ESRF	**Experiment title:** Interfacial ice melting under high hydrostatic pressure	**Experiment number**: SC-4145
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Report:

The goal of the high energy x-ray diffraction experiment SC-4145 at ID31 was to study interfacial premelting in ice/clay nano composites. Below the melting point of bulk water, the formation of a quasi liquid layer was observed for the ice/vermiculite and ice/kaolin system. The thickness of this interfacial premelting layer is gradually increasing with temperature. For both minerals, a similar thickness of about 2 nm is reached 3 K below the bulk melting point. This corresponds to less than three times the ice Ih lattice spacing along the c-axis. For higher temperatures, the quasi liquid layer thickness follows a logarithmic growth law. Here, pronounced differences are observed between the charged vermiculite and uncharged kaolin minerals.

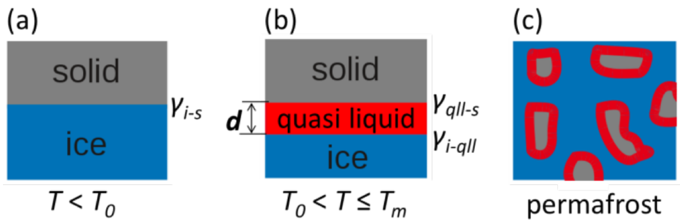

Fig. 1. (Color online) Sketch for premelting at ice/solid interfaces. (a) Ideal ice/solid interface with interfacial tension γ_{i-s}. (b) Above the onset temperature T_0 a thin qll of thickness d is formed before bulk melting sets in at T_m. (c) In natural ice/solid composite materials such as permafrost, the premelting mechanism is also affected by impurities, confinement and the geometry of the system.

During our experiment at ID31 in April 2016, we employed high energy x-ray diffraction (XRD) to study the interfacial melting in ice/vermiculite and ice/kaolin composites. Vermiculite and kaolin are phyllosilicate clay minerals, forming planar platelets with a large aspect ratio and a large specific surface area. Well defined vermiculite samples of high purity were obtained by chemical processing the natural mineral. This suppresses geometry and impurity driven effects, allowing a direct interpretation of the extracted qll growth law d(T) by physical models for intrinsic interfacial premelting. From comparison between the results obtained for charged vermiculite and uncharged kaolin clays we extract information on the relevant molecular interactions governing the intrinsic interfacial melting mechanism.

High energy x-ray diffraction at beamline ID31, ESRF was employed to study the ice content in the clay composite materials (71 keV x-ray energy, 0.5 mm x 0.4 mm beam size). As internal XRD calibration standard, 1 wt.% CeO_2 was added to the clays. Cylindrical pellets (6 mm diameter, 15 mm length) were prepared by uniaxial compacting the water soaked materials at approx. 100 bar (Fig. 2a). The resultant water content of the samples, determined by thermogravimetric analysis after the XRD measurements, were 26.5 wt.% and 20.1 wt.% for vermiculite and kaolin respectively. The pellets were placed inside a temperature controlled titanium cell (-60 ^{o}C < T < 30 ^{o}C, stability better than ±0.005 ^{o}C). To increase thermal contact and to avoid water evaporation during the measurements, the cell was filled with 2,2,4-trimethylpentane. After rapidly cooling the sample to -60 ^{o}C and equilibration for 40 min, XRD measurements were made while stepwise increasing the temperature until complete melting was observed. For each temperature, at least two series of 117 independent scattering patterns were collected by rotating (±6^{o}, 0.5^{o} steps) and translating (±2 mm, 0.5 mm steps) the sample along the cylinder axes. This procedure allowed the collection of representative and reproducible XRD averages. Scattered intensities were recorded on a CdTe hybrid pixel area detector (PILATUS3 X CdTe 2M, Dectris, 1478x1679 pixels, 172 µm pixel size). The 117 2D datasets were normalized by their integrated CeO_2 (111) Bragg intensities and averaged (Fig. 2b). No singular intense Bragg spots

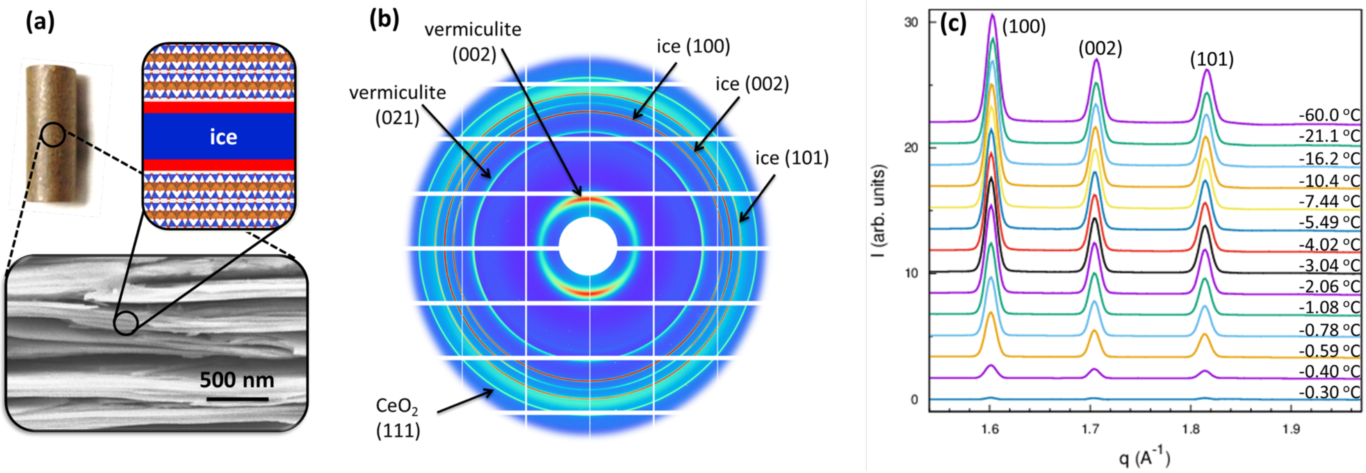

Fig. 2. (Color online) (a) Photography of a compacted vermiculite/H_2O pellet, SEM image of the modified dry vermiculite, sketch of interfacial ice melting in porous sheet silicates (ice: blue, qll: red, not to scale). (b) 2D XRD pattern of vermiculite/ice composite at -60 ^oC. (c) Radial averaged XRD difference patterns between partially frozen samples at -60 $^oC \leq T < 0$ ^oC and the molten sample at +0.8 ^oC.

were observed in the 2D data. This indicates the absence of large ice crystals, formed by water clustering during freezing of the composite sample. Therefore, the integrated intensity of the Bragg reflections provides a quantitative measure of the ice content. After radial averaging, a high temperature pattern of the molten sample and a linear background were subtracted (Fig. 2c). Integrated (100), (002), and (101) Bragg intensities of ice Ih were determined from fitting a Gaussian peak shape to the XRD data. For all three ice Bragg reflections, the same temperature dependence was observed. Finally, the average qll layer thickness was determined from the specific surface area and the water fraction of the sample by taking into account the Debye-Waller factors [1] and assuming full crystallization at -60 ^oC [2].

Below the bulk melting point, the intensities of the ice Ih Bragg reflections rapidly increase (Fig. 2c). This corresponds to a decrease of the qll thickness (Fig. 3). At $T_m - T = 0.5$ K we find a thickness of 4.5 nm for H_2O/vermiculite and 8 nm for H_2O/kaolin respectively. These values are larger than the 2 nm to 4 nm observed by x-ray reflectivity at the interface between single crystalline ice and amorphous SiO_2 [2] and quartz [3] respectively. However, for both clays the observed qll thicknesses are much smaller than the 12 to 50 nm found at free ice surfaces [4,5]. This dependency indicates that aside from the specific water properties, the interfacial premelting mechanism is strongly influenced by the interactions with the solid substrate. In the temperature range between the bulk melting point T_m and $T_m - T = 2$ K the qll thickness d(T) follows a logarithmic dependency (Fig. 3, straight solid lines). No signs of a cross-over from logarithmic law to power law behavior at high temperatures were found in our data. This indicates that in this temperature range interfacial premelting is dominated by exponentially decaying short-ranged interactions rather than long-ranged van der Waals force [6-9].

Below $T_m - T = 3$ K the qll thickness slowly decreases for both clay minerals. A similar cross over in the growth law was predicted for systems where the qll thickness at high temperatures is dominated by ions [10]. However, in this temperature range the qll thickness is below 2 nm. This corresponds to less than three times the 0.736 nm lattice spacing of ice Ih along its c-axis [11]. Therefore, it is expected that thermodynamic models, based on mean-field approximations, come to their limits. This suggests that the concepts behind the derivation of the logarithmic growth law depicted in Eqn. (3) and the Debye length, governing ion induced premelting are no longer applicable. Therefore, we suggest that this cross over is caused by a transition from a continuous melting process to discrete interfacial layer by layer melting [12,13]. This interpretation is supported by the identical transition temperatures between the two melting regimes for both clay minerals. In addition, below

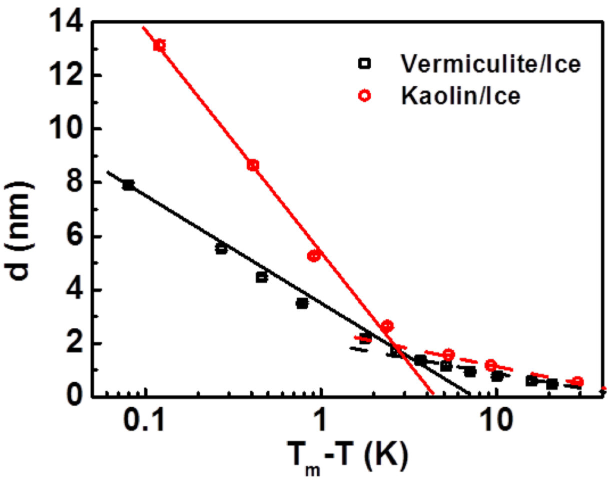

Fig. 3. (Color online) qll thickness d vs. temperature below melting T_m - T for vermiculite (black squares) and kaolin (red circles) composite samples extracted from the intensity of the ice (100), (002), (101) Bragg reflections. Fits to the data points in the in the low (T_m - T > 3 K, dashed lines) and high temperature (T_m - T < 3 K, solid lines) regime were obtained by linear regression of d ln(T_m - T).

T_m - T = 3 K we find a very similar qll growth law d(T) for the vermiculite and kaolin systems, prepared by different procedures. In contrast to perfect interfaces, the clay surfaces exhibit inhomogeneity on the molecular length scale. Therefore, the discrete steps in thickness vs. temperature get blurred, leading to the observed slowly decreasing qll thickness.

In conclusion, we determined the interfacial ice melting in two well characterized ice-nanocomposite model systems comprised of a charged and an uncharged clay. Above T_m - T = 2 K the qll thickness is quantitatively described by a logarithmic growth law. This indicates that interfacial premelting of ice is governed by exponentially decaying short-ranged interactions. Around a qll thickness corresponding to two to three times the lattice parameter along the c-axis of ice Ih i.e. at T_m - T ~ 3 K a cross over to another temperature dependency was observed. This observation is attributed to a transition between a continuous interfacial melting process and discrete layer by layer melting at low temperatures.

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