

**Wednesday 10 July 2013, Moorfoot & Kilsyth Rooms, 11:00-13:00**

**Geosciences and extreme conditions I - Molecular systems**

## **Putting the squeeze on energetic materials - high-pressure neutron diffraction studies of a melt-cast explosive**

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2,4-dinitroanisole (DNAN) is an energetic material, developed as an insensitive replacement for TNT in melt-cast explosive formulations. While DNAN-based formulations demonstrate greatly reduced sensitivity to accidental initiation compared to those using TNT, issues remain with the replacement of TNT with DNAN. For instance, DNAN-based formulations have demonstrated catastrophic levels of irreversible growth during heat-cycling, with volume increases of up to 15% reported.

In order to investigate the role of polymorphism in the irreversible growth of DNAN, high-pressure and variable-temperature neutron and x-ray diffraction studies have been performed. The phase diagrams of both form-I and -II of DNAN have been explored for the first time.

In the case of DNAN-II, two high-pressure phase transitions were found, one above 0.16 GPa (DNAN-III) and the second above 3.4 GPa (DNAN-IV). No further phase transitions were noted up to 5.88 GPa. In addition, variable temperature studies demonstrated that the DNAN-II to DNAN-III transition also occurs when DNAN-II is cooled below 267 K. The thermal expansion of the DNAN-II/III lattice was investigated from 150 K to 363 K, demonstrating that an abrupt change in the thermal behaviour of lattice parameters occurs at the DNAN-II/III transition. From these combined crystallographic studies, the structure of DNAN-III has been solved, showing it is closely related to DNAN-II. A DNAN-I/III transition was not found during variable temperature studies on DNAN-I, as may be expected given the dissimilarity between the DNAN-I and DNAN-II structures. The role of polymorphic transitions in the melt-cast processing of DNAN will also be discussed.

## **The structure of ice VII on the approach to symmetrisation (first neutron diffraction measurements up to 80 GPa)**

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The symmetrisation of the hydrogen bonds in water was first speculated on in 1964 by Kamb and Davis [1] and investigated theoretically in 1972 by Holtzapfel [2], who used a simple double-Morse potential model. In subsequent decades, the formation of ice X, as symmetric ice came to be known, has been extensively studied. Neutron-diffraction studies of deuterated ice D<sub>2</sub>O [3,4] are particularly useful in characterising structure, as they yield the only direct measurements of the proton (deuteron) density distribution. However, to date, the maximum accessible pressures (<30 GPa) for such measurements have confined these studies to a regime where the water molecule geometry remains essentially unchanged from ambient pressure[4].

Here, we present the implementation of diamond-anvil-cells for neutron powder diffraction at the Spallation Neutron Source, Oak Ridge TN. This new capability permits routine structural measurements up to 80 GPa. We will show data on crystalline D<sub>2</sub>O up to these pressures, approaching the symmetrisation transition. Our refinements show the first direct structural measurements of the structure in ice under these conditions. The details of this behaviour will be presented as will the new cell designs that have permitted the measurement of refinable neutron powder data in this new high-pressure regime.

[1] B. Kamb & B.L. Davis PNAS 52 1433 (1964).

[2] W.B. Holtzapfel J. Chem Phys 56, 712 (1972).

[3] W.F. Kuhs J. Chem. Phys. 81 3612 (1984). 4.R.J. Nelmes et al Phys. Rev. Lett. 81 2719 (1998).

**(invited) The polymorphism of ice**

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The water molecule is one of the most abundant molecular species in the universe, and it is of fundamental importance across the natural sciences. In fact, the water / ice system has been a pioneer for research into important phenomena such as high-pressure polymorphism, pressure-induced amorphisation, negative thermal expansion and polyamorphism.

This talk gives an overview of our recent efforts exploring the phase diagram of ice. This includes the discovery of three new antiferroelectric phases of ice, which we named ices XIII, XIV and XV. Furthermore, the structure of the 'ordinary' ice, hexagonal ice I, is investigated using total scattering techniques, and methods for quantifying stacking disorder in ice I are presented. New structure – spectroscopy correlations, which may be relevant for hydrogen-bonded materials in general, are introduced. To conclude, the effects of stacking disorder on the shapes of snowflakes are discussed.

**Translational and rotational diffusion in water in the GPa range**

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Water has been systematically investigated since centuries and essentially all its properties have been measured with high accuracy at ambient conditions [1]. However, the development of new techniques and methodologies allowing to investigate water in unexplored conditions constantly feeds with new results the debate on water properties and discloses new routes for the understanding of its uniqueness.

We recently developed a new setup for the Paris-Edinburg (PE) press that allows measuring hydrogenated liquid diffusion and molecular reorientation by quasi-elastic neutron scattering in the GPa range (up to 5 GPa), i.e. one order of magnitude higher pressures than what possible up to present. The diffusion of water in the GPa-range is, crucial for a variety of scientific issues in natural sciences spanning from problems relevant for volcanology and environment, to models of water in planetary interiors [2].

Here we present the first measurements of the translational and rotational diffusion coefficient of water at high temperature (400K) as a function of pressure, up to the melting point of ice VII. We show that under these extreme conditions new and unexpected effects emerge and that high temperature dense water does not behave as a simple liquid [3].

- [1] Water: A Comprehensive Treatise, ed. F. Franks (Plenum, New York, 1972), Vol. 1, Chap. 12.
- [2] C. Cavazzoni et al., Science 283 (1999),44 - 46.
- [3] L.E. Bove et al., Science (2013), submitted.

## Structural phase transitions in sodium niobate with temperature and pressure by powder neutron diffraction

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NaNbO<sub>3</sub> exhibits unusual complex sequence of structural phase transitions, which are not clearly understood. We review our systematic neutron diffraction measurements as a function of temperature (T=15 K to 1075 K at P=0) and pressure (up to 11 GPa at T= 300 K) to study the structures and understand the phase transitions. On lowering the temperature from 1075 K, we observe successive transitions from cubic to tetragonal (T<sub>2</sub>), and to orthorhombic (T<sub>1</sub>) phases as a result of the condensation of zone boundary M and R point instabilities, respectively. Further, on lowering the temperature, we find orthorhombic S (<795 K), R (<755 K) and P (<680 K) phases that are linked to freezing of zone boundary phonons along the line T with (q= ½, ½, g) with g = 1/12, 1/6 and ¼ respectively [Phys. Rev B 83, 134105 (2011)]. Below 300 K, we find unambiguous experimental evidence for coexisting ferroelectric phase with an antiferroelectric phase over a wide range of temperature [Phys. Rev B 76, 024110 (2007)]. Based on our detailed temperature dependent neutron diffraction studies, the phase diagram of sodium niobate is presented that resolves existing ambiguities in the literature about different structures. The high pressure measurements carried out up to 11 GPa at ambient temperature indicate transition from Pbcm to Pbnm phase [Appl. Phys. Lett. 101, 242907 (2012)]. These transitions are characterized by appearance and disappearance of superlattice reflections in the powder diffraction patterns.

## Specific features of detonation nanodiamonds by small-angle neutron scattering

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Detonation nanodiamonds (DND), ultra-fine single crystals of cubic diamond with a diameter of 4-5 nm (X-ray diffraction data) formed during an explosion of oxygen-imbalanced explosives, represent a highly attractive material in nanotechnology including biomedical applications. The paper summarizes the applications of small-angle neutron scattering (SANS) in the structural characterization of DND with respect to various levels of their organization both in powders and liquid dispersions, where they form different kinds of aggregates because of the extremely high specific surface area. In addition to the previous results [1,2] it has been shown that the basic units of DND reveal a complex inner structure comprising a spatial diffusive transition from the diamond state of carbon in the crystalline bulk to its graphitic-like state at the surface. The continuous radial density profile over the whole particle volume conforming to a simple power law has been proposed to describe this transition. A theory of the small-angle scattering combining the diffusive properties of the DND particles and their polydispersity has been developed and experimentally tested. Besides branched clusters (fractal dimension ~2.3, size above 100 nm) formed in colloidal DND solutions a fraction of compact and comparatively small aggregates (size ~10 nm) has been revealed. Its extraction and re-dispergation make it possible to achieve highly concentrated (up to 20 wt. %) and at the same time stable solutions. [1] W. Miiller et al., J. Am. Chem. Soc. 134, 3265 (2012).

[1] M.V.Avdeev, V.L.Aksenov, L.Rosta, Diamond Related Matter. 16 (2007) 2050

[2] M.V.Avdeev, N.N.Rozhkova, V.L.Aksenov, V.M.Garamus, R.Willumeit, E.Osawa, J. Phys. Chem. C 113 (2009) 9473