at $T_s = -49.5^\circ\text{C}$ and with a saturation ratio $S=1.4$. ($\times 700$)
b: 180 sec after (a)

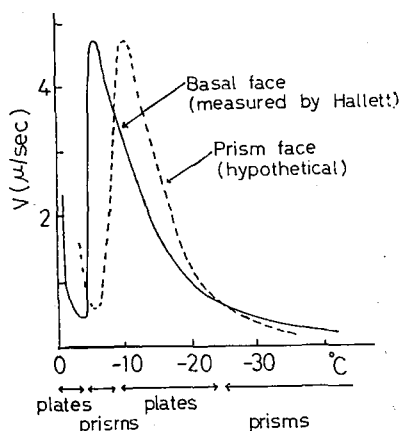


Fig. 4. The temperature variation of the velocity, v , of a layer-propagation (250 Å thick deduced) on the basal face (measured by Hallett) and the prism face (hypothetical, after Hobbs and Scott)

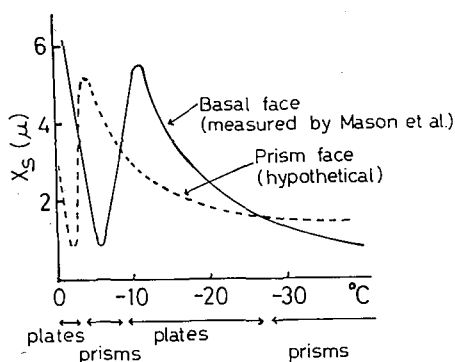


Fig. 5. The temperature variation of the mean migration distance x_s of a water molecule on the basal face (measured by Mason *et al.*) and the prism face (hypothetical, after Mason *et al.*)

vary with temperature in a similar manner, using eq. (1), in which $v \propto x_s$, if $x_s \gg h$.

Mason *et al.* attempted to obtain more direct measurements of x_s . Their method is based on the following assumptions. If two neighbouring growth layers develop at constant temperature and supersaturation and are separated by a distance greater than $2x_s$, they will travel independently at constant speed. But, if their separation is less than $2x_s$, their collection zone will overlap, and will mutually interfere and slow down as they compete with each other for the diffusing current of molecules. Therefore, the critical separation at which they just begin to slow down may be taken as $2x_s$. Mason *et al.* (1963) obtained in this manner a set of measurements of x_s at different temperatures as shown in Fig. 5.

The variation of x_s with the temperature obtained by Mason *et al.* is remarkable and is quite similar in general character to that obtained by Hallett from his measurements of the velocity of growing step, but there exists an important difference in temperature at which the maximum appears on each curve (in Figs. 4 and 5). Hallett obtained the maximum at -6°C as shown in Fig. 4, while Mason *et al.* obtained the maximum at -11°C as seen in Fig. 5. No information has been given to interpret this discrepancy, which may possibly lead to a contradiction between the two different explanations suggested by Mason *et al.* (1963) and by Hobbs and Scott (1965) for the variation of crystal habit with temperature.

III. Re-Examination on the Velocity of Step-Propagation Over the Basal Surface of Ice

For the purpose of checking the validity of either of the experimental results obtained by Hallett and by Mason *et al.*, the velocity of step-propagation over the basal

surface of ice crystal was re-examined by the present author. Measurements of x_s in Mason's method were abandoned, because the change in the rate of closing of two steps seems to be rather obscure.

The apparatus used is shown in Fig. 6. Thermoelectric refrigeration using p and n bismuth telluride was adopted in a two-stage cascade cooling system composed of a thermoelectric panel (B) set up by 10 elements in series for maintaining sub-zero temperatures, and a thermoelectric element (C) for spot-cooling under the microscope. A small, well insulated box (A), $32 \times 30 \times 15$ mm, which could be cooled to any temperature to -35°C by regulating the DC current in the panel (B) at the bottom of the box was used. A thin ice sheet was placed on the bottom of this box as a vapour source. A small fan inserted through the wall kept the water vapour of the air in equilibrium with the ice at the bottom of the box.

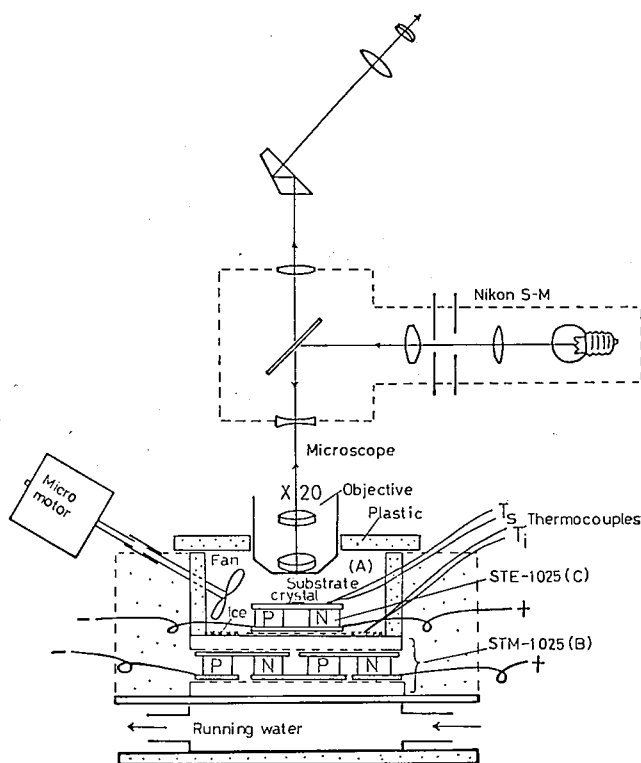


Fig. 6. Experimental apparatus

A thin plate of covellite with a fresh cleavage surface upwards was placed on the copper cold plate of the thermoelectric element (C), and cooled to the desired temperature (-50°C at the lowest) by increasing the DC current to the element.

The ice crystal growing on the cleavage surface of covellite was viewed with the aid of a vertical illuminator, and photographed simultaneously. When the substrate temperature T_s , was lower than that of the ice at the bottom, T_i , the supersaturation, s , over the substrate was roughly estimated by the temperature difference $T_i - T_s$.

All measurements were made under a constant excess vapour density of $0.21 \text{ g}\cdot\text{m}^{-3}$ (approximately 10% supersaturation at -10°C and 50% at -30°C) for the temperature range between -7 and -50°C . No satisfactory measurements have been made at temperatures above -7°C , though Hallett and Mason *et al.* succeeded to get some data in this temperature range. Ice crystals were not observed to nucleate at temperatures higher than -7°C on the cleavage surface of covellite. Unsuccessful trials were made in such a way as to increase the substrate temperature above -7°C after ice nucleation had took place.

Since the initiation of step-propagation was unpredictable, all the events were recorded on time-lapse 16 mm colour photographs, when thin coloured crystals grew laterally to certain diameters approaching each other or any obstacle on the cleavage surface of covellite. Thus the step-propagation over the basal face of the thin ice crystal was photographed, from the very time of the beginning in one to six frames per second depending on the rate of advance of the phenomena. After processing, the successive stages in the step-propagation were reproduced every proper number of the frame on the screen of Filmotion (16 mm film analyzer) and the velocity of propagation was determined for each step.

The thickness of the ice crystals may be estimated in the following manner using the ICI chromaticity diagram (Evans, 1948). Using the notation given in Fig. 7 the path difference between successive beams is simply $2n_1d_1 \cos \phi_1$, since the phase changes with reflection at the upper and lower surfaces of the ice film are both equal to π ,

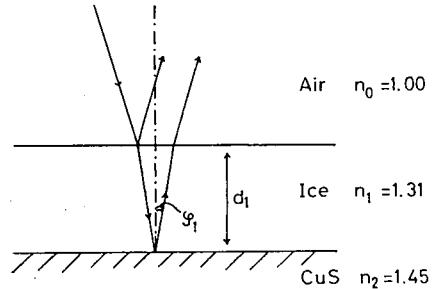


Fig. 7. Interference in an ice layer on a covellite surface

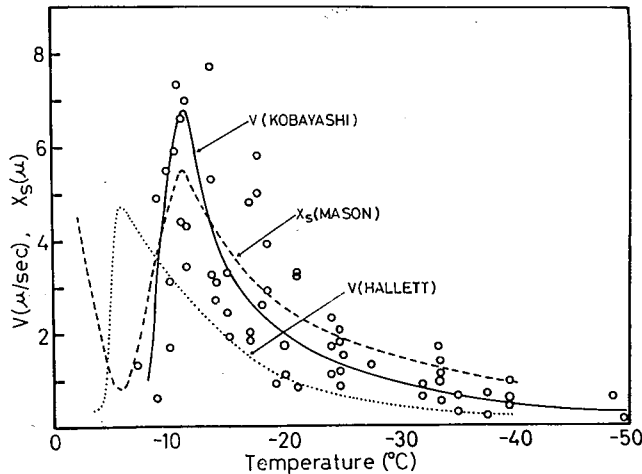


Fig. 8. Temperature variation of the velocity of a layer-propagation (250 Å thick deduced) on the basal face obtained by the present author. Excess vapour density: $0.21 \text{ g}\cdot\text{m}^{-3}$. Curves obtained by Hallett and by Mason *et al.* are also shown for comparison

since $n_0 < n_1$, and $n_1 < n_2$. If $2n_1d_1 \cos \varphi_1 = m\lambda$, where m is an integer, the reflected energy will show a maximum for that wave length, λ , and the film will possess a characteristic hue.

The results of the present experiment are plotted in Fig. 8. Plotting was made for the lateral growth velocity of a layer of 250 Å thickness deduced from any layer thickness by the relation between thickness and velocity, for the convenience of comparing with that of Hallett's experiment.

Although no data were available above -7°C in the present experiments, the data obtained by the author represent a better coincidence in general tendency with those obtained by Mason *et al.* than those obtained by Hallett, as can be clearly seen in Fig. 8. It must be emphasized that the velocity, v , of a growing step over the basal face give its maximum at -11°C in the same manner as in the case of Mason *et al.*'s measurements. Hallett's data giving a maximum at -6°C seem to be incorrect. Between 0 and -6°C Hallett and Mason *et al.* obtained a similar tendency in which v or x_s falls rapidly with the decreasing temperature.

It may be concluded, therefore, that the velocity v , or the mean migration distance x_s , over the basal face represents a remarkable characteristic showing a rapid fall to a minimum at -6°C , a sharp increase to a maximum at -11°C and thereafter a gradual fall with the decreasing temperature down to -50°C or lower.

This variation with the change in temperature is extraordinary and quite suggestive for explaining the variation of ice crystal habit with the changes in temperature.

IV. On the Suggested Mechanisms of Habit Change of Ice

Mason *et al.* (1963) have attempted to explain the variation of ice crystal habit with temperatures in terms of the relative rates of x_s for the basal and prism faces. Since no experimental data are available on x_s for the prism face, they assumed that the curve would be of a same general shape for the basal face but of a rather different amplitude and a slight displacement towards higher temperatures. The two curves could then intersect at three points as shown in Fig. 5 to give four temperature ranges in which the ratio of x_s for the basal and prism faces alternates between being larger than, and smaller than, unity. For example, at temperatures between -8 and -25°C the migration distance x_s is shown as being greater on the basal than on the prism face. They considered that this leads to a net migration of material from the basal to the prism faces, to a more frequent nucleation of layers on the prism faces and to the crystal developing as a plate. Between -3 and -8°C the situation is reversed, implying that the crystal should develop as a prismatic column. In this manner they have given a possible explanation to the transitions which are observed in the sequence of plates—prisms—plates—prisms as the temperature is lowered from 0 to -90°C .

Recently, Hobbs and Scott (1965) defined the collection distance, x_c , as the distance from the step at which the concentration of adsorbed molecules C_s is equal to the fraction $(1-e^{-1})$ of the concentration at a distance far from the step. They pointed out that the collection distance of a growing step, x_c , is not, in general, equal to the mean migration distance x_s of adsorbed molecules on the surface. And they showed

that, below -3°C the experimental results on v are qualitatively explicable in terms of their theoretical derivation and analysis for x_c .

In view of the assumption that x_c can not be equated to x_s , Hobbs (1965) now stands against Mason *et al.* offering a new idea to explain the habit change of ice crystals. From his calculation it is evident that the concentration of adsorbed molecules C_s is very much lower in the neighbourhood of a step than for a point far removed from the step. Therefore, whilst a step is within a collection distance, x_c , of the edge of the crystal, where adjacent basal and prism faces intersect, the probability of a new step being nucleated at the edge will be reduced. Assuming that in the absence of a step close to the edge both crystal faces have an equal probability of nucleating a new step, he infers the face which has the greater velocity v of step-propagation will nucleate a larger number of steps in a given time than will the other faces*. Thus he infers that if the temperature is such that the velocity v on the basal face is greater than that on the prism face the crystal will grow faster in the c -direction and develop as a prismatic column.

If Hobbs' ideas are correct, the velocity v on the basal face should be greater than that on the prism in the temperature ranges from -4 to -10°C and from -22 to -90°C , but the reverse should be found from 0 to -4°C and from -10 to -22°C , if it should be applied for the actual transition in ice crystal habit.

This can not be the case if Mason *et al.*'s measurements, as shown in Fig. 5, are valid. It may be easily recognized in Fig. 4, that the curve obtained by Hallett for the velocity v on the basal face is in a favourable location to draw a hypothetical curve for the prism face (dotted line) in such a manner as suggested by Hobbs.

The results of the present analysis, however, showed in the foregoing that Hallett's measurements were incorrect. Therefore, Hobbs' idea to explain the habit change can not be adopted for the actually observed habit change in ice crystals.

To make a step forward in examining Mason's idea for the mechanism of habit change of ice, the experimental determination of v on the prism face is urgently required.

* Objections may be raised as follows; the face which has greater velocity v of step-propagation has the longer collection distance x_c than that of the other face. Supposing a new step can not be nucleated until a step moves into a further distance x_c from the edge, both the basal and prism faces must have an equal chance for nucleating steps in a given time.

In a private communication Hobbs stated that the objection would be a valid one if the concentration of adsorbed molecules at a large distance from the face of a step were the same on both the prism and basal faces.

He now supposes that the probability of nucleating a new step is proportional to C_{∞} , the concentration at large x , which is given in his paper (Hobbs, 1965, eq. (18)) by

$$C_s = C_{\infty} = \frac{(A_v - A_s)C}{kC + A_v - A_s} \quad \text{at } x = \infty$$

Since k is different for different crystallographic faces so is C_{∞} . C_{∞} will also be temperature dependent due to temperature dependence of k . Hence, at certain temperatures, the C_{∞} for the basal face will be greater than the C_{∞} for the prism face, while at other temperatures the reverse may hold.

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