Prism and Other High-Index Faces of Ice Crystals Exhibit Two Types of Quasi-Liquid Layers

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**ABSTRACT:** Surface melting of ice significantly governs a wide variety of phenomena in nature. We recently succeeded in directly observing the surface melting on ice basal faces (Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 1052–1055) by our advanced optical microscopy, which can detect 0.37-nm-thick elementary steps on basal faces. However, the direct observation of surface melting on the other prism and high-index faces remains an experimental challenge. To fully obtain a comprehensive understanding, we need to examine the surface melting on these faces. Here we show the appearance of two types of quasi-liquid layers (QLLs) on prism and high-index faces just below the melting point. We quickly raised the temperature of ice crystals and then observed prism and high-index faces during a roughening process. We found that with increasing temperature, round liquid-like droplets ($\alpha$-QLLs) first appeared at temperatures higher than $-1.4$ to $-0.5$ °C, and then thin liquid-like layers ($\beta$-QLLs) also appeared at temperatures higher than $-0.8$ to $0.3$ °C, as in the case of basal faces. This result demonstrates that the presence of two types of QLL phases with different morphologies plays an intrinsically important role in the surface melting of ice crystals, irrespective of face indexes. We also revealed that the roughening process was caused thermally.

1. **INTRODUCTION**

Ice is one of the most abundant materials on the earth, and hence its phase transition is closely related to various fields. Surface melting of ice crystals governs surface properties of ice just below the melting point. Then, it is well-known that the surface melting of ice affects a wide variety of phenomena such as the generation of thunder,\textsuperscript{1,2} regulation,\textsuperscript{3–4} frost heave,\textsuperscript{7,5} the conservation of foods, ice-skating,\textsuperscript{5,3,6} the preparation of a snow man,\textsuperscript{3} in addition to crystal growth of ice crystals.\textsuperscript{2,7} Therefore, it is crucial to understand the surface melting of ice crystals.

The surface melting of ice crystals just below the melting point forms the liquid called “quasi-liquid layers” (QLLs) on ice crystals. After Faraday first proposed the existence of QLLs in 1842, many studies confirmed the formation of QLLs by various methods such as ellipsometry,\textsuperscript{8} optical reflectometry,\textsuperscript{9} nuclear magnetic resonance,\textsuperscript{10,11} glancing angle X-ray scattering,\textsuperscript{12,13} sum-frequency vibrational spectroscopy,\textsuperscript{14,15} and atomic force microscopy.\textsuperscript{16–18} All of these measurements reported that thickness of QLLs significantly increased with increasing temperature. To obtain further understanding of dynamic behaviors of QLLs, it is essential to directly visualize ice crystal surfaces at the molecular level under atmospheric pressure.

We and Olympus Engineering Co., Ltd. have developed laser confocal microscopy combined with differential interference contrast microscopy (LCM–DIM)\textsuperscript{19} which can visualize individual elementary steps (0.37 nm in thickness) on ice basal faces.\textsuperscript{20,21} Then we succeeded in observing the appearance of two types of QLLs with different morphologies (drop and thin-layer shapes) on ice basal faces: round liquid-like drops and thin liquid-like layers were named $\alpha$- and $\beta$-QLL phases, respectively.\textsuperscript{22} This result on ice basal faces demonstrates that the conventional picture of surface melting needs crucial corrections, since it has been thought that one QLL phase appears uniformly on ice crystal surfaces.

In contrast, on prism and other high-index faces of ice crystals, how does surface melting proceed? Several studies have reported that on prism faces, surface melting occurs at lower temperature than on basal faces.\textsuperscript{7,8,23} Prism faces show a roughening transition at about $-2$ °C, and then high-index faces appear at temperatures higher than $-2$ °C. However, so far there exists no molecular-level visualization study on these faces. Hence, to fully obtain a comprehensive understanding of surface melting of ice crystals, we need to directly observe surface melting on prism and other high-index faces by LCM-DIM.

However, after once high-index faces were formed by the roughening transition of prism faces, the molecular-level visualization of surface morphologies by LCM-DIM becomes difficult, since such high-index faces show a macroscopically round shape. Then we focused our attention on the fact that the surface melting is a relatively fast phenomenon: QLLs of several nanometers to several tens of nanometers in thickness were formed within several tens of seconds on basal faces.\textsuperscript{21,22}
We expected that we can observe surface melting on prism and high-index faces before ice crystals become fully rounded. Then we quickly raised the temperature of a sample ice crystal, and attempted to observe prism and high-index faces during the roughening process by LCM-DIM.

2. EXPERIMENTAL METHOD

A confocal system (FV300, Olympus Optical Co. Ltd.) was attached to an inverted optical microscope (IX70, Olympus Optical Co. Ltd.), as explained in our recent studies. A super luminescent diode (Amonics Ltd., model ASLD68-050-B-FA: 680 nm) was used for the LCM-DIM observations. The LCM-DIM system (Figure S1A) used in this study included all of the improvements reported in our recent study for the observation of elementary steps on ice crystal surfaces.

An observation chamber had upper and lower Cu plates, whose temperatures $T_{\text{sample}}$ and $T_{\text{source}}$ were separately controlled using Peltier elements (Figure S1B). At the center of the upper Cu plate, a cleaved AgI crystal (a kind gift from emeritus professor G. Layton of Northern Arizona University), known as an ice nucleating agent, was attached using heat grease. Temperatures of the upper and lower Cu plates were first set at $T_{\text{sample}} = 20.0$ and $T_{\text{source}} = -15.0 \degree C$, respectively. Water vapor was then supplied to the inside of the chamber by nitrogen gas bubbled through water (flow rate: 500 mL/min). Ice crystals were grown on the lower Cu plate for 1 h; these ice crystals were used as a source of water vapor in the subsequent process. Then, the water–vapor supply was stopped, and the chamber was kept airtight. The temperatures of the upper and lower Cu plates were then kept at $T_{\text{sample}} = -15.0$ and $T_{\text{source}} = -13.0 \degree C$, respectively. Then the ice crystals grown on the lower Cu plate were evaporated, and water vapor was supplied to the cleaved AgI crystals. The majority of ice crystals grown on the upper Cu plate showed basal faces perpendicular to the optical axis because of heteroepitaxial growth (inset of Figure S1B). However, a small number of ice crystals were randomly nucleated and grown with their prism faces perpendicular to the optical axis. The surfaces of such prism faces were observed by LCM-DIM. Note that the prism faces of the sample ice crystals thus obtained did not include strain caused by the lattice mismatch during the heteroepitaxial growth on the AgI crystals. By separately controlling $T_{\text{sample}}$ and $T_{\text{source}}$, the growth temperature of the sample ice crystals and the supersaturation of the water vapor were adjusted independently. Other details of the observation chamber, such as the calibration of $T_{\text{sample}}$ and the evaluation of supersaturation $\sigma = (P - P_0)/P_0$ (here $P$ is the water vapor pressure in the observation chamber, and $P_0$ is the solid–vapor equilibrium pressure) were reported in our recent study.

3. RESULTS AND DISCUSSION

The roughening of prism faces and the subsequent appearance of macroscopically round crystal surfaces composed of high-index faces become an obstacle to the molecular-level observation on ice crystal surfaces, as explained in the Introduction. Hence, we first observed the roughening process of prism faces directly, and then examined the time scale on which the rounding of crystal surfaces started to affect the molecular-level surface observation.

Figure 1A shows the surface morphology of a prism face observed at $T_{\text{sample}} = -4.4 \degree C$ under a supersaturated condition. As explained in our previous paper, the differential interference contrast of all LCM-DIM images shown in this study was adjusted as if an ice crystal surface was illuminated by a light beam slanted from the upper-left to the lower-right direction. To obtain this image, a raw LCM-DIM image was processed according to the method explained in Figure S2 of the Supporting Information. A black arrowhead presents an elementary step of 0.39 nm in thickness. Concentric elementary steps repeatedly emerged from the positions marked by cross marks in Figure 1A. All elementary steps laterally advanced in the lower-right direction (a black arrow). These results show that at temperatures lower than $T_{\text{sample}} = -4.4 \degree C$, prism faces are flat at the molecular level, showing the terrace–step–kink structure.

In contrast, when we raised $T_{\text{sample}}$ to a temperature higher than the roughening transition temperature $T_{\text{rough}}$, which was about $-4$ to $-2 \degree C$ in this study, the surface morphology of the prism face was changed significantly. Several tens of seconds after $T_{\text{sample}}$ became higher than $T_{\text{rough}}$, distances between adjacent elementary steps decreased significantly (Figure 1B). Then the contrast of elementary steps on the prism face disappeared. We could observe the beginning of the rounding of the crystal surface at the molecular level, as the slight decrease in the brightness of prism faces from their peripheries. The sample surface gradually looked dark (Figure 1C), and finally we could rarely see reflected light from the sample surface (Figure 1D). Then we could not observe the surface morphology at the molecular level anymore. These results demonstrate that due to the roughening transition, the facets of prism faces disappeared, and then high-index faces appeared. In our similar observations, the time periods, after which the molecular-level surface observations became impossible, were 15 min to 7 h, depending on the rates of temperature increase and finally achieving temperatures.

Furukawa and Elbaum reported that the rounding of prism faces is due to thermal roughening, which proceeds even under equilibrium conditions. In contrast, Sei and Gonda reported that the roughening is due to kinetic roughening which occurs when the chemical potential difference between an ice crystal and water vapor is larger than a certain critical
value. In this paper, we could observe the roughening process, when we reduced the chemical potential difference (Figure 1) by increasing $T_{\text{sample}}$ (keeping $P$ constant). Hence, we concluded that the roughening of prism faces proceeds thermally. The decrease in the distances between adjacent elementary steps (Figure 1B) corresponded to the decrease in step ledge free energy of elementary steps with increasing $T_{\text{sample}}$.

Next we tried to investigate the time scale of surface melting on prism and high-index faces, to verify whether we can observe surface melting before the macroscopic rounding due to the roughening transition. We quickly raised $T_{\text{sample}}$ to temperatures just below the melting point, and then observed the prism and high-index faces during the roughening transition.

Figure 2 shows a surface morphology of prism and high-index faces after we raised $T_{\text{sample}}$ from $-2.9$ to $-0.9$ °C at a rate of 0.4 °C/min (for 5 min). This rate was 20 times faster than that (0.02 °C/min) applied to basal faces in our previous study. Black contrast appearing on the sample surface shows that the surface became slightly rounded. In addition, note that hemispherical objects with a diameter of about 3 μm appeared (a white arrowhead). The upper-left and lower-right sides of the hemispherical objects look brighter and darker, respectively. These differential interference contrasts of the hemispherical objects demonstrate that the hemispherical objects were convex and bulged from the ice crystal surface.

To examine whether the hemispherical objects were solids or liquid, we further observed the hemispherical objects in detail. As shown in Figure 3 and Movie 1: The coalescence of round liquid-like droplets ($\alpha$-QLLs) on prism and high-index faces, we could observe the coalescence of adjacent hemispherical objects. During the coalescence, two hemispherical objects (white arrowheads) were deformed just like “liquid droplets” (Figure 3B and C). Then, finally, one hemisphere object was formed (Figure 3D) due to its interfacial free energy. These results clearly demonstrate that the hemispherical objects were liquid that appeared just below the melting point. Therefore, we concluded that the hemispherical objects correspond to the round liquid-like droplets ($\alpha$-QLLs), which were found on ice basal faces in our previous study. From the observations shown in Figures 1–3, we can also conclude that the appearance of $\alpha$-QLL phases on prism and high-index faces is significantly faster than the rounding process of prism faces by the roughening transition. We could reproducibly observe the appearance of $\alpha$-QLL phases at temperatures higher than $-1.4$ to $-0.5$ °C.

To explore what would happen at temperatures higher than those adopted in Figures 1–3, we raised $T_{\text{sample}}$ further, and observed prism and high-index faces by LCM-DIM. Figure 4 and Movie 2: The appearance of thin liquid-like layers ($\beta$-QLLs) beneath $\alpha$-QLLs.
and high-index faces after we raised \( T_{\text{sample}} \) from \(-2.9 \) to \(-0.4 \) °C at a rate of \( 0.5 \) °C/min (for 5 min). As shown in Figure 4A, thinly layered objects (half-black/white arrowheads) spontaneously appeared beneath \( \alpha \)-QLL phases (a white arrowhead). To easily distinguish the thinly layered objects, outlines of individual thinly layered objects shown in Figure 4A were marked by solid lines in Figure 4B. Dashed lines in Figure 4B show the positions where the contrasts of the thinly layered objects disappeared due to the macroscopically round shape of the ice crystal surfaces. Figures 4C and D were taken 16.1 and 32.2 s after Figures 4A and B, respectively. As shown in Figure 4 and Movie 2: The appearance of thin liquid-like layers (\( \beta \)-QLLs) beneath \( \alpha \)-QLLs, \( \alpha \)-QLL phases and the thinly layered objects gradually became smaller and larger, respectively.

Finally, the sample ice surface was completely covered with the thinly layered objects.

To examine whether these thinly layered objects were solids or liquid, we further in situ observed the coalescence of adjacent thinly layered objects. As shown in Figure 5 and Movie 3: The coalescence of \( \beta \)-QLLs on prism and high-index faces, two adjacent thinly layered objects (half-black/white arrowheads) coalesced with each other, showing significant fluidity.

As explained above, we found, for the first time, that on prism and high-index faces of ice crystals, two types of QLL phases (\( \alpha \)- and \( \beta \)-QLL phases) with drop and thinly layered shapes appear spontaneously, as on basal faces. In Figure 6, we summarized the results obtained on prism and high-index faces in this study, and those obtained on basal faces in our previous paper.22

\( T_{\text{rough}} \) and the appearance temperatures of \( \alpha \)- and \( \beta \)-QLL phases exhibited relatively wide dispersion (Figure 6A). The roughening transition and the appearances of \( \alpha \)- and \( \beta \)-QLL phases occurred at temperatures higher than \(-4 \) °C, \(-1.4 \) °C, and \(-0.3 \) °C, respectively. The temperature range of the appearance of \( \alpha \)-QLL phases appears to overlap with that of \( \beta \)-QLL phases. However, during one experiment, with increasing temperature \( \beta \)-QLL phases always appeared at higher temperature than \( \alpha \)-QLL phases.

At temperatures lower than \( T_{\text{rough}} \) (\(-2 \) to \(-4 \) °C), the prism faces observed in this study were flat at the molecular level, and no QLL phase appeared. In contrast, many studies29–31 so far have reported that surface melting occurred at much...
lower temperature (e.g., −40 to −30 °C). One possible explanation for this discrepancy is the effects of strain. Our previous study revealed that strain caused by lattice defects, such as dislocations and microdefects, significantly induces the appearance of α- and β-QLL phases. Therefore, we expected that the ice single crystals grown in our studies included much less strain than those grown in other previous studies.

In addition, Figure 6 demonstrates that the appearance temperatures of the α- and β-QLLs on the prism and high-index faces (A) were similar to those on basal faces (B). In contrast, many studies reported that on prism faces, surface melting occurs at lower temperature than on basal faces. At this moment, we have no experimental evidence that explains this discrepancy in the temperature ranges of surface melting. One hypothetical explanation for this discrepancy is also based on the effects of strain. The ice crystals used for the observation of basal faces were heteroepitaxially grown on the AgI substrates, possessing strain caused by the lattice misfit (1.5%). In contrast, the ice crystals used for the observation of the prism faces were randomly grown, being free from the heteroepitaxial strain. Therefore, we expected that the smaller amount of strain in the crystals for the prism-face observation exhibited a higher temperature of surface melting, resulting in the similar temperature ranges of the surface melting on the basal and prism faces.

To reveal the relation between the appearance of QLLs and strain caused by defects on ice crystal surfaces, we need to examine whether dislocations and microdefects on prism and high-index faces also induce the appearance of two QLL phases as in the case of basal faces. On basal faces, α-QLLs reproducibly appeared on the positions at which screw dislocations were located. However, on prism and high-index faces, such observation was technically very difficult because of the following reason. On prism faces, screw dislocations were always located at edges of ice crystals (Figure 1), as on basal faces (the reason is still unclear). But after the rounding (roughening) process started, edges of prism faces were the first to become rounded and hence quickly appeared black (Figure 2). Therefore, on the edges of prism and high-index faces, due to their quick blackening, it was unacceptable to observe the appearance of α-QLLs. In addition, on basal faces, β-QLLs appeared from the surface beneath which microdefects were embedded. However, on prism and high-index faces, we could not so far reveal such a relation. This issue will become an important challenge in the future.

In this study, we tried to measure the thicknesses of the two QLL phases on prism and high-index faces. However, we could not succeed in measuring them for the following reasons. In the case of basal faces, they do not show the thermal roughening, and they are flat at the molecular level up to their melting point. Hence, we could wait until α-QLLs become large enough (several 10–100 μm in diameter) to measure their three-dimensional (3D) profile using interference fringes. However, in the case of prism and high-index faces, the diameters of α-QLLs observed in this study reached only 3 μm (Figure 2), probably because we needed to measure α-QLLs before ice crystals became fully rounded. Therefore, because of the small size of α-QLLs, we could not measure their 3D profile using interference fringes. In contrast, β-QLLs became large enough to measure their 3D profile using interference fringes: prism and high-index faces were covered with β-QLLs. However, the thickness of β-QLLs was smaller than the detection limit of interferometry (≤several tens of nanometers). Since the differential interference contrast of β-QLLs was significantly higher than that of an elementary step, we expected that the thickness of β-QLLs was about one to several tens nanometers.

As summarized in Figure 6, we found that, irrespective of the plane indices, two types of QLL phases emerge spontaneously on ice crystal surfaces. This result demonstrates that two types of QLL phases play intrinsically important roles in the surface melting of ice crystals. To fully understand the roles of the two QLL phases, we need to directly measure physical properties of two QLL phases. Therefore, we are planning to develop a Raman spectroscope combined with LCM-DIM in the near future.

4. CONCLUSIONS

In this study, we quickly raised the temperature of the sample ice crystals, and observed the prism and high-index faces before the ice crystals became fully rounded. Then we found that on prism and other high-index faces, round liquid-like droplets and thin liquid-like layers (α- and β-QLL phases) spontaneously appear at temperatures higher than −1.4 to −0.5 °C and −0.8 to −0.3 °C, respectively. These results strongly suggest that the presence of two QLL phases plays an intrinsically important role in surface melting of ice crystals.

During the increase in the temperature of the sample ice crystals, we kept the water vapor pressure constant (reduced the chemical potential difference between the ice crystal and the water vapor), and observed the roughening processes. From this observation, we concluded that the roughening of prism faces proceeds thermally.

ASSOCIATED CONTENT

Supporting Information

Schematic drawings of the experimental setups, image processing performed to obtain LCM-DIM images, and captions for the movies. The Supporting Information is available free of charge on the ACS Publications website atDOI: 10.1021/acs.cgd.5b00438.

Web-Enhanced Features

Movies of the coalescence of the bulk liquid-like droplets (α-QLLs) on prism and high-index faces (Movie 1), the appearance of thin liquid-like layers (β-QLLs) beneath α-QLLs on prism and high-index faces (Movie 2), and the coalescence of β-QLLs on prism and high-index faces (Movie 3) are available as video files in the HTML version of the paper.
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Author Contributions
H.A., G.S., and Y.F. designed the research performed by H.A., G.S., and K.N. S. produced the experimental system. H.A., G.S., and Y.F. wrote the paper. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
LCM-DIM, laser confocal microscopy combined with differential interference contrast microscopy; QLL, quasi-liquid layer

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