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Phase behaviour of methane clathrate under conditions relevant to Titan's interior

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1. Introduction

Microporous gas hydrates – known as clathrates – are common on the Earth and are also thought to be abundant in the outer Solar System [1]. The conditions for the existence of clathrates prevail throughout the Solar System and they are considered to be abundant from the Martian permafrost to the surfaces and interiors of many icy satellites [7]. These materials have been extensively studied in the range 0 – 5 GPa at ambient temperatures [2-5]; however, their behaviour in the range close to the dissociation (or melting) point is not well known at all, with some suggesting the occurrence of a face-centred cubic (sII) phase, and others that the clathrate becomes unstable with respect to mixtures of solid methane and ice. The high-pressure behaviour underpins planetary modelling; for example, the behaviour of methane hydrate in the ranges 0–6 GPa and 100–400 K is crucial to accurate modelling of Saturn's largest moon, Titan where clathrates are hypothesised to be the source of CH_4 in Titan's atmosphere [6].

In order to address these problems we are carrying out a program of investigation using neutron diffraction to investigate the phase behaviour of methane clathrate close to its dissociation temperature in the 0.6–2.5 GPa region. Our goals were to obtain data to provide the first *in-situ* diffraction-based evidence for the phase behaviour of methane clathrate near to its high-pressure dissociation temperature (along with a control measurement at room temperature for comparison with other workers), to obtain P-V curves along two isotherms for each of the phases observed, and to complete structure refinements of all three clathrate polymorphs, thereby allowing us to carry out a full audit of the methane concentration in each phase as a function of pressure (including cage occupancies).

Thus far we have successfully completed our RT measurements and will make the higher temperature observations in July 2013; we anticipate being able to report our findings from this second experimental run at the EPSC.

2. Experimental

Methane clathrate (deuterated so as to satisfy the requirements of the neutron scattering measurements) was prepared in a steel pressure vessel by exposing frozen D_2O powder to ~ 122 bar of CD_4 gas at −10°C for five months. This was extracted under liquid nitrogen, powdered, and loaded into a Paris-Edinburgh opposed anvil press. Once sealed under load, the mixture was warmed until it completely melted, and was subsequently re-crystallised *in situ* by increasing the load into the stability field of the sI methane clathrate. A phase-pure specimen in equilibrium with fluid was thereby obtained and neutron powder diffraction data were measured on increasing load (at RT).

3. Figures

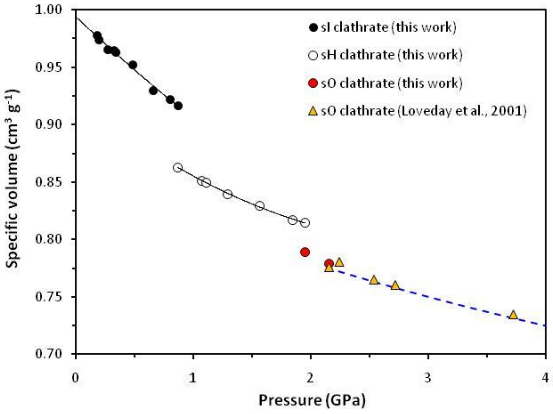

Figure 1. P-V curve obtained in this work along the room-temperature isotherm. Solid lines are equations of state fitted to our observations and the dashed line is an equation of state fitted to the data of Ref [3].

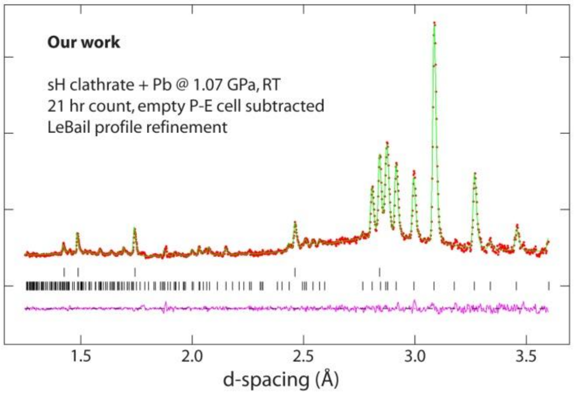

Figure 2. Neutron powder diffraction pattern of the sH clathrate; filled red circles are the measurements and the green line is a structural model fitted to the data (the difference is shown by the pink line underneath). Vertical tick marks indicate the positions of Bragg peaks from the Pb pressure marker (top) and from the clathrate (bottom). Compare these data with Figure 3 in Ref. [8].

4. Results

During our room-temperature compression we found the expected series of phase transitions, from sI → sH at 0.87 GPa and sH → sO at 1.96 GPa (Fig. 1); in both cases we observed phase co-existence. Importantly, we initially formed sH clathrate *without* ice VI, the water evolved during the phase transition remaining liquid. This allowed us to collect a very high quality dataset from phase-pure sH clathrate in the absence of contaminant ice peaks (Fig. 2). Ice VI crystallised subsequently, at 1.3 GPa, and remained present after the transition from sH to sO. At 2.16 GPa, the specimen was warmed in an effort to melt the accessory ice VI and a small amount of solid methane, thus leaving sO clathrate + liquid. This was only achieved after reaching 380 K and then reducing the pressure slowly to 2.3 GPa). A final low-noise dataset was acquired from the specimen of sO clathrate + liquid. In addition to the RT compression curve (specific volume against pressure, shown in Fig. 1), we are presently working on complete structure refinements of all three clathrate polymorphs, thereby allowing us to carry out a full audit of the methane concentration in each phase as a function of pressure (including cage occupancies), something which was not done in recent work by others [8].

It is important to observe that, upon decompression at 370 K, we found the sO clathrate co-existing with liquid; we did not observe any breakdown to solid methane and ice. The diffraction data permit no ambiguity in this observation, which agrees perfectly with the work of Kurnosov et al [2]. Nevertheless, we will return to this region of the phase diagram in our second experimental run and will report on the reproducibility of our observations.

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