Epitaxial Freezing of Supercooled Droplets on Ice Surfaces*

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Abstract

The structure and orientation of ice crystals in a water droplet frozen on a prismatic or a basal plane of ice substrate at temperature down to −23°C were investigated.

On the prismatic plane above −20°C the droplet froze into a single crystal, which had the same orientation as the substrate ; between −21°C and −23°C about 30% of the droplets polycrystallized, at least one of the crystals in the droplet having the same orientation as the substrate.

Meanwhile, on the basal plane the droplet always froze into a single crystal above −10°C, while at −11°C about 50% of the droplets and at −14°C and below all of them polycrystallized. In most cases of monocrystallization on the basal plane, the crystal had the same orientation as the substrate, but a misorientation resulting from a rotation of the crystal by less than 10° around the c-axis was found in a few cases of freezing at −11°C or below. In case of the polycrystallized droplet no crystal had the same orientation as the substrate, differently from the polycrystallization on the prismatic plane. Instead, every crystal and the substrate had in common the direction of one of the a-axes each other ; and the c-axis of the former was parallel to the direction of one of the 0−0 bonds of the latter other than the one parallel to the c-axis of the former.

As for the polycrystallized droplet frozen below −18°C on the basal plane the number of crystals was large and all possible six orientations were usually realized, giving a hexagonal arrangement of Laue spots specific to them.

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Contents

I. Introduction

Freezing of a supercooled droplet on impacting an ice substrate has long been recognized to play an important role in forming a natutal polycrystal snow and also in the growth process of hail and rime. Hallett (1964) first experimented in a supercooled water droplet by letting it impact an ice substrate and found that the structure and orientation of a crystal grown in the droplet depended on both the temperature and the orientation of the substrate.

Since then, similar experiments have been conducted by various authors (Higuchi and Yosida, 1966 ; Levi and Aufdermaur, 1970 ; Aburakawa and Magono, 1972 ; Macklin and Rye, 1974 ; Levi, deAchâval and Lubart, 1974 ; Levi, Nasello and deAchâval, 1980 ; Wainscoat and Macklin, 1982). They were mostly concerned in the orientation of a crystal relative to that of the substrate. They found consequently that the distribution of orientation shows some peaks depending on the temperature and the orientation of the substrate ; and that despite some discrepancies among their results, they seem not discrepant about the peak around 70° when the droplet polycrystallized on the basal plane of the substrate.

Among the measurements of axial angles between spatial branches of natural polycrystalline snow by various authors, the most comprehensive are probably the measurement carried out by the Magono group of Hokkaido University in the early 1970's (Lee, 1972 ; Uyeda and Kikuchi, 1976 b). According to their results, a peak is found around 70° in all kinds of polycrystalline snow crystals namely, spatial dendrites, radiating assemblage of dendrites, crossed plates and combination of bullets (Uyeda and Kikuchi, 1976 b).

Since polycrystalline snow crystals except the radiating assemblage of dendrites have been considered polycrystalline in their embyonic stage, Uyeda and Kikuchi conducted an experiment of spontaneous freezing of a supercooled water droplet suspended at the interface of dichloroethane liquid and parafin liquid and measured the angle between the c-axes of the neighboring crystals (Uyeda and Kikuchi, 1976 a). They found that, though two peaks, one around 25° and the other around 75°, appeared in the distributions of angles, only the latter remained after the annealing of the frozen droplet. Later, they conducted an experiment of heterogeneous freezing of a supercooled water droplet by seeding it with a needle of a single crystal of ice (Uyeda and Kikuchi, 1980). Then polycrystallization occurred in the shape of a hemisphere most frequently when it was seeded with a basal plane of the single crystal. Both the angle between the c-axes of the neighboring crystals and that between the c-axis of one crystal and that of the seeding crystal had a peak around 75° in the distribution of angles.

It was Kobayashi, Furukawa, Kikuchi and Uyeda (1976) who explained the appearance of these peaks on the basis of the calculation of the angle of two c-axes of a possible twin crystal of ice ; they determined that the angle is 70.3° for a $[30\bar{3}4]$ twin. Kobayashi, Furukawa, Takahashi and Uyeda (1976) also suggested that, if the twin is a penetrating type, the portion shared in common should have a cubic structure. Subsequently Takahashi (1981)

proved thermodynamically the possibility of formation of a cubic embryo in supercooled water ; he considered that some of the eight {111} planes of a cubic embryo might serve as a basal plane of a hexagonal ice which will be grown later. In this case, the c-axes of two hexagonal portions will make an angle of 70.5°. On the other hand, Furukawa (1982) made clear that the $(30\bar{3}4)$ and $(30\bar{3}8)$ planes constitute favorable mirror planes for the twin crystal of ice from the viewpoint of the C. S. L. (Coincident-Site Lattice) theory. Recently, Whally (1981) stated that Scheiner's halo is an indication of evidence in favor of the presence of a cubic ice in the atmosphere, but a question remains to be solved about the optical properties of the cubic ice. Verification of the explanations proposed above and clarification of the mechanism of polycrystallization call for more accurate measurements.

In the earlier experiments the orientation of crystals in a frozen droplet was deduced from hoar grown on the droplet by supplying water vapor afterward to simulate natural snow growth. In such a case as well as in natural snow, the orientation of a growing crystal will undergo distortion for many reasons. To avoid it Uyeda and Kikuchi (1980) made the direct determination of the orientation of a crystal using the optical method with the universal stage despite that it had an error up to 5°.

The present study will use both X-ray Laue photography and the optical method. The former is to obtain atomically accurate crystallographic relations between individual crystals in a frozen droplet as well as between them and a substrate. As has been known from the results of other scientists' previous experiments, probably the most interesting phenomenon will be polycrystallization which will occur only when the droplet impacts (or is seeded by) the basal plane. In this connection the droplet impacting a prismatic plane will be treated briefly. Also interesting in the texture (from, arrangement and number of crystals) of the frozen droplet, the optical investigation of which is the easiest for a general consideration of growth of an ice crystal in supercooled water.

Following this introduction, the preparation of samples and the methods of investigation will be briefly described in Chapter II. Secondly the results of optical observations will be given in Chapter III. Next X-ray Laue photographs taken will be analyzed in Chapter IV ; particularly, it will be shown that in the case of polycrystallization of a droplet on the basal plane the angle between the c-axes of any two neighboring crystals and that between the c-axis of a crystal and that of the substrate are 70.5°, as predicted by Takahashi. It will be shown then in Chapter V that, when the crystal and the substrate have the same orientation optically, they are in fact in the same orientation in atomic order. The results of observations of the surface with the scanning electron microscope will be given then in Chapter VI, the surface structure of the substrate being considered to play an important role in determinig the crystal orientation of the impacting droplet. Finally some kinematical explanations will be given in Chapter VII for the observed results presented in Chapters III and IV.

II. Experimental Procedures

II. 1. *Freezing of Supercooled Droplets on Ice Surfaces*

A small piece of ice, 0.5~1 mm in thickness and 10×10 mm^2 in surface area, was cut out as an ice substrate from either a single crystal of Mendenhall glacier or and artificially grown single crystal, the surface of which was so chosen as was exactly the basal or the prismatic plane with the aid of the X-ray method. A thin dendrite plate grown in the melt and a thin hexagonal hoar crystal were used as substrates also.

The substrate was put in a cold room at temperatures ranging from −8°C to −23°C and water of 0°C was sprayed with an atomizer horizontally about 2 m above the substrate. The size of the sprayed water droplets ranged from 100 to 300 μm in diameter. According to Stokes' equation, the terminal velocity of a water droplet 300 μm in diameter in an environment of −10°C is 2.9 m/sec. However, because of natural convection in the cold room, the droplets stayed in the air long enough to attain the environmental temperature (Kuhn and Mason, 1968) and also impacted the substrate with a much less speed than the calculated terminal velocity. The impact, thus caused no catastrophic deformation of the droplet, serving mainly to break up the state of supercooling, and ice was formed in a hemispheric shape on the ice substrate.

II. 2. *Method of Optical Observation*

As mentioned in the introduction, the texture of a frozen droplet (namely, the from, arrangement and number of crystals in it) was investigated with a polarizing light microscope, which also gave information of the orientation of the crystals.

For this observation, the top of the frozen hemisphere was carefully planed with a razor blade so as to make the surface of the top parallel to the surface of the substrate as much as possible. As the height of the hemisphere was of the order of 100 μm, its thickness came to ammount to 40 to 60 μm after planing, while the thickness of the substrate was 500 to 1000 μm as mentioned in the preceding section.

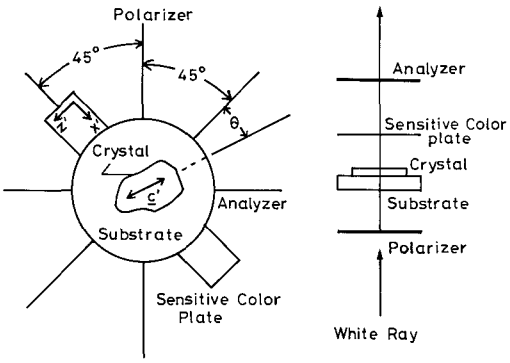


Fig. 1 Schematic illustration of an optical system used for analyzing. Retardation : $R=530(nm)+d(n_2-n_1)$ for $\theta=0°$, bluish. $R=530(nm)-d(n_2-n_1)$ for $\theta=90°$, yellowish.

Clear images of such thin crystals on a thick substrate were obtained by placing a sentitive color plate of 530 nm between the specimen and the analyzer as schematically shown

in Fig. 1, where a bidirectional arrow c' indicates the direction of the projection of the c-axis of the ice crystal subjected to observation. Suppose that ice crystal is in the extinction position (either the c-axis is parallel to the observation axis or the angle θ in Fig. 1 is equal to $\pm$ 45°). Then as is well known it shows no effect on the color of the image regardless of its thickness. It is because the retardation of the two rays through the analyzer is solely determined as 530 nm by the sensitive color plate, which gives rise to a pinkish red color. On the other hand, if the crystal is either the adding position ($\theta=90°$), the retardation is 530 nm plus or minus $d(n_2-n_1)$, respectively, where, d is the thickness of the crystal and (n_2-n_1), the difference of the refraction indices of ice, is about 0.004. For a thin crystal with the value of d sufficiently less than 530/0.004 nm (108 μm), these value of retardation give either a bluish (for the adding position) or a yellowish (for the subtracting position) color. In the intermediate positions ($\theta\neq 0°$, $\pm 45°$, $\pm 90°$), it is hard to define the color because of the emergence of not two but four rays with different intensities ; but around the adding position, namely, $-20° < \theta < +20°$, the color is bluish, while around the subtracting position, namely $70° < \theta < 110°$, the color is yellowish.

When crystals on the substrate were actually observed the substrate was placed always in the extinction position, which is automatically fulfilled if the basal plane constitute the surface of the substrate. To find the direction of c' of a crystal on the substrate, one only needs to rotate the specimen so as to make the color of the crystal just as the same as that of the substrate. Then the angle θ is either plus or minus 45°. On a further rotation by 45° the sign is determined by the color change of the crystal.

In case that the prismatic plane constitutes the surface of the substrate, the substrate is first brought in the extinction condition without the sensitive color plate. If a crystal lends quite the same color as the substrate when the sensitive color plate is inserted, we may conclude that c' is either parallel or perpendicular to the c-axis of the substrate. Further optical determination of c' was not attempted in this case.

II. 3. *X-ray Observation*

Optical observations mentioned above give only partial information of the orientation of the crystals. More complete and accurate information will be most conveniently obtained by X-ray Laue photographs. A white beam about 500 μm in diameter was irradiated perpendicularly to the surface of the substrate, namely, parallel to either the [0001] direction (in case the basal plane constitutes the surface of the substrate) or the $[10\bar{1}0]$ derection (in case the prismatic plane constitutes the surface of the substrate) of the substrate. And a transmission Laue photograph was taken, which thus simultaneously produced spots due to both the substrate and the crystals. If spots other than those of the well-defined pattern of the substrate were absent, it was concluded that the crystals had the same orientation as the substrate ; otherwise, some crystals must have been misoriented, whose orientation relative to that of the substrate could be deduced from photograph. As the photograph contained

spots due to all crystals, the orientation of an individual crystal might not be identified by this method. But combined with the result of an optical observation, sufficient information can be obtained concerning the orientations of the crystals for a later discussion, as shown in Chapter IV.

The accuracy of determination of the relative orientation by the Laue photograph was about $\pm$ 0.5° in the present study. When it was concluded from a Laue photograph that a crystal has the same orientations as the substrate, the coincidence of the orientations was further checked with an X-ray topography with an accuracy of $\pm 5\times10^{-4}$ rad (0.03°). The detail of it will be given in Chapter V.

III. Results of Optical Observations

III. 1. *Droplets Frozen on the Prismatic Plane*

It is well known that natural snow crystals are mostly surrounded by the basal and the prismatic plane, as they are the most stable ones of the ice crystal in terms of energy. When snow crystals fall through supercooled clouds, accretion of water droplets will hence occur on both kinds of the planes. However, few misorientated crystals are found on the prismatic plane of the snow crystals, showing that the water droplets impacting the prismatic plane are mostly incorporated into the mother crystal. Uyeda and Kikuchi (1980) showed that at a

Fig. 2 Microphotograph of polycrystalline droplets frozen on the prismatic plane at −21°C. Orientation of the largest crystal coincides with that of the substrate.

temperature range from −17°C to −26°C, the possibility of polycrystallization of a water droplet seeded with the prismatic plane is about a half of that seeded with the basal plane. In this connection an experiment which will present an interesting insight from the point view of cloud physics.

Summarized, the results of such an experiment in the present study are as follows : Above −20°C, droplets impacting the prismatic plane always froze as a single crystal with the same orientation (including the a-axis as verified by Laue photographs) as the substrate. Even at lower temperatures of −21°C to −23°C, only 30% of the droplets polycrystallized. Moreover, even in the case of polycrystallization, the largest of the crystals had the same orientation as the substrate, as indicated by the colors of the crystals in a typical polarizing light microphotograph of droplets frozen at −21°C on the prismatic plane (Fig. 2). No regularity was found then in the orientation of the misorientated crystals.

III. 2. *Droplets on the Basal Plane*

On the basal plane, the texture and the orientation of frozen droplets show characteristic dependence on temperature. Above −10°C, the droplets always froze as a single crystal, while polycrystallization occurred in a half of the droplets at −11°C and in all at −14°C and below.

A typical microphotograph of monocrystallized droplets is shown in Fig. 3A, where the sample was frozen at −8°C. In the case of monocrystallization, the color of the crystal did not change by the rotation of the sample and remained the same as that of the substrate, showing that the c-axis of the crystal was normal to the surface of the substrate, namely, having the same orientation as that of the substrate.

In the case of polycrystallization, the texture of the frozen droplet changed sharply at −18°C. A polarized light microphtograph of the droplets frozen at −14°C shown in Fig. 3B is typical of that of the polycrystallized droplets frozen above −18°C. As seen from the photograph, the crystals were rather fat in their form and irregularly arranged (in two dimensional cross section). On the other hand, as exemplified in Fig. 3C by a microphotograph of the droplets frozen at −21°C, the crystals frozen below −18°C were bar-like in their form and arranged in a regular manner in which the long axis of the bar was parallel to one of the three directions intersecting at an angle of 60°. Moreover, the parallel bars made up a few grains of the same interference color. Three dimensionally, the crystals obtained above −18°C must have been of the form of a lump, while the group of the parallel bars obtained below −18°C of the form of a pack of the parallel platelets.

By the method described in Section II. 2, the projection of the c-axis of a bar-like crystal on the surface of the substrate was proven to be normal to the long axis of the bar. Despite their irregular arrangement, the c-axes of the crystals frozen above −18°C were also proven to be parallel to one of three directions intersecting one another at an angle of 60°, quite similarly to the case of the polycrystallized droplet frozen below −18°C. The critical

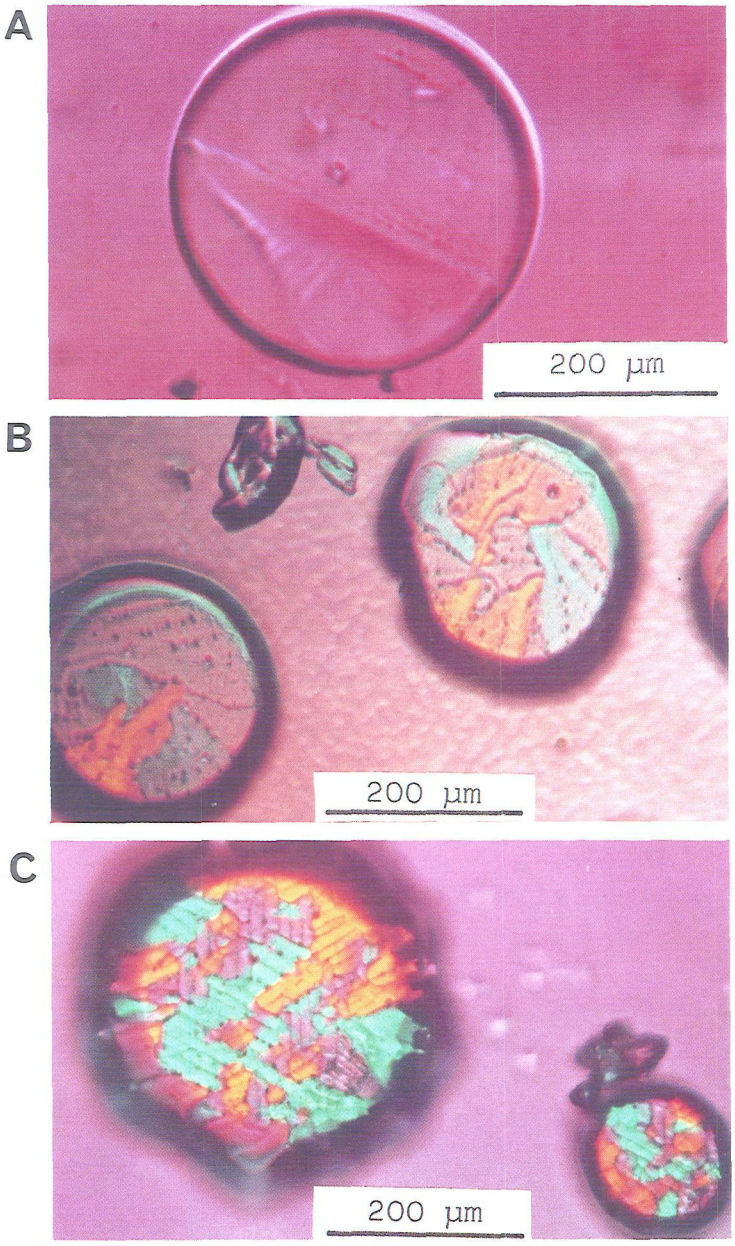


Fig. 3 Microphotographs of droplets frozen on the basal plane observed under crossed polarized light.
(A) frozen at −8°C, (B) −14°C, (C) −21°C.

temperature of −18°C affecting the texture seemed to have little effect on the orientation of the c-axis of the crystal. No crystal with the c-axis of the same orientation as that of the substrate was found in the polycrystallized droplets on basal plane, irrespective of the frozen temperature.

III. 3. *Number of Crystals in a Polycrystallized Droplet on the Basal Plane*

A comparison between Figs. 3B and 3C suggests that the number of crystals in a polycrystallized droplet on the basal plane increases with lowering temperature. In Fig. 4, the number is plotted against the frozen temperature of droplets about 250 μm in diameter, where each open circle represents an average of 50 droplets. The number actually increases exponentially with lowering temperature from −11°C to −18°C, where it levels off. The number as well as the form of the crystals shows no remarkable change from −18°C to −23°C, the lowest temperature in the present study, as was implicitly mentioned in the preceding section.

The number naturally depended on the diameter of the droplet. In Fig. 5, the number is plotted against the diameter of a droplet frozen at −15°C and −20°C. As seen from the figure, at both temperatures, the number increases with increasing diameter as expected. In particular, at −20°C, it increases quadratically. Namely, the average size of the crystal is independent of the diameter of the droplet.

This is clearly shown in Table 1, which is compiled from the data represented in Fig. 5 by open circles, each showing the average number of crystals of all droplets of the same diameter observed in the present experiment. It follows from the average area of 4×10^{-4} mm^2 in the Table that an average ratio of the length to the width of the bar is about 4, as

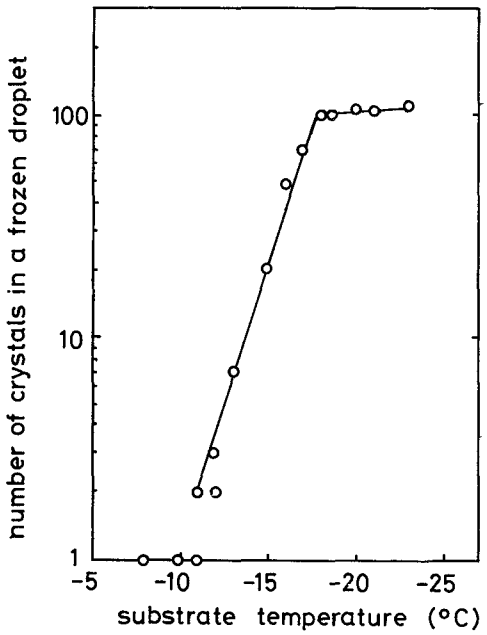
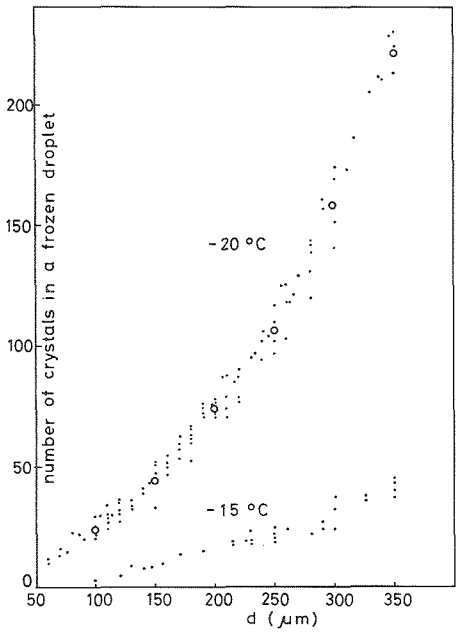


Fig. 4 Relation between the average number of crystals in a frozen droplet about 250 μm in diameter and the substrate temperature.

Table 1

diameter of a droplet(mm)	number of crystals	area per crystal(mm^2)
0.1	24	3.3×10^{-4}
0.15	44	4.0
0.2	75	4.2
0.25	106	4.6
0.3	157	4.4
0.35	221	4.3

Relations between the diameter of a droplet and an average area per crystal (frozen at −18°∼−23°C).



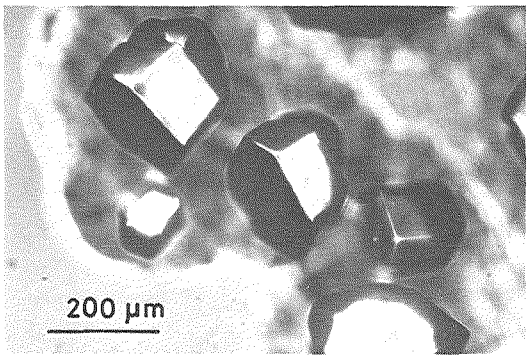


Fig. 6 Microphotograph of crystals grown at −11°C by supplying water vapor to droplets frozen at −15°C.

Fig. 5 Relation between the number of crystals in a droplet of various diameters frozen at −15° and −20°C.
One dot corresponds to one droplet and an open circle to the average of droplets having the same diameter.

the width of the bar is about 10 μm.

It must be noted that not all of the crystals in the frozen droplet were capable of growing when water vapor was supplied to it. Figure 6 is a photograph of crystals grown on polycrystallized droplets frozen at −15°C by supplying water vapor at an environmental temperature of −11°C. Only one or two crystals were grown on one droplet which probably had at least 10 crystals. The technique of growing hoar can determine the orientation of only one or two of the many crystals in a frozen droplet.

IV. Analysis of the Laue Photographs of a Frozen Droplet on the Basal Plane

IV. 1. *Laue Photographs of Monocrystalline Droplet*

As was mentioned in Section III. 2, optical observations revealed that all the monocrystalline droplets on the basal plane had the same orientation of the c-axis as the substrate. The Laue photographs of them taken in a manner described in Section II. 3, usually gave only the well-known hexagonal pattern of the substrate shown in Fig. 8B, proving that the orientation of the frozen droplets was completely, that is, with regard not only to the c-axis but also to the a-axes, same as that of the substrate.

However, in a few cases of freezing at −11°C or −12°C, the Laue photographs of them

produced a double image of the hexagonal pattern exemplified in Fig. 7 of a monocrystalline droplet frozen at −11°C on the basal plane. In the figure one can easily recognize that a pattern similar to that of Fig. 8B (rotated by about 60°) consists of brighter spots ; and also that the remaining less bright spots make up a similar pattern rotated counterclockwise by about 8°. It was then concluded that in this case the frozen droplet is misoriented from the substrate by the rotation around the common c-axis of about 8°.

Such rotational misorientations are found in nature in twelve-branched snow crystals. Kobayashi and Furukawa (1976) measured the angle of misorientation of 116 such crystals and found three peaks at 30°, 27° and 22° in its frequency histogram. They also reported no angle of misorientation less than 10°. In the present care, however, three out of about 150 monocrystalline droplets were misoriented and all these three had angles of misorientation less than 10°.

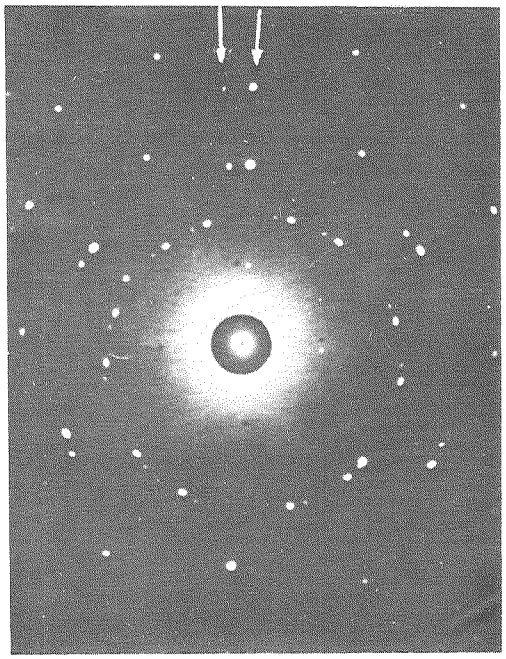


Fig. 7 Laue photograph of a monocrystallized droplet frozen at −11°C on a substrate. The droplet and the substrate misorientated from each other by a rotation of about 8° around the common c-axis.

IV. 2. *Laue Photographs of Polycrystalline Droplets*

Optical observations showed that despite rather a clear distinction in texture between droplets frozen at temperatures above and below −18°C, the orientations of crystals in both kinds of the droplets were governed by such a simple rule that the projection of the c-axis on the surface of the substrate is parallel to one of the three directions intersecting one another at an angle of 60°. Then it is suggested that spots due to crystals in a Laue photograph of a polycrystalline droplet on the basal plane will show a three-fold symmetry if at least three areas each different in interference color are found in the corresponding polarized light microphotograph of the droplet.

A Laue photograph of a polycrystalline droplet frozen on the basal plane below −18°C is given in Fig. 8A, while given in Fig. 8B is the Laue photograph of the substrate as mentioned before. An illustration of Fig. 8A is shown in Fig. 9, where open circles represent the spots solely due to the crystals. Contrary to expectation, they show a six-fold symmetry instead of a three-fold one. Then it follows that two directions of the c-axis must exist for

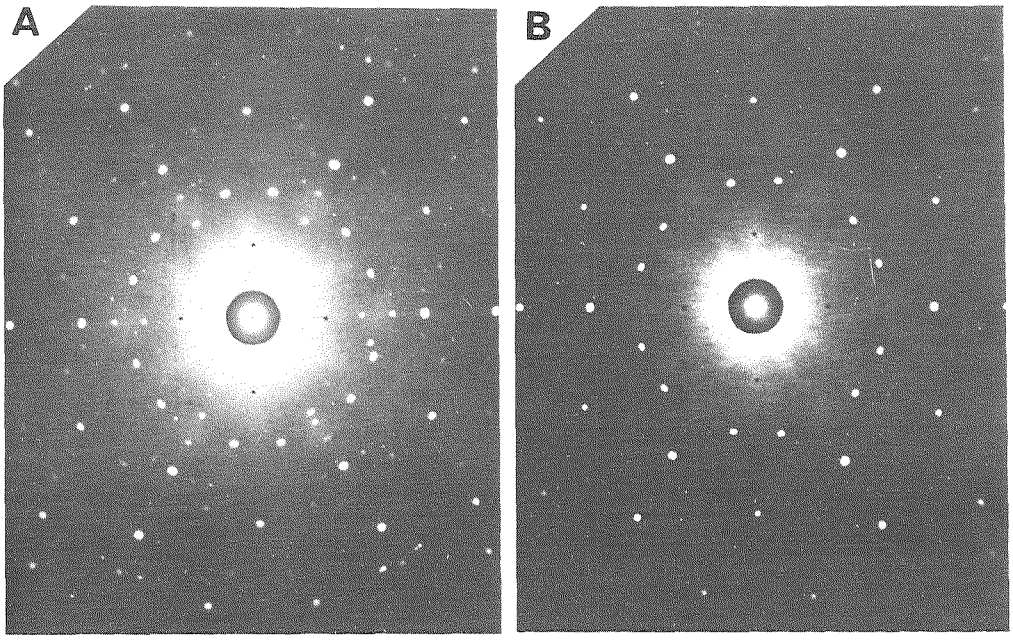


Fig. 8 (A) Typical Laue photograph of a droplet frozen below −18°C with spots due to both the droplet and the substrate. (B) Laue photograph of the substrate only.

crystals having the same color in the polarized light microphotograph.

In a Laue photograph of a polycrystalline droplet frozen above −18°C, part of the spots shown by open circles in Fig. 9 are absent. It reveals clearly then that the six-fold symmetry of the open circles in Fig. 9 is caused rather by six kinds of symmetrically arranged crystals than by some six-fold symmetry of a kind of crystal

IV. 3. *Possible Orientation of Crystals*

As mentioned in the introduction, both observations and theories by other researchers strongly suggest that in a polycrystalline droplet frozen on the basal plane the angle among c-axes of the crystals and the substrate was around 70°. One may consider then that the spots shown by the open circles in Fig. 9 are due to such tilted crystals.

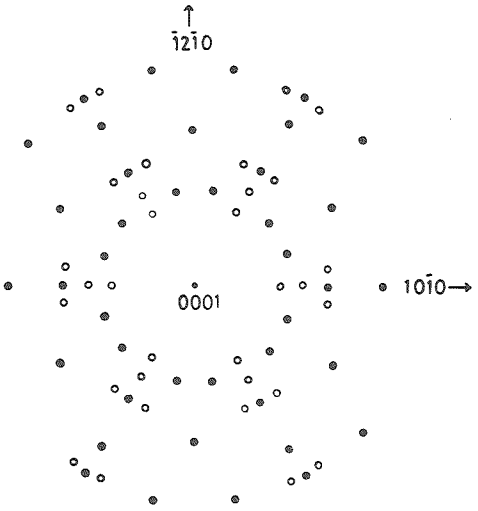


Fig. 9 Schematic illustration of positions of Laue spots of Fig. 8A. Open and solid circles represent respectively Laue spots due to the crystals in the droplet and to the substrate.

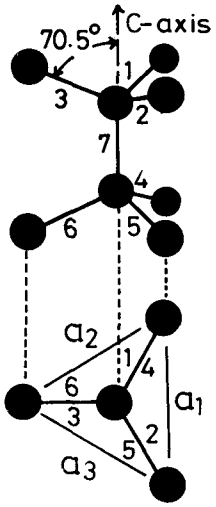


Fig. 10 Oxygen atoms form a tetrahedral configuration in ice I_h. The angle between the direction of the O-O bond (1~6) and the c-axis is 70.5°.

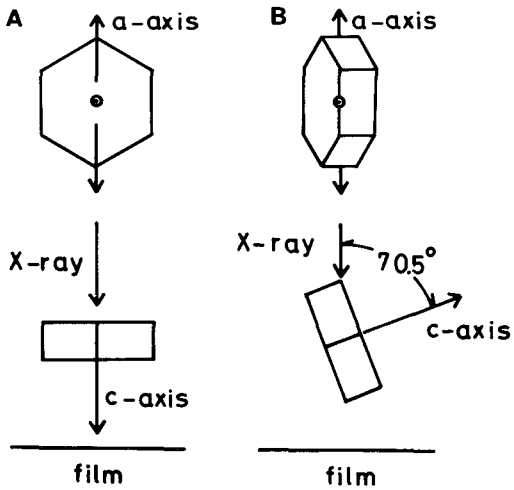


Fig. 11 Relative positions of the X-ray beam and the ice sample with beam parallel to directions of O-O bonds. (A) Parallel to the c-axis ; (B) Parallel to another of the O-O bond directions.

Now, oxygen atoms in ice I_h arrange themselves to make a tetrahedral configuration as illustrated in Fig. 10. The Laue photograph shown in Fig. 8B was taken with the arrangement shown in Fig. 11A, where the upper part shows the front view, while the lower the top view. As seen from the figure, one of the a-axes of the sample is placed parallel to the axis of the goniometer. The X-ray beam is irradiated parallel to the c-axis, or to the direction of an O-O bond labeled with 7 in Fig. 10.

A rotation of the ice sample around the axis of the goniometer by 70.5° changes the arrangement from Fig. 11A to Fig. 11B, where it is easily seen that the X-ray beam is now parallel to the direction of another O-O bond (labeled with 3 or 6 if the a_1 -axis in Fig. 10 is parallel to the axis of the goniometer). Laue photographs taken with this arrangement are given in Figs. 12A and 12B. In the former the ice sample was sufficiently large, while in the latter it was of the order of 100 μm in linear dimensions. As the intensity of diffraction is proportional to the irradiated volume, the number of recognizable spots is smaller in Fig. 12B than in Fig. 12A. For a crystal (or assembly of crystals of the same orientation) in a frozen droplet, one may expect at most the spots in Fig. 12B and more safely the encircled and indexed spots in Fig. 13, which is an illustrated map of Fig. 12B.

It is obvious that a reverse rotation of the sample by the same amount around the same axis gives rise to a mirror image of Fig. 13 with respect to the vertical axis in the figure. When patterns obtained by similar rotations around the other a-axes are combined, then a six-fold symmetric pattern of Fig. 14 is produced, which is just the same as the pattern made

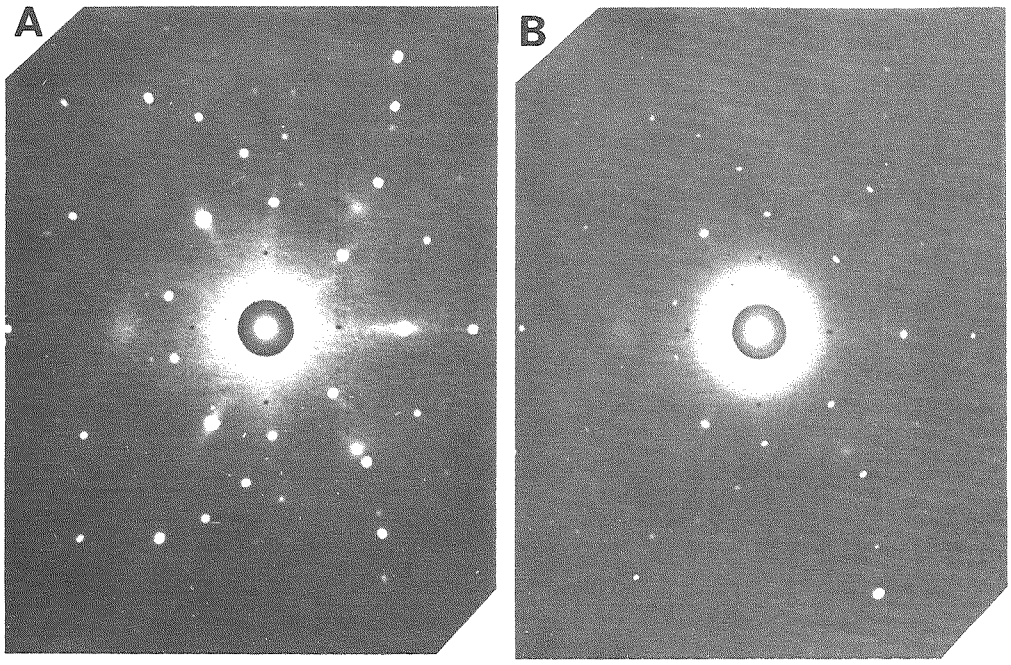


Fig. 12 Laue photographs of a single crystal of ice taken in the arrangement illustrated in Fig. 11B :
(A) of a sample larger than the X-ray beam area and (B) of a sample about half of it.

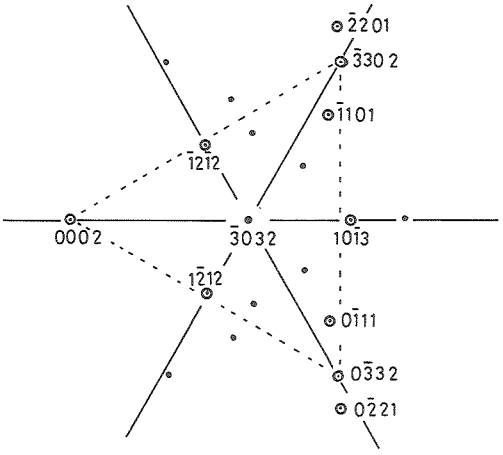


Fig. 13 Reproduced spots from the Laue photograph shown in Fig. 12. Only the indexed spots are likely to appear for a sample of the order of 100 μm in linear dimensions.

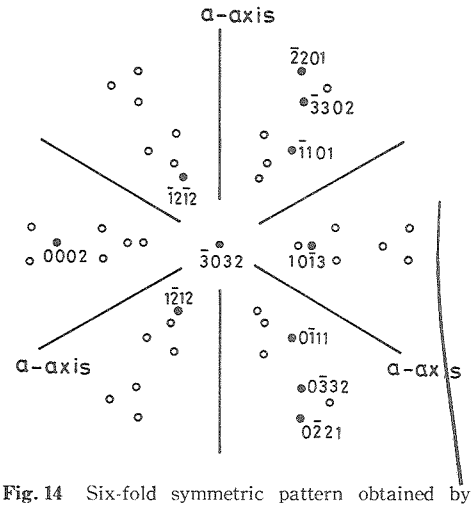


Fig. 14 Six-fold symmetric pattern obtained by combining the pattern produced after rotating the sample by 70.5° around each of the three a-axes.

up of the open circles in Fig. 9.

Thus, the Laue photograph of Fig. 8A can be understood to be made by the substrate and crystals arranged in six different orientations, each having the c-axis tilted by 70.5° from that of the substrate and one common a-axis direction with the substrate. In the case of a polycrystalline droplet on the basal plane frozen above −18°C, not all of the six orientations are realized ; and so, the Laue photograph comes to lose the six-fold symmetry.

IV. 4. *Optical Structure and Crystal Orientation of a Polycrystalline Droplet on the Basal Plane*

As was described previously, in the polarized light microphotograph of a polycrystalline droplet on the basal plane crystals are divided into at most three groups by interference colors. Now, it is obvious that the direction of an a-axis of each group is parallel to that of an a-axis of the substrate. Particularly, it constitutes the long axis of a bar-like form in the case of a droplet frozen below −18°C.

Each group having the same interference color is further subdivided into two subgroups by the orientation of the c-axis. Tilting by 70.5° from the c-axis of the substrate, the c-axis of each of the two subgroups is mirror-symmetrical with respect to the plane determined by the common a-axis and the c-axis of the substrate. The six c-axis orientations are parallel to the six O-O bonds of the substrate, but not parallel to its c-axis. These facts seem to support the existence of cubic nuclei proposed by Takahashi (1981).

V. X-ray Topography of an Ice Substrate with Frozen Droplets

The previous two chapters helped clarify the orientations of crystals in a frozen droplet on the basal plane of an ice substrate. However, two questions remain to be answered. The first question is : Is there really no crystal with the same orientation as the substrate in a polycrystalline droplet? Such a crystal can be recognized neither from Laue photographs, nor from polarized light microphotographs if it underlies misoriented crystals. The second question is concerned with the intrinsic limitation of Laue photographs in the accuracy of determination of the orientation of an ice crystal, the error amounting to about 0.5° in the present study. In other words, this question is on the accuracy more severe than 0.5° for the validity of the coincidence of such orientations of a monocrystalline droplet and the substrate that are determined from Laue photographs.

X-ray topographs of an ice substrate with frozen droplets were taken in anticipation of possible answers to these questions, using the method of X-ray diffraction topography (Lang's method).

As seen from a diagram of the scheme of this method shown in Fig. 15, a quasi-monochromatic (K_α and K_β) X-ray beam collimated through the first and the second slit irradiates a sample, while the third slit is so positioned that only a diffracted K_α beam

satisfying a specified Bragg condition can go through it to reach a film. By scanning the sample and the film simultaneously, the diffraction pattern of the whole crystal is recorded on the film. The method has an orientational accuracy of about 5×10^{-4} rad (0.03°). This means that, if a frozen droplet in Fig. 15 is misorientated from the substrate by more than that amount, the diffraction from the frozen droplet has no effect on the image on the film, while if not, the inner structure of the frozen droplet will be seen on the film together with that of the substrate.

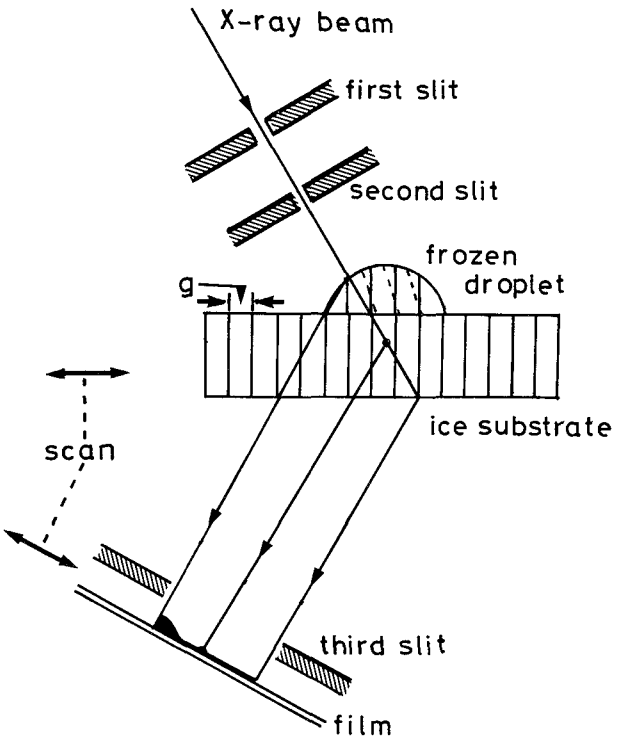


Fig. 15 Schematic diagram of Lang's method, g representing a diffraction vector (normal to the diffraction plane). If the orientation of a frozen droplet coincides with that of the substrate, the diffraction condition satisfied by the substrate will also be realized by the droplet.

A topography of the substrate with droplets, the latter being frozen at −10°C and proven by both Laue and polarized light photographs to be in the same orientation as the substrate, is shown in Fig. 16A, where the droplets are seen as gray spots, which are considered due to complicated inner structure (like a large number of imperfections) of the droplets. The droplets, thus contributing to the image on the film, are considered to be in the same orientation as the substrate with an accuracy of 0.03°,

On the other hand, Fig. 16B is a topography of the substrate with droplets frozen at −17°C. In the topography the droplets are identified only by their peripheries, across which the dislocation lines of the substrate are seen continuously and within which no new imperfections are seen. It shows that no crystals with the same orientation as the substrate are present within the peripheries (or in the droplets).

VI. Surface Topography of the Basal Plane

As described in Chapters III and IV, the texture and orientation of a frozen droplet on the basal plane of an ice substrate showed a clear dependence of them on the environmental

temperature, which on the one hand directly determined the intensity of supercooling of the droplet and on the other was considered to have had an effect on the surface topography of the substrate. The dependence of the surface topography on the environmental temperature will be described in this chapter.

Use of the scanning electron microscope may be the best way to observe the surface topography of a material. However, in case of ice at such very high temperatures as is met in the present freezing experiment the direct observations of it with the scanning electon microscope is not practical because of its high vapor pressure. Therefore, a Formvar replica of the surface of ice, prepared with a replication technique invented by Schaefer (1950) and later developed by Higuchi (1957, 1958), was observed with the scanning electron microscope.

Observations of a Formvar replica of the ice surface with the scanning electron microscope have been carried out earlier by Kuroiwa (1969) and Shinha (1977). They used a Formvar solution at a relatively high concentration (5~6%) in order to create evaporating and/or dislocation etch pits on the ice surface during the slow evaporation of the solvent. However, the present experiment found such etch pits undesirable. Hence, a more dilute Formvar solution (1~2%) in ethylene dichroride was used.

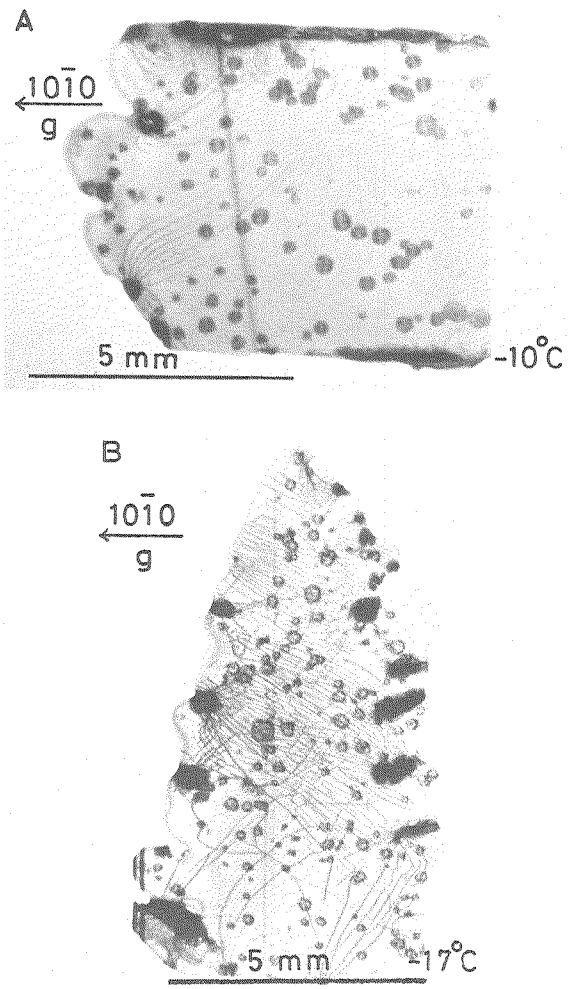


Fig. 16 X-ray topographies produced by scanning of the basal plane of an ice substrate with frozen droplet on it. (A) : frozen at −10°C ; (B) : at −17°C.
[10$\bar{1}$0] reflection ; Mo-K$_\alpha$ radiation.

Procedures to make a replica are as follows : A Formvar solution and an ice sample are put in a cold room at a desired temperature. After both the sample and the solution have attained the room temperature, part of the surface of the sample is coated with a small

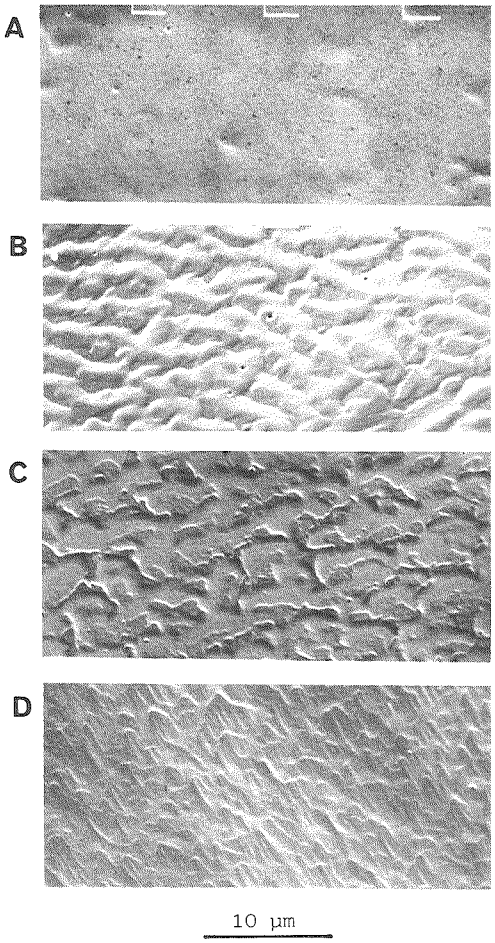


Fig. 17 The scanning electron micrographs of the replicas of the basal plane made at (A) −9°C, (B) −12°C, (C) −14°C, (D) −21°C.

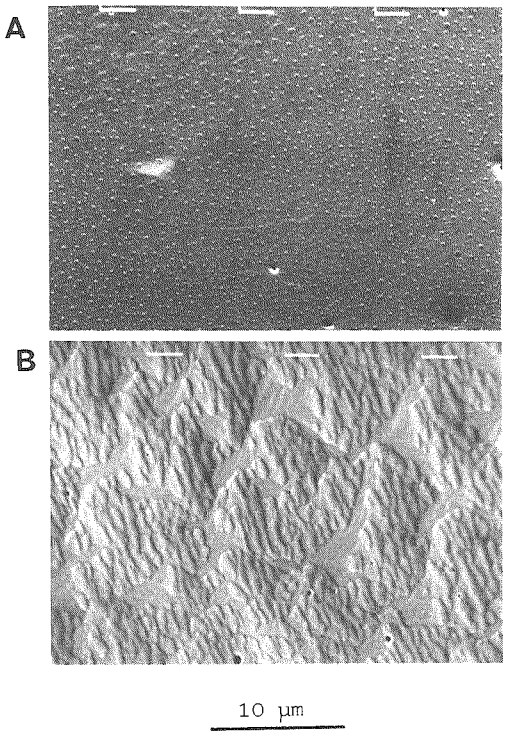


Fig. 18 Surface topographies of a cleaved basal plane at (A) −9°C and (B) −12°C.

quantity of the solution, whose solvent evaporates so fast as in about five minutes that few etch pits are created on the ice surface. Then, the remaining Formvar film is stripped off the ice surface and laid upside down on a glass slide. The surface of the film, which replicated the ice surface, is later decorated by the sputtering of Au ions.

The possibility of chemical etching of the ice surface with a Formvar solution has often been suspected, for the solubility of water in ethylene dichloride is 0.914% by weight at 0°C. But in the present experiment the Formvar solution was saturated with ice so that such chemical etching was impossible.

The scanning electron micrographs of the replicas made at the environmental temperatures of −9, −12, −14 and −21°C of arbitrary parts of the basal surface of an ice sample $5\times5\times0.5$ cm^3 in dimensions are given in Figs. 17A to D, respectively. The ice sample was cut from a block of a single crystal from Mendenhall glacier, whose surface was as carefully

prepared parallel to the basal plane as possible and then finished by evaporation.

A most striking fact seen from these figures is that the surface is very smooth at −9°C while fairly rough at lower temperatures. This fact is not due to the method of preparation of the ice surface as seen from a comparison between Figs. 18A and B, which are the scanning electron micrographs of a cleaved basal plane of ice at −9° and −12°C respectively.

It has been generally considered that the higher is the temperature the rougher is the surface. The apparent contradiction revealed above may be explained by the existence of a quasi-liquid layer at −9°C, which has become generally accepted both from theoretical (Fletcher, 1968 ; Kuroda and Lacmann, 1982) and experimental standpoints (Kvlividge et al., 1974 ; Mizuno and Hanafusa, 1980).

The roughness of the surface at the lower temperatures seemed to be divided into three types depending on temperature. In the first type, roughness appears around −12°C, the surface being covered with parallel grooves as seen in Fig. 17B ; in the second type, roughness appears between −14°C and −17°C, with a network of grooves as seen in Fig. 17C ; and in the third type, roughness appears below −18°C, the surface becoming scaly as seen in Fig. 17D.

It is not easy to describe such divergent kinds of roughness quantitatively. But an attempt was made to assign a number per unit area ($\pi\,(\frac{250}{2})^2\ \mu m^2$) to each of the three types in the following manner : The numbers of grooves, knots of networks and scales to the first, second and third, respectively. The result of such an analysis is given in Fig. 19, where the numbers in the area of a circle of a diameter of 250 μm are plotted against temperature.

It is surprising to find that these rather arbitrarily defined numbers assigned to the surface roughness depended on temperature in a very much similar manner to the number of crystals in a polycrystalline droplet (Fig. 4 in Sec. III. 3).

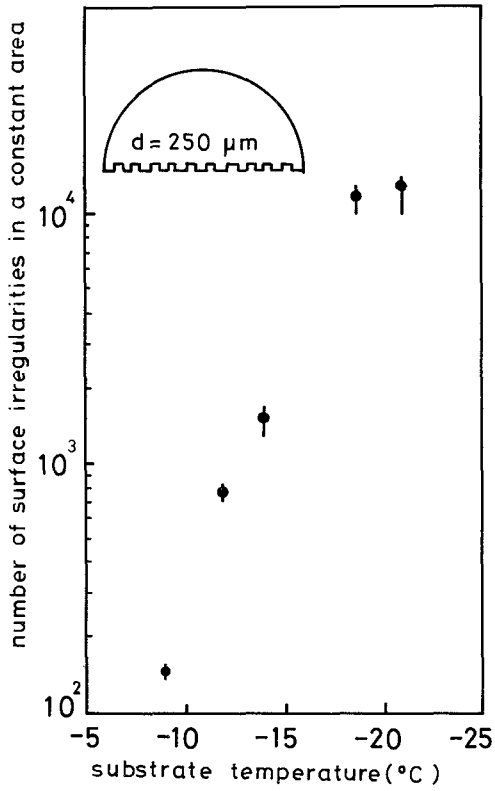


Fig. 19 Number of surface irregularities in a constant area plotted against the substrate temperature.

VII. Discussion

As shown in Chapter IV, the orientation of a crystal in a polycrystallized droplet on the basal plane of an ice substrate was such that the angle between the c-axis of the crystal and that of the substrate was 70.5° and the crystal and the substrate had in common the direction of one of the a-axes. Kobayashi, Furukawa, Takahashi and Uyeda (1976) proved that this orientational relation is given if the crystal and the substrate are both "epitaxially connected" to one cubic ice in such a manner that the basal planes of the former are "identical with" two nonparallel {111} planes of the latter. Here, both the descriptions of "epitaxially connected" and "identical with" mean that all oxygen atoms on the boundary plane are in normal positions with regard to both the cubic and the hexagonal lattice. This implies then that the a-axes of the hexagonal lattice are in the ⟨110⟩ directions of the cubic lattice. Since any two {111} planes have one common ⟨110⟩ direction, it is obvious that the crystal and the substrate have one common a-axis direction. On the other hand, it is easily proven that any two nonparallel {111} planes make an angle of $\cos^{-1} 1/3$ or 70.5°. Hence, the c-axis of the crystal and that of the substrate, each normal to one {111} plane, make that angle.

As mentioned ealier, the orientation of a crystal was determined with as accuracy of less than 0.5°. Hence, it is almost certain that each misorientated crystal and the substrate were connected by a cubic nucleus as Kobayashi et al. (1976) proposed.

Now, Takahashi (1981) showed that cubic nuclei are more stable than hexagonal ones in

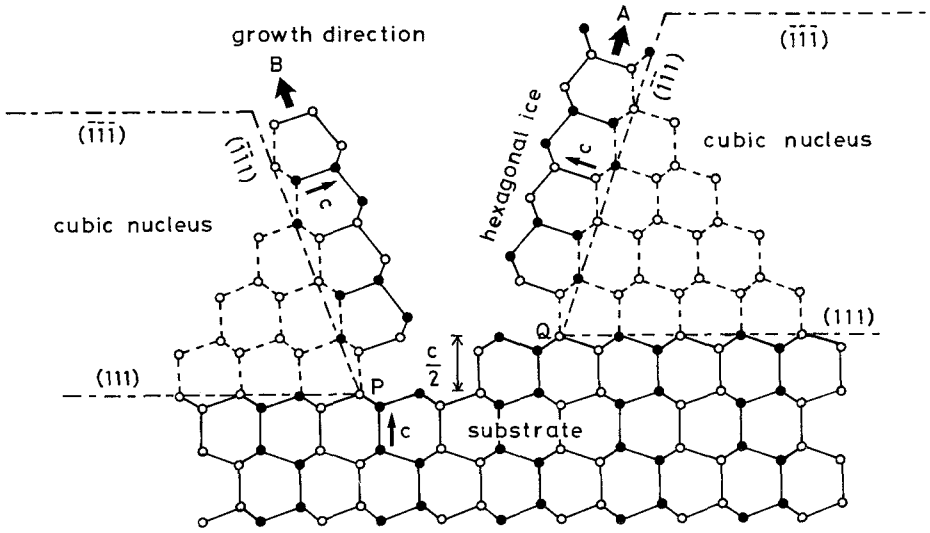


Fig. 20 Schematic illustration of the lowest step on the basal plane projected on the $(11\bar{2}0)$ plane, which generates the crystals orienting one another oppositely.

supercooled water, if the degree of supercooling is strong enough. He also discussed the relative frequency of formation of cubic and hexagonal nuclei on the basal plane of a substrate covered with supercooled water. He suggested then that below about −12°C the formation of cubic nuclei becomes noticeable and below −18°C both nuclei appear almost evenly.

In the present experiment, nuclei may be considered to be formed either *in* the droplet and later connected to the substrate or directly *on* the substrate. However, it is difficult to accept the first process because almost all of the crystals in the present experiment indicated that their nuclei were "epitaxially connected" to the substrate, except only three out of about 150 monocrystalline droplets showing a rotation around the c-axis, as described in Sec. IV. 1. Then, according to Takahashi, even at −18°C or below, both hexagonal and cubic nuclei must exist on the substrate. Then, a question will arise about why only the cubic nuclei grew into visible crystals of hexagonal structure.

Before discussing the question, let us answer another simple one : Why are there six possible orientations of the c-axis when there are only three pairs of parallel {111} planes not normal to the basal plane of the substrate?

For the sake of clarity, suppose that the cubic nuclei have the form of an octahedron surrounded by eight {111} planes and its (111) plane is connected to the basal plane of the substrate. Now, in an hexagonal ice, there are two kinds of basal planes c/2 apart from each other as shown in Fig. 20, which represents the projection of the oxygen lattice of the substrate with two cubic nuclei (the parts with dotted bonds) adjacent to the $(11\bar{2}0)$ plane of the substrate. It is obvious from the projection that the nuclei must be orientated as shown in the figure, with points P and Q being the vertexes of the octahedron. Without loss of generality, the plane on to which a new hexagonal lattice is added can be considered to be the $(\bar{1}\bar{1}1)$ plane of the individual nucleus. Thus, the $(\bar{1}\bar{1}1)$ plane of the nucleus gives two different possible directions of the c-axis depending on the kinds of basal planes on to which the uncleus is connected.

The newly added lattices and the substrate have in common the direction of one of the a-axes normal to the plane of the paper. The two possible directions of the c-axis are then mirror symmetric with respect to the plane determined by this common a-axis and the c-axis of the substrate, as was postulated in the explanation of the six-fold symmetry in Sec. IV. 3.

It must be noted here that, if such a mirror symmetric pair of c-axes are observed in a polycrystallized droplet, the surface of the substrate will certainly be made up of both kinds of basal planes.

The appearance of a new hexagonal lattice on the cubic nuclei, which is essential for the growth of a misorientated crystal, is most easily understood by the local heating of water due to the growth of nuclei. According to Takahashi, formation process of nuclei on the {111} planes of a cubic ice is the same as that on the (0001) plane of an hexagonal ice. Hence, when water temperature rises higher than −12°C or so, only hexagonal nuclei can be formed on the

{111} planes of the grown cubic nuclei.

Now, let us return to the first question about why crystals with the same c-axis direction as the substrate were not observed in a polycrystallized droplet despite that hexagonal nuclei were supposed more numerous than cubic nuclei. The question may be partly answered by the "wedge-shaped shrinking process" of unfavorably orientated crystals frequently observed in crystal growth from a supercooled melt. A brief explanation of this process will be given for the present case.

For the sake of convenience, ice will be hereafter called "normal" if its c-axis is parallel to the c-axis of the substrate, and called "slant" otherwise. When cubic nuclei have been covered with an hexagonal ice, the boundary may be such that small points of a slant ice are scattered in a normal ice. Since ice grows faster in the direction normal than parallel to the c-axis, the points of the slant ice will grow into fan-like plates protruding into water and running over the normal ice in its a-axis directions. (Such protrusion is possible because of the supercooling of the droplet.) Eventually these plates will make a network of tilted walls on the normal ice.

Cross section normal to the substrate surface of the boundary at this stage are shown in Fig. 21, where for the sake of simplicity only the cases in which the c-axis of the two walls and the c-axis of the normal ice are on the same plane. Suppose that the normal and the slant ice have the same growth rate parallel to the c-axis. Then, the dotted line in the figure will constitute the boundary between them in the final stage. In every case the normal ice continues to shrink, making a flat wedge, whose ratio of height to base is given in the caption of the figure.

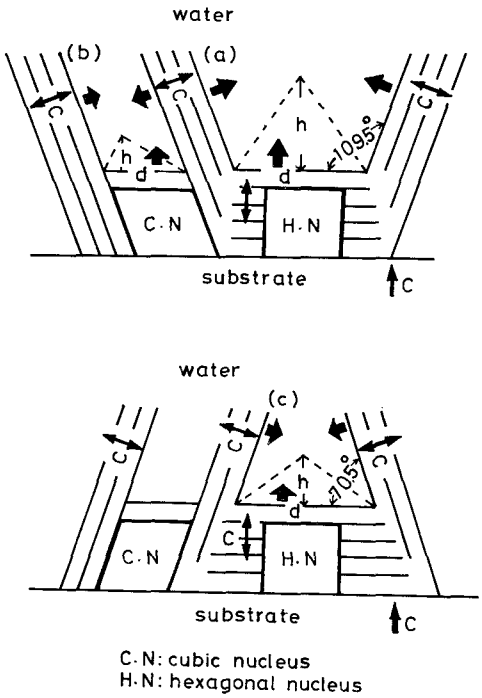


Fig. 21 Wedge-shaped shrinking process.
(a) $h/d=\frac{1}{2}\tan 54.75°=0.70$
(b) $h/d=\frac{1}{2}\sin 70.5°=0.47$
(c) $h/d=\frac{1}{2}\tan 35.25°=0.35$

A photograph of the vertical cross section of a polycrystallized droplet on the substrate shown in Fig. 22 seems to suggest that this is a mechanism by which the normal ice becomes extinct.

If the number of cubic nuclei are only two or three in a droplet 250 μm in diameter, the base on the wedge may reach to 100 μm and the height to 50 μm. These large wedges may recognized in the polarized light photographs of the vertical section such as shown in Fig. 22.

However, they have not searched after systematically. They may be recognized in the horizontal photographs described in Sec. III. 2 also. At least in these horizontal photographs, they are not observed as described in that section. It may be considered that cubic nuclei were large in number than the grown crystals and that the number of crystals were reduced as a result of unification or recrystallization after the normal ice had vanished.

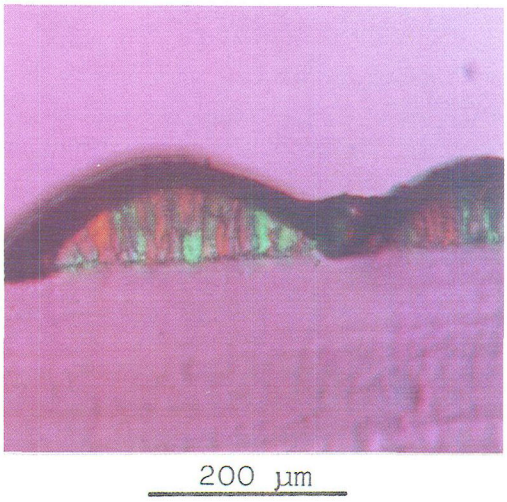


Fig. 22 Vertical section of droplets frozen at −21°C on the basal plane.

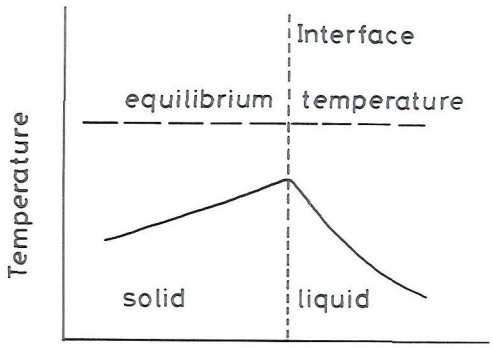


Fig. 23 Schematic illustration of temperature distribution at the interface at the moment a droplet impacts against and freezes on the ice substrate.

Finally, the following brief consideration will be given to the forms of crystals. When a supercooled water droplet freezes on an ice substrate, the temperature will have such a distribution as is shown in Fig. 23, with a large negative gradient in the part of water, especially near the interface. Under the conditions, the advancing interface is unstable in form ; that is, once a protuberance is generated on the boundary, it grows into the part of water faster than into the other part of the interface (Weinberg and Chalmers, 1952). As mentioned earlier, ice grows faster in the direction normal to the c-axis than in the direction parallel to it. Hence a protuberance occurs at the tip of a slant ice. The subsequent growth of the protuberance depends on water temperature. When supercooling is weak, it grows as a thick plate, whereas, when strong, it grows as a dendrite, which eventure must be a cause of differentiating the form of a crystal between above and below −18°C. When a protuberance grows it generates heat locally ; as a result the heat prohibits another protuberance from growing within the effective distance of the heat. The local heating is not so sensitive to temperature that the distance will not change much in a temperature range from −18°C to −23°C. It may explain constant spacing of the platelets in this temperature range.

VIII. Concluding Remarks

As mentioned in the introduction, the main purpose of the present study is to determine as accurately as possible the orientation of a crystal grown in a supercooled water droplet impacting an ice substrate at various environmental temperatures. In this connection, a droplet frozen on a substrate was observed using polarized light microscopy and X-ray Laue diffraction, by which the orientation of a crystal was determined with an accuracy of 0.5°. Besides, the texture of the frozen droplet was revealed by optical observations.

While observational results on the droplet frozen on the prismatic plane of the substrate were rather limited to the confirmation of earlier results by other researchers, those on the droplet frozen on the basal plane gave important information on the growth mechanism of a crystal in supercooled water covering an ice substrate.

The most important of the results was that, in the case of polycrystallization of a droplet on the basal plane, which inevitably occurred below −14℃ and was found to occur up to −12℃, there were only six possible orientations of a crystal. Since they coincided with the orientations predicted by Kobayashi, Furukawa, Takahashi and Uyeda (1976), it may be said that the existence of a cubic lattice between the substrate and the crystal postulated by them has been experimentally confirmed.

The temperature dependence of the texture of the polycrystallized droplet was explained by considering the subsequent growth of cubic and hexagonal nuclei, which were assumed to be formed epitaxially on the basal plane of the substrate according to Takahashi's theory (Takahashi, 1981). It was pointed out in the consideration that the surface of the substrate should have two kinds of basal planes half a unit (modulo one unit) apart in order that a pair of crystals will be realized with their orientations being mirror-symmetric to each other with respect to the plane determined by one of the a-axes and the c-axis of the substrate.

Close proportionality of the number of crystals and the number on surface irregularities seen from a comparison of Figs. 4 and 19 seems to suggest that more subtle relations exist between the surface structure and the texture of the droplet, which remain to be clarified in future.

Acknowledgments

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