GROWTH MECHANISMS OF SINGLE ICE CRYSTALS GROWING AT A LOW TEMPERATURE AND THEIR MORPHOLOGICAL STABILITY

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Single ice crystals were grown in air at low pressure (0.3 Torr) and 760 Torr at -30°C and various constant supersaturations \( \sigma \). As a result, it is considered that the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces of many ice crystals growing in air at -30°C grow by a nucleation mechanism except for low supersaturation \( \sigma < \) about 2%. In addition, the stability of the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces of ice crystals growing in air at -30°C and 760 Torr was investigated.

1. Introduction

It has been found that both column-like and plate-like ice crystals grow in air at 760 Torr at temperatures below -20°C [1,2]. Recently, Kuroda and Lacmann [3] and Kuroda [4] have theoretically pointed out that the habit of ice crystals growing in air at 760 Torr below -20°C depends not only on temperature but also on supersaturation. Therefore, Gonda and Koike [5] have experimentally studied the habit of ice crystals growing in air at 760 Torr below -20°C as functions of temperature and supersaturation. According to this experiment, it has been shown that except for the habit of ice crystals growing at low supersaturation (below about 2%), the habit of minute ice crystals of 15 \( \mu \)m in size coincides with the result obtained from the theory [3,4], but the habit of large ice crystals with skeletal structures above 100 \( \mu \)m in size does not coincide with the theory. At the same time, Kuroda and Lacmann [3] and Kuroda [4] have claimed theoretically that the \( \{0001\} \) and \( \{10\overline{1}0\} \) faces of ice crystals growing at temperatures below -20°C, at water saturation grow by a nucleation mechanism. However, the validity of the theory has not been confirmed experimentally, that is, at very low supersaturation ice crystals may grow by other mechanism than a nucleation mechanism.

In the next place, the stability of the \( \{10\overline{1}0\} \) faces of polyhedral ice crystals growing from the vapor phase has been studied experimentally as functions of supersaturation and crystal size [5,6]. The results coincided qualitatively with the numerical calculations of Kuroda, Irisawa and Ookawa [7]. Moreover, it is necessary to investi-
gate the interface stability of polyhedral ice crystals growing from the vapor phase because it is considered that the interface stability depends not only on supersaturation and crystal size but also on crystal shape and the pressure of air.

The purpose of this study is to investigate the growth mechanisms of single ice crystals growing at $-30^\circ$C in air at low pressure in which the effects of the diffusion field of water vapor can be neglected and to investigate the stability of the \{0001\} and \{10\overline{1}0\} faces of polyhedral ice crystals growing in air at 760 Torr as functions of supersaturation, crystal size and crystal shape etc.

2. Experimental procedures

The outlines of the growth chamber have been described in a previous paper [5]. For the trans-

Fig. 2 Supersaturation dependence of the habit of single ice crystals growing in air at low pressure and at $-30^\circ$C: (a) for ice crystals of 100 $\mu$m; (b) for ice crystals of 300 $\mu$m.
port of water vapor from the top to the bottom of the chamber, an ice plate for supplying water vapor and a growth substrate (cover glass) were set on the upper inner and the lower walls of the chamber, respectively. To keep the temperature of the substrate constant, the electric current flowing through the thermoelectric cooling panels set at the bottom of the chamber was controlled by a thermal regulator. To keep the temperature of the ice plate for supply of water vapor constant, the same operations were carried out. Thus, the error in the temperatures of the water vapor source and the growth substrate remained less than ±0.05°C. Ice crystals were nucleated in air by inserting sufficiently rarefied silver iodide smoke of about 3 cm³ into the chamber. Minute ice crystals formed in the air fell on the cover glass set at the bottom of the chamber. To investigate the growth mechanism of ice crystals at −30°C under environmental conditions where the effects of the diffusion field of water vapor could be neglected, single ice crystals were grown in air at 0.3 Torr and at various constant supersaturations. Second, to investigate the interface stability of ice crystals growing at −30°C, single ice crystals were grown at various constant supersaturation in air at 760 Torr in which the effects of the diffusion field of water vapor played a important role. We observed in situ ice crystals using a differential interference microscope.

3. Experimental results

Fig. 1 shows a schematic example of ice crystals predominantly growing in air at low pressure (0.3 Torr), at −30°C and 3% supersaturation. At a supersaturation below about 2%, long solid prisms (whisker-like crystals $c/a > 1.0$, here $c/a$ is the ratio of axial lengths) predominantly grow in air at

![Graph](image_url)

Fig. 3 Normal growth rate versus supersaturation relations of the (0001) and (1010) faces for ice crystals of 100 μm grown in air at low pressure and at −30°C: □, • and ○: mean values of long solid prisms ($c/a > 1.0$), of columns ($c/a > 1.0$) and of plates ($c/a < 1.0$), respectively; (a) (0001) face, (b) (1010) face.
Fig. 4 The change in shapes of the (0001) and (10\bar{1}0) faces of ice crystals grown in air at 760 Torr, at −30°C and 22% supersaturation: (a) 3, (b) 6, (c) 21, (d) 38, (e) 61, (f) 121 min.

low pressure and −30°C (figure is not shown). As shown in fig. 1, however, a relatively long solid prism \((c/a = 2.5–5.0)\) grows predominantly at a supersaturation of 3.0%. The ratio of axial lengths of the crystal \(c/a\) is nearly constant with increasing crystal size.

Fig. 2 shows the supersaturation dependence of the habit of ice crystals growing in air at low pressure and at −30°C. For ice crystals of 100 \(\mu\)m in size (a), long solid prisms (whisker-like crystals \((c/a > 1.0)\) grow in high frequency at a supersaturation below about 2%, while at a supersaturation above about 3%, plate-like ice crystals \((c/a < 1.0)\) grow in high frequency. For ice crystals of 300 \(\mu\)m in size (b), at a supersaturation below about 2%, long solid prisms \((c/a > 1.0)\) grow in high frequency in the same way as ice crystals of 100 \(\mu\)m. At a supersaturation between about 3 and 5%, column-like ice crystals \((c/a > 1.0)\) grow in high frequency. Moreover, at supersaturations above about 6%, plate-like ice crystals \((c/a < 1.0)\) grow in high frequency. As shown in this figure, the habit of ice crystals growing at −30°C depends not only on temperature but also on supersaturation and crystal size.

Fig. 3 shows the normal growth rate versus supersaturation relations of the \((0001)\) and \((10\bar{1}0)\) faces of polyhedral ice crystals of 100 \(\mu\)m in size growing in air at low pressure and at −30°C. As shown in the figure, at a supersaturation below about 3%, the normal growth rates of these faces seem to be non-linear with the supersaturation \(\sigma\). At a supersaturation above about 4%, the growth rates of these faces seem to be linear with the supersaturation and they seem to gradually approach Hertz–Knudsen equation when \(\alpha = 0.27\). The condensation coefficient \(\alpha\) is the pre-factor in the Hertz–Knudsen equation

\[
R = a V_m \sqrt{(P - P_i)/2 \pi m k T}.
\]

where \(V_m\) is the molecular volume of H2O, \(P\) the
Fig. 5 Stability limits of the (0001) and (10\,\bar{1}0) faces of column-like ($c/a > 1.0$) and plate-like ($c/a < 1.0$) ice crystals grown in air at 760 Torr and at $-30^\circ$C; $\sigma^*$ and $\sigma^{**}$ mean the limit of stable growth, respectively: (a) column-like ice crystal, (b) plate-like ice crystal.

actual vapor pressure, and $P_i$ the equilibrium vapor pressure of ice. Meanwhile, the habit of ice crystals growing in air at low pressure and at $-30^\circ$C is transformed from long solid prisms ($c/a \gg 1.0$) to columns ($c/a > 1.0$) to plates ($c/a < 1.0$) with increasing supersaturation.

Fig. 4 shows an example of the stability of the (0001) and (10\,\bar{1}0) faces of ice crystals growing in air at 760 Torr and at $-30^\circ$C and a supersaturation of 22%. At 3 min after ice nucleation (a), it is obvious that skeletal structures are formed on the (0001) and (10\,\bar{1}0) faces of plate-like ice crystal ($c/a < 1.0$). It is seen that the growth rate along the $c$-axis of the crystal is larger than that along the $a$-axis as time elapses. After 21 min (c), the skeletal structures of the (10\,\bar{1}0) faces begin to disappear, but the skeletal structures of (0001) faces develop more than in the early stages of growth. After 38 min (d), the skeletal structures on one side of the (0001) faces begin to disappear, and after 61 min (e), those on the other side begin to disappear. After 121 min (f), both the (0001) and the (10\,\bar{1}0) faces of the crystal developed optically smooth surfaces (stable growth).

Fig. 5 shows the supersaturation and crystal size dependences of the stability limit of the (0001) and (10\,\bar{1}0) faces of (a) column-like ($c/a > 1.0$) and (b) plate-like ($c/a < 1.0$) ice crystals growing in air at 760 Torr and $-30^\circ$C. As shown in the figure, the stability limit of the (0001) and (10\,\bar{1}0) faces of column-like and plate-like ice crystals depends on both supersaturation and crystal size. In the figure, it is seen that the (0001) faces of column-like ice crystals become unstable at lower supersaturation than the (10\,\bar{1}0) faces and the unstable region of the (0001) faces is larger than the (10\,\bar{1}0) faces, and vice versa in case of plate-like ice crystals.

Incidentally, polyhedral ice crystals grow in air at low pressure, at $-30^\circ$C and a supersaturation of 5%. However, even under the same temperature and supersaturation, skeletal ice crystals grow in air at 760 Torr.

4. Discussions

Kuroda and Lacmann [3] and Kuroda [4] theoretically pointed out that the (0001) and (10\,\bar{1}0) faces of single ice crystals growing at temperatures below $-20^\circ$C grew by a nucleation mechanism under conditions of water saturation. According to
the experiments accomplished in air at low pressure (see fig. 2), long solid prisms (whisker-like crystals $c/a \gg 1.0$) are formed at a supersaturation below about 2%, while relatively long solid prisms ($c/a = 2.5-5.0$) are formed at supersaturation between 3 and 5%. Furthermore, as shown in fig. 3, for supersaturation $\sigma < \text{about } 3\%$, the growth rates of the (0001) and (1010) faces of the crystals seem to be non-linear with $\sigma$; for $\sigma > \text{about } 4\%$, the growth rates of these faces seem to be linear with $\sigma$ and they are closer to the Hertz–Knudsen equation when $\alpha = 0.27$. Furthermore, if we also consider the results shown in fig. 5, it is considered that the (0001) and (1010) faces of many ice crystals growing in air at $-30^\circ\text{C}$ grow by a nucleation mechanism except for low supersaturation below about 2%. In addition, by recent observations of growth steps on the (0001) and (1010) faces of ice crystals growing in air at 250 Torr, it is considered that the growth model of ice crystals growing in air at $-30^\circ\text{C}$ is the Birth and Spread nucleation. This experimental result coincides with the theory of Kuroda et al. [3,4].

In the next place, it can be seen in fig. 5 that the stability limit of the (0001) and (1010) faces of column-like ($c/a > 1.0$) and plate-like ($c/a < 1.0$) ice crystals growing in air at 760 Torr at $-30^\circ\text{C}$ depends on both supersaturation and crystal size. This result agrees well with previous results [5,6] and the numerical calculations of Kuroda, Irisawa and Ookawa [7]. Moreover, in case of column-like ice crystals, the (0001) faces become unstable at lower supersaturation than the (1010) faces and vice versa in case of plate-like ice crystals. This means that the stability limit of ice crystals depends not only on supersaturation and crystal size but also on the ratio of axial lengths $c/a$.

5. Conclusions

Single ice crystals were grown in air at low pressure (0.3 Torr) and 760 Torr, at a temperature of $-30^\circ\text{C}$ and various constant supersaturations. The growth mechanisms and the stability of the (0001) and (10\Bar{1}0) faces of the crystals were investigated. The results obtained in this study are as follows:

1. The (0001) and (10\Bar{1}0) faces of many ice crystals, grown in air at $-30^\circ\text{C}$, grow by a nucleation mechanism except for low supersaturation below about 2%. This experimental result coincides with the theory of Kuroda et al. [3,4].

2. The stability limits of the (0001) and (10\Bar{1}0) faces of column-like ($c/a > 1.0$) and plate-like ($c/a < 1.0$) ice crystals grown in air at 760 Torr at $-30^\circ\text{C}$ depend on both supersaturation and crystal size. This result agrees well with previous results [5,6] and the numerical calculations of Kuroda, Irisawa and Ookawa [7].

3. The (0001) faces of column-like ice crystals ($c/a > 1.0$) grown in air at 760 Torr and at $-30^\circ\text{C}$ become unstable at lower supersaturation than the (10\Bar{1}0) faces, and vice versa in the case of plate-like ice crystals ($c/a < 1.0$). This means that the stability limit of ice crystals depends not only on supersaturation and crystal size but also on the ratio of axial lengths $c/a$.

4. In order to study the growth mechanism and interface instability from the microscopic point of view, observations of step growth on the surfaces of ice crystals grown from the vapor are being carried out in our laboratory. The result will be published in the near future.

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