	Experiment title: **Equation of State of Ice in the Temperature range 300-1000 K up to 80 GPa**	**Experiment number**: HS2156
Beamline:	**Date of experiment**: from: 18.06.03 to: 23.06.03	**Date of report**: 24.08.04
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Report:

Aim of the experiment :

It was shown from various experimental and theoretical investigations that compression of ice to around 62 GPa induces the proton delocalisation of the O-H···O bond. The first experimental proof of this transition was obtained in this team more than 10 years ago.[1] At low temperature this delocalisation, due to a quantum effect, is the first step to the so-called symmetric ice X. At high temperature the role of thermal hoppings or ionic defects may become predominent. Actually it was proposed from computation that above 1200 K and 60 GPa there is a "melting" of the proton sublattice: this state is called superionic.[2]

The goal of the current investigation is threefold, i) it is to obtain a complete p, V, T equation of state (EOS) which could provide thermodynamics information such as volume, expansivity, in the pressure range up to 80 GPa and from 300 to 1000 K; ii) to locate the onset of the proton translational disorder through the treatment of the EOS ;[3] and iii) to search a possible modification of the EOS related to the expected strong increase of the ionicity at high T-p correlated with the superionic state.

Experimental

Ice was compressed in large x-ray conical aperture (74°) membrane diamond cells (MDAC) designed in our laboratory. The heater of the DAC consisted of an electric heating sleeve surrounding the body of the cell and in addition an oven surrounding the diamond anvils. This device is placed in vacuo, into a chamber equipped with windows for the incident and diffracted x-ray beams. The temperature was determined thanks to a thin thermocouple soldered on the brass diamond centering piece. Preindented rhenium gaskets were utilized. For internal pressure calibrants doped Sm^{2+} strontium borate and gold (or platinium) powder were placed in the gasket hole which was filled with liquid H_2O. High pressure powder diffraction was performed in an angle dispersive method on beam line ID09A using a MAR 345 image-plate detector. The monochromatic x-ray beam ($\lambda \sim 0.41$ Å) was collimated down to 50 x 50 μm^2 and «cleaned up» close to the cell using fine slits to avoid contamination by gasket scattering. During exposure times, the DAC was rocked through ± 3° in order to improve the powder statistic. In the p-T range of the present investigation, ice is cubic (at 295 K water crystallizes into solid VI at 0.9 GPa then at ~ 2 GPa it transform to solid VII, space group $Pn\bar{3}m$). At ~5 GPa the cell parameter is a ~3.25 Å and with a wavelength of the incident x-ray beam around 0.41 Å the various hkl Bragg reflections 110, (111), 200, 211, (220), (310) were observed (observation of the reflections between brackets depends on the experimental conditions, *e.g.* in some instances the 111 reflection, due only to hydrogen atoms, was observed up to 40 GPa).

Results

During this run the investigations were performed in a pressure range exceeding 80 GPa at 402 and 700 K giving a total of 49 (p,a,T) data points (more than 150 data points with the HS-1841 run performed in 2002). For the time being the effects of uniaxial stress component were not analysed and only raw data are discussed below. The raw data were fitted with the so-called Vinet EOS (see in reference 3) which involve the three "zero-pressure" parameters, lattice parameter, bulk modulus and its first pressure derivative: a_0, B_0 and B'_0, respectively. Actually the strong correlation between these parameters prevent consistent determinations. To partly solve this difficulty, the **expansivity** for the hypothetic "atmospheric" solid VII was constrained to a reasonable value and so the $a_0(T)$ parameter was fixed for each isotherm. Presently in the 295-700 K temperature range the bulk modulus B_0 and B'_0 found around 15 GPa and 5.5 respectively with no significant temperature dependence. For each isotherm the pressure dependence of the lattice parameter appears to be continuous in the whole pressure domain; however different regimes may exist as mentioned above and may be emphasized if a linear representation of the EOS is used. Applying this procedure we found a negative shift of the transition pressure towards the proton delocalised state, which is estimated around 50 GPa at 700 K whereas it is ~ 62 GPa at room temperature. [3]

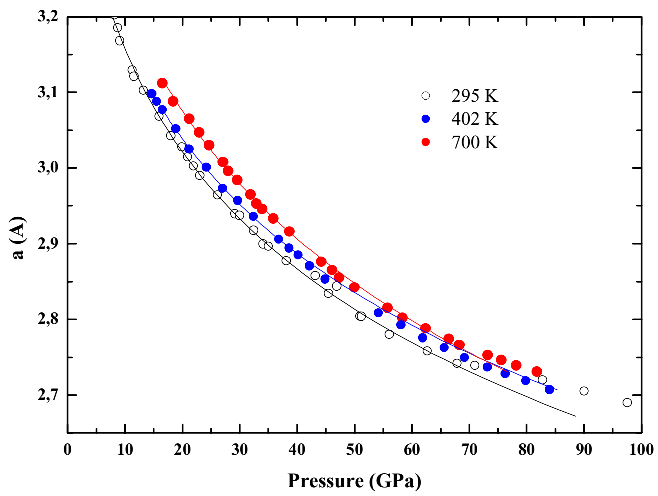

Figure 1 Lattice parameter of ice VII at 295, 402 and 700 K. Symbols: data points. Solid lines: fit according to the EOS of Vinet et al. The discrepancy with the Vinet EOS at high pressure is assigned to the setup of the proton disorder.

References

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