THE GROWTH MECHANISM AND THE HABIT CHANGE OF ICE CRYSTALS GROWING FROM THE VAPOR PHASE

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Polyhedral ice crystals are formed at a few % supersaturation in order to clarify experimentally the growth mechanism and the habit change of ice crystals growing in low air pressure at a temperature of 0 to −30°C. On the basis of the normal growth rates versus supersaturation, in situ observation of ice crystal surface and the advance rates of steps versus supersaturation, it is concluded that the {0001} and {1010} faces of ice crystals grow by the vapor–quasi-liquid–solid (V–QL–S) mechanism at a temperature of 0 to −2°C, while they grow by the BCF mechanism at a temperature of −2 to −30°C. The habit change with temperature of ice crystals growing in low air pressure is explained by the temperature dependence of the condensation coefficient of the {0001} and {1010} faces.

1. Introduction

The growth of ice crystals from the vapor phase is one of the important problems of cloud physics, glaciology and crystal growth. The change in morphology of ice crystals growing in air of 1.0 × 10^5 Pa with temperature and supersaturation has been studied by Nakaya [1], Kobayashi [2], Hallett and Mason [3], etc. It is well known that the change in morphology of ice crystals growing in air and other gases depends also on the volume diffusion of water molecules towards the crystal surface and also on the transportation of the heat released by sublimation [4–6]. Therefore, ice crystals have been formed under conditions where the resistance of the volume diffusion of water molecules and the transportation of the latent heat of sublimation is ignored in order to study the habit change of ice crystals growing from the vapor phase [7–10].

Recently, Kuroda and Lacmann [11] and Kuroda [12] have theoretically interpreted the mechanism of the habit change with temperature of ice crystals growing in air of 1.0 × 10^5 Pa at water saturation, on the basis of the anisotropy of the growth mechanism of ice crystals and its temperature dependence. In these papers, the so-called vapor–quasi-liquid–solid (V–QL–S) mechanism has been proposed in order to interpret the habit of ice crystals growing at a temperature near the melting point. After that, the existence of a quasi-liquid layer has been confirmed by ellipsometry [13] and NMR [14] measurements. On the other hand, the off-faceted morphology of ice crystals growing from the vapor phase has been observed at a temperature near the melting point [9,15]. The purpose of this paper is to form polyhedral ice crystals under conditions where the resistance of the volume diffusion of water molecules and the
transportation of the latent heat of sublimation is ignored, and to clarify experimentally the growth mechanism and the habit change of ice crystals growing in low air pressure of 40 Pa at a temperature of 0 to $-30^\circ$C.

2. Experimental

2.1. Growth chamber and temperature control system

Fig. 1 shows the experimental apparatus for in situ observation of ice crystals growing from the vapor phase. The surface temperature of a glass substrate (G) is kept at a desired temperature by controlling the electric current (2 to 5 A) which flows to the thermoelectric modules attached at the bottom surface of the chamber using a PID type temperature controller (V). A copper–constantan thermocouple as a sensor of the temperature controller is attached at the position between the bottom surface of the chamber and the upper surface of the thermoelectric modules. In this experiment, the temperature of the growth substrate (G) is held constant with an accuracy of 0.01$^\circ$C.

The temperature of the ice plate (F) for a water vapor supplier is controlled by adjusting finely an electric current which flows to the thermoelectric modules. The heat released from the thermoelectric modules is removed by circulating the isopropyl alcohol cooled at a desired temperature using the circulating refrigerators (Z).

The growth temperature is recorded through a digital thermometer (b). The analog output of the thermometer (b) is digitized using a digital electronic voltmeter (c) and its values are recorded in a microcomputer (d) through a GP-IB (general purpose interface bus) interface unit (g). The temperature difference between the ice plate (F) for the water vapor supplier and the upper surface of the growth substrate (G) is digitized using a digital electronic voltmeter (a) and recorded in the microcomputer (d) through the GP-IB interface unit (g). The thermocouples (h, i) are made of 0.1 mm copper–constantan wires and the growth temperature and the temperature difference between the water vapor supplier and the growth substrate are measured with accuracy of 0.01$^\circ$C.

The growth temperature, the temperature difference, etc are recorded using a microcomputer (d) with the method described below.

(1) The time sequence of the growth temperature, the temperature difference and the supersaturation are recorded using a CRT monitor (f). The experimental data are printed out using an impact dot matrix printer (e) when the experiments are finished.

(2) When a key of the keyboard is pushed, the growth time, the growth temperature and the temperature difference are recorded in a floppy disk and printed out by a printer (e).

2.2. Vacuum system

A rotary vacuum pump (U) is connected to the growth chamber in order to evacuate the air in the growth chamber. The air pressure in the chamber is measured using a Pirani vacuum gauge (S). In order to avoid the inflow of impurities into the chamber, a cooling coil tube (T) is inserted between a rotary vacuum pump (U) and the growth chamber. A three-way vacuum cock (I) is opened when silver iodide smoke is supplied or the air in
the chamber is evacuated. A cock (2) is closed when an ice crystal grows at a desired growth condition.

2.3. Optical system

In the present experiment, a reflex-type differential interference microscope (H) was used to observe the surface structure of ice crystals growing on the growth substrate (G). We must minimize the light which reflects at the positions except for the ice crystal surface in order to increase the detection sensitivity of the microtopography on the ice crystal surface. Therefore, a glass window of 0.2 mm in thickness is coated with a nonreflection film and the under-surface of the substrate glass of 0.2 mm in thickness is blackened with black oily ink.

As the reflection factor of light on the ice crystal surface is comparatively small, a 50 W halogen lamp is used to detect the microtopography of the ice crystal surface. A green interference filter and a heat insulating filter are also inserted into the optical path in order to increase the resolving power of crystal images and to decrease the heating of ice crystals by the irradiation of the light. In this experiment, a 2/3 inch TV camera (M) with high resolving power (above 650 lines in horizontal resolution) and high sensitivity (0.3 lux in minimum intensity) is used. A VHS-type video tape recorder (P) or a U-matic video tape recorder (Q) through a video timer (N) is used to detect the crystal images.

3. Experimental results

3.1. The habit change of ice crystals with temperature

Ice crystals were grown on a glass substrate of 0.2 mm in thickness in low air pressure of 40 Pa at a temperature of 0 to −30°C. The reason why the ice crystals were grown in low air pressure of 40 Pa is that under this air pressure, the resistance of the volume diffusion of water molecules can be ignored. Under these growth conditions, where the resistance of the transportation of the latent heat

![Fig. 2. Ice crystal grown in low air pressure of 40 Pa at −0.7°C and at 1.7% supersaturation: (a) 0, (b) 6.4, (c) 7.1, (d) 7.4, (e) 7.6 and (f) 8.7 min.](image)
of sublimation can be also ignored, the surface supersaturation becomes equal to the bulk supersaturation.

Fig. 2 shows an example of an ice crystal grown in low air pressure of 40 Pa at \(-0.7^\circ\)C and 1.7% supersaturation. The \(c\) and \(b\)-axes are shown by arrows. This crystal was photographed from the direction of the \(a\)-axis. Photos \(a\) and \(f\) indicate the positive pictures, while photos \(b\) to \(e\) indicate the negative pictures. It is known from photo \(b\) that the ice crystal at \(-0.7^\circ\)C grows as a plate-like crystal with smooth \(\{0001\}\) face. On the other hand, although the \(\{1010\}\) facets are also observed in the growth stage (b), they disappear in the growth stage (c). The dark part in the center of the crystal corresponds to a glittering part because photos \(b\) to \(e\) are negative pictures. As seen in the figure, an ice crystal growing at \(-0.7^\circ\)C grows as a plate-like crystal.

Fig. 3 shows an example of an ice crystal grown in low air pressure of 40 Pa at \(-30^\circ\)C and 2.7% supersaturation. As the size ratio \(c/a\) of the ice
crystal grown at $-30^\circ$C is 1.4, this crystal is a columnar crystal. The habit change of an ice crystal growing in low air pressure at relatively low supersaturation with temperature is described in detail in a previous paper [16].

Fig. 4 shows the length along the $c$- and $a$-axes of an ice crystal grown at $-30^\circ$C and 2.7% supersaturation versus the time elapsed. Solid and open circles show the experimental values of the length along $c$- and $a$-axes of the ice crystal, respectively. For example, the growth rates of the \{0001\} and \{1010\} faces of the ice crystal were calculated from this figure using the method of least squares. That is to say, the growth rates of the \{0001\} and \{1010\} faces can be obtained as the gradient of straight lines in this figure. The growth rates of only one ice crystal versus supersaturation were measured at various constant supersaturations by repeating many times the growth and the evaporation of the same ice crystal.

3.2. Normal growth rates of an ice crystal versus supersaturation

The normal growth rates of an ice crystal were measured as a function of supersaturation in order

Fig. 5. Normal growth rates of the \{0001\} and \{1010\} faces of an ice crystal grown in low air pressure of 40 Pa at (a) $-1.0^\circ$C and (b) $-1.9^\circ$C versus supersaturation.

Fig. 6. Normal growth rates of the \{0001\} and \{1010\} faces of an ice crystal grown in low air pressure of 40 Pa at (a) $-3.1^\circ$C and (b) $-7^\circ$C versus supersaturation.

Fig. 7. Normal growth rates of the \{0001\} and \{1010\} faces of an ice crystal grown in low air pressure of 40 Pa at (a) $-15^\circ$C and (b) $-30^\circ$C versus supersaturation.
to study the growth mechanism of the ice crystal growing in low air pressure at various constant temperatures.

Fig. 5 shows the normal growth rates of an ice crystal grown in low air pressure of 40 Pa at (a) \(-1.0^\circ C\) and (b) \(-1.9^\circ C\) versus supersaturation. The dotted lines represented by the Hertz–Knudsen equation, the solid curves and the alternate long- and short-dash curves show the theoretical curves of the Hertz–Knudsen equation which gives the maximum growth rates, the BCF mechanism [17] and the V–QL–S mechanism [18], which shows the growth mechanism of ice crystal covered with a quasi-liquid layer where screw dislocations outcrop on the quasi-liquid/ice interface. The solid and open circles show the experimental values of the normal growth rates of the \{0001\} and \{10\overline{1}0\} faces of an ice crystal, respectively.

The growth rates of only one ice crystal grown at various constant supersaturations were measured by repeating many times the growth and the evaporation of the same ice crystal. Here, the surface supersaturation is corrected by measuring the evaporation point of an ice crystal at every measurement. Therefore, a very low dispersion in the normal growth rates was achieved.

From a comparison of the experimental values and the theoretical curves, it is understood that the \{0001\} and \{10\overline{1}0\} faces of an ice crystal grown at \(-1.0^\circ C\) grow by the V–QL–S mechanism. On the other hand, it is understood that the \{0001\} face of an ice crystal grown at \(-1.9^\circ C\) grows by the BCF mechanism, while whether the \{10\overline{1}0\} face of the ice crystal grows by the BCF mechanism or the V–QL–S mechanism is not determined from only fig. 5.

Fig. 6 shows the normal growth rates of the \{0001\} and \{10\overline{1}0\} faces of an ice crystal grown in low air pressure of 40 Pa at (a) \(-3.1^\circ C\) and (b) \(-7^\circ C\) versus supersaturation. In the figure, the dotted lines represented by the Hertz–Knudsen equation, the solid curves and the alternate long- and short-dash curves show the theoretical ones of the Hertz–Knudsen equation, the BCF mechanism and the V–QL–S mechanism, respectively. The other dotted lines show the asymptotes of the BCF curves. The solid and open circles show the experimental values of the normal growth rates of

### Table 1

<table>
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<tr>
<th>Temperature (°C)</th>
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Fig. 8. Surface structure of the (0001) and (1010) faces of ice crystals evaporating in low air pressure of 40 Pa at −1.0 and −1.4°C, respectively. Photos (a), (b) and (c) are the evaporation process at 0.2% subsaturation; photos (d), (e) and (f) are the evaporation process at a subsaturation near ice saturation: (a) 0, (b) 18 and (c) 60 s; (d) 0, (e) 10 and (f) 49 s.

the (0001) and (1010) faces, respectively. As shown in the figures, it is seen that the experimental values of the normal growth rates of the (0001) and (1010) faces of an ice crystal grown at −3.1 and −7°C coincide with the BCF theoretical curves, respectively.

Fig. 7 shows the normal growth rates of the (0001) and (1010) faces of an ice crystal grown in low air pressure of 40 Pa at (a) −15°C and (b) −30°C versus supersaturation. The dotted lines represented by the Hertz–Knudsen equation, the solid curves and the other dotted lines show the theories of the Hertz–Knudsen equation, the BCF mechanism and the asymptotes of the BCF curves, respectively. The solid and open circles are the experimental values of the normal growth rates of the (0001) and (1010) faces, respectively. As shown in the figures, it is seen that the experimental values of the normal growth rates of the (0001) and (1010) faces of an ice crystal grown at −15 and −30°C coincide with the BCF theoretical curves, respectively.

Table 1 shows the experimental values of the condensation coefficient α₁, which means the adsorption probability of water molecules from the vapor phase on an ice crystal surface, the critical supersaturation σ₁, where the normal growth rate versus supersaturation relation is transformed from quadratic to linear, the evaporation energy of a water molecule, $W$, the specific energy of a step at vapor/ice interface, $\gamma$, and at quasi-liquid/ice interface, $\gamma_{dl}$, the self-diffusion constant of water
Fig. 9. Surface structure of the (0001) and (1010) faces of ice crystals grown in low air pressure of 40 Pa at −30 °C. Photos (a), (b) and (c) are the growth process at 2.5% supersaturation; photos (d), (e) and (f) are the growth process at 2.0% supersaturation; the arrow shows the direction of the c-axis: (a) 0; (b) 2 and (c) 19 s; (d) 0; (e) 90 and (f) 180 s.

molecules in quasi-liquid layer, $D_{ql}$, and the mean migration distance of water molecules on ice crystal surface, $x_s$. For the sake of the comparison, the theoretical values [11,18] of $W$, $\gamma$, $\gamma_{ql}$ and $x_s$ are also shown together with the measurement under pure water vapor conditions [8] and the NMR measurement [14]. Here, the intervals of confidence for $\alpha_1$, $\sigma_1$ and $W$ are two digits before and after the decimal point and those for $\gamma$, $\gamma_{ql}$, $D_{ql}$, and $x_s$ are one digit before and after the decimal point. It is understood from the table that the experimental values of $W$ and $\gamma$ agree approximately with the theoretical ones. On the other hand, it is understood that the experimental values of $\gamma_{ql}$ are smaller by an order of magnitude than the theoretical ones, while the values of $D_{ql}$ are

Fig. 10. Advance rates of steps on the (0001) and (1010) faces of ice crystals grown in low air pressure of 40 Pa at (a) −7 °C, (b) −15 °C and (c) −30 °C versus supersaturation, respectively. The solid and open circles show the experimental values of the (0001) and (1010) faces, respectively.
larger by an order of magnitude than the value of the NMR measurement. The explanation of \( \alpha_1 \) is described in a later section.

### 3.3. In situ observation of ice crystal surface

In order to clarify the growth mechanism of ice crystals growing in low air pressure at a temperature of 0 to \(-30^\circ C\), the experimental values of the normal growth rates of an ice crystal versus supersaturation were compared with various growth theories. As the growth mechanism of ice crystals depends on their surface microstructure, in situ observation of their surface structure must be done.

Fig. 8 shows the surface structure of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces of an ice crystal evaporating in low air pressure of 40 Pa at \(-1.0\) and \(-1.4^\circ C\), respectively. Photos a to c show the evaporation process at 0.2% subsaturation. When we carefully observe the crystal surface, the evaporation pits are observed on the \( \{0001\} \) facet. On the other hand, photos d to f show the \( \{10\overline{1}0\} \) faces of an ice crystal evaporating at a subsaturation near ice saturation. A \( V \)-shaped evaporation groove running vertically to the \( c \)-axis may be concerned with a stacking fault outcropping on the \( \{10\overline{1}0\} \) facet. Many evaporation pits are seen near the edges of the \( \{10\overline{1}0\} \) facet with further evaporation.

On the basis of many in situ observations of the surface structure of ice crystals growing and then evaporating under low air pressure, it is understood that the evaporation preferentially occurs at the positions where a stacking fault or dislocations with screw component outcrop, and in the growth stage, they act as the center of growth. That is to say, a one-to-one correspondence was experimentally found between the growth hillocks formed on the growing ice crystal surface and the evaporation pits in the evaporation stage [19].

Fig. 9 shows the surface structure of an ice crystal growing at \(-30^\circ C\). Photos a to c show the surface structure of the \( \{0001\} \) face. The dislocation density at \(-30^\circ C\) is smaller than that of \(-15^\circ C\). In these photographs, there is only one growth hillock (arrow ↑). On the other hand, photos d to f show the surface structure of the \( \{10\overline{1}0\} \) face. A white spot in the center of the \( \{10\overline{1}0\} \) face is the air cavity formed between the ice crystal and the growth substrate in the early growth stage. The black spot which exists at the right hand side of the \( \{10\overline{1}0\} \) face may be dust adhered on the lens of the microscope. The video scanning lines are also seen obliquely at the bottom of the left. In these photographs, no growth hillock is observed on the \( \{10\overline{1}0\} \) face, but a small-angle boundary is observed in the center of the \( \{10\overline{1}0\} \) face. It was confirmed by many surface observations that some dislocations with screw component existed at the position where the small-angle boundary outcropped.

### 3.4. Advance rates of steps versus supersaturation

In order to determine the growth mechanism of polyhedral ice crystals grown in low air pressure, the advance rates of steps versus supersaturation were measured together with the normal growth rates of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces versus supersaturation and in situ observation of ice crystal surface.

Fig. 10 shows the advance rates of steps on the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces of ice crystals grown at (a) \(-7^\circ C\), (b) \(-15^\circ C\) and (c) \(-30^\circ C\) versus supersaturation. In this figure, the solid and open circles show the experimental values of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces, respectively. The solid and dotted curves show the BCF theoretical ones of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces, respectively, which were calculated using the critical supersaturation \( \sigma_1 \) and evaporation energy \( W \) (table 1). Here, the mean migration distances \( x \) of admolecules on the ice crystal surface were chosen so as to fit the experimental values at a supersaturation below \( \sigma_1 \). It is understood that the experimental values of the advance rates of steps on the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces agree approximately with the BCF theoretical curves at each temperature and at a supersaturation below \( \sigma_1 \).

### 4. Discussion

The normal growth rates of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces versus supersaturation and in situ
observation of the ice crystal surface and the advance rates of steps versus supersaturation of ice crystals grown in low air pressure of 40 Pa at a temperature of 0 to −30°C and at a few % supersaturation were measured in order to clarify the growth mechanism and the mechanism of the habit change of polyhedral ice crystals with temperature.

The growth mechanism and the habit change with temperature of polyhedral ice crystals growing in low air pressure of 40 Pa at a few % supersaturation are summarized in fig. 11. As shown in the figure, the limiting habit of the ice crystals changes with decreasing temperature as follows: the hexagonal plate grows at a temperature of 0 to −4°C, the hexagonal column grows at −4 to −10°C, the hexagonal plate grows again at −10 to −21°C and the hexagonal column grows at a temperature below −21°C. On the other hand, the {0001} and {1010} faces of ice crystals growing at a temperature of 0 to 2°C grow by the V–QL–S mechanism [18], and those at a temperature of −2 to −30°C grow by the BCF mechanism [17]. The growth mechanism of ice crystals grown at a temperature of 0 to −2°C, which was determined in the present study, coincides with that proposed by Furukawa et al. [13].

In order to clarify the mechanism of the habit change of ice crystals with temperature, we must study the surface kinetics of water molecules on ice crystal surface in molecular level. As for the first step, the condensation coefficient \( \alpha_1 \) of the \{1010\} face decreases monotonously with decreasing temperature in the temperature range of 0 to −3°C, but increases monotonously with decreasing temperature in the temperature range of −3 to −30°C. On the other hand, the condensation coefficient \( \alpha_1 \) of the {0001} face repeats the rise and fall with decreasing temperature. As a result, in the temperature range of 0 to −4°C, the hexagonal plate grows because \( \alpha_1 \{1010\} > \alpha_1 \{0001\} \); in the temperature range of −4 to −10°C, the hexagonal column grows because \( \alpha_1 \{0001\} > \alpha_1 \{1010\} \); in the temperature range of −10 to −21°C, the hexagonal plate grows because \( \alpha_1 \{1010\} > \alpha_1 \{0001\} \) and at a temperature below −21°C, the hexagonal column grows because \( \alpha_1 \{0001\} > \alpha_1 \{1010\} \).

![Fig. 11. Growth mechanism and the habit change of polyhedral ice crystals growing in low air pressure at a few % supersaturation with temperature.](image)

![Fig. 12. Condensation coefficient \( \alpha_1 \) of the {0001} and {1010} faces of polyhedral ice crystals as a function of temperature. The solid and open circles show the values of the {0001} and {1010} faces, respectively.](image)
As for the second step, as the condensation coefficient \( \alpha_i \) depends on the surface microstructure of growing ice crystal, for example, we must measure the slope of the growth hillocks which are formed on the \{0001\} and \{1010\} faces as a function of temperature and supersaturation. If these measurements are carried out, the temperature dependence of the habit change of ice crystals growing from the vapor phase will be explained more clearly.

5. Conclusions

The normal growth rates of the \{0001\} and \{1010\} faces versus supersaturation, in situ observation of ice crystal surface and advance rates of steps on the \{0001\} and \{1010\} faces versus supersaturation were measured in order to clarify the growth mechanism and the temperature dependence of the habit change of ice crystals growing in low air pressure of 40 Pa at a few % supersaturation. The results obtained by the present experiments are as follows.

1. The limiting habit of polyhedral ice crystals growing in low air pressure of 40 Pa at a few % supersaturation changes repeatedly with decreasing temperature, such as hexagonal plate → hexagonal column → hexagonal plate → hexagonal column.

2. Ice crystals grown under the conditions described above grow by the V–QL–S mechanism at a temperature of 0 to \(-2^\circ\)C, but grow by the BCF mechanism at a temperature of \(-2\) to \(-30^\circ\)C.

3. The habit change of polyhedral ice crystals growing in low air pressure at a few % supersaturation with temperature can be explained by

the temperature dependence of the condensation coefficient \( \alpha_i \) of the \{0001\} and \{1010\} faces.

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References