

**THERMAL EXPANSION AND PHASE CHANGES IN METHANE AND NITROGEN AT PLUTO TEMPERATURES.** H.E.A.Brand<sup>1</sup> and H.E. Maynard-Casely<sup>2</sup>, <sup>1</sup>Australian Synchrotron, 800 Blackburn Rd., Clayton, Victoria, 3168, helen.brand@synchrotron.org.au <sup>2</sup>Australian Centre for Neutron Scattering, ANSTO, Lucas Heights, Locked Bag 2001, Kirawee 2232, Australia.

### Introduction:

Some of the most striking images from the New Horizons fly-by of Pluto were of the towering mountains surrounded by seemingly flowing glacial terrain (Figure 1) [1]. The explanation for this terrain has its basis in crystallography, where at 44 K the strength of the hydrogen bond endows water ice with the resilience to build such mountains, while the rotational disorder in the solid structure of methane [2] and nitrogen [3] allow these materials to flow plastically even at 44K. These interpretations have been strengthened by the spectral observations that correlate these materials to the respective terrains [4].

In order to undertake accurate modelling of the geological features on Pluto the physical properties of the constituent materials must be well constrained. There is much still to be understood about the interactions and structural behaviours at these frigid temperatures, and crystallographic investigations can play a vital role in characterising these.

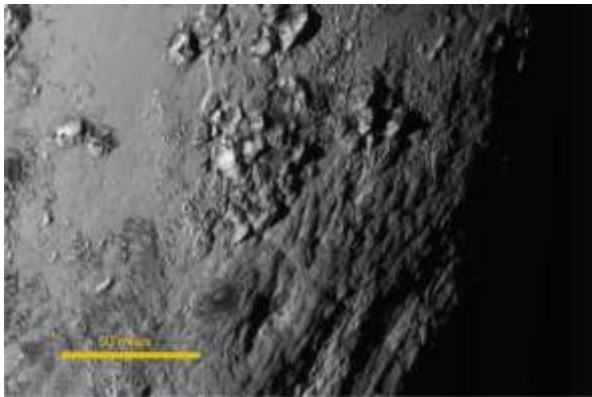


Figure 1 - Close-up images near Pluto's equator taken by the New Horizons spacecraft, showing mountains thought to be composed of water ice rising 3,500 meters above seemingly flowing glaciers of nitrogen and methane. Image credit: NASA, John Hopkins University Applied Physics Laboratory and Southwest Research Institute.

Although water-ice has been the subject of intensive laboratory studies, the same cannot be said of methane and nitrogen. The thermal

expansions of these materials have been investigated [5], but only to a lowest temperature of 40 K and using techniques which were largely insensitive to, in particular, the hydrogen positions within methane.

Thus, the aim of the experiments reported here is to investigate the structures of the phases formed and determine the thermal expansion of methane and nitrogen over temperatures relevant to Plutonian processes using neutron diffraction.

### Experimental method:

The lack of form factor upon neutron diffraction measurements (which is a constraint upon x-ray diffraction) allows the accurate characterisation of anisotropic structural effects and volume changes through phase transitions. Despite the large incoherent scattering from hydrogen, the methane experiment persisted in the use of hydrogenous methane (rather than substituting for deuterated methane), as it has been noted that the phases transition temperatures differ between these forms. Methane and nitrogen gas were condensed to liquids within a vanadium can, mounted in an orange cryofurnace on the WOMBAT high intensity powder diffraction instrument at the Australian Centre for Neutron Scattering. The samples were then cooled to 6 K (nitrogen) and 8 K (methane), and diffraction data collected in 2 K increments to 78 K (for nitrogen) and 92 K (for methane). Data were collected for 1 hour per pattern for CH<sub>4</sub> and 15 minutes per pattern for N<sub>2</sub>.

### Preliminary results and discussion:

Nitrogen and methane both exhibit structural changes between 20 and 40 K. Methane was known to have two cubic structure forms (phase I and II) in the temperature range studied, we observe the II – I transition at 22 K, Figure 2, which shows the volume – temperature relationship for methane.

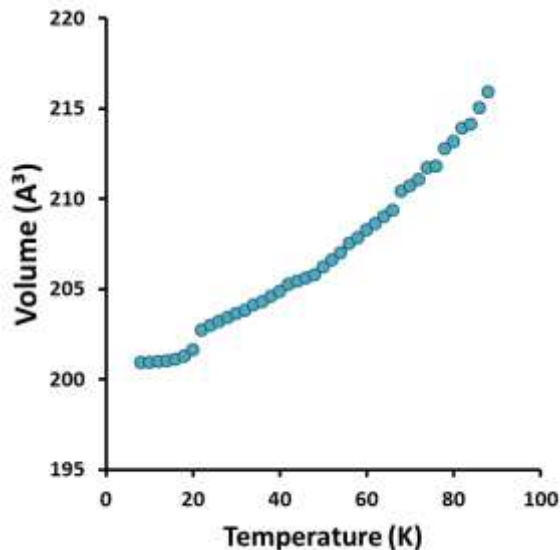


Figure 2. Unit-cell volume expansion of methane with temperature from 6 – 90K.

Nitrogen also is known to undertake two forms at low temperature (cubic  $\alpha$  phase and hexagonal  $\beta$  phase). Figure 3 shows the diffraction of nitrogen between 6 and 70 K. There is a very obvious phase change at 38K where we observe the  $\alpha$  to  $\beta$  transition. This represents a significant density (figure 4) and relative volume change.

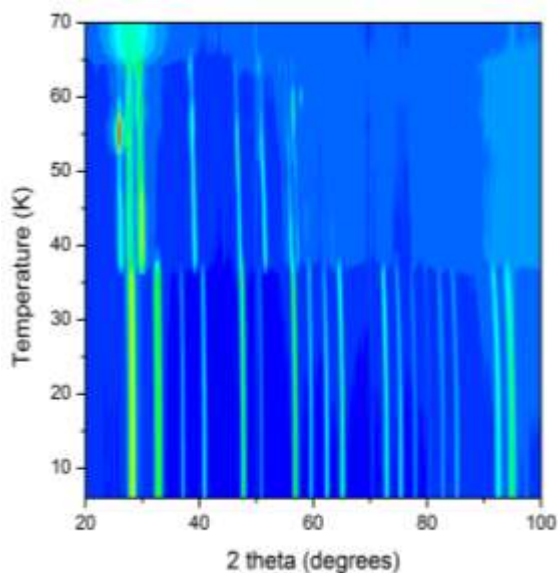


Figure 3 – Thermodiffractogram of nitrogen upon heating from 6- 70K. This shows the expansion of the materials as well as the  $\alpha$  to  $\beta$  phase change at 38 K.

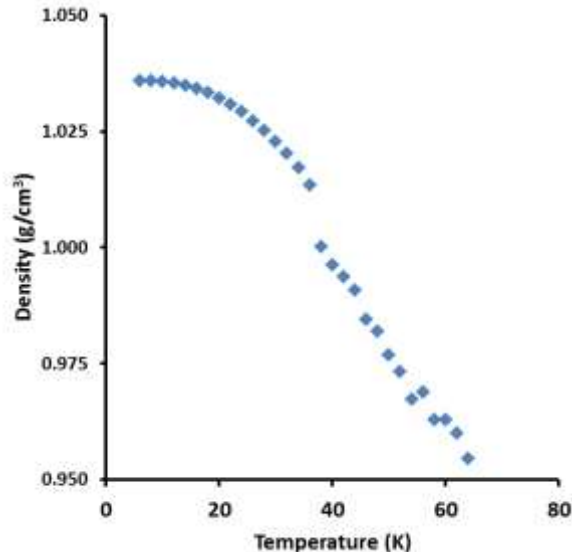


Figure 4. Density changes with temperature for N<sub>2</sub>.

This phase change in nitrogen is particularly interesting for plutonian studies as it is within the range of surface temperature variation on Pluto. This has implications for weathering processes which may be catalyzed by a volume change process, much like freeze-thaw weathering on Earth but in the solid state. Additionally, as can be seen in Figure 3, we observed significant changes in the preferred orientation of solid nitrogen with temperature – an observation we wish to pursue further.

We will present the structural details of these transformations, as well as the coefficients of thermal expansion and their consequences for the terrain and processes on Pluto.

**References:** [1]. Moore, J.M., et al., *Science*, 2016. 351(6279): p. 1284-1293. [2]. Press, W., *Journal of Chemical Physics*, 1972. 56: p. 2597. [3]. Press, W., B. Janik, and H. Grimm, *Zeitschrift für Physik B Condensed Matter*, 1982. 49(1): p. 9-16. [4]. Grundy, W., et al., *Science*, 2016. 351(6279): p. aad9189. [5]. Heberlein, D., E. Adams, and T. Scott, *Journal of Low Temperature Physics*, 1970. 2(3): p. 449-463.

#### Acknowledgements

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