Roughening Transition Observed on the Prism Facet of Ice

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Single crystals of ice are grown from vapor, and viewed by means of an interference microscope. The basal facet persists until melting, but the prism facet disappears above about $-2\,^\circ\mathrm{C}$, the surface taking a dome shape. With the temperature dropping from near $0\,^\circ\mathrm{C}$, a facet reappears at $-1.35\,^\circ\mathrm{C}$. The measured curvature just above the transition is consistent with the prediction of a "universal curvature jump" by Jayaprakash, Saam, and Teitel. The surface curvature near the facet edge is also measured.

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Roughening transitions are a matter of current interest, both for their relevance to equilibrium crystal shapes [1] and for applications to surface chemistry and catalysis. One of the most intriguing predictions of roughening theory is that of the "universal curvature jump," [2] the conjecture that the crystal shape at the center of a facet changes discontinuously from flat (radius of curvature infinity) to round (finite radius of curvature) at the roughening temperature T_R appropriate to that orientation. Unfortunately, the phenomenon has been difficult to observe due to experimental challenges of obtaining equilibrium shapes. Furthermore, for finite-sized crystals the facets may disappear from view below T_R, in that their lateral extent simply shrinks below resolvable size.

So far, crystals of solid He have provided the most fruitful system for the study of the roughening transition and its relation to equilibrium crystal shape [3]. Access to the latter is provided by the bath of superfluid He in which samples are prepared. A curvature jump consistent with the theory was found by Wolf *et al.* [4] on the *c* facet. Heyraud and Métois have studied small crystals of Au [5], NaCl [6], Pb [7], and In [8]. They clearly observed a large fraction of rounded surface in familiar materials at elevated temperatures. In the latter two materials they also observed the appearance of various distinct facets in growth shapes at progressively lower temperatures [9]. Closest to the respective melting points, only the lowest-order facets remained. Recently, Maruyama has observed small crystals of Xe and Kr growing in a completely rounded shape with temperature above $T\sim0.8T_M$, consistent with the disappearance of low-order facets above a roughening transition [10].

This Letter describes the observation of a curvature jump consistent with thermodynamic roughening on the prism facet of ordinary H_2O ice. Ice possesses a number of advantages in the study of crystal shapes: an easily accessible temperature range, high vapor pressure, and high scientific interest due to its important atmospheric functions. Most studies of ice have concentrated on dendritic shapes, such as snowflakes. Colbeck has worked on ice crystals grown extremely slowly, and found evidence for disappearance of facets below the melting temperature [11]. Unfortunately (for the current purposes), his experiments were conducted in the presence of a full atmosphere of air, which impeded diffusion through the vapor, and consequently the relaxation of growth forms to equilibrium shapes by that mechanism.

For this work, single crystals of ice were prepared *in situ* from vapor, following loosely the method of Beckmann [12]. A copper chamber is evacuated by a LN2-trapped mechanical pump, cooled to $T\sim-10\,^\circ\mathrm{C}$, and then exposed to a flask of degassed, deionized water at room temperature. Water vapor transfers into the chamber, lining the walls with a layer of ice which ensures a large vapor reservoir of uniform temperature. Near the center of the chamber is an independently cooled sample stage exposing a surface of cleaved mica. Both the chamber and sample stage cooling are provided by thermoelectric junctions. Temperature is determined by a thermistor underneath the substrate, calibrated by measurements of the vapor pressure in the chamber. To nucleate a sample, the stage is cooled, and the chamber walls warmed slightly in order to overcome the nucleation barrier. Even at these low temperatures, the first depositions are always supercooled water. When ice does form, it is as a coarse polycrystalline film. By repeatedly evaporating and recondensing, a single seed may be isolated which, with luck, displays an orientation where a facet lies parallel to the substrate. Crystalline orientation is determined by the growth shapes of small seeds, as shown in Fig. 1.

Focused on the sample stage is an interference microscope. It is of a Linnik type [13], forming Newton's rings by interference between the sample and a distant reference mirror. Straight, parallel "wedge" fringes are generated by a flat surface; a spherical surface produces concentric "bulls-eye" fringes. The field of view is 1.80

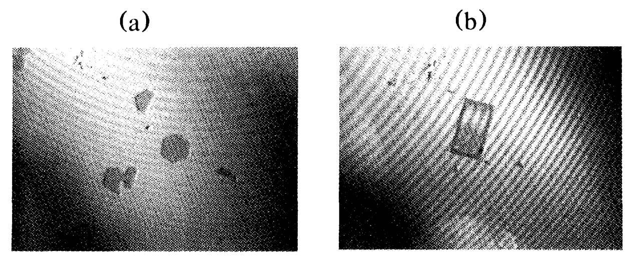

FIG. 1. Seeds of small growing ice crystals. (a) Hexagonal, basal orientation; surrounded by others of random orientation. (b) Rectangular, prism orientation.

$\times 1.35$ mm, and one fringe represents a height change (relative to the reference mirror) of $\lambda/2=2947$ Å. The images are captured by video camera and recorded on a commercial VCR.

After isolating a single seed, it is grown over a period of several days. Crystals can be held for many weeks with no obvious change in shape. The microscope focus is readjusted to form fringes on the image of the facet. The overall crystal shape can be observed through a window in the chamber, but is not directly measurable due to the limited field of the microscope. The area of interest here is the center portion at the very top of the crystal, where the interference microscope provides sensitivity to changes in the surface morphology.

Growth of ice crystals at low temperatures ($T \sim -9\,^\circ$C) confirms many of the observations now familiar from the He and metal crystallite studies. Most of the surface in the equilibrium shape is rounded, i.e., already roughened in those orientations. Facets form a small portion of the total surface area. Their size is exaggerated dynamically by growth due to the high concentration of steps in the vicinal orientations, and diminished by sublimation. Small crystals growing fast become completely faceted, displaying hexagonal (basal) or rectangular (prism) shapes.

On samples nucleated with the basal plane exposed, the "low-temperature" growth behavior persists up to the triple point. Figure 2 shows such a crystal at a temperature of $-0.3\,^\circ$C. The persistence of the facet indicates that the roughening temperature is not reached for this orientation before bulk melting destroys the crystal.

By contrast, the prism facet exposed on the crystal produced from the seed shown in Fig. 1(b) grew in two distinctly different modes as the temperature rose toward melting. Below $\sim -3\,^\circ$C, the behavior of this facet was similar to that of the basal facet. By $\sim -2\,^\circ$C, however, the facet began to round over, gradually losing both the extent of its flat area and the edge which defined it. The crystal was kept slowly growing throughout the observation in order to accentuate any microscopic facet which might exist. It was impossible to find precisely the temperature at which this flat-to-round transition took place. Lowering the temperature, however, a round-to-flat transition was found at $-1.35\,^\circ$C. Interferograms and deduced surface profiles from the most careful run are shown in Fig. 3. At $-1.2\,^\circ$C the shape was that of a smooth dome. Figure 3(b) shows an interferogram of the surface, with the fringes centered near the peak of the dome. In Fig. 3(c) the fringes are displaced, by tilting the microscope reference mirror, to show more clearly that no flat region exists at the dome peak. At $-1.35\,^\circ$C a flat spot appeared, indicated by the spread of the region of uniform grey scale in Fig. 3(e) (fringes centered), and the straightening of the fringes near the center in Fig. 3(f) (fringes displaced). As the temperature was lowered further, the crystal recovered the broad flat facet it had previously [Fig. 3(h)]. This process of disappearance and reappearance of the facet was repeatable on this crystal, with no apparent change in the transition temperature.

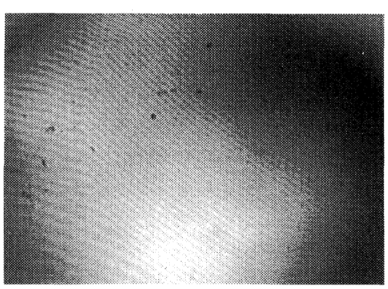

FIG. 2. Facet spreading across the surface of a growing, basal-oriented crystal, $T=-0.3\,^\circ$C.

The interference patterns in Fig. 3 provide considerable quantitative information. During these measurements the sample was growing at a rate of ~ 50 Å/sec. (Well below T_R such a growth rate did have a significant effect on the crystal shape, spreading the facet and sharpening its edge. Above $\sim -2\,^\circ$C the shape seemed to lose its dependence on growth rate.) First, the radius of curvature may be obtained from Figs. 3(a) and 3(b), above the transition. The thickness was measured independently, by focusing through the crystal onto the mica substrate, and was found to be 3.5 mm. A height change of $3\pm\frac{1}{4}$ fringes over a radius of 0.5 mm indicates a radius of curvature of 140 ± 12 mm. Jayaprakash, Saam, and Teitel make a specific prediction for the ratio of the crystal thickness (i.e., the distance from the center of the crystal to the center of the facet) to the radius of curvature at the surface [2]:

$$z_0/R_c=(2/\pi)f_0 d^2/k_B T\,.$$

According to the data $f_0=109$ ergs/cm^2 [14], $d=a_0\sin 60°$, $a_0=4.52$ Å [15], $T_c=272$ K, and $z_0=3.5$ mm, we get $R_c=124$ mm. The measurement exceeds the theoretical prediction by 13%.

Another prediction of roughening theory concerns the shape of the facet edge below T_R. This should be governed by a Pokrovsky-Talapov exponent [16], so that the height of the surface varies as $-y\sim(x-x_0)^{3/2}$, where x_0 is the radius of the facet. Mean-field theory also indicates a power-law dependence, but with an exponent equal to 2 [17]. The surface profile displayed in Fig. 3(d) covers a small range of surface orientations, from 0° to $\sim 1.3°$ with respect to the facet, and a range in the parameter $[(x-x_0)/z_0]^{1/2}$ from 0 to 0.4. The same profile data are presented in Fig. 4 on log-log scales. A least-squares fit to the solid points gives an empirical exponent of 1.74, fitted over the entire range. The extrapolated slope is very sensitive to the placement of the $y=0$ point, representing the facet radius x_0. Also shown in Fig. 3(d) are hollow symbols, representing the choice of x_0 which would imply an exponent of 1.5 (squares), or 2 (circles). The effect on the log-log plot is

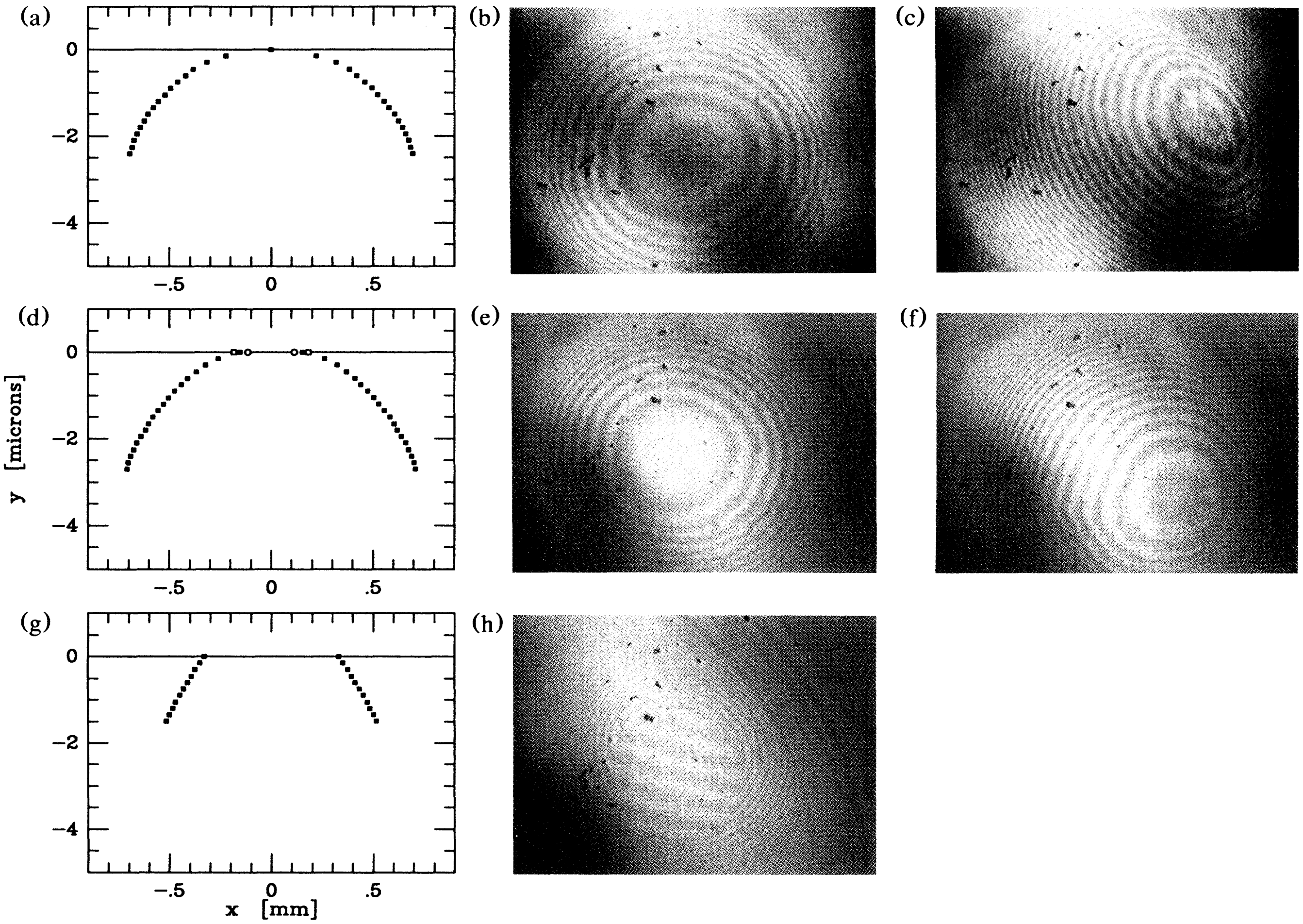

FIG. 3. (a),(d),(g) Profiles deduced from measurements of fringes in (b),(e),(h). Hollow symbols in (d) are explained in the text. The horizontal scale is maintained throughout. The apparent vertical scale is magnified 300 times. (b) Prism facet has disappeared at $T=-1.2\,^{\circ}\mathrm{C}$. The a-axis orientation is still vertical. (c) Tilting the interferometer reference mirror, there is no break in the slope to indicate a facet. (e) Lowering the temperature to $T=-1.35\,^{\circ}\mathrm{C}$, the facet reappears. (f) Now tilting the mirror, the change in slope is apparent. (h) The facet at $T=-2.8\,^{\circ}\mathrm{C}$.

shown by the same symbols in Fig. 4. Note that the match to the smaller exponent is best for smallest x, consistent with a leading exponent of $\frac{3}{2}$, followed by a correction with exponent 2. Indeed, the angular width of the critical region where the $\frac{3}{2}$ exponent prevails should shrink to zero with decreasing T_R-T. Ideally the vicinal contour measurement would be made farther from T_R, but then the steady growth has a strong effect on the profile and the current technique is not applicable. A better determination of the critical exponent should be made in an experiment which can reach true equilibrium. The short response times of crystal shape to changes in growth drive observed during this experiment suggest that time scale to relax to equilibrium may not, in fact, be inordinately long.

A different sample in the same orientation did not undergo the rounding transition. Instead, cracks and grooves in the surface were exposed, above $T\sim-1.2\,^{\circ}\mathrm{C}$. These were oriented primarily perpendicular to the c axis, so they were probably planar faults originating at the substrate. Presumably they pinned the surface, preventing the long-wavelength fluctuations which would be responsible for rounding it at the roughening temperature. On cooling, the transition from rounded growth to the anisotropic low-temperature growth mode took place very near T_{tr}. The faults may have provided a sink for mobile steps on the surface, effectively stretching it flat, or another mechanism, adsorbed impurities being the most likely, may distinguish the behavior of the two crystals. In the case of He, small concentrations of ^{3}He have been shown to affect the roughening temperature of the c facet of ^{4}He [18].

The transition temperature measured here is in the range where one might expect surface melting, as opposed to surface roughening. The samples were prepared, in fact, for a study of melting. The unanticipated loss of

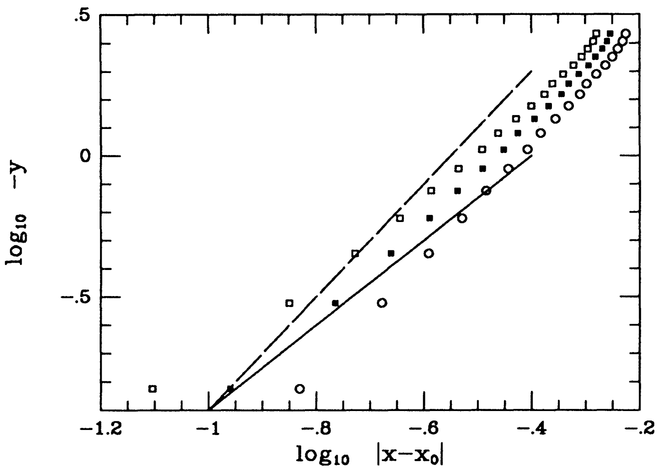

FIG. 4. Log-log plot of the profile data in Fig. 3(d). The solid line represents a slope of $\frac{3}{2}$, the dashed line a slope of 2. Hollow symbols correspond to choices of facet radius x_0 which brings a least-squares fit to one or the other of these slopes.

the facet preempted the latter work, but on approaching the triple point, droplets were observed forming on the surface, indicating that the liquid did not form a wetting film on the ice even at the triple point. Similar droplets also appeared on the basal facet.

Another interesting observation is that between the faceting and melting temperatures the height of the growing surface became unstable on the scale of the wavelength of light, forming hills and valleys in the interference image, superimposed on the smooth dome. Closer to melting, these disturbances diminished, the surface becoming smooth to the resolution of the interferometer, until the droplets formed. Lowering the temperature, the interval of instability reappeared, and again vanished before the appearance of the facet. Perhaps this is a signal of unstable growth above T_R, followed by a smoothing due to incipient, but incomplete, surface melting.

In conclusion, these observations demonstrate a roughening transition in the prism orientation of ice. Quantitative measurements are consistent with the prediction of a universal curvature jump. The shape of the critical region is suggestive of a Pokrovsky-Talapov transition. This study also indicates the usefulness of ice as a material for the study of equilibrium crystal shapes, and of the interference microscope for sensitivity to surface curvature in the region of greatest interest.

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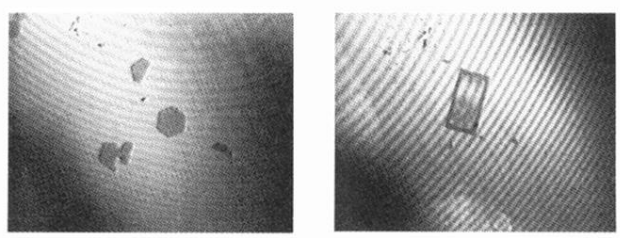
(a) (b)



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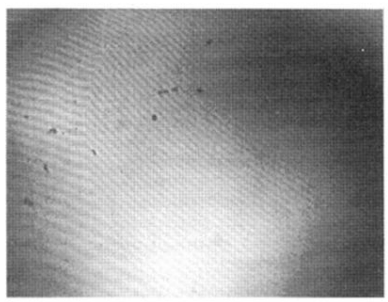
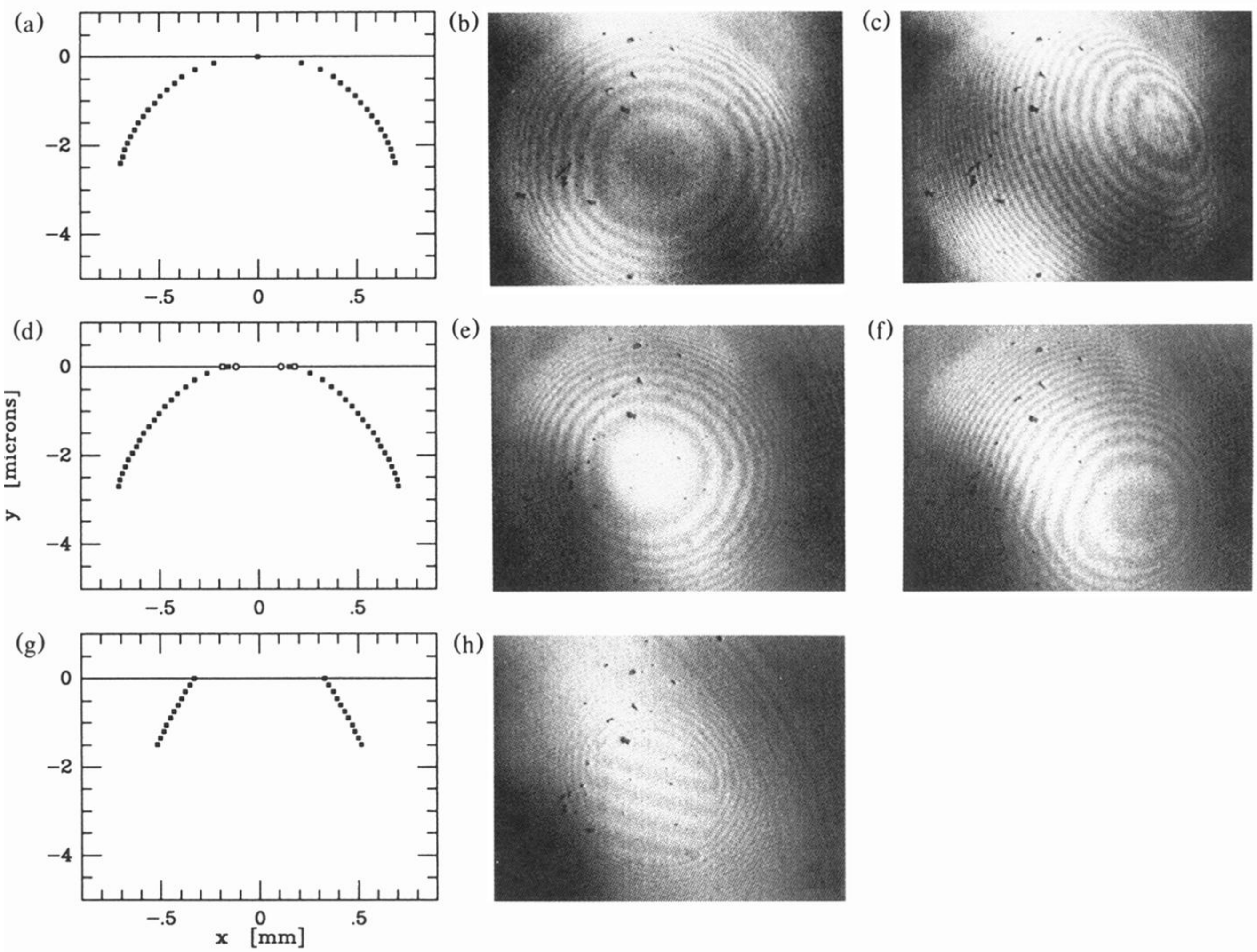


FIG. 2. Facet spreading across the surface of a growing, basal-oriented crystal, $T = -0.3\,^{\circ}\mathrm{C}$.



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