	Experiment title: Equation of State of Ice in the Temperature range 300-1000 K up to 80 GPa	**Experiment number**: HS1841
Beamline: ID09A	**Date of experiment**: from: 06-mars/07-mai 02 to: 09-mars/09-mai-02	Date of report:**22-August 02**
Shifts:	**Local contact(s)**: Dr. Michael HANFLAND	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Philippe Pruzan*, Frédéric Datchi*, Jean-Claude Chervin*, Bernard Canny*, Physique des Milieux Condensés, UMR 7602, B77, Université Pierre et Marie Curie 75252 Paris cédex 05.

Report:

Aim of the experiment

At room temperature (295 K) the equation of state (EOS) of ice was carefully investigated in the megabar range, [1-4] on the other hand there is a paucity of data at low and high temperature. The present experiment aims at obtaining the EOS in the 295-600 K temperature range up to ~80 GPa. The goal is threefold, -first it is to obtain a complete p, V, T equation which could provide thermodynamics information such as volume, expansivity, -second it is to determine the pressure and temperature evolution of the proton disorder through the locus of the pseudo-transition lines given in Fig. 1 specifically the line assigned to the statistical symmetrization of the bond, -and third it is to search a possible modification of the EOS related to the expected strong increase of the ionicity at high T-p which likely leads to a superionic state.[5]

Experimental

Ice was compressed in the membrane diamond cell (MDAC) designed in our laboratory ; the full 4θ x-ray apertures of the various cells used were around 46°. High pressure powder diffraction was performed in an angle dispersive method on beam line ID09A using a MAR 345 image-plate detector. In the p-T range of the present investigation ice is cubic (water crystallizes into solid VII, space group $Pn\bar{3}m$). At ~5 GPa the cell parameter is ~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). The thermostat of the DAC consists of an electric heating sleeve surrounding the body of the cell. The temperature was determined thanks to a thin thermocouple soldered on the brass diamond centering piece. The thermocouple temperature *vs* the experimental hole temperature was previously calibrated at atmospheric pressure. For the pressure measurement we used the ruby or the doped Sm^{2+} strontium borate luminescence lines;[6] in most cases gold or platinum powder was placed in the experimental volume, and the pressure calibrations of Anderson and Jamieson,[7] which correlate the lattice parameters with p and T, were used.

Results

Eleven runs were performed along isobaric and isothermal paths. In the first part of the experiment, we failed to rich pressures above 30 GPa because of systematic failure of the gaskets that contained the samples at high temperature. To take this into account, we changed the way the gaskets were prepared for the second part of the run, which allowed us to achieve pressures up to 90 GPa at 500 K. Isothermal investigations were performed around 400, 500 and 600 K respectively. At 400 and 600 K the maximun pressure was ~30 GPa, it was 90 GPa at 500 K. The p-T range investigated is given in Fig. 1. For the time being the effects of uniaxial stress component were not analysed and only raw data are discussed below. Within the experimental accuracy the temperature effect is clearly visible up to ~30 GPa and consistent with a positive expansivity : systematic departures between the (various) runs performed at different temperatures are observed. As expected on further compression the temperature effect is less marked if not negligible. The raw data were fitted with the so-called Vinet EOS.[8] In the p-T range investigated the bulk modulus B_0 and its first pressure derivative B'_0 were found around 15 GPa and 5 with no systematic temperature dependence. The extrapolated zero-pressure lattice parameter, termed a_0, was found to increase less than 1 % from 295 to 600 K. Actually the number of parameters in the EOS is too large and correlations among them prevent reliable determinations. It is required to constraint a_0 or B_0, or both, from data obtained with different investigations. For instance it is planned to use the lattice parameters values along the VII-L melting curve which are going to be obtained from the Experiment HS 1685 (Datchi *et al.*). Information on B_0 can be obtained from Brillouin spectroscopy, it would be relevant also to constraint this parameter.

Preliminary conclusion and perspective

We plan the following :

i) Carrying out the investigation at higher pressure and temperature, specifically data are required above 600 K, furthermore the density of data points in the p-T range investigated must be homogeneous, this involves further investigations at 400 and 600 K.

ii) The data treatment must include the effect of non-hydrostatic compression, in other words the effect due to uniaxial stress component (USC). This USC has to be taken into account to obtain the corrected value of the cell parameter under hydrostatic compression. Evaluation of the USC will be the next step in the treatment of the present data.

iii) In the fitting procedure of the data with the EOS (*e.g.* Vinet EOS) constraints based on the results of the cell parameter along the melting curve will be imposed. This will permit to obtain more reliable values of B_0 and B'_0 and to assess their temperature dependences.

<u>**References**</u>

1. R.J. Hemley et al., **Nature** (London) 330, 737 (1987).
2. E. Wolanin, Ph. Pruzan, J.C. Chervin, B. Canny, M. Gauthier, D. Hausermann, M. Hanfland, Equation of state of ice VII up to 106 GPa. **Phys. Rev. B** 56, 5781 (1997).
3. Ph. Pruzan, E. Wolanin, M. Gauthier, J.C. Chervin, B. Canny, D. Hausermann, M. Hanfland, Raman Scattering and X-ray diffraction of ice in the megabar range. Occurrence of a symmetric disordered solid above 62 GPa. **J. Phys. Chem**. 101, 6230 (1997).
4. Paul Loubeyre, R. Le Toullec, E. Wolanin, M. Hanfland, and D. Hausermann, **Nature**, 397, 503 (1999).
5. C. Cavazzoni, G.L. Chiarotti, S. Scandalo, E. Tosatti, M. Bernasconi, M. Parinello, **Science** 283, 44, 1999.
6. F. Datchi, R. Le Toullec, P. Loubeyre, **J. Appl. Phys.** 81, 3333 (1997).
7. Anderson *et al.* **J. Appl. Phys.** 65, 1534 (1989). Jamieson *et al.*, **High Pressure Research in Geophysics** 27 (1982).

8. Useful comments on the most commonly used EOS are given by R.E. Cohen *et al.*, **American Mineralogist** 85, 338 (2000).
9. F. Datchi, P. Loubeyre and R. LeToullec, **Phys. Rev. B**, 61, 6535 (2000)

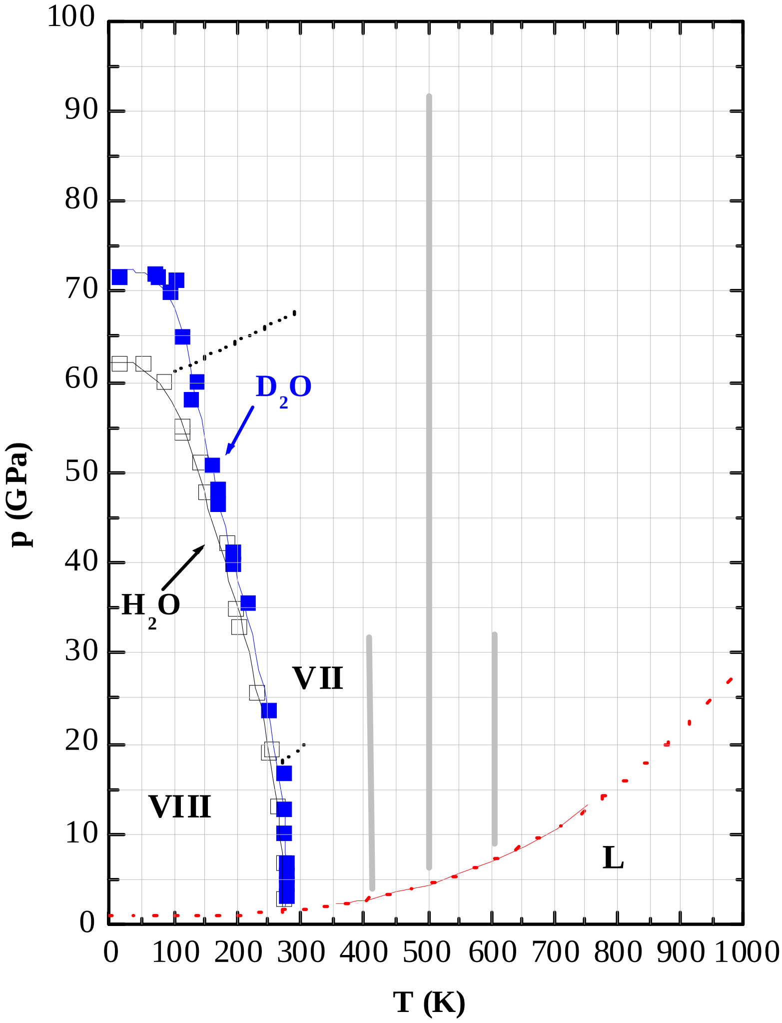

Figure 1. Phase diagram of Ice in the VII-VIII region (black and blue lines). Black dots : pseudo-transition lines for the proton ordering : at ~60 GPa dynamic symmetric solid. Red : melting line.[9] Light grey lines : domains investigated in the present work.