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Tip splitting in dendritic growth of ice crystals

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Ice crystals growing vertically upwards in quiescent ultrapure water have been investigated at small subcoolings in the range of $0.035 < \Delta T < 1.0$ K. At subcooling less than 0.35 K, dendritic tips split and the tip radius R_2 drops because two tips replace one when viewed from the basal plane. The growth velocity and the tip radius of the edge plane of the dendrite, however, are found to remain independent of time and unaffected by the morphological instabilities in the basal plane. In contrast, when the subcooling is greater than 0.35 K, the tips seem to grow with an invariant shape. The shape of drops of water that are in equilibrium with solid ice is observed to be close to a circular disk. From the shape of these drops, the anisotropy of the surface energy in the edge plane, which is an ellipse, is estimated to be about 30%, while the basal plane is found to be indistinguishable from a circle, despite the hexagonal structure of ice. We speculate here that tip splitting in ice dendrites may be a morphological instability caused by the coupling between lack of anisotropy in the basal plane and natural convection, which becomes significant at small ΔT.

I. INTRODUCTION

The growth of crystals from pure subcooled melts produces dendrite structures in which the leading tip of the main stem propagates in the preferred crystallographic direction. These reproducible patterns have small dimensions and large curvature, and they occur in nature due to the competition between the effect of the surface energy of the solid-liquid interface and the rate of heat removal from the surface into the subcooled melt. Surface tension depresses the melting point and reduces the driving force for heat transfer of an interface which is convex to the melt and this stabilizes the solidification front.

Ice is highly anisotropic with a rich structure in the basal plane and virtually no structure in the edge plane. We report here splitting of the tips of the basal plane which appears to be unique to crystals, such as ice, which have hexagonal-close-packed structure. Succinonitrile, in sharp contrast, forms symmetric dendrites that propagate in all three dimensions with stable tips.

Anisotropy has been reported to play a crucial role in dendritic solidification. Kessler, Koplik, and Levine [1,2] developed theoretical models for the solidification of weakly anisotropic substances. They showed that some degree of anisotropy is essential to form dendritic patterns, which consist of a leading tip followed by a stream of sidebranches, and lack of anisotropy leads to tip splitting. This idea has led to a wealth of demonstrations of tip splitting in fluid-fluid systems, such as Hele-Shaw flow, which are inherently isotropic. Ben-Jacob *et al.* [3] and Chen and Wilkinson [4] have etched grooves on the walls containing the fluid to induce dendritic patterns with stable tips. Couder *et al.* [5,6] observed the fluid-fluid interface develop into a dendritic structure when an air bubble is placed on the interface in order to break the isotropy of the system and thereby to avoid tip splitting. Therefore it seems clear that anisotropy stabilizes the tips by directing the growth into favorable crystallographic directions. However, these studies of fluid-fluid interfaces are limited to two-dimensional or axisymmetric systems. We will show here that the three-dimensional nature of anisotropy has a significantly different effect on the growth of ice dendrites, which undergo tip splitting unlike their axisymmetric counterpart.

Huang and Glicksman [7] and Glicksman and Singh [8] have demonstrated the fourfold symmetry of the anisotropy in surface tension by observing the shape of liquid droplets which are in equilibrium with the solid phase. We report here measurements of anisotropy in surface tension for the ice-water system. We will show that the shape of the equilibrium drop is close to a circular disk. Therefore the degree of anisotropy is very small in the basal plane and is very large in the edge plane. Hexaoctyloxytriphenylene also has a hexagonal-close-packed structure. Its equilibrium shape has been studied by Oswald [9], who found it to be close to a circular disk.

Surface attachment kinetics plays a very important role by limiting the growth normal to the basal plane as discussed by Fujioka and Sekerka [10]. The growth along the basal plane, however, is governed by heat transfer. Thus the anisotropy of ice is three dimensional.

All of the experiments on dendritic crystal growth have been performed on earth and gravity induces convection in the melt as observed by Kallungal and Barduhn [11] and Glicksman and Huang [12]. Ananth and Gill [13] showed that Earth's gravity enhances the growth rate and reduces the tip radius. The Grashof number, which indicates the significance of convection in the system, gets larger as the subcooling is decreased. The subcoolings employed in our experiments are as low as 0.035 K. Fujioka [14], Kallungal and Barduhn [11], and Tirmizi and Gill [15,16] reported the growth rate and tip radii of ice dendrites at relatively large subcoolings. These investigators did not discuss the occurrence of tip splitting in any of their experiments.

II. EXPERIMENT

The growth cell that was used is similar to the one used by Glicksman, Schaefer and Ayers [17] for succinonitrile experiments. It is made of Pyrex glass and consists of several parts designed to ensure free growth of ice crystals as shown in Fig. 1. In order to investigate the effect of dissolved air in water on dendritic growth of ice, two cells with water of different levels of purity were used. One cell was operated in open air. The other was hermetically sealed and filled with air-free, pure water using vacuum distillation and several melting and freezing steps which were carried out in a way that ensured that dissolved air was removed from the water.

Nucleation is induced by liquid nitrogen and the dendrite propagates along a capillary and emerges from the tip of the capillary to grow freely in subcooled water. In general, ice dendrites grow in arbitrary directions with respect to the microscope-camera system. Therefore to investigate the effect of thermal (natural) convection induced by gravity on ice crystal growth, and photograph the edge and basal planes accurately, a system was designed which allows 360° rotation and ± 30° tilting. This system enabled us to achieve any desired orientation as dendrites emerged from the capillary tip.

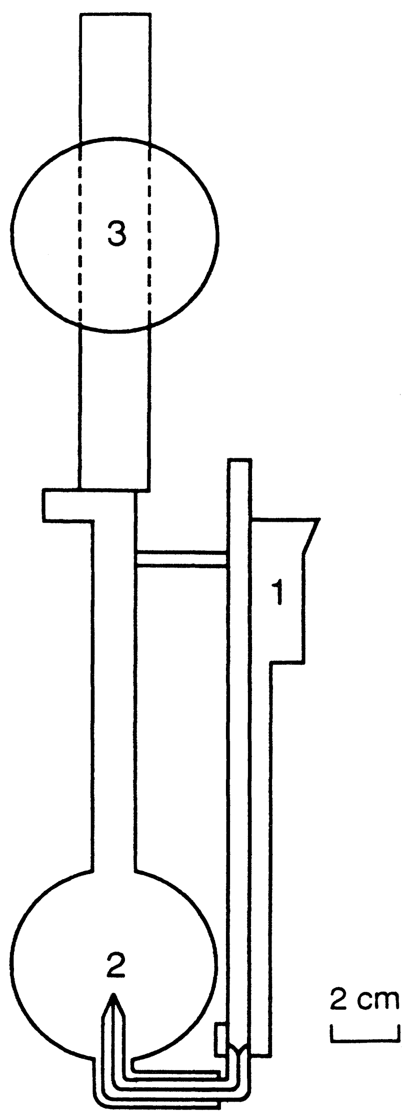

FIG. 1. Schematic diagram of growth cell. (1) Nucleation chamber. (2) Crystal growth chamber. (3) Rotating and tilting system.

Once the crystal emerges from the capillary tip, photographs of dendrite are taken and the time elapsed is recorded. The negative films are then used to calculate the tip radii of the basal and edge planes as a function of time by the formulas $R_1, R_2 = w^2/8l$. The width of the crystal is w at a distance l from the tip of the dendrite. The distances w and l are measured by the Microcalc-1 image analysis system made by the Ram Optical Instrument Co. In this system the image is magnified against a standard grid and is transmitted to the monitor via a microscope and a charge-coupled device (CCD) camera. The calculated values of $w^2/8l$ are found to be independent of l indicating that the shape of the tip of an ice dendrite can be approximated well by an elliptical paraboloid having an aspect ratio $A = R_2/R_1$. The errors in the measurements of V_G, R_1,andR_2 are less than 5%, 10%, and 10%, respectively.

A. Temperature control and measurement

The growth cell is kept inside a constant-temperature bath containing an ethylene glycol solution as the coolant. In order to measure the temperature of constant temperature bath, the precision thermistor (Model S-25, Serial No. 329, Thermometric Inc.), calibrated by the National Institute of Standards and Technology (NIST), is located just beside the crystal-growth chamber. The electrical resistance of the thermistor is measured indirectly with a digital nanovoltmeter (Model 181, Keithly Instruments, Inc.). The voltage is read when a steady current is passed through the thermistor from a constant current source (Model CS-1000B, Cryocal Inc.). The voltage measured by the procedure can be converted to resistance and thus the bath temperature can be obtained by using a calibration table of resistance and temperature. The temperature of the bath is controlled by a precision temperature controller (Model 123, Bayley Instrument Co.) and a portable cooling unit (Model PCC-13A-3, Blue M Electric Co.).

With these control assemblies, the bath temperature was recorded to be stable to ±2 mK for over 10 h as shown in Fig. 2. In the range of subcooling $0.2 < \Delta T < 0.35$ K, the total observation time for dendritic growth is less than 1 h during which time the constant-temperature bath can be controlled within ±1 mK.

B. Triple-point measurement and purity

The level of purity of the water in the closed growth cell was determined by measuring the triple point. Vacuum distillation together with alternate melting and freezing of the melt to eliminate dissolved air enabled us to fill

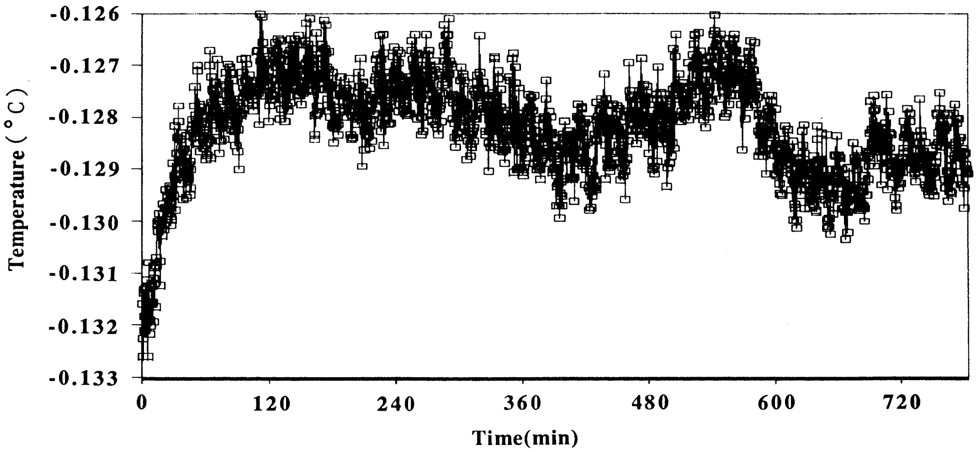

FIG. 2. Stability of constant temperature bath.

the triple-point cell [18–22] with pure water and the same procedure was used to fill the growth cell.

The triple points of our cell and the master cell, which is manufactured by Jarrett Instrument Co., were measured by using the sheath method [22,23] and they are shown in Figs. 3(a) and 3(b), respectively. The difference in the triple points between 100%-pure water and our cell was found to be less than 0.5 mK. Thus the purity level of the water in the closed cell can be estimated using the following equation:

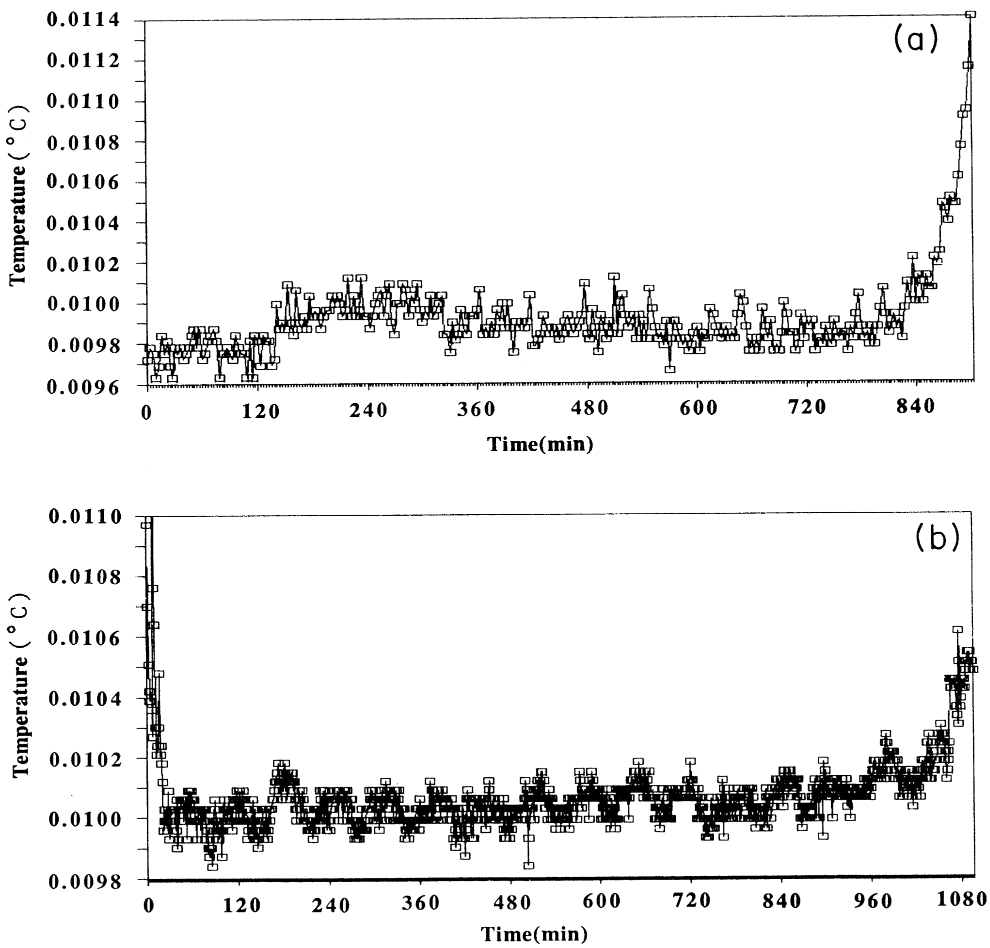

FIG. 3. Triple point of water. (a) Our cell, (b) NIST standard cell.

$$\Delta T_f = T_f - T_e = \frac{R_g T_f^2}{L} X \ , \tag{1}$$

where T_f is the triple point of pure substance, T_e the corresponding temperature for the actual sample with an infinitesimal amount of impurity, X the mole fraction of impurity, R_g the gas constant, and L the latent heat of fusion. By using Eq. (1), it is found that the purity of the water obtained by vacuum distillation followed by alternate melting and solidification is over 99.999%. In measuring the triple point of water with this cell, the pressure head will cause the temperature to be slightly lower than that for zero head because the pressure gradient dP/dT in the water is negative and of order 10^{-6} K/cm [23], which is negligible.

III. RESULTS AND DISCUSSION

We found that the tip of fully developed ice dendrites splits in the basal plane at subcoolings less than about 0.35 K. Figure 4 illustrates the growth of an ice crystal with tip splitting at a subcooling of 0.35 K. Figure 4(a) is taken 2.5 min after the crystal emerged from the capillary tip. At this subcooling the radius of curvature of the tip of the basal plane is about 120 μm. During the first 5.5 min, the ice dendrite grows in a shape preserving manner and then the tip splits as shown in Fig. 4(b). Consequently, the tip radius of the basal plane drops, as shown in Fig. 8 for several values of the undercooling, because two tips replace one. For a short time, both of the leading tips grow simultaneously. Then, one of these tips becomes dominant, while the other is retarded as a sidebranch, which eventually orients itself at an angle of about 60° to the main stem. Figure 4(c), which is taken at 8.3 min, shows that the tip again is growing steadily and has recovered its original radius. This process is repeated as illustrated in Fig. 4(d). However, it does not occur at constant time intervals. The tip radius in Fig. 4(d) is larger than that in Fig. 4(b) because the time elapsed after splitting was slightly longer. In contrast, the edge plane of the tip never splits. Figure 5 shows the edge view of the dendrite, at $\Delta T = 0.35$ K, taken during the same experiment in which the basal plane underwent tip splitting. Clearly, the radius of curvature R_1 remains independent of time and it is about 30 times smaller than that of the basal plane.

As the subcooling is decreased, the time for the tip splitting process to repeat itself increases. Figure 6 shows the photographs of the tip splitting phenomenon at $\Delta T = 0.09$ K. Figures 6(a) and 6(b) were taken at 3 min and 25 min, respectively. During this period, the ice crystal grows slowly to form a dendrite. Finally, it becomes a fully developed dendrite and then the tip becomes unstable and splits as can be seen from Figs. 6(c) and 6(d), which were taken at 1 h 32 min and 1 h 53 min, respectively.

At $\Delta T > 0.35$ K, tip splitting was never observed and the dendrites grew in a shape preserving manner. As an example, consider Fig. 7, which shows a double exposure photograph taken at $\Delta T = 0.80$ K. The first exposure is at 2 min 10 sec and the time interval is 11 sec. Thus the tip of the basal plane seems to grow with an invariant shape at $\Delta T > 0.35$ K and, at $\Delta T < 0.35$ K, the radius of basal plane R_2 changes with time due to tip splitting as shown in Fig. 8. R_2 decreases when the tip splits and then increases until it splits again. Often the tip does not split in the middle with respect to the main axis (a axis). Then the tip radius of the basal plane decreases less than shown in Fig. 4. There seems to be a unique maximum value for R_2 for a given ΔT before splitting occurs. On the other hand, the tip radius of the edge plane R_1 is observed to be independent of time after an initial transient period as can be seen clearly in Fig. 9 for subcoolings less than 0.1 K for which changes occur relatively slowly. Figure 10 shows the basal plane of the dendrite at various stages of growth at $\Delta T = 0.35$ K. These pictures are traced from a video system which records the patterns in real time as they occur in the experiments.

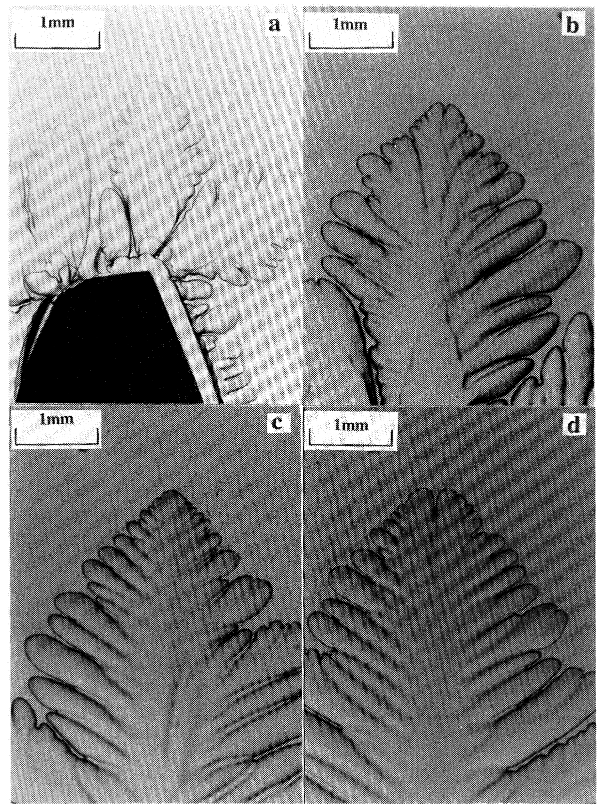

FIG. 4. Tip splitting of ice dendrite with time ($\Delta T = 0.35$ K): (a) $t = 2.5$ min; (b) $t = 5.5$ min; (c) $t = 8.3$ min; (d) $t = 10$ min.

Another interesting observation in this experiment is that the growth velocity remains constant, at fixed ΔT, even while tip splitting is occurring and the shape is changing profoundly. Figure 11 shows the growth velocity with time during tip splitting. This indicates that the growth velocity of the tip is not affected much by the morphological instability of the basal plane. This implies that overall growth kinetics of ice dendrites are governed mainly by the curvature of the edge plane because the curvature of the edge plane is much greater than the curvature of the basal plane. As mentioned earlier, we could

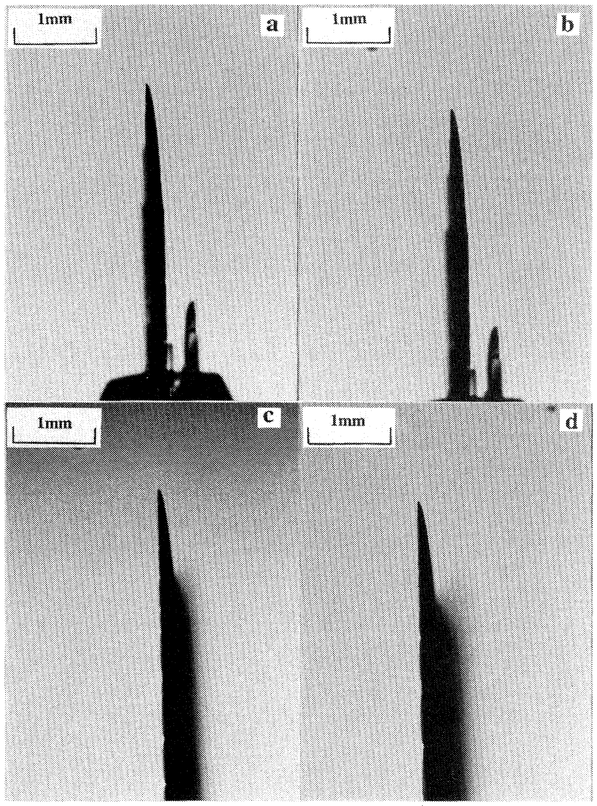

FIG. 5. Edge view of ice dendrite with time ($\Delta T = 0.35$ K): (a) $t = 4$ min; (b) $t = 5$ min; (c) $t = 11.5$ min; (d) $t = 12.5$ min.

not observe any change in the tip radius of the edge plane during tip splitting. Therefore it appears that heat transfer, which determines the rate of propagation of the dendrite, is not influenced by tip splitting.

Crystalline anisotropy arises from the orientation dependence of the surface energy and of the interfacial attachment kinetics which act simultaneously to encourage the growth of the ice dendrite along its main stem. The Gibbs-Thomson relationship for the three-dimensional case can be expressed as [24]

$$T_e = T_m - \frac{T_m}{L}\left[\gamma(\theta,\phi)(\kappa_1+\kappa_2) + \frac{\partial^2\gamma}{\partial\theta^2}\kappa_1 \frac{\partial^2\gamma}{\partial\phi^2}\kappa^2\right], \quad (2)$$

where γ is the surface energy, κ_1 and κ_2 are the principle curvature, and θ and ϕ are the orientation angles. Kessler, Koplik, and Levine [1,25], Meiron [26], Benamar and Moussallam [27], and Barbieri, Hong, and Langer [28] included the effect of fourfold anisotropy of surface energy in their models of dendritic growth and showed that $\sigma^* = (2\alpha d_0/V_G)(\kappa/2)^2 \propto \epsilon^{7/4}$ for weakly anisotropic substances such as succinonitrile. ϵ is the degree of anisotropy; α is the thermal diffusivity of the melt; κ is the curvature of dendritic tip, d_0 is the capillary length scale which is given by $d_0 = T_m \gamma c_p / L^2$, γ is the surface tension, and c_p is specific heat of the melt. These models, called microscopic solvability theory, indicate that dendrites cannot have stable growth without anisotropy. Pieters and Langer [29] showed that the solidification front becomes dendritic and decorated with a stream of sidebranches instead of being needle shaped, in response to minute temperature fluctuations, known as

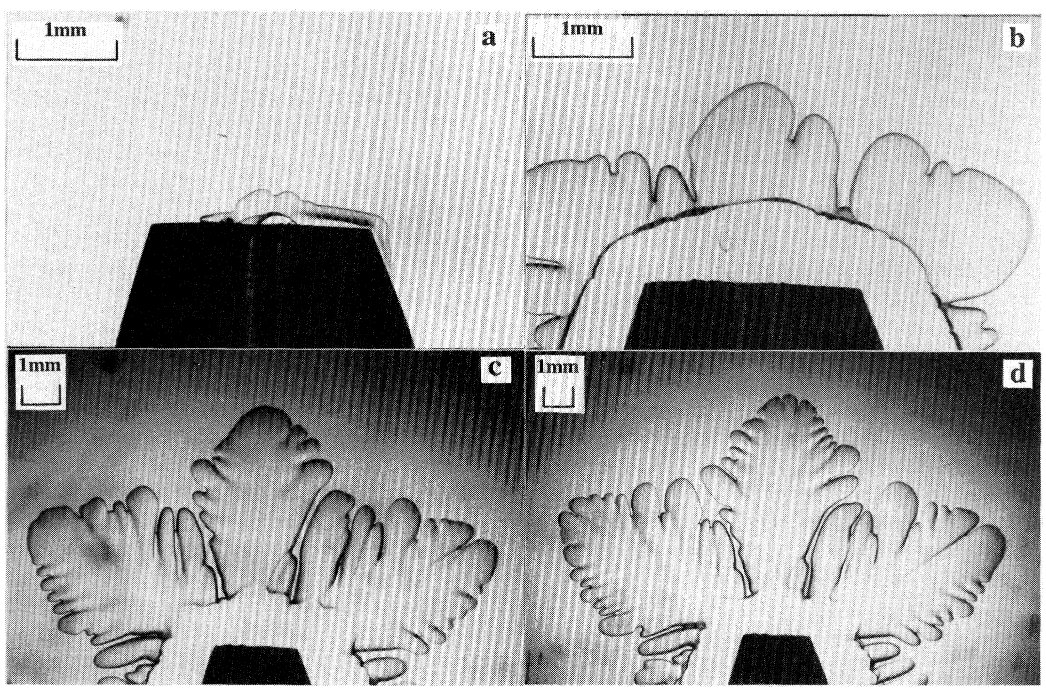

FIG. 6. Tip splitting of ice dendrite with time ($\Delta T = 0.09$ K): (a) $t = 3$ min; (b) $t = 25$ min; (c) $t = 1$ h 32 min; (d) $t = 1$ h 53 min.

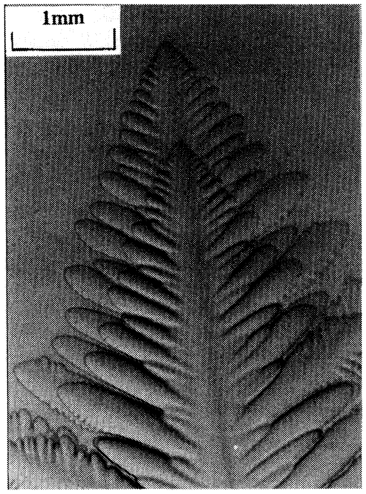

FIG. 7. Double-exposure photograph at $\Delta t = 0.80$ K ($t = 2$ min 10 sec, interval is 11 sec).

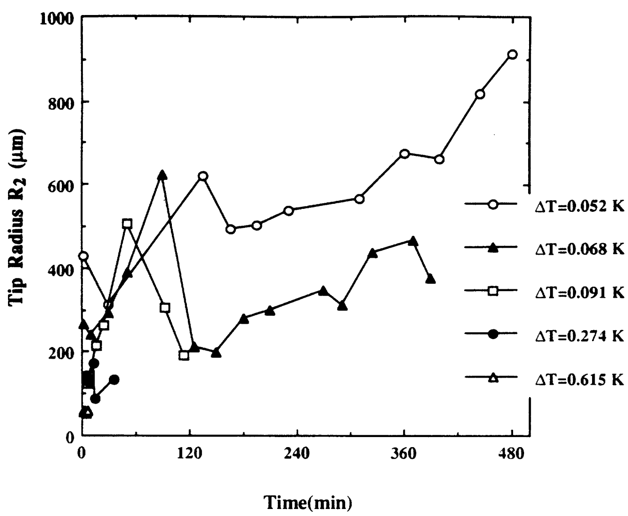

FIG. 8. Radius of curvature in basal plane R_2 with time.

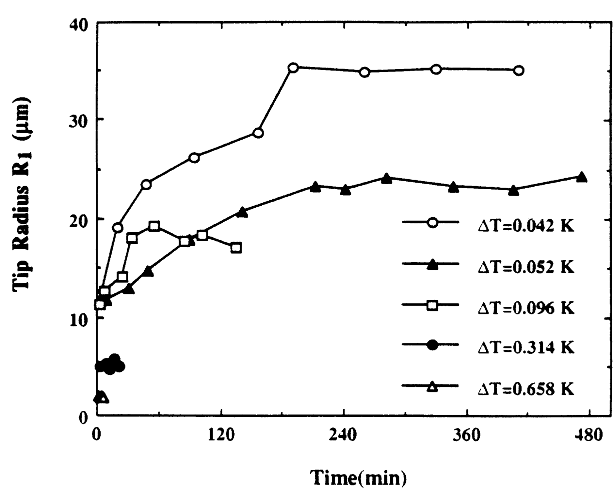

FIG. 9. Radius of curvature in edge plane R_1 with time.

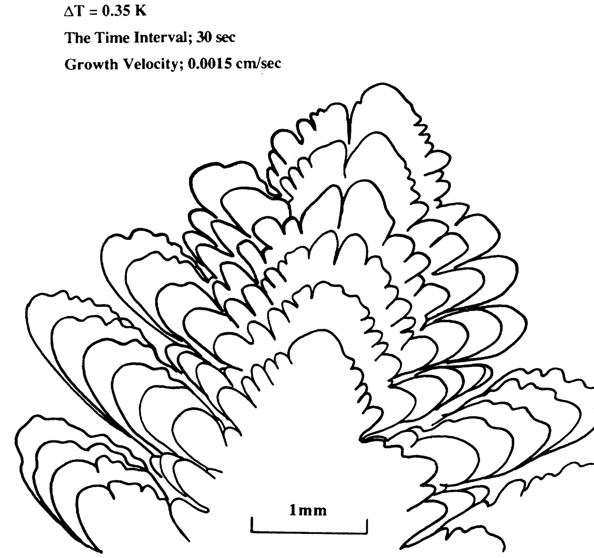

FIG. 10. Development of tip splitting morphology at $\Delta T = 0.35$ K at 30-sec time intervals.

noise, in the melt. Kessler, Koplik, and Levine [2] argued that this noise can induce tip splitting in materials that have a degree of anisotropy ϵ less than a certain critical value. Therefore we attempted here to estimate the degree of anisotropy for ice.

A measure of the anisotropy of the solid-liquid interfacial energy can be obtained from the equilibrium shape of liquid droplets which are surrounded by a solidified matrix as shown by Huang and Glicksman [7] for SCN (succinonitrile). Since the temperature on the surface of the droplet is independent of position in Eq. (2), the polar variation of surface energy leads to variation in the shape of the surface. Therefore one can obtain, from Eq. (2), the shape of the droplet in each plane as

$$r(\theta) = r_0(1 + \epsilon_m \cos m\theta) , \tag{3}$$

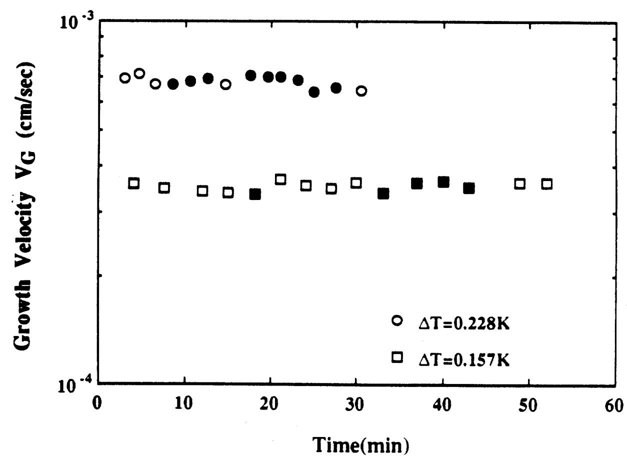

FIG. 11. Growth velocity of the dendritic tip of ice through the tip splitting event. ●■, split tip data; ○□, recovered tip data.

where r_0 is the arithmetic average of the radii of the liquid droplets at equilibrium. The degree of symmetry in the surface energy is m. For ice, $m=6$ in the basal plane and $m=2$ for the edge plane. ϵ_m is the degree of anisotropy of the material, which can be determined by the following equation:

$$\epsilon_m = \frac{r_{\max} - r_{\min}}{r_{\max} + r_{\min}} . \tag{4}$$

If the interfacial energy of a given material is isotropic, the equilibrium shape will be spherical and ϵ_m is zero. As ϵ_m increases the equilibrium shape will deform to minimize the total surface energy. We will apply Eqs. (3) and (4) independently to the basal and edge planes of the drop of water in equilibrium with ice.

The equilibrium shape of water droplets was observed in an ice matrix as shown in Figs. 12(a) and 12(b). Figures 12(a) and 12(b) show the top and side views, corresponding to the basal and edge planes, respectively. These experiments are performed by immersing the cell containing the droplets into the constant temperature bath for more than two days to achieve solid-liquid equilibrium. The photographs indicate that the shape of the basal plane is nearly circular despite its sixfold symmetry and the edge plane looks like an ellipse with twofold symmetry. Thus the three-dimensional equilibrium shape of water droplets seems to be close to a circular disk. The degree of anisotropy of the edge plane ϵ_2 was estimated by using Eq. (4) and was found to be approximately 0.3. Due to the small magnitude, we can only obtain rough estimates of ϵ_6 which vary from 0.001 to 0.003. Therefore, based on microscopic solvability theory, it seems plausible that the growth of the edge plane is morphologically stable, but that of the basal plane is unstable to small perturbations, due to the small value of ϵ_6, and undergoes splitting of the tip in response to noise, such as flow driven by gravity. It should be mentioned, however, that several aspects of the solvability theory are yet to be clarified as discussed by Xu [30]. Since capillarity depends on the mean curvature of the dendritic tip, we define the stability constant σ^* accordingly and it is shown to be independent of the Stefan number $S=\Delta T/(L/c_p)$ in Fig. 13. For subcoolings less than 0.35 K we choose the maximum value of R_2 since R_2 changes with time. Figure 13 also shows that σ^* for ice is higher than that for succinonitrile and pivalic acid as one might expect from the solvability theory.

Figure 14 shows the ratio of characteristic fluid velocity V_{nc} to the growth velocity of the ice dendrite V_G versus dimensionless subcooling. At $\Delta T<0.35$, the effect of natural convection on ice crystal growth, as indicated by the characteristic fluid velocity, becomes stronger than the apparent convection created by the moving boundary as the subcooling decreases, and it is interesting to note that the tip splitting also begins to occur at about 0.35 K. The characteristic fluid velocity was calculated by using the thermal convection analogy $Gr=Re^2$ and is given by $V_{nc}=\sqrt{g\beta\Delta T R_m}$. Gr and Re are the Grashof and Reynolds numbers, respectively, g is the gravitational constant, β is the coefficient of volumetric expansion, and R_m is the effective length scale which is taken to be $R_m=2R_1R_2/(R_1+R_2)$. The thermal convection analogy has been shown to yield reasonable estimates of natural convection for succinonitrile dendrites by Ananth and Gill [31].

It is found that the tips of dendrites growing either in water saturated with air (99.99% of purity) or in air-free, vacuum distilled water (99.999% of purity), begin to split at the same temperature, $\Delta T \approx 0.35$ K, and in the same manner. Therefore dissolved air does not play a role in tip splitting instabilities.

Recently, the tip splitting phenomenon was observed in the anisotropic Hele-Shaw fingering experiments of Ben-Jacob *et al.* [32]. They explained this phenomenon as resulting from a "mismatch" between surface tension and

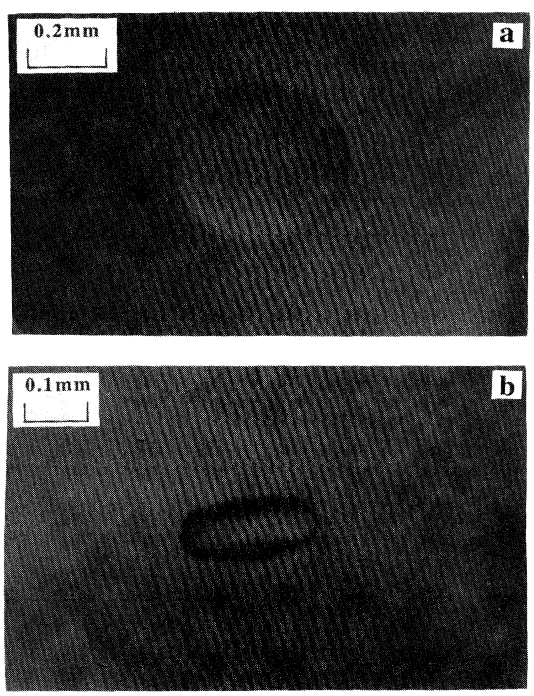

FIG. 12. Photographs of the equilibrium shape of water in the ice matrix: (a) basal plane, (b) edge plane.

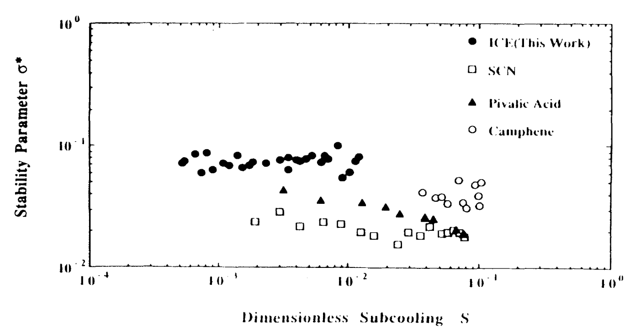

FIG. 13. Stability parameter as a function of dimensionless subcooling S; SCN [7]; pivalic acid [33]; camphene [34].

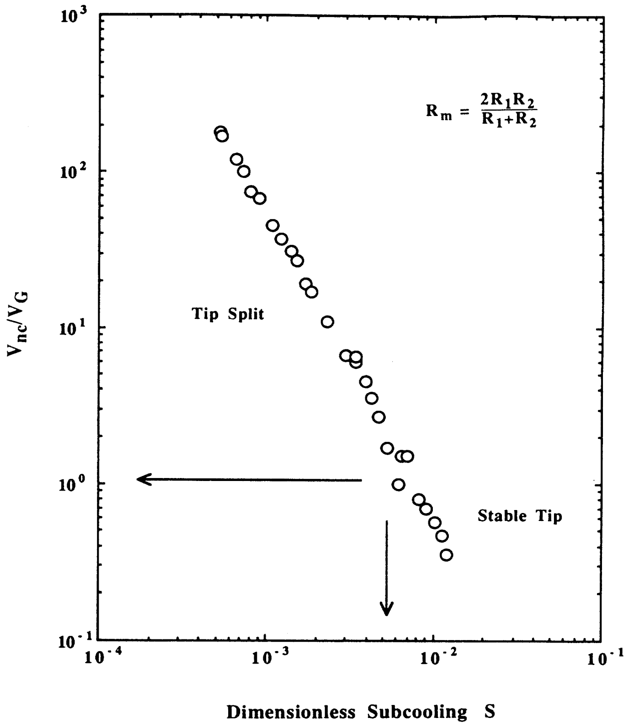

FIG. 14. Comparison of growth velocity with characteristic fluid velocity as a function of dimensionless subcooling.

kinetic anisotropies. Hele-Shaw flow with fingering is a fluid-fluid interaction which is influenced by external force field and geometry effects. In contrast, our experiments relate to a fluid-solid interface in which the crystal lattice plays an important role. Furthermore, the nature of surface attachment kinetics is not known well for the ice-water system. Therefore at the present time it is not clear that the idea of a mismatch as used by Ben-Jacob *et al.* can be applied to interpret the tip splitting of ice identities.

The growth velocity and tip radius of the basal and edge planes were measured at subcoolings of 0.035−1.0 K. As ΔT is increased, V_G increases from 2×10^{-5} to 2×10^{-2} cm/sec, while R_1 decreases from 40 to 1 μm and R_2 decreases from 1200 to 30 μm. Thus the growth Péclet number $P=V_GR_1/\alpha$ changes from 5×10^{-5} to 2×10^{-3} as ΔT increases. At these low subcoolings, convection driven by gravity is significant. Therefore the theory of Horvay and Cahn [35] underpredicts the Péclet number. A detailed discussion of the kinetic data and comparison with convection theory of Ananth and Gill [36] for the growth of an elliptical paraboloid will be discussed in a forthcoming paper.

IV. CONCLUSIONS

We have observed that tip splitting of ice dendrites occurs when the water is subcooled less than 0.35 K. Also, for water-ice the anisotropy of surface energy in the edge plane is measured to be about 30%, while that for the basal plane is small. Furthermore, natural convection becomes increasingly important as subcooling is reduced below 0.35 K. These experimental observations suggest that the splitting of the tips of ice dendrites may result from the effect of coupling between morphological instabilities created by the very weak anisotropy of the surface energy of the tip of the basal plane and convective flow, which increases the rate of heat transfer. The hexaoctyloxytriphenylene dendrite for which tip splitting has been mentioned, but not shown or discussed [9], also has a hexagonal close-packed structure like ice. However, tip splitting has not been reported for dendrites of succinonitrile, pivalic acid, or ammonium bromide (NH_4Br) in free growth, all of which have cubic structure.

ACKNOWLEDGMENTS

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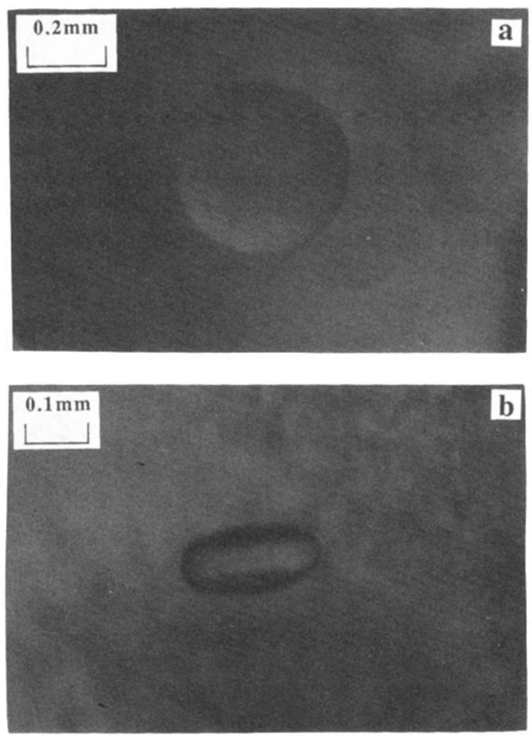

FIG. 12. Photographs of the equilibrium shape of water in the ice matrix: (a) basal plane, (b) edge plane.

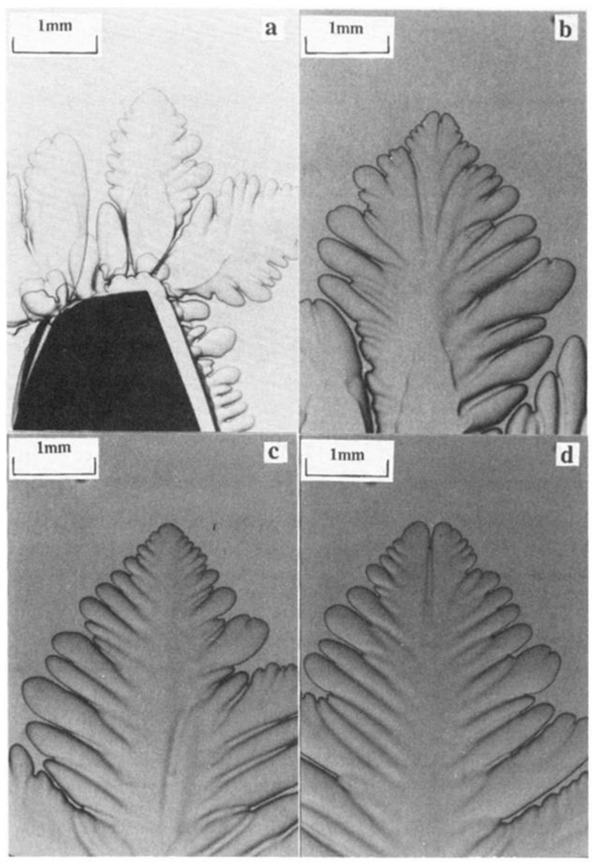

FIG. 4. Tip splitting of ice dendrite with time ($\Delta T = 0.35$ K): (a) $t = 2.5$ min; (b) $t = 5.5$ min; (c) $t = 8.3$ min; (d) $t = 10$ min.

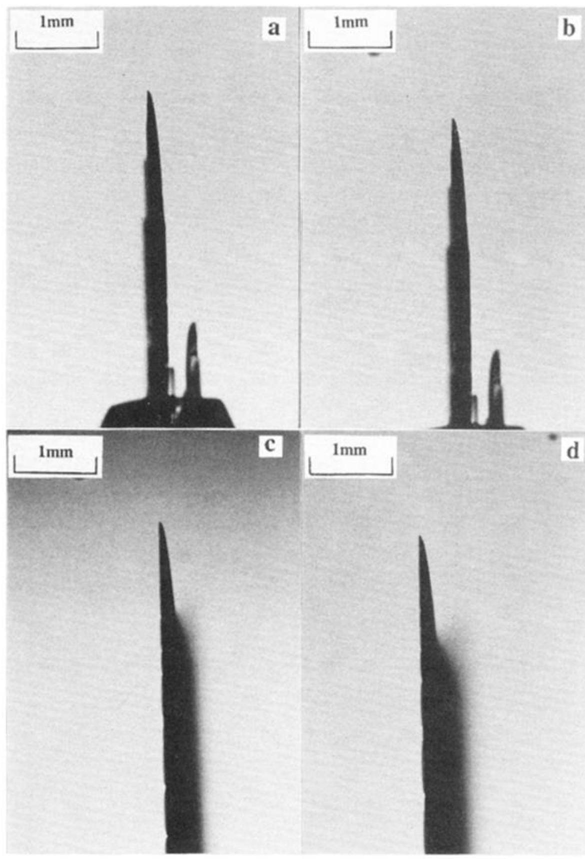

FIG. 5. Edge view of ice dendrite with time ($\Delta T = 0.35$ K): (a) $t = 4$ min; (b) $t = 5$ min; (c) $t = 11.5$ min; (d) $t = 12.5$ min.

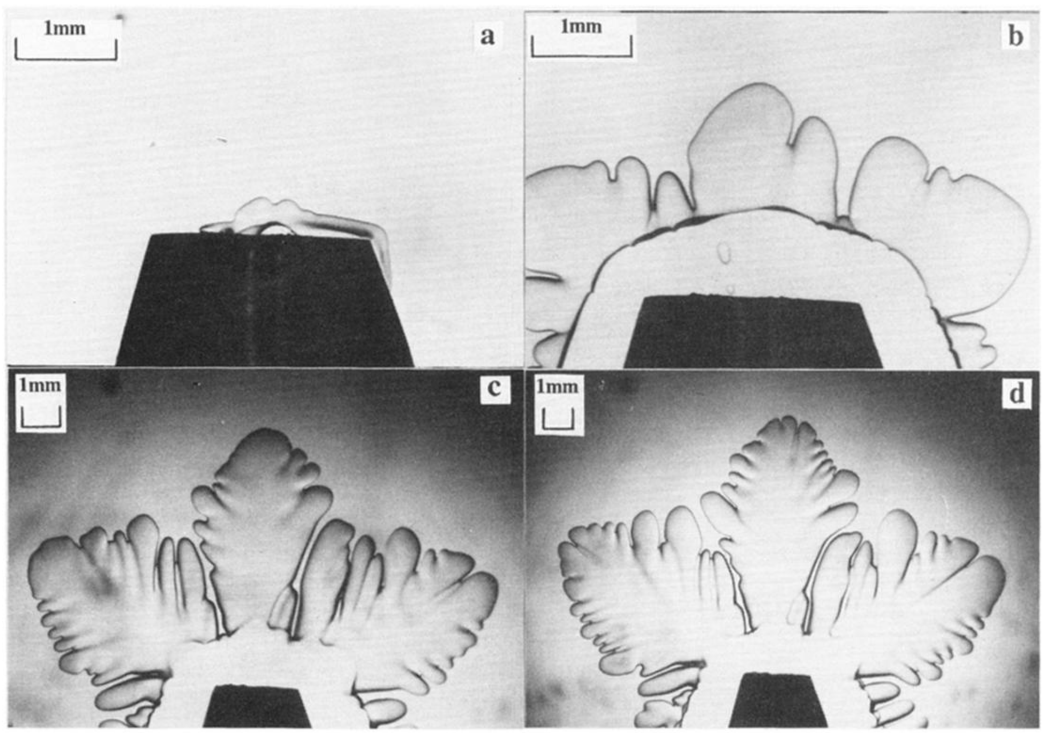

FIG. 6. Tip splitting of ice dendrite with time ($\Delta T = 0.09$ K): (a) $t = 3$ min; (b) $t = 25$ min; (c) $t = 1$ h 32 min; (d) $t = 1$ h 53 min.

FIG. 7. Double-exposure photograph at $\Delta t = 0.80$ K ($t = 2$ min 10 sec, interval is 11 sec).