ESRF	**Experiment title:** Influence of electric fields on the surface/interface melting of ice	**Experiment number**: SI-1341
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We have started to investigate the pre-melting of ice at the ice/SiO_2 interface in the presence of electric fields employing high-energy x-ray reflectivity. In earlier experiments we have studied pre-melting phenomena of ice extensively, leading to both a fully established sample preparation technique and a robust experimental setup at ID15A [1-5]. A clear change of the interfacial structure was observed depending on the applied electric field strength indicating an induced additional layer between the ice and the syubstrate. Unfortunately, we could not complete the experiements due to the loss of two ice samples caused by two major power breakdowns affecting the entire ESRF facility.

The ice samples were sandwiched between two smooth Si(100) substrates in a parallel plate capacitor configuration.A homogeneous electric fields was applied across the two interfaces. The sample thickness was chosen such that both interfaces could be accessed during the experiment via a vertical translation. Prior to contacting the ice samples with the substrates, the basal plane of the ice samples was oriented normal to the interface using in situ x-ray diffraction.

In order to be able to apply electric fields as new parameter a high voltage-proof setup has been constructed (Fig 1). It is based on a two-cycle cooling system: In the outer cycle, a compressor provides the necessary cooling power being transferred by a heat exchanger to the inner cycle. The latter directly circulates around the sample and employs heptane as cooling agent. The chamber itself consists of a double-walled glass cylinder on top of a stainless steel socket. The outer volume can be evacuated, preventing the windows of the inner part from icing. During operation, heptane enters the glass cylinder through 120 thin capillaries in the socket to maximize heat exchange between the socket and the liquid. Regulating the heating power of the cartridges inside the socket, we can control the temperature around the sample. We used two thermo resistors (PT100) placed below and above the sample holder, which could be introduced or removed quickly during the experiment via a stainless steel rod. This rod also served as a connection of the upper

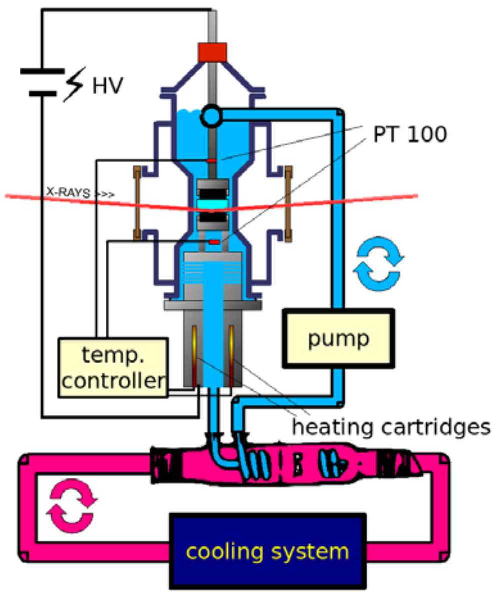

Fig 1. Sketch of the setup.

substrate to the upper electrode of the high voltage power supply.

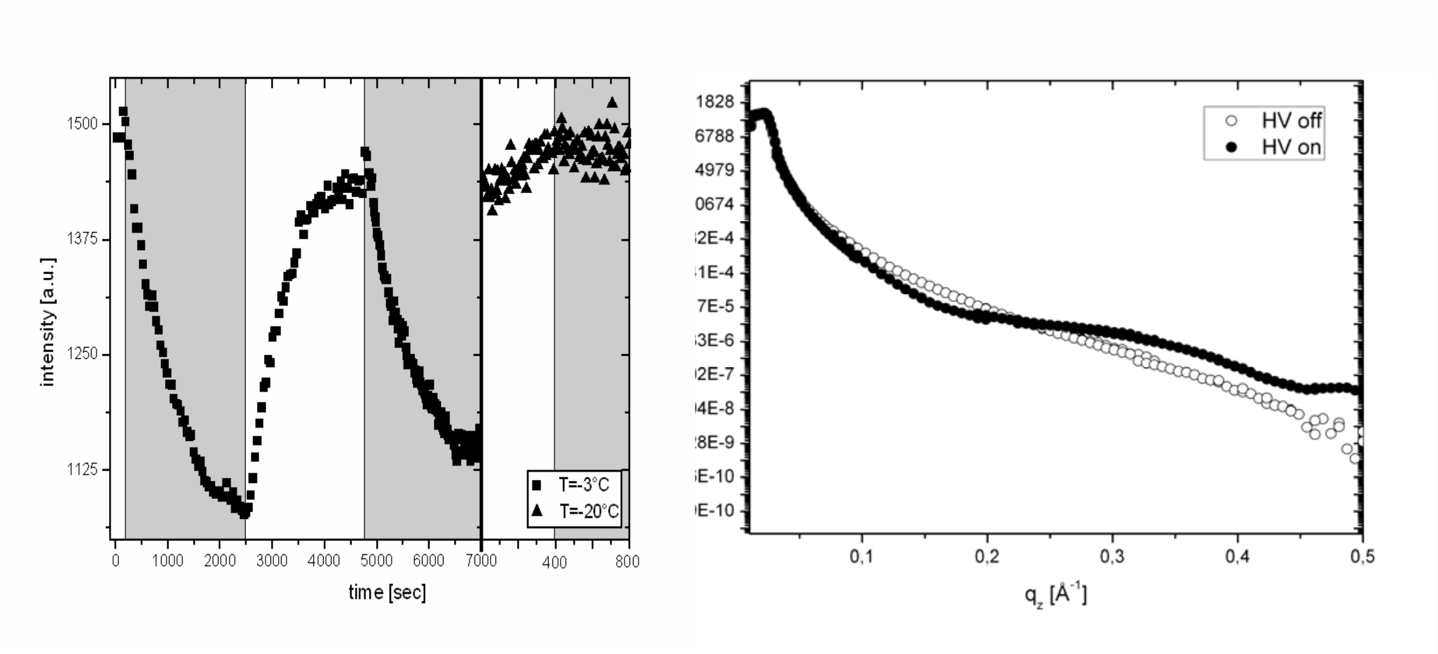

Fig 2. Left: Time dependent change of the measured reflected intensity at q_z=0.32Å^{-1} with and without an applied electric field of 0.5x10^6 V/m switched on at T= - 3°C and T= - 20°C. Shaded areas indicate that the electric field is switched on. Right: Reflectivity at T= - 3°C before application of high voltage (full circles) and after several hours of exposure at 2.5kV (corresponding to a field strength of 0.5x10^6

Since the water molecule has a dipolar character, it is expected that strong electric fields affect the stabilty of ice and thus its pre-melting behaviour [6,7]. Results from STM measurements indicate electro-freezing of water at room temperature at field strengths of about 10^6 V/m [8] - a region that is accessable with our setup. After having acquired reflectivity data at a fixed temperature without electric fields we probed the structure of the interface with gradually increasing field strength. In order to improve time resolution, we first sampled the intensity at various q_z positions on the reflectivity curve in timescans. By way of example, the left part of Fig 2 demonstrates clearly that the intensity at q_z=0.32Å^{-1} shows a reversible response to an applied electric field of 2.5kV (corresponding to 0.5x10^6 V/m) at T=-3°C, whereas at T=-20°C no effects were observed. This strongly suggests an electric field effect on the pre-melting of ice, since the two temperature have been chosen above and below the onset of pre-melting (T_m= -17^{o}C [1]).

The observed effect shows up clearly in the complete reflectivity curves (Fig 2, right). Surprisingly, we found that exposure to high voltages over several hours leads to destructive (or at least non-reversible changes on the time scale of our experiments) effects at the interface. This reduces the amount of reliable data, which can be sampled with a single sample. The above mentioned loss of two samples did not allow us to investigate the field effects on the pre-melting of ice systematically. Further experiments are therefore needed to understand our observations. Our preliminary results point to the appearance of an additional layer induced by the applied electric field rather than to a simple change of the thickness of the quasi-liquid layer.

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