ESRF	**Experiment title:** Single-crystal x-ray diffraction of ice VII at high pressure and high temperature: effect of disorder on the thermodynamics of melting.	**Experiment number**: HS-1685
Beamline: ID30	**Date of experiment**: from: 8/12/01-19/05/02 to: 11/12/01-22/05/2002	**Date of report**: 22/08/2002
Shifts: 18	**Local contact(s)**: Pierre BOUVIER, Anne-Marie DHAUSSY	*Received at ESRF:*

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Report:

The aim of this experiment was threefold: (1) obtain an accurate measurement of the volume of H_2O ice VII along the melting line; (2) obtain structural information on ice VII at high pressure and temperature; and (3) follow the evolution of the superlattice reflections observed in previous single-crystal x-ray diffraction experiments at room temperature. We have performed angle-dispersive diffraction on two different single crystals of ice VII grown from the melt in the sample chamber of a diamond anvil cell (DAC).

We used a DAC specifically designed for high temperature operation, with a large (74°) x-ray aperture provided by the use of boron carbide supporting plates. High temperatures were achieved through the use of an external resistive heater whose geometry provides very homogeneous and well defined temperature conditions. Temperature was measured by a thermocouple in contact with one of the diamond anvils and pressure was obtained through luminescence measurements of a ruby ball and $SrB_4O_7:Sm^{2+}$ compound, on one hand, and x-ray diffraction of the gold liner surrounding the sample, on the other hand. In the first part of the run, we used the MAR 345 image plate detector to collect the diffraction patterns and in the second part, the Brukker CCD. Image analysis and integration have been performed with FIT2D.

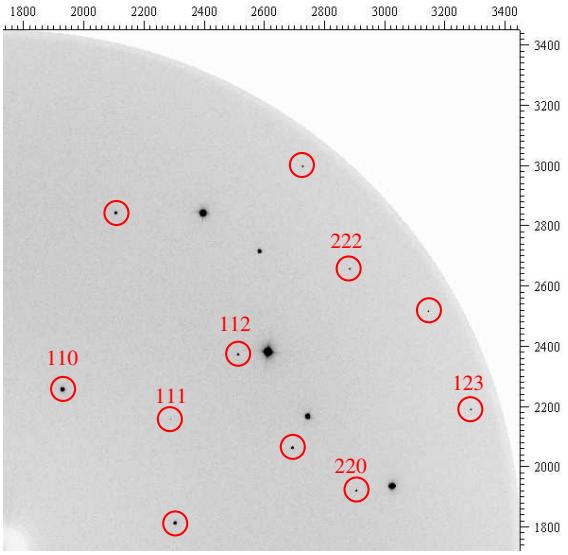

Figure 1 : upper-right quadrant of a typical image plate obtained during the experiment, using the MAR detector. The circled reflections are those from the ice VII single crystal inside the DAC sample chamber at ~3 GPa. The other reflections originate from the diamond anvils.

As shown in figure 1, high quality single-crystal diffraction images could be obtained, with a large number of reflections (up to 24 belonging to 8 different class groups). In particular, we could follow the (111) reflection from one of the studied single crystal (the other one being ill-oriented in that purpose), which is solely due to diffraction from the hydrogen atoms. About 110 data points have been collected along 8 isobars spanning the P-T range between 2.9 GPa and 10 GPa, and from room temperature to slightly below the melting temperature [1] corresponding to each scanned pressure (see Fig. 2). Isobars around 5 GPa and 6 GPa were measured on both single crystals to check for consistency. Temperature increments were of 10 to 25 K. Pressure was kept constant within about ±1 kbar of the nominal pressure, as indicated by either the ruby or $SrB_4O_7:Sm^{2+}$ compound. Pressure as deduced from the diffraction pattern of the gold liner and calculated with the EOS derived by Anderson et al. [2] served as an additional check, although less precise (fluctuations of up to 10 percent of the nominal pressure was observed).

All the observed reflections are consistent with the *bcc* lattice of ice VII; no phase transitions was detected, as expected. One result of this study is that we never observed the superlattice reflections that appeared in the single-crystal experiments at room temperature[3]. Although the second single crystal was ill-oriented in that purpose, we could

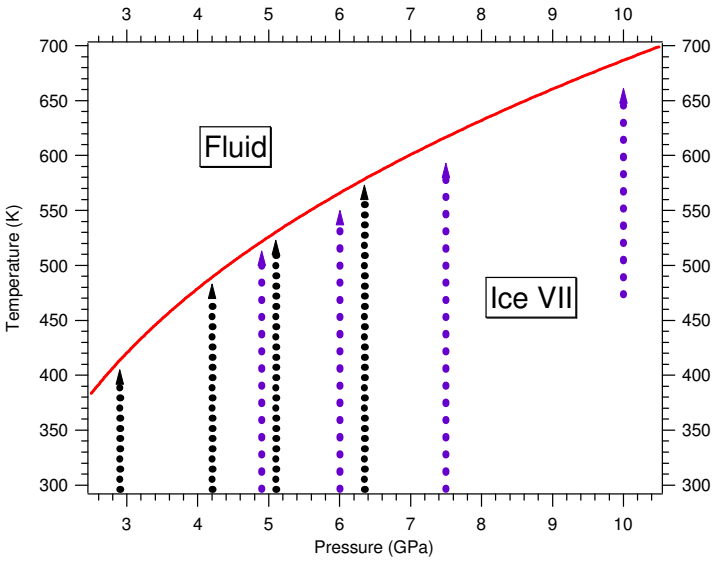

Figure 2 : Pressure-temperature paths followed during the experiment. Conditions close to isobaric ones were kept. The two different colors indicate paths for the two studied single-crystals. The red line shows the melting curve of ice VII [1].

clearly follow the (111) and (222) reflections from the first single crystal, as mentioned above. The superlattice reflections were previously observed in energy-dispersive mode, at the same diffraction angles as the (111) and (222) ones and at an energy approximately half that of the (111). Hence, if these reflections had been present here, they should have appeared along the radial lines connecting the (111) and (222) reflections and the center of the diffraction image, at an angle approximately half that of the (111). We recall here that these reflections never appeared in powder x-ray nor neutron diffraction patterns of ice VII. However they were present in every single-crystal experiments at the ESRF using energy-dispersive (polychromatic) mode. More work is needed to elucidate this phenomenon.

Figure 3 shows the evolution with temperature of the lattice parameter *a* normalized to its room temperature value for each isobar. Data analysis is still ongoing so this only represents preliminary results. The lines are fits to the data using a polynomial form for the thermal expansion parameter $\alpha(P,T) = \frac{1}{a_0}\frac{\partial a}{\partial T}\Big|_P$. Clearly, the thermal expansion coefficient has a non-linear temperature dependence at high pressure and exhibits an interesting evolution with pressure: whereas the initial expansion from RT at the two lowest pressures (2.9 and 4.2 GPa) is positive, it seems to reach a slightly negative minimum around 5.1 GPa before rising up again at higher pressures (6 and 7.5 GPa). The next steps of this analysis will be to extract from the data the volume along the melting curve and build an equation of state *P-V-T* that can account for the observed evolution.

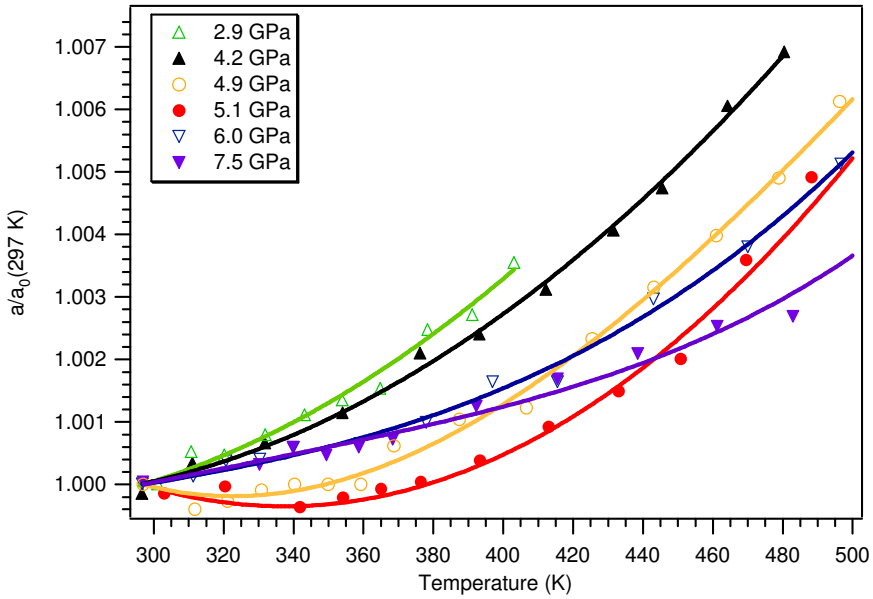

Figure 3 : Evolution with temperature of the normalized lattice parameter of ice VII along the studied isobars.

References:

[1] F. Datchi, P. Loubeyre and R. LeToullec, Phys. Rev. B, **61**(10), 6535 (2000)

[2] O. Anderson, D. Isaak and S. Yanamoto, J. Appl. Phys. **65**(4), 1534 (1989)

[3] P. Loubeyre, et al., *Nature*, **397**,503 (1999)