

**PS18.03.12 THE STRUCTURE OF IN-SITU ICES III AND V.** C. Lobban<sup>1</sup>, J.L. Finney<sup>1</sup> and W.F. Kuhs<sup>2</sup>, <sup>1</sup>Dept. of Physics & Astronomy, UCL, London WC1E 6BT, UK, <sup>2</sup>MKI, Universität Göttingen, D-37077 Göttingen, Germany

The degree of hydrogen ordering within ices III and V is controversial, very little structural work having been done on these phases under their stable conditions of high pressure. Instead samples have generally been quenched to liquid nitrogen temperatures and recovered to ambient pressure, the results of such structural studies differing from conclusions drawn from dielectric, calorimetric and spectroscopic measurements under pressure. We have previously attempted to study these phases under pressure using a helium gas pressure system. However, the helium diffused into the system forming helium hydrate, resulting in great difficulty in forming the desired ice phases. More recently, during an experiment designed to look at argon clathrate, under argon pressures of up to 5kbars, we found that temperature reduction under pressure led to the formation of ice V rather than the clathrate. As starting from the liquid led to a very poor powder, more recent work has established that ices III and V can be prepared from powdered ice Ih, again under argon pressure. We have already collected one data set on ice III under pressure which clearly shows a small amount of partial ordering. We also have two experiments scheduled for the study of these systems on HRPD at ISIS and D2B at ILL. Structural refinements will be presented from all these experiments, with particular emphasis on the hydrogen orderings in the two phases.

**PS18.03.13 EVIDENCE OF A SYMMETRIC DISORDERED ICE ABOVE ~62 GPa FROM RAMAN SCATTERING AND X-RAY DIFFRACTION INVESTIGATIONS.** E. Wolanin,\* Ph. Pruzan,\* M. Gauthier,\* J.C. Chervin,\* B. Canny,\* D. Hausermann,\*\* M. Hanfland\*\*, \*Physique des Milieux Condensés (URA 782), Université P. & M. Curie, B 77, 4, place Jussieu F-75252 Paris Cedex 05, France, \*\*E.S.R.F., B.P. 220 F-38043 Grenoble Cedex, France

Experimental investigations of ice and deuterated ice, using Raman scattering at low temperature and x-ray diffraction at 300 K, were performed in the diamond anvil cell at pressure on excess to 100 GPa.

One of the main feature of the ice phase diagram above 2 GPa is the VII-VIII order-disorder antiferro-paraelectric transition whose locus was determined by Raman scattering. Analysis of the behavior of the VII-VIII transition temperature  $T_c$  vs pressure, points out three pressure regimes for the proton disordering. In particular the drop of  $T_c$  to 0 K at 62 GPa is consistent with the proton delocalization between two neighbouring oxygens.

Our x-ray investigation performed at 300 K confirms the Pn3m structure for ice VII for pressures above 100 GPa. Using a treatment based on the universal equation of state (EOS) of Vinet, our x-ray data exhibits three pressure regimes for the EOS consistent with our Raman results. Ice adopts a disordered structure with a proton delocalization along the O-O direction. This structure is very likely a step before the ordered symmetric ice.

**PS18.03.14 HIGH-PRESSURE ROTATION PHASE OF ICE VI.** Gabuda S.P., Institute of Inorganic Chemistry, Novosibirsk, Russia

The proton magnetic resonance (PMR) was used to study the molecular mobility in high pressure phases of ice. The routine continuous line NMR spectrometer was equipped with a special high-pressure vessel of beryllium bronze for registration of PMR spectra of samples being under the pressures up to 2 GPa. During the study it was found that the narrow PMR line of liquid water remains almost unchanged when the pressure exceeds the value of ice VI crystallisation (0.8 GPa at room temperature). The broad NMR line of solid water (ice) arises only when the hydrostatic pressure is 1.3 GPa or more. The half-widths and mean square widths (or second moment  $M$ ) of this line are pressure independent from 1.3 to 1.5 MPa. But the numerical value  $M=9.0\pm 0.5$  G<sup>2</sup> of recorded spectra are much less, than  $M \approx 40$  G<sup>2</sup>, computed for the ice VI structure. It should be noted that  $M$  value of NMR spectrum of ice Ih is 36 G<sup>2</sup>, that is close to the expected rigid lattice ice VI value.

The observed behaviour of PMR spectra of water under the high pressure correlates very closely with the behaviour of PMR spectra of  $H_2S$  at decrease of the temperature. Reasoning from the correspondence between the low temperature behaviour of molecular crystals and of those at high pressures one can conclude that at approximately 0.8 GPa water crystallises into the superplastic phase, and at 1.3 GPa it undergoes a transformation into the "rotation" phase. The real rigid high pressure crystal lattice of ice VI probably is formed only when the pressure is more, than 1.5 GPa (at room temperature).

**PS18.03.15 HIGH PRESSURE STRUCTURAL STUDIES OF ALKALI MANGANESE(III) FLUORIDES.** Carlson, S., Xu, Y., Norrestam, R<sup>1</sup>, and Hålenius, U.<sup>2</sup>, <sup>1</sup> Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden, <sup>2</sup>Mineralogy, Swedish Museum of Natural History, Box 50007, S-10405 Stockholm

The crystal structures of alkali manganese(III) fluorides are being investigated by X-ray diffraction techniques at pressures up to 50 kbar, using MoK $\alpha$  radiation from a rotating anode equipment and a diamond anvil cell (Diacell Products). For one of the sodium manganese fluorides a reversible isosymmetric phase transition (22 kbar) has been observed. Studies on the structural features of this transition, based on single crystal data and on visual spectra collected around the phase transition, are currently being performed. The structure refinements converge smoothly to R values below 0.08. The preliminary results indicate that the phase transition implies reorientations of the static Jahn-Teller prolate distortions of the coordination octahedra around the manganese(III) ions. An interpretation of the visual spectra further confirms these results. Current investigations include studies of manganese(III) fluorides with other alkali ions.