The Structure of Ice Grown in Bulk Supercooled Water

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ABSTRACT

The structure of ice grown in water supercooled to temperatures between −2C and −7.5C has been studied and recorded by flash photography. The ice structures formed below −3C are not co-planar with the basal planes of the seed crystals but are split into two, and occasionally more, segments. At temperatures below −5.5C secondary splitting occurs on the major growth segments, the complexity of the structure increasing with increased supercooling. A stepped growth mechanism has been suggested to explain these observations. The three-dimensional structures so formed are sufficiently complex to retain unfrozen liquid and so give rise to spongy ice.

1. Introduction

The fact that there is a limit to the rate at which heat may be transferred from an object undergoing accretion in a supercooled cloud, and that this limit is an important factor in determining the nature of the ice deposited, is now well known (List, 1959; Macklin, 1961). If the rate of arrival of droplets is greater than a certain value only a fraction of the accreted droplets can freeze. The resulting structure is an open-mesh matrix of ice which retains the unfrozen water something after the manner of a wet sponge. Icing tunnel experiments have shown that such deposits occur at ambient temperatures as high as −5C and may contain as much as 70 per cent of unfrozen liquid. Heat transfer theory predicts that the ice deposited on large hailstones is of this kind and it has been suggested this accounts for at least some of the irregular features observed on such stones (Macklin, 1961).

From the physical point of view the mechanism of the freezing of water under accretion conditions is a complicated process. The radial growth rates of hailstones in clouds whose liquid water concentrations are a few g m^{-3}, are of the order of 10^{-3} to 10^{-2} cm sec^{-1}, and forced convection heat transfer is sufficient to freeze water at about this rate (see Table 1). However, the growth rate of ice in supercooled water is 1 cm sec^{-1} at −5C and increases rapidly as the temperature is lowered (see, e.g., Bolling and Tiller, 1961) so that as pointed out by the writers elsewhere (Macklin and Ryan, 1964) it appears that there are two phases in the freezing process. The first phase occurs in a very short time after a newly arrived droplet impinges on a surface and is nucleated. During this interval the temperature gradients within the liquid are extremely high as the droplet is supercooled by at least several degrees. The growth of ice is very rapid (greater than 1 cm sec^{-1}) and only a fraction of the liquid turns to ice at the expense of the remainder which is warmed towards 0C. As this occurs, the temperature gradients quickly diminish until finally they are so small that the factor dominating the growth is the rate of heat transfer to the environment. This is the second phase of the freezing process and is two orders

TABLE 1. Radial growth rates and maximum rates of heat transfer from spherical hailstones.

[The growth rates have been calculated from a formula given by Ludlam (1958) assuming a water concentration of 5 gm^{-3}, a collection efficiency of unity, a mean hailstone density of 0.9 g cm^{-3}, and the maximum rates of heat transfer, which occur when the surface temperatures of the stone are 0C, from experimental data given by Macklin (1963). The equivalent freezing rates have been obtained by dividing the rates of heat transfer by the quantity $0.9(L_f+\sigma T)$, L_f being the latent heat of fusion of water, σ the specific heat of water and T the ambient temperatue. When the growth rate exceeds the freezing rate, spongy ice is formed.]

Hailstone radius (cm)	0.5	1	2	3
Growth rate (10^{-3} cm sec^{-1}) at				
− 5°C	2.4	3.4	4.8	5.9
−10°C	2.5	3.6	5.0	6.2
−20°C	2.7	3.9	5.5	6.7
−30°C	3.0	4.2	6.0	7.3
Maximum rate of heat transfer (10^{-3} cal cm^{-2} sec^{-1}) at				
− 5°C	30	26	22	19
−10°C	58	48	41	37
−20°C	103	89	74	67
−30°C	142	120	101	91
Equivalent freezing rate (10^{-3} cm sec^{-1}) at				
− 5°C	0.45	0.38	0.32	0.29
−10°C	0.92	0.77	0.65	0.59
−20°C	1.93	1.65	1.39	1.25
−30°C	3.2	2.7	2.3	2.0

of magnitude or more slower than the first phase. It is, however, the initial phase which primarily determines the ice structure. The second phase is essentially a consolidating process, the ice being laid down on the structure formed during the first phase. The amount of ice formed during the initial freezing depends on the degree of supercooling; at −20C, for example, the fraction initially frozen is approximately one quarter of the total mass.

Because of the complexity of the accretion process, it is simpler to study first the growth of ice in bulk supercooled water. For the reasons given above, this is of fundamental importance in determining the ice structure in deposits formed by accretion, particularly spongy ice. Preliminary experiments by the writers showed that at supercoolings below −5C three-dimensional ice structures are produced, and that below −5.5C these are sufficiently complex to retain unfrozen liquid (Macklin and Ryan, 1962).

Three-dimensional ice structures have been reported also by Yamaji (1959) and Chalmers (1961) in supercooled aqueous solutions. Although ice has an essentially hexagonal structure, these workers found that twelve primary growth directions occur, six on each side of the basal (*a*-axis) plane, their projections onto the basal plane coinciding with the normal *a*-axis growth directions for ice. The angle between the growth directions and the basal plane varies from 0 to 30 degrees depending on the supercooling, the concentration of the solution and the nature of the solute. Recently, Hallett (1963) has published photographs showing similar structures growing in supercooled water droplets a few millimetres in diameter.

The present paper describes some features of the growth of ice in bulk supercooled water and discusses its relevance to ice formed by the accretion of supercooled droplets.

2. Experimental procedure

In the preliminary experiments referred to above, the writers simply nucleated singly distilled water which had been supercooled in glass test-tubes. It was subsequently discovered that, once the ice had reached the side of the vessel, it grew along the surface of the glass more quickly than through the supercooled liquid. This caused the structure to become more complicated as throughout most of the volume of the water the ice grew in from the sides of the vessel rather than from the single point of nucleation, and, as shown by Knight (1962), the orientation of ice growing along a glass substrate can change considerably. This undoubtedly served to increase the mechanical strength of the structure and its ability to retain unfrozen water. To some extent this effect could be overcome by using vessels made of plexiglass as the growth rate along this material was found to be considerably slower than along glass at the same temperature.

To investigate the phenomena more fully and to overcome the effects of the sides of the containing vessel, experiments have been carried out using cubic plexiglass vessels of 4.2 cm internal dimensions. These were filled to a depth of 1.5 to 2 cm of water and chilled to a predetermined temperature by a glycol-water cooling bath in a deep freeze unit. They were then removed from the bath, placed on a stand in another part of the refrigerator, and nucleated with a crystal of ice. Using conventional 35 mm flash photography, the ensuing growth was photographed before it reached the sides of the vessel.

The water used for these experiments was triply distilled. An analysis showed that it contained impurities to the extent of 1 ppm by weight, the main impurity being silica, presumably coming from the final stage of the still which was constructed of quartz. The concentration of soluble impurities was determined using a flame photometer. Several tests showed that the Na^+ ion content of the water actually nucleated was between about 0.01 and 0.1 ppm, the K^+ ion concentration being less than this. The extent of gaseous impurity was not determined but it is probable that the water used was virtually saturated with air at room temperature (15 to 20C). Conductivity measurements gave values for the specific resistance of approximately 10^6 ohms which is the value to be expected from dissolved carbon dioxide.

The crystals used for nucleation were thin dendrites several millimeters long by 1 mm or so across grown in slightly supercooled water (−0.3 to −1C). Each was frozen onto a wire attached to a simple mechanical device so that the crystal could be lowered at a rate of about 0.3 mm sec^{-1} until it just touched the surface of the water. In all cases the seed crystal was mounted so that its *a*-axis plane was directed downwards into the liquid. It was found from experience that it was necessary to maintain the seed crystal close to 0C prior to nucleating, otherwise a large number of crystals was formed. This is thought to be due to the frosting of the crystal at colder temperatures, the small frost crystals breaking off when the seed crystal was lowered into the liquid surface. The photographs were taken with the camera looking vertically downwards; in some cases two photographs were taken simultaneously, one camera being arranged as described above, the second camera pointing horizontally, i.e., parallel to the upper surface of the liquid.

The greatest difficulty experienced was in obtaining an accurate measure of the degree of supercooling of the water just prior to nucleation. To achieve this a second control vessel containing a dilute water-glycol mixture was used, the temperature of which was measured by copper-constantan thermocouples. The specific heat of the glycol-water mixture used was only slightly less than that of pure water (about 1 per cent) so that its rate of cooling was virtually equal to that of pure water. This was confirmed by warming samples of both pure water and the mixture and determining their cooling rates. To reduce thermal gradients within the sample to a minimum, both vessels were given sufficient time in the cooling bath for the glycol-water sample to attain a temperature within 0.3C of the bath temperature. Then the vessel containing the pure water was removed from the bath, nucleated and photographed. It was not always possible to maintain the region of the deep-freeze unit where the latter processes were carried out at precisely the desired temperature so the time between taking the vessel from the bath and nucleating was noted and the control vessel, whose temperature could be accurately determined, subjected to the same conditions. In this way it is considered that the temperature of the water sample, including possible thermal differences throughout the volume of the vessel was ascertained to within ±0.3C in nearly all cases. The lowest temperature reached with the present apparatus and sample volumes was −7.5C. This proved sufficient to cover the range of phenomena which could be recorded satisfactorily with the photographic techniques employed.

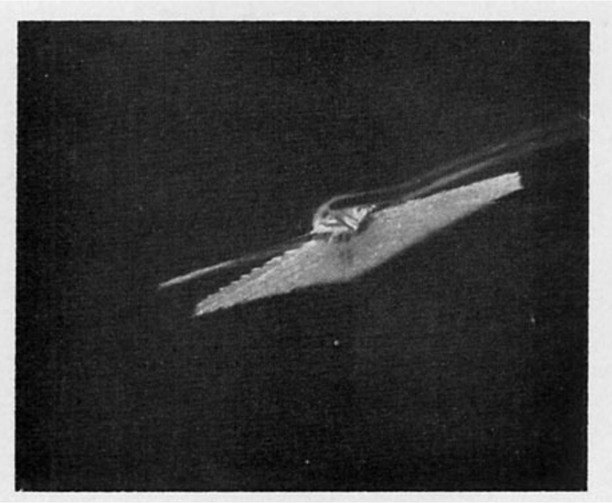


FIG. 1. Ice structure formed at −3.7C. (×3.3.)

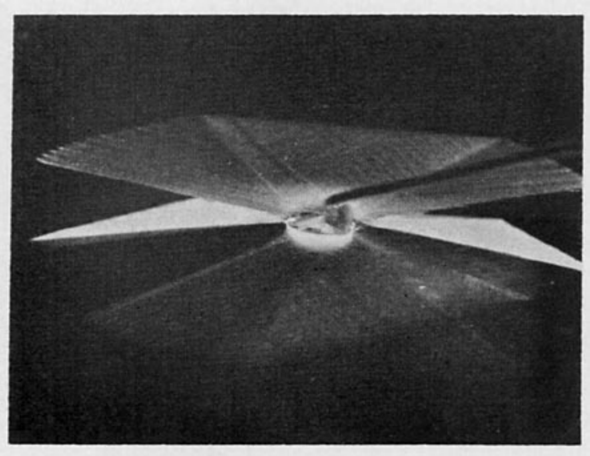
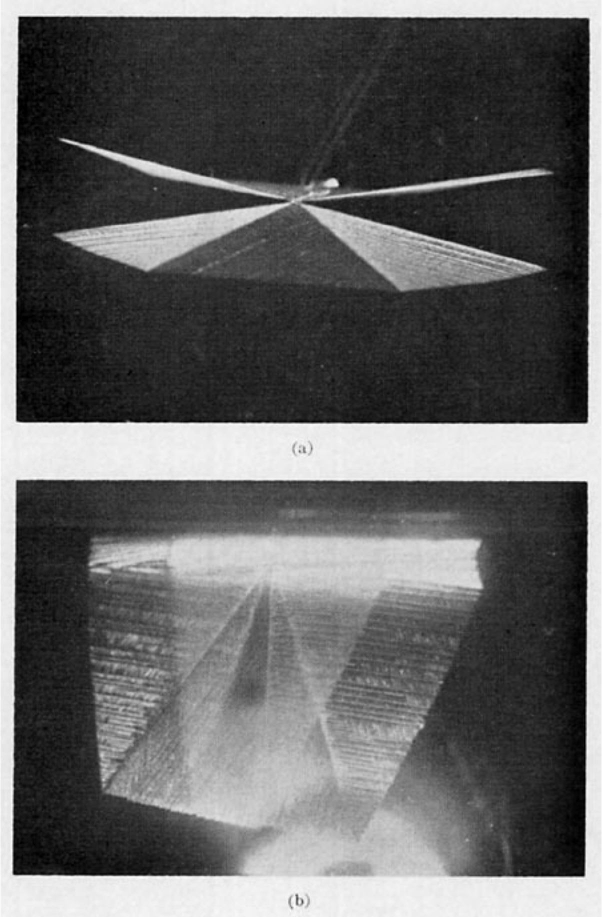


FIG. 2. Ice structure formed at −4.6C. (×3.1.)

3. Results and observations

Even at temperatures as high as −3C the ensuing growth in the supercooled water was not co-planar with the seed crystal, i.e., in the *a*-axis plane, but was split into two, and occasionally more, segments. This could



(a)

(b)

FIG. 3. Ice structure formed at −5.2C. (a) photograph taken with the camera looking vertically. (×2.9.) (b) photograph taken with the camera looking horizontally. (×3.1.)

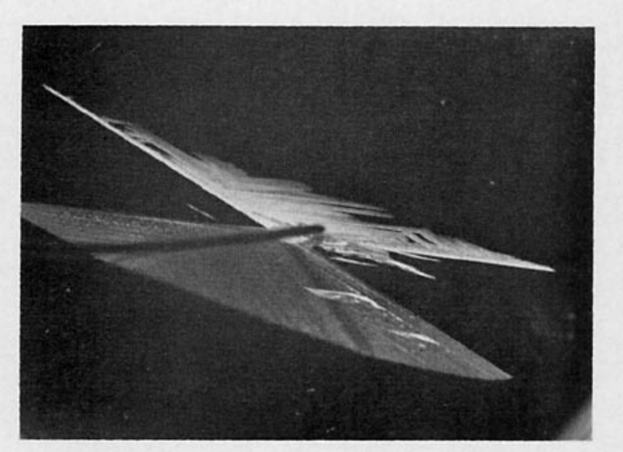
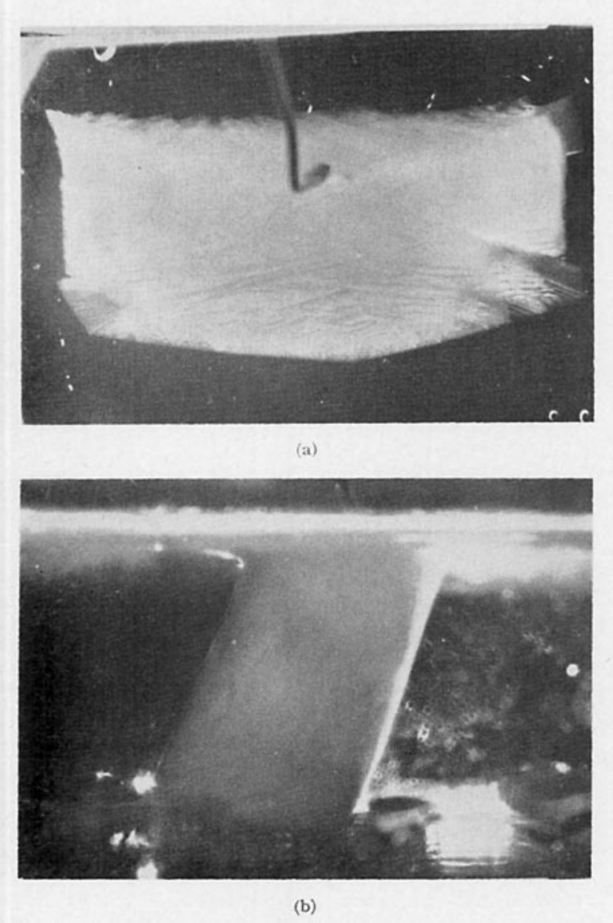


FIG. 4. Ice structure formed at −6.1C. Secondary splittings have occurred on the major growth segments. (×2.8.)

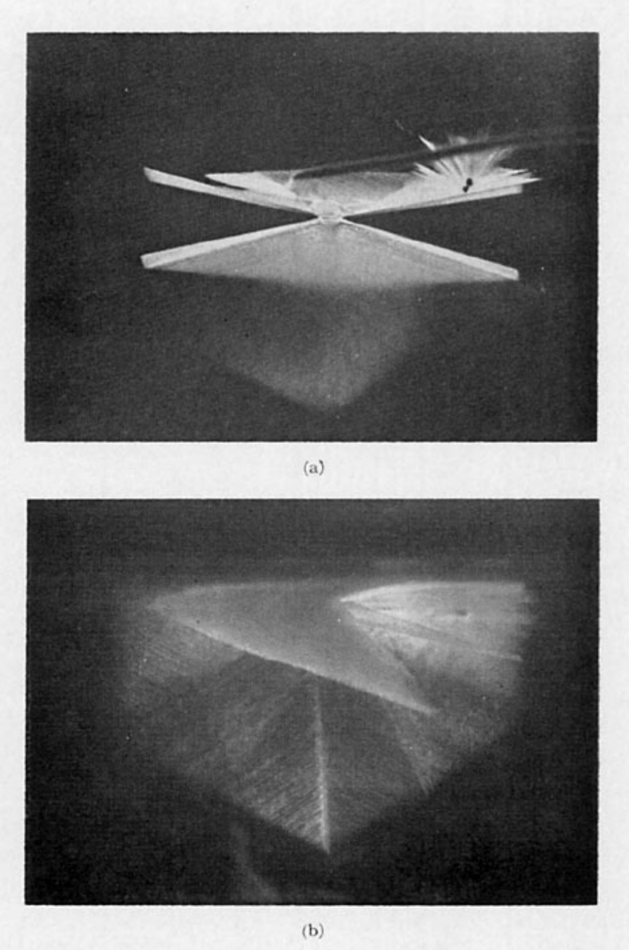
be seen easily by visual inspection and by using a low power microscope. The structures obtained at temperatures −3.7C, −4.6C and −5.2C are shown in Figs. 1 to 3, respectively. In these photographs which were taken from above, the ice segments can be seen growing down into the liquid. The segments stem from the single point of nucleation. This is best seen in Fig. 3a where the thin dendrite used as a seed crystal is directed almost vertically downwards; the ensuing growth segments are symmetrically placed about the plane of the dendrite.[1] These are similar to the structures reported by Yamaji (1959) and Chalmers (1961). In addition to the major segments grown down into the liquid, one or more planes sometimes grew across the liquid surface (Fig. 2). At supercoolings below about −5.5C, secondary splitting was observed on the major growth planes (Fig. 4). This first occurred on the outer parts of the growth segments but as the temperature was lowered, the structures became more and more complicated, secondary splitting occurring both on the inside and the outside of the segments so that the structures grew virtually as a "solid" mass (Fig. 5). At these temperatures the growth rate exceeded 1 cm sec^{-1}. An interesting phenomena is shown in Fig. 6: in this instance a major growth segment struck a small dust particle floating on the surface of the liquid. Immediately ice grew outwards in all directions.

There are two further observations of relevance. Frequently an ice plane striking the edge of the perspex vessel was "reflected" and grew back into the liquid. This occurred whenever there were regions of liquid in the vicinity of the walls that were still supercooled. Secondly, examination under a microscope showed that there was some modification of the structures after the initial freezing had terminated. Small pieces of ice, a few millimeters long and 100 or so microns diameter broke away from the segments and could be seen floating on the surface of the liquid. This occurred even though the vessel was kept at a temperature below 0C so that it could not have been due to melting.


(a)

(b)

Fig. 5. Ice structure formed at −6.4C. (a) photograph taken with the camera looking vertically. (×2.7.) (b) photograph taken with the camera looking horizontally. (×3.0.)


(a)

(b)

Fig. 6. Ice structure formed at −5.9C showing the effect of dust motes on the growth: (a) photograph taken with the camera looking vertically. (×3.0.) (b) photograph taken with the camera looking horizontally. (×3.1.)

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[1] To fully appreciate the photographs which are in effect plan views it is suggested that the reader might wish to construct the three-dimensional model of the structures described below and depicted in Fig. 7.

4. Discussion

In ice, which has hexagonal symmetry, there are three *a*-axes in the basal plane. In normal dendritic growth, therefore, there are three pairs of primary growth directions which emanate from the point of nucleation. This is commonly seen in well formed snowflakes for example. The major growth segments formed in supercooled water also have an essentially hexagonal symmetry but it was observed that they are non-planar. As far as could be ascertained by visual and microscopic examination each individual sector is apparently planar but the three sectors comprising a segment are inclined to each other so that the segment is bent at each primary growth direction. This may be seen in Fig. 3a, particularly in the upper segment. From a study of the ice growth it was apparent that the structures shown in Figs. 1-3 are all parts of the structure shown schematically in Fig. 7a in which there are twelve primary growth directions, their projections onto the basal plane coinciding with the normal growth directions for ice. As mentioned above Chalmers (1961) also came to this conclusion. The reason that the complete structure is not seen in the photographs is simply that the nucleation was effected at the surface of the liquid and growth could only take place downwards. The actual structure produced in the liquid depends on the orientation of the nucleating crystal and two typical cases are shown in Figs. 7b and c.[2]

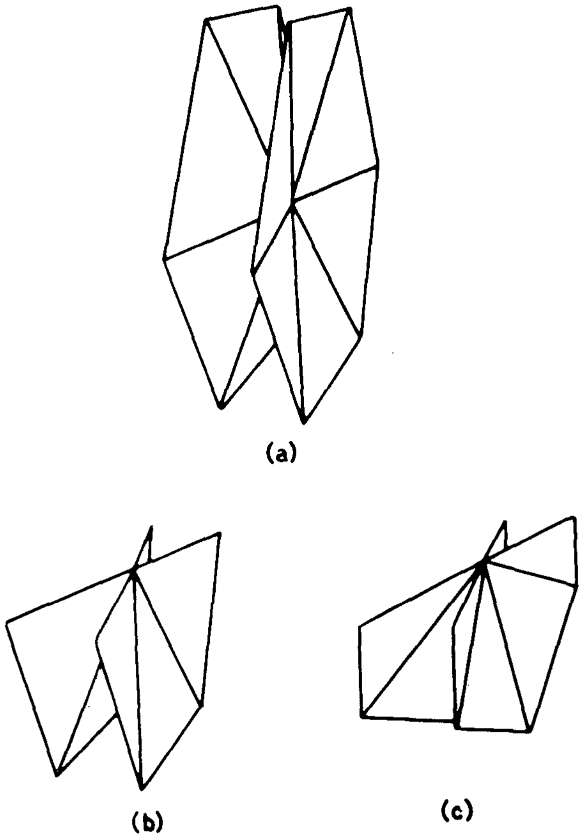

FIG. 7. Schematic representation of the ice structures: (a) complete structure with twelve primary growth directions emanating from the central point of nucleation and symmetrically placed about the basal plane of the seed crystal. (b) and (c) typical structures in the liquid.

The dendritic structure of each individual sector in the major growth segments is seen in Fig. 3b and Fig. 6b. In the center sector there is a discontinuity where the dendrites coming from each bordering primary growth direction have approached each other. There are however no corresponding discontinuities in the other two upper surfaces. In Fig. 3 the growth in the center sector from the right hand primary growth direction has persisted in preference to the growth from the left hand primary growth direction. In the outer sectors growth has ensued from the primary growth directions bordering the center sector. This occurs because the latent heat can be dissipated more readily within the bulk of the liquid than at the surface. Undoubtedly the relative dominance of growth from each primary direction is governed by heat transfer considerations.

Using three-dimensional geometry it is possible to deduce from the photographs with reasonable accuracy the angles of splitting between the corresponding primary growth directions. The angle increases from 11 degrees at −3C to 30 degrees at −6C (Fig. 8). Splitting was not observed above −2.9C; below −6.5C the structures were too complicated to enable reliable measurements to be made.

As mentioned above there were occasions when ice planes grew over the surface of the water and when more than two major segments resulted from a single nucleation. These effects were possibly due to slight frosting of the seed crystals as mentioned above or to slight vibrations of the seed crystal on its supporting wire at

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[2] In some more recent experiments, we have observed that the structure of ice grown in supercooled sugar solution is of the same form as that described here for supercooled water. However, because the rate of growth of ice in the sugar solution is considerably slower than that in pure water (by a factor of one or two orders of magnitude depending on the concentration), it is possible to nucleate the sugar solution within the bulk liquid and not just at the surface. In this case the complete three-dimensional structure shown schematically in Fig. 7a is formed. It is worth pointing out also that the structures described here explain the main shapes of crystals formed in trays of supercooled sugar solution which are being used for detecting atmospheric ice nuclei, namely, the hexagonal and rectangular shapes. The hexagonal shape is produced when a small hexagonal plate formed in the fog above the tray falls flat on the surface and the rectangular shape when a needle-shaped crystal alights horizontally on the surface (see Bigg and Macklin, 1957; Burley 1964). At the sugar concentrations and supercoolings normally used for this technique, the subsequent ice growth shows pronounced secondary splitting. In the former case the *c*-axis is normal to the liquid surface and the structure formed is basically one of the pyramidal halves of Fig. 7a, yielding apparently normal hexagonal growth. In the latter case the c-axis is horizontal and the manner of nucleation is the same as in the present experiments. The ice growth is then virtually identical in form with that shown in Fig. 5a, so that, when viewed from above, the ice structure appears rectangular. Further details of these experiments will be discussed elsewhere.

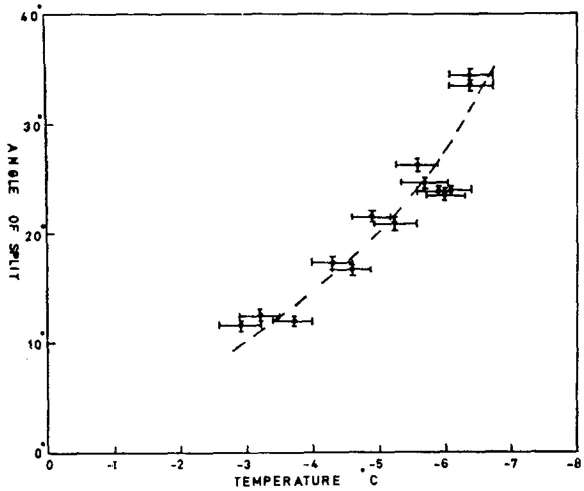

FIG. 8. The angle between pairs of primary growth directions as a function of temperature.

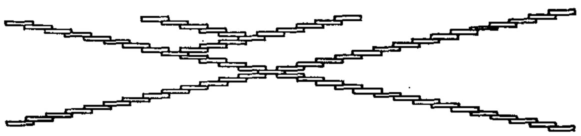

FIG. 9. Formation of the ice structures by the proposed stepped growth mechanism (adapted from Mason, Bryant and Van den Heuvel, 1963).

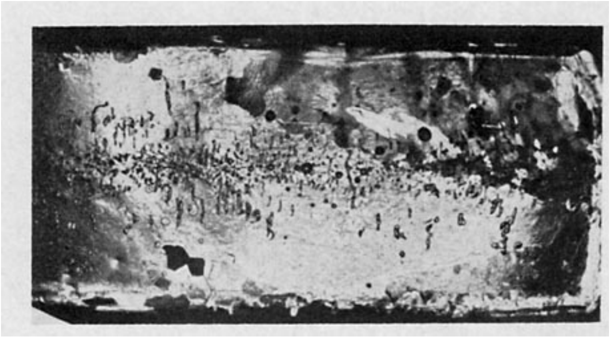

FIG. 10. Thin ice section between crossed polaroids showing the crystal structure. The nucleation point is on the right hand side of the photograph. (×1.9.)

the moment of nucleation. The former effect, however, could be similar to that observed by Hallett (1960) in water which was barely supercooled. He found that if the *a*-axis plane of the nucleating crystal is inclined at an angle to the liquid surface crystal growth occurs along the surface as well as into the liquid. In the present experiments it was not possible to ensure that the basal plane of the nucleating crystal was normal to the surface.

As far as could be determined from direct observation and from the photographs, the secondary growth segments have the same features as the major growth segments and the sectors in the secondary growth segments are parallel to those in the corresponding major ones. This suggests that the mechanism responsible for the initial splitting is responsible also for the secondary growth. However, the secondary growth does not take the same symmetrical form as the primary growth. The asymmetry is governed presumably by the heat flow within the liquid. The heat of fusion released by the major growth segments warms the nearby liquid inhibiting temporarily other growth in its own direction of propagation. The secondary segments grow predominantly in a direction opposite to that of the parent plane because the thermal gradient is greater in that direction, the heat of fusion having had a longer time to dissipate. The spacing and subsequent development of the secondary segments is undoubtedly determined by such considerations since these govern the free energy gradient required for crystallization (see, e.g., Tiller 1963). These heat transfer effects may explain also why the secondary splitting occurs at an apparently lower temperature than the initial splitting. At the instant of nucleation the temperature of the liquid is the measured temperature. Immediately, however, the temperature at the interface of the liquid and the ice surfaces rises and the ensuing growth is determined by a smaller temperature difference than that of the nucleation. If a "critical" supercooling is required for the initial splitting a corresponding lower bulk liquid temperature is required before the onset of secondary growth.

It is not possible to determine from the present experiments the precise crystallographic orientations in the ice formations. Chalmers (1961) simply states that the primary growth directions are not rational directions in the crystal structure. An examination of Figs. 3b and 6b shows that the individual sectors have a typically dendrite structure. It is tempting, therefore, to assume that each is an *a*-axis plane. As the adjacent sectors are inclined to each other, such an assumption requires that there be two inclined *a*-axis planes which stem from the same primary growth direction. This suggests a twinning mechanism but it is difficult to explain the continuous temperature dependence of the angle of splitting on this basis. Further a four-fold twinning of each *a*-axis direction would be required to explain the symmetry of the structures about the nucleation point. A probable mechanism is that proposed by Mason, Bryant and Van den Heuval (1963) to explain the hopper structure of ice crystals grown from the vapor phase under moderate and high supersaturations, namely, that the ice grows in a step-like manner shown schematically in Fig. 9. A somewhat similar stepped-growth mechanism has been used also by Niegish and Swan (1960) to explain the formation of pyramidal polythene crystals grown from solution. The angle of splitting is then determined by the ratio of the height of the step to the distance between steps that is, by the ratio of the growth velocities parallel to the *c*-axis direction and to the basal plane; further, secondary growth can form in the way indicated in the diagram.

One important implication of such a mechanism is that the ice structures are then single crystals. In an attempt to confirm this, ice structures have been produced in plexiglass test tubes at supercoolings ranging from 6.8 to 10.0C. The manner of nucleation and the purity of the samples were the same as in the above experiments. After permitting these to freeze solid in the cooling bath, thin sections were made by melting the ice between warm metal plates and the crystal orientation determined by examining them between crossed polaroids (see, e.g., Macklin, 1961). A typical section is shown in Fig. 10. The point of nucleation in this section was in about the center on the extreme right and three large crystals, seen as different shades of grey, have grown out from this point. Near the edges of the section, however, there are numerous small crystals (more readily discerned in the thin section itself which is colored when placed between crossed polaroids). Thus, while there are large areas which are single crystals the whole structure is not of the same orientation. There are, however, several difficulties with this technique. Movement of the seed crystal after initial nucleation can easily disrupt the structure. Disruption can occur also due to mechanical stresses arising during the complete solidification of the liquid as this tends to take place from the outer surface of the vessel inwards to the center. Perhaps equally important is that this manner of freezing causes the resultant crystal orientations to be determined at least in part by the orientation of the ice formed at the edges of the vessel. The fact that the dendrites undergo re-orientation when they strike the surface of the vessels undoubtedly explains the reason for the large number of small crystals near the edges of the section. It is not surprising, therefore, that the whole sections are not of uniform orientation. On the other hand, the existence of large single crystals radiating out from the point of nucleation indicate that the secondary growth is definitely preferentially orientated. If this were not the case a larger number of smaller crystals would have been produced during the complete freezing.

Some support for the stepped-growth mechanism proposed above is given also by the experiments of Hallett (1963) on the freezing of 1 to 3 mm diameter drops supercooled to temperatures as low as −20C, on a single crystal ice substrate. He found that if the substrate was at 0C and wet the drops froze as a single crystal with the orientation of the substrate irrespective of the temperature of the drop. This also occurred if both the temperature of the ice surface and the temperature of the drop were above −5C. If the temperatures of the drop and substrate were below −5C, more than one crystal was formed. From the photographs published by Hallett, these were apparently due to more than one point of nucleation. A similar effect was observed in the present experiments when the seed crystal was not near 0C.

It is admitted, however, that neither the sections nor Hallett's observations can be regarded as conclusive justification for the mechanism proposed and further work is being carried out to clarify this.

5. Application to the growth of ice formed by accretion

The ice structures grown in water initially supercooled below −5.5C to −6C will retain unfrozen liquid and in this sense they may be regarded as "spongy." As suggested previously (Macklin and Ryan, 1962) this retention is thought to be due simply to interfacial forces between the liquid and solid. The ice structures formed in the plexiglass vessel were less complicated and consequently mechanically weaker than the ice formed in glass test tubes at the same supercooling. The reason for this is the re-orientation of the ice as it grows along the glass (Knight, 1962). While the three-dimensional structures shown in the photographs may be regarded as a basis for the formation of spongy ice under accretion conditions, it is unlikely that they would occur in so perfect a form. The arrival of the droplets at the surface at speeds greater than several meters a second would presumably cause disruption and re-orientation of existing structures, and asymmetry would result from local thermal gradients in the film. The subsequent modification of the structures and the probable reflection of ice planes at the existing liquid-solid and the liquid-air interfaces would serve to complicate and strengthen the ice deposits, as would also the accretion of ice particles and other foreign motes in addition to the supercooled droplets.

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