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Studies on the Freezing of Water. (I)

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In order to study the freezing of water in a shallow dish, the authors devised a shadow photograph method. Using this method, successive photographs were taken of the freezing initiated with and without seeding. Regular forms of crystal, produced on water surface and in water, have been classified into four crystal forms; needle form, feather-like form, disc crystal and steller crystal. A disc crystal grows into a steller crystal. This process is also shown by successive photographs.

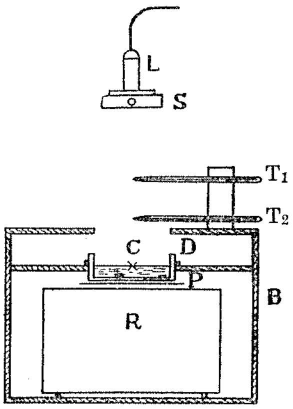
§ 1. Introduction

Freezing of water has been described in detail by many workers. Among them, B. WEINBERG,[1] W. A. BENTLEY[2], and W. J. ALTBERG[3] have reproduced photographs of ice crystals.

In research on the freezing proceess, it is very difficult to take photographs of ice crystals. The authors devised a very simple and useful method — the shadow photograph method, and achieved a tolerable success. The experiments were carried out in a cold chamber of the Institute of Low Temperature Science belonging to our University.

§ 2. Experimental Procedure

The apparatus for the shadow photograph method is shown in Fig. 1. In this figure, an ice crystal C formed on water surface in a shallow glass dish D is illuminated downwards by a point light source L. Thus a shadow of the ice crystal is projected onto photographic paper P, which is placed closely under the bottom of the dish D. This bottom is made of a glass plate. Giving suitable exposure by the shutter S, a clear photograph of an ice crystal can be obtained. It is also possible to observe directly the shadow of a crystal projected on a white paper placed at the position of the photographic paper. A lamp of the lamp—and scale for a galvano-



L : Light source
S : Shutter
C : Ice crystal
D : Shallow dish
P : Photographic paper
B : Wooden box
R : Water reservoir
T_1 & T_2 : Thermometer

Fig. 1. Apparatus

meter was early used for the point light source. But later a small electric torch bulb was found very suitable on account of its intense light and small filament. Also the shutter was replaced by an electric switch. The distance from the light source L to the bottom of the dish was 65 cm. The dish had a diameter of 7 cm and was 3 cm in depth. The depth of water was 2.6 mm at 10 cc of water and 5.2 mm at 20 cc. In order to make sure that the water was cooled only from its free surface, a large water reservoir R was placed under the photographic paper in wooden box B. The apparatus was set in the cold chamber. Two thermometers T_1 and T_2 were placed at posions 6 cm and 10 cm respectively from the dish bottom, to measure the air temperature above water surface. At the moment of exposure, those thermometers were moved aside. The water used in the experiment was distilled and non-distilled. The latter material was once filtered with a filter paper.

§ 3. Freezing Process

It is well-known that "the only certain way to initiate freezing intentionally is to seed water with suitable crystal"[4]. In the present experiment, freezing was initiated in two ways. One was to seed water with ice crystals and the other was to cause water to freeze naturally without artificial seeding. However, the latter does not correspond to spontaneous nucleation. The authors call the latter case, as a matter of convenience, the "natural freezing". Further discussion on this problem will be offered below in C.

In the following experiment, the shallow dish containing water at room temperature was brought into the cold chamber before beginning each experiment.

(*a*) *Natural freezing*

Photos. 1a–1d in Pl. I are successive photographs in this case. Needle-like crystals spring forth from the periphery of the dish and grow out towards the centre of the field. These needle-like crystals soon take a feather-like form as shown in Photos. 1b and 1c. In Photo. 1c, all crystals are exclusively on the water surface or in the water, not on the glass plate of the dish bottom. Four irregular forms of ice crystals in Photo. 1d are growing on the glass plate of the bottom.

It is difficult to determine the vertical position of each crystal by only one photograph. But a series of successive photographs gives some information about this point. In the course of the experiment, vertical positions of crystals are easily determined by direct touches with a fine wire.

Sometimes in the course of natural freezing, ice crystals growing on the water surface were found apart from the periphery. Such cases are shown in successive photographs 2a and 2b in Pl. I and 3a–3f in Pl. II. The stellar crystal in the former shows slight displacement between two photographs. In general, a floating crystal drifts slowly on water surface. This is one way to determine the vertical position of a crystal. In Photo. 3a, the first appearance is a crossed needle, which is also on water surface. In Photo. 3e, three needles and also one crossed needle have grown out on water surface without artificial initiation during the process of freezing.

The feather-like crystal on water surface in Photo. 3b shows an interesting further crystal growth. In the course of its growing, it spreads out barbed vanes, which are not parallel to the water surface. As soon as they reach the glass plate of the bottom, they transform their crystal form into a new irregular form creeping on the glass plate. This transition of crystal growth is seen in Photo. 3c and also in Photo. 3d. The crystal form after the transition is not always irregular. In Photo. 3d, the needle-like crystal crossing obliquely at the centre of the field takes a simple needle form after the transition.

In Photos. 3e and 3f, some crystals of a needle form show intense black lines on their sides. These black lines are probably due to the reflected light on crystal surfaces. The distance between a crystal and its black line often changes during the growing.

Experimental condition of Photos. 1a–1d, 2a–2b and 3a–3f are shown in TABLE I. In TABLE I, and II, "time" means the moment at which each photograph is taken, measured from the first photograph of each series. T_1 and T_2 are the air temperature of 6 cm and 10 cm respectively above water surface. T_r is room temperature of the cold chamber, and T_w is water temperature of the reservoir R. "v" is the volume of water contained in the glass dish.

TABLE I.

No. of Photo.	time (min.)	T_1 (°C)	T_2 (°C)	T_r (°C)	T_w (°C)	v (cc)
1a	0	−11∼−13	−13∼−14	−14∼−15	4	20 (non-distilled)
1b	1					
1c	2					
1d	3					
2a	0	−5∼−6	−6	−8	6	10 (non-distilled)
2b	1					
3a	0	−4∼−6	−6∼−7	−6∼−8	3	20 (non-distilled)
3b	4					
3c	6					
3d	11					
3e	18					
3f	36					

(b) *Freezing initiated with seeding*

Successive Photographs 4a and 4b in Pl. III are initial stage of growing after seeding with a small hoar crystal put on the water surface. In this case, growing crystals are of needle form. When water surface is partially covered with some ice crystal, the same effect as that of seeding was obtained by stirring the water with a thermometer. Two series of successive photographs in this case are shown in Photos. 5a–5c and 6a–6f. Photo. 5a shows freezing surface before the stirring, and Photo. 5b is immediately after it. The stirring was carried out at the central part of the field. Successive Photographs 6a–6f show the freezing process after the stirring. In these two series, many regular and irregular forms of ice crystals grow on water surface at the same time. The experimental conditions of Photos. 4a–4b, 5a–5c and 6a–6f are given in TABLE II.

TABLE II.

No. of Photo.	time (min.)	T_1 (°C)	T_2 (°C)	T_r (°C)	T_w (°C)	v (cc)
4a	0	− 14	− 16	− 17	8	20 (non-distilled)
4b	1					
5a	0	− 6	− 7	− 8	6	20 (non-distilled)
5b	0.5					
5c	4					
6a	0	−5∼−6	−7∼−8	−7∼−8	11	20 (distilled)
6b	0.5					
6c	1.0					
6d	1.5					
6e	2.0					
6f	2.5					

(*c*) In regard to seeding, it is at present worth while reconsidering the accidental initiation of crystallization which occured in the case of natural freezing of the preceding experiments. As the upper space of the cold chamber is occupied by refrigerator pipes covered with hoar crystals, the air of the chamber contains hoar crystals and their fragments. Then, it is probable that the accidental initiation of crystallization is due to seeding with those ice particles which fell into the water surface.

§ 4. Crystal Form and Crystal Growth

In this article, the objects of our discussion are concerned only with ice crystals formed on water surface and in water, and do not include crystals formed on glass plate. Ice crystals formed on a glass plate in water are related to window ice.[5]

(*a*) BENTLEY[6] early classified ice crystals formed from liquid water into six kinds; lanceolate, discoidal, solid hexagonal, flower-like, spandrellic forms, and corallin. The authors classified them in somewhat different way, but this classification is only provisional. Ice crystals of regular types can be classified into four forms; (1) needle form, (2) feather-like form, (3) disc crystal, and (4) stellar crystal.

1) *Needle form.* Ice crystals in Photo. 1a all belong to this form.

They soon grow up into a feather-like form through a needle-with-knobs. The crossed needle found in Photo. 3a in Pl. II is also one of this form, but it shows spatial structure in its later stage of growth as shown in Photo. 3f. In freezing initiated by stirring, many types of needles are produced. Some of them grow up from deformed forms of disc-crystal.

2) *Feather-like form.* This type has two kinds, the one is a needle form in its early stage, the other is feather-like in its early stage of growth shown in Photo. 3b in Pl. II. Two barblike vanes take three different features. The first is symmetrical on both sides, the second is unsymmetrical, and the third shows only one vane on one side.

3) *Disc crystal.* This type is produced only in freezing initiated by seeding. It is very thin and flat, and has no trace of air bubble in it. This type grows into a stellar crystal through the stage of a notched disc D_2 in Fig. 2. In early stage of a notched disc crystal, it shows no mark of hexagonal symmetry, but in its later stage it takes a form of hexagonal symmetry with six main branches radiating in stellar form. This process of growing is precisely shown about the disc marked D in Photos. 6a–6f in Pl. IV. Deformed disc crystals are often produced, and their common type is semicircular or spandrellic form which grow into different forms as shown in Fig. 3.

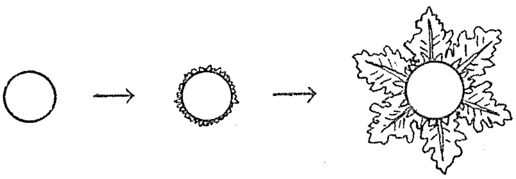


Fig. 2. Growth of disc crystal

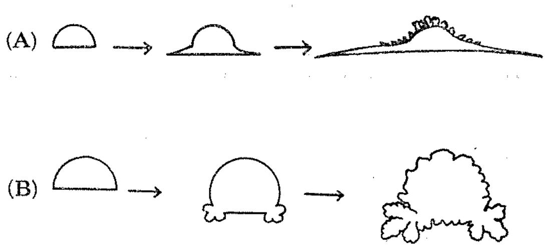


Fig. 3. Two types of growth of semicircular disc crystal

(*b*) Most conspicuous phenomena in freezing initiated by seeding are varieties of crystal forms on water surface, and similarities are seen in the structure of growing parts in each different crystal at the later stage of growth. The former suggests the difference of the initial condition of each crystal in microscopic dimension, and the later suggests the identical effect of thermal condition on each crystal growth of different crystals.

In the preceding experiments, water temperature was measured only in the case of Photos. 5a–5c and 6a–6f, from the beginning of experiments to the appearance of natural freezing before the stirring. In both cases, natural freezing occured at about $-0.5°C$. But these measurements are not accurate as the water depths are so shallow that only the bulb of the thermometer can be immersed in water. The rate of crystallization of water is very sensitive to temperature variation, and it reaches 3.32–5.27mm/sec at $-2.0°C$.[7] Then in our experiments, water is probably not very supercooled. Air temperatures above water surface fluctuated within 2°C because of the presence of observers. TABLES I and II show only mean values of air temperature in the course of experiments.

§ 5. Concluding Remarks

In respect to the preceding experiment, the authors' misgivings are concerning the discrepancy of the shape between original crystals and their shadow photograhs. When a thin glass plate is immersed perfectly in water, an outline of its shadow photograph agrees with its original shape, and it is about 2% larger than the original size under the same conditions as those of the preceding experiments. This difference in size will be caused by the divergence of light from the light source, and a bulb with some extension of filament. But when a glass plate is partially immersed, it shows its magnified shadow with irregular outlines. It is impossible to compare simultaneously the shadow photograph with the direct measurement of an original crystal. But a floating ice plate on water surface exposes only one-eleventh of its total thickness above the water surface. Then the lateral extension of disturbed water surface attached to the periphery of an ice crystal is probably very small as compared with the horizontal dimension of a thin crystal. The deformation of the shadow caused by the periphery will be very small.

With regard to the inner part of a crystal, a shadow photograph shows more complicated structure owing to refraction and reflection of light in the crystal or on the crystal surface. Direct observation and microscopical observation do not show such a complicated feature.

In comparison with BENTLEY's photographs,[2] it is probable that his method of photographing gave rise to a tendency to attach particular importance to crystals having a slow rate of crystallization. Slender needles and some stellar crystals of dendritic form, as shown in Photo. 2a, have a fast rate of crystallization.

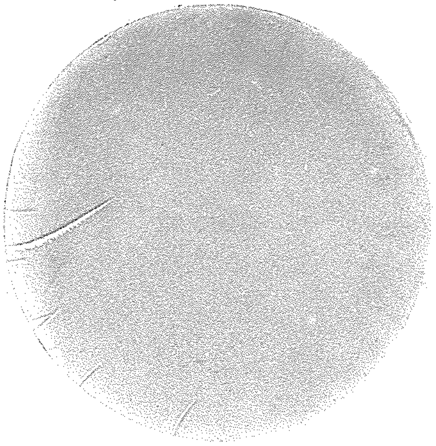
In 1949, IMAI[8] proposed an explanation regarding the growing of a disc crystal into a needle form. His explanation is based on the inclination of a disc crystal in relation to the water surface. In our photographs, a deformed disc crystal of semicircular form shows no mark of any inclination.

On the whole, disc crystals and stellar crystals are more suitable than crystals having spatial structure as the objects of the present method. The results of further investigation on disc crystals under controlled conditions will be published in a succeeding paper in this journal.

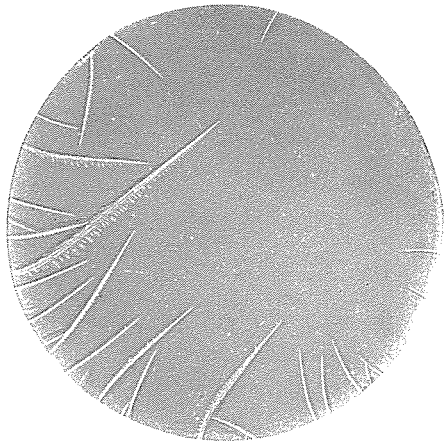
In conclusion we wish to express our sincerest gratitude to Prof. U. NAKAYA for his helpful guidance and encouragement throughout this work. We also express our gratitude to the Institute of Low Temperature Science for the permission to use the cold chamber laboratory. Our thanks are also due to Mr. M. KUMAI for his useful suggestions.

References

1) WIENBERG, B., *Phys. Rev.* **27** (1908), 509.
2) BENTLEY, W. A., *Month. Weath. Rev.* **35** (1907), 439 and 512.
BENTLEY, W. A. & HUMPHREYS, W. J., *Snow Crystals* (1931) pp. 221 and 222.
3) ALTBERG, W. J., *Trans. of the Meeting of the Int. Commission of Snow and of Glaciers,* (1936), 373.
ALTBERG, W. J., *Acta Physicochimica U. R. S. S.* **9** (1938), 725; **11** (1939), 287).
4) DORSEY, N. E., *Properties of Ordinary Water Substance* (1940), p. 416.
5) NAKAYA, U., *The Formation of Ice Crystals.* (Compendium of Meteorology, (1952), p. 208.)
6) BENTLEY, W. A., *Month. Weath. Rev.* **35** (1907), 512.
7) See reference 4) p. 645.
8) IMAI, I., *On the Freezing of Water. Seppyo* (*J. of the Japanese Society of Snow and Ice*) **11** (1949), 10 (in Japanese).



1a × 0.84



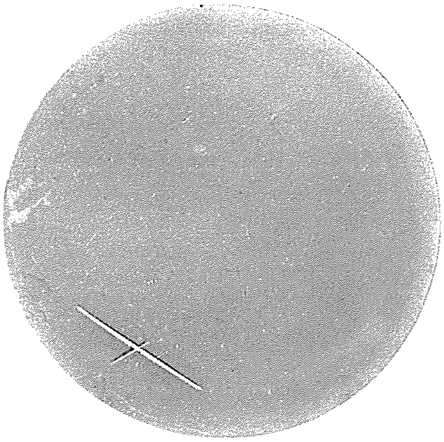
1b × 0.84

1c × 0.84

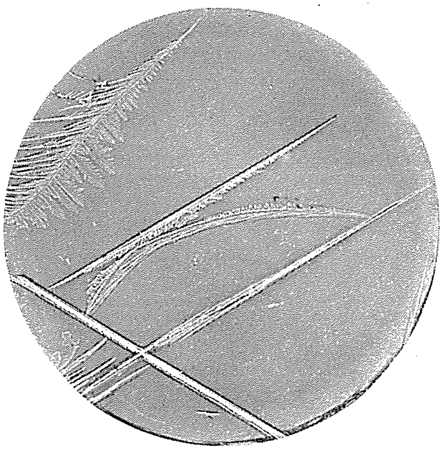
1d × 0.84

2a × 0.84

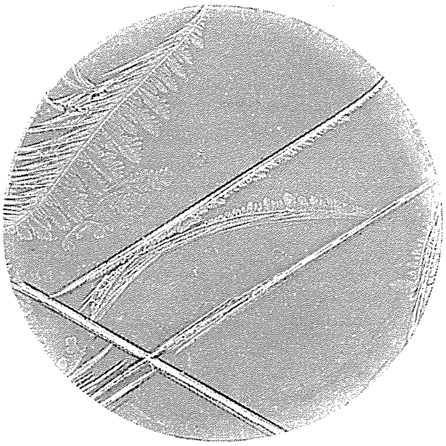
2b × 0.84



3a × 0.84



3b × 0.84

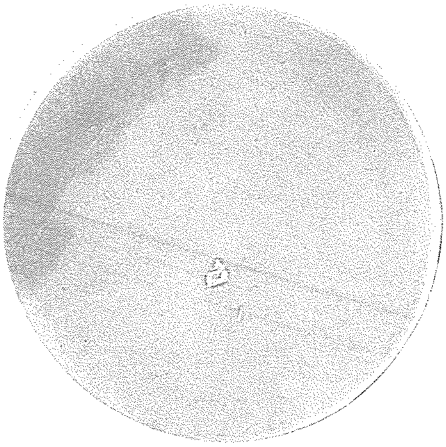


3c × 0.84

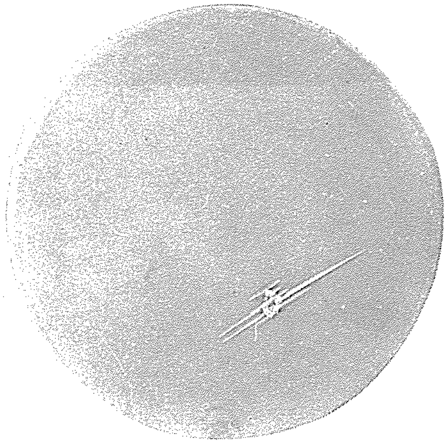
3d × 0.84

3e × 0.84

3f × 0.84

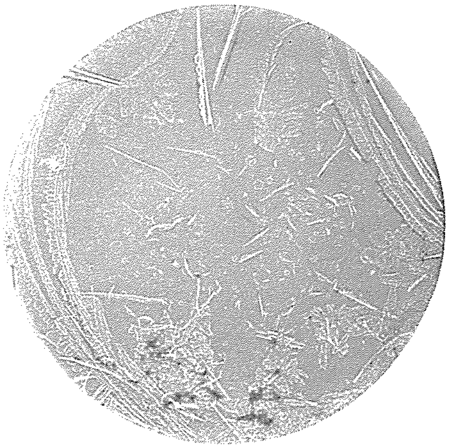


4a × 0.84

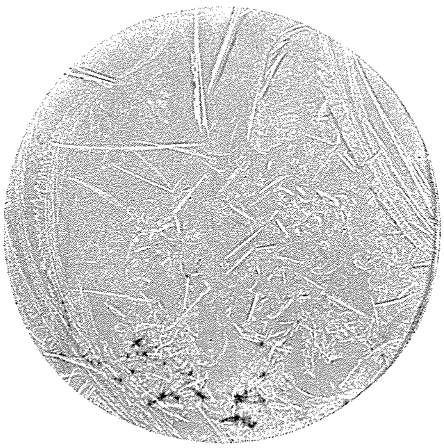


4b × 0.84

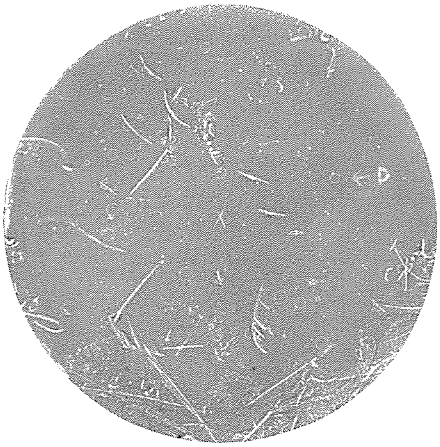
5a × 0.84



5b × 0.84



5c × 0.84



6a × 0.84

6b × 0.84

6c × 0.84

6d × 0.84

6e × 0.84

6f × 0.84