

**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.

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

**FA5-MS07-O3****Probing Strong and Weak Interactions in  $Mg(BH_4)_2$  and  $NH_3BH_3$  by Diffraction Under High Pressure.**

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We present a structural diversity of two light hydrogen storage materials,  $Mg(BH_4)_2$  and  $NH_3BH_3$ , uncovered in high-pressure diffraction experiments. A phase transition in  $Mg(BH_4)_2$  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  $Mg(BH_4)_2$  structures, which show nearly two-fold variation of density ( $d$ , g/cm<sup>3</sup>):

- 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  $BH_4$  groups via H-B-H edges;
- repulsive interactions define a deformed tetrahedral  $MgB_4$  environment and a set of stable  $MgH_8$  polyhedra;
- the  $MgH_8$  nodes are linked by the linearly-coordinated  $BH_4$  ligands into various framework structures; the frameworks

are similar to the covalently-bonded MOFs, i.e. they can be porous, interpenetrated etc.;

- reconstruction of strongly bound  $\text{Mg}(\text{BH}_4)_2$  coordination frameworks is kinetically hindered, giving rise to a coexistence of various metastable polymorphs.

Structural evolution of ammonia borane  $\text{NH}_3\text{BH}_3$  manifests itself in two phase transitions, below 293 K at ambient pressure and above 1.1 GPa at room temperature, relating a disordered  $I4mm$  structure to the ordered polymorphs with  $Pmn2_1$  and  $Cmc2_1$  structures. The later has been solved from diffraction data, positions of N and B atoms and orientation of  $\text{NH}_3$  and  $\text{BH}_3$  groups were finally assigned with a help of first principles DFT calculations. Group-theoretical analysis identifies a single two-component order parameter, combining ordering and atomic displacement mechanisms and linking the orientationally disordered parent phase  $I4mm$  with three ordered distorted structures. We propose a generic phase diagram for  $\text{NH}_3\text{BH}_3$ , by mapping three experimentally found and one predicted phases as a function of temperature and pressure, along with the evolution of the corresponding structural distortions. The role of N-H...H-B dihydrogen bonds in the stability of  $\text{NH}_3\text{BH}_3$  polymorphs is examined.

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**Keywords:** high pressure; synchrotron powder diffraction; hydrogen storage

#### FA5-MS07-O4

**High Pressure Anelastic Behaviour of  $\text{Fe}_x\text{O}$ .** Leonid Dubrovinsky<sup>a</sup>, Anastasia Kantor<sup>a</sup>, Innokenty Kantor<sup>a</sup>, Michael Krisch<sup>b</sup>, Alexei Bossak<sup>a</sup>. <sup>a</sup>BGI, Bayreuth University, Germany. <sup>b</sup>ESRF, France.

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Elastic properties of solids are among the most important for solid Earth geophysics, engineering, and solid-state physics. Elastic moduli can be determined from pressure-volume relations (static or shock-wave compression), from acoustic waves velocity measurements (ultrasonic interferometry), or from dispersion curves of acoustic phonon branches (neutron, x-ray or light inelastic scattering). In the case of an ideal elastic solid the elastic moduli determined using different techniques should coincide within the experimental error (with the conversion factor between isothermal and adiabatic moduli). However, if any anelastic relaxation exists and the equilibrium strain for a given stress is achieved only after certain finite time interval, the effective elastic moduli measured by different methods would systematically vary, depending on sampling frequency. Anelasticity in a solid appears due to defects or other crystal imperfections when the energy minimum is achieved not only by varying the atomic geometry but also by changes in the materials' mesostructure (e.g. structure with a characteristic length larger than the crystal unit cell

size).

We have chosen non-stoichiometric  $\text{Fe}_x\text{O}$  as a candidate for a strongly anelastic material. Although  $\text{Fe}_x\text{O}$  has been intensively studied for several decades, many of its properties including elastic behaviour remain controversial and not well understood. A combined single-crystal inelastic x-ray scattering (IXS) and x-ray diffraction (XRD) study of synthetic wüstite  $\text{Fe}_{0.95}\text{O}$  at elevated pressure revealed increasing the difference in the bulk modulus determined from static (XRD) and dynamic (IXS) measurements upon compression. We explain and quantitatively describe this observation by anelastic relaxation in wüstite. The reanalysis of previous results put some more evidence for relative good coincidence for bulk moduli and systematic difference for  $K'$  between static and dynamic measurements.

**Keywords:** high pressure; FeO; anelastic behaviour

#### FA5-MS07-O5

**Pressure Induced Homothetic Volume Collapse in Si and Ge Clathrates** Alfonso San Miguel<sup>b</sup>, Denis Machon<sup>b</sup>, Jean-Christophe Blancon<sup>b</sup>, Colin Bousige<sup>b</sup>, Sylvie Le Floch<sup>b</sup>, Régis Débord<sup>b</sup>, Vittoria Pischedda<sup>b</sup>, Pierre Toulemonde<sup>a</sup>. <sup>a</sup>Institut Néel, Grenoble, France. <sup>b</sup>LPMCN, Université Lyon 1 and CNRS, Lyon, France.

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Since the discovery of a pressure induced isostructural homothetic volume collapse (HVC) of silicon type I clathrates [1,2], different models have attempted with limited success to explain this remarkable transition which can be associated with up to ~10% of atomic volume reduction. Recently, different studies [3,4] point out to some form of disorder in the silicon host framework associated to the volume collapse in clathrates, which detail nature has not been well characterized. The pressure induced isostructural HVC in clathrates could be related to pressure induced amorphization preserving the crystal topology recently predicted in zeolites [5] making of the HVC a more general behaviour in nanocage-like materials. We have combined high pressure EXAFS at the Ba L3-edge in  $\text{Ba}_8\text{Si}_{46}$  and at the Ge k-edge in the  $\text{Ba}_8(\text{Si}_{1-x}\text{Ge}_x)_{46}$  mixed clathrates to obtain a local image of the evolution of the host and guest structures at the HVC transition and understand its physical origin. The full set of obtained data allow us to present a novel picture on the mechanism governing this notable phase transition.

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**Keywords:** clathrate; EXAFS; high pressure