

MS67.28.4*Acta Cryst.* (2005). A61, C87**Anomalous Thermal Expansion in Cyanide-bridged Molecular Framework Materials**Karena W. Chapman, Cameron J. Kepert, *School of Chemistry, University of Sydney*. E-mail: chapmank@chem.usyd.edu.au

We have recently uncovered unprecedented negative thermal expansion (NTE) behaviour in a broad family of molecular framework materials,[1] remarkable in exhibiting coefficients of thermal expansion ($\alpha = d\ell/dT$) up to three times those of known existing materials. The mechanism underlying this unusual phenomenon involved the thermal population of librational modes, which results in a net contraction of non-nearest neighbour bond lengths.

The structural flexibility and control inherent in such molecular frameworks present a unique opportunity to systematically investigate this NTE behaviour and the influences of framework topology, composition and host-guest interactions.

These studies have combined conventional Bragg crystallographic techniques with consideration of diffuse scattering which allow the dynamic aspects of the structure to be probed. These techniques include single crystal x-ray diffraction at laboratory and synchrotron sources, neutron and synchrotron powder diffraction, and total neutron scattering and high energy x-ray scattering for pair distribution function analysis and reverse Monte Carlo modelling.

[1] Goodwin A.L., Kepert C. J., *Phys. Rev. Lett.*, 2005, *submitted*.

Keywords: thermal expansion, lattice vibrations, pair distribution function

MS67.28.5*Acta Cryst.* (2005). A61, C87**In-situ Synchrotron XRD Studies of Combustion Processes**Gilberto Artioli, *Dipartimento di Scienze della Terra, Università di Milano*. E-mail: artioli@iunmix.terra.unimi.it

Synchrotron based diffraction techniques are powerful tools for the characterization of the crystal phases involved in fast chemical reactions. The flexibility of the instrumental setup and the brilliance of the source allow for optimal selection of the experimental parameters, so that reliable structural information can be obtained even on metastable or transient species.

Two in situ experiments were selected, related to the high temperature combustion processes on catalytic materials. In both cases the full-profile analysis of the diffraction data, including cell parameters, phase abundance, peak width, and Rietveld-type structure refinement yield a wealth of information on the reaction mechanisms and kinetics.

In the first case, the burning of the organic template within the cavities of a high-silica MFI zeolites has been followed in situ using the ESRF BM-8 translating image plate [1]. The structural refinements allow quantification of the template occupancy in the channels, and the dimensionality of the diffusion kinetics of the reaction products [2]. In the second case, the combustion of methane over iron oxide catalysts has been followed by coupled XRD and gas MS, gaining insight on the changes taking place in the solid state catalysts during the production of hydrogen [3].

[1] Meneghini C., et al., *Journ. Synch. Rad.*, 2001, **8**, 1162. [2] Milanesio M., et al., *J. Am. Chem. Soc.*, 2003, **125**, 14549. [3] a) Gemmi M., et al., *Journ. Appl. Cryst.*, 2005, *in press*; b) Ghisletti et al., *this conference*.

Keywords: in-situ dynamic XRD, catalysts, reaction kinetics

MS68 LIQUIDS AND AMORPHOUS SYSTEMS AT HIGH PRESSURE**Chairpersons:** Christopher Tulk, Dennis Klug**MS68.28.1***Acta Cryst.* (2005). A61, C87**Intermediate Range Chemical Ordering in H₂O, Si and Ge under Pressure**Chris J. Benmore^a, R.T. Hart^a, Q. Mei^{a,b}, D.L. Price^c, J. Yarger^b, C.A. Tulk^c, D.D. Klug^d, ^a*Argonne National Laboratory, Argonne, IL, 60439 USA*. ^b*University of Wyoming, Department of Chemistry,**Laramie, Wyoming 82071-3838, USA*. ^c*HIFR and SNS project, Oak Ridge National Laboratory, Oak Ridge TN 37831, USA*. ^d*National Research Council of Canada, Ottawa, Ontario K0A 0R6, Canada*. E-mail: benmore@anl.gov.

Neutron and x-ray diffraction data for low, high and very high density amorphous and liquid water, silicon and germanium have been compared in terms of the first sharp diffraction peak in the structure factor and at the radial distribution function level. The low density amorphous and high density liquid forms of water, Si and Ge are shown to have very similar structures if the contributions from the hydrogen correlations in water are neglected. The very high density liquid forms of Si and Ge are also analogous, but differ slightly from amorphous and liquid water by the way in which the interstitial atoms or molecules are pushed into the nearest neighbour shell. Both the low and very high density forms show a higher degree of chemical ordering compared to the high density form.

Keywords: amorphous diffraction, liquid structure, intermediate range order of glasses

MS68.28.2*Acta Cryst.* (2005). A61, C87**Evolution of the Structure of Amorphous Ice - from LDA through HDA to VHDA**Roman Martonak, D. Donadio, M. Parrinello, *Computational Science, Department of Chemistry and Applied Biosciences, ETH Zurich, c/o USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland*. E-mail: martonak@phys.chem.ethz.ch

We report results of molecular dynamics simulations of amorphous ice for pressures up to 22.5 kbar [1,2]. The high-density amorphous ice (HDA) as prepared by pressure-induced amorphization of Ih ice at T=80 K is annealed to T=170 K at various pressures to allow for relaxation. Upon increase of pressure, relaxed amorphous ice undergoes a pronounced change of structure, ranging from the low-density amorphous ice (LDA) at p=0, through a continuum of HDA states to the limiting very high-density amorphous ice (VHDA) regime above 10 kbar. The main part of the overall structural change takes place within the HDA megabasin, which includes a variety of structures with quite different local and medium-range order as well as network topology and spans a broad range of densities. The VHDA represents the limit to densification by adapting the hydrogen-bonded network topology, without creating interpenetrating networks. The connection between structure and metastability of various forms upon decompression and heating is studied and discussed. Comparison with experimental results is presented and some conclusions concerning the relation between amorphous ice and supercooled water are drawn.

[1] Martonak R., Donadio D., Parrinello M., *Phys. Rev. Lett.*, 2004, **92**, 225702. [2] Martonak R., Donadio D., Parrinello M., *J. Chem. Phys.*, *in press*.

Keywords: amorphous solids, water, ice

MS68.28.3*Acta Cryst.* (2005). A61, C87-C88**Structure of High-pressure Liquids: X-ray Diffraction and RMC Modelling**Shinji Kohara^a, Yuichi Akahama^b, Yasuo Ohishi^a, László Temleitner^c, László Pusztai^c, Masaki Takata^a, Haruki Kawamura^b, ^a*Japan Synchrotron Radiation Research Institute, Hyogo, Japan*. ^b*University of Hyogo, Hyogo, Japan*. ^c*Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, Budapest, Hungary*. E-mail: kohara@spring8.or.jp

With the arrival of the latest generation of synchrotron sources and the introduction of advanced insertion devices (wiggler and undulators), the high-energy ($E > 30$ keV) X-ray diffraction technique has become feasible, leading to new approaches in the quantitative study of the structure of simple liquids at high pressure.

We report reliable diffraction data of high-pressure liquids in a diamond anvil cell (DAC), measured at the Spring-8 high-energy X-ray diffraction beamline BL04B2 using 37.6 keV X-rays. Moreover, we performed reverse Monte Carlo modelling [1] to investigate structural modification of the liquids under high pressure. The

resulting large structural models (sets of thousands of atomic coordinates) were subjects of geometrical analyses: distributions of the number of first neighbours, as well as local angular correlations have been calculated. In the cases of molecular liquids investigated (like the case of liquid O₂), correlations between orientations of neighbouring molecules have been characterized.

[1] McGreevy R.L., Pusztai L., *Mol. Simul.*, 1988, **1**, 359.

Keywords: high-pressure X-ray diffraction, diamond anvil cells, computer modelling liquids

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Acta Cryst. (2005). A61, C88

X-ray Diffraction Study in Liquid Cs up to 9.8 GPa

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An x-ray diffraction study of liquid Cs at high pressure and temperature has been conducted in order to characterize the structural changes associated with the complex melting curve and phase transitions observed in the solid phases [1, 2, 3, 4]. At 3.9 GPa a discontinuity in the density of the liquid accompanied by a decrease in the coordination number from about 12 to 8 marks a change between simple and non-simple liquid regime [5].

The specific volume of liquid Cs, combined with structural analysis of the diffraction data, strongly suggest the existence of an electronic hybridization above 3.9 GPa similar to that reported on compression in the crystalline phase.

Further, *ab-initio* calculations with cluster of 264 atoms confirm the structural results obtained experimentally and reinforce the hypothesis of the electronic hybridization driven by compression of the solid and of the liquid.

[1] Kennedy G.C., Jayaraman A., Newton R. C., *Phys. Rev.*, 1962, **126**, 1363.

[2] Jayaraman A., Newton R. C., McDonough J.M., *Phys. Rev.*, 1967, **159**, 527. [3] McMahan A.K., *Phys. Rev. B*, 1984, **29**, R5982. [4] Tsuji K. et al., *J. Non-Cryst. Sol.*, 1990, **117/118**, 72. [5] Falconi S. et al., *Physical Review Letters*, 2005, *in press*.

Keywords: caesium, high pressure, liquids

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CdSb under Pressure: Compound Decomposition, New Phase Formation and Amorphization

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Application of high pressure offers wide possibilities to produce new materials in crystalline and amorphous states. The Cd-Sb alloy system has at ambient pressure one intermediate compound of equiatomic composition, CdSb, orthorhombic, space group *Pbca*, with 16 atoms in the unit cell. On pressure increase to 7.3 GPa, we observed a transition from CdSb-*oP16* phase to a new state that is interpreted as a two-phase mixture of a simple hexagonal Sb-rich phase and a hexagonal close packed phase of (almost pure) Cd. At 8.4 GPa, lattice parameters are for the *sh* phase (space group *P6/mmm*) $a = 3.066(1)$ Å and $c = 2.860(1)$ Å, and for Cd-*hcp* phase (space group *P6₃/mmc*) $a = 2.93(1)$ Å and $c = 5.165(1)$ Å, close to those reported for pure Cd at this pressure. On pressure decrease, the two phase mixture state is observed down to 1 GPa and below 1 GPa, an amorphous phase is observed. The halos of the amorphous phase of CdSb sample correspond to $Q_1 = 2.004$ Å⁻¹ and $Q_2 = 2.953$ Å⁻¹. The full width at half maximum of the halos corresponds to the correlation length 12-15 Å. The amorphous phases formed in binary alloys Zn-Sb, Cd-Sb and Al-Ge after pressure action are close to tetrahedral nets and correspond to nearly 4 el./atom composition [1,2].

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[1] Belash I.T., Degtyareva V.F., Ponyatovskii E.G., Rashchupkin V.I. *Sov. Phys. Solid State*, 1987, **29**, 1028. [2] Degtyareva V.F., Belash I.T., Ponyatovskii E.G. *Phys. Stat. Solidi (a)*, 1991, **124**, 465.

Keywords: high-pressure phases, decomposition, amorphization

MS69 ELECTRON CRYSTALLOGRAPHY ON ORGANIC CRYSTALS AND BIOMOLECULES

Chairpersons: Hans Hebert, Ute Kolb

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Electron Diffraction from a Beam of Laser-aligned Proteins: Progress Report

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The use of diffraction patterns from aligned molecular beams has been proposed as an approach to the structure determination of proteins that are difficult to crystallize [1]. Polarized laser light is used to align the molecules in the beam. By cooling a beam of hydrated proteins to low temperature, sufficient alignment for diffraction purposes might be possible. Therefore an arrangement has been suggested [2] consisting of continuous, orthogonal, intersecting electron (or X-ray), molecular and laser beams. Limited coherence of the electron beam ensures that no interference occurs between the wavefields scattered by different molecules within the electron beam. The diffraction pattern is a sum of the intensities of the identical patterns from the many hydrated molecules within the beam at any one time. The two-dimensional electron diffraction pattern accumulates continuously at the detector for a fixed laser and molecular orientation before being read out. Repeating this process for many orientations would allow tomographic reconstruction of the molecule. An electron diffraction camera with a water droplet source, a polarized laser beam and a LaB₆ electron gun is currently under development. Initially we use micron size water droplets and dope them with large particles like TMV, since they are easier to align. Preliminary results with this instrument will be presented.

[1] Spence J., Doak T., *Phys. Rev. Lett.*, 2004, **92**, 198102–198104. [2] Spence J.C.H., Schmidt K., et al., *Acta Cryst.*, 2005, **A61**, 237–245.

Keywords: electron diffraction, protein structure determination, image reconstruction

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Methods Development and Software Engineering for 2D Electron Crystallography

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Electron crystallography of 2D crystals (2D-EX) of membrane proteins has allowed atomic models of these proteins to be built (1,2). Several advantages of this method over 3D x-ray crystallography can be identified, such as preserving the protein in a more native state or imaging of the crystal with direct amplitude and phase retrieval. Nevertheless, this method has not yet matured to the point of routine use. We pursue the goal to establish 2D-EX membrane protein crystals as a complementary method (next to x-ray crystallography and structural NMR) for resolving atomic resolution structures of biological macromolecules. To this end, we are in the process of implementing and refining the methods utilized by the pioneers of the field (1,2), as well as following novel methodological and algorithmic approaches. In parallel, we are developing an image processing library and toolkit (3), tailored to the specific requirements of these methods.

[1] Henderson R., Baldwin J.M., Ceska T.A., Zemlin F., Beckmann E., Downing K.H., *J. Mol. Biol.*, 1990, **213**, 899. [2] Murata K., Mitsuoaka K., Hirai T., Walz T., Agre P., Heymann J.B., Engel A., Fujiyoshi Y., *Nature*, 2000, **407**, 599. [3] Philippsen A., Schenk A.D., Stahlberg H., Engel A., *J.*