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Novel Molecular Materials for Hydrogen Storage Applications

Maddury Somayazulu

Geophysical Laboratory, Carnegie Institution of Washington

5251 Broad Branch Rd. NW, Washington DC, 20015

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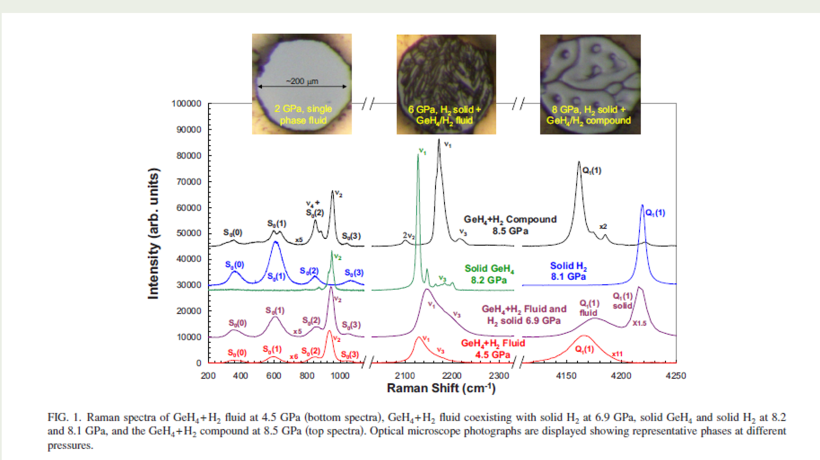
GEOPHYSICAL LABORATORY

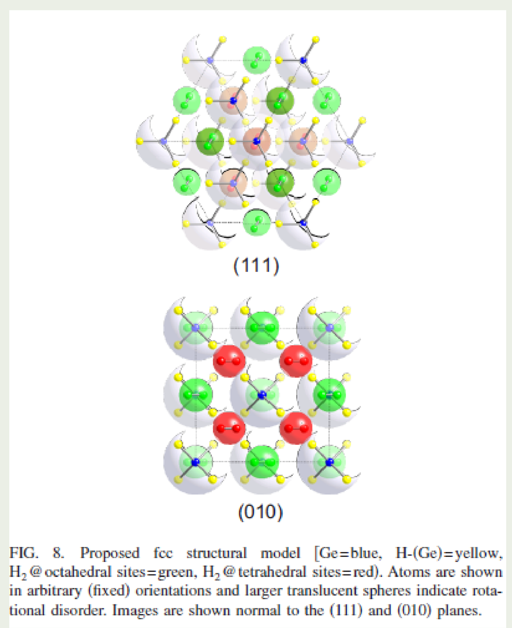
BES009

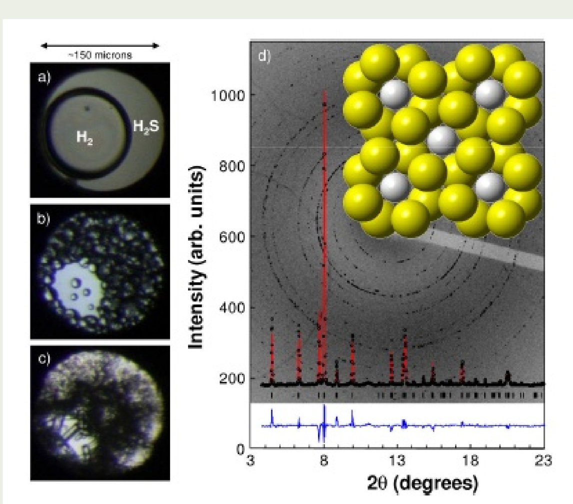
Collaborators: Robert. G. Potter, Timothy Strobel, Wilson Wannene, Viktor Struzhkin, Dhanesh Chandra and Russell J Hemley

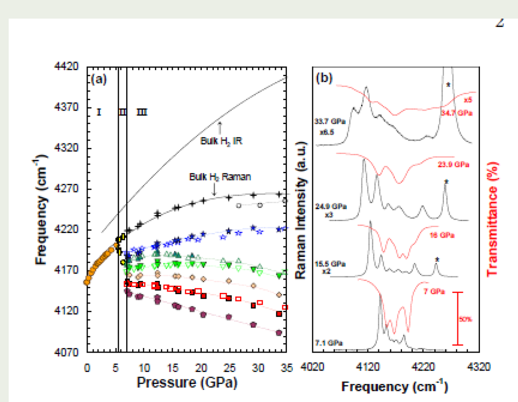
Motivation and Goals : We propose to use high pressure to help design and understand new classes of materials suitable for reversible hydrogen storage using a suite of experimental techniques such as Raman and IR spectroscopy, X-ray and neutron scattering and also investigate site specific interactions of storage materials with molecular hydrogen at high pressures. These studies on systems such as NH_3BH_3-H_2; SiH_4-CH_4-GeH_4-H_2; Xe-H_2 have yielded new compounds and insights into interaction of H_2 with other molecular systems.

H_2S-H_2; SiH_4-H_2 and GeH_4-H_2 binary systems – tuning intermolecualr interactions with pressure



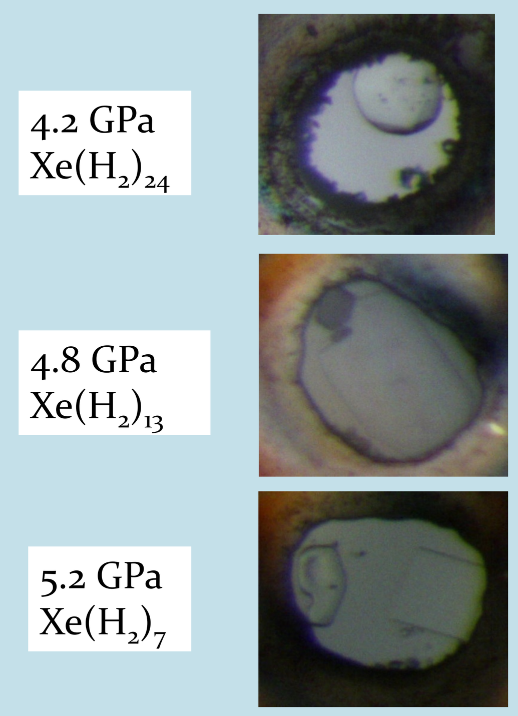


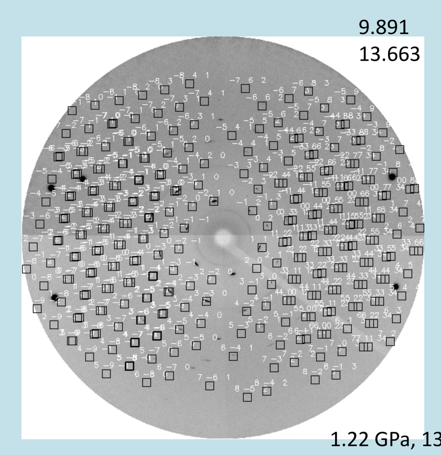


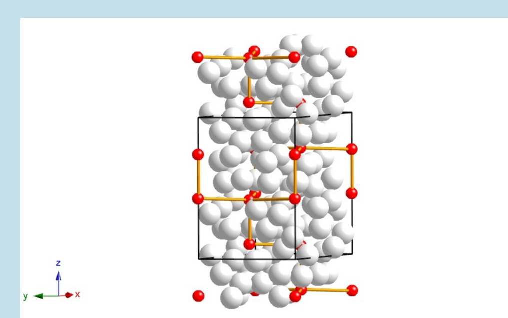


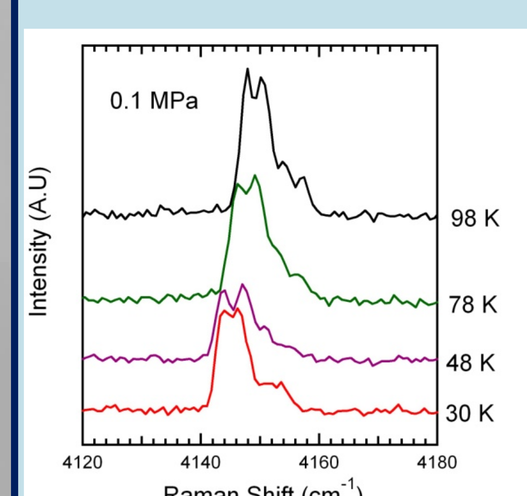
- CH_4+H_2
  - Compound formation, small perturbations from bulk molecular hydrogen (Somayazulu et al, Science, 1996)
- SiH_4+H_2
  - Compound formation, abnormally strong intermolecular interaction with hydrogen (T. Strobel et al, PRL, 2009)
- GeH_4+H_2
  - Compound formation?
  - Even stronger perturbation to H_2? (T. Strobel et al, J. Chem. Phys, 2010)
- H_2S +H2
  - Host-Guest structure?
  - Hydrogen bonding evolution with pressure results in a novel clathrate structure. (T. Strobel et al, PRL, 2011)

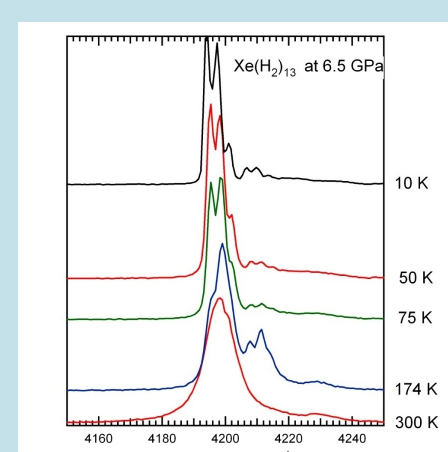
$Xe(H_2)_{24}$ – the most hydrogen-rich van der waals solid stable at 90 K and 1 atm.

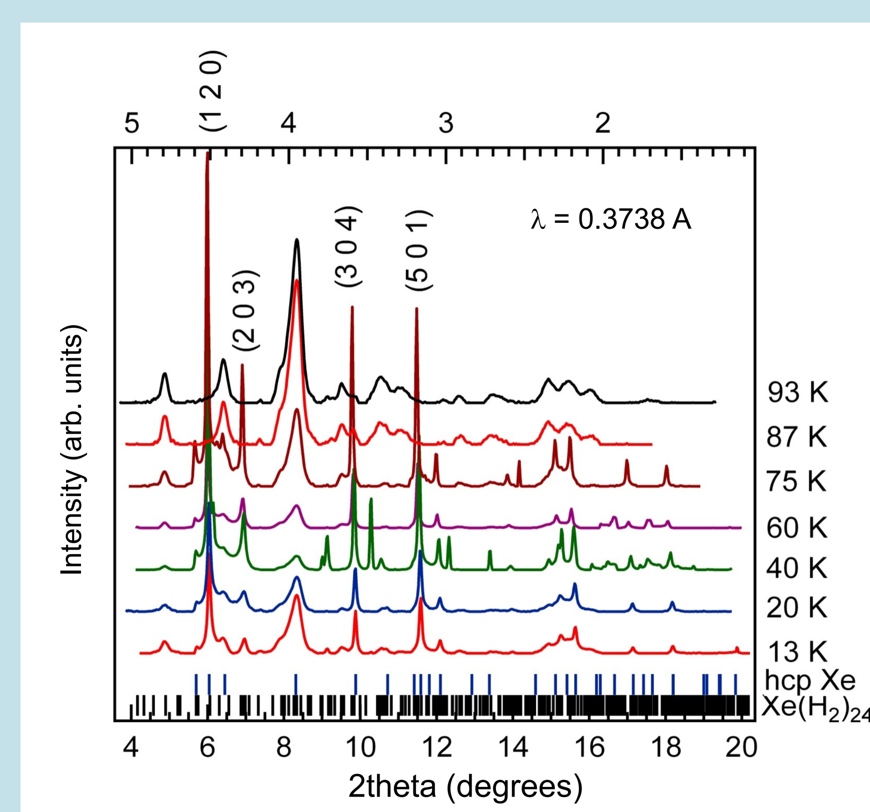












1. $Xe(H_2)_{24}$ the most hydrogen-rich solid known is stable at 1 atm and 90 K.
2. In comparison to $Ar(H_2)_2$ and in fact other binary molecular solids, packing does not seem to play the vital role in this compound formation. First signs of true vdW bonding ?
3. Surprisingly, although Xe-H bond formation has been observed at relatively benign P-T conditions, we don't observe any evidence for Xe-H bond formation even in xenon rich mixtures.
4. At ambient temperatures, no xenon-rich solids are found to occur

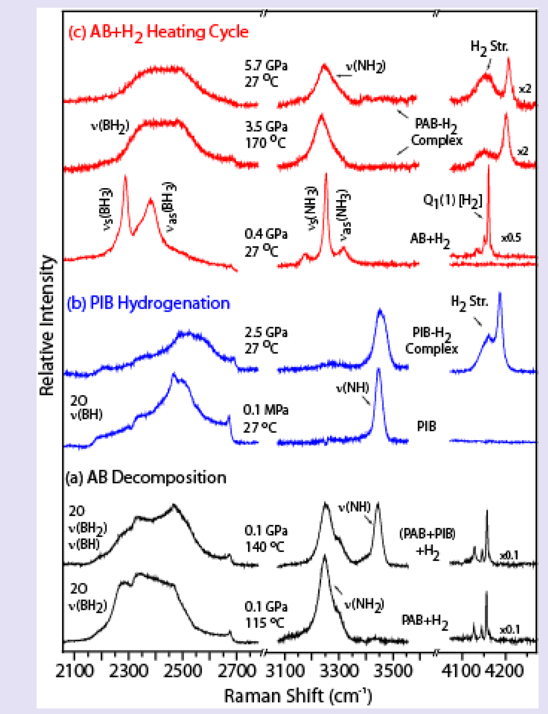
Somayazulu et al, Nature Chem. (2010)

Ammonia Borane and related materials

Complexation kinetics much faster (and lower pressure) than AB-H_2!

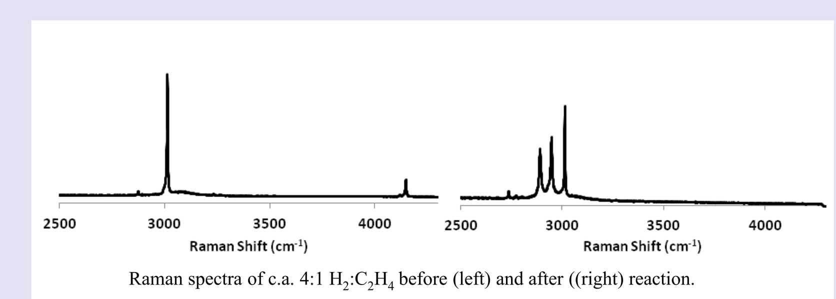
Reaction of 'clean' PIB with H_2 (2.5 GPa, RT)

Decompose AB to PAB / PIB



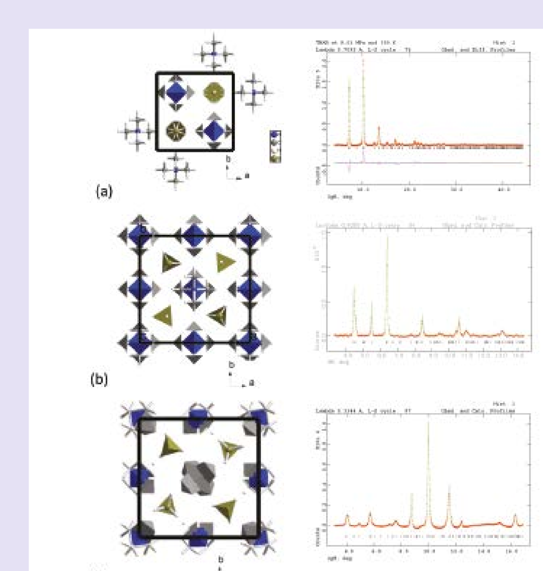
H_2 Complexes with PAB & PIB

Chellappa et al. ChemPhysChem (2010)



Me_2NHBH_3/H_2 mixtures were found to hydrogenate ethylene and carbon dioxide at room temperature and pressures above 0.5 GPa. Raman spectra of c.a. 4:1 H_2:C_2H_4 before (left) and after ((right) reaction. [Potter et al, J. Chem. Phys. (communicated)]

Pressure induced Phase transitions in TMAB.



Raman spectroscopy and synchrotron powder diffraction reveal a sequence of pressure induced ohase transitions in Tetramethylammonium-borohydride at 5 and 20 GPa. [Allen Dalton et al, J. Phys. Chem A (2011)]