

**P.20.03.25***Acta Cryst.* (2005). A61, C468**High Pressure Studies of Molecular Systems at the ESRF**Iain D. H. Oswald, Mohamed Mezouar, *European Synchrotron Radiation Facility, Grenoble, France*. E-mail: oswald@esrf.fr

High-pressure has been shown to be a powerful tool for the study of polymorphism in molecular systems, and the effect of pressure on soft organic systems is an area of great current scientific interest (Boldyreva [1], Oswald *et al.* [2]). Most of the research performed at the high-pressure beamline at the ESRF (ID30/ID27), however, has been confined to characterization of hard materials. Recent studies by Fourme *et al.* [3] have successfully used ID30 to probe the effects of pressure on biological systems. The study of small molecules at high pressure acts as an ideal bridge between these two very different areas of research.

This paper describes structural studies of molecular systems performed at the ESRF on ID27. Gas-driven membrane diamond anvil cells (mDAC) were used to perform the experiments at high pressure and high temperature. The facilities available to the user at ID27 allow both single-crystal and powder diffraction to be used. This is a great advantage for the study of molecular solids since many of these systems undergo destructive phase transitions. The ability change collection strategy from single crystal diffraction studies to powder studies whilst the sample is still *in situ* allows the user to continue the study to higher pressure despite the deterioration of the crystal.

[1] Boldyreva E.V., *J. Mol. Struct.*, 2004, **700**, 151. [2] Oswald I.D.H., Allan D.R., Day G.M., Motherwell W.D.S., Parsons S., *Cryst. Growth & Des.*, 2005, *in press*. [3] Fourme R., Kahn R., Mezouar M., Girard E., Hoerentrup C., Prangé T., Ascone I., *J. Synchrotron Rad.*, 2001, **8**, 1149.

**Keywords:** high pressure, molecular systems, synchrotron radiation

**P.20.04.1***Acta Cryst.* (2005). A61, C468**"Poor-men" High Pressure Cell for Single Crystal X-ray Crystallography**Dmitry S. Yufit, Judith A. K. Howard, *Department of Chemistry, University of Durham, Durham, DH1 3LE, UK*. E-mail: d.s.yufit@durham.ac.uk

A simple "moderate-high" pressure cell for single crystal X-ray crystallography at the pressure up to 1KBar has been developed. The simple design provides good visibility of the crystal during the data collection, straightforward optical alignment, easily controllable pressure, no blind areas for X-rays and simple loading procedure. The cell can be used for studying crystals under gas as well as hydrostatic pressure. The crystal is placed in the quartz capillary, connected by a quartz-metal seal to the specially modified high pressure valve. A special attachment for the cell mounting on a goniometer of Bruker CCD diffractometer has been designed and unusual data collection procedure has been developed. Our experience in operating the cell, potential pitfalls and possible future applications of the new cell and data collection mode will be described. The cell has been tested with several molecular organic crystals and the results of the tests will be presented.

**Keywords:** high-pressure crystallography, data collection method, pressure cell

**P.20.06.1***Acta Cryst.* (2005). A61, C468**The Effect of High Pressure on the Topology of Organic Systems**Peter A. Wood<sup>a</sup>, Simon Parsons<sup>a</sup>, Elna Pidcock<sup>b</sup>, <sup>a</sup>*Department of Chemistry, University of Edinburgh, Edinburgh, UK*. <sup>b</sup>*Cambridge Crystallographic Data Centre, Cambridge, UK*. E-mail: p.a.wood@sms.ed.ac.uk

The effect of high pressure on a crystal structure is dependent on the delicate balance of forces. Recent work has shown that in many cases the application of high pressure has the effect of compressing a structure anisotropically. This is exemplified by alanine [1], which

compresses significantly in the b and c directions, but only slightly in the a-direction.

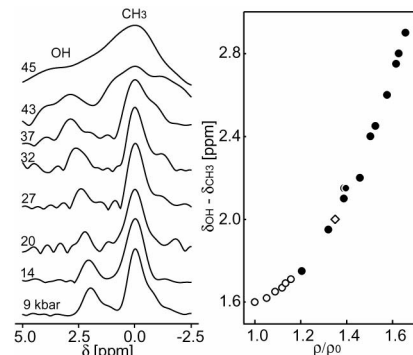
There are a range of methods for analysing the change in structure due to pressure, one which gives a useful overall picture of the molecular symmetry works by partitioning the structure into Voronoi-Dirichlet polyhedra (VDPs) [2]. It is often the case that the application of hydrostatic pressure causes the structure to become more locally symmetric. Using these VDPs it is possible to see structures tend towards standard hard-sphere packing structures such as BCC, FCC and HCP as the pressure is increased.

[1] Dawson A., *PhD Thesis*, The University of Edinburgh, 2003. [2] Blatov V. A., Shevchenko A. P., Serezhkin V. N., *J. Appl. Cryst.*, 1999, **32**, 377.

**Keywords:** high pressure, small-molecule crystallography, crown ethers

**P.20.06.2***Acta Cryst.* (2005). A61, C468**Hydrogen Bonding and Dynamics of Methanol by High-pressure Diamond Anvil Cell NMR**Takuo Okuchi, George D. Cody, Ho-kwang Mao, Russell J. Hemley, *Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*. E-mail: t.okuchi@gl.ciw.edu

Liquid methanol at densities up to  $\bar{n}/\bar{n}_0 = 1.7$  was studied by NMR with a specially designed diamond anvil cell and radio frequency probe [1-2]. Methyl and hydroxyl resonances have been separately observed at pressures to 43 kbar which exceeds equilibrium freezing pressure of methanol. The chemical shift difference between methyl and hydroxyl protons increases nonlinearly with increasing density, indicating an accelerative decrease in hydrogen bond length (Figure). Analysis of spin-lattice relaxation rates of hydroxyl and methyl protons indicates that compression enhances intermolecular proton exchange and selectively reduces motion of the hydroxyl protons. Collectively these observations reveal that hydrogen bonding interaction in liquid methanol increases significantly with compression, inhibiting the liquid-solid transition even above the freezing pressure.



[1] Okuchi T., *Phys. Earth Planet. Inter.* 2004, **143-144**, 611. [2] Okuchi T., Hemley R.J., Mao H.K., *Rev. Sci. Instrum.* 2005, **76**, 026111.

**Keywords:** methanol, NMR, high pressure

**P.20.06.3***Acta Cryst.* (2005). A61, C468-C469**Structural Relationships between Amorphous Ices at High Pressure**John Stephen Loveday<sup>1</sup>, R.J. Nelmes<sup>1</sup>, M. Guthrie<sup>1</sup>, C.L. Bull<sup>1</sup>, T. Strässle<sup>2</sup>, S. Klotz<sup>2</sup>, G. Hamel<sup>2</sup>, <sup>1</sup>*School of Physics & Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, UK*. <sup>2</sup>*Physique des Milieux Condensés, Université P et M Curie, 4 Place Jussieu, 75252 Paris, France*. E-mail: j.loveday@ed.ac.uk

The various forms of amorphous ice provide the principal experimental tests of the proposal that supercooled liquid water undergoes a first order liquid-liquid transition at pressure [1]. Up to now most experimental studies of these amorphous ices have been performed at ambient pressure on quench recovered samples and results have proved inconclusive and in any case do not probe the pressure range of the proposed transition. We present *in-situ* neutron diffraction studies of the various forms of amorphous ice which provide for the first time and accurate view of the relationships between the phases.

[1] Poole H., Sciortino F., Essmann U., Stanley H.E., *Nature*, 1992, **360**, 324-328.

**Keywords:** high pressure, neutron diffraction, amorphous ice

#### P.20.07.1

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#### High-Temperature X-ray Study of Zn-substituted $\text{Cu}_2\text{V}_2\text{O}_7$

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A room temperature X-ray study has been performed on the Zn-substituted  $\beta\text{-Cu}_2\text{V}_2\text{O}_7$  [1, 2], however no study of the  $\text{Cu}_2\text{V}_2\text{O}_7$  -  $\text{Zn}_2\text{V}_2\text{O}_7$  solid solutions has been yet done under high temperature *in situ*. Such studies are important as there are two known polymorphs of  $\text{Zn}_2\text{V}_2\text{O}_7$  and three polymorphs of  $\text{Cu}_2\text{V}_2\text{O}_7$ , both high-temperature modifications ( $\beta'$ - $\text{Zn}_2\text{V}_2\text{O}_7$  [3] and  $\beta'$ - $\text{Cu}_2\text{V}_2\text{O}_7$  [4]) are not retained on quenching at a practicable rate.

High-temperature X-ray analysis of the  $\text{Cu}_{2-x}\text{Zn}_x\text{V}_2\text{O}_7$  solid solutions ( $0 \leq x \leq 0.7$ ) was carried out in the temperature range of 25°-770°C *in situ*. With substitution of Cu by Zn temperatures of the  $\alpha \rightarrow \beta'$  and  $\beta \rightarrow \beta'$  phase transitions decreased, and both phase transitions changed their features and character in comparison with pure  $\text{Cu}_2\text{V}_2\text{O}_7$ .

As the main difference between the  $\beta'$ - $\text{Cu}_2\text{V}_2\text{O}_7$  and  $\beta\text{-Cu}_2\text{V}_2\text{O}_7$  structures involves the V-O-V angle in the  $[\text{V}_2\text{O}_7]^{4-}$  groups decreasing sharply upon quenching, a concentration dependence of structural parameters for both Zn-substituted structures was established and probable cause for the  $\beta' \leftrightarrow \beta$  phase transition was given.

[1] Nord A.G., Stefanidis T., *Mat. Res. Bull.*, 1985, **20**, 845. [2] Schindler M., Hawthorne F.C., *J. Solid State Chem.*, 1999, **146**, 271. [3] Krasnenko T.I., Zubkov V.G., Tyutyunnik A.P., Zolotukhina L.V., Vasyutinskaya E.F., *Crystallography Reports*, 2003, **48**, 35. [4] Petrova S.A., Zakharov R.G., Rotermel M.V., Krasnenko T.I., Vatolin N.A., *Doklady Chemistry*, 2005, **400**, 30.

**Keywords:** vanadates, structural transitions, temperature

#### P.20.07.2

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#### A Furnace for *in situ* Time Resolved Diffraction with Gas Flow

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The understanding of chemical reactions has become a major challenge in the development of new materials and processes, and the improvement of existing industrial processes. *In situ* time resolved diffraction is one obvious solution, and the use of synchrotron sources coupled with outstanding detectors such as RAPID2 [1] allows the collection of refinable patterns in times as short as 1s [2].

In order to observe the reactions in different non-ambient conditions, we designed a furnace able to perform classical temperature dependent experiments, but also allowing a gas to flow through the capillary. This unique design is highly interesting, especially for the study of reactions occurring in the presence of oxidative or reductive conditions (e.g. catalysis). The use of this device and of a synchrotron source was already proven and we were able to observe an oxidation occurring in less than 20s! [3].

The furnace designed for these experiments is slimmer than the length of the capillary, and can reach temperatures up to 950°C. A rotating seal is used for the gas insertion (alternatively it can be connected to a vacuum line). It is fixed on the goniometer allowing the spinning of the capillary. The gas is collected at the other side of the furnace and can be studied with a gas analyzer.

[1] Berry A., Helsby W.I., et al., *Nucl. Instr. Meth. Phys. Res. A*, 2003, **513**, 260. [2] Cernik R.J., Barnes P., et al., *J. Synchrotron Rad.*, 2004, **11**, 163. [3] Jacques S., Leynaud O., et al., *in preparation*.

**Keywords:** *in situ* diffraction, time-resolved, red-ox reactions

#### P.20.08.1

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#### A Parametric Approach to Single Crystal Diffraction Data Analysis

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Snapshots of molecular crystal structures using single crystal diffraction at a single temperature yield a determination that is sufficient for many purposes. However, for systems that are undergoing change, characterisation of the structure at a series of temperatures is vital. There has been a recent increase in the number of such variable temperature studies being undertaken; however, measurements have been traditionally performed at rather few temperatures. There is relatively little evidence to date of single crystal diffraction studies involving the exploitation of data sets of an evolving molecular structure at many temperatures (say, for example, 50-100) in the more parametrically challenging regime.

We have been developing novel ideas regarding both experimental protocol and data analysis which could maximise the information content available from laboratory single crystal X-ray diffraction data. The basic idea behind the approach is that, when analysing variable temperature data, one is not examining sets of unrelated parameters at individual different temperatures, but the evolution of the fundamental parameters throughout the whole experimental period. One can thus treat the data as an ensemble and, by defining the temperature evolution of a parameter by a suitable function, fit all the data simultaneously to a single continuously evolving structural model. The approach will be outlined and selected examples of its application given.

**Keywords:** data analysis, refinement methods, structure analysis

#### P.20.09.1

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#### A Combined Raman-X-ray Powder Diffraction Study at Non-ambient Condition

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Raman spectroscopy can often help to overcome the well-known limitations of X-Ray Powder Diffraction (XRPD) alone by providing additional information on samples containing light elements and/or disordered moieties and/or amorphous phases. We designed and carried out a combined Raman-XRPD *in situ* experiment to exploit the complementarities of the two techniques in investigating the kinetics of a transformation occurring in the solid state at non-ambient conditions. The experimental setup was tested on a simple solid-state to solid-state transformation, consisting in a phase transition occurring at 330K to octakis(isobutyl)-octasilsesquioxane. The crystal structure of the RT phase was solved by single crystal X-Ray diffraction [1], whereas the high temperature (HT) phase was only recently discovered by some of us. The *ab initio* solution of the high T crystal structure was hampered by the poor quality of the 330 K XRPD pattern. Monitoring the transformation simultaneously using the Raman technique combined to XRPD allowed a full structural characterization of the HT phase and in particular:

- i) to understand that the phase transition was strongly correlated to the features of the isobutyl moieties;
- ii) to monitor the possible radiation damage;
- iii) to carefully check the temperature of the system (exploiting the Stokes/anti-Stokes ratio of the Raman bands).

[1] Bassindale, et al., *Dalton Trans.*, 2003, 2945.

**Keywords:** powder diffraction under non-ambient condition, Raman spectroscopy, kinetics