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With the notable exceptions of water, ammonia and a very limited number of other examples, there have been relatively few high-pressure structural studies of simple molecular compounds. Such studies can provide fascinating information about intermolecular interactions and pressure-induced phase transition, in particular hydrogen-bonding interactions. Recent results for thiourea and urea obtained from the experiments on neutron beamlines at the UK ISIS facilities have shown a very rich high-pressure behaviour [1].

In the light of these results, we have undertaken neutron and synchrotron studies on thiourea dioxide, which has been selected by virtue of its interesting ambient pressure structure [2].

We report a phase transition between a powder sample of orthorhombic phase I of thiourea dioxide to a new monoclinic phase II at a pressure of 0.54 GPa. This transition has also been observed in a single crystal sample at a pressure of 0.45 GPa. We also report an unusual isostructural transformation in thiourea dioxide at 6.8 GPa that involves the formation of a new hydrogen bond.

[1] Marshall W.G., *ISIS Annual Report*, 2003. [2] Sullivan R.A.L., Hargreaves A., *Acta Cryst.*, 1962, **15**, 675.

Keywords: polymorphism, high pressure phase transitions, hydrogen bonding polymorphism

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The Effect of Pressure, and Formation of new Polymorphs of the Amino Acids L-cysteine and L-serine

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The application of pressure (<10 GPa) has proved a successful way of probing materials, particularly biologically important building blocks such as amino acids to understand the significance of hydrogen bonding interactions in these simple organic molecules [1].

On application of pressure, even systems comparable to each other have been shown to have remarkably different properties. Orthorhombic L-cysteine and L-serine-I, both of which have similar packing arrangements are examples of this. Under pressure, L-cysteine initially undergoes a much larger reduction in volume than L-serine-I, until at much higher pressure (c.a. 4 GPa) a single-crystal to single-crystal phase transition was observed. L-serine-I also undergoes a similar phase transition (c.a. 5 GPa) [2], however, although both phase transitions in L-serine-I and orthorhombic L-cysteine occur through the compressibility of soft interactions, the resulting high-pressure polymorphs are far different.

Pressure studies between ambient and 10 GPa are not only providing a useful way to investigate polymorphism of materials, but the information obtained on increasing pressure is beginning to give us an appreciation of the compressibility of intermolecular interactions under these pressure.

[1] Dawson A., Allan D.R., Clark S.J., Belmonte S.A., David W.I.F., McGregor P.A., Parsons S., Pulham C.R., Sawyer L., 2005, *accepted for publication*. [2] Moggach S., Morrison C.A., Allan D.R., Parsons S., Sawyer L., *Acta Cryst.*, 2005, **B61**, 58-68.

Keywords: high-pressure, polymorphism, amino acids

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Absence of Halogen Bonding in the High-pressure Structure of Chlorotrimethylsilane

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Halogen...halogen interactions are usually considered as the next most important cohesion forces, apart from the hydrogen bonds, governing the arrangement of molecules in crystals [1]. Such interactions are observed in many compounds containing halogens.

The interactions of one halogen atom with the lone pair of another halogen atom forms intermolecular bridges. The chlorine...chlorine interactions belong to the most fundamental supramolecular synthons [2].

Meanwhile in the structure of chlorotrimethylsilane determined at low temperature [3] no halogen...halogen interactions are observed. Therefore we have undertaken the high-pressure study of this compound to check if short chlorine...chlorine contacts would exist in the compressed crystal. We have determined the crystal structure of chlorotrimethylsilane at 0.3 and 0.6 GPa. At these pressures the crystal is orthorhombic, space group Pmn2₁, whereas the crystal frozen at low temperature crystallized in monoclinic space group P2₁/m. It occurs that also in this new high-pressure phase of C₃H₉ClSi no close chlorine...chlorine contacts are observed.

[1] Metrangolo P., Resnati G., *Chem. Eur. J.*, 2001, **7**, 2511. [2] Bosch E., Barnes C.L., *Cryst. Growth Des.* 2002, **4**, 299. [3] Bushmann J., Lentz D., Luger P., Röttger M., *Acta Cryst.*, 2000, **C56**, 121.

Keywords: weak interactions, high-pressure crystallography, noncovalent bonding

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High-pressure Crystal Phase of 1,2-ethylenediamine

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1,2-Ethylenediamine (H₂N CH₂ CH₂ NH₂) is the simplest of α,ω -alkanediamines. Its m.p. is 284.29 K [1], and it was crystallized at low temperature and its structure determined at 213 K [2] and 130 K [3]. The crystals are monoclinic, space group P2₁/c, $a = 5.047(2)$, $b = 7.14(2)$, $c = 5.475(2)$ and $\beta = 115.36(3)$ [3] (hereafter phase II).

In our study we have crystallized C₂H₈N₂ by pressure-freezing in Merrill-Bassett diamond-anvil cell. In this way three distinct phases of C₂H₈N₂ have been obtained and their structures determined: phase II with the unit cell parameters similar to those listed above for the low-temperature phase; phase I (which is stable at lower pressure and higher temperature, than for phase II) – monoclinic, space group P2₁/c $a = 5.031(10)$, $b = 5.132(3)$, $c = 7.167(5)$, $\beta = 110.60(12)^\circ$ at 0.3 GPa and 293(2) K; at 1.5 GPa the crystal is transformed to phase III with the unit-cell doubled.

The structures have been solved by direct methods and refined by full matrix least squares.

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Keywords: crystal growth, high-pressure structure determination, hydrogen bonds in organic crystals

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Probing Polymorphism with High Pressure

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In recent years, work at Edinburgh has shown that pressure-induced crystallisation of simple organic compounds from the pure liquid results in the generation of new polymorphs [1]. Attempts to induce polymorphism in more complex, higher melting compounds (such as pharmaceuticals) have been much less successful. This is because thermal decomposition usually occurs long before the pressure-elevated melting temperature is reached.

We have instead developed a technique for growing single crystals from solution at high pressure that removes excessively high temperatures and provides an opportunity to study high-pressure crystallisation from different solvent systems [2]. We report how the power of this technique, in combination with ambient-pressure conventional polymorph screening processes, is not only successful in

identifying known polymorphs of organic molecules, but also completely new polymorphs, and solvates, as illustrated by the nootropic drug piracetam, for which new polymorphs and hydrates were prepared and characterised at pressures below 1.0 GPa [3].

We believe that this methodology has the potential to make a significant impact for the discovery of new polymorphs and solvates.

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Complex Structures in Barium at High Pressure

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Barium has a bcc structure at ambient pressure, transforms to an hcp phase II at 5.5 GPa, and then to phase IV at 12 GPa which transforms to another hcp phase at 45 GPa. Phase IV is characterised by complex structures and a number of different forms. IVa, which exists from 12 to 12.5 GPa, was the first example discovered of a composite incommensurate host-guest structure in an element [1]. The structure comprises a 'host' framework, with 8 atoms in a tetragonal unit cell, and chains of 'guest' atoms that lie in channels formed by the host framework. These chains form tetragonal and monoclinic guest structures that are incommensurate with the host along the *c*-axis of the host. Similar composite structures have now been found in Sr, K, Rb, As, Sb and Bi. In barium above 12.5 GPa, there is a IVb form with the same host structure as IVa but with the guest chains forming an orthorhombic structure. There is evidence of further structural changes to a IVc form at ~16 GPa and a IVd form at ~18 GPa [1]. New structural studies have revealed these to have remarkably complex structures.

[1] Nelmes R.J., Allan D.R., McMahon M.I., Belmonte S.A., *Phys. Rev. Letters*, 1999, **83**, 4081.

Keywords: high-pressure crystallography, barium, phase transitions

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Structures and Phase Transitions of CuInSe₂ under High Pressure

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The ternary compound semiconductor CuInSe₂ has a rich variety of potential applications and has stimulated a substantial number of experimental and theoretical studies. In previous high-pressure energy-dispersive powder diffraction studies of this material, the structural phase transition from the tetragonal chalcopyrite phase to the face-centred cubic at 7.6 GPa have been reported [1]. This NaCl-like structure exists up to 29 GPa, the highest pressure obtained in their experiment. We have embarked on a re-examination of the high-pressure structures and transitions in CuInSe₂ using angle-dispersive powder diffraction techniques with the image-plate detector on station 9.1 at the SRS Daresbury Laboratory, U.K. We find the same structural phase transition as has been previously reported up to 29 GPa. On further compression, we have obtained extensive data through a next phase transition at 39.2 GPa. This newly discovered phase has now been identified as an orthorhombic distortion of the NaCl structure. This high pressure phase is stable up to 53.2 GPa, the maximum pressure reached for this experiment.

[1] Tinoco T., Polian A., Gomez D., Itie J.P., *phys. stat. sol. (b)*, 1996, **198**,

433.

Keywords: ternary chalcopyrite, high-pressure X-ray diffraction, diamond anvil cells

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Resolution of the Intermediate High Pressure Phase of PbTe

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The lead chalcogenides PbX (X=Te, Se, S) are narrow-gap semiconductors (group IV-VI), which crystallise at ambient conditions in the cubic NaCl (B1) structure. It has been known for 20 years that they transform at ~3-6 GPa to an intermediate phase, and at higher pressures to the 8-fold coordinated CsCl (B2) structure. There has been much controversy on the crystal structure of the intermediate high pressure phase [1,2,3].

We report recent X-ray powder diffraction obtained at synchrotron sources under pressure, that allowed us to solve the structure of the intermediate phase of PbTe, from simulated annealing techniques and Rietveld refinement: the phase transition at 6 GPa is not to the GeS (B16) or TlI (B33) type structures as previously reported, but to an orthorhombic Pnma structure, with cell parameters *a*=8.157(1), *b*=4.492(1), *c*=6.294(1) Å at 6.7 GPa. This structure corresponds to a distortion of the low pressure NaCl structure with a coordination intermediate between the six-fold B1 and the eightfold B2 structure. These new results may modify the admitted paths of phase transitions between the B1 (NaCl) and B2 (CsCl) structures.

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Keywords: high-pressure structure determination, semiconductor structures, synchrotron powder diffraction

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Structural Study of Solid Mercury at High Pressures

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Liquid mercury solidifies at about 1.2 GPa at room temperature. After solidification, it undergoes several structural phase transitions under high pressure. The highest-pressure \bar{a} -phase with the hcp structure appears above about 37 GPa [1], which is reported to be stable to at least 67 GPa [2]. We have investigated the structural stability of the \bar{a} -phase at ultrahigh pressures.

Angle-dispersive powder x-ray diffraction experiments have been done with the diamond-anvil cell at high pressures at room temperature on the beam line 10 XU at Spring-8. The \bar{a} -phase was found to be stable up to 193 GPa, the highest pressure investigated. The *c/a* axial ratio continuously decreased with pressure from 1.73 at 50 GPa to 1.64 at 193 GPa. The equation of state for the \bar{a} -phase was obtained over the pressure range 50-193 GPa. The bulk modulus and its pressure derivative for the \bar{a} -phase at 50 GPa were determined as 292 GPa and 5.5, respectively.

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Keywords: mercury, high pressure, diamond anvil cells

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High Pressure Effect on Bonding Nature in KMnF₃

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