Cubic Ice Captured by *In Situ* Transmission Electron Microscope

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Nearly a hundred years ago, the Nobel laureate Linus Pauling proposed based on the 'ice rule'[1] and residual entropy theory that the structural entropy of ice is the same for common hexagonal ice (Ih) with tetrahedrally coordinated water molecules assembling into a hexagonal close-packing manner and cubic ice (ice Ic) in a cubic close-packing manner.[2] Whalley also claimed that a special halo called Scheiner's halo which was occasionally observed since almost four hundred years ago is caused by the refraction of light at the specific truncated octahedral surface of ice Ic in diamond cubic structure.[3]

However, the search for ice Ic in laboratories has been accompanied by a continuous dispute. German scientist Hans König first carried out electron diffraction characterization of ice condensed by water vapor at low temperature with a transmission electron microscope (TEM), claiming that the ice crystals grown by this method were ice Ic.[4] Together with the many subsequent experiments that also claimed to obtain ice Ic, the diffraction results, however, cannot exclude hexagonal ice, thus failed to prove that ice Ic has been obtained.[5] These accumulated diffraction results lead to the conclusion that the previously claimed ice Ic is actually stacking disordered ice (ice Isd), which is formed by random stacking of cubic and hexagonal sequences.[6]

Recently, based on diffraction results, two groups of scientists obtained pure-phase ice Ic by heating ice XVII to 160 K in vacuum[7] or degassing a C_2 hydrogen hydrate at 100 K,[8] respectively. The reason for different ice I crystals obtained by these experiments is still unclear, and the existence of ice Ic in the atmosphere is still a mystery.

Now an *in situ* TEM study has captured the pure-phase ice Ic formation process.[9] Huang *et al.* shows that in the vacuum of TEM column, residual water vapor condensed on a cryogenic substrate leads to a mixture of pure-phase ice Ic and single-crystalline ice Ih in separate growth paths. Especially, it is the real-space imaging that directly displays the crystallization process of ice Ic formation at the molecular resolution. This ultra-high spatially resolved real-space tracking characterization of individual crystallites one by one conclusively demonstrates the crystalline structure of vapor-deposited ice crystals. By tracking the ice formation process, two types of low-energy defects in ice Ic are also present. More intriguingly, defects dynamics are visualized when taking electron beam as both a probe and an energy-perturbation source.

The mixing of ice crystallites of polytypes unveiled in the vapor deposition experimental results may explain why the mixed cubic and hexagon peaks are present upon similar conditions in the previous diffraction experiments. In addition to unambiguously demonstrating the pure-phase ice Ic formation from vapor deposition, the unveiled preferential nucleation of ice Ic provides new insights into the heterogeneous nucleation of ice I. The real-space visualization of the microscopic details of the ice Ic crystal formation process is present, which paves the way for the deep understanding of the complex phase transition phenomenon of ice formation.

Despite these advancements, there is still more to learn about ice Ic. For example, the preferential for ice Ic nucleation under different conditions, such as supercooling or supersaturation, is still not fully understood.

Future research in the field of ice Ic will likely focus on addressing these knowledge gaps. More profoundly, future experimental and computations studies warrant developments to gain a deeper understanding of the microscopic kinetics of ice-Ic nucleation and crystallization under ambient conditions. Additionally, there may be opportunities to explore the practical applications of ice Ic, such as deicing of cryo-surfaces and cryopreservation.

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