

for biological compounds, such as sugars and polysaccharides. The molecule of EG is a triple rotor about the O-C, C-C and C-O bonds. Following the common assumption that each of the rotors can assume 3 positions, the molecule can exist as $3^3=27$ conformers of which 10 are unique [1]. We have looked at the crystal structures of EG frozen at varied thermodynamical conditions. This study also pertains to a basic problem of the relation between the conformational preferences of isolated molecules and their conformation adopted in the crystalline state [2]. Till now one EG structure crystallized by temperature freezing was determined at 130 K: crystal was orthorhombic, in $P2_12_12_1$ (phase I) with $Z'=1$ [3]. Two new crystal phases of EG have been obtained by *in-situ* pressure-freezing in a Merrill-Bassett DAC [4]. These new crystal structures were solved straightforwardly by direct methods in space group $P2_1$ at 1.2 and 2.0 GPa (phase II), and in space group $Pbcn$ at 2.2 GPa (phase III).

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The structure and nature of ice VII to 20 GPa

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Ice VII has a simple average structure in which the oxygens form a body-centred cubic (bcc) arrangement and the protons are disordered over two off-centre sites in H-bonds that connect the oxygens into two interpenetrating tetrahedral networks. However, there is a complication in that the oxygens are disordered over a number of sites that are displaced $\sim 0.1\text{Å}$ from the mean bcc positions [1]. The protons must also be disordered over several sites around their mean position. The direction of these displacements affects both the number of sites – and hence the number of structural configurations – and the geometry of the H-bonds. Some possible displacement directions would require there to be a range of quite different bondlengths, which could have implications for understanding the bond centring to ice X at much higher pressures. Because of the small magnitude of the displacements, it is difficult to obtain a decisive determination of their direction. But overcoming this problem is crucial to a full understanding of the ice VII phase. There are also other questions about this phase, including the nature of its short-range structure, the possibility of incommensuration [2] and some form of discontinuity around 14 GPa (~ 18 GPa in the deuterated form) [3]. We will report a range of studies, using both neutron and x-ray diffraction techniques, that provide new information on the structural disorder and also on the evidence for or against any change in structure in the range up to 20 GPa.

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High pressure X-ray cell for soft matter

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There is currently high demand for development of techniques that will allow probing of the time-dependent structural behaviour of out-of-equilibrium soft condensed matter systems. An ideal technique for monitoring and triggering the structural evolution of such systems within the millisecond regime is time resolved X-ray diffraction, employing pressure as the triggering variable. Using pressure jumps to trigger structural change has several major advantages over other methods, e.g. temperature jumps: The pressure step propagates at the speed of sound and thermodynamic equilibrium is achieved far more rapidly than the rate of acquisition, bi-directional pressure jumps propagate at the same speed, if structural changes are fully reversible, pressure jumps can be repeated with identical experimental parameters to allow for data averaging, pressure does not normally disrupt intramolecular bonds below 2GPa (20 kbar) While changing pressure is an ideal technique for studying phase changes, it is technically challenging which has limited its use as a common laboratory technique. We have recently used synchrotron light and the pressure jump technique to elucidate and investigate a novel liquid crystalline mesostructure in a hydrated lipid system and are now developing a high performance, robust and user friendly facility for investigation of soft condensed matter systems at high pressure. This facility will be freely available to users at Diamond Light Source and it is hoped that this will allow this highly advantageous technique to become accessible to a much wider section of the community than is currently possible.

Keywords: soft condensed matter, high pressure X-ray diffraction, lipid mesophases

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High-pressure structural studies of pharmaceutical materials

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The phenomenon of polymorphism is of crucial importance to many industries including the pharmaceutical, pigments and energetics industries. Polymorphism is an extremely interesting research topic for the structural scientist, however, the appearance of an unidentified polymorph during the production of an active pharmaceutical ingredient (API) can cause serious problems for both the production and processing of the pharmaceutical. The physical properties of an API e.g. solubility and hence bioavailability can vary dramatically depending on the polymorph that is isolated and so the emergence of a new polymorph requires a cessation of production together with a full investigation of the polymorphism exhibited by the API. For this reason the pharmaceutical industry places great

importance in understanding the polymorphic behaviour of APIs and so employs polymorph screening techniques in an attempt to sample a variety of different crystallization conditions. The large diversity of crystallization conditions provides the pharmaceutical industry with the confidence that all possible polymorphs of an API have been isolated. High-pressure techniques can provide a complementary method for exploring polymorphism and solvate formation in molecular solids. They are particularly useful for the identification and characterization of new forms that do not appear through standard crystallisation techniques such as those employed in conventional polymorph screens performed under ambient conditions. High-pressure methodologies are well-suited for obtaining so-called “disappearing” or elusive polymorphs in a reproducible manner. This presentation will highlight a number of different examples of polymorphism exhibited by pharmaceutical materials when subjected to high pressures.

Keywords: high-pressure crystallography, pharmaceuticals, polymorphism

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Kinetics and mechanisms of pressure-induced phase transitions of ternary model biomembrane systems

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Lipid bilayers, which provide valuable model systems for biomembranes, display a variety of polymorphic phases, depending on their molecular structure and environmental conditions, such as pH, ionic strength, temperature and pressure. By using calorimetric, spectroscopic and diffraction techniques, the temperature and pressure dependent structure and phase behavior of one- and two-component lipid systems, differing in chain configuration and headgroup structure, have been studied in recent years [1-3]. Very little is known about the phase behavior of the biologically more relevant heterogeneous three-component lipid systems, in particular about their kinetic and non-equilibrium behavior. We present data on structural and kinetic aspects of lamellar-to-lamellar lipid bilayer phase transitions of a three-component lipid mixture DOPC:DPPC:cholesterol, which serves as a canonical model raft mixture taking into account the heterogeneity of natural membranes. Applying static synchrotron small-angle x-ray scattering measurements and the pressure-jump relaxation technique in combination with time-resolved measurements (TRSAXS), the various temperature and pressure dependent phases and the kinetics of the lipid phase transformations have been investigated over a temperature range from 10 to 80 °C at pressures from ambient up to 3 kbar (300 MPa). Transitions in both the forward and reverse directions have been measured. The results are discussed in the light of possible kinetic mechanisms and are compared with the results of other lipid mesophase transitions.

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Keywords: lipid phase transitions, TRSAXS, pressure perturbation

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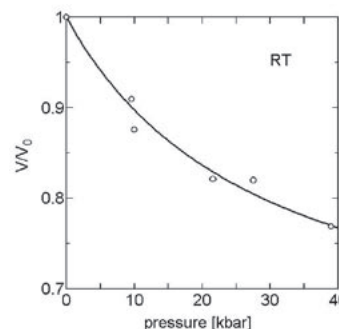
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Equation of state for the low-pressure crystalline phase of tin tetraiodide

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A series of experimental studies on determination of the melting curve of the low-pressure crystalline phase (CP-I) of a molecular crystal tin tetraiodide and its polyamorphism (presented in this congress) has been performed since 2001 onward, utilizing the beam line BL14B1 of SPring-8 in Japan. A multi-anvil press consisted of 6 tungsten carbide anvils with a center flat of 10mm or 6mm was employed to cover a pressure range up to about 6GPa. In situ energy-dispersive synchrotron x-ray diffraction measurements were carried out (refer to Fuchizaki et al., 2004, for details as to the experimental setup). During this period of research sufficient diffraction data for the CP-I structure have been accumulated to construct the equation of state (EOS). In fact, the compression data obtained at room temperature were fitted to corrected second-order Murnaghan's EOS (Fuchizaki, 2006) as depicted in the figure. The bulk modulus and its pressure derivative at ambient conditions turned out to be 7.31GPa and 3.91, respectively. Contribution from the thermal pressure to the EOS will be discussed, together with the results obtained through molecular dynamics simulations.



Keywords: equations of state, high pressure, molecular crystals

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Molecular dynamics simulation study on liquid tin tetraiodide

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Recently, a pressure-induced liquid-to-liquid phase transition has been found in tin tetraiodide (Fuchizaki, presented in this congress). The polyamorphism in this substance, including two solid amorphous states found previously, can be understood in a unified way based on the pseudo-binary regular solution model. The high-pressure amorphous state, which forms beyond ~15GPa on compression at room temperature, was shown to be attained by molecular dissociation, whereas the low-pressure amorphous state consists of randomly oriented molecules. In this context, the high-pressure liquid phase may be attained by polymerization of molecules from the low-pressure molecular liquid state. In order to understand the mechanism of the transition, molecular dynamics simulations were carried out. The molecule was regarded as a rigid tetrahedron. The intermolecular interaction was modeled by van der Waals interactions between