# Radiation-Induced Premelting of Ice at Silica Interfaces

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(Received 20 May 2009; published 24 August 2009)

The existence of surface and interfacial melting of ice below 0 °C has been confirmed by many different experimental techniques. Here we present a high-energy x-ray reflectivity study of the interfacial melting of ice as a function of both temperature and x-ray irradiation dose. We found a clear increase of the thickness of the quasiliquid layer with the irradiation dose. By a systematic x-ray study, we have been able to unambiguously disentangle thermal and radiation-induced premelting phenomena. We also confirm the previously announced very high water density (1.25 g/cm$^3$) within the emerging quasiliquid layer.

DOI: 10.1103/PhysRevLett.103.095502 PACS numbers: 68.08.De, 61.05.cm, 61.20.Ne, 61.80.Cb

Ice is abundant in our Solar System and throughout the Universe. Most of it is unprotected from the high-energy particle and photon irradiation from outer space. Organic life as known to us is bound to the liquid form of $H_2O$, water, which is stable only in a small corridor of environmental conditions, in particular, in the narrow temperature and pressure range between the solid-liquid and the liquid-vapor coexistence lines. Therefore, a detailed understanding of the various phenomena which could increase the stability range of water is crucial. In this context, the premelting of ice at surfaces [1–4] and interfaces [5–7] below 0 °C has been the focus of scientific interest and is held responsible for many naturally occurring phenomena [8,9]. The emerging quasiliquid layer could also serve as a reservoir of liquid $H_2O$ at temperatures below the bulk melting point. The frequently posed question as to whether life could have developed and survived on other planets could be related to this surface phenomenon and its occurrence in harsh environments, especially under the influence of high-energy radiation.

In the thermal melting of ice at a smooth ice-$SiO_2$ interface, a logarithmic growth law of the thickness of the quasiliquid layer (QLL) has been found upon approaching the bulk melting temperature $T_m$, i.e., $L(T) = \xi \ln((T_m - T_0)/(T_m - T))$, where $T_0$ denotes the onset temperature for the formation of the QLL and $\xi$ the correlation length within the QLL [6].

In this Letter we describe x-ray reflectivity studies of the effect of radiation on the formation of a QLL at the interface of ice and $SiO_2$. High-energy x rays induce radiation damage via secondary electron cascades produced by photoelectric absorption and Compton scattering. The impact of both processes is enhanced in the interfacial region due to the approximately 5 times larger scattering cross section in the denser $SiO_2$ substrate (see Fig. 1). The secondary electrons interact with the ice by inelastic scattering, which leads to an increase of ionic defects in the ice, as chemical bonds of the water molecules are broken. It has been shown that ionic impurities lead to an increase in the thickness of the QLL [10]. The impact of irradiation on interfacial melting might therefore also depend on the conductivity of the substrate and its ability to neutralize charges at this interface. In addition, irradiation can lead to amorphization by increasing the mean molecular displacement [11].

Ice-$SiO_2$ interfaces were prepared from single crystalline ice produced by repeated zone refinement [12] in contact with fused silica (thickness 12.7 mm, diameter 25.4 mm, Wave Precision, Moorpark, CA) and quartz (thickness 12.7 mm, 25.4 × 25.4 mm$^2$, (0001) orientation, misalignment ±0.1°, Crystec, Berlin, Germany), respectively. Both substrates (surface roughness <4 Å) were sonicated in a soap solution and acetone, followed by immersion overnight in a 5% solution of chromium trioxide in concentrated sulfuric acid and extensive rinsing with purified water. The hydrophilic substrates were bonded to basal (0001) oriented ice crystals using the procedure described elsewhere [6,13].

X-ray reflectivity measurements were performed at the high-energy beam line ID15A of the European Synchrotron Radiation Facility (Grenoble, France). A sketch of the geometry is shown in Fig. 2. More details about the experimental setup can be found in Ref. [13]. By

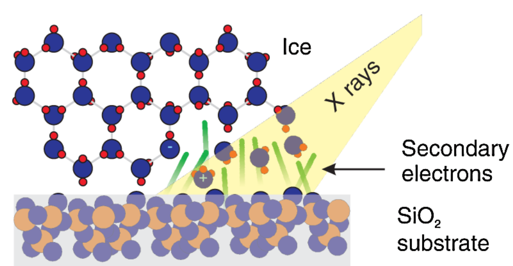


FIG. 1 (color online). Sketch of the radiation damage. Illumination of the $SiO_2$ substrate with x rays creates secondary electrons that destroy bonds between and inside the water molecules.

 

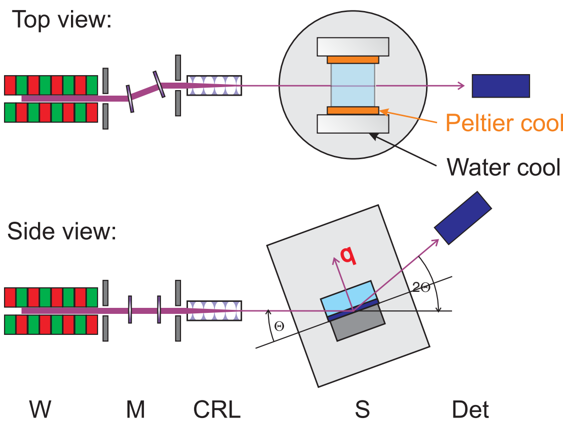


FIG. 2 (color online). Sketch of the experimental setup with the radiation source (W), monochromator (M), focusing element (CRL), sample chamber (S), and detector (Det).

focusing the high-energy x-ray beam (70 keV, $\Delta E/E = 0.3\%$) with an aluminum compound refractive lens we obtained an average flux of approximately $5 \times 10^{10}$ photons per second and a vertical spot size of less than 5 $\mu$m at the sample position. The focused beam is penetrating the bulk ice from the side, allowing selective and full illumination of the $SiO_2$ interface even at glancing angles. A homogeneous sample temperature was achieved by symmetric cooling with two Peltier elements. Several calibrated Pt-100 sensors melted into the ice verified the temperature stability as better than 5 mK.

X-ray reflectivity is the method of choice to probe the electron density profile perpendicular to an interface with atomic or molecular resolution. For a single, perfectly smooth interface the monotonically decaying Fresnel reflectivity curve is obtained. In a single- or multilayered system modulations of the reflectivity curve are expected that allow an accurate determination of the layer thickness and electron density.

The reflectivity was measured with a linearly increasing radiation dose (with time) and a nonmonotonic temperature profile. Typical reflectivity curves obtained at $-1\,^{\circ}$C at both amorphous and crystalline $SiO_2$ interfaces are shown on the left side in Fig. 3 as function of momentum transfer $q$. The electron density profile at the interface was reconstructed from the experimentally determined reflectivity curves. For this, the simulated electron density profile was cut into slabs of 0.1 Å thickness. The reflectivity was then calculated using the Parratt formalism [14], which is also applicable to thin layers with high roughness as present in this study. The fitting procedure was coded in a genetic algorithm. The best fits and the electron density profiles retrieved from the model are shown in Fig. 3. Similar to the results of our previous studies [6] we found strong evidence for the formation of a QLL with a density significantly larger than the density of ice, albeit with increasing thickness as a function of radiation dose. It is important to note that, at both interfaces, no indication of

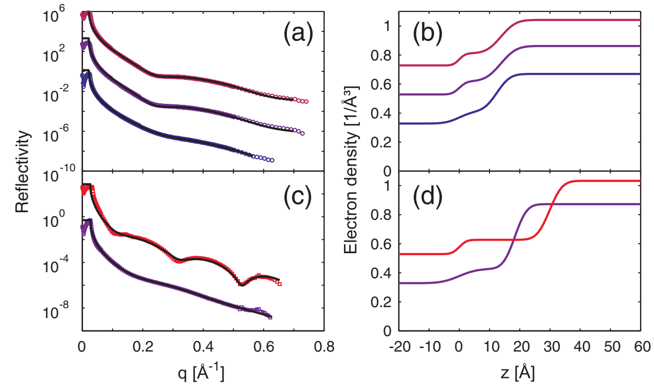


FIG. 3 (color online). Left: Reflectivity obtained at $-1\,^{\circ}$C from the ice-silica (a) and the ice-quartz (c) interface. Best fits according to the model described in the text are shown as lines. For clarity the curves are shifted vertically by a factor of 1000 with increasing radiation dose. (b) and (d): Corresponding electron density profiles retrieved from the model. Profiles with higher irradiation are shifted by adding 0.2 $Å^{-3}$.

interfacial melting was observed at the start of the experiments when the deposited radiation dose was still small. Apparently, a minimum radiation dose is required to trigger interfacial melting. A similar effect has been observed earlier [6].

The significance of the irradiation process for the interfacial melting of ice becomes immediately apparent in the analysis of the thickness of the QLL as a function of the temperature below melting $T_M - T$ alone [see Fig. 4(a)]. The data show no clear dependence on temperature. In order to separate the influence of temperature and irradiation, we monitored the increase of the layer thickness with irradiation at a constant temperature [see Fig. 4(b)].

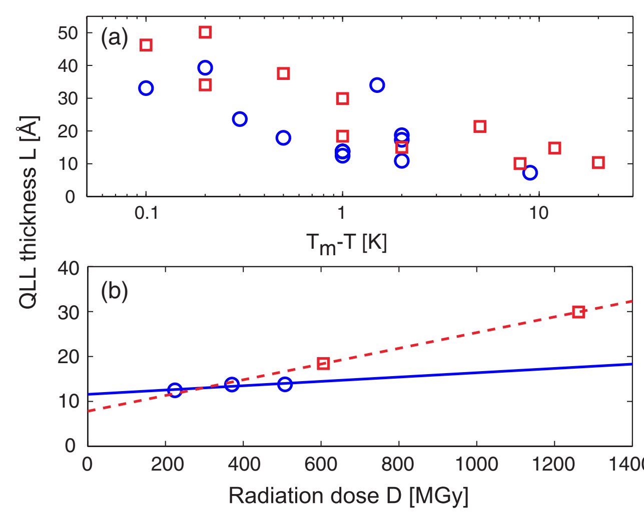


FIG. 4 (color online). (a) Growth of the thickness of the QLL at the ice-silica (circles) and ice-quartz (squares) interfaces as a function of the temperature below melting. (b) Increase of the QLL thickness with radiation dose at $-1\,^{\circ}$C. The lines are guides for the eye.

In order to separate radiation-induced and thermal premelting, the complete data set has been fitted with a modified growth law

$$L(T, D) = \alpha D + \xi \ln\frac{T_m - T_0}{T_m - T}, \quad (1)$$

where the onset temperature $T_0$, the correlation length $\xi$ and a constant radiation-induced growth parameter $\alpha = \partial L/\partial D$ are free parameters. $D$ is the radiation dose and $L$ the thickness of the QLL. The local incident x-ray flux (photons/s/mm$^2$) changes as a function of the incident angle of the focused x-ray beam on the interface. Throughout the measurement of each reflectivity curve it varies in a nonlinear manner as a function of time and location on the interface. As the simplest approach for the analysis, we have used averaged values for the integrated irradiation, which are subject to a significant experimental error. However, there is no indication that the probed area would have a spatially heterogeneous electron density profile parallel to the interface. On average, within 1 h of beam time, 10 MGy are deposited inside the ice.

For the ice-silica interface we found a value of $\alpha = 16$ Å/GGy, while a slightly higher value of $\alpha = 21$ Å/GGy was obtained for the ice-quartz interface. This scales well with the higher density of the quartz, as most of the secondary electrons are created in the substrate.

Equation (1) does not take into account the minimum radiation dose needed to trigger the premelting. We incorporate this effect by introducing an additional fit parameter $D_0$ and replacing $D$ with $D - D_0$. However, due to the limited number of data points no significant value could be obtained. Likewise, for very high radiation doses a saturation effect is expected, as the radiation damage can be annealed faster. In addition, the radiation-induced growth is expected to drop by a factor of 5 once the thickness of the QLL is larger than the electron path length in ice. None of these effects have been observed in the limited beam time. For these reasons Eq. (1) is only valid for intermediate irradiation doses.

The coefficient $\alpha$ was not constant for the duration of the experiment of several days, as assumed by Eq. (1). This may be due to the difficulties in the accurate determination of the integrated radiation, an additional temperature dependence of the coefficient, or an aging effect of the ice.

Figure 5 summarizes the result of fitting both data sets employing Eq. (1) (dashed lines) and shows the thermal part ($\alpha = 0$) of the interfacial melting. The residual scattering in the experimental data is attributed to a possibly nonconstant value of $\alpha$. Layer thicknesses measured at temperatures below the onset temperature have negative values, since a QLL can only be observed after irradiation. The solid line shows the growth law without radiation effects, the layer thickness is zero below $T_O$. We also included two measurements taken at the end of the experiment (solid diamonds) which clearly show a strongly enhanced layer thickness. Most likely this is due to irreversible modifications of the silica interface. A more detailed understanding of these changes would require systematic long-term studies.

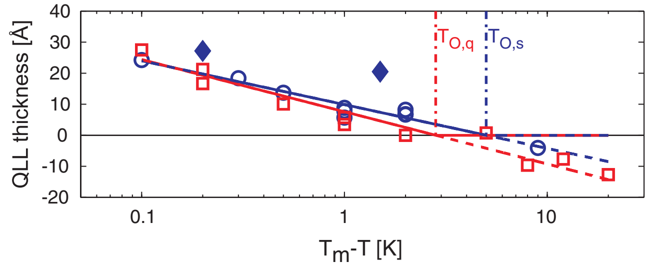


FIG. 5 (color online). Thermal part of the thickness of the QLL for the ice-silica (circles) and ice-quartz (squares) interface. The dashed lines represent the best fits to Eq. (1). The solid lines show the growth law that would be observed using nonirradiative methods. Measurements done after irreversible modifications of the interface (diamonds) have not been included in the fit.

The parameters for the thermal part of the growth law for the thickness of the QLL are $\xi = 6.1$ Å and $T_0 = -5\,°\mathrm{C}$ for the ice-silica interface and $\xi = 7.3$ Å and $T_0 = -2.8\,°\mathrm{C}$ for the ice-quartz interface, respectively. The slightly higher value for the ice-quartz interface and its higher onset temperature might be indicative of an influence of the underlying crystalline lattice or the difference in interface energy, e.g., due to the different surface density of hydroxyl groups.

Figure 6 shows the density of the QLL obtained for all measurements as a function of irradiation. The QLL appears after passing a threshold value $D_{\mathrm{min}}$, which is not only material dependent (choice of substrate) but also energy dependent because of the energy dependence of the Compton and photoelectron yield. The density appears to be constant with a value of 1.25 g/cm$^3$. This value is in good agreement with the results from earlier studies [6]. Because of the reversibility of the thermal part of the interfacial melting, it can be ruled out that the large value

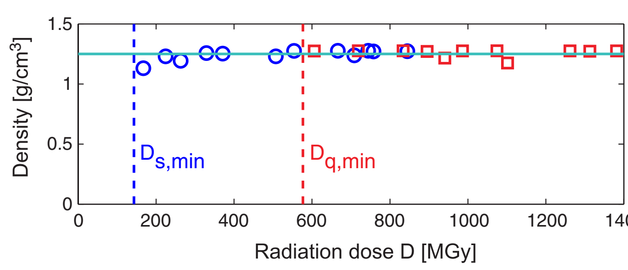


FIG. 6 (color online). Density of the quasiliquid layer as a function of irradiation for the ice-silica (circles) and for the ice-quartz (squares) interface. The solid line indicates the density of VHDA. The dashed vertical lines mark the minimum radiation dose $D_{\mathrm{min}}$ required to initiate interfacial melting at the ice-silica (s) and at the ice-quartz (q) interface.

of the density in the QLL is induced by the segregation of impurities to the interface. The density of the QLL is found to be close to the density of very high-density amorphous ice (VHDA) [15]. It has therefore been speculated that the local structure of the water in the quasiliquid layer is similar to the structure of high-density amorphous ice [6], indicating the stabilization of a high-density liquid in nanoconfinement. Note that a confined water phase with similar density has also been found in zeolites [16], indicating again a significant densification of water in nanoconfinement.

The formation of this surface phase requires repositioning of the water molecules, i.e., a certain mobility of the water molecules which would be enhanced by radiation-induced defects. This defect hypothesis would create a natural link between the observed premolten layer and the radiation dose.

The radiation-induced loss of long-range order in ice has already been studied for particle [17,18] and photon [19,20] irradiation in outer space conditions. Inelastic neutron scattering studies [21] showed that radiation-induced amorphization in ice is comparable to thermal melting. It is therefore expected to lead to the annealed form of high-density amorphous ice (HDA) [21,22]. Laffon *et al.* [19] showed that amorphous ice produced by x-ray irradiation at 20 K densifies upon annealing at higher temperatures. Irradiation with high-energy photons during reflectivity measurements seems to have a similar effect on the QLL, which has an even higher density than HDA. This might result from a combination of confinement and radiation effects. To our knowledge, this is the first report of radiation-induced loss of long-range order in ice at close to ambient conditions.

The radiation-induced growth presented in this work is different from the results published earlier [6], where the thickness of the QLL did not depend on the amount of irradiation and was fully reversible with temperature. This difference is striking, as both studies were performed at ice-$SiO_2$ interfaces. At this point it remains an open question whether the observed difference is related to the fact that in the earlier studies a thin $SiO_2$ film ($\approx 20$ Å thickness) on top of a silicon substrate was used instead of bulk $SiO_2$. Because of the higher electrical conductivity of silicon, this could affect the accumulation of surface charges due to radiation effects. The importance of surface charging in synchrotron experiments has been shown in a recent study [23]. Furthermore, hydrofluoric acid was used in the preparation by [6]. As HF has a high diffusion rate in ice [24,25], remaining contaminants might have influenced the properties of the ice surface.

In conclusion, we have observed interfacial melting of ice at the interface between ice and $SiO_2$ by high-energy reflectivity. The most striking observation is that the thickness of the quasiliquid layer grows with irradiation. A quantitative analysis of the effect is difficult due to the limited amount of beam time available; however, this is the first report of radiation-induced amorphization of ice close to the melting point. The QLL exhibits a density similar to the density of VHDA. Our study supports the idea that this high-density phase is related to the creation of irradiation defects at the interface.

The authors wish to thank S. Engemann (MPI für Metallforschung) for support and discussion.

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