H_2O Under Pressure

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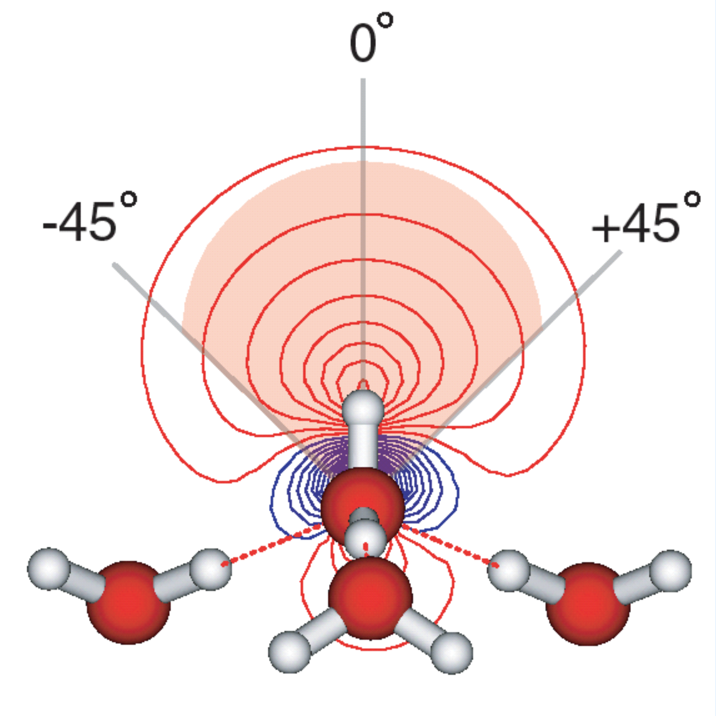
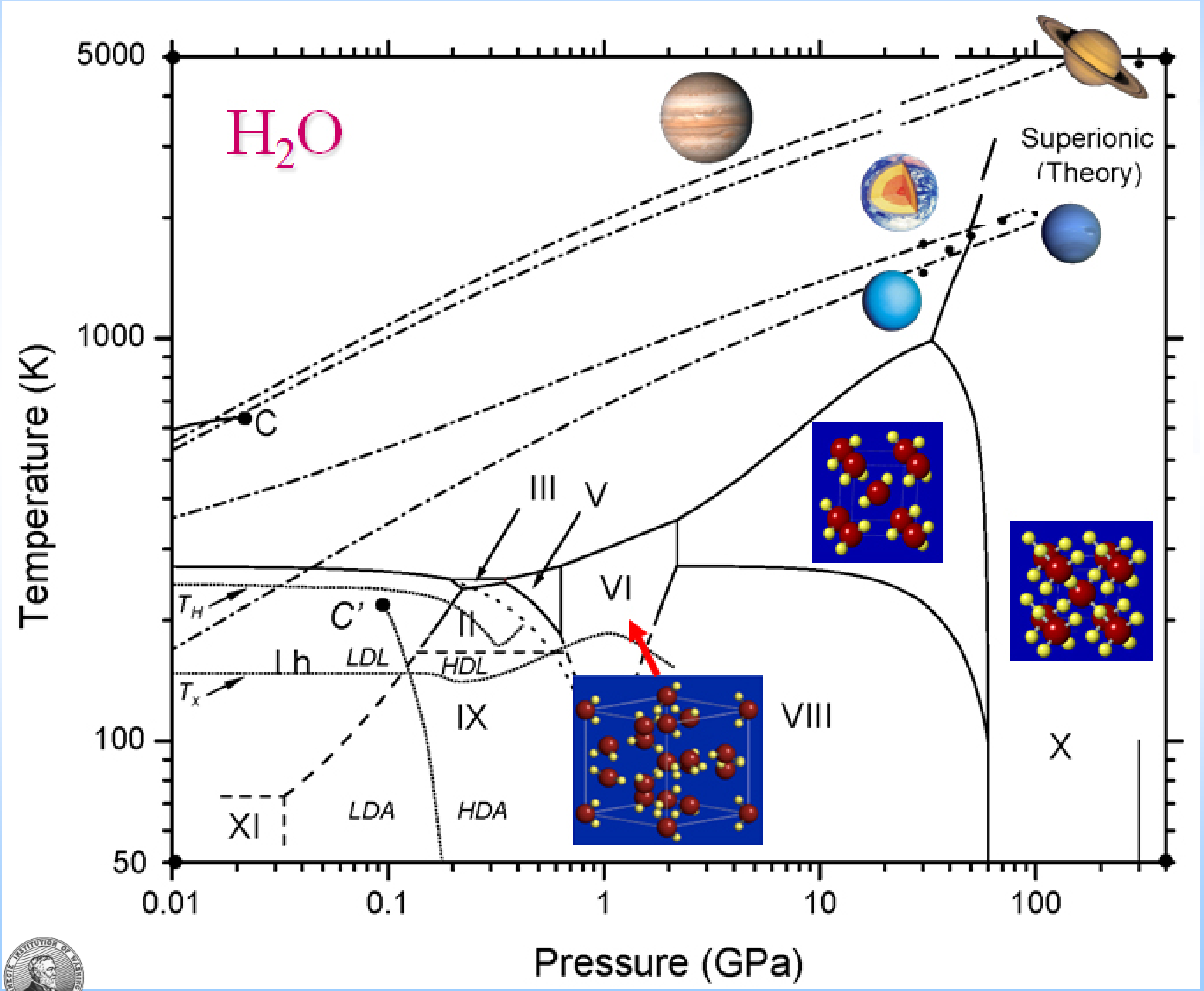


Workshop on Fundamental Challenges in our Understanding of the Physics and Chemistry of Water, January 16-17, 2015

High-pressure behavior of water continues to present new questions and surprises

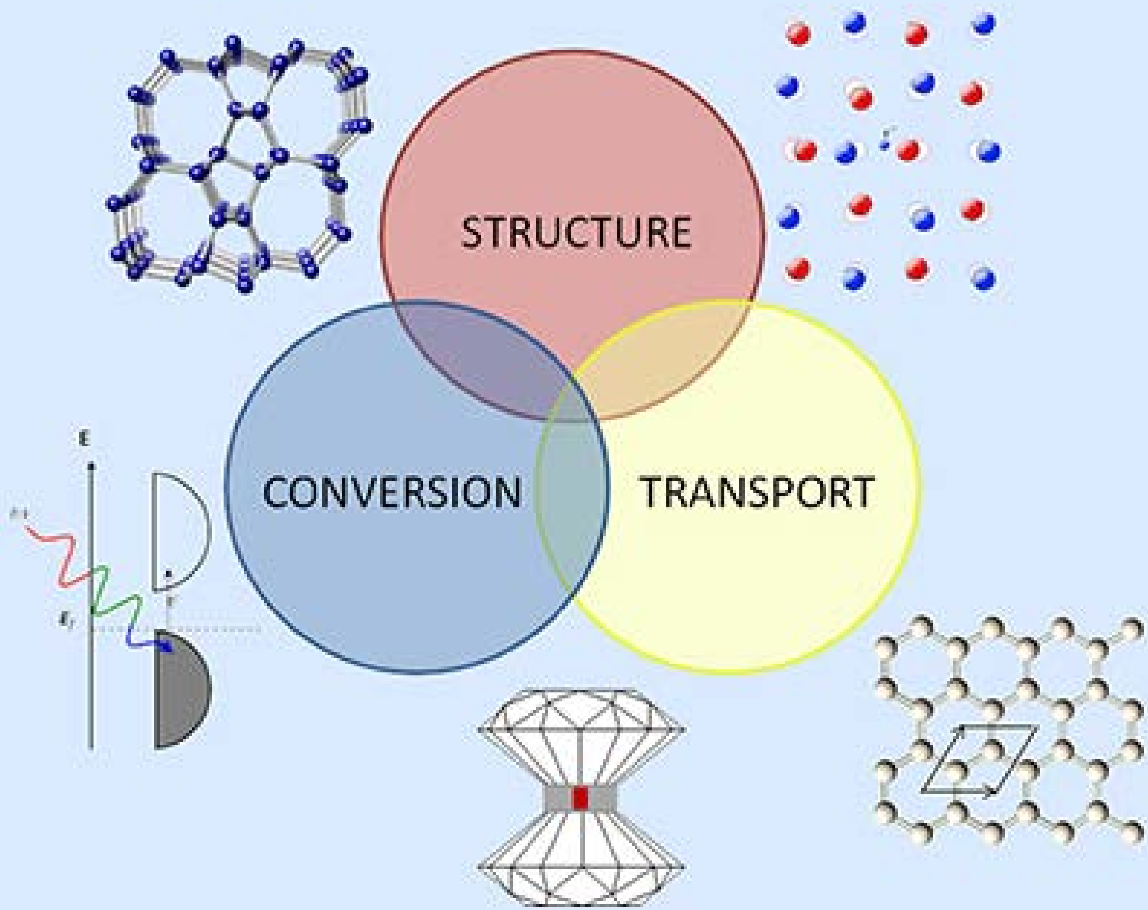


- **Origin of stability?** ***~20 stable and metastable phases***
- **Novel transitions?**
  - ***non-molecular***
  - ***amorphization***
  - ***superionic***
  - ***liquid/liquid trans***
- **High *P-T* fluid?**
- **Electronic prop.?**
- **New chemistry?**
- **Breakdown of H_2O?**
- **Supporting life at extreme *P-T*?**

EFree Energy Frontier Research in Extreme Environments Center

DOE Energy Frontier Research Center

Mission: **To accelerate the discovery and synthesis of new energy materials using extreme conditions**



Carnegie:

- **Director:** R. J. Hemley
- **Assoc. Director:** T. S. Strobel
- **Admin.** S. Gramsch, M. Phillips
- **Carnegie Partners:** R. Boehler, Y Fei, D. Kim, Z. Liu, H. K. Mao, V. Struzhkin, W. Yang

University Partners:

- **Penn State:** J. Badding, N. Alem, Crespi
- **Cornell:** R. Hoffmann, N. Ashcroft
- **Colorado School Mines:** C. Taylor
- **Caltech:** B. Fultz
- **Lehigh:** K. Landskron

DOE Facilities

- ***APS, ANL (X-ray)***
- ***SNS, ORNL (Neutron)***
- ***NSLS II, BNL (IR)***

U.S. DEPARTMENT OF ENERGY Office of Science

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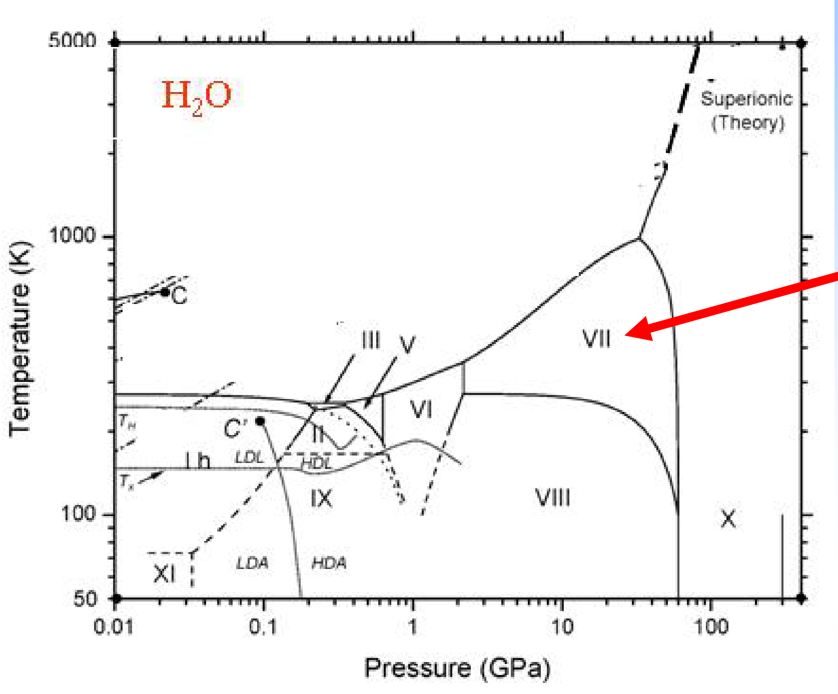
Continuing puzzles in ice VII



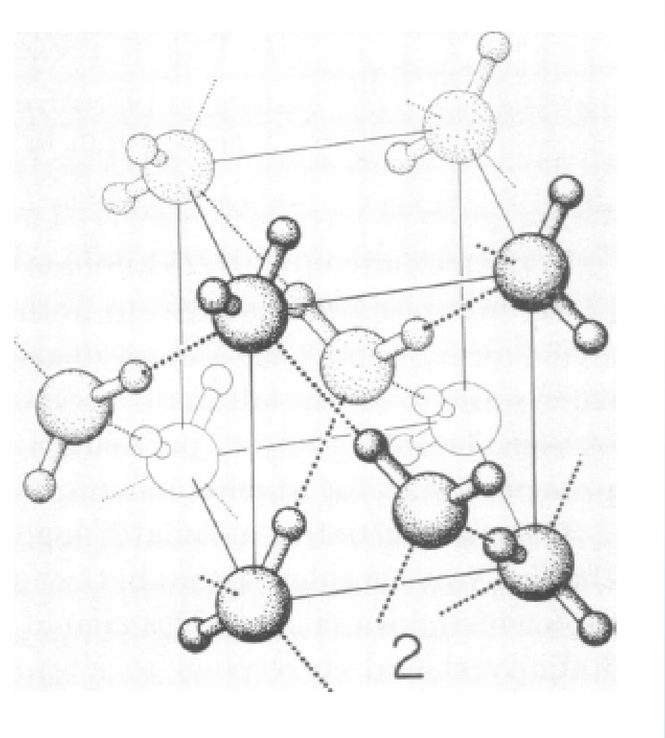
[Kamb & Davis, *PNAS* (1964)]

*ICE VII, THE DENSEST FORM OF ICE**

By Barclay Kamb and Briant L. Davis

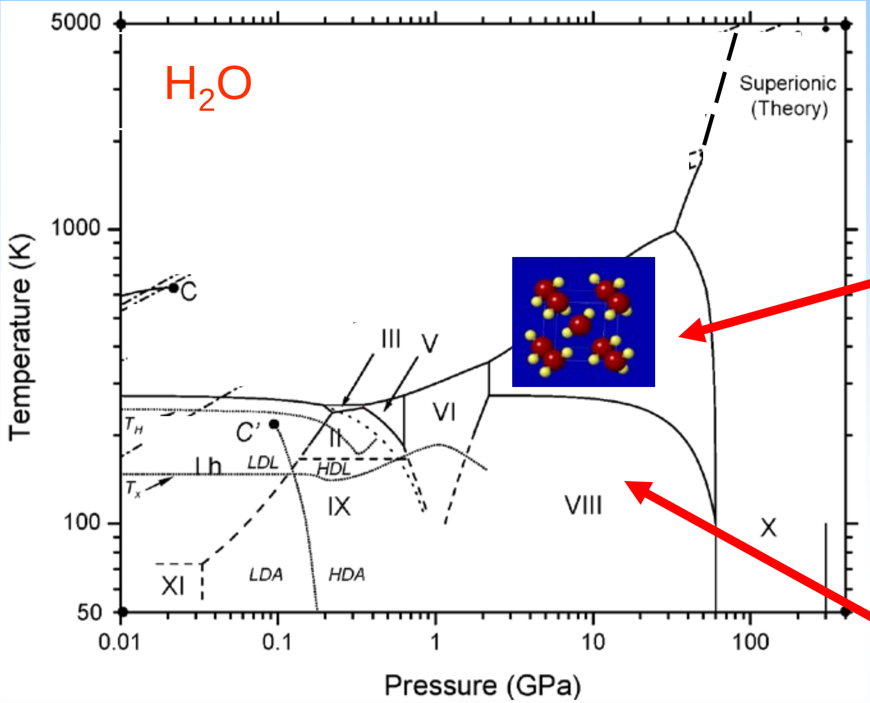
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, AND SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY, RAPID CITY

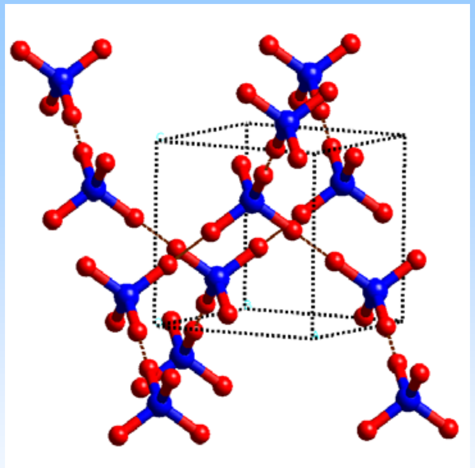
Communicated by Linus Pauling, October 19, 1964



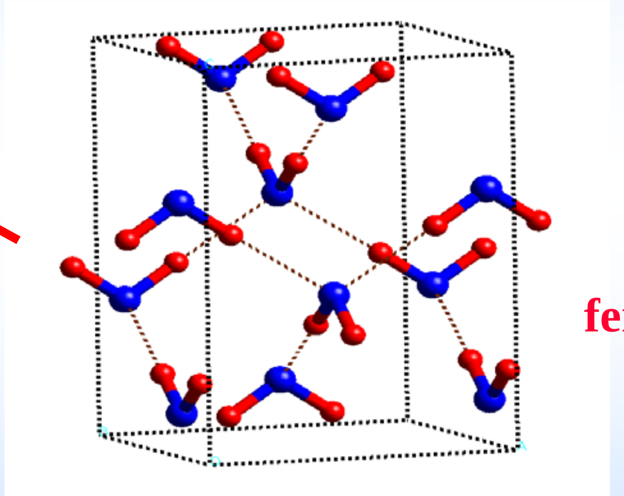
- O atoms lie on bcc lattice
- Two interpenetrating ice Ic lattices
- Retains tetrahedral motif seen in lower pressure ice phases
- Predicted H-bond symmetrization

Continuing puzzles in ice VII

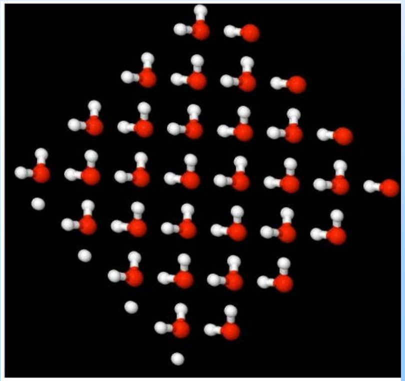




Ice VII proton disordered



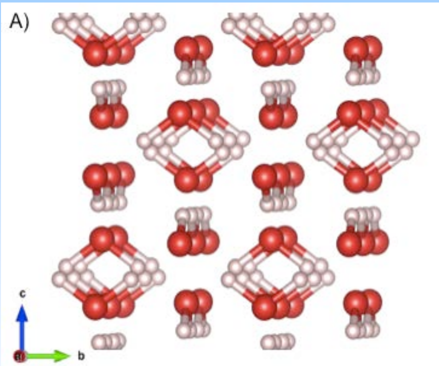
Ice VIII anti-ferroelectric



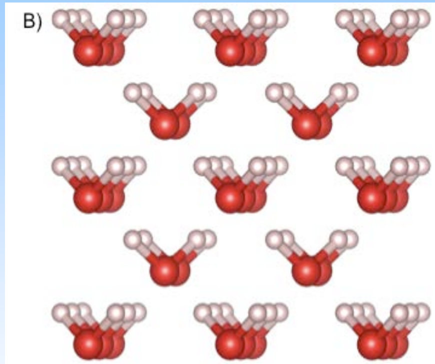
Hypothetical polar ice VIII (ferroelectric)

- ***Nature of the proton ordering***
  [Kuhs et al., *J. Chem. Phys.* (1984)]
- ***Structural transitions observed in ice VII***
  [Somayazulu et al. *J. Chem. Phys.* (2008)]
- ***Is there a ferroelectric form?***
- ***Higher P-T behavior?***

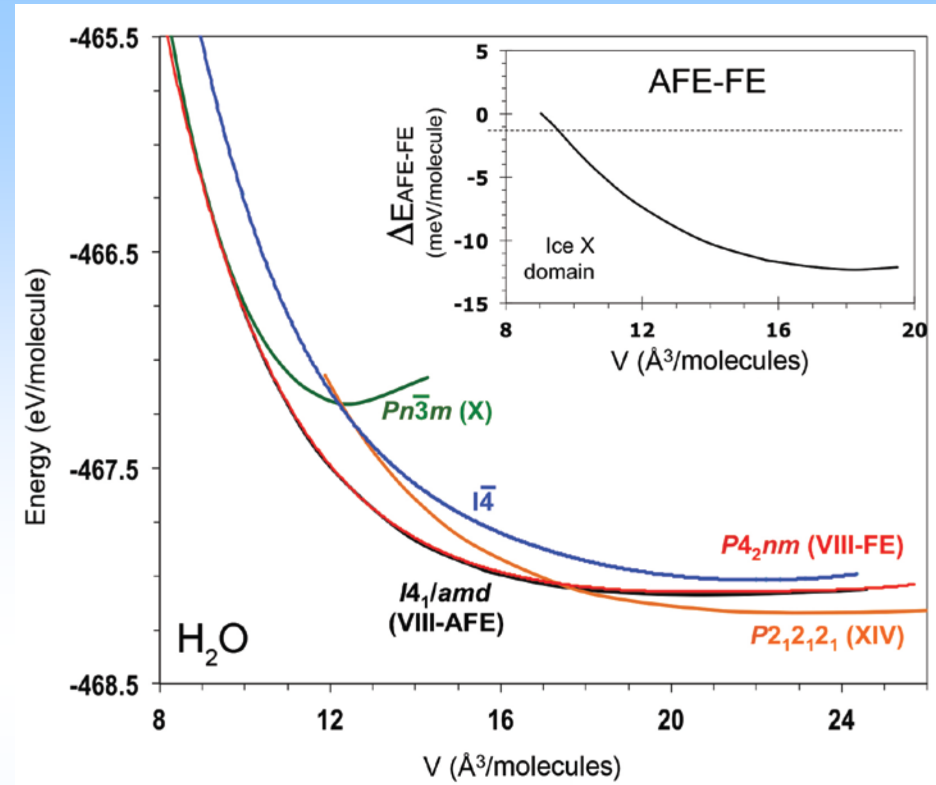
Ferroelectricity in dense H_2O

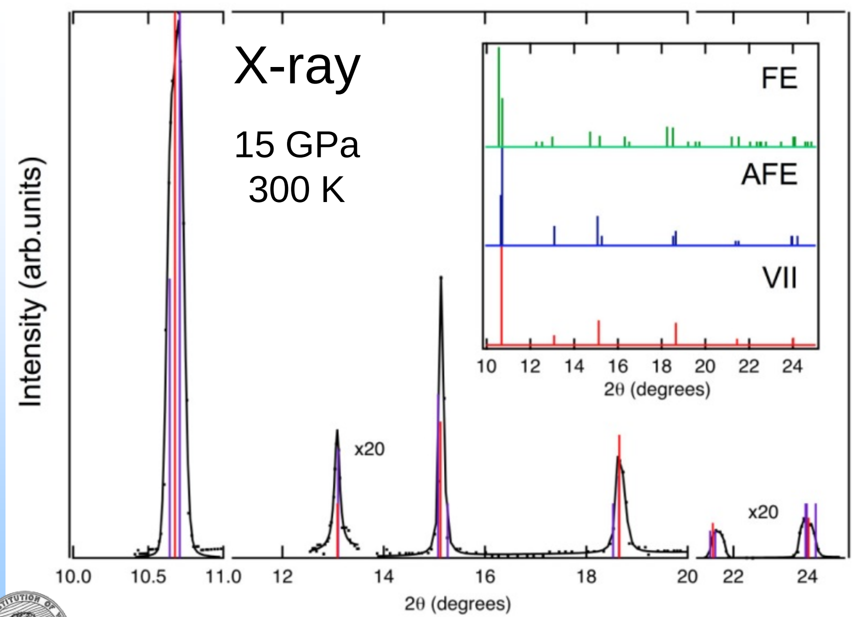


Anti-Ferroelectric (VIII-AFE)



Ferroelectric (VIII-FE)

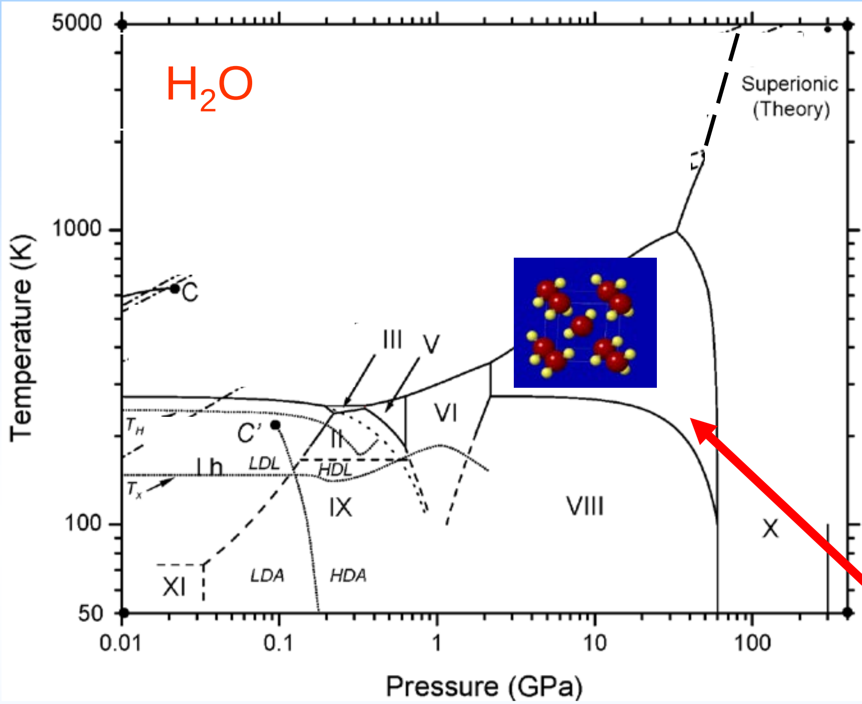




- **AFE-FE nearly degenerate**
- **Fit to x-ray data**
- **Mixed domains of FE and AFE**
- **Stabilized by pressure and epitaxial growth?**

[Caracas & Hemley, *to be published*]

Water splitting in dense ice

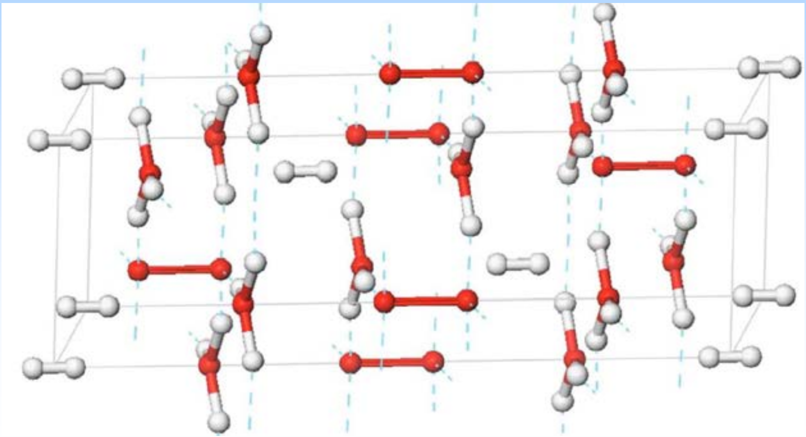


- Molecular alloy of H_2-O_2
- Metastable energetic material
- Similar results found for NH_3

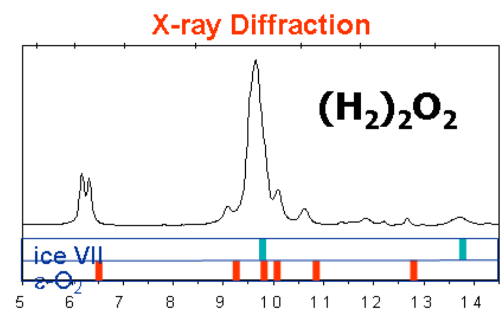
  [Lazor *et al*., to be published]
- Mechanism not understood

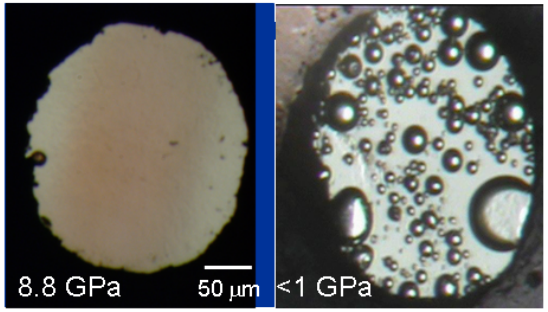
THEORY: 'When is H_2O not water?'

[Pickard & Needs, *J. Chem. Phys.* (2007)]



[W. Mao *et al*., *Science* (2006)]



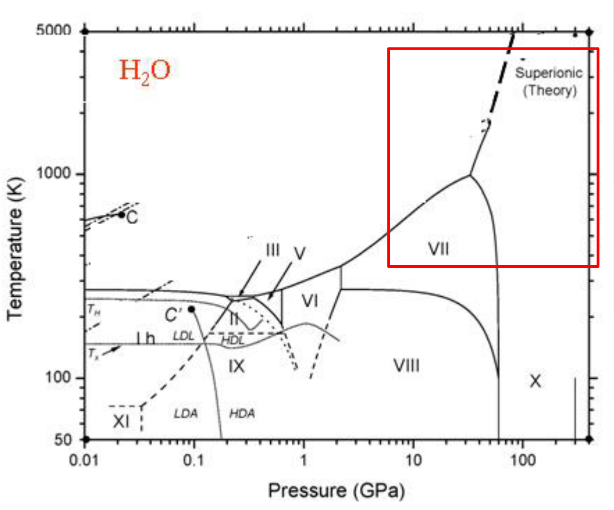


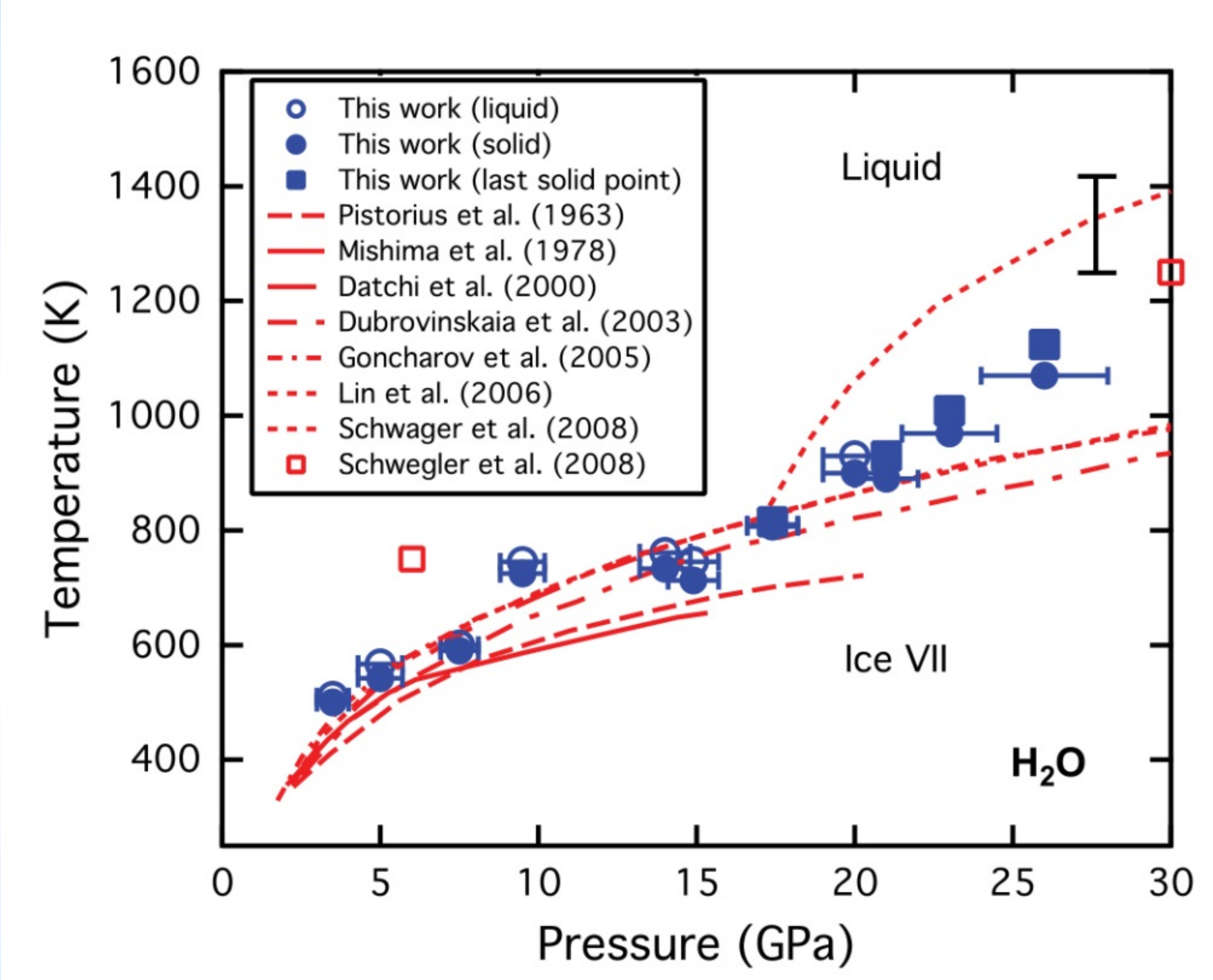
X-ray-induced reaction

Hard (>7 keV) x-ray photons

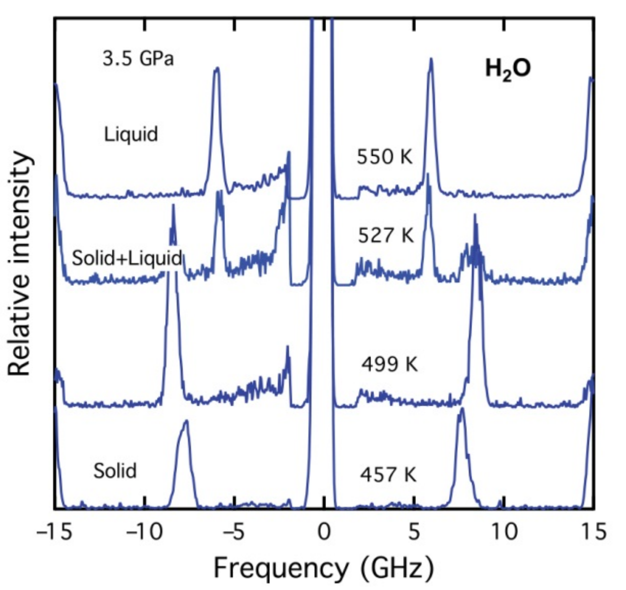
Improved measurement of high *P-T* melting

[Ahart et al., *High Pressure Res.* (2014)]





High P-T Brillouin Scattering

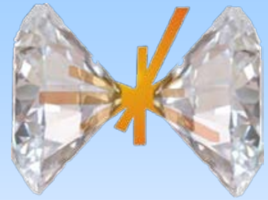


- **Clear melting signature**
- **v_s (eos) for high *P-T* liquid**
- **High P-T relations, structures, dynamics?**

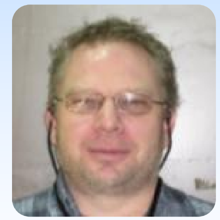
Neutron scattering at extreme *P-T* conditions

- **Underutilized (compare x-ray)**
- **Low-*Z* cross sections (*e.g*, D)**
- **Extensively used at low *P-T***
- **Previous limit 27 GPa**

  [Guthrie, *Ph.D. thesis* (2002)]
- **Transitions at higher pressure**

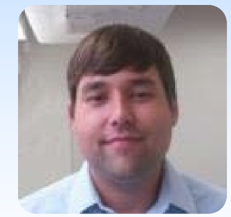


SNAP: Spallation Neutrons at Pressure

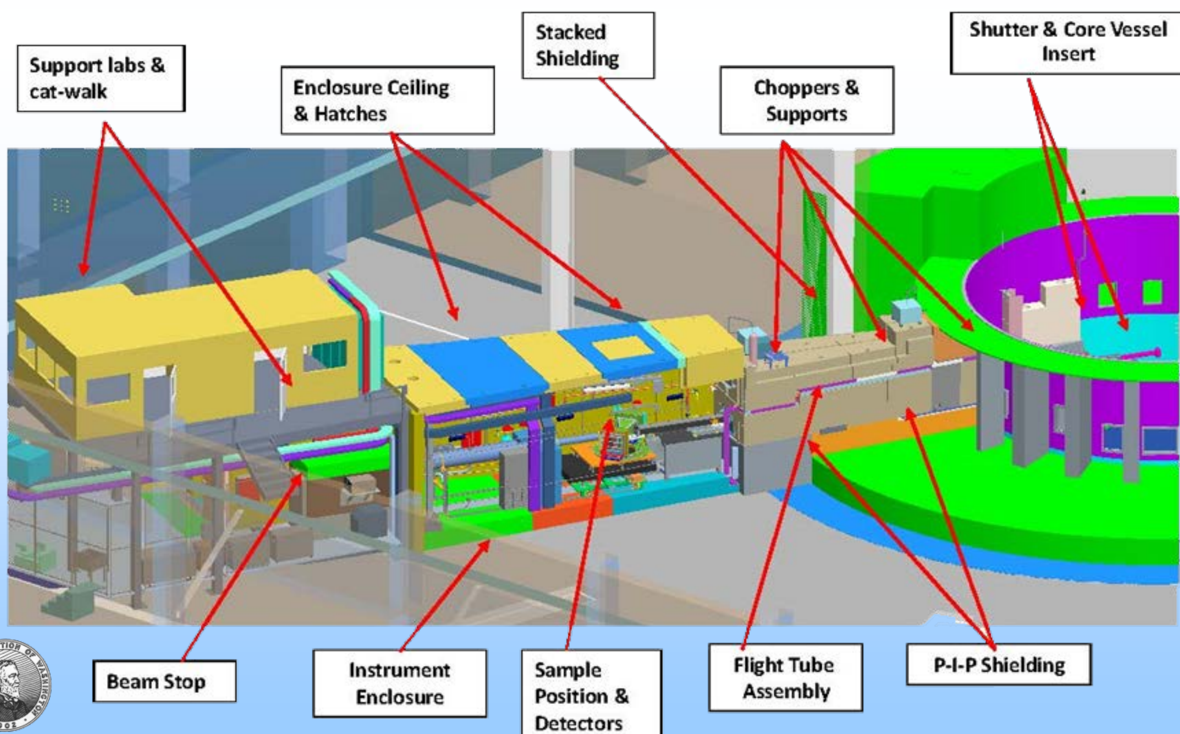


C. A. Tulk

A. M. dos Santos



J. Moliason



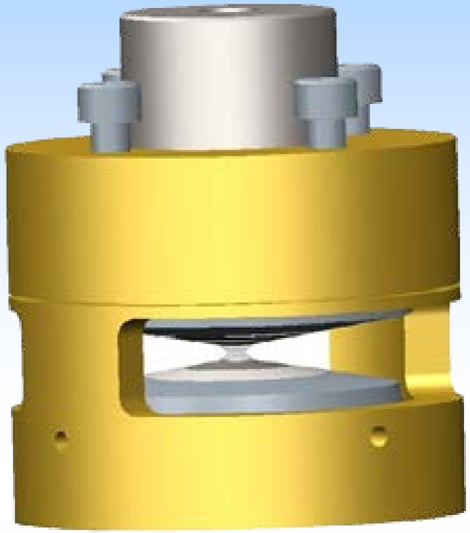
Spallation Neutron Source

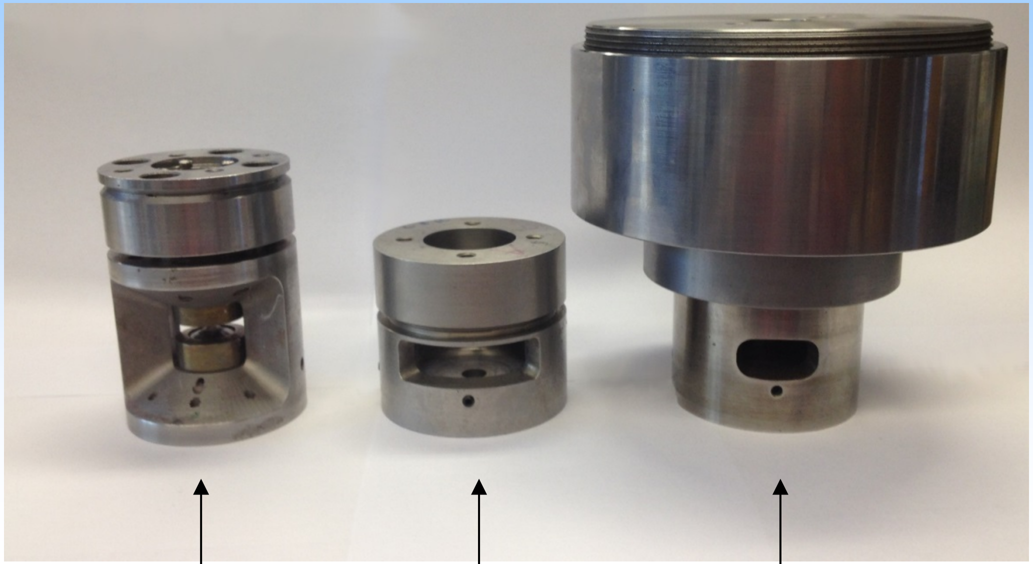
SNAP's dedicated high pressure diffractometer, came online 2006

Highly versatile: can study single crystals, powders, liquids

New cell designs of high-pressure neutron scattering

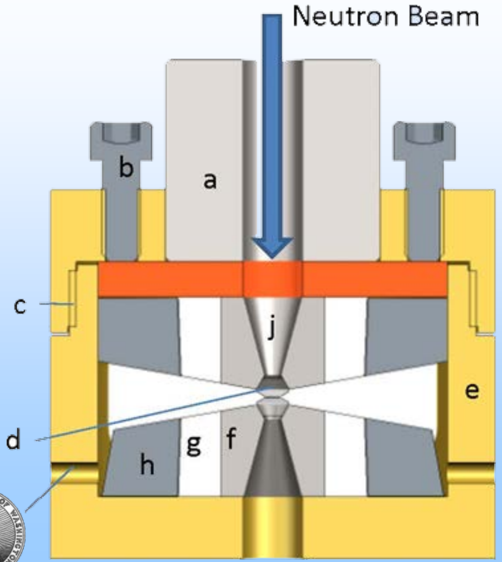
Enhancing sample volume

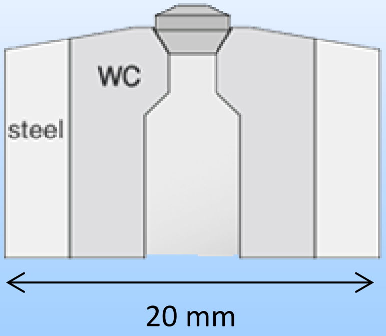


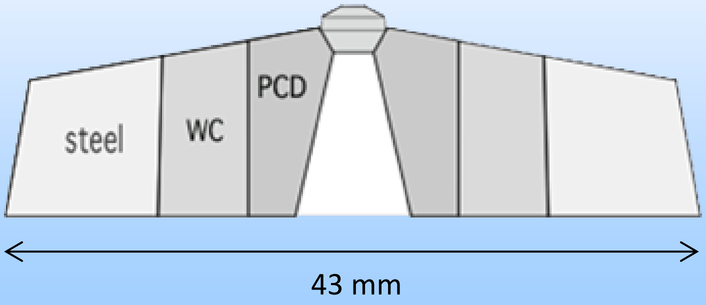


2008 2013 2014

R. Boehler

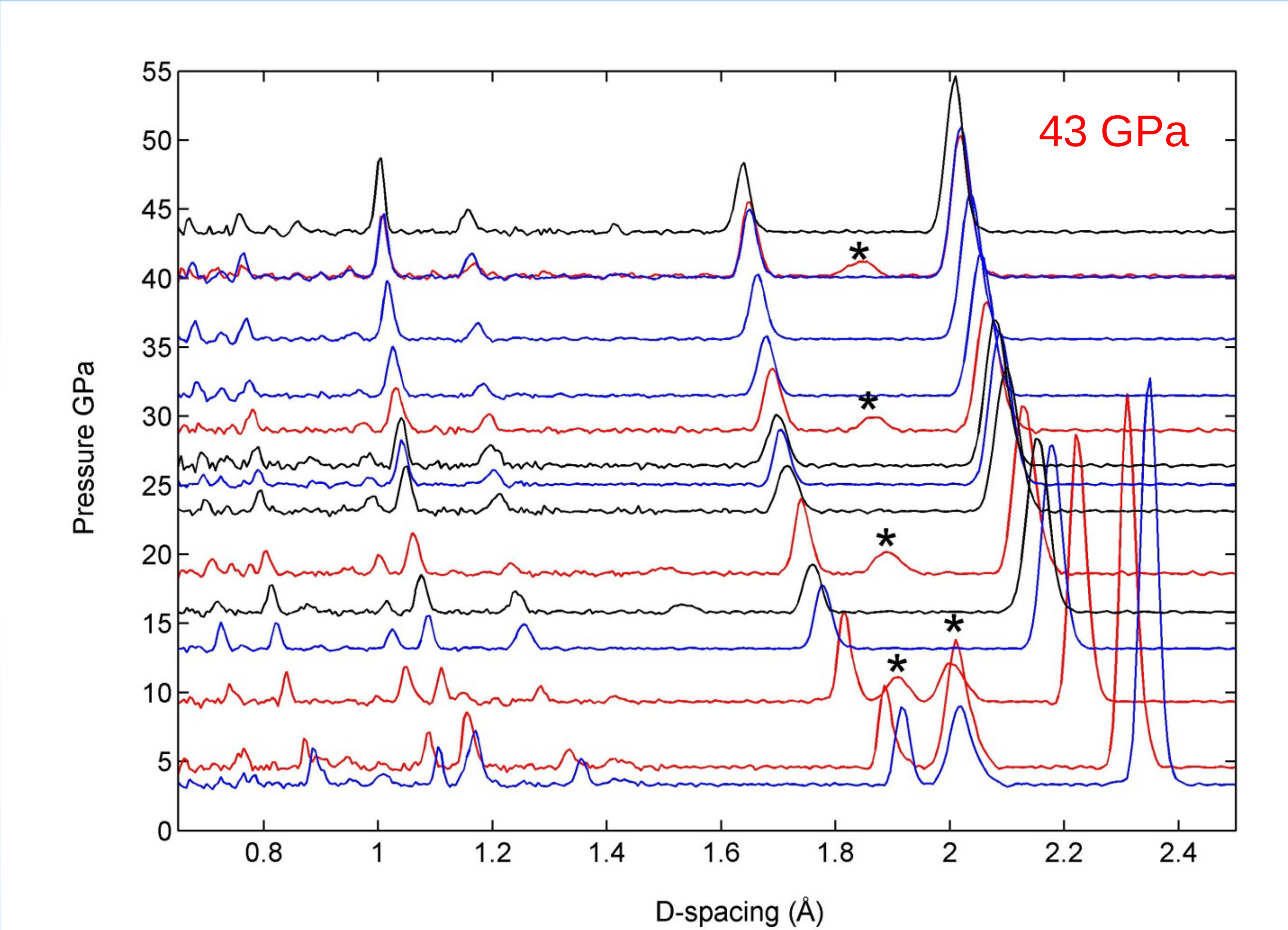


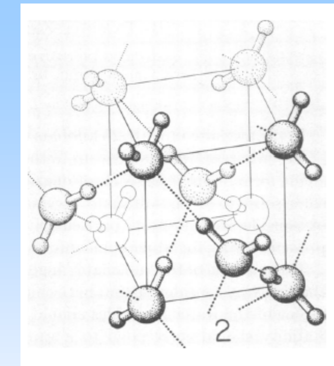




[Boehler et al., *High Pressure Res.* (2013)]

Neutron diffraction of ice VII (300 K)





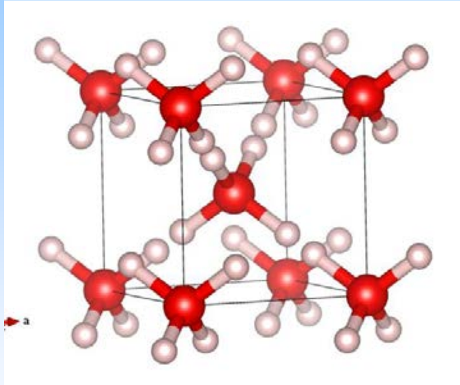
0.05 mm³ D_2O ice VII (6 hour datasets)

~50 ug sample!

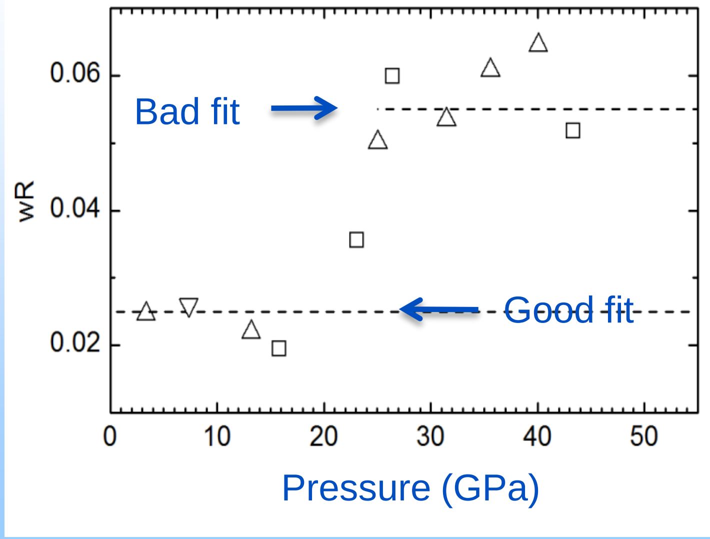
- **Excellent S/N to 50 GPa**
- **Shifts in positions and intensities**

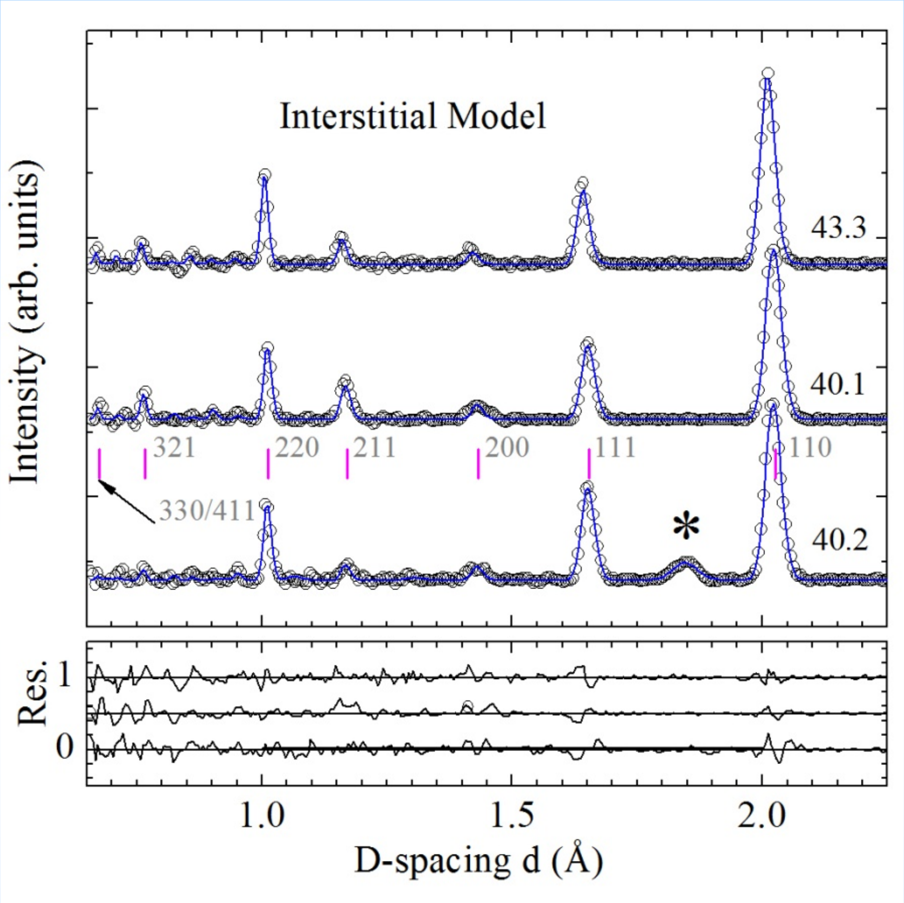
[Guthrie et al., *PNAS* (2013)]

Failure of the conventional model for ‘proton centering’



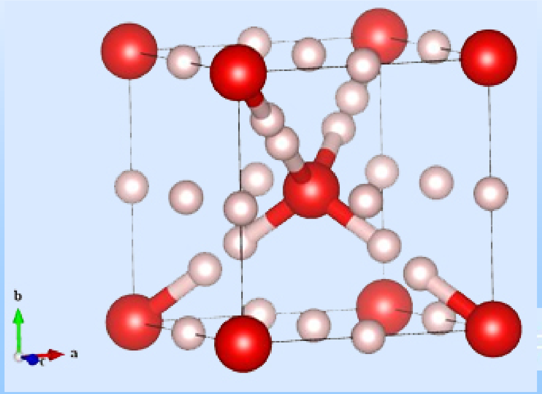
- Rietveld refinement
- Low pressure data agree well with previous work
- Abrupt reduction in quality of fit above 25



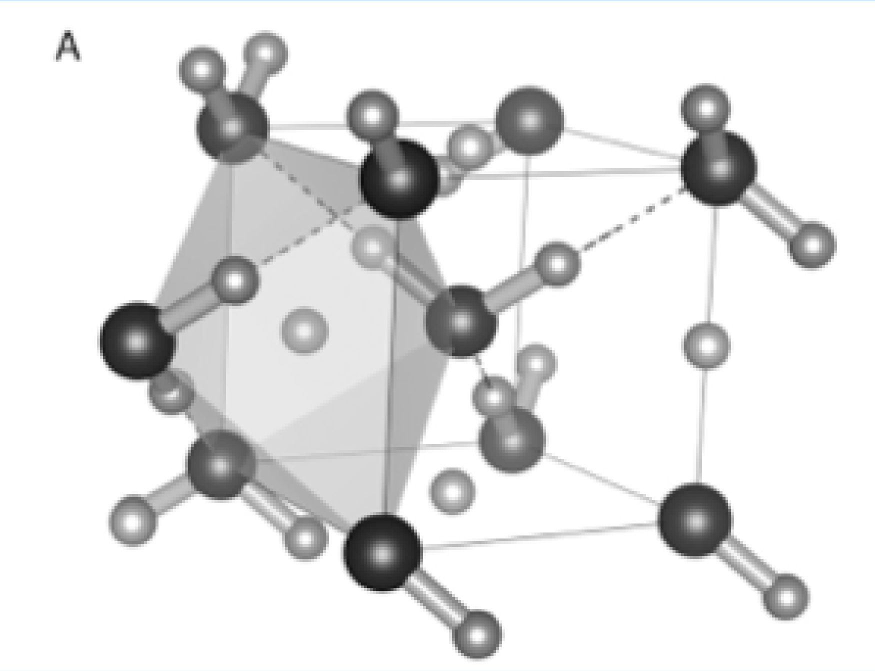


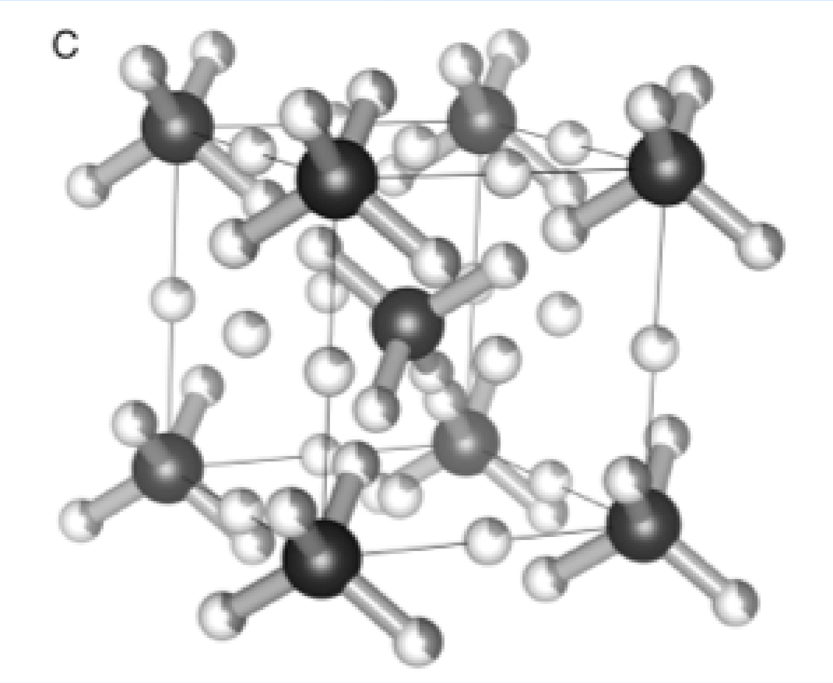
Observed intensities consistent with scattering density in the octahedral voids of O lattice

[Guthrie et al., *PNAS* (2013)]



Interstitial protons in ice VII above 30 GPa (300 K)



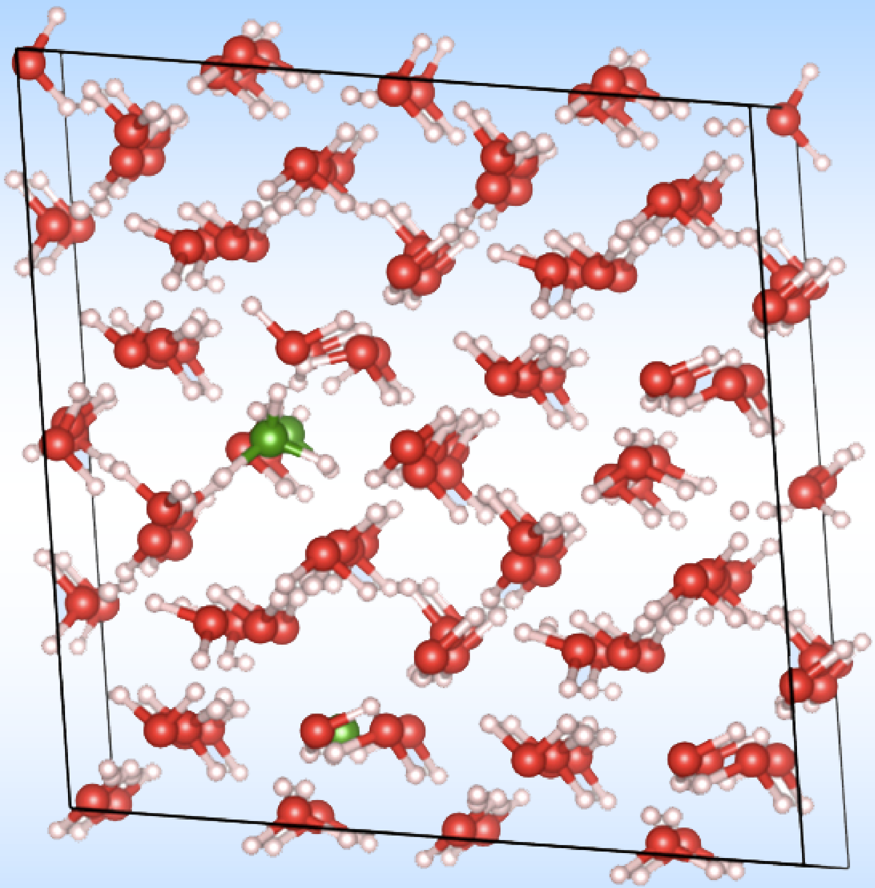


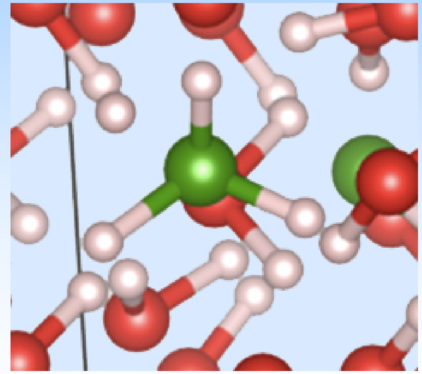
[Guthrie *et al.* PNAS (2013)]

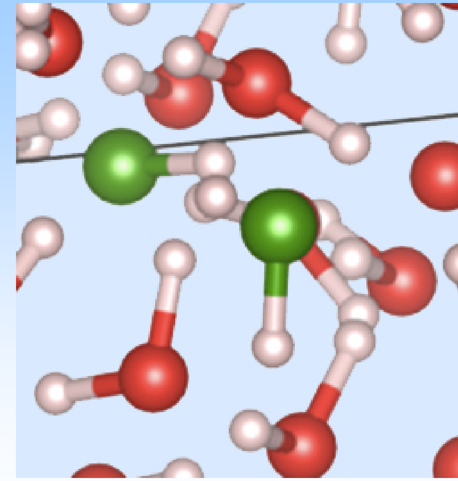
- **Not reproduced by DFT calculations (classical nuclei)**
- **Quantum diffusion? (path integrals?)**
- **Improved theory or other models?**

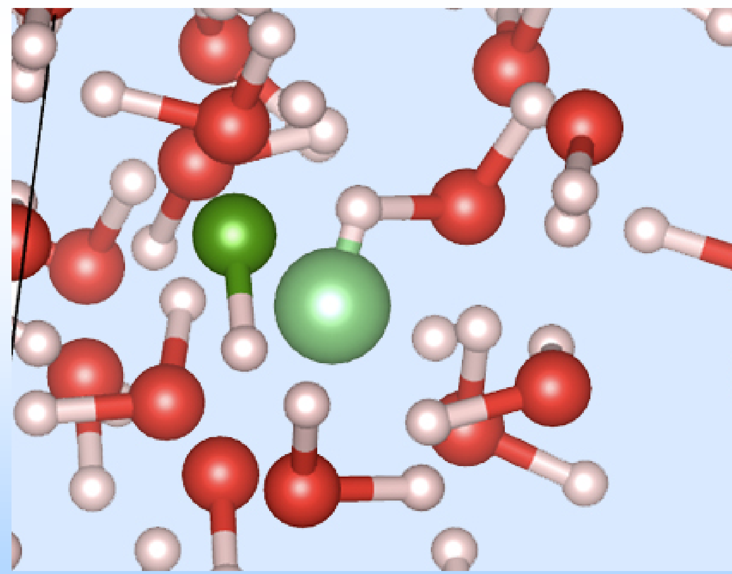
Partial dissociation to form additional defects

MD DFT-GGA (50 GPa, 300 K)







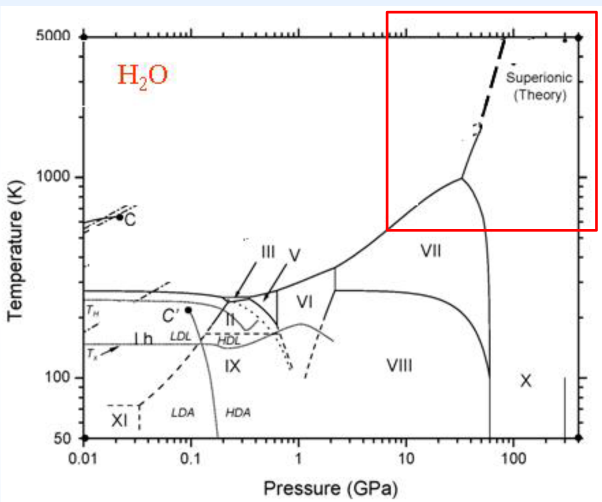


- Partial breakdown of H_2O
- H_3O…OH defects
- H-H-O-H molecules

[Caracas et al. *in preparation*]

Interstitial protons and superionicity

(Meta)stability of interstitial H defects at high temperatures



low-P

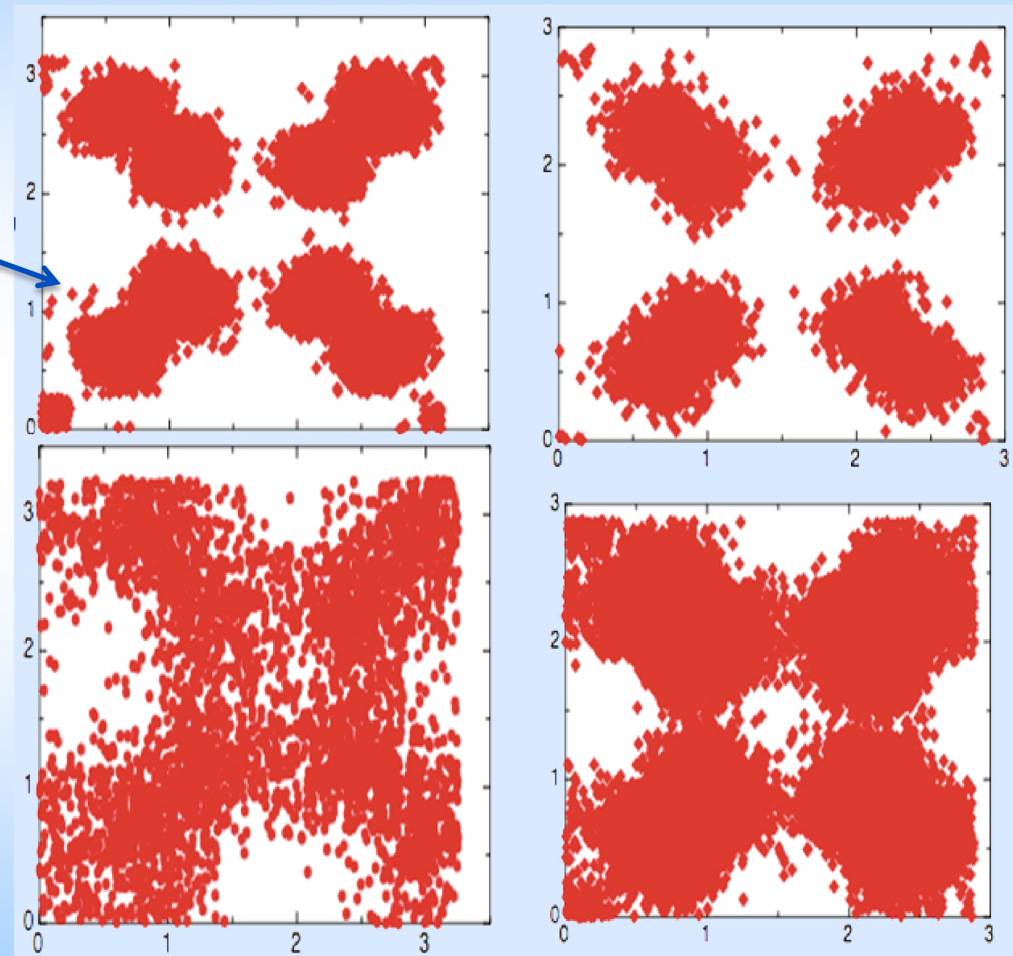
high-P

300 K:

Interstitial H defect ?

1000 K:

Melt/ Super-ionic?

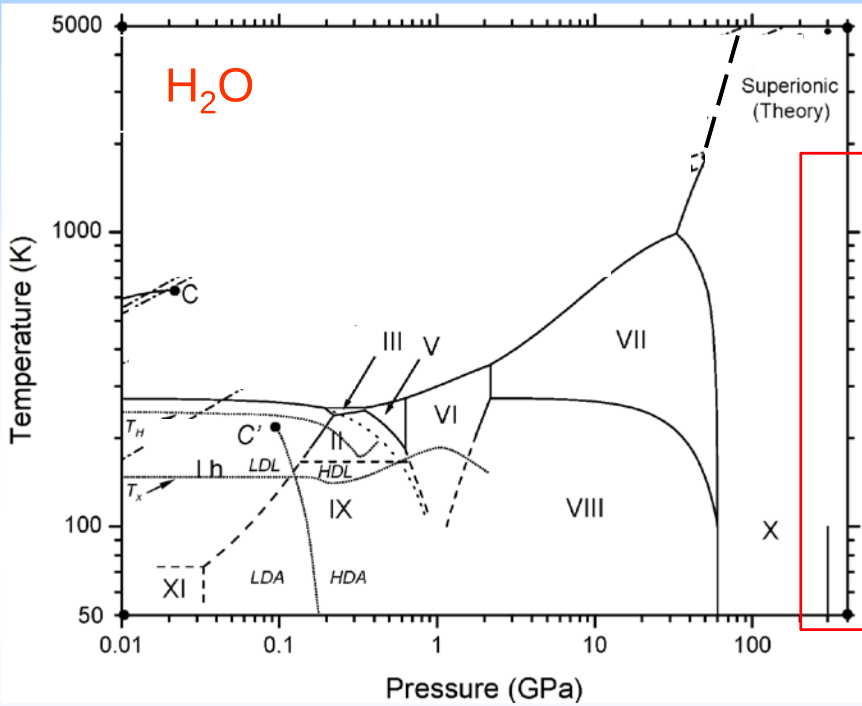


Need confirmation by neutron scattering

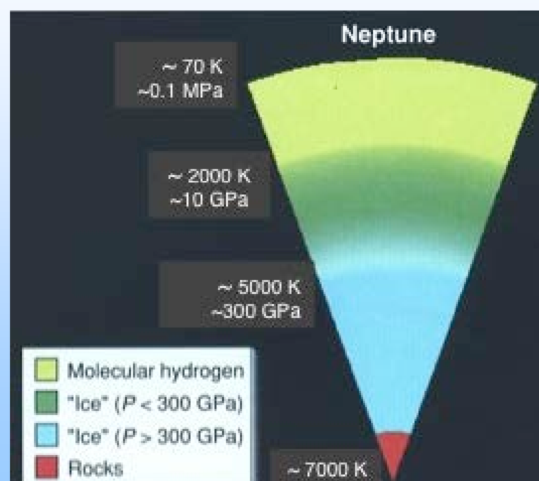
MD DFT-GGA (50 GPa, 300 K)

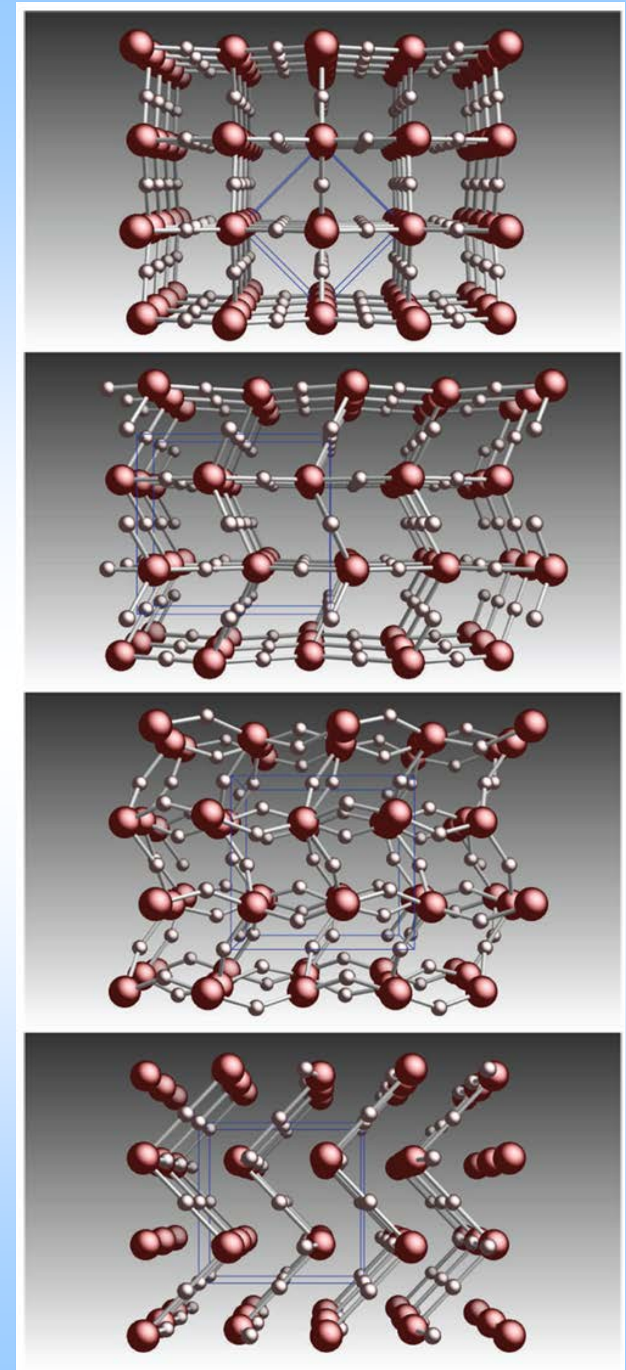
[Caracas et al. *in preparation*]

Ultrahigh-pressure phases of H_2O: *theoretical predictions*



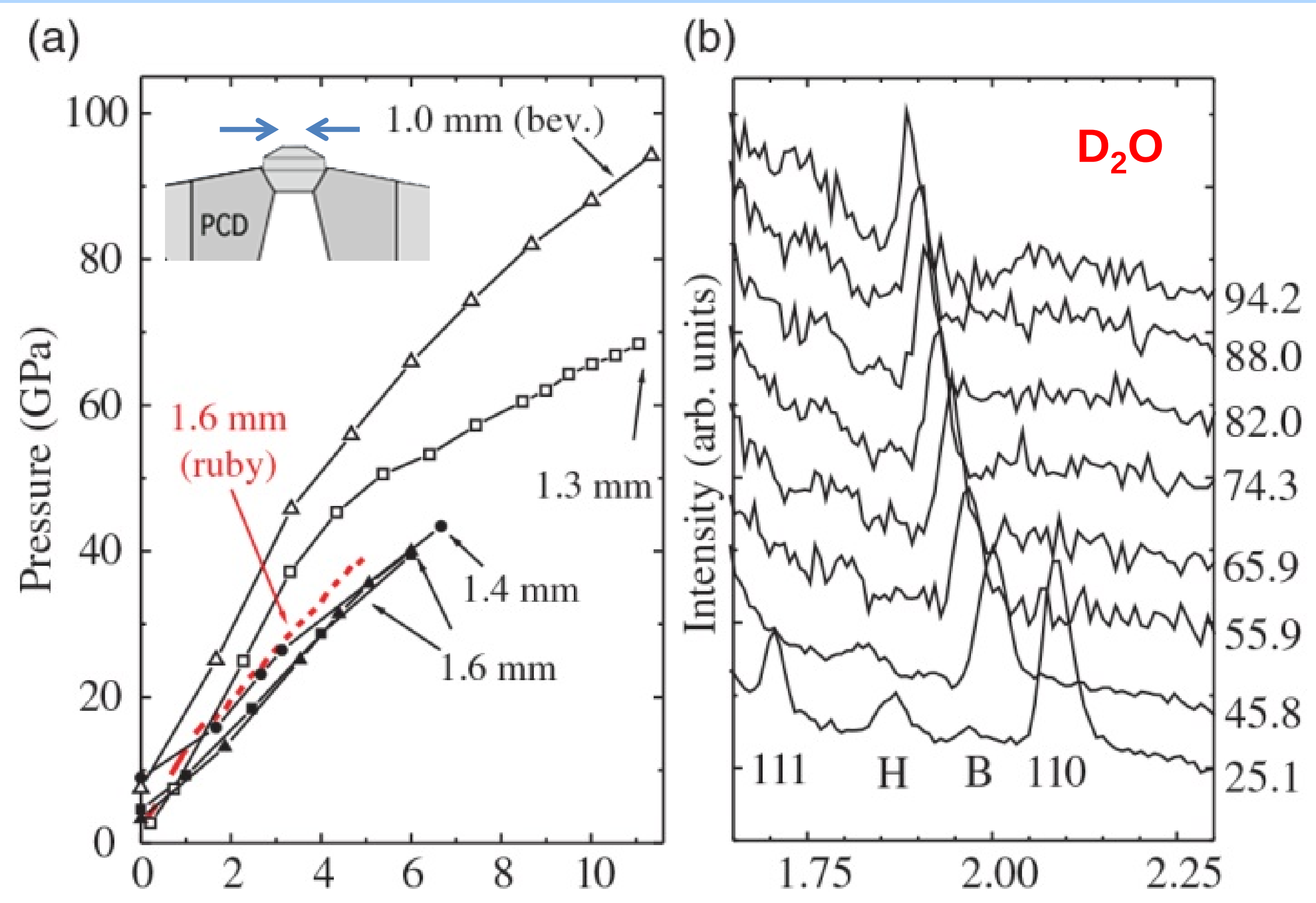
[Militzer *et al. Phys. Rev. Lett*. (2010); see also Caracas, *ibid.* (2008); Hermann *et al., PNAS* (2012)]

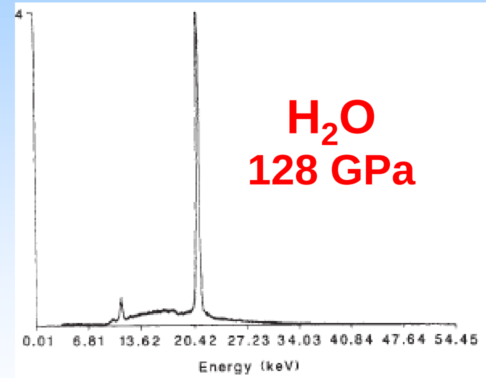




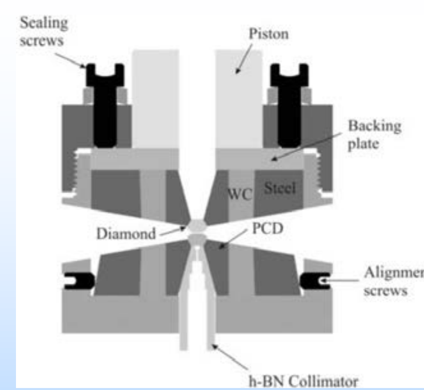
Neutron diffraction at megabar pressures

X-ray H_2O





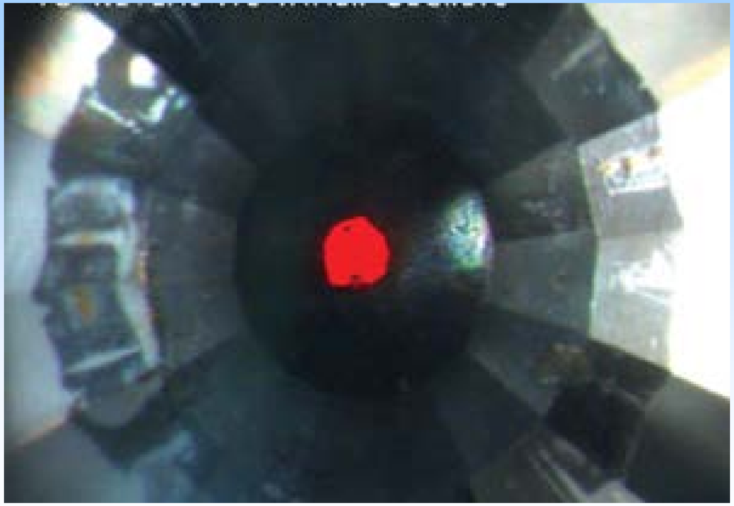
[Hemley et al., *Nature* (1987)]



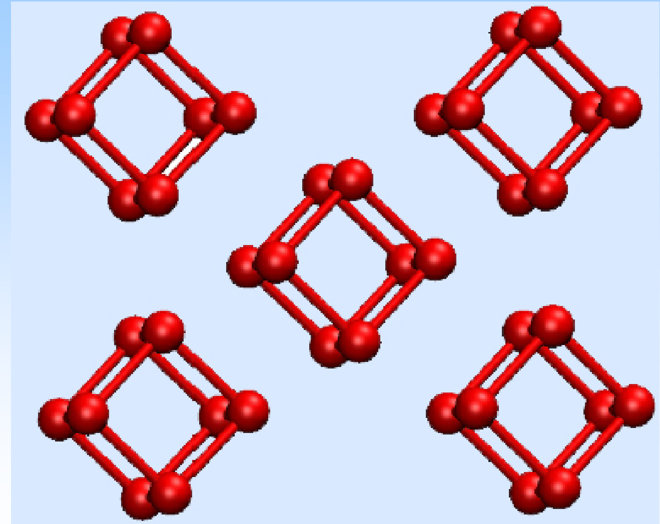
Increase sample volume by x100 at 100 GPa
(10^{-4} mm^3 to ~2 x 10^{-2} mm^3)

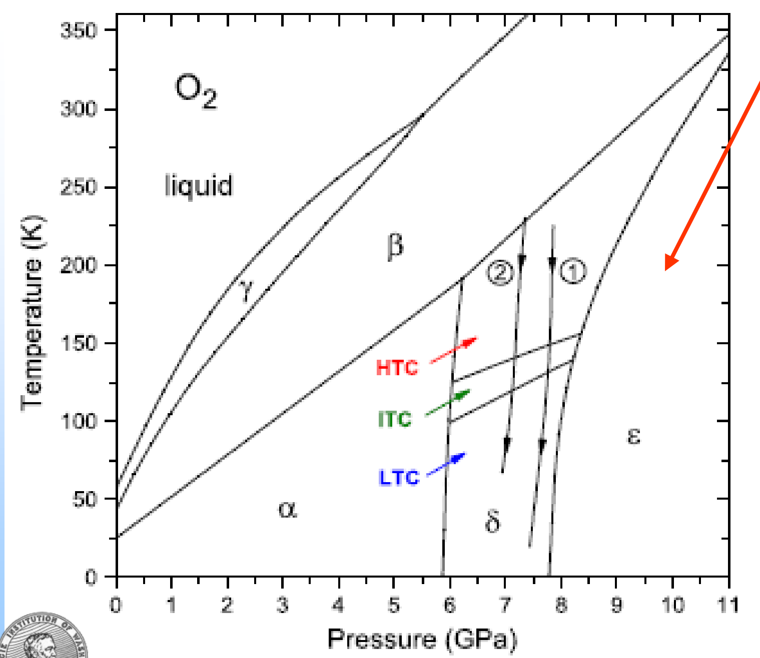
[Boehler et al., *High Pressure Res.* (2013)]

Oxygen under pressure

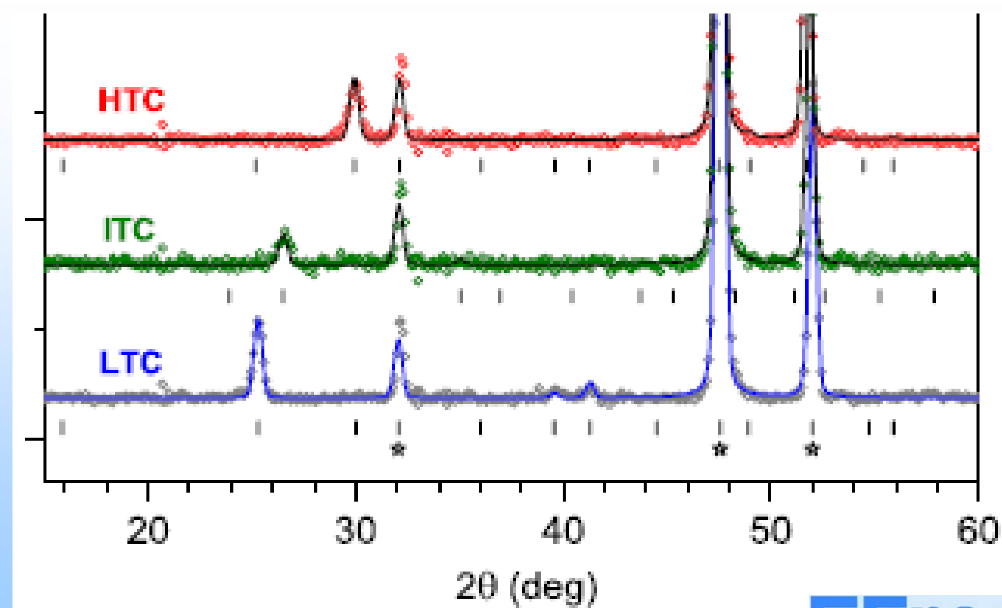


ε-oxygen: $(O_2)_4$ clusters (>8 GPa)



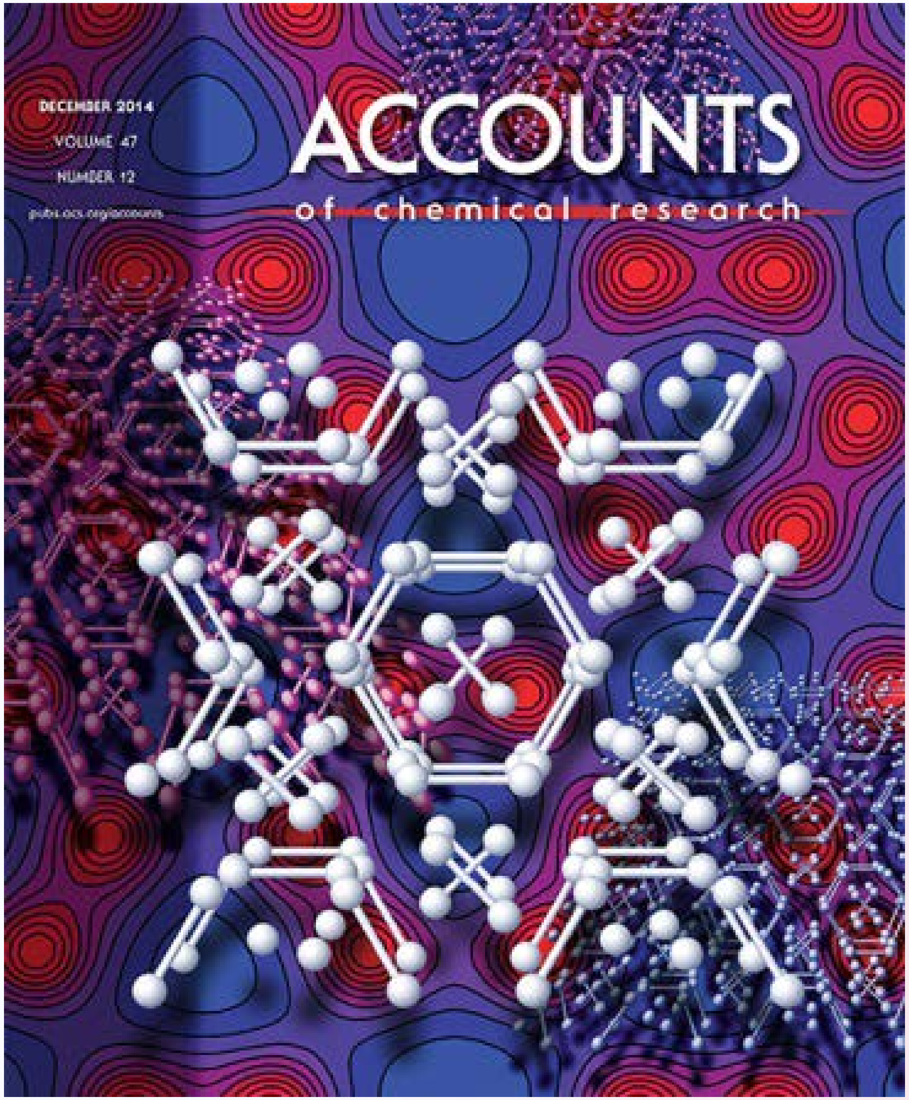


Neutron scattering shows magnetic collapse



[Klotz et al., *Phys. Rev. Lett.* (2010)]

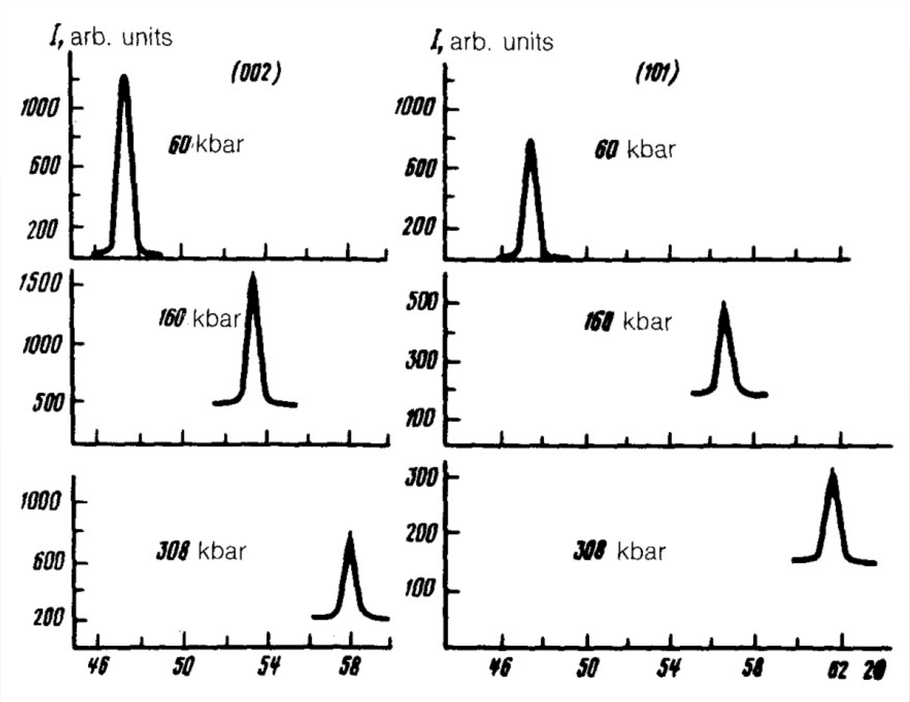
Hydrogen under pressure



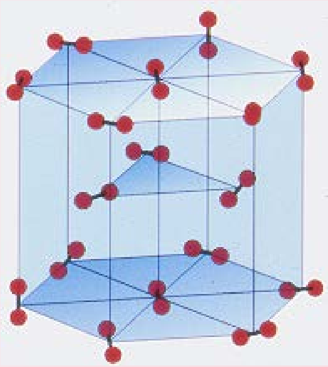
'Graphenic' hydrogen at 230 GPa (phase IV)

[Naumov & Hemley, *Accts. Chem. Res.* (2014)]

Neutron diffraction of D_2 to 30 GPa (phase I)

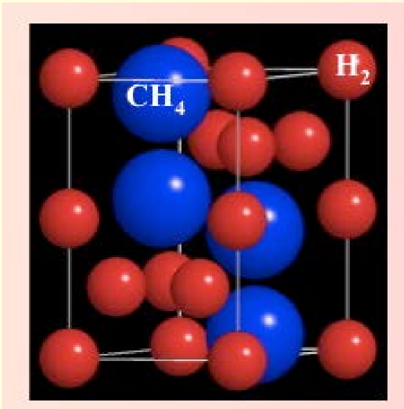


[Glazkov et al., *JETP Lett.* (1988)]



Rotational disordered hcp

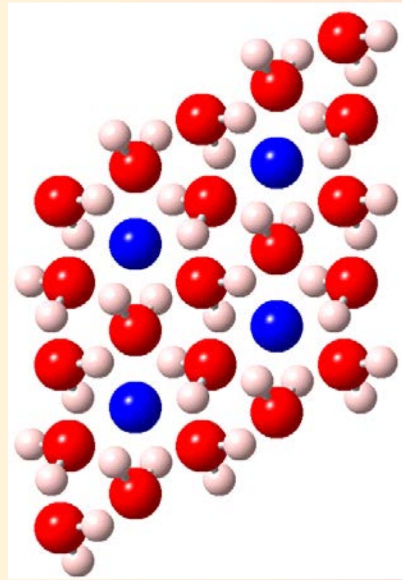
Novel Dense Molecular Compounds



$CH_4(H_2)_4$

33.4 wt% H_2

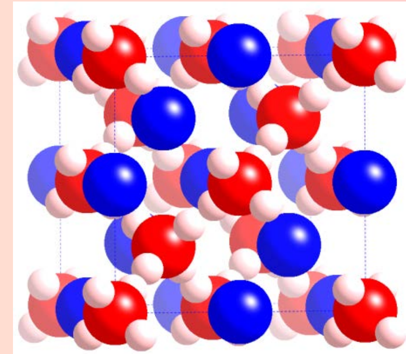
[Somayazulu *et al., Science* (1996);
W. Mao *et al. Chem. Phys. Lett.* (2005)]



$(H_2O)_2H_2$

α-quartz-type

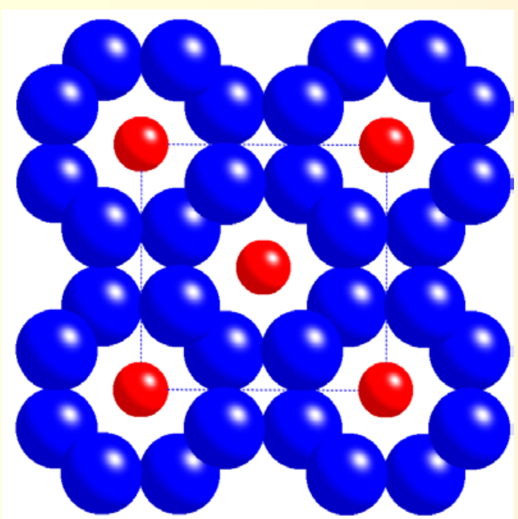
[Strobel et al.,
J. Phys. Chem.
(2011)]



H_2O-H_2

11.3 wt% H_2

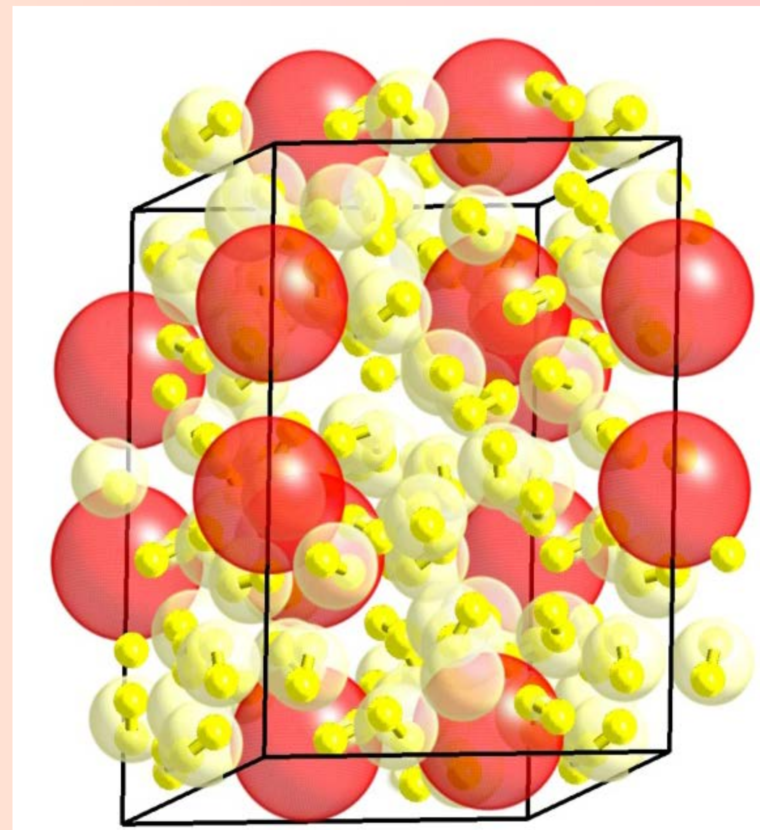
[Vos et al., *Phys. Rev. Lett.* (1993)]



$(H_2S)_2H_2$

Al_2Cu type

[Strobel et al.,
tPhys. Rev. Lett.
(2010)]



$Xe(H_2)_7$

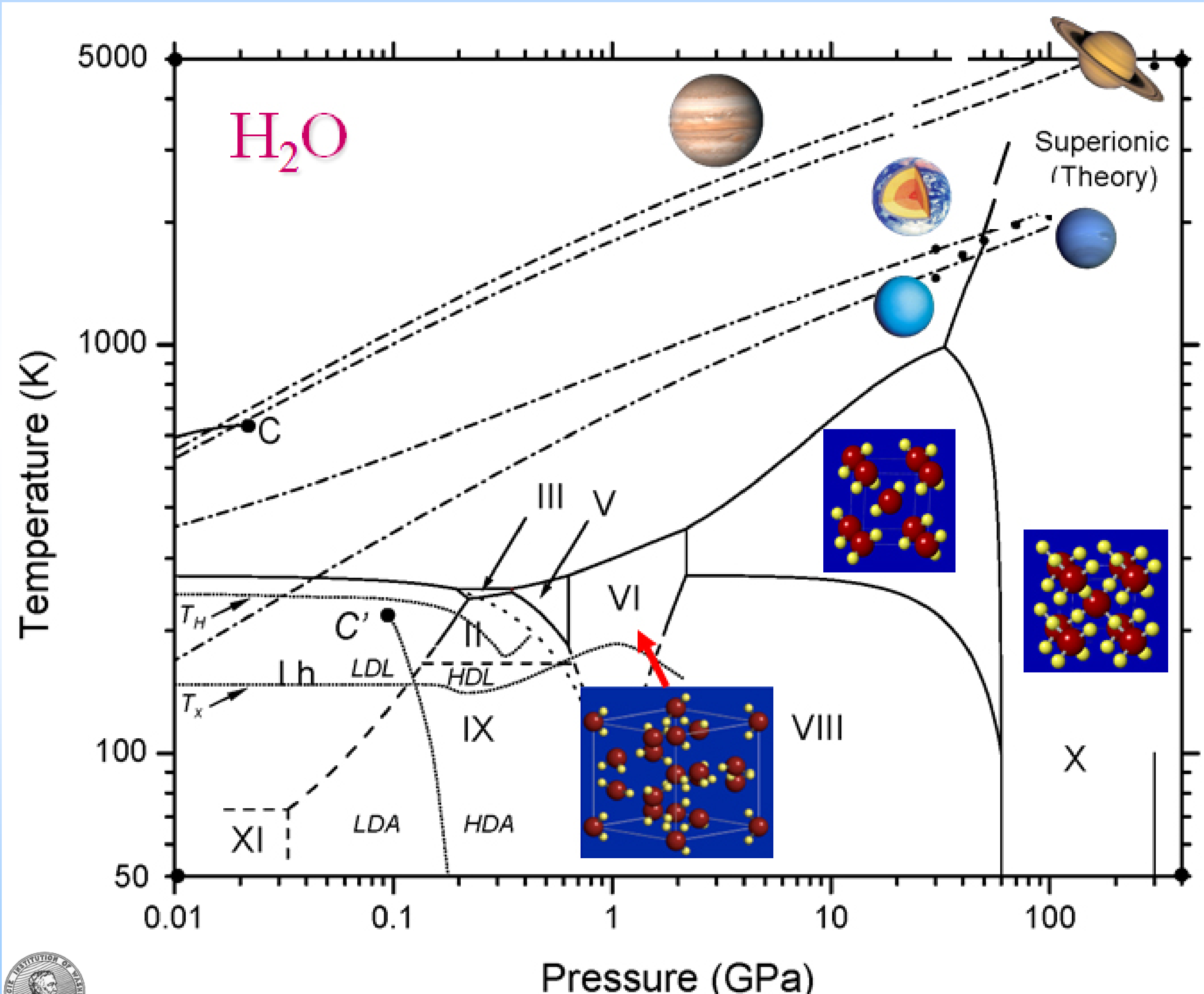
Insulating to >255 GPa

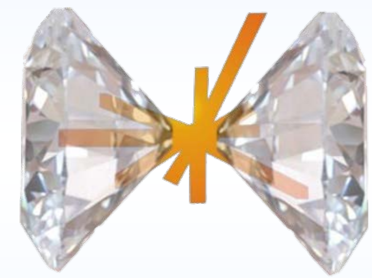
[Somayazulu et al., *Nature Chem.* (2009)]

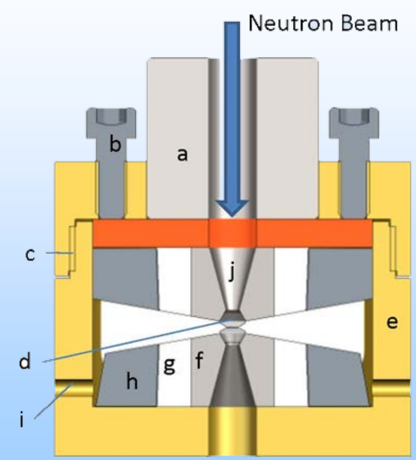
Higher pressure: Superconductor: T_c = 190 K (!)

[Eremets et al., *to be published*]

A bright future for studies of the behavior of water under extreme conditions







ACKNOWLEDGEMENTS

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Razvan Caracas (Lyon)
Neil Ashcroft (Cornell)
Roald Hoffman (Cornell)
A. Hermann (Cornell)

Financial Support

DDOE/SC/BES, DOE/NNSA, A. P. Sloan Foundation, N.S.F., Carnegie Institution