

FA5-MS07-O1**High-Pressure Studies of Small-Molecule Systems.**

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The revolution in small-molecule single-crystal x-ray diffraction studies brought about by the introduction of CCD area detectors has allowed the routine study of extremely complex molecular systems that would have proved intractable by any other means. With the greater expectation on the level of difficulty of structural problem that can now be tackled successfully, there has been an accompanying increase in the scope of structural work that is now being attempted – from the investigation of the crystal structure itself at fixed conditions to a whole range of parametric studies exploring the response of the structure to an external perturbation: e.g. photo-excitation; the intercalation of gas guest molecules into a host lattice; the response of the structure to an applied magnetic field; and structural change induced by the alteration of thermodynamic variables. While variable temperature studies have been extremely routine for a number of years, it is the use of high pressure that has demonstrated the greatest recent increase in interest. This is due to the development of both data collection and analysis procedures along with improved diamond-anvil cell design, which allow the full advantage of CCD area detectors to be exploited. This greatly increases the scope, and complexity, of structural work that can now be undertaken relatively routinely and makes high-pressure diffraction far more applicable to a whole range of materials of direct interest to the chemical crystallography community. In this talk the development of high-pressure single-crystal x-ray diffraction techniques for CCD area detector diffractometers will be discussed and a number of studies on challenging small-molecule systems will be described.

Keywords: small-molecule; single-crystal; high-pressure

FA5-MS07-O2**Incommensurate Structures in Elements at Megabar Pressures.**

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Since the discovery of the incommensurate host-guest structure under pressure in elemental Ba in 1999 [1], many incommensurate structures have been found in various elements across the periodic table (see [2] and references therein). In this presentation, we review the incommensurate structures found in elements at high pressures and report the details of our recent studies on incommensurately modulated structure in S and a host-guest structure in As. Sulphur becomes metallic and superconducting above 90 GPa with $T_c = 10$ K forming an incommensurately modulated crystal structure at 300 K. By studying the crystal

structure of metallic sulphur at low temperatures close to the superconducting transition, we find a charge-density wave instability, responsible for the structural modulation, to be in competition with the superconducting state [3].

The phase transitions in As are followed with x-ray diffraction on pressure increase from a simple cubic structure to the incommensurate host-guest structure [4] and further to 1 Mbar where As transforms to a body-centered cubic structure. We discuss the reasons for an appearance and stability of such complex structure in a simple element between two very simple cubic structures.

[1] R. J. Nelmes, D. R. Allan, M. I. McMahon, and S. A. Belmonte, *Phys. Rev. Lett.* 83, 4081, 1999. [2] M.I. McMahon, R.J. Nelmes, *Chem. Soc. Rev.* 35 943, 2006. [3] O. Degtyareva et al., *Phys. Rev. Lett.* 99, 155505, 2007. [4] O. Degtyareva, M. I. McMahon, and R. J. Nelmes, *Phys. Rev. B* 70, 184119, 2004.

Keywords: high-pressure phase transitions; powder X-ray diffraction; incommensurate structures

FA5-MS07-O3**Probing Strong and Weak Interactions in Mg(BH₄)₂ and NH₃BH₃ by Diffraction Under High Pressure.**

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We present a structural diversity of two light hydrogen storage materials, Mg(BH₄)₂ and NH₃BH₃, uncovered in high-pressure diffraction experiments. A phase transition in Mg(BH₄)₂ at 1.1-1.6 GPa is accompanied by a volume collapse of more than 20%. The high-pressure phase is stable at ambient conditions; its structure was solved from powder diffraction data in the sp. gr. $P4_2nm$. It represents a new structure type which may be a true ground state of magnesium borohydride. Its structural evolution was studied as a function of pressure and temperature. On heating to 100°C at ambient pressure it transforms back into the alpha-phase. We analyze observed and hypothetical Mg(BH₄)₂ structures, which show nearly two-fold variation of density (d , g/cm³):

- the discovered $P4_2nm$ phase, $d = 0.99$ at ambient conditions;
- alpha-phase ($d = 0.78$), first reported in the sp. gr. $P6_1$ and then revised in $P6_122$ [1]. Its structure contains an unoccupied void, accounting for 6.4% of space;
- beta-phase forms above 180°C and is stable at ambient temperature; its $Fddd$ structure [2] has lower density ($d = 0.76$), but contains no unoccupied voids;
- theoretically predicted highly porous $I-4m2$ and $F222$ ($d = 0.56, 0.54$) and dense $I4_1/amd$ ($d = 1.01$) phases [3, 4].

We identify the following building principles:

- Mg atom coordinates four BH₄ groups via H-B-H edges;
- repulsive interactions define a deformed tetrahedral MgB₄ environment and a set of stable MgH₈ polyhedra;
- the MgH₈ nodes are linked by the linearly-coordinated BH₄ ligands into various framework structures; the frameworks