

PHASE BEHAVIOUR OF METHANE HYDRATE UNDER CONDITIONS RELEVANT TO TITAN'S

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Introduction: Clathrate hydrates are common on the Earth and are also thought to be abundant in the outer Solar System [1-2]. Clathrates have been extensively studied in the range 0 – 80 GPa, principally at ambient temperatures [3]; however, the behaviour of methane clathrate at pressures and temperatures thought to reflect the interior of the larger icy satellites (i.e., close to their dissociation point) have not been examined in detail and there are some outstanding questions. High-pressure behaviour underpins planetary modelling efforts; for example, the behaviour of methane hydrate in the ranges 0 – 5 GPa and 100 – 500 K is crucial to models of Saturn's largest moon, Titan, where clathrates are hypothesised to be the source of the dense N₂, CH₄ atmosphere [4]. To address these, we carried out a series of experiments using the PEARL high-pressure neutron diffraction instrument at the ISIS facility of the STFC Rutherford Appleton laboratory near Oxford, UK. This contribution presents the results of our findings.

Experimental Method: Methane clathrate (deuterated so as to satisfy the requirements of the neutron scattering measurements) was prepared in a steel pressure vessel by exposing frozen D₂O powder to ~ 122 bar of CD₄ gas at -10°C for five months. Once sealed under load, the sample was loaded into a null-scattering gasket of a Paris-Edinburgh press, and subsequently transferred into its loading cradle and hoisted into position in the PEARL beamline. The sample was subjected to increasing loads firstly at room temperature and in subsequent loadings at elevated temperatures, approaching 400 K. The diffraction data obtained were exported as GSAS-format raw files for Rietveld refinement and analysis [5].

Results: This neutron powder diffraction study has provided *in-situ* diffraction based evidence for the phase behaviour of methane clathrate near to its high-pressure dissociation temperature, and the first direct measurement of the melting point of structure sO methane clathrate. The sequence of phase changes observed along the room-temperature isotherm agree well with expectations based on previous studies. We observed that upon compression, the primitive-cubic structure I (sI methane clathrate transforms to the hexagonal structure H (sH) phase at ~0.870 GPa, and then

at ~1.955 GPa, transforms to an orthorhombic “filled ice” structure, dubbed sO. In each transition, high-pressure ice (phases VI and VII were exsolved as the residual hydrate became more concentrated in methane. The data obtained were also used to find the bulk and axial incompressibilities of each phase, and the volume change at each phase transition.

More interestingly, at temperatures close to the dissociation curve, we observed some new behaviour. In particular, a mixture of sH clathrate + ice VI compressed at 325 K underwent partial melting of the clathrate component when compressed above 1.64 GPa. This suggests a downward curvature of the sH dissociation line above ~ 1.5 GPa such that it intersects the melting curve of ice VI. That there is a region where ice is stable and methane clathrate is not has implications for the release of methane from the deep mantle of a large icy satellite.

By contrast, the melting curve of sO clathrate must be above the melting line of ice VII since we observe sO clathrate co-existing with liquid at 2.3 GPa, 370 K.

An outline phase diagram illustrating these results will be presented.

References: [1] Fortes A.D. and Choukroun, M. *Space Sci. Rev.* 153(1-4), 185-218, 2010. [2] Mousis, O., et al. *Faraday Discuss.* 147, 509–525, 2010. [3] Loveday, J.S. et al. *Phys. Chem. Chem. Phys.* 10, 937-950, 2008. [4] Loveday, J. S., et al. *Can. J. Phys.* 81, 539-544, 2003. [5] Larsen, A. C. and Von Dreele, R.B. Los Alamos National Laboratory Report No. LAUR 86-748, Los Alamos, New Mexico, 2000