ESRF	**Experiment title:** Interfacial melting of ice	**Experiment number**: SI-899
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Report:

Water is omnipresent on earth and the basis of our life. It shows numerous anomalies, which are still not all understood. Among these unusual properties is the melting behavior of ice, which exhibits two extraordinary features. One is pressure melting, mediated by the anomalous density increase upon melting. The other is surface melting, where a (quasi)liquid layer forms at the surface at temperatures below the bulk melting point. This phenomenon has been observed in other materials, but is particularly pronounced in the case of ice. This is surprising, as for surface melting the density increase upon melting is energetically unfavorable.

There is experimental evidence that at ice-solid interfaces, interfacial premelting can occur, the same way as surface melting does. However, probing well-defined ice-solid interfaces with high spatial resolution has not been possible so far due to the lack of adequate methods to access deeply-buried interfaces. We have recently developed a scheme for probing such deeply-buried interfaces based on the use of high-energy X-ray microbeams.[1] This technique has now been applied to study model ice-solid interfaces.[2] For the first experiment of this kind, we have chosen a ice-SiO_2(-Si) interface, which can be easily prepared and might serve as a model for ice-mineral interfaces as they occur in nature.

High-purity single crystal ice with basal (00.1) orientation has been contacted with the cleaned substrate. A special sample cell has been constructed which allows a very stable temperature control using Peltier devices. The aforementioned high-energy X-ray scheme has been used to perform X-ray reflectivity measurements at the buried ice-SiO_2 interface in a temperature range from -25°C to -0.036°C.

The measured reflectivity curves are shown in Fig. 1a (open circles). It can be seen that interference fringes appear upon heating which is a direct signal for the formation of an additional layer with different density. The density profiles across the interface have been reconstructed with the dynamical Parrat formalism and the fits are shown in Fig. 1a as solid lines. Fig. 1b shows two examples for such density profiles: For -25°C where the quasiliquid layer has not yet formed and for -0.036°C where it has reached a thickness of 5.5 nm. The layer thickness and the density are plotted as a function of temperature in Fig. 2. The layer thickness follows in good approximation a logarithmic growth law known from wetting theory. The growth amplitude hints to increased density correlations in the quasiliquid layer (0.84 nm compared to 0.45-0.8 nm for bulk water). The density of the quasiliquid is much higher than that of bulk water and close to the density of the high-density amorphous (HDA) form of ice (1.17 g/cm^3), suggesting a close structural relationship. In current water theories the HDA ice is the vitreous counterpart of a postulated high-density liquid (HDL) form of water. As interface melting is an equilibrium phenomenon, the quasiliquid is more likely to be identified with the HDL water than the metastable HDA ice. This would be the first time that one of the postulated water phases has been stabilized. Confinement scenarios like interface melting might offer a way to study these phases.

We plan to extend our studies of ice-solid interfaces to various substrates in order to investigate the influence of the substrate morphology and chemistry.

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[1] Reichert, H., Honkimäki, V., Snigirev, A., Engemann, S., and Dosch, H. A new X-ray transmission-reflection scheme for the study of deeply buried interfaces using high-energy microbeams. Physica B **336**, 46-55 (2003).

[2] Engemann, S., Reichert, H., Dosch, H., Bilgram, J., Honkimäki, V., Snigirev, A. Interfacial melting of ice in contact with SiO$_2$. *Submitted to Phys. Rev. Lett.*

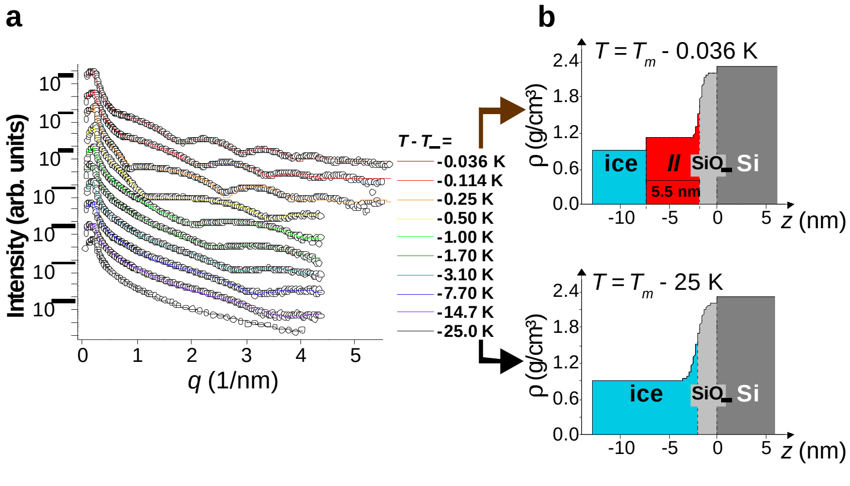

Figure 1

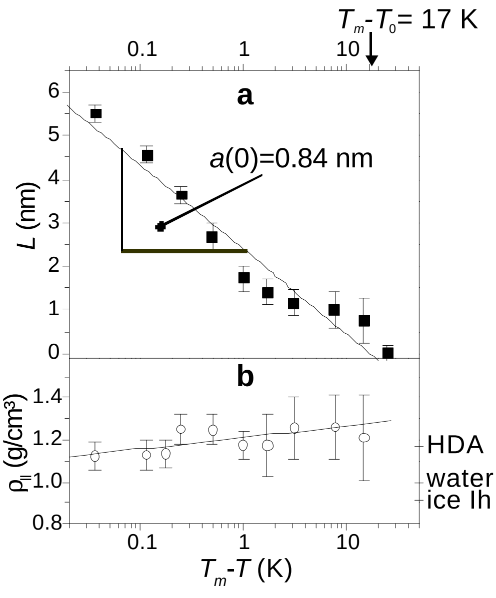

Figure 2