Snow Crystal Habit Changes Explained by Layer Nucleation

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ABSTRACT

Critical supersaturations have been measured for the vapor growth of ice crystals on both the basal and prism faces between −16° and −0.4°C. The values are low: approximately constant at 0.4% for the prism face, less for the basal face between −3° and −9°C, but greater at higher and lower temperatures. The transitions between tabular (platelike) and columnar growth habits that occur near −3° and −9°C are thus directly understandable in terms of layer nucleation as the growth mechanism, without explicitly considering the surface migration of water molecules or spiral steps. These low values of critical supersaturation are consistent with a disordered ice surface, but not with a surface melt layer, even at −1°C.

1. Introduction

Explaining the complicated growth habit variation that natural and artificial snow crystals exhibit as a function of temperature and supersaturation has been a fundamental problem for several decades. In this paper, we present a new set of data that suggests that layer nucleation is the growth mechanism responsible for the formation of most snow crystals. A brief history of experimental work on snow crystal habit along with relevant topics from crystal growth theory will be followed by a more complete discussion of the layer nucleation mechanism, both in general and as applied to snow crystals. Then we present our experimental results that support the layer nucleation mechanism.

2. Background

a. Snow crystal growth experiments

The first major experimental work on snow crystal growth was by Nakaya and his colleagues, reported in his book (Nakaya 1954). This work established the main temperature dependencies: plates from 0° to −3° or −4°C, needles between roughly −3° and −9°C, plates from −9 to about −22°C, and columnar crystals at lower temperatures. Nakaya used a convection cloud chamber, which complicated the interpretation because supersaturation was not well controlled. Marshall and Langleben (1954) deduced supersaturation values and interpreted the habit changes in terms of both temperature and supersaturation. Hallett and Mason (1958) grew ice crystals in a diffusion cloud chamber and showed that supersaturation had little effect on the transition temperatures between columnar ($c/a > 1$) and tabular ($c/a < 1$) crystals. (See Fig. 1 for definitions of c and a.) Their results established that the primary habit, $c/a > 1$ or $c/a < 1$, is largely independent of supersaturation and thus requires a mechanism that depends only on temperature. The habit diagram that is cited most often was constructed by Kobayashi (1961) by consolidating previous results along with his measurements of ice growth on a fiber at supersaturations lower than liquid water saturation and is reproduced as Fig. 2. Other measurements of ice crystal growth on a fiber and at low supersaturation were not in complete agreement with Kobayashi's results (Rottner and Vali 1974; Colbeck 1983; Wang and Fukuta 1985; Keller et al. 1980). However, growth shapes observed in free fall at liquid water saturation (Gonda 1980; Takahashi and Fukuta 1988; Takahashi et al. 1991) do support the results in Fig. 2. In contrast, experiments of ice crystal growth on a substrate (Shaw and Mason 1955; Lamb and Scott 1972; Beckmann and Lacmann 1982; Sei and Gonda 1989) have produced more isometric ($c = a$) crystals at high supersaturations than those reported in Fig. 2.

The systematic investigation of ice crystals on covellite (CuS) surfaces (Hallett 1961; Mason et al. 1963; Kobayashi 1965a; Anderson and Hallett 1979; Cho and

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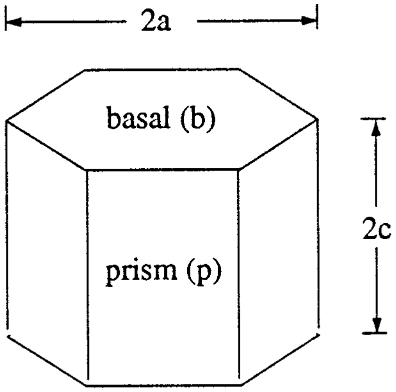

FIG. 1. Dimensions and faces of a solid prismatic ice crystal.

Hallett 1984a,b) dealt with thin, basal, epitaxial crystals of ice exhibiting interference colors in reflected light, allowing their thicknesses to be measured. Temperature could be controlled accurately but supersaturation less so, partly because there were always many ice crystals competing for vapor. It was found that these crystals often did not thicken in spite of substantial supersaturation, showing that the basal surfaces were free of spiral steps and the supersaturation was below the critical value for layer nucleation [defined after Eq. (8)]. Growth steps on the basal ice surface were initiated when crystals grew together or ran into a step on the substrate surface, so the step heights and rates of step advance across the ice surface could be measured. Values of both the step interaction distances (the separations at which two steps reduced each other's speed) and the individual step speeds oscillated with temperature. Since the steps grow largely by migration of water molecules across the ice surface, a "mean migration distance" could be deduced, and this had a similar, strong temperature dependence. This migration distance was used in Mason et al. (1963), along with a similar one assumed for the prism face of ice, to explain the variation of the *c*/*a* ratios of ice crystals grown from the vapor as a function of temperature.

The approach to the snow crystal habit problem taken here bypasses the surface molecular migration distance. We start with the complete crystal growth process, from vapor diffusion to surface incorporation, and then ask which growth mechanism best fits all observations.

b. Crystal growth theory

Snow crystal growth occurs when water vapor molecules diffuse through the air, strike the surface, and become incorporated into the crystal. Ventilation has a significant effect on the growth of large snow crystals in the atmosphere, but since it does not completely eliminate the vapor diffusion process, its neglect here does not alter our conclusions. The net diffusive flux (number of molecules $\mathrm{s}^{-1}\ \mathrm{m}^{-2}$) through the air to the surface of a solid isometric ($c = a$) crystal of mean radius r is (Pruppacher and Klett 1978)

$$\text{net flux} \approx \frac{D}{r}(N_\infty - N_s) \equiv \frac{D}{r}N_{\mathrm{eq}}(\sigma_\infty - \sigma_s), \quad (1)$$

where D is the diffusion constant of water vapor in air, N the vapor concentration (number of molecules m^{-3}), and σ is the supersaturation defined by $(N - N_{\mathrm{eq}})/N_{\mathrm{eq}}$. The subscripts ∞, "s," and "eq" indicate far-field, surface (at a crystal corner), and equilibrium quantities (at the crystal temperature), respectively. Equation (1) is

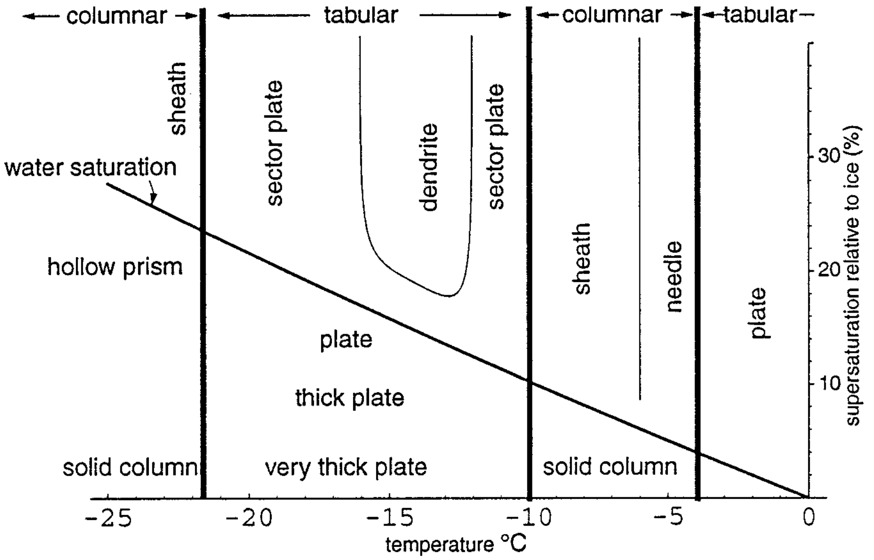

FIG. 2. Ice crystal growth habits as a function of temperature and supersaturation far from the crystal surface, according to Kobayashi (1961). Water saturation curve is the ice supersaturation of liquid water equilibrium at the environmental temperature.

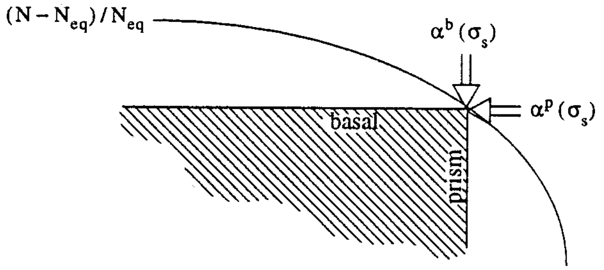

FIG. 3. Adjacent to the corner, surface supersaturation is the same for both adjoining faces. We assume here that the layers nucleate at the crystal corners.

exact only for a sphere but will be generalized below to allow for $c \neq a$ and different growth rates on the basal and prism faces. The vapor impingement rate is

$$\text{flux striking surface} = \frac{\overline{v}}{4} N_s, \qquad (2)$$

where $\overline{v}$ is the mean speed of a vapor molecule in air ($\sim$500 m s^{-1}). The rate of molecules leaving the surface depends on the surface concentration of mobile molecules, which depends on the supersaturation, and is given by

$$\text{flux leaving surface} = \frac{\overline{v}}{4} N_{\text{eq}}[1 + (1 - \alpha)\sigma_s], \qquad (3)$$

where α is the condensation coefficient (also called the deposition coefficient). Condensation coefficients are functions of the surface supersaturation and the surface properties of the face. Equation (3) indicates that the number desorbing per second is the same as at equilibrium when $\alpha = 1$, but equals the impingement rate when $\alpha = 0$. The net number exchanged between surface and vapor is given by the difference between Eqs. (2) and (3),

$$\text{net flux} = \alpha \frac{\overline{v}}{4} N_{\text{eq}} \sigma_s, \qquad (4)$$

which must equal the right-hand side of Eq. (1). Equation (4) illustrates that α can be interpreted as the fraction of molecules striking the surface that grow into the crystal: it must vary between 0 and 1. Experimental evidence suggests (Nelson 1993) that the condensation coefficients for both the basal face (α^{b}) and prism face (α^{p}) of ice approach a value close to 1 when σ_s becomes large. But, in general, $\alpha^{\text{b}} \neq \alpha^{\text{p}}$ and can be significantly less than 1 at low supersaturations.

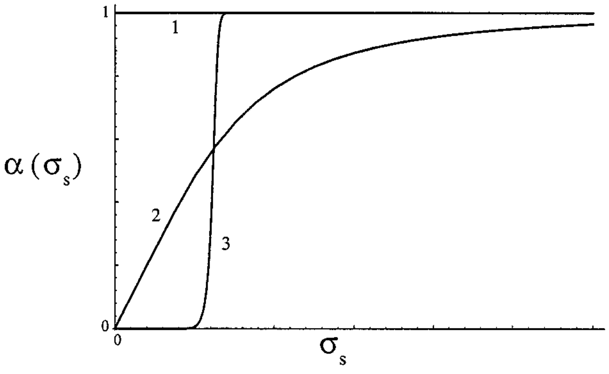

FIG. 4. The condensation coefficient functions for the three growth mechanisms: rough interface growth (1), spiral steps (2), and layer nucleation (3). As the surface supersaturation increases above the critical value, the layer nucleation rate falls below that given by Eqs. (7) and (8), and saturates at one because the step spacing on the face rapidly decreases with diminishing effect on the growth rate (Burton et al. 1951). Also, the available area for nucleation, being between the crystal edge and the closest step, rapidly decreases with increasing supersaturation, thus causing A to decrease. The actual curve for layer nucleation on ice might be different; in particular, if a step collects molecules from the higher side then the layer nucleation curve should not saturate as quickly.

For an infinitely sharp edge, the surface supersaturation is virtually identical on the face regions immediately adjacent to either side of the edge (Fig. 3).[1] In this case, Eq. (4) indicates that the ratio of the flux on the basal face to that on the prism face is simply the ratio of the respective condensation coefficients near the edge. It follows that

$$\frac{dc/dt}{da/dt} = \frac{dc}{da} = \frac{\alpha^{\text{b}}(\sigma_s)}{\alpha^{\text{p}}(\sigma_s)}. \qquad (5)$$

The problem of explaining the habit changes becomes the problem of explaining the ratio of the condensation coefficients: tabular growth requires $\alpha^{\text{b}}/\alpha^{\text{p}} < 1$ and columnar growth $\alpha^{\text{b}}/\alpha^{\text{p}} > 1$. Surface migration from one face to another can change dc/da, but it should not alter the above requirement. Equations (1), (4), and (5) illustrate two important points: the surface supersaturation (σ_s), which is generally much smaller than the ambient supersaturation (σ_∞), is the relevant parameter for crystal growth, and the growth shape is always determined by the condensation coefficients even if the total mass uptake is vapor diffusion controlled.

There are presently three established crystal growth mechanisms that should be considered as possibilities on snow crystals: 1) "continuous" growth at a rough interface, 2) growth from one or more spiral steps (originating at line defects such as screw dislocations), and 3) growth by layer nucleation. Figure 4 shows the $\alpha(\sigma_s)$ functions for each of them. In the case of continuous growth, there can be no facets because the growth rate increases continuously with σ_s, whereas the existence of a facet implies the same growth rate over a range of σ_s. Except possibly

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[1] The supersaturation is not precisely identical on the face regions adjoining an edge for two reasons. First, the edge is probably rounded on the molecular scale so the flat face regions where growth layers start on the two faces are separated. Second, the surface supersaturation used in these equations are averaged over regions within about one vapor mean free path normal to each face such that Eq. (2) is exact. The impacts of these qualifications are not assessable in quantitative detail, but given the small scale of the rounding and vapor mean free path in comparison to the crystal sizes considered here, they should have a minor effect on the following argument.

for the tips of ice dendrites, snow crystals are faceted, so continuous growth is not a tenable growth mechanism for snow crystals.

Growth from spiral steps is the mechanism described in cloud and ice physics texts (Young 1993; Pruppacher and Klett 1978; Hobbs 1974) because it is the most common growth mechanism found on many other crystals (Frank 1982, 1993). In the simplest case, the condensation coefficient for spiral steps is given by

$$\alpha(\sigma_s) = \frac{\sigma_s}{\sigma_1} \tanh\left[\frac{\sigma_1}{\sigma_s}\right], \qquad (6)$$

where σ_1 is proportional to the edge free energy of a two-dimensional embryo and inversely proportional to the surface migration distance (Burton et al. 1951). These dependencies of σ_1 come about because the step spacing in the spiral depends upon the critical radius (hence the edge energy), which limits the curvature at the center of the spiral, but the step spacing is only important relative to the mean migration distance. For spiral steps with their centers near the corner, the ratio of the growth rate on the basal to that on the prism face lies between $\sigma_1^{\mathrm{p}}/\sigma_1^{\mathrm{b}}$ and 1. Since the growth shape of sector plates or dendrites with $c/a \sim 0.01$ indicate that $dc/da \leq 0.01$, growth from spiral steps requires $\sigma_1^{\mathrm{p}}/\sigma_1^{\mathrm{b}} \leq 0.01$ for these thin tabular crystals. (Similarly, $\sigma_1^{\mathrm{p}}/\sigma_1^{\mathrm{b}} \geq 10$ for long columns.) But measurements (Sei and Gonda 1989) instead indicate that $\sigma_1^{\mathrm{p}}/\sigma_1^{\mathrm{b}}$ varies between about 0.9 and 3.6, so spiral steps cannot easily produce the extremely anisotropic growth habits that are observed. Another indication that the spiral step mechanism does not dominate ice growth from the vapor is the fact that growth does occur at low ambient supersaturations and temperatures near −3°C and from −10° to −15°C without the line defects needed for spiral steps (McKnight and Hallett 1978; Mizuno 1978).

We conclude that neither continuous growth nor spiral step growth fit observations of snow crystal growth, and now consider the last crystal growth mechanism: layer nucleation.

3. Growth by layer nucleation

Despite their initially uniform environment, snow crystals grow in very anisotropic shapes. Other examples of highly anisotropic crystal growth rates in such environments include whiskers (which presumably contain an axial screw dislocation), whose thinness is due to the extreme slowness of layer nucleation on their large-area faces (Lewis 1975).

The growth rate by layer nucleation is the layer height times the layer nucleation rate. At low growth rates, when each new layer is complete before the next is nucleated, the nucleation rate is

$$\text{number/sec} = Ae^{-\Delta G^*/kT}, \qquad (7)$$

where ΔG^* is the Gibbs free energy for formation of a critical embryo on the surface, k is Boltzmann's constant, and the exponential term times the concentration of mobile, single water molecules on the ice surface is the steady-state concentration of critical embryos. The prefactor A is the product of the concentration of these single water molecules and the rate at which a critical embryo gains one molecule. It is proportional to the following: crystal area, supersaturation, molecular vapor density at equilibrium, and the square of the mean surface migration distance (Lewis 1975). Assuming an area of 1000 μ^2, a surface supersaturation of 1%, 0°C, and a mean surface migration distance of 1 μ, then

$$A \approx 10^{21}\ \mathrm{s}^{-1}. \qquad (8)$$

We will define the critical supersaturation (σ_{cr}) as the supersaturation at which growth is barely perceptible, which for our experiment had the value of one layer per second (i.e., 3 μm in 3 h), and will use the above value for the prefactor. Since $\Delta G^* = \pi a_0 \gamma^2/kT\sigma_s$ for a circular disc embryo (Burton et al. 1951), where γ is the edge free energy of a new layer and a_0 is the area occupied by a molecule on the surface, then the growth rate change for a given change, $\Delta\sigma_s$, near σ_{cr} is $10^{21\Delta\sigma_s/\sigma_{\mathrm{cr}}} \sim 100$ for $\Delta\sigma_s/\sigma_{\mathrm{cr}} = 0.1$.[2] Similarly, the change in growth rate for a 10% change in γ is $\sim 10^4$. Thus, if layer nucleation is the growth mechanism there should be an experimentally sharp threshold (at σ_{cr} by definition) between zero and an easily measurable growth rate as one changes the supersaturation while keeping the temperature constant. Note also that if the edge-free energies of the basal and prism faces are slightly different, the difference in growth rates will be enormous: a small temperature change that produces a slight change in the relative values of the edge free energies could completely alter the primary habit.

To summarize, arguments in support of layer nucleation as the mechanism of snow crystal growth, are the following.

- It easily produces the (very) anisotropic growth rates that are observed.
- Only small changes in surface properties (γ^{b}, γ^{p}) can cause an abrupt transition from thin plates to long needles and vice versa.
- Growth by layer nucleation has been inferred from some studies of ice crystals grown at low supersaturations in the laboratory.
- In addition, the fast-growth directions of branched, sector snow crystals would not remain fixed along the crystallographic a axes, as they are observed to do, unless growth occurred by layer nucleation (see appendix).

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[2] With the above definition of critical supersaturation, the layer nucleation rate is $10^{21(1-\sigma_{\mathrm{cr}}/\sigma_s)}$, where $\sigma_{\mathrm{cr}} = \Delta G^*\sigma_s \log[e]/21kT$. When σ_s increases from σ_{cr} to $1.1\sigma_{\mathrm{cr}}$, the growth rate increases a hundred fold. If there is more than one step on the crystal face the nucleation rate is smaller than that given by Eqs. (7) and (8). This is discussed in more detail in the caption for Fig. 4.

However, there also are the following problems with layer nucleation as the growth mechanism.

1) There has been no evidence that the relative values of critical supersaturation vary in the right manner to explain snow crystal shapes.
2) Ice crystal growth measurements on a substrate usually fit Eq. (6) better than Eq. (7).
3) Growth rates should be much more anisotropic at low supersaturation than has been reported. In particular, the low supersaturation habits shown in Fig. 2 are not expected from layer nucleation.
4) Snow crystals are expected to contain imperfections that should strongly affect low supersaturation growth rates.

These arguments against layer nucleation as the surface mechanism of habit change can only be resolved through measurement of critical supersaturations. After describing our experiment and results, we will address these problems.

4. Method and procedure

The experimental technique (Nelson and Knight 1996) was designed especially for good control at low values of supersaturation, with a single crystal growing at the end of a fine capillary (10 μm OD) in a 2-cc chamber within a constant-temperature bath. The vapor source was a puddle of supercooled LiCl solution with volume much bigger than the crystal so that the supersaturation was effectively constant during growth and independent of growth rate. Supersaturation could be determined within about 0.03% (Nelson and Knight 1996). It was calculated using Raoult's law and the temperature decrease from the temperature at which the solution was in equilibrium with ice. The latter was determined by measuring the temperature at which, upon slow warming, the crystal just started to evaporate.

The experimental procedure was to supercool and then nucleate pure water in the capillary. The expansion extruded a drop onto the capillary tip, which froze virtually always into a single crystal. Then by manipulating the temperature, the frozen drop could be evaporated and the crystal regrown from the vapor at temperatures selected to give any value of supersaturation within the range determined by the amount of LiCl in the puddle. Crystals often were evaporated and regrown several times to cover a range of supersaturations. It was much more common to observe critical supersaturations on a basal than on a prism face in this experiment, presumably because imperfections were more common on the prism faces, although we have no indication of the type of imperfection nor do we know if they were caused by the capillary.

A strong advantage of this particular experimental setup over previous studies is the fact that the capillary terminates within the crystal, so that it contacts at most one basal and two prism faces out of the eight faces on the solid prismatic crystal. It was observed that the contact of the crystal with the exterior of the capillary does stimulate growth, since critical supersaturations were not seen on faces that contacted the capillary. The crystal usually had a corner at the location where the capillary penetrated the surface, a phenomenon also seen in the photos from Kobayashi (1961), leaving one basal and four prism faces free. This compares with growth on a substrate, which provides at most one free face if that face is exactly parallel to the substrate, and growth on a fiber, which can have two to six free faces, but four or less if the fiber penetrates one corner.

The other advantages of this technique are positive control of supersaturation by controlling the temperature of the isothermal system and the ability to have only a single crystal growing so that there is no competition between crystals for the vapor supply. This makes the environmental supersaturation probably as well defined as one can achieve working at atmospheric pressure and in the gravitational field. For the very low growth rates in these experiments, the assumption that the temperature is uniform is very good.

Probably the major disadvantages of the present method are the inability to change the temperature and supersaturation independently during crystal growth, the difficulty of getting high quality photographs through several centimeters of fluid and two windows, and the annoyance of waiting for the water in the very fine capillary to freeze out to the end. Also, accessible supersaturations are limited to the value corresponding to saturation with respect to supercooled water and below.

5. Results

Measured critical supersaturation values for the basal and prism faces are shown in Fig. 5 as a function of temperature. The data comes from 25 crystals exhibiting a critical supersaturation on one or both basal faces and 18 crystals showing a critical supersaturation on one or more prism faces. Hence, each data point represents observations of several crystals using a fixed concentration of salt solution. There was no indication of different measured values for different crystals under the same conditions: error bars for the basal face indicate uncertainty in the supersaturation at which growth started. No error bars means that the uncertainty is about the size of the filled square. The larger uncertainties are due to making observations at larger intervals of supersaturation. The basal face shows a strong temperature dependence with a minimum of about 0.15% near −5°C. Uncertainty estimates for the prism face data are different because the data is less complete. We could not easily measure an upper limit to the critical supersaturation so we rely largely on our observations of symmetric growth of all prism faces. The reason for this difference is twofold; the crystal was usually oriented in a position to view the normal growth of the basal

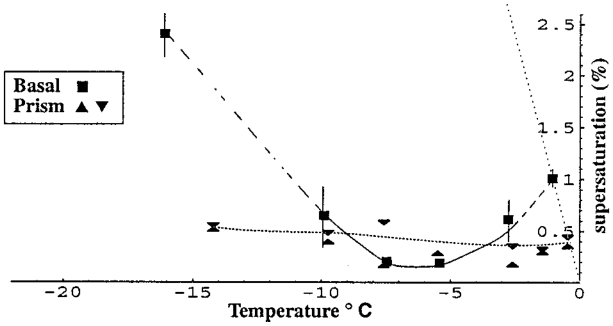

FIG. 5. Measured critical supersaturations at which growth was just observable for the ice basal and prism faces (~3 μm in 3 h). Error bars for basal face data were estimated from the temperature interval between observed growth and nongrowth. The solid curve is dashed at its ends because the data do not define slopes there. The upper limits of the prism face critical supersaturation data (downward-pointing triangles) were estimated from observations of equal growth on all prism faces (compare Figs. 6a and 6b). At −5.5°C an upper limit was not recorded. Lower limits (upward-pointing triangles) are the highest supersaturations at which nongrowth of one or more prism faces was observed. The steep dotted line is the supersaturation of supercooled liquid water (compare to Fig. 2), and the lower dotted line passes through the prism face data. The effect that growing faces had on reducing the supersaturation on the nongrowing faces was estimated by inserting the measured growth rates and values of h^b, h^p for the centers of the faces (Nelson 1994) into Eq. (9) and was found to be less than 10% for the extreme crystal shapes in the experiments. Its effect is not included in the data.

faces, which precluded viewing normal growth of most prism faces, and growth of one prism face (presumably from a spiral step) could apparently induce growth on a neighboring face that previously had not been growing even when the supersaturation was kept constant. That this latter behavior was observed on prism faces but not basal faces might be because a line dislocation normal to the growing prism face will eventually intersect a nongrowing neighboring face, thus promoting growth on both of them. The critical supersaturations (dotted line) for the prism face are within the ranges from the upward- and downward-pointing triangles and do not depend strongly upon temperature but remain constant over this range at about 0.4%.

The highest temperature data were obtained with pure water as the vapor source, starting very close to 0°C and cooling until growth was observed. Thus, the critical supersaturation must be above liquid water saturation for temperatures above −1°C on the basal and −0.4°C on the prism faces.

Examples of crystals are shown in Fig. 6. The critical supersaturation in the example in Fig. 6a was exceeded for prism faces and all six grew at the same rate, but one basal face did not grow measurably while the other grew just fast enough to remain in contact with the capillary. The crystal in Fig. 6b showed no growth on the two prism faces closest to the capillary tip and on the basal face not in contact with the tip. Occasionally, a free crystal face that did not grow was observed to start growing after neighboring faces had grown farther up the capillary. Then this face would continue to grow after lowering the supersaturation, albeit at a slower rate. We hypothesize that the growth on neighboring faces introduced a line defect, perhaps originating from the contact with the capillary, to the previously nongrowing face. Growth of ice along a solid, foreign surface could produce dislocation-generated spiral steps, and that might also explain the second problem with the layer nucleation mechanism noted in section 3. The third and fourth arguments against layer nucleation, the lack of extreme habits in previous experiments at low supersaturation and the influence of imperfections on growth, will be discussed in the next section.

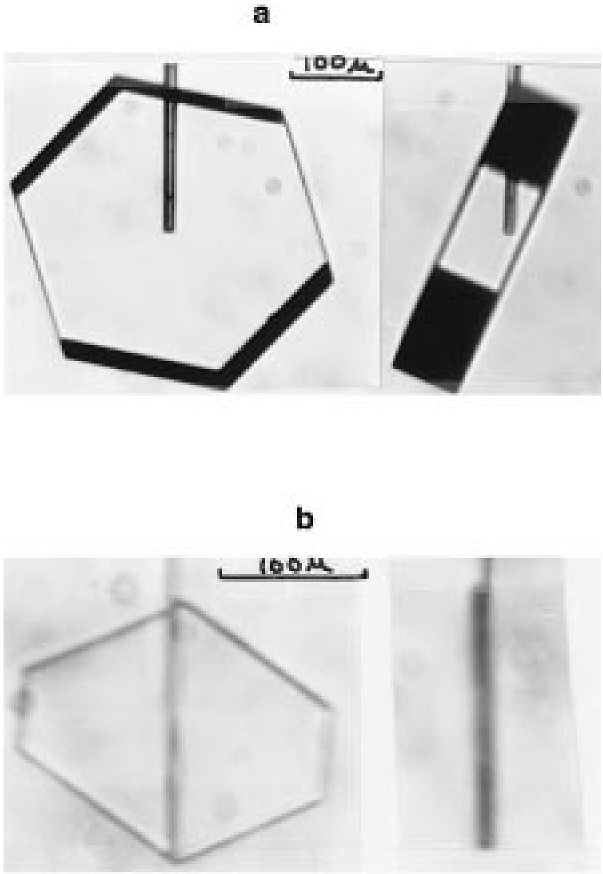

FIG. 6. (a) Front and side view of crystal grown at −15°C and 1.5% supersaturation. (b) Same as (a) except at −7.4°C and 0.15% supersaturation.

6. Discussion

a. *The mechanism of habit change*

The most important finding of this study is the following observation: the critical supersaturations for the basal and prism faces cross near two temperatures, −3° and −9°C, which are appropriate to explain the axial ratio c/a changes in the habit diagram shown in Fig. 2. Therefore, these data negate the first argument against

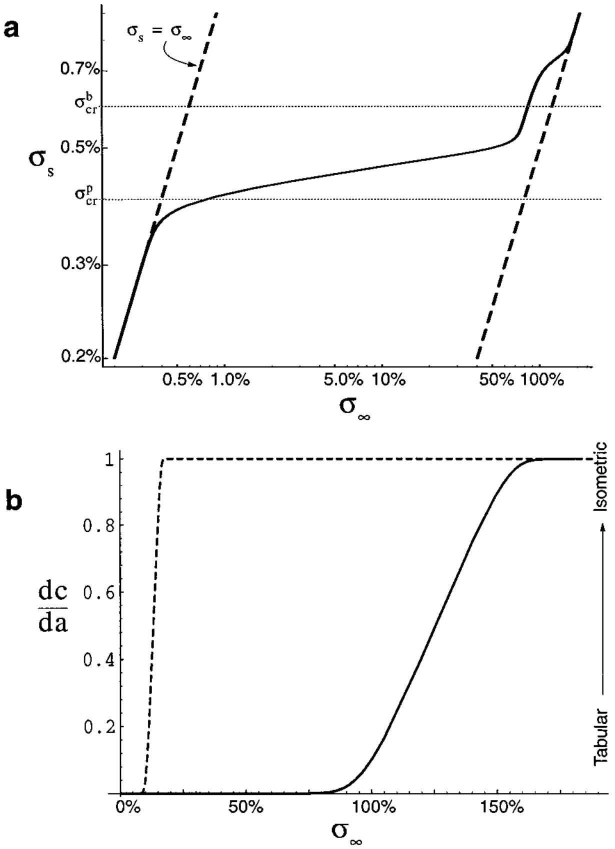

FIG. 7. (a) Surface supersaturation as a function of ambient supersaturation for layer nucleation. Solid curve is σ_s at a corner from Eq. (10) for $a' = 200$, $\sigma^p_{cr} = 0.4\%$, $\sigma^b_{cr} = 0.6\%$, and $c = a$. Dashed curve on the left is $\sigma_s = \sigma_\infty$, and the dashed curve on the right is σ_s when $\alpha^b = \alpha^p = 1$. Note the flattening of $\sigma_s(\sigma_\infty)$ near $\sigma_s = \sigma^p_{cr}$ and σ^b_{cr}. (b) Solid curve is the ratio of growth rates on the basal and prism faces for the conditions in (a). The only change for the dashed curve is the vapor diffusivity was increased by a factor of 10 while keeping the crystal size the same (i.e., $a' = 20$). This illustrates why growth at high supersaturation with reduced air pressure results in more isometric growth.

layer nucleation as the surface mechanism of habit change and are consistent with the premise that layer nucleation can produce the transitions at −3° and −9°C from tabular to columnar growth. However, the question of the large growth-rate anisotropy has not been fully answered: since $\sigma_\infty \gg \sigma_{cr}$ in clouds composed mainly of supercooled water, why should small differences between σ^b_{cr} and σ^p_{cr} lead to large differences in growth rate? The following answer is based on the simplifying assumption that the crystal contains no spiral-step-forming imperfections. Although this is probably not correct, the argument should also apply qualitatively to the more realistic case that we discuss later.

The surface supersaturation is much less than the ambient supersaturation because the crystal is rapidly depleting the surrounding air of vapor molecules. However, for this depletion to take place, the surface supersaturation must be just above the lowest critical supersaturation. The net result is that the surface supersaturation remains close to the lower critical value, so that virtually all of the growth must be on one face and practically none on the other. Introducing two different types of crystal faces (basal and prism) into the analysis changes Eq. (1) to a form containing two shape-dependent factors; $h^b(c/a)$, and $h^p(c/a)$, which represent the dependence of the vapor diffusion field on the growth rates of each face:[3]

$$h^b(\text{net flux to basal})c + h^p(\text{net flux to prism})a = DN_{eq}(\sigma_\infty - \sigma_s). \tag{9}$$

Using this equation, together with Eq. (4) for both crystal faces, we can solve for σ_s, the surface supersaturation at the corner,

$$\sigma_s = \frac{\sigma_\infty}{1 + a'(\alpha^p h^p + \alpha^b h^b c/a)}, \tag{10}$$

where $a' \equiv \bar{v}a/4D$. (Here, $a' \sim 5a$ for a in μm and is typically larger than 100). For layer nucleation, $\alpha^{b,p}$ are highly nonlinear functions of σ_s, therefore, a closed form solution to Eq. (10) is not possible. Instead, we plot the surface supersaturation as a function of ambient supersaturation in Fig. 7a for the case that $\sigma^b_{cr} > \sigma^p_{cr}$. When $\sigma_\infty \leq \sigma^p_{cr}$ the root of Eq. (10) (σ_s) is trivial: $\sigma_s = \sigma_\infty$. This is shown by the initial increase of σ_s in Fig. 7a. As σ_∞ increases further, σ_s moves into the transition region between $\alpha^p \approx 0$ and 1 and stays there until σ_∞ is quite large. Since this occurs over a small range of σ_s near σ^p_{cr}, where growth is most anisotropic (Fig. 7b), layer nucleation can easily account for the high degree of anisotropy of snow crystal shapes. If spiral steps are present, the anisotropy would be less when the crystals are small as described below. Surface migration between adjoining faces is not needed for this explanation of the anisotropy, although it might also play a role when a crystal face becomes very thin (such as at the ends of needles and dendrite arms). Note also that σ_s is much smaller than the ambient supersaturation even when $\sigma_\infty \gg \sigma^p_{cr}$ or σ^b_{cr} so assuming that $\sigma_s = 0$ in a diffusional growth rate calculation (i.e., diffusion-limited growth) should be accurate, and this is in agreement with experiment (Takahashi et al. 1991; Takahashi and Fukuta 1988). If $a' \to 0$ (by removing the air from the environment, or, equivalently, by increasing the vapor diffusivity), then the root of Eq. (10) again becomes trivial: $\sigma_s \to \sigma_\infty$, but in this case σ_∞ can be much larger than the critical values. Thus, the growth rate anisotropy

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[3] The h functions describe the vapor density anywhere external to the crystal roughly in proportion to the area of each face. They depend on position and crystal shape, but for the vapor density at the corners of a cylindrical crystal, $h^b \sim 0.4a/c$, h^p increases monotonically with c/a and is approximately 0.3 at $c = a$. A more complicated crystal would require a different h function for each flat region on the crystal surface. Approximate functions for $h^b(c/a)$ and $h^p(c/a)$ can be found in Nelson and Baker (1996).

should disappear when the air pressure is reduced and the ambient supersaturation is significantly above the critical values (above 17% in the conditions of Fig. 7b). This prediction is in agreement with several experiments of ice crystal growth at low air pressure (Gonda 1980; Isono et al. 1957; Beckmann and Lacmann 1982).

The present results also indicate that the growth rate anisotropy should be greater at −15°C than at −7°C because the difference in critical supersaturations is larger at −15°C. This is in agreement with laboratory measurements of small freely falling ice crystals in a supercooled water cloud (Gonda 1980).

The experimental results in this work show extremely anisotropic growth at very low supersaturation, which is consistent with the layer nucleation mechanism. (In Fig. 6 the anisotropy is limited only by the capillary and the time of growth.) These results conflict directly with previous observations of nearly equidimensional growth at low supersaturation (Kobayashi 1961; Rottner and Vali 1974; Colbeck 1983). Furthermore, many observations and experiments have shown the most anisotropic growth of snow to be a high supersaturation phenomenon, not low. We offer the following discussion as suggestions toward the resolution of these difficulties: the problem of explaining natural snow crystal shapes at high and low supersaturations, and the discrepancy in experimental results.

Snow crystals usually start by the freezing of supercooled liquid droplets several to a few tens of microns in diameter. Although they are often single crystals, stresses generated during freezing[4] would likely generate self-perpetuating (spiral) steps on all faces. We will assume that the starting ice from which snow crystals grow contain spiral steps on all faces, but their number is fixed: further growth from the vapor does not produce more spiral steps. There are no laboratory data to support or refute this assumption, but it is consistent with current knowledge of crystal growth. Figure 4 illustrates that growth from spiral steps should control growth rates at low supersaturations. It is only at higher supersaturations that layer nucleation is expected (Lewis 1975) and observed (De Yoreo et al. 1994; Malkin et al. 1995) to dominate growth over spiral steps. However, when the ambient supersaturation is above the lowest critical value, layer nucleation should gradually dominate growth as the snow crystal increases in size in the following way.

Consider the starting ice as a frozen droplet in the shape of a sphere. At low supersaturation, the first stage is for faceted patches to appear on the six prism faces, the two basal faces, and possibly pyramidal faces (Gonda and Yamazaki 1978). Then the regions between the basal and prism faces grow out to form a solid and nearly isometric hexagonal column. Once the column is completely filled out, growth proceeds at spiral steps from the dislocations that emerge on the faces. Figure 8a is a simplified picture of the ice structure at this stage. Dislocations that intersect the surface are represented as lines and are drawn normal to the surface because this would likely minimize the internal energy of the crystal. Therefore, as growth continues on the facets, their points of emergence will stay near the face centers (Fig. 8b), so that dislocation-free areas near the edges grow larger and larger. As the solid column grows at constant ambient supersaturation, the relative values of surface supersaturation at the edges, as compared to the face center, increase along with the tendency for steps to nucleate near the edges (Frank 1974; Nelson and Baker 1996). This leads to hollowing at the face centers, as shown in Fig. 8c, which we will denote as the start of stage two. The question now is, do dislocations affect growth during this stage?

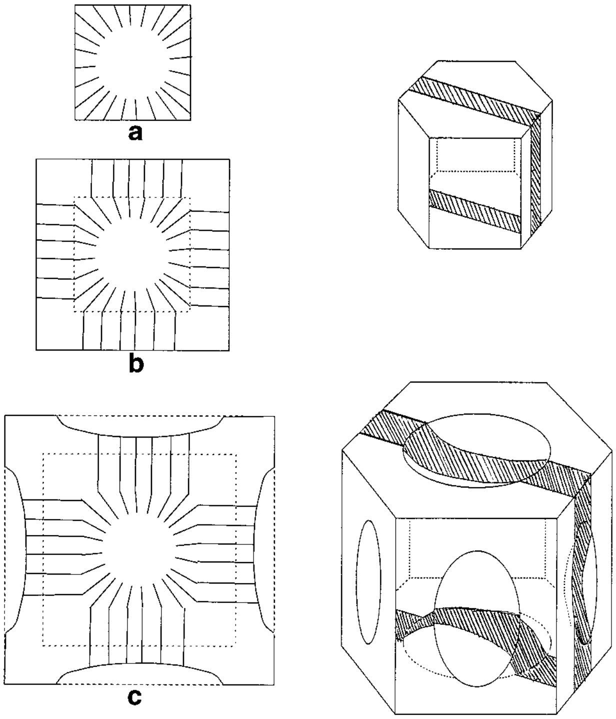

Fig. 8. (a) A schematic of a slice through an isometric crystal (illustrated at right) immediately after the basal and prism faces have covered the crystal surface. The lines indicate line dislocations that lead to spiral steps on a surface. In (b), the crystal faces have grown from the vapor, but since the dislocation outcrops remain near the centers of the faces, perfect crystal regions near the corners increase in area. (c) Owing to their being exposed to higher supersaturations, the edge regions grow faster, thus creating a faceted rim, and separate from the slower growing center regions of crystal (hollows) that contain the spiral step sources.

Eventually, all dislocation emergent points should be in the hollows and thus below the level of the leading

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[4] Possibly from one or more of the following: temperature gradients, expansion upon freezing of trapped liquid pockets, and lattice mismatch between ice and the freezing nucleus (or other nonsoluble material in the droplet). Note that the first two of these were probably negligible in our experiment.

growth surfaces. If there are equal numbers of dislocation of opposite sign, all with the same Burgers vector, then dislocation-induced spiral growth steps on the leading growth surface cancel out, leaving that surface perfect and thus growing solely by layer nucleation. However, it is more likely that there will be an excess of one sign over the other, and then we expect, after some step coalescence, to have a single step of height corresponding to the amount of that excess to travel around the face perimeter as shown in Fig. 9a. As the circumference of this rim increases so that the time for the step to complete a revolution becomes longer than the time to nucleate new layers, layer nucleation will begin to dominate growth. Once this occurs, narrower protrusions (needles in the case of columnar growth, and arms for tabular crystals) should eventually form that further isolate the emergent points of dislocations to regions of relatively small supersaturation, thus suppressing the influence of dislocations even more. Figure 9b shows a schematic of a needle that sprouted from the corner of a columnar crystal and is growing exclusively by layer nucleation because of this isolating effect.

The above represents what is probably the usual case: growth with some spiral steps. The result is that the initial growth is not very anisotropic, but after growth proceeds, and in particular, after a face hollows, growth becomes controlled by layer nucleation and hence very anisotropic. This transition to very anisotropic growth occurs much faster at higher supersaturations both because larger sizes develop faster, but also because hollowing occurs at smaller sizes (Nelson and Baker 1996). Although our argument is primarily speculation at present, the X-ray diffraction topographic study of dislocations in vapor-grown ice by Mizuno (1978) shows just the tendencies expected from this hypothesis. However, there are cases where growth rates are very anisotropic without hollowing and at low supersaturations. We frequently observed this in our experiments because it was common for one or more faces to be free of spiral steps. It has also been observed on snow crystals at low temperatures (Shimizu 1963), presumably for the same reason.

Finally, there is a close connection between layer nucleation and spiral steps. If the surface migration distance is nearly the same on both faces, then the face with the lower critical supersaturation would grow faster than the other face even when growth is from spiral steps[5] because the spacing between steps in a spiral is proportional to the edge-free energy of a new layer (Burton et al. 1951). This links the present measurements to previous observations of habit change in negative crystals (Knight and Knight 1965; Furukawa and Kohata 1993). These latter results were almost certainly examples of dislocation-controlled growth and exhibited habit changes at nearly the same temperatures as snow crystals but were much less anisotropic in growth rate.

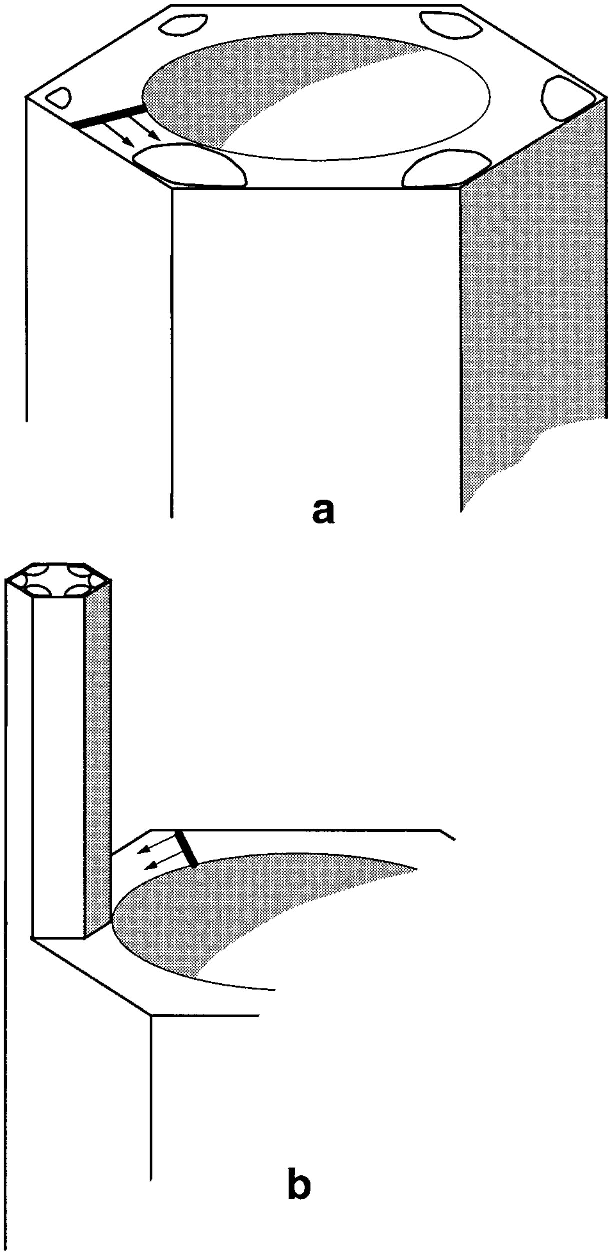

FIG. 9. (a) The rim area of a columnar crystal is growing by the single step (dark line with arrows indicating direction of motion) formed by dislocation outcrops hidden in the hollow region of crystal. Layer nucleation at the corners is also shown. In (b), a corner region is growing fast enough to sprout a needle. The needle grows only by layer nucleation because any step formed by a dislocation outcrop in the hollow remains on the rim. An actual needle crystal would likely have several needles along the rim, each growing from a different corner and connected to its neighbor by concave regions of rim.

The contradictory experimental results can be explained by substrate effects. In the laboratory, all pre-

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[5] Either from a single spiral step on each face, or for spiral steps sources randomly distributed in sign and position (Burton et al. 1951).

vious experiments that allowed long growth times have involved flat substrates or fibers and there has been no systematic selection for the measurements to be made on free faces. Beckmann and Lacmann (1982) reported critical supersaturations for faces in contact with a flat substrate, but the values were not reproducible and there was no systematic difference between the values on the prism and basal faces. Kobayashi (1961) found limiting c/a ratios of 1.4 for temperatures below $-22°$C, 0.8 for temperatures between $-22°$ and $-10°$C, and ‘‘thick columns’’ above $-10°$C, but his crystals were penetrated by a fiber, and the results were not confined to free faces and also exhibited significant scatter. In contrast, the results we have given here are limited to free faces; the faces in contact with the capillary grow at all supersaturations.[6] Although our results presented here show more anisotropic growth at low supersaturations, there are plausible reasons for this: when spiral steps are absent from several crystal faces the growth anisotropy is extreme at low values of σ_∞. This concludes our discussion of the third and fourth difficulties with layer nucleation as the mechanism of snow crystal habit change.

Some authors have argued that surface migration from one face to another plays a role in the formation of crystal habit (Mason et al. 1963; Mason 1993; Kuroda and Lacmann 1982; Frank 1982). Surface migration from the slower face to the rim of the faster-growing face could significantly increase the growth rate of the latter (Sears 1955a) during branching and hollowing when the faster-growing faces are very thin and could reduce the growth rate on the former (Frank 1982). Our present experiments cannot rule these effects out; we have only argued that they are not needed to explain the main features of snow crystal growth. Explaining quantitatively the extreme snow habits at high values of σ_∞, is a problem that requires further study because of these and other possible influences on growth, but since the analysis would need to take into account the more complicated shapes of ice crystals growing at high supersaturations and large sizes, this will not be easy to carry out. Layer nucleation on freely growing snow crystals and substrate effects on laboratory-grown crystals can explain most experimental and observational data on ice vapor growth that we know about.

Table 1. Critical supersaturations for a variety of materials. Data are from the following sources: Sears (1955b): Cd, Ag, Zn, CdS; Loper et al. (1971): Cd; Sears (1956): Hg; Stein and Meyer (1980): KCl; and Keller (1991): NaCl. Theoretical critical supersaturations and a summary of the data prior to 1974 are in Lewis (1974).

Material	$\frac{T(\text{melt}) - T}{T(\text{melt})}$	Measured critical supersaturation (%)	Theoretical critical supersaturation (%)
ice	0.005–0.055	0.15–2.5	20
Cd	0.036–0.12	300–700	280–440
Ag	0.091	900	300
Zn	0.10	200	600
Hg	0.10	3×10^4	4×10^8
CdS	0.16	30	
KCl	0.43	600	
NaCl	0.46	2900	

b. Implications for the nature of the ice–air interface

The simplest theoretical estimate of the critical supersaturation for vapor growth is based on the assumption that the riser of a step has the same interfacial energy as the flat surface, so that the step energy is simply the area of the step riser times the interfacial energy. Using the measured ice-vapor surface energy, 100 ergs cm^{-2} (Ketcham and Hobbs 1969), with a step height of 3 Å, the above assumption results in a critical supersaturation of approximately 20% instead of the measured 0.2%–2%. Table 1 contains measured critical supersaturations and the values calculated as above for a variety of vapor-grown crystals. In comparison to other vapor-grown crystals, the measured ice values are small and the discrepancy between theory and experiment large. This discrepancy can be resolved if the surface region undergoes gradual disorder as the surface is approached from the bulk. This is suggested by experiment (e.g., Golecki and Jaccard 1978) and molecular dynamics calculations (Kroes 1992; Nada and Furukawa 1994). Cahn (1960) showed that the critical supersaturation for growth can be much less than that from the simplest estimate in this case. Jackson et al. (1967) argued that Cahn’s theory does not apply to the solid–vapor interface but introduced a theory without this restriction that qualitatively reached the same conclusion. Bartley (1978) argued that molecular reconstruction at the edges of critical embryos can lead to low values of critical supersaturation.

Some authors have suggested that the ice–vapor interface contains a melt layer at equilibrium and that layer nucleation occurs from this ‘‘quasi liquid’’ (Kuroda and Lacmann 1982; Fukuta and Lu 1994). There is little doubt that the ice surface is rather badly disturbed at temperatures not far below zero, and the undecided issue is whether it is more realistic to view it as a liquid layer or, more traditionally, as a partially disordered crystal right up to the vapor interface. In terms of layer nucleation, a low energy barrier is expected either way. If the nucleation event occurs at the bottom of the quasi liquid, the barrier might be comparable to that of ice from supercooled water: if instead it occurs at the vapor interface, the lower energy barrier is caused by the lower step energy resulting from surface disorder.

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[6] It is worth noting that the nucleation of a new growth layer on a facet where it contacts a substrate is expected to depend critically upon the angle the facet makes with the substrate surface as well as upon the nature of the substrate itself. Any critical supersaturation values below or equalling those for free faces can be anticipated. Another possible substrate influence is the introduction of spiral step sources into the growing crystal.

Hillig (1958), supported by Sperry (1965) and Wilen and Dash (1995), found the critical supercooling for layer nucleation on the basal plane from liquid water to be 0.02°C, which corresponds to a supersaturation of 0.02%. This is approximately 10 times lower than the lowest critical supersaturation measured here (on the basal plane at −6° or −7°C) and roughly 50 times lower than that on the basal plane at about −1°C, where the critical supersaturation line meets the line representing saturation with respect to supercooled water (Fig. 5).[7] Thus if the model of the ice growth by layer nucleation at the base of a quasi liquid layer is correct, then the quasi liquid cannot be very much like ordinary liquid water. In fact, this discrepancy would be even larger if the quasi liquid were more icelike since the edge energy between the ice and quasi-liquid layer would be smaller. Furthermore, Hillig (1958) and Miksch (1963) found no critical supersaturation for growth at the prism face from liquid water at atmospheric pressure. The presence of such a barrier in growth from the vapor argues in the same direction. Thus, it appears more likely to the authors that the layer nucleation takes place at the vapor interface and that the view of the ice surface as a liquid layer is not a useful idealization for crystal growth processes.

It is clear that the fundamental reason why ice growth habits vary as they do must wait for a better understanding of the ice surface than exists at present. There is a surface transition of some kind on the basal face with decreasing temperature, as shown by step growth studies (Hallett 1961; Mason et al. 1963; Kobayashi 1965a; Cho and Hallett 1984b), face growth rate studies (Lamb and Scott 1972), and the present results. The present work does not show a similar transition on the prism face (in contrast to Lamb and Scott) and, therefore, does not support the conjecture (Mason et al. 1963; Mason 1993) that the prism face might have a transition displaced a few degrees in temperature from that on the basal face.

c. Comparison to previous studies

All previous measurements of critical supersaturation have been for ice growing on a substrate. Shaw and Mason (1955) observed critical supersaturations up to about 10%, but the values varied from crystal to crystal under the same conditions. Kobayashi (1965b) observed ice whisker growth at temperatures between −40° and −60°C at supersaturations up to 3% indicating that the critical supersaturation for the prism face is approximately 3% at these low temperatures. Cho and Hallett (1984a) observed a lack of growth on the basal face at temperatures above −3°C and below −7°C, but not in the column growth regime in between these temperatures, even at supersaturations less than 1%. The low critical supersaturations found here for basal face growth are below 0.4% in this range. Their experiments involved basal faces of epitaxial crystals on covellite, which are influenced by epitaxial strain, making quantitative use of some of the results difficult. Beckmann and Lacmann (1982) grew ice crystals from a pure vapor and occasionally observed growth as a function of supersaturation that fit Eq. (7) reasonably well. The resulting critical supersaturations were close to those reported herein, but the authors could not resolve a difference between the basal and prism faces.

Partial agreement with the present results also comes from the measurements of growth rates of basal and prism facets of ice intersecting a substrate in a pure water vapor environment at an excess vapor density of 10 μm Hg and a range of temperatures (Lamb and Scott 1972). They found a strong maximum in the growth rate normal to the basal plane from about −4° to −8°C. This vapor pressure is equal to a supersaturation that crosses the critical supersaturation curve of Fig. 5 at −4° and −9°C, which is in remarkable agreement with our results if their basal face growth maximum was due to layer nucleation. However, they also found a maximum in growth on the prism plane from about −9° to −17°C, which cannot be easily explained by layer nucleation since our measurements do not indicate a reduction in critical supersaturation for the prism face in this region. As noted in footnote 6, the growth of faces that intersect a substrate is expected to be more complicated than that of free faces.

The observations of small, round, basal discs of ice growing from the vapor reported by Keller et al. (1980) also cannot be explained at present. We also observed this phenomenon on occasion. The rounded interfaces parallel to the *c* axis became faceted as the crystal grew, though in some cases, thickening appeared to be very slight. As mentioned in section 2b, a rounded interface implies that nucleation is not rate controlling, contrary to the discussion in Keller et al. (1980), and it remains difficult to understand why small and/or thin crystals alone should have rounded, growing interfaces. A surface impurity that becomes diluted and hence less active as the crystal grows is a possible explanation for this effect.

7. Conclusions

Layer nucleation can explain the primary features of snow crystal growth habits: the changes in *c*/*a* ratio near −3° and −9°C, and the extreme values of *c*/*a*. It is also consistent with some of the secondary features: the crystal orientation of some sector axes (see appendix) and the relatively high degree of symmetry of dendritic and sector plate crystals. The arguments for layer nucleation being the mechanism were already strong (Frank 1974, 1982;

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[7] In making this comparison, the assumption is that there is no barrier to equilibration of the liquid layer with the vapor, that all of the metastability exists between the layer and the crystal. Thus ΔG^* is the same whether viewed between vapor and crystal or between liquid layer and crystal so it can be calculated equivalently from either supersaturation or supercooling. This device is commonly used in nucleation calculations (e.g., Fletcher 1962).

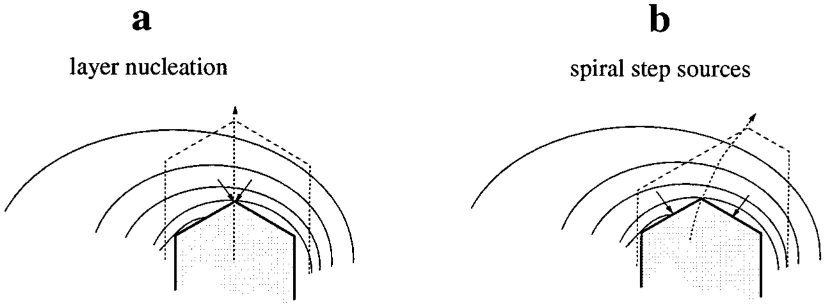

FIG. A1. Growth of a sector arm or branch in a gradient of supersaturation (indicated by asymmetric supersaturation contours around the crystal). In (a), growth layers are nucleated at the tip, resulting in equal growth on both adjacent faces and straight growth of the tip. In (b), growth occurs from spiral steps fixed to the ends of line imperfections, resulting in unequal growth on the adjacent faces and curved tip growth.

Knight 1972), and the mechanism had been proposed by several other researchers (Keller et al. 1980; Mason et al. 1963; Kuroda and Lacmann 1982; Fukuta and Lu 1994), but the present results are the first to implicate directly the values of critical supersaturation for layer nucleation growth on different faces as the cause of the habit change. Surface migration of water molecules between adjacent faces of ice may play a role here as well, but it is not needed to explain the main features.

A fundamental understanding of snow crystal growth mechanisms must come from better knowledge of temperature-dependent, structural changes on the basal and prism faces. That understanding is needed to explain the step velocity results (Hallett 1961; Mason et al. 1963; Kobayashi 1965a; Cho and Hallett 1984a,b) as well as the temperature dependence of the critical supersaturations revealed in the present work. Also, it is not known if spiral steps occur on snow crystals and whether they influence the crystal shape.

The present experiments need to be extended to lower temperature and with controlled amounts of impurity. Also, in light of the disparity in the prism face results between our measurements and those of Lamb and Scott (1972), more measurements should be done on the prism face. In addition, it would be interesting to examine the highest subzero temperatures with great care because of the possibility of layer nucleation occurring after liquid condensation on the surface (vapor–liquid–solid growth) when the vapor is slightly supersaturated with respect to liquid water.

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APPENDIX

Direction of Sector Branches

One difference between layer nucleation and spiral step growth was illustrated in Fig. 4. Another one comes from the fact that layer nucleation occurs fastest wherever the surface supersaturation is highest. This is in contrast to spiral step sources, which are fixed to line imperfections. An expected manifestation of this difference is shown in Fig. A1. Layer nucleation should occur at the tip of a sector arm because the surface supersaturation is usually largest there. Since the nucleation rates of layers on each face on either side of the tip are determined by the supersaturation at the tip, both faces grow at the same rate, thus forcing the tip along a straight line even when there is a lateral gradient of supersaturation, as shown in Fig. A1a. With spiral step growth, a vapor density gradient causes the supersaturation at the spiral centers on adjacent faces to be different, because they are not immediately adjacent to the tip. The tip would grow toward the direction of the higher supersaturation, as shown in Fig. A1b. Observations of sectors grown in gradients show clearly that Fig. A1a represents the actual case. Figure A2 shows one example, grown in a chamber built to replicate Nakaya's apparatus 4. [See Nakaya (1954, 159, Fig. 289). More examples are shown in Figs. 299, 312, 339, 445, and 476a of the same reference.] The gradient is manifested by the unequal development of the prism faces adjoining the tip. Therefore, this supports the argument for growth by layer nucleation. Even in the absence of vapor density gradients, competition between spirals results in significant changes in growth rate of a crystal face (Lubetkin and Dunning 1978; Onuma et al. 1994), so if sector arms grew by spiral ledges then the arms would probably meander, in contradiction to observation (Nakaya 1954). Yamashita (1976) discussed and illustrated the distinction between straightness and curvature of sector axes in detail.

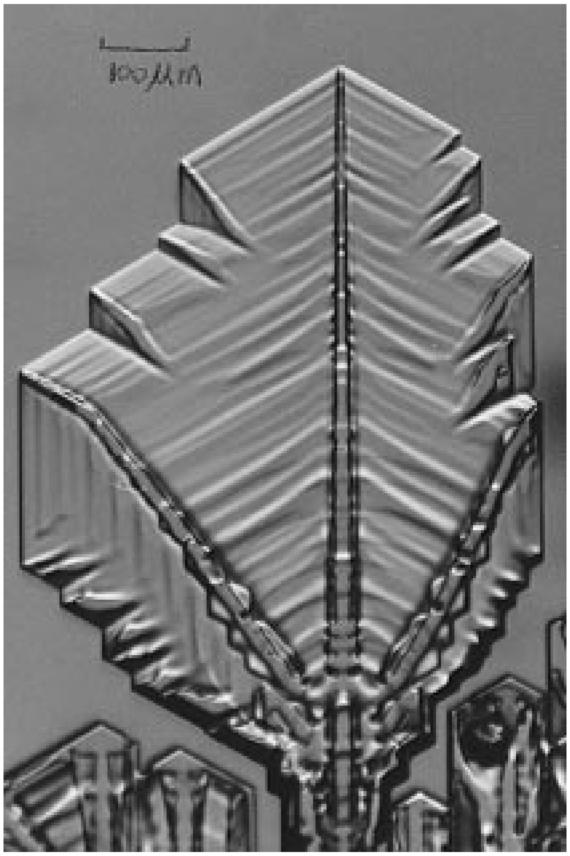

FIG. A2. Sector grown at −17.5° C, approximately saturation with respect to liquid water. The central spine is straight and accurately at 60° to the two prism facets at the top because the growth rate on both facets is controlled by the supersaturation right at the tip. However, the shape shows higher supersaturations to the left than to the right. The two other spines are not parallel to *a* axes, because nucleation at their tips only controlled the growth at one side, while the other side received steps that nucleated at the main tip. The one at the left curved to become parallel to an *a* axis when it was cut off from steps originating at the tip of the primary spine.

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