

Investigating planetary ices with neutrons.

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The large icy moons of our Solar System are, as the name indicates, dominated by water ice, and water bonded with other species, such as ammonia, and possibly salts such as magnesium sulfate. The size of these icy moons is such that their ice mantles may be 800-900 km deep, yielding P-T regimes of 0-2 GPa and 50-400 K. This parameter space is ample to allow for rich polymorphic diversity, which in turn has consequences for the structure and evolution of these worlds, typified by the evidence for geological activity (tectonism and cryovolcanism) seen on Europa, Ganymede, and recently Titan.

For water ice, the phase diagram is well known to 2 GPa; however, at low temperatures, kinetics prevent the location of equilibrium phase boundaries on the time-scale of a typical experiment. Furthermore, the equations of state of important phases, such as ice VI, are poorly characterised. The phase diagram of ammonia dihydrate is not well known at all; the structures and thermoelastic properties of the high-pressure phases have never been measured. The hydrates of magnesium sulfate (epsom salt, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and Fritzsche's salt, $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$) are even more poorly understood.

Using powder neutron diffraction techniques we are able to make in situ phase identification at the same time as measuring the molar volume. Hence, we can determine accurate equation of state (EOS) parameters and identify new phases. Knowledge of the equilibrium phase diagrams and EOS parameters are essential to constructing realistic structural models of icy moon interiors. Accurate EOS data, both from experiments and *ab initio* simulations, also permit the calculation of equilibrium phase stability (via the Gibbs Free Energy); thereby circumventing the kinetic inhibition found in

low-temperature experiments.

In experiments at the ISIS neutron spallation source, Rutherford Appleton Laboratory, U.K., using the HRPD, PEARL/HiPr, and OSIRIS beamlines, we have achieved the following:

- The first accurate thermal expansion and bulk modulus measurements of helium-free ice II, ammonia dihydrate I (ADH I), and the low-pressure phase of epsom salt.
- Identification of several new high-pressure phases of ammonia dihydrate. ADH II is formed from phase I at ~ 0.41 GPa at 175K, and transforms to phase III when warmed to 190 K at 0.55 GPa. ADH IV appears to be the liquidus phase at ~ 200 K, 0.6 GPa, and has been observed up to pressures exceeding 4 GPa in the Paris-Edinburgh cell. ADH IV breaks down above ~ 180 K when pressurised over 4.5 GPa to a mixture of ice VIII and bcc ammonia monohydrate phase VI (N.B., this mixture was previously misidentified in our earlier work as a single phase, ADH V). The dehydration of ammonia dihydrate under pressure is similar to the well-known dehydration of salt hydrates - such as epsomite - under pressure. Below 180 K, ADH IV appears to transform to a bcc crystal structure akin to AMH VI, and this is referred to as ADH VI.
- Collection of the first high resolution neutron diffraction data from Fritzsche's salt.

In future work, we shall be studying ammonia hemihydrate - to validate *ab initio* computer models - and the higher hydrates of sulfuric acid, which may be important mineral species in the crust of Jupiter's moon Europa.