NEUTRON DIFFRACTION STUDIES OF PLANETARY ICES. A. D. Fortes,[1] I. G. Wood,[1] K. S. Knight,[2] J. P. Brodholt,[1] M. Alfredsson,[1] and L. Vočadlo[1]. [1]Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, United Kingdom (*andrew.fortes@ucl.ac.uk*), [2]ISIS facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire, OX11 0, United Kingdom.

Introduction: Many of the icy satellites in the outer Solar System contain significant quantities of water, either in the form of pure ice or combined with other substances to form hydrates. The structure and evolution of these icy moons is determined by the physical properties of their component ices; their thermal expansivity, incompressibility, and phase stability. We are therefore engaged in a programme of study to measure the physical characteristics of candidate materials using neutron diffraction techniques. Neutrons are powerful probes of low molecular-weight solids, hydrogen-bearing species in particular, and their penetrative power allows one to study materials even in complex sample environments, such as pressure cells and cryostats. In practice, we measure the variation in molar volume of a solid as a function of pressure and temperature; this leads to derivatives in P and T, such as thermal expansivity and compressibility. Furthermore, we can observe phase transitions *in situ*, and collect diffraction data which may lead to a successful solution of the new polymorph's structure.

In this contribution, we present the results of our work on a high-pressure polymorph of solid water - ice II - and the heptahydrate of magnesium sulfate – epsomite. Our work on ammonia dihydrate is presented in a companion abstract and poster presentation [1].

Ice II (D_2O): Surprisingly little is known of the thermoelastic properties of this ice polymorph; bulk moduli and thermal expansion coefficients have been estimated from just a few data points [2].

Ice II is formed by compression of ice Ih to ~0.25 GPa at 225K, where the transformation takes a few minutes. Two gas pressure vessels were used, one made of Aluminium 7075 alloy, rated to 0.45 GPa, and one made of TiZr null-scattering alloy, rated to 0.55 GPa. Diffraction patterns were collected at a number of P and T points in the stability field of ice II, and then the samples were recovered to ambient pressure at 110 K. Argon was used as the pressure transmitting medium since it does not enter the ice II structure, as helium does. However, in spite of exercising great care, argon plugs frequently blocked the pressure capillary, leading to the loss of much high-pressure data. Nevertheless, a good isothermal compression curve was acquired at 225 K; from this, the zero-pressure bulk modulus was found to be 12.2 GPa.

Data were collected on ice II at atmospheric pressure (Fig. 1) whilst warming from 4 K to 160 K (where the sample irreversibly transformed to the cubic polytype of ice I). Slight offsets were seen between each run, caused by small differences in the position of the sample in the neutron beam, and were dealt with by normalising the data sets to have the same volume at 55 K. Clearly, ice II does not exhibit the negative volume thermal expansion coefficient seen in ice Ih at low temperature [3].
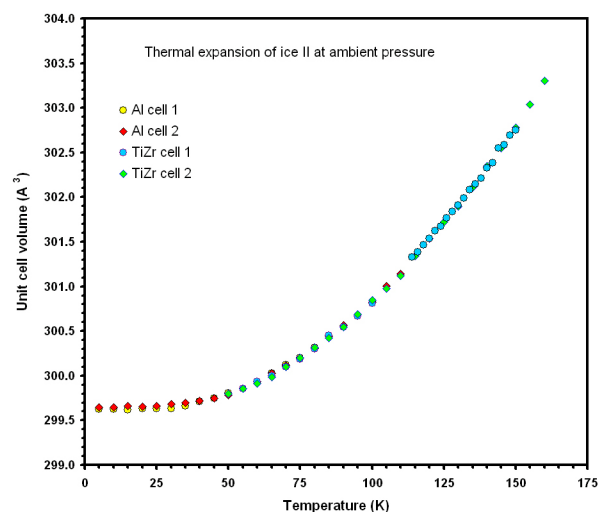

Figure 1. Plot of the unit cell volume of D_2O ice II against temperature for samples recovered at atmospheric pressure. The plot depicts four data sets, acquired in different sample environments, normalised so as to have the same value at 55 K.

Epsomite ($MgSO_4 \cdot 7D_2O$): Kargel [4] postulated that interactions between the volatile and chondritic components of icy moons during their formation would yield brines of $MgSO_4$ and Na_2SO_4. Freezing these brines produces minerals like epsomite ($MgSO_4 \cdot 7H_2O$), MS12 ($MgSO_4 \cdot 12H_2O$), and mirabilite ($Na_2SO_4 \cdot 10H_2O$). We have begun our investigations of these salt systems with epsomite.

The neutron diffraction data do not show any change in the crystal structure at low temperatures. However, there are some interesting changes in the behaviour of the crystal; whilst epsomite has a strictly *positive* volume thermal expansivity from 1.8 - 300 K, the *a*-axis of the orthorhombic unit cell has *negative* linear thermal expansivity up to ~250 K, before turning positive (see Fig. 2). Further single-crystal work is

needed to establish the underlying mechanism for this behaviour.

Compression to 0.55 GPa in a TiZr pressure vessel (using Ar gas) allowed us to measure the bulk and linear incompressibilites at 290 K. The bulk modulus, 21.5 GPa, is in agreement with earlier compressibility studies [5] elastic modulus measurements [6], and unpublished *ab initio* calculations by one of us (ADF). The *a*- and *c*-axes are both of similar stiffness (linear incompressibilities ≈ 73 GPa) and are much stiffer than the *b*-axis (linear incompressibility ≈ 55 GPa) at 290 K, in agreement with calculations. We suspect that the *a*-axis may be much softer in the low-T regime where it exhibits negative thermal expansion.

No phase change to a denser polymorph was seen, even after four hours at 0.55 GPa. This is in agreement with Bridgman [5] and Grasset *et al*. [7], and does not necessarily contradict Livshits *et al*. [8], who observed a phase transition at 0.45 GPa; the deuteration of our sample is very likely to shift phase boundaries to slightly higher pressures.

Conclusions: Our goal in measuring the equation of state of ice II is to be able to calculate its stability relative to ice Ih, and so locate the equilibrium phase boundary at low-T. The position of this boundary has implications for the evolution of objects such as Rhea [9]. More work is needed to achieve this.

The thermoelastic behaviour of epsomite at temperatures pertinent to icy moons (50-150K) is clearly very different to its behaviour at terrestrial room temperature, highlighting the importance of these kinds of studies in understanding planetary materials. Knowing the densities of these hydrates under the appropriate conditions allows us to determine volume changes attending hydration; reactions implicated in the formation of certain features on Ganymede [10].

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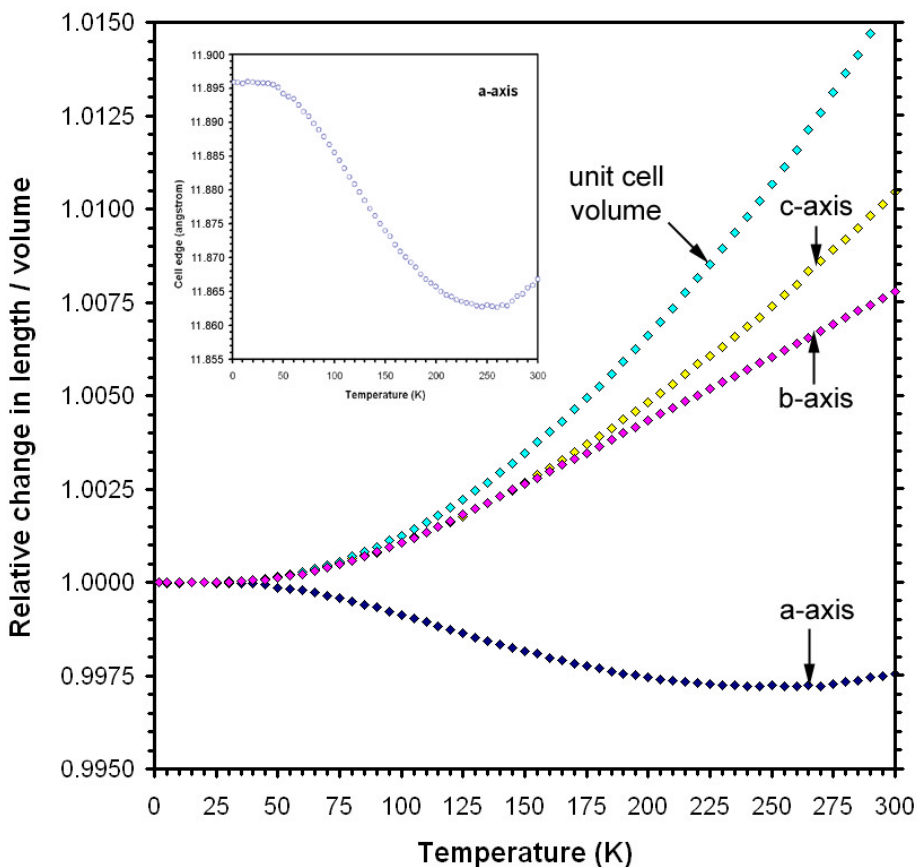

Figure 2. The relative change in length of the unit cell edges (i.e., a / a_0, b / b_0, c / c_0) and volume (V / V_0) in deutero-epsomite from 1.8 − 300 K. The inset shows the absolute change in the length of the a-axis over the same temperature range.