High Temperature Superconductivity in Dense Hydrogen Systems

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Quantum Matter: Computation Meets Experiments
Aspen Center for Physics - Mar. 10, 2020

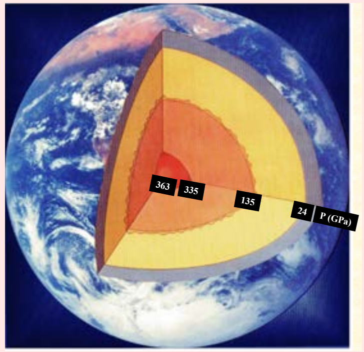
OUTLINE

1. Background/Context
2. Superconductivity and Pressure
3. Dense Hydrogen
4. Superhydrides
5. New Materials

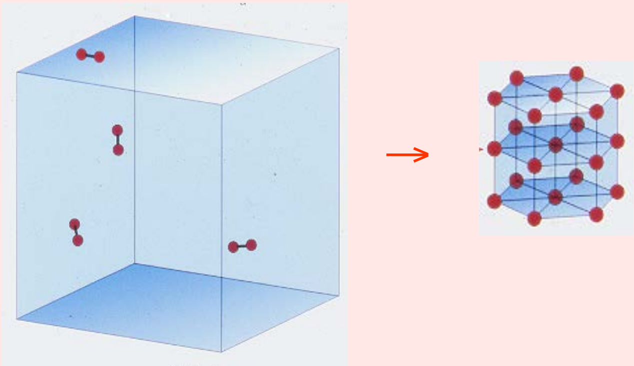
THEMES

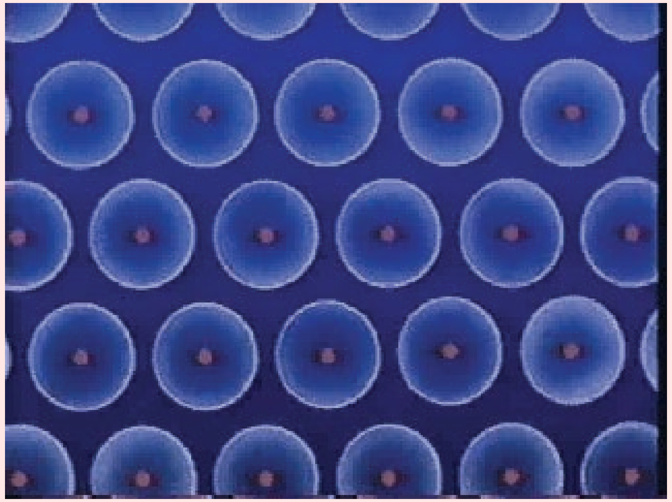
- ***Hydrogen in Extremes***
- ***Computation/Experiment Synergy***
- ***'Materials by Design'***

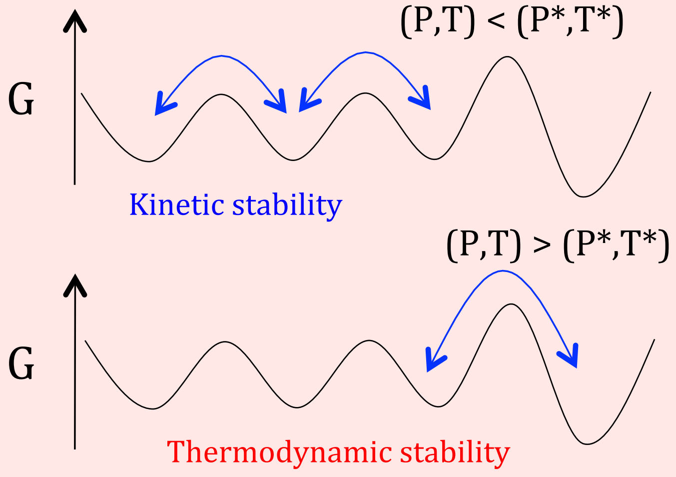
Materials at High Pressure

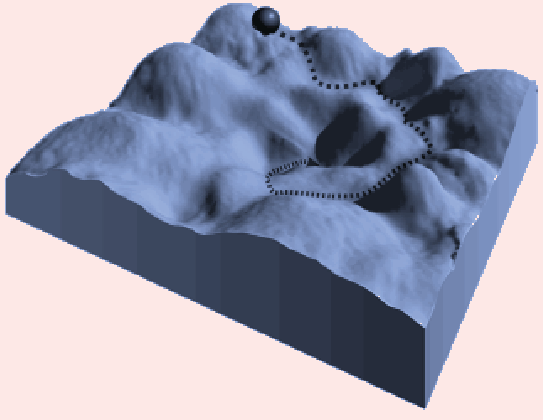


360 GPa









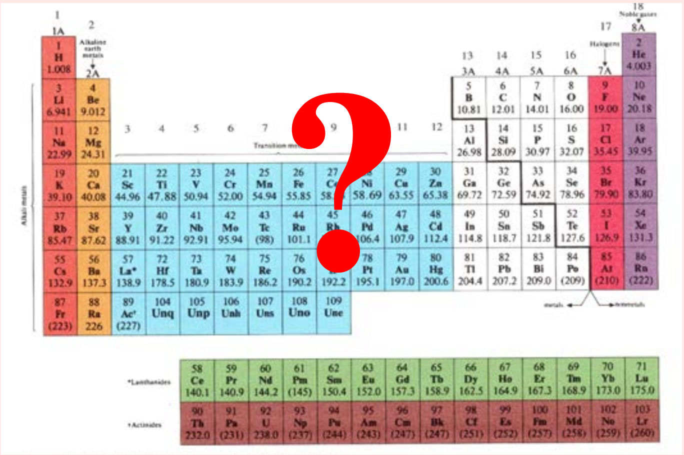
Exploring Energy Landscapes in the Search for New Materials and Phenomena

>100's GPa (to ~TPa)

~ eV energies

valence electrons

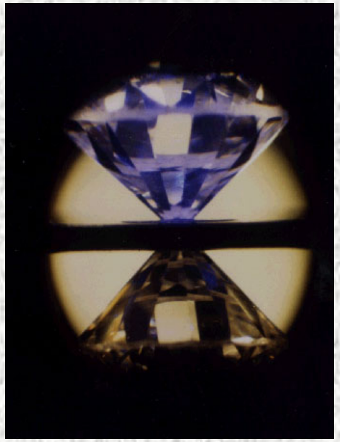
$$P = -\frac{\partial E}{\partial V}$$

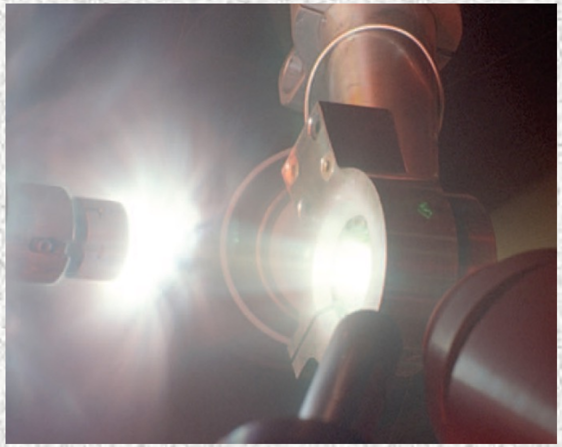


EXPERIMENTS

COMPRESSION TECHNIQUES

Static | *Dynamic*



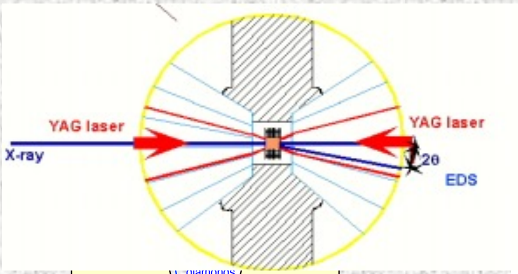


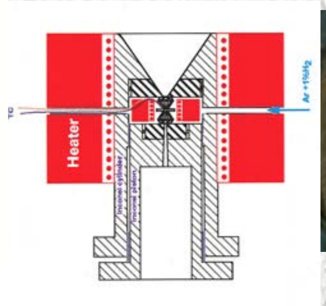
>100's GPa (to ~TPa)

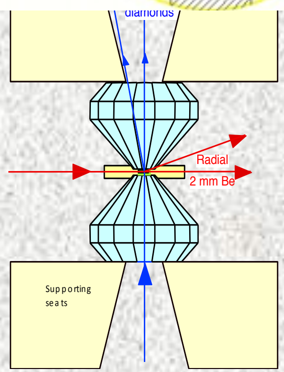
~ eV energies

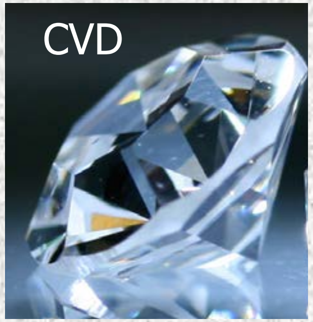
>100's Mbars (1 Gbar)

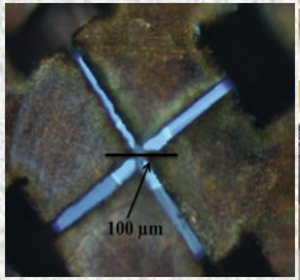
~ keV energies

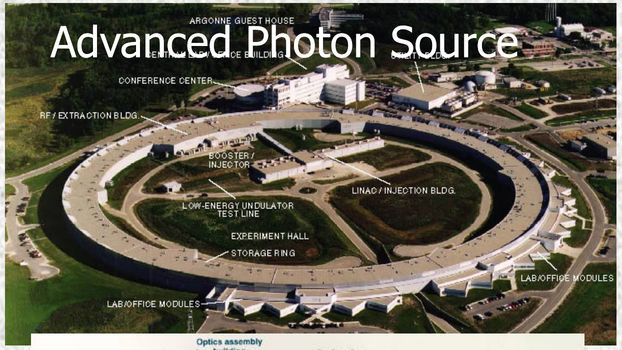


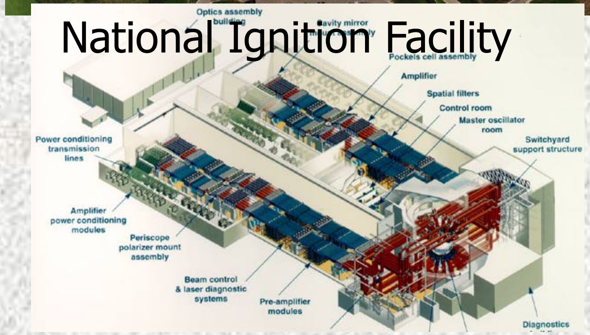












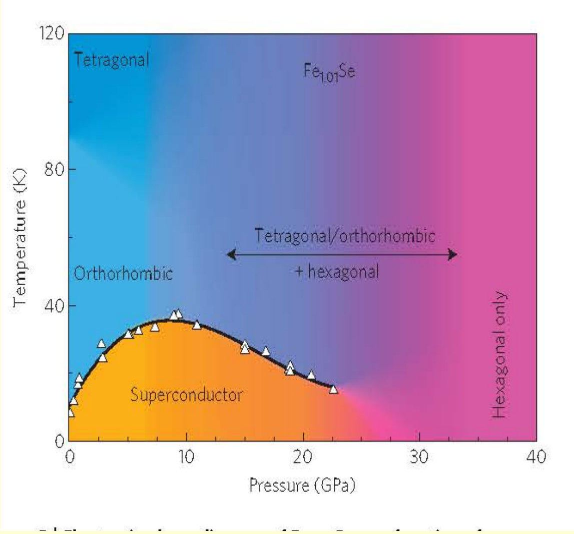
COMPUTATIONS

- **Density Functional**
- **Path Integral, Quantum Monte Carlo**
- **Structure Search Methods**

Pressure Effects on Superconductors

Sn and In

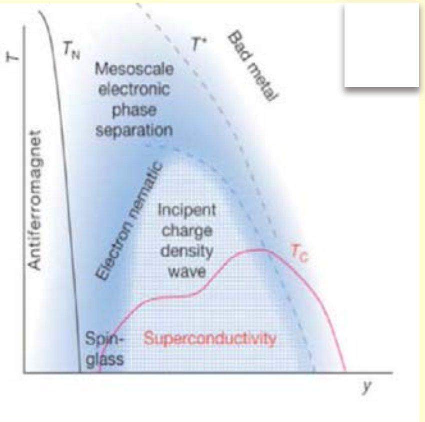
[Sizoo and Kamerlingh Onnes, *Commun. Phys. Lab. Univ. Leiden* (1925)]



$Fe_{1.01}Se$

T_c = 36.7 K (8.9 GPa)

[Medevdev et al., *Nature Mat.* (2009)]

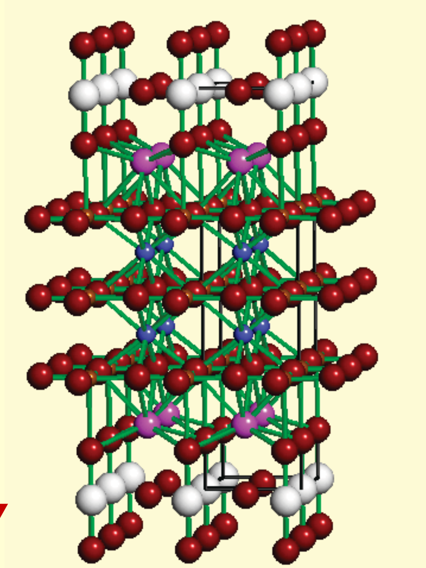


[Fradkin & Kivelson (2012)]

$HgBa_2Ca_2Cu_3O_{8+\delta}$

T_c = 164 K (30 GPa)

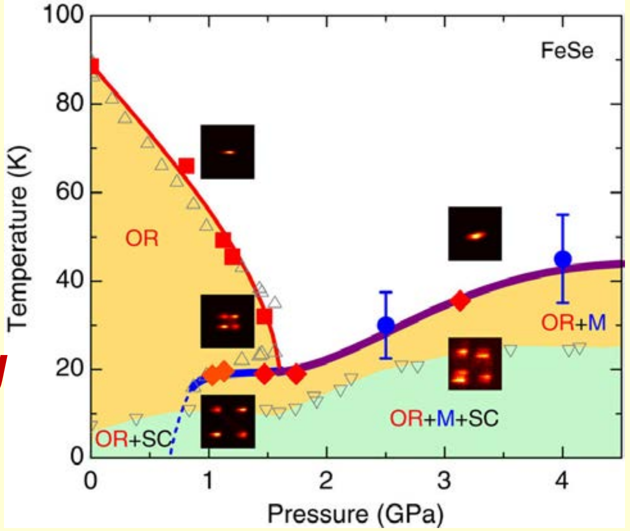
[Gao *et al.*, (1994); Lokshin *et al.* (2002)]



Electrical Conductivity
Magnetic Susceptibility
X-ray Diffraction

Electrical Conductivity
Magnetic Susceptibility
X-ray Diffraction
Mossbauer Spectroscopy
Nuclear Forward Scattering

Low P-T Phase Diagram

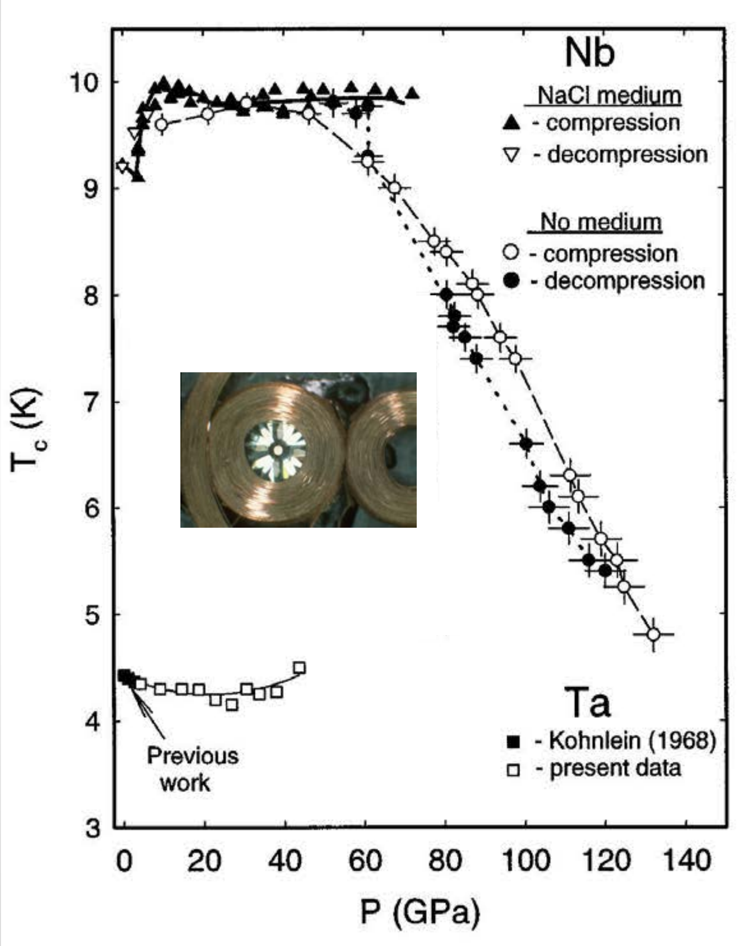


[Kothapalli et al, *Nature Comm.* (2016)]

High Pressure and Superconductivity

Superconductivity at Megabar Pressures

Niobium

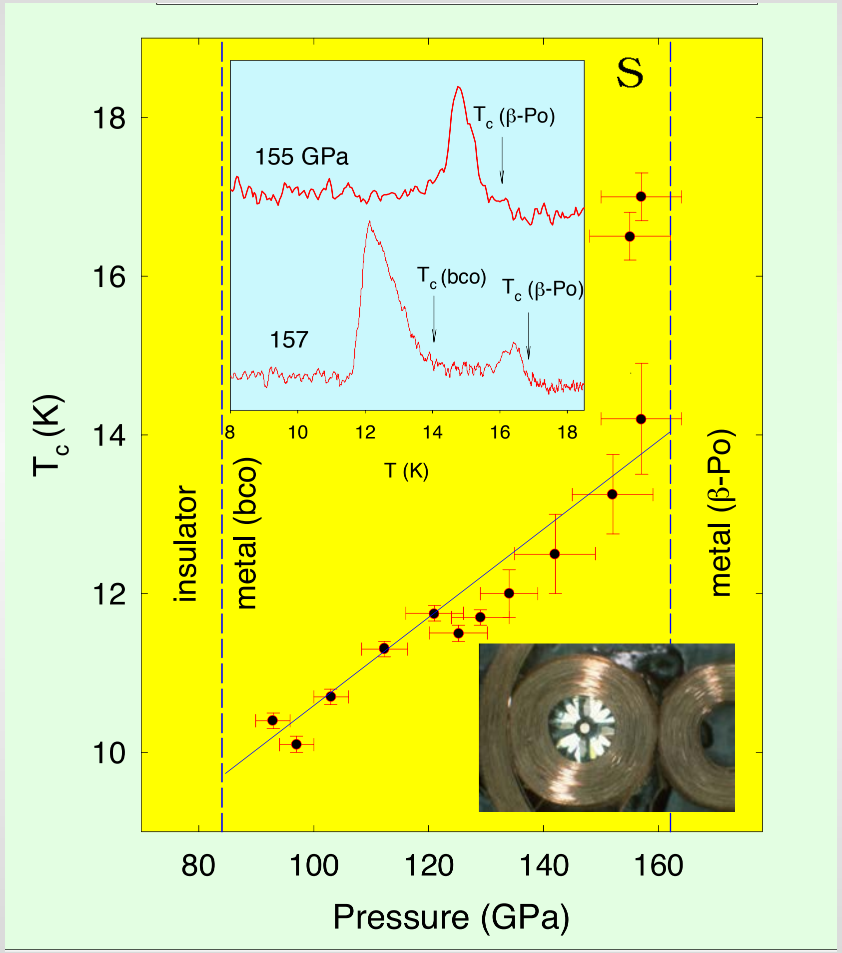


T_c = 9.8 K at 80 GPa

(magnet. suscept.)

[Struzhkin et al., *Phys. Rev. Lett.* (1997)]

Sulfur

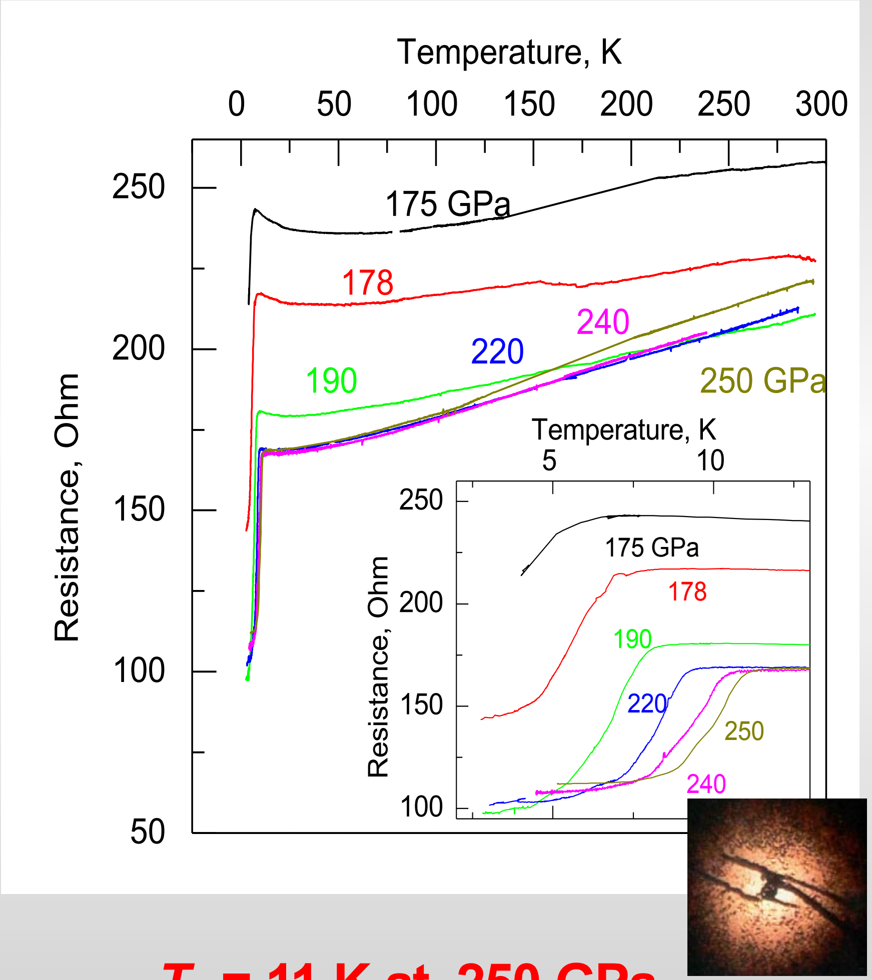


T_c = 17 K at 160 GPa

(magnet. suscept.)

[Struzhkin et al., *Nature* (1997)]

Boron



T_c = 11 K at 250 GPa

(electrical conductivity)

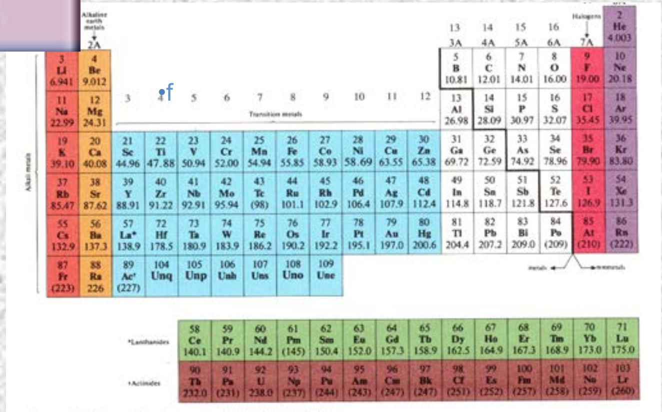
[Eremets et al., *Science* (2001)]

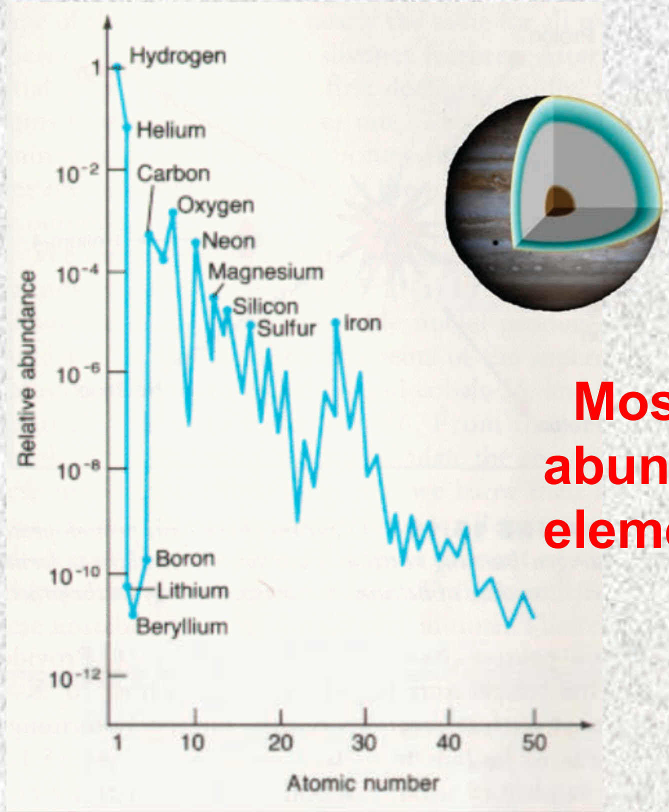
ELEMENT ONE

"Let's start at the very beginning, a very good place to start…"

The Sound of Music
Rogers and Hammerstein

Starting point for chemistry

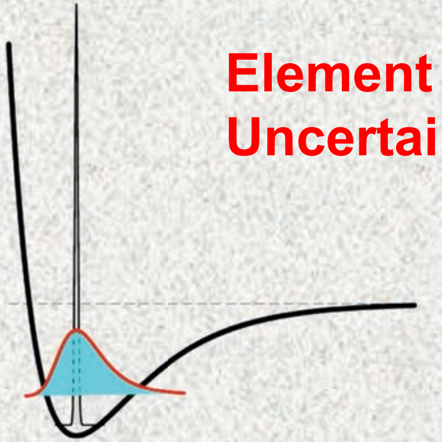




Most abundant element

$$\hat{H} = \sum_{i}^{\text{nuclei}} \hat{T}(i) + \sum_{j}^{\text{electrons}} \hat{T}(j) + \sum_{k}^{n} \sum_{l}^{e} \hat{V}(k,l) + \sum_{m}^{e} \sum_{n>m}^{e} \hat{V}(m,n) + \sum_{o}^{n} \sum_{p>o}^{n} \hat{V}(o,p)$$

Test of fundamental theory



Element of Uncertainty'

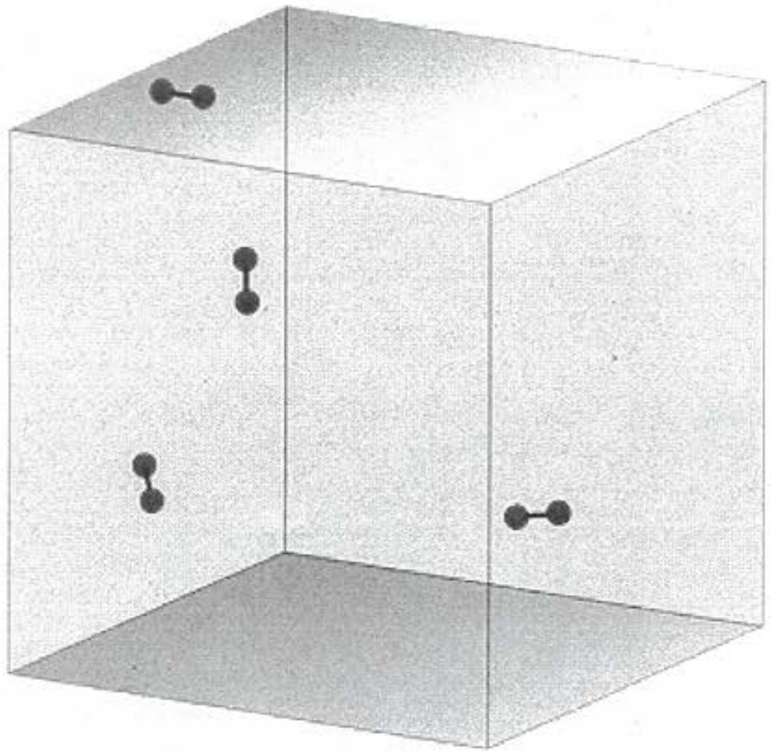
Metallic and Superconducting Hydrogen

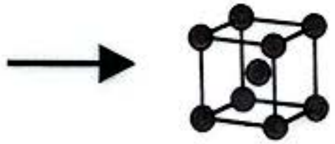
DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

On the Possibility of a Metallic Modification of Hydrogen

E. WIGNER AND H. B. HUNTINGTON, *Princeton University*

(Received October 14, 1935)





> 25 GPa

VOLUME 21, NUMBER 26 PHYSICAL REVIEW LETTERS 23 DECEMBER 1968

METALLIC HYDROGEN: A HIGH-TEMPERATURE SUPERCONDUCTOR?

N. W. Ashcroft
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 3 May 1968)

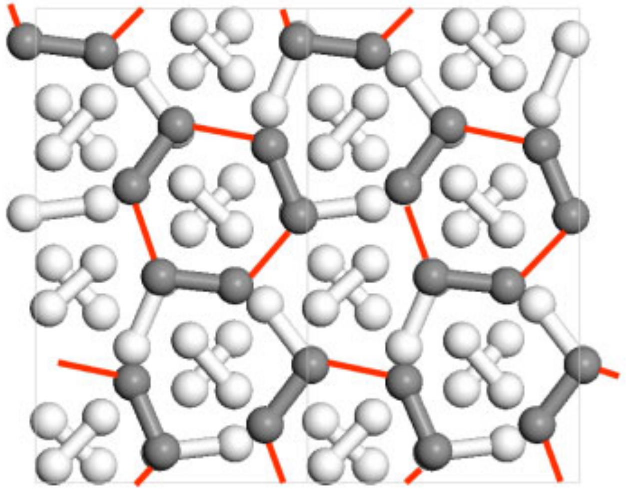
Bardeen-Cooper-Shrieffer (BCS)

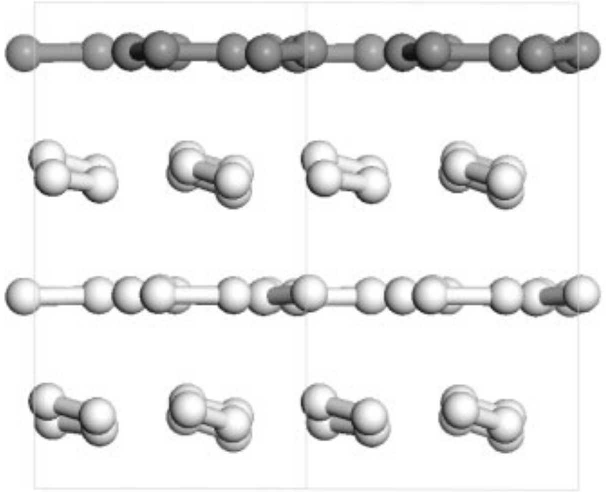
Phonon-mediated; high Θ_D

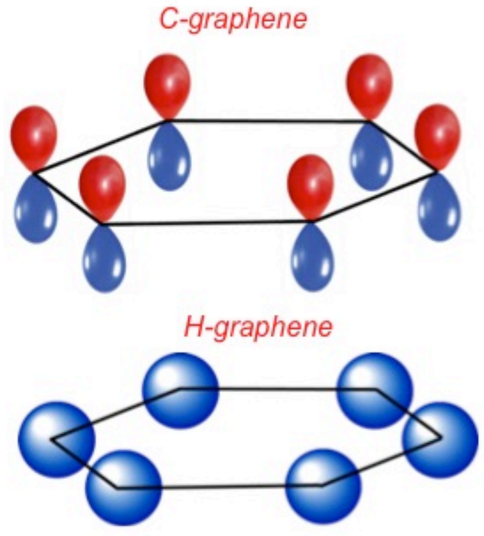
$$T_c = 0.85\Theta_D \exp(-1/N_0 V),$$

T_c >> 300 K?

Dense Molecular Hydrogen



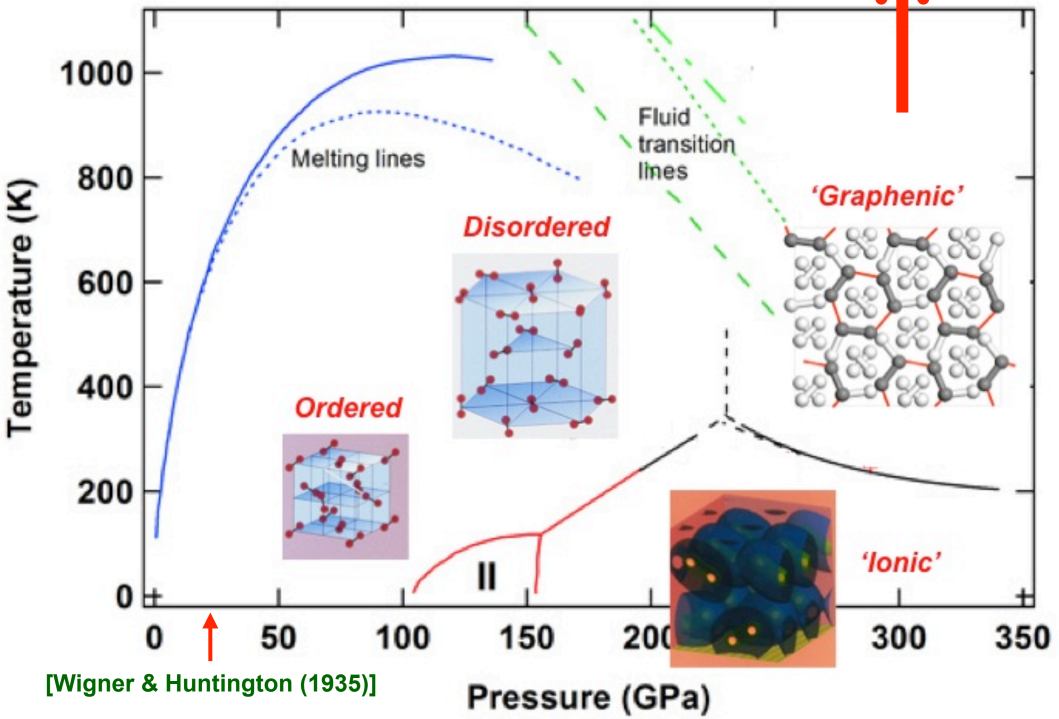




H_6 **'aromatic cluster'**

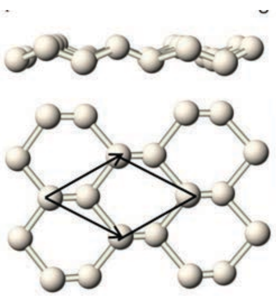
[Naumov & Hemley, *Acct. Chem. Res.* (2014);
see also, LeSar & Herschbach, *J. Phys. Chem.* (1981);
Dixon et al., *Faraday Disc.* (1977)]

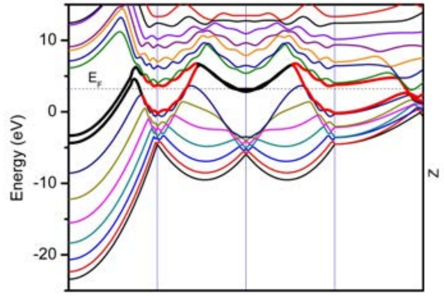
[Pickard & Needs,
Nature Phys. (2007)]

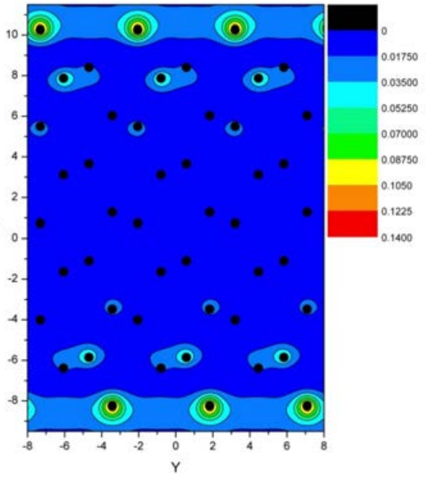


[Wigner & Huntington (1935)]

Predicted Topological Semimetal

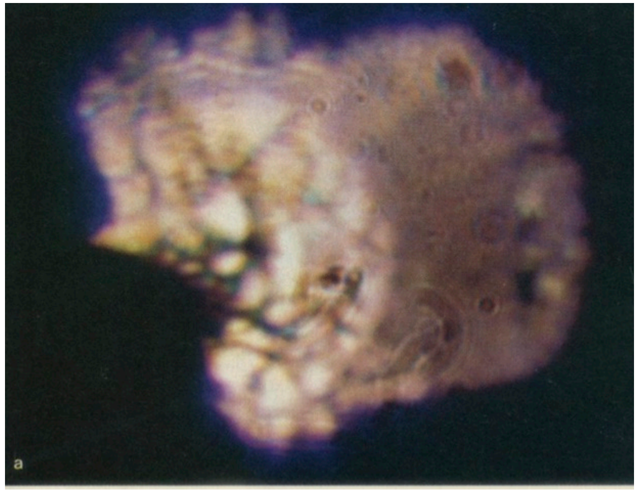






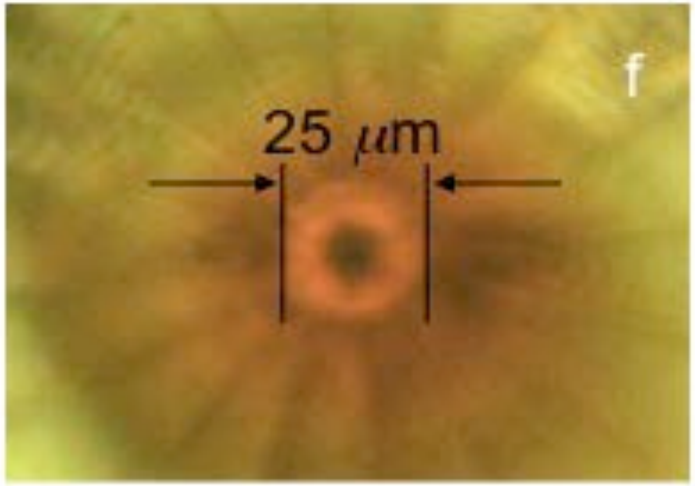
[Naumov & Hemley,
Phys. Rev. Lett. (2016)]

Is Hydrogen Metallic at these *P-T* Conditions?



>200 GPa, 77 K

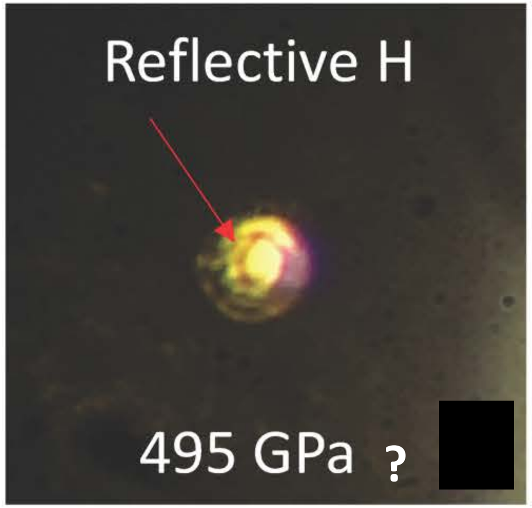
[Mao & Hemley, *Science* (1989)]



360 GPa, 100 K

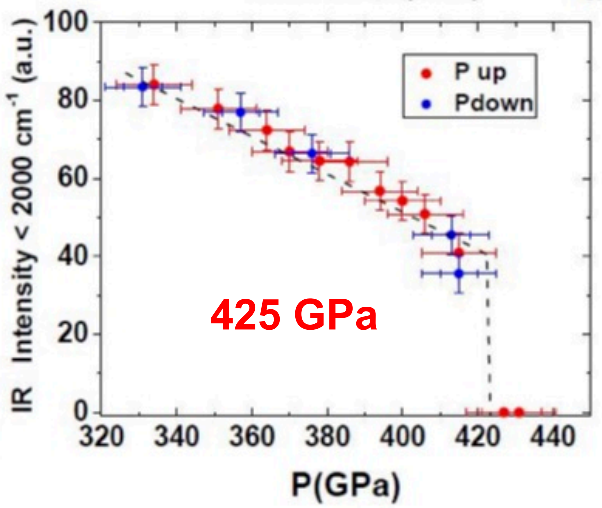
[Zha et al., *Phys. Rev. Lett.* (2012)]

- ***Semiconducting/ Semimetallic***



[Dias & Silvera, *Science* (2017)]

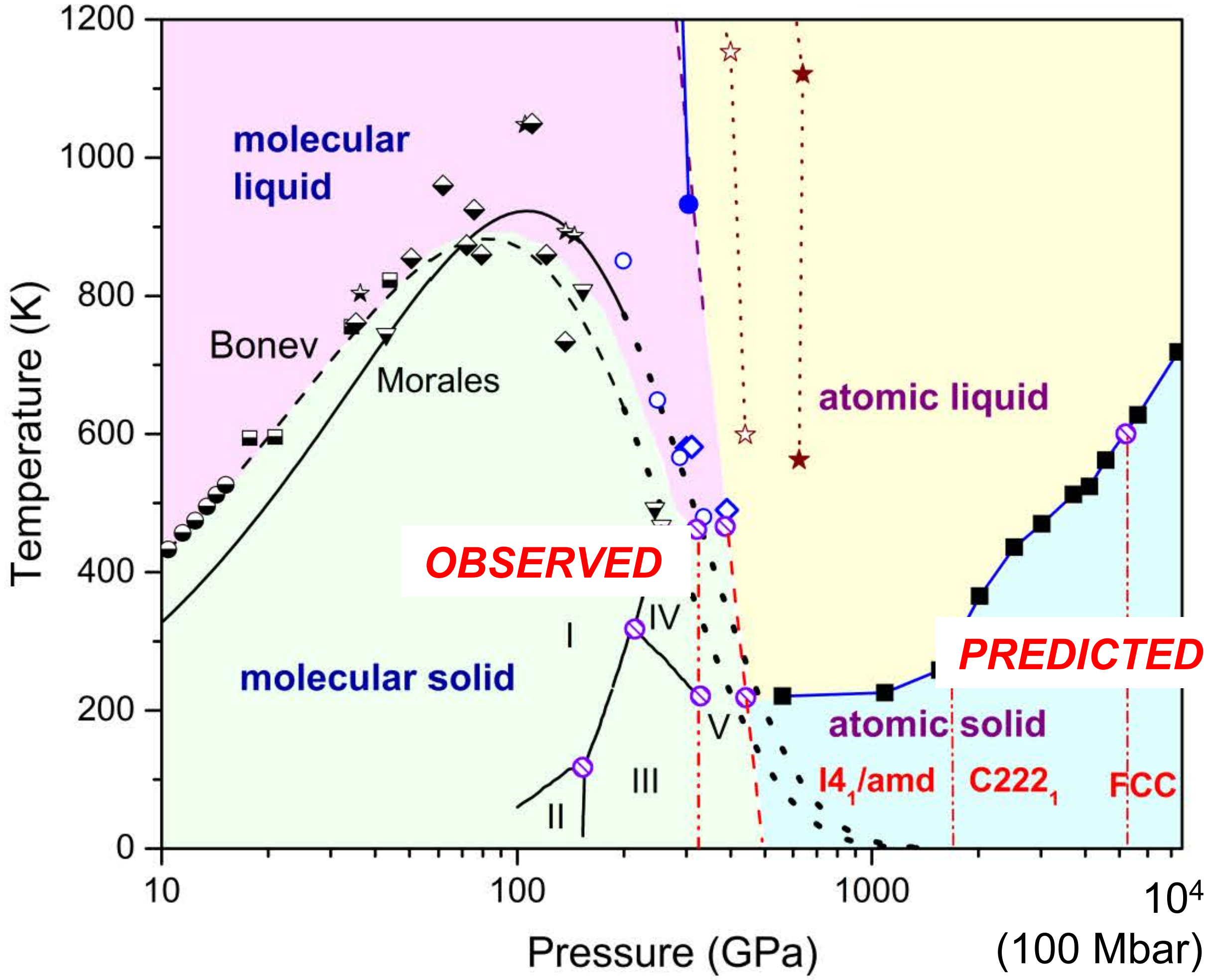
Infrared Absorption



[Loubeyre et al. Nature (2020)]

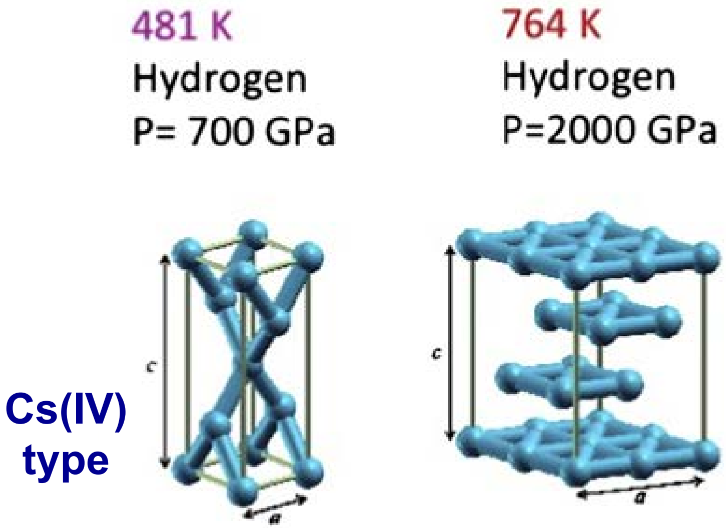
- ***Atomic Metallic?***

Hydrogen at Higher Pressures



[Geng et al., *Phys. Rep.* (2016)]

HIGH T_C SUPERCONDUCTIVITY

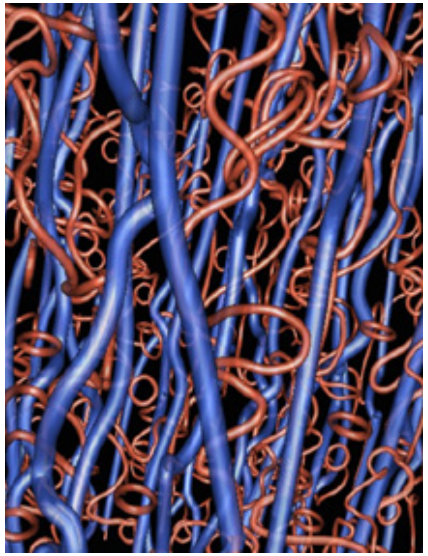


[see, McMahon et al., *Rev. Mod. Phys.* (2012)]

Superconducting Superfluid?

> 400 GPa

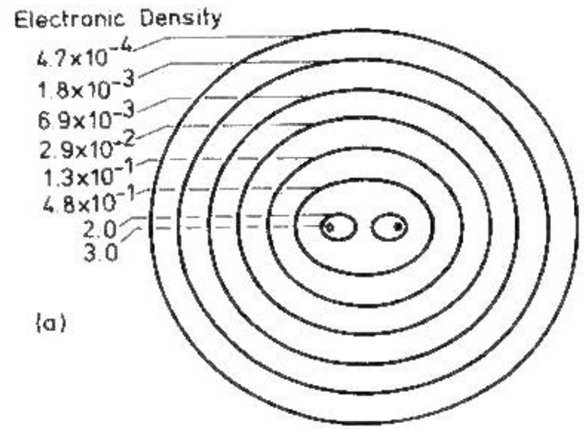
[Babaev et al., *Nature* (2004); *Phys. Rev. Lett.* (2005)]



- ***'Utrahigh' T_c Superconductor (e.g., >700 K)?***
- ***Superfluidity/Superconductivity?***

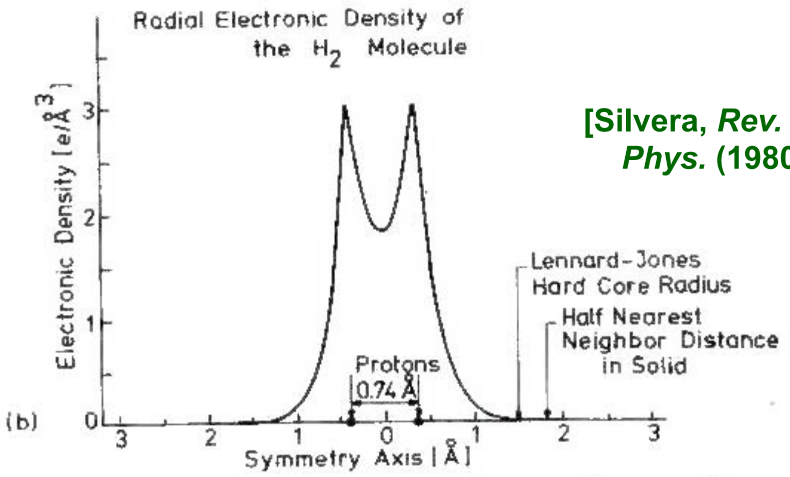
Breaking the Bond with Compression and Chemistry

DIATOMIC HYDROGEN



Charge Density

E_b = 4.52 eV



[Silvera, *Rev. Mod. Phys.* (1980)]

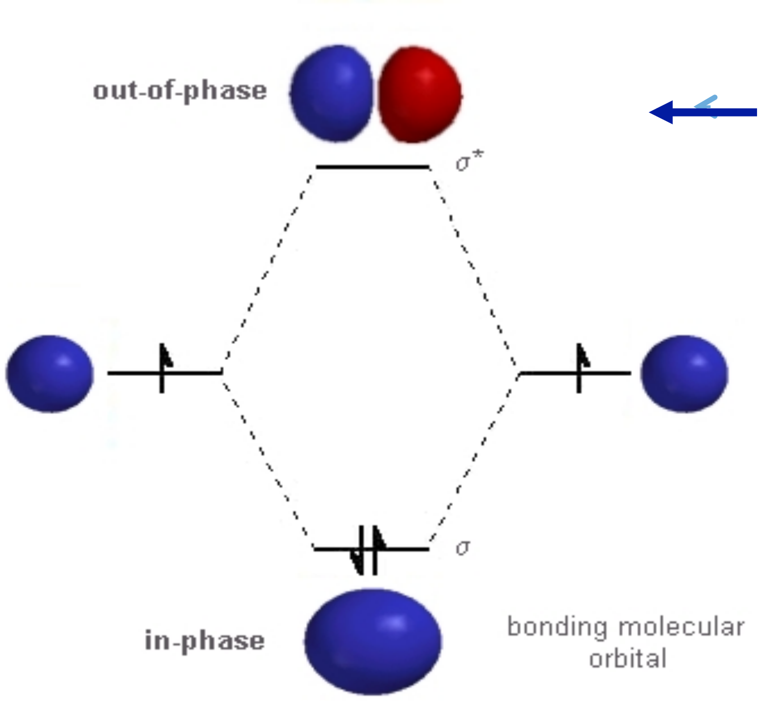
VOLUME 50, NUMBER 17 PHYSICAL REVIEW LETTERS 25 APRIL 1983

Approaches for Reducing the Insulator-Metal Transition Pressure in Hydrogen

A. E. Carlsson and N. W. Ashcroft

Laboratory of Atomic and Solid State Physics and the Materials Science Center, Cornell University, Ithaca, New York 14853

(a) Impurity stabilization (chemical doping)
(b) Electron-hole pair creation



electron doping to destabilize H_2

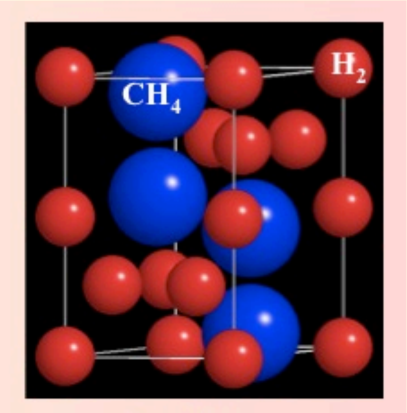
"Chemical Pre-Compression"

[Ashcroft, *Phys. Rev. Lett.* (2004)]

Reluctant Alkali or Tenacious Halogen?

[Ashcroft, *Phys. World* (1995)]

Novel Dense Molecular Compounds



$CH_4(H_2)_4$

33.4 wt% H_2

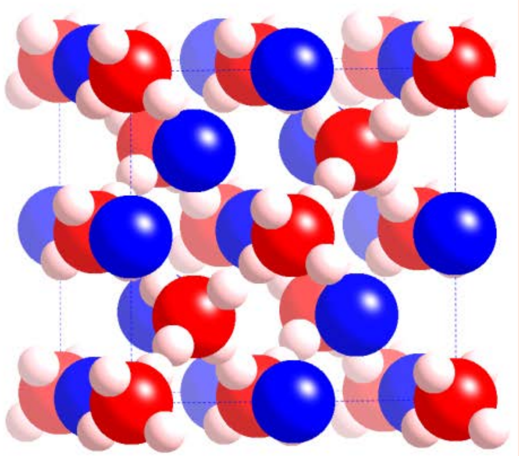
[Somayazulu *et al., Science* (1996);
W. Mao *et al. Chem. Phys. Lett.* (2005)]

H_2O-H_2

'Stuffed ice VII'

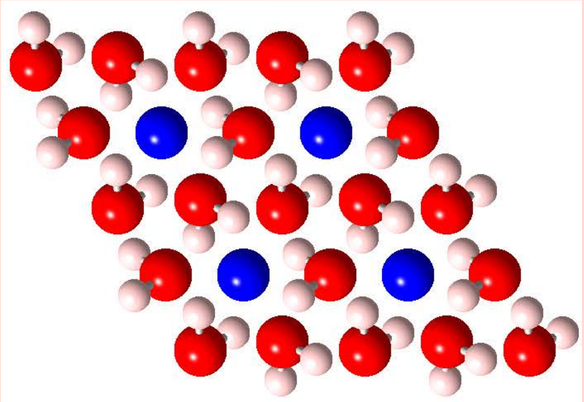
11.3 wt% H_{2D}

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

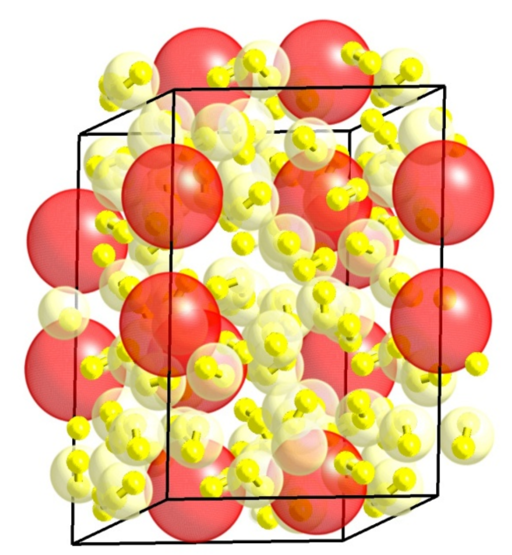


$(H_2O)_2H_2$

Quartz-type ice



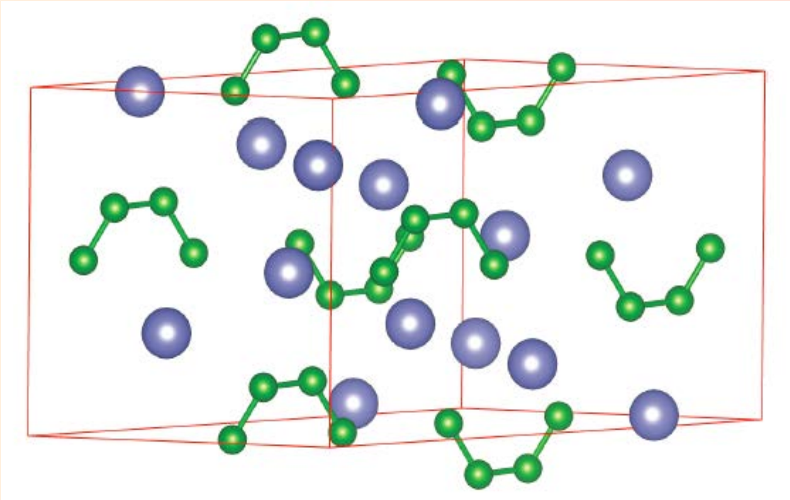
[Strobel et al., *J. Am. Chem. Soc.* (2016)]



$Xe(H_2)_8$

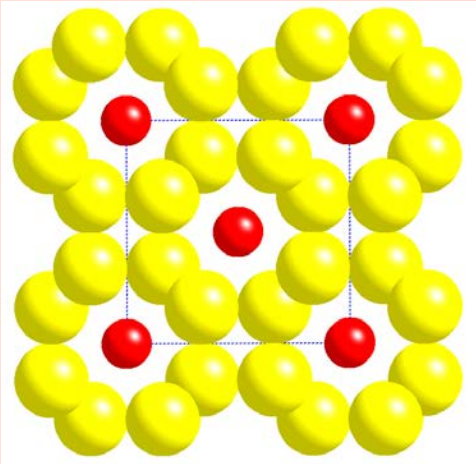
[Somayazulu et al.,
Nature Chem. (2009)]

$Xe_3(N_4)_n$



[Somayazulu *et al., in preparation*]

$(H_2S)_2H_2$



Al_2Cu type

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

➢ ***PRECURSOR TO*** H_3S

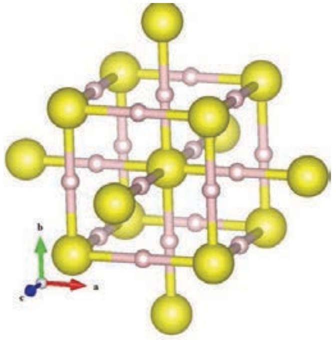
Success of Structure Search Methods

Predicted Very High-T_c Superconductors at 100-300 GPa

[*e.g.*, Ma, Oganov, Pickard, Zurek]

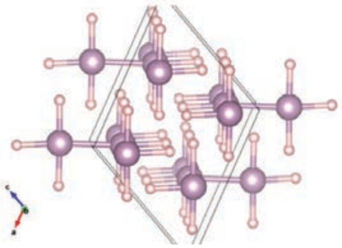
OBSERVED

SH_3
T_c = 203 K



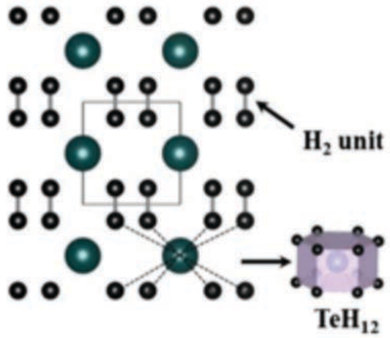
[Li et al., *J. Chem. Phys.* (2014); Duan *et al., Sci. Rep.* (2014); Drozdov et al., *Nature* (2015)]

PH_3
T_c = 100 K



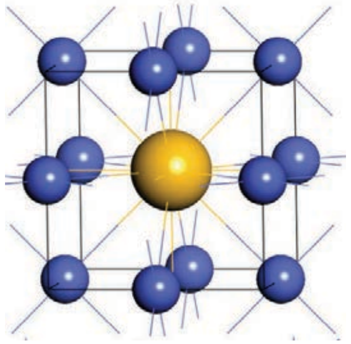
[Liu *et al., JPCC* (2016); Shamp *et al. JACS* (2016); Drozdov et al. arXiv (2016)]

TeH_4
T_c = 107 K



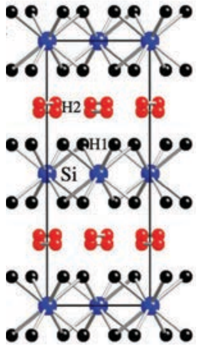
[Zhong *et al., PRL* (2010)]

$GeH_4(H_2)_2$
T_c = 153 K



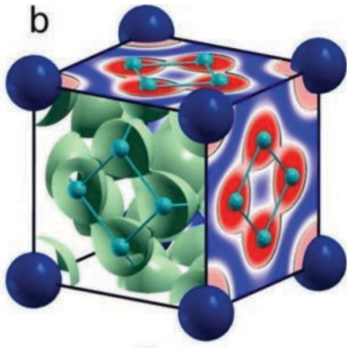
[Jin *et al., PNAS* (2010)]

$SiH_4(H_2)_2$
T_c = 107 K



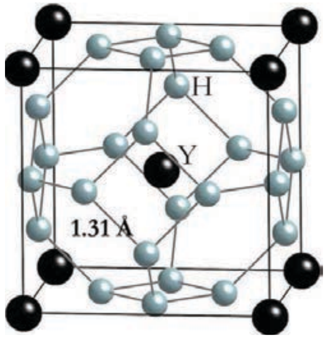
[Li *et al., PNAS* (2010)]

CaH_6
T_c = 235 K



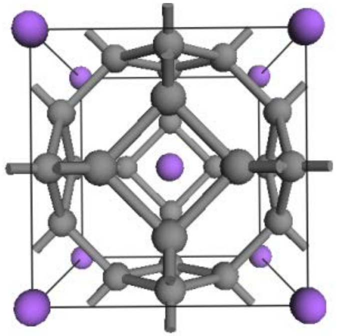
[Wang *et al., PNAS* (2012)]

YH_6
T_c = 251 K



[Li *et al., Sci. Rep.* (2015)]

NaC_6
T_c = 116 K



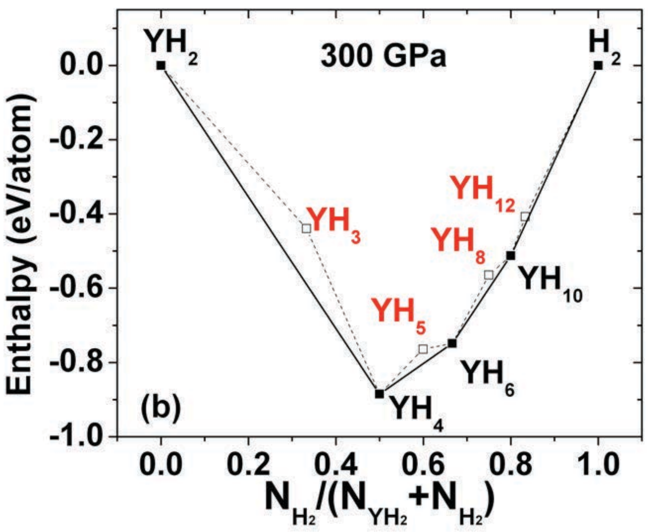
[Lu *et al., Phys. Rev. B* (2016)]

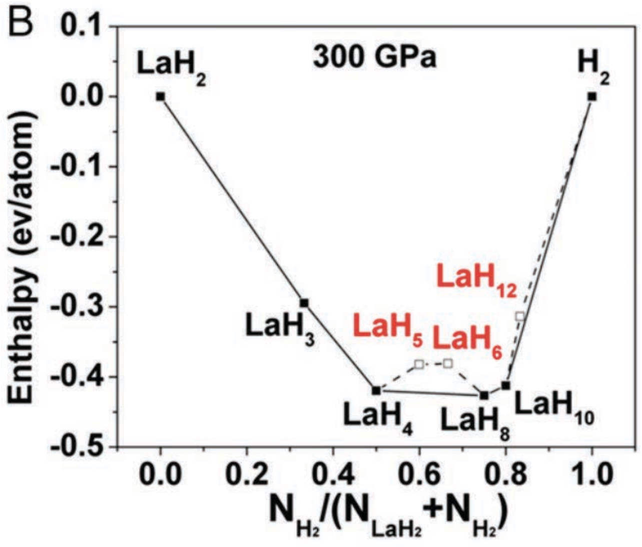
Higher Hydrides?

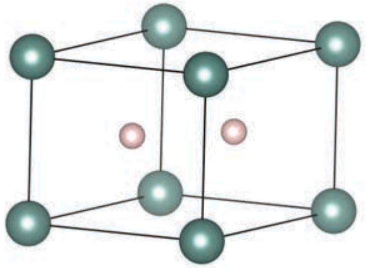
Rare Earth – Hydrogen System

DFT Structure-Search (CALYPSO)

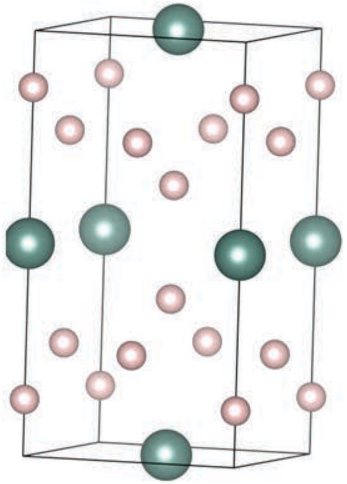
[Liu *et al.*, *PNAS* (2017)]



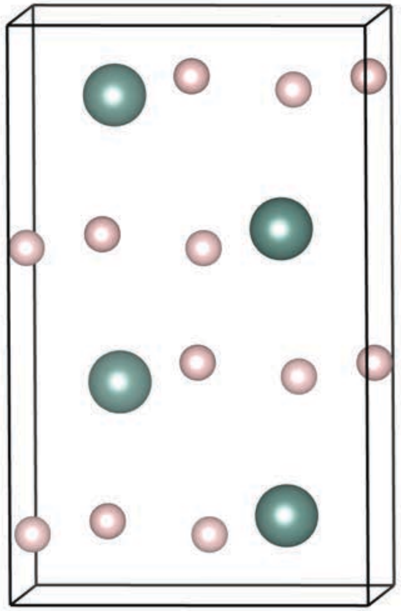




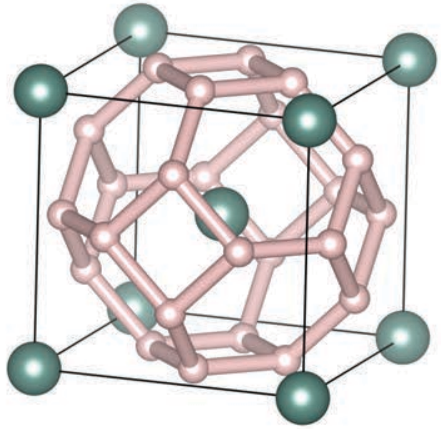
AH_2



AH_4

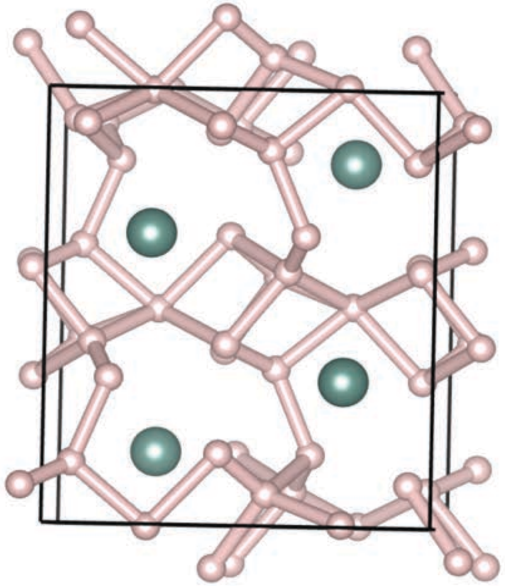


AH_3

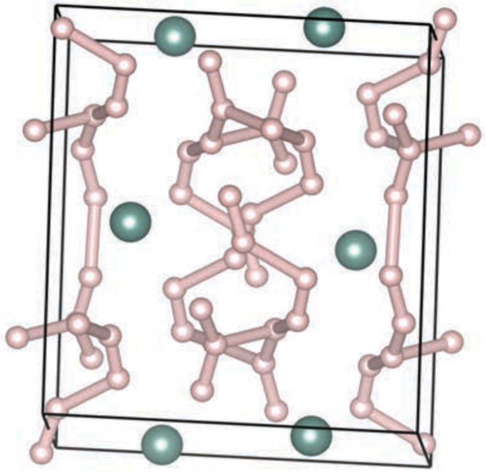


AH_6

Superhydrides (AH_n n > 6)



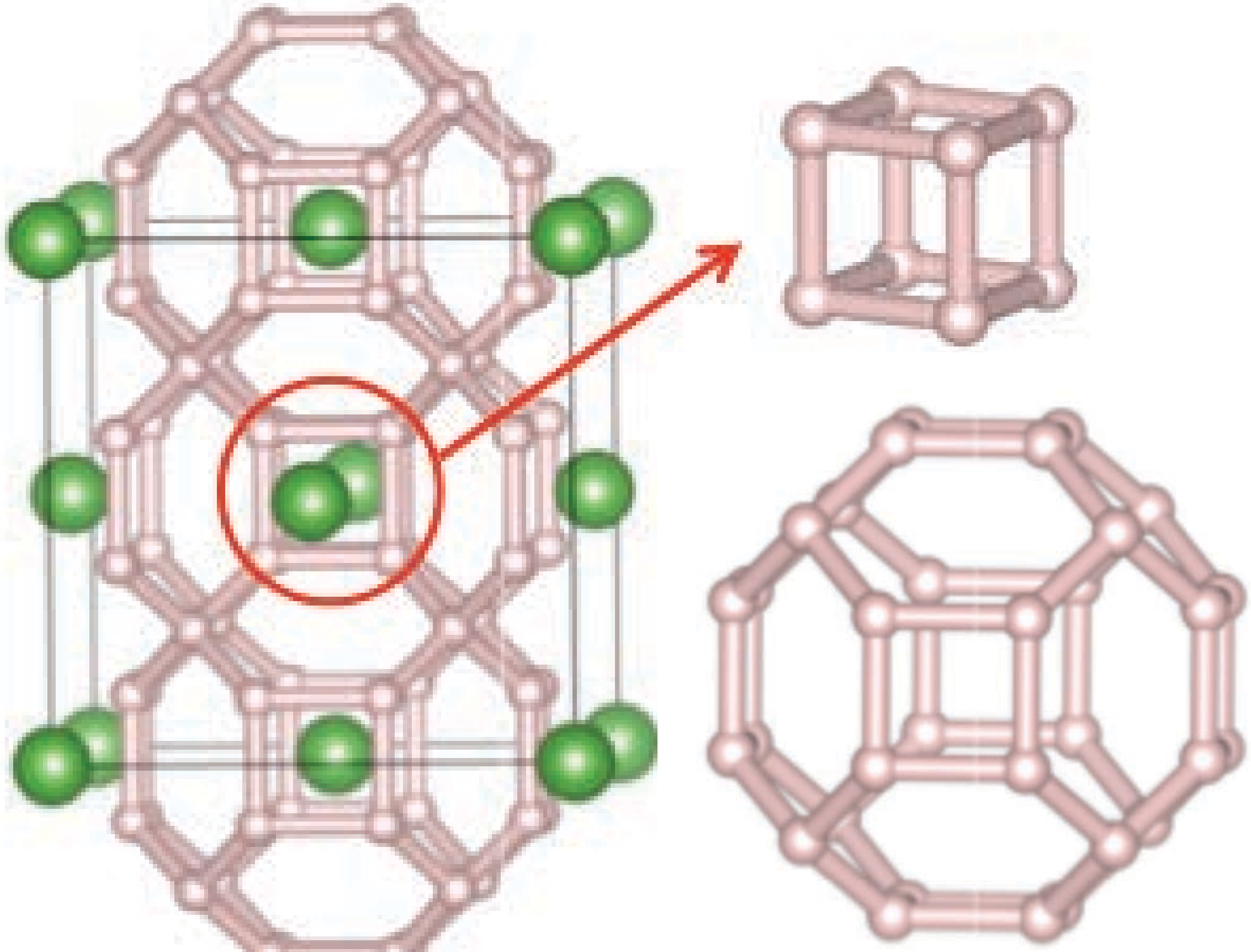
AH_8



AH_{12}

Predicted La and Y Superhydrides

'Novel' Clathrate Structure Type

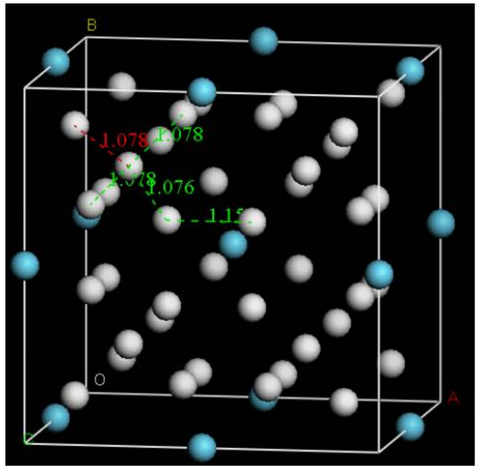


$[4^6 6^{12}]$

LaH_{10} and YH_{10} predicted stable >200 GPa

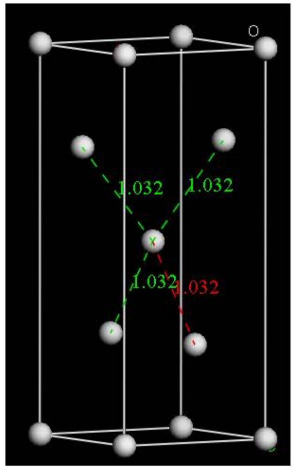
[Liu et al., *PNAS* (2017); Peng et al., *Phys. Rev. Lett.* (2017)].

LaH_{10}



FCC-LaH_{10} at 300 GPa

Atomic H

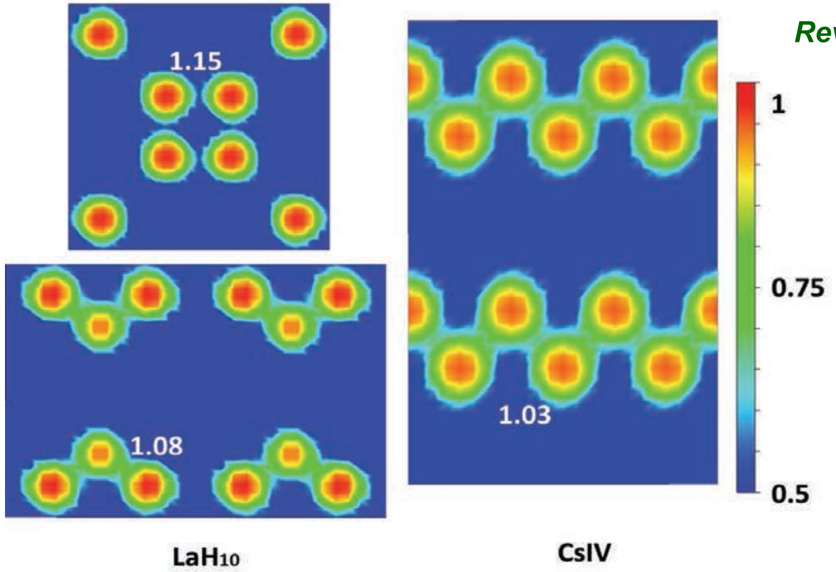


CsIV at 300 GPa

H-H distances ~ 1.1 A

Predicted Stable >500 GPa

[McMahon et al., *Rev. Mod. Phys.* (2012)]



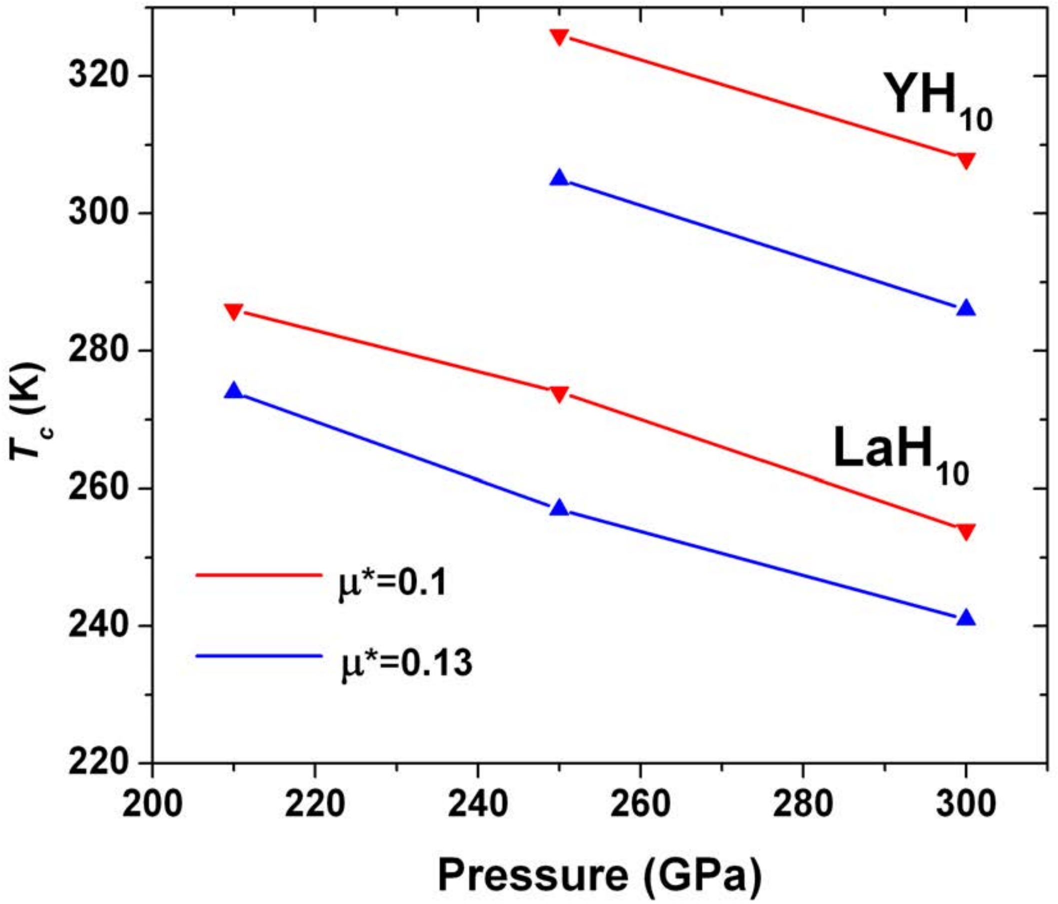
Electron Localization Function

similar s-p hybridization

[Liu *et al.*, *Phys. Rev. B* (2018)]

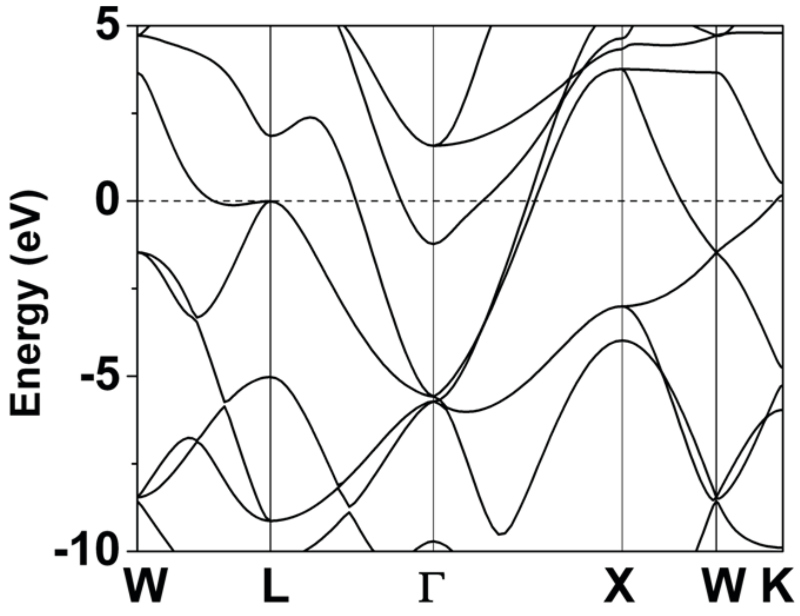
Predicted La and Y Superhydride Superconductors

T_c versus pressure

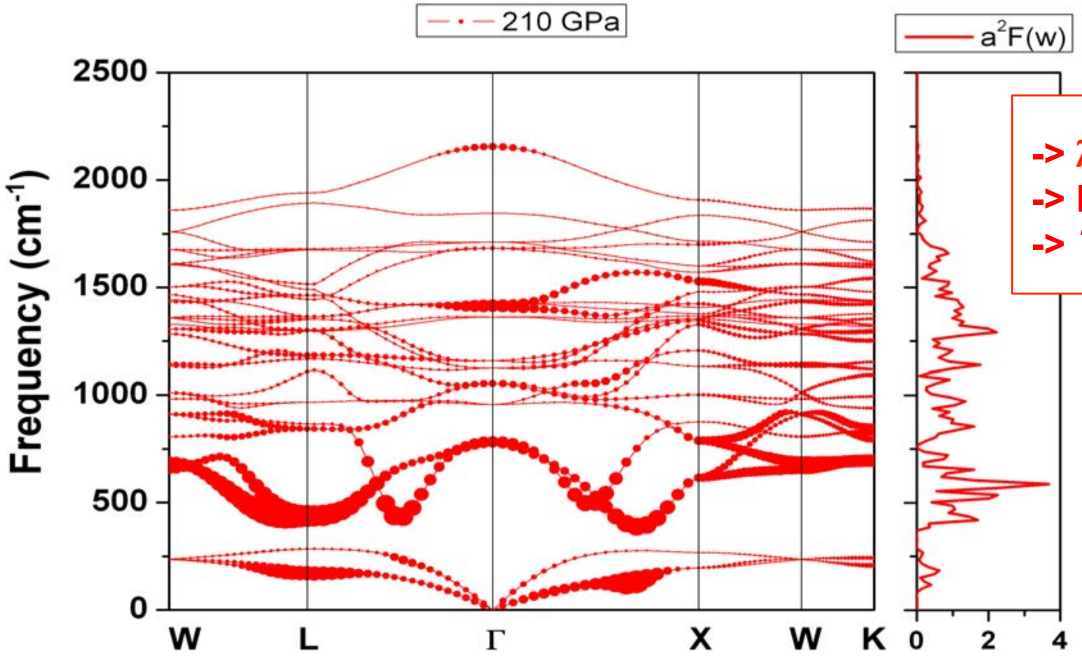


$$T_c = \frac{\omega_{\log}}{1.2}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]$$

[Liu et al., *PNAS* (2017)]



LaH_{10}

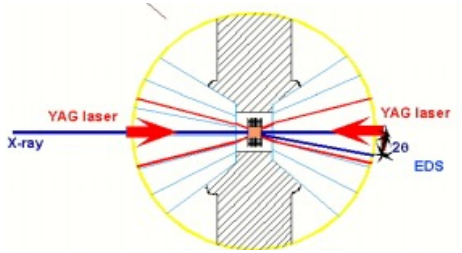


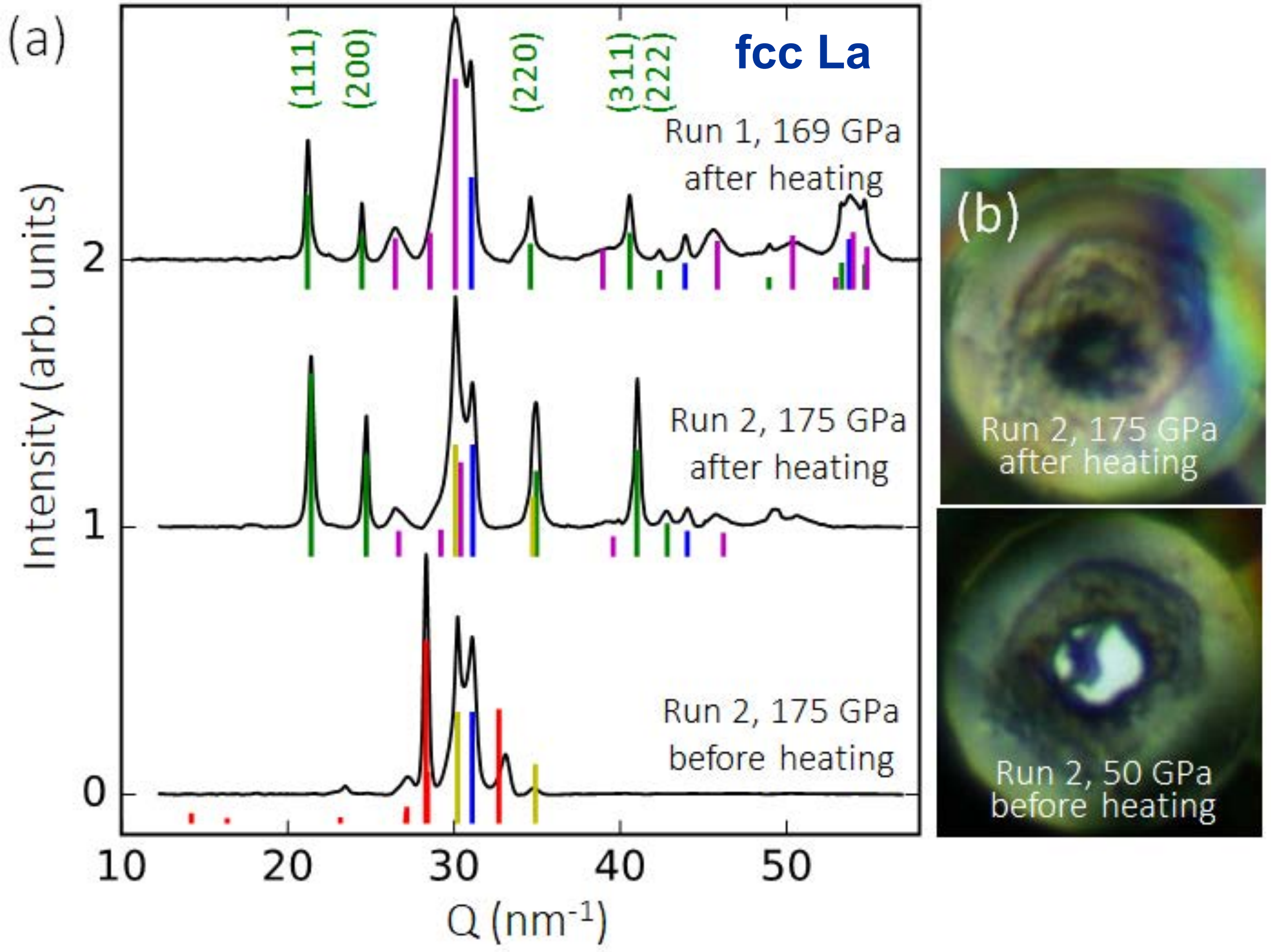
-> λ
-> EPC
-> T_c

Synthesis of Lanthanum Superhydride

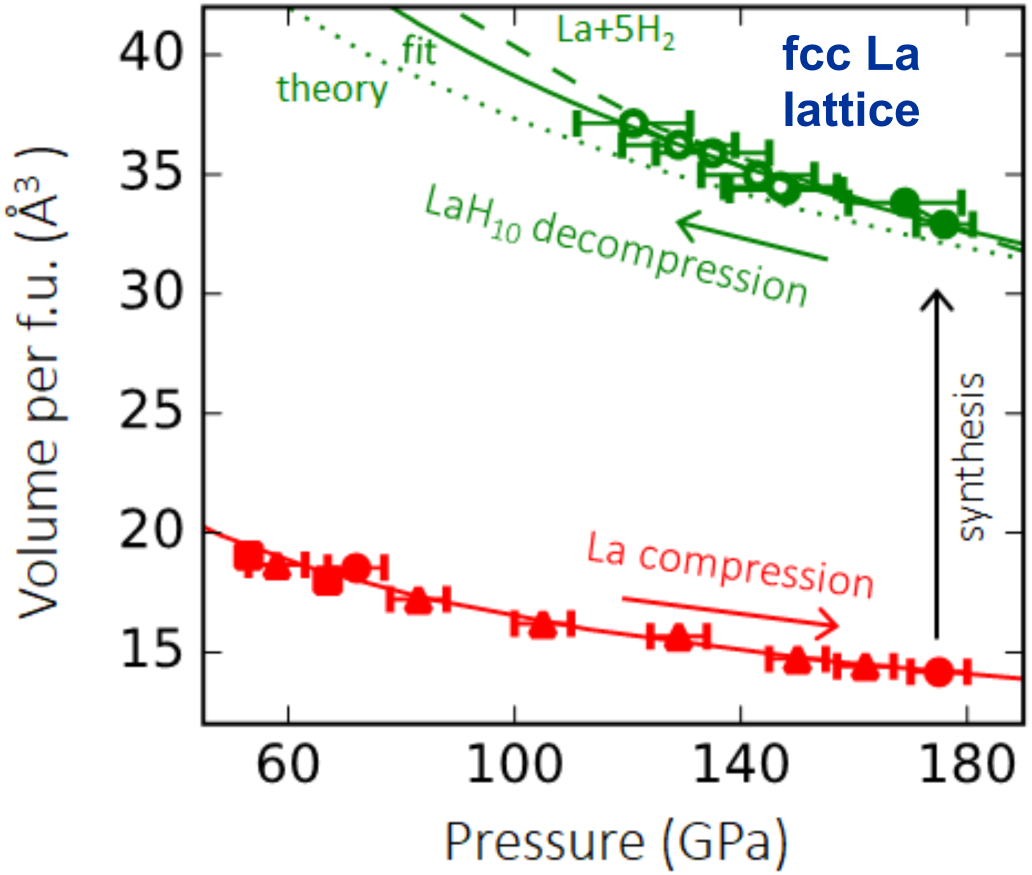
X-RAY DIFFRACTION

Laser heated La + H_2



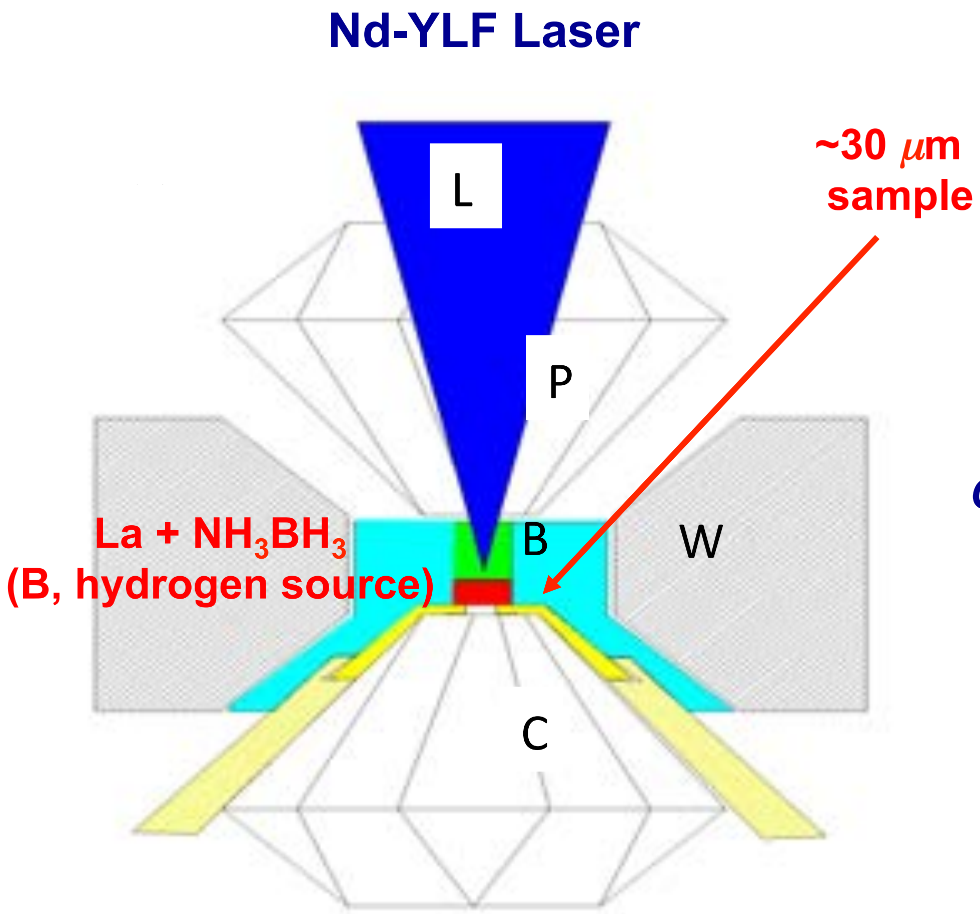


P-V EOS

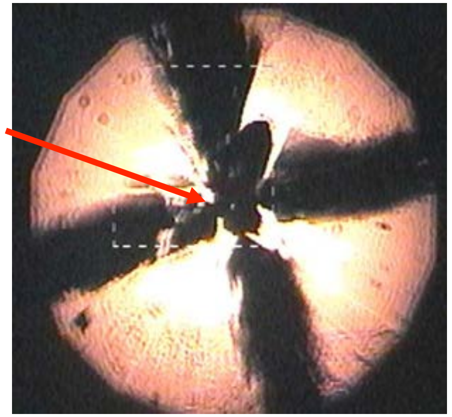


[Geballe *et al.*, *Angew. Chem.* (2018)]

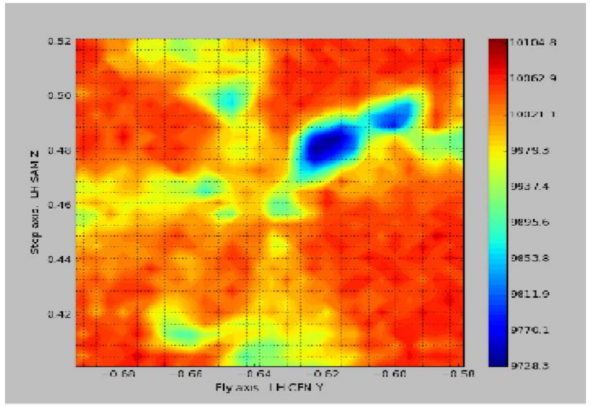
Lanthanum Superhydride Resistance Measurements



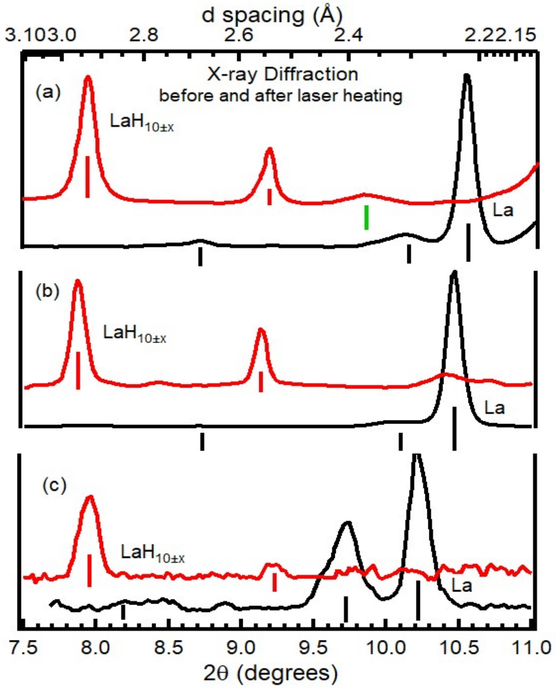
SCHEMATIC

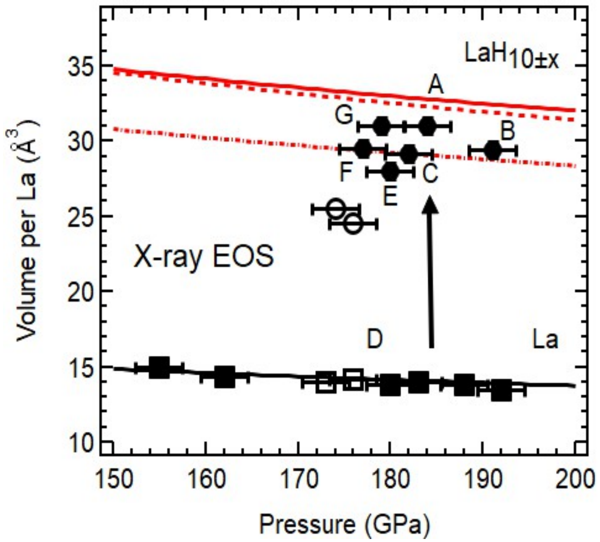


OPTICAL MICROSCOPY



X-RAY RADIOGRAPHY

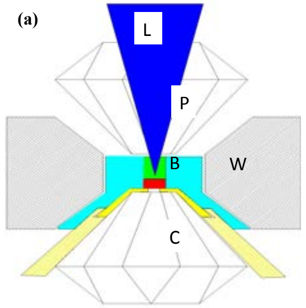


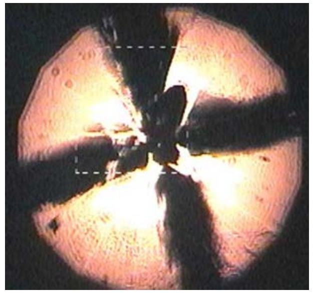


[Hemley *et al., Superconductivity and Pressure,* Madrid (May 2018)]
[Somayazulu *et al., Phys. Rev. Lett.* (2019)]

Lanthanum Superhydride Resistance Measurements

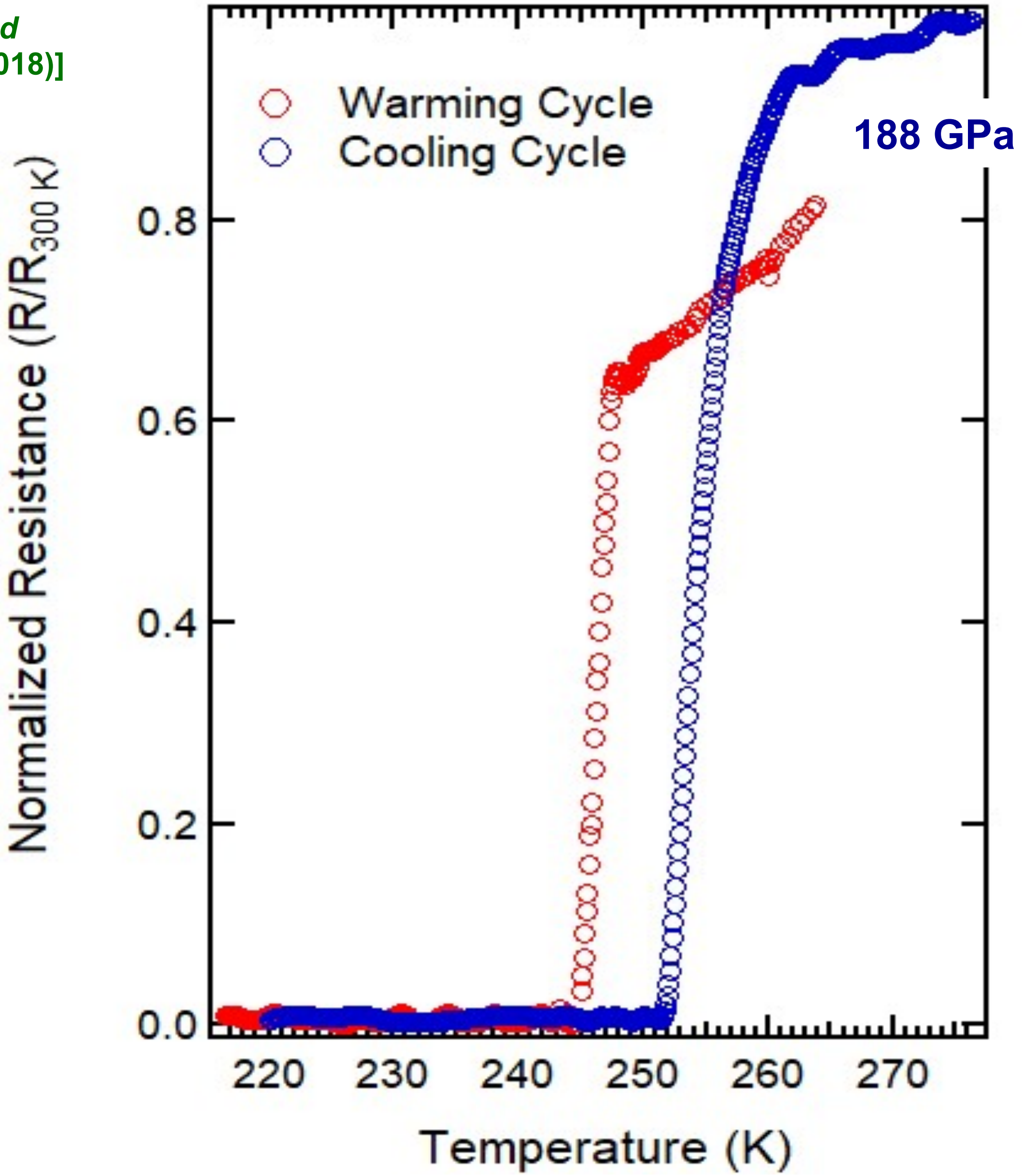
[Hemley *et al.*, *Superconductivity and Pressure*, Madrid (May 2018)]

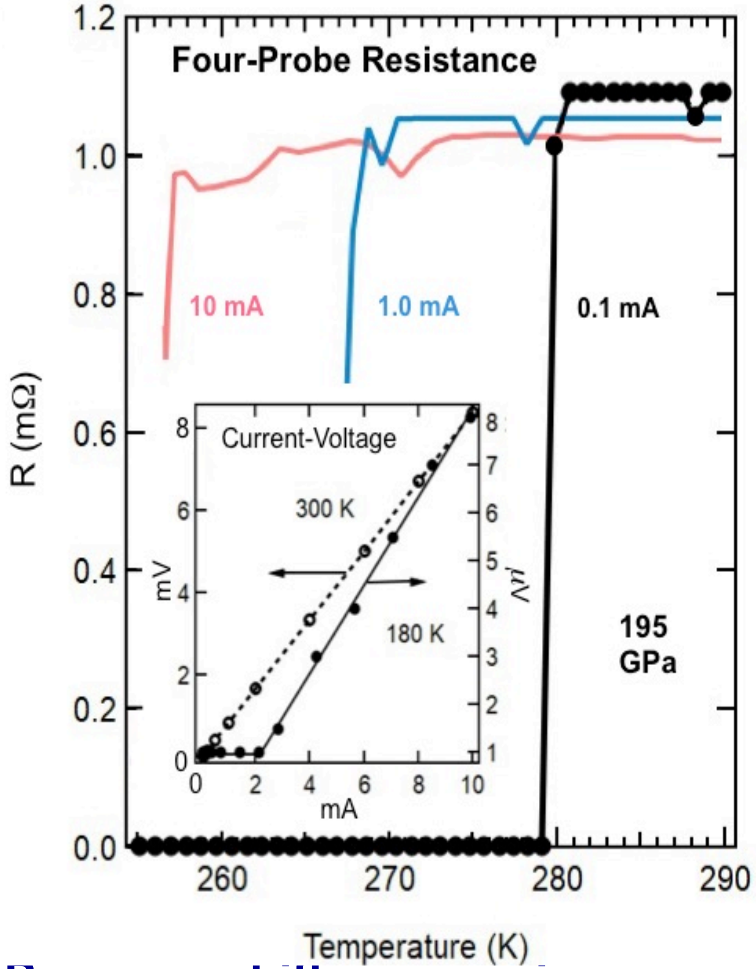




Following laser heating synthesis to 1200 K

4 PROBE



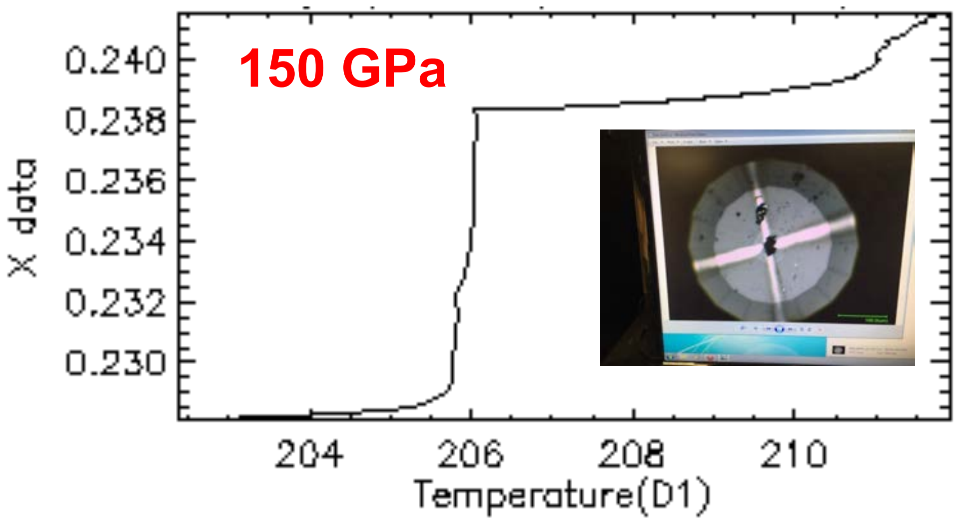


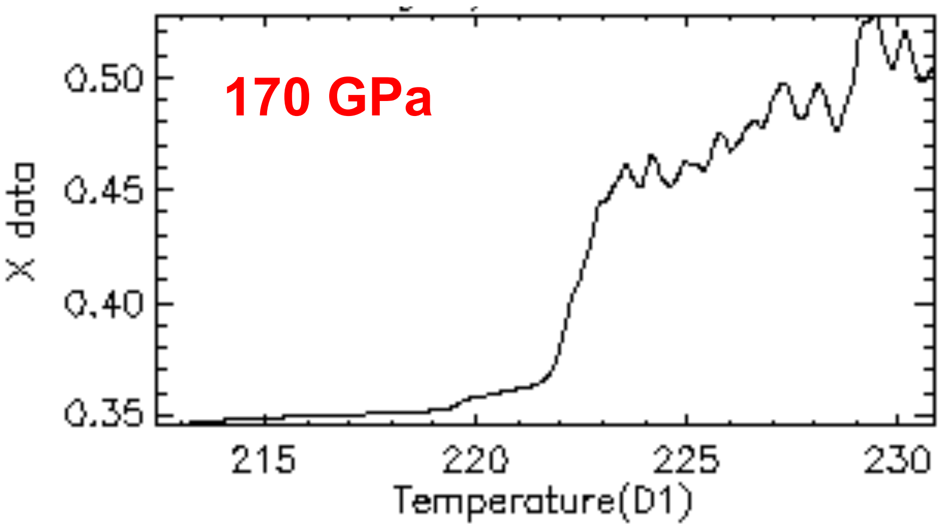
- Pressure shift on warming
- Conductivity onset varies with synthesis conditions
- Reproducible onsets to >260 K

[Somayazulu *et al.*, *Phys. Rev. Lett.* (2019)]

Subsequent Experimental Work

Synthesis at 150 GPa

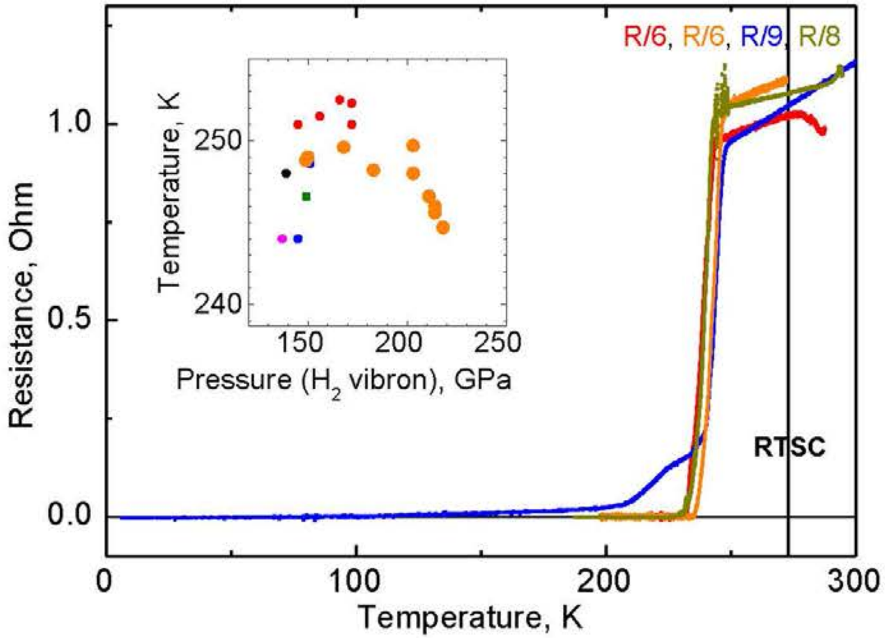




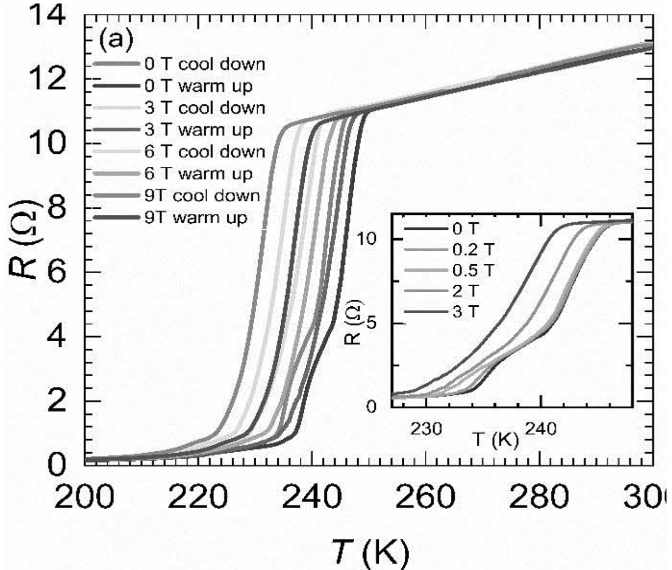
- T_c = 206-225 K: *R3m*

[Ahart et al., to be published]

Other Work



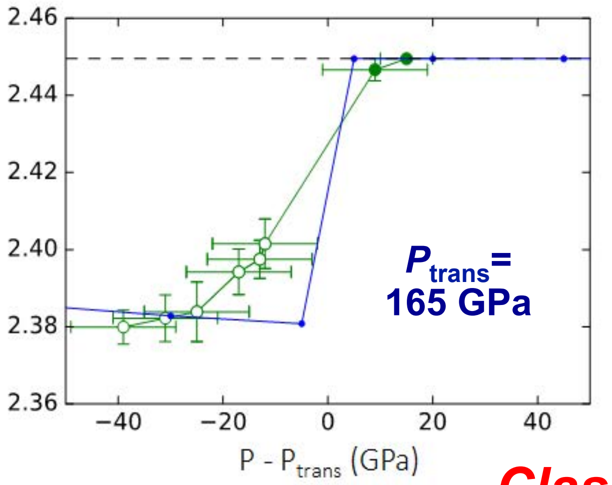
; Drozdov et al., *Nature* (2019)]

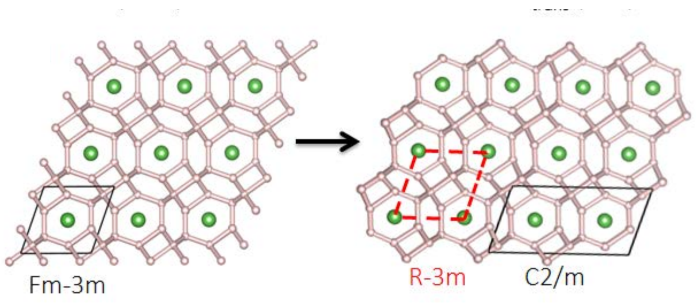


- **Confirm LaH_{10} high T_c**
- **Different synthesis (e.g., 150 GPa)**
- **T_c shift with field**

Phase Transition and Dynamics in LaH_{10}

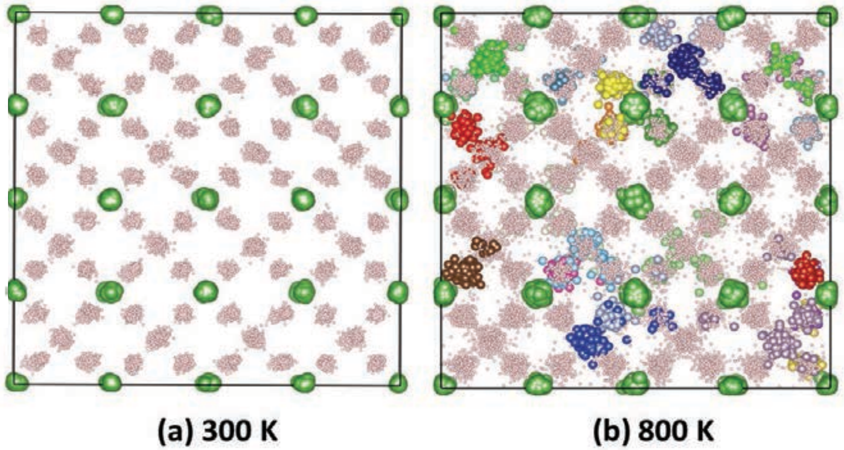
Displacive Transition





[Geballe *et al.*, *Angew. Chem.* (2018)]

Quantum (PI) MD



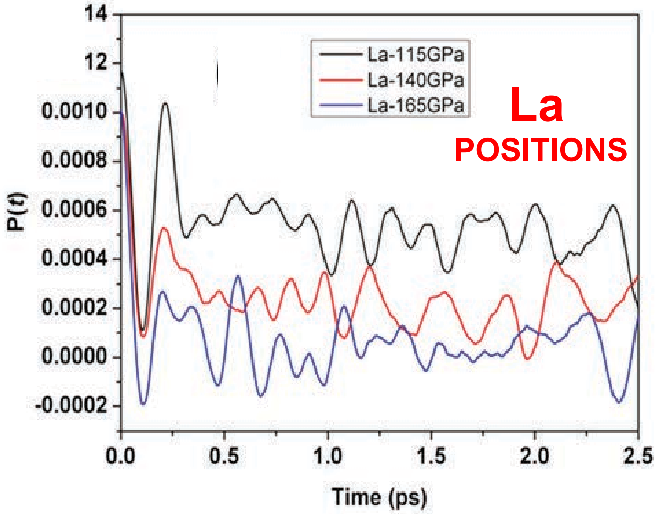
- Highly quantum H-lattice: rms δH = 20% of r(H-H)
- Sublattice melting at higher temperature

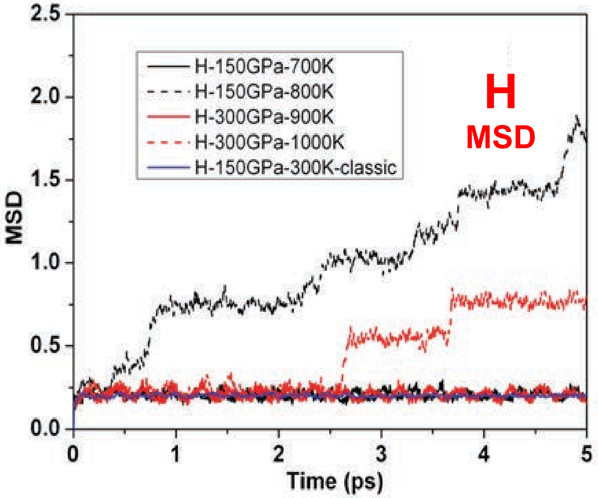
[Liu *et al.*, *Phys. Rev. B* (2018)]

- 'Giant' H ZPM (H_3S): breakdown of Migdal

[Jarlborg & Bianconi, *Sci. Rep.* (2016)]

Classical MD

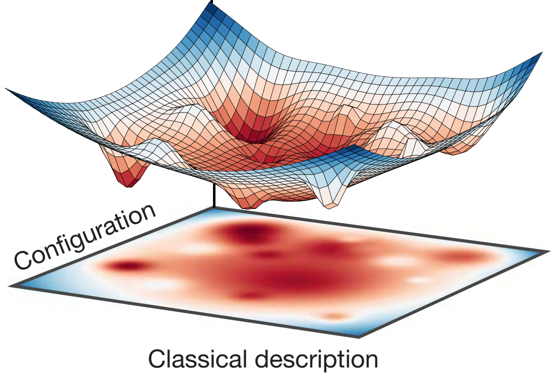


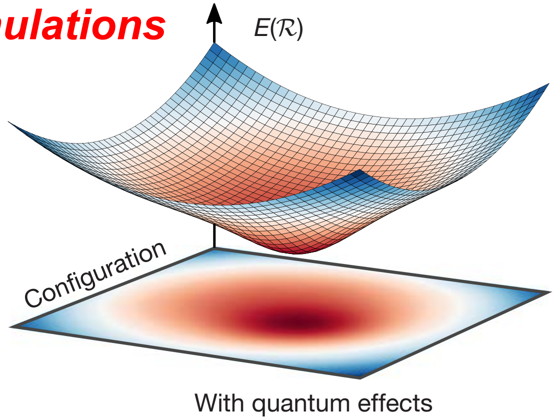


- Strongly anharmonic in *Fm*3*m*
- Lowers *Fm*3*m*-*R*3*m* transition pressure

[Liu *et al.*, *Phys. Rev. B* (2018)]

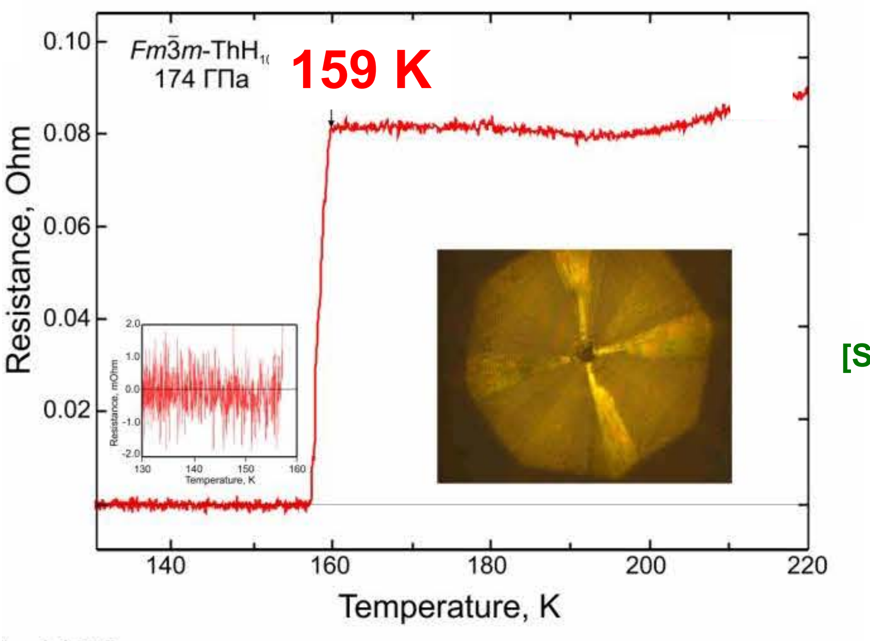
Extended Simulations





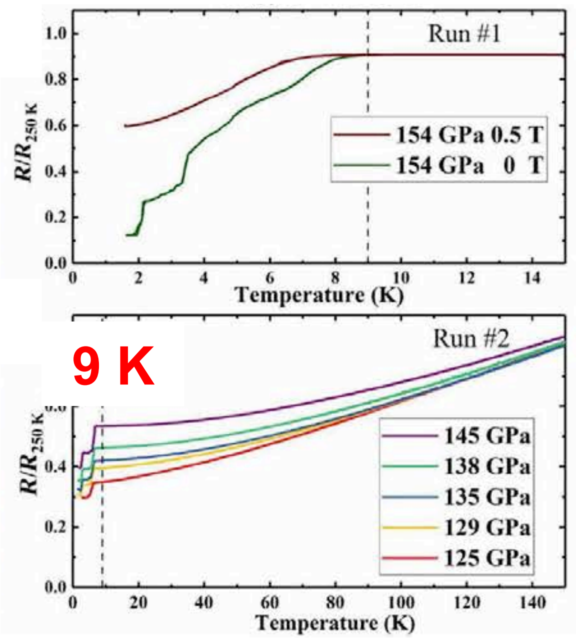
[Errea et al., *Nature* (2020)]

Recent Developments: Other Superhydrides



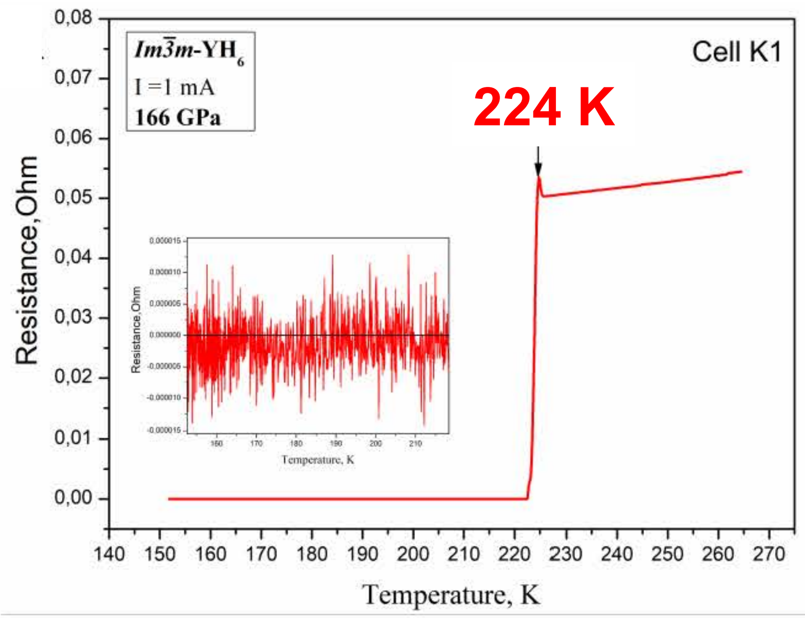
ThH_{10}

[Semanok et al., arXiv (2019)]



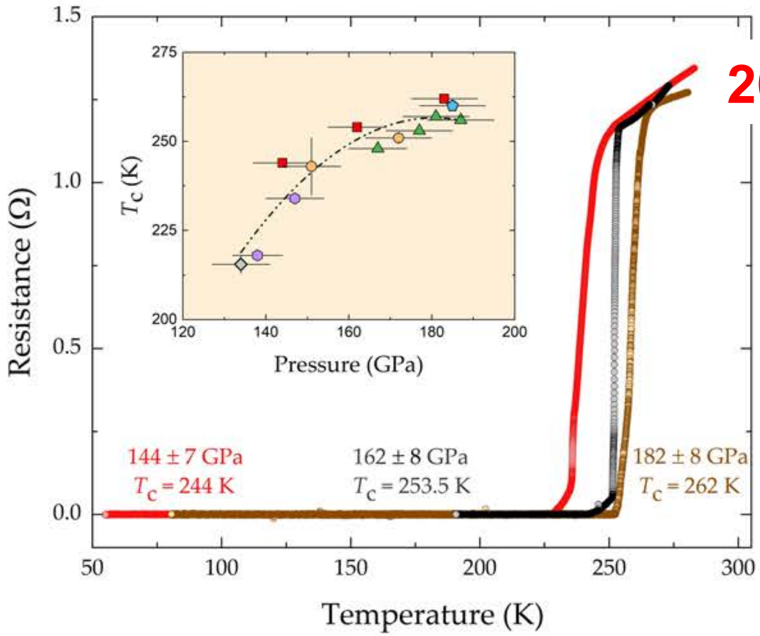
PrH_9

[Zhou et al., *Sci. Adv.* (2020)]



YH_6

[Troyan et al., arXiv (2019)]



262 K

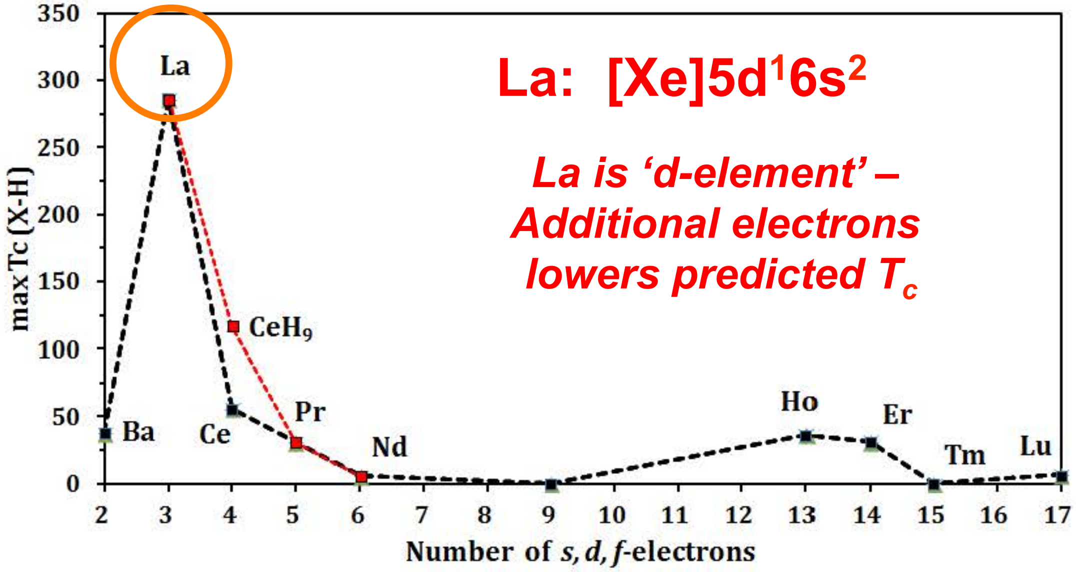
$YH_{9,10}$

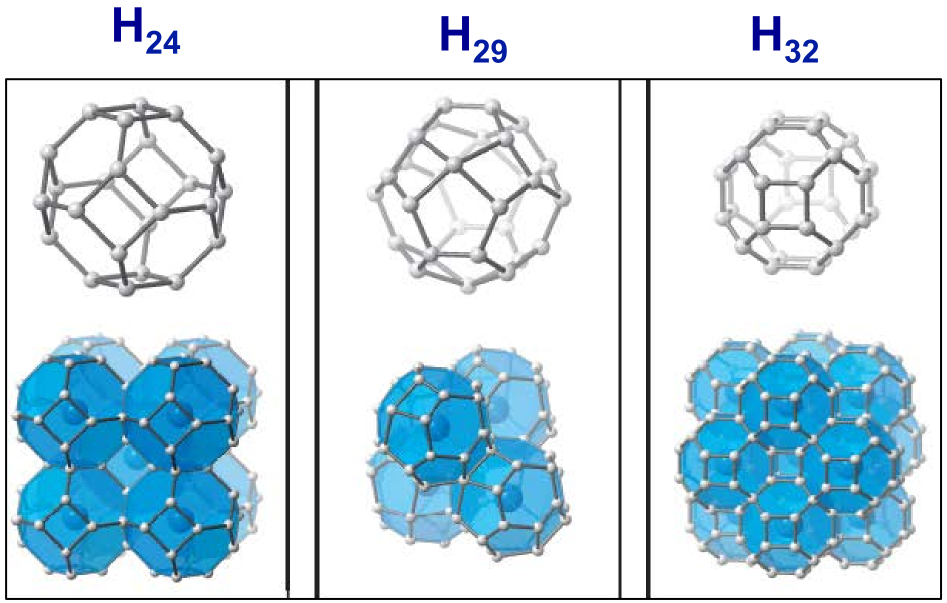
[Snider et al., submitted]

Emerging Systematics

- **H-cage structures**
  - Higher T_c in larger cages
- **Electron-doping of H lattice**
  - Laδ+ charge transfer to H cages
  - Laδ− mixed H^-H^+ [Liu et al., *Phys. Rev. B* (2019)]
  - Why La (Y, rare earths)?

[Semenok et al., arXiv (2019)]





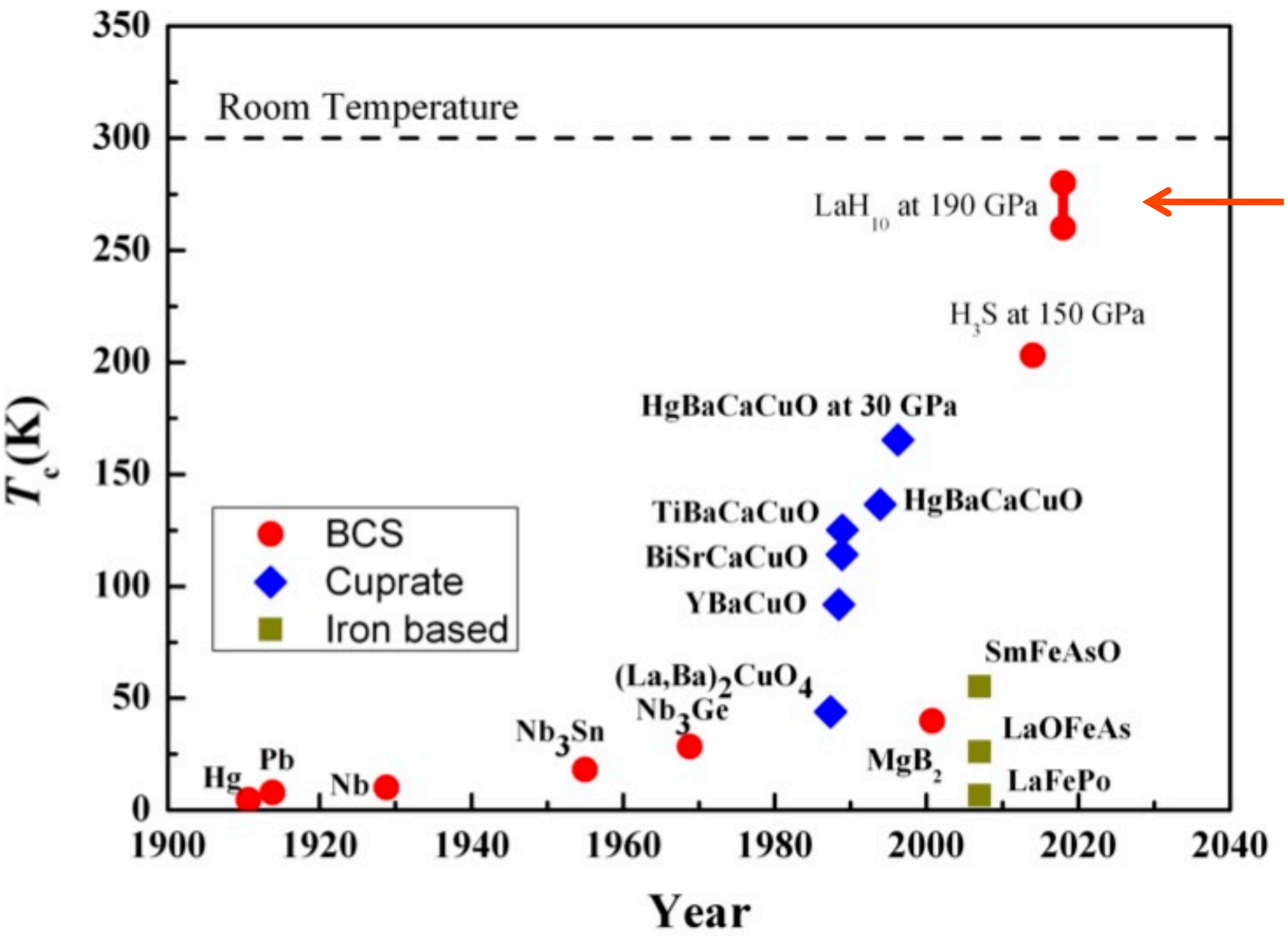
[Liu et al., *PNAS* (2017); Peng et al., *Phys. Rev. Lett.* (2017); Zurek and Bi, *J. Chem. Phys.* (2019)]

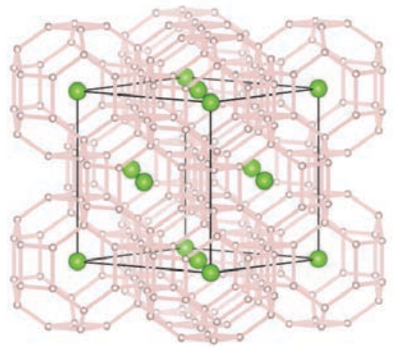
- **Dominant role of H**
  - All high T_c hydrides [Quan et al., arXiv (2019)]
- **Fully quantum system**
  - Phase stability

    [Liu et al., *Phys. Rev. B* (2018); Errea et al. *Nature* (2020)]
  - Pairing

    [Jarlborg & Bianconi, *Sci.. Rep.* (2016)]

Towards Hot Superconductivity

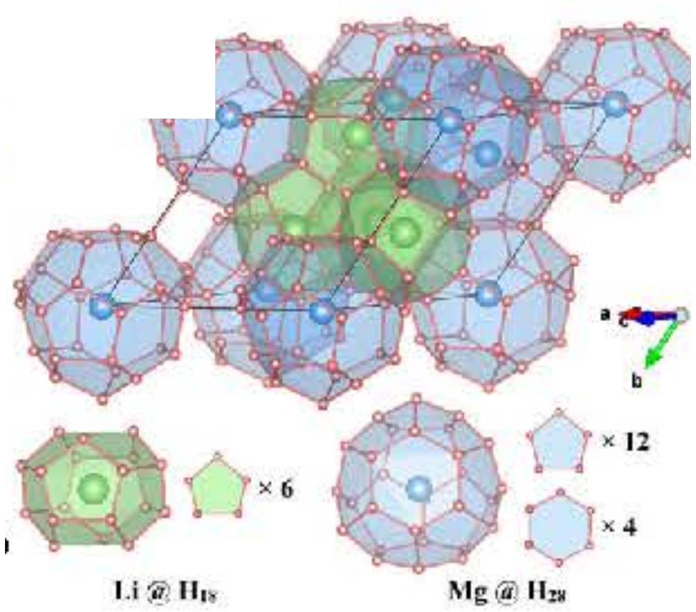


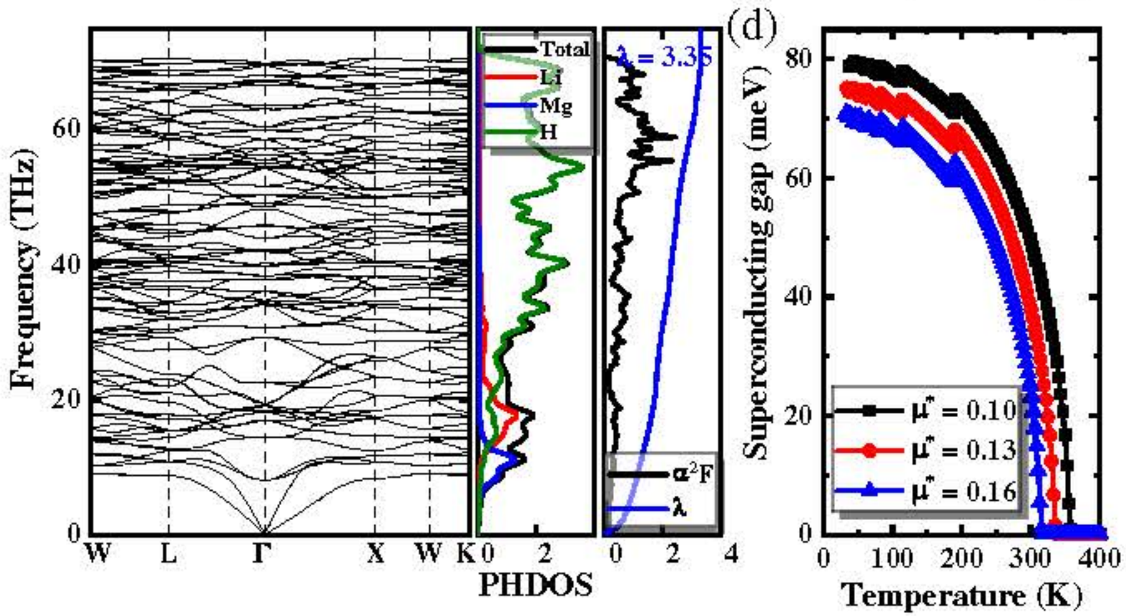


- **Mechanism?** [Mazin, *'Extraordinarialy Conventional', Nature* (2015)]
  - ***full quantum*** **treatment**
- **Still higher T_c?**
  - ***More complex chemistries***
- **Recovery to ambient?**
  - ***H analog materials***

[Hemley, Ahart, Liu, & Somayazulu, *Superconductivity and Pressure*, Madrid, May 2018]

Ternary and More Complex Hydrides





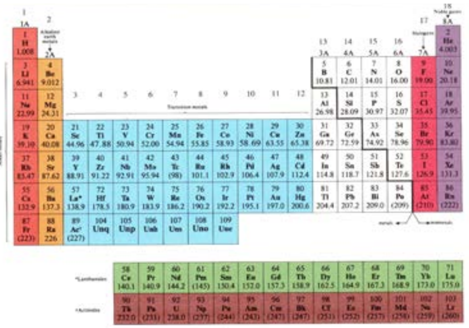
Li_2MgH_{16}

Predicted T_c to 470 K!

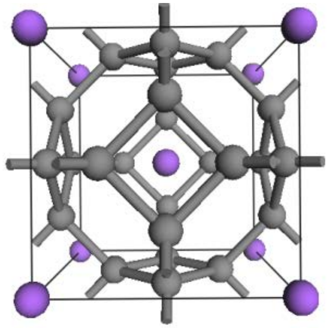
(250 GPa)

[Sun et al., *Phys. Rev. Lett.* (2019)]

S-Se-H, Li-La-H…



C-'X'-H **Sodalite-based**



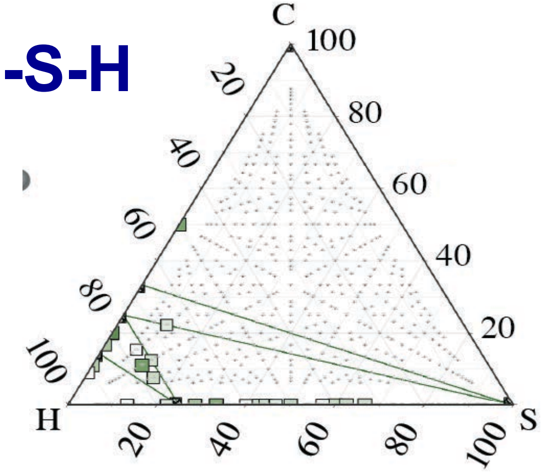
NaC_6

Predicted T_c = 116 K

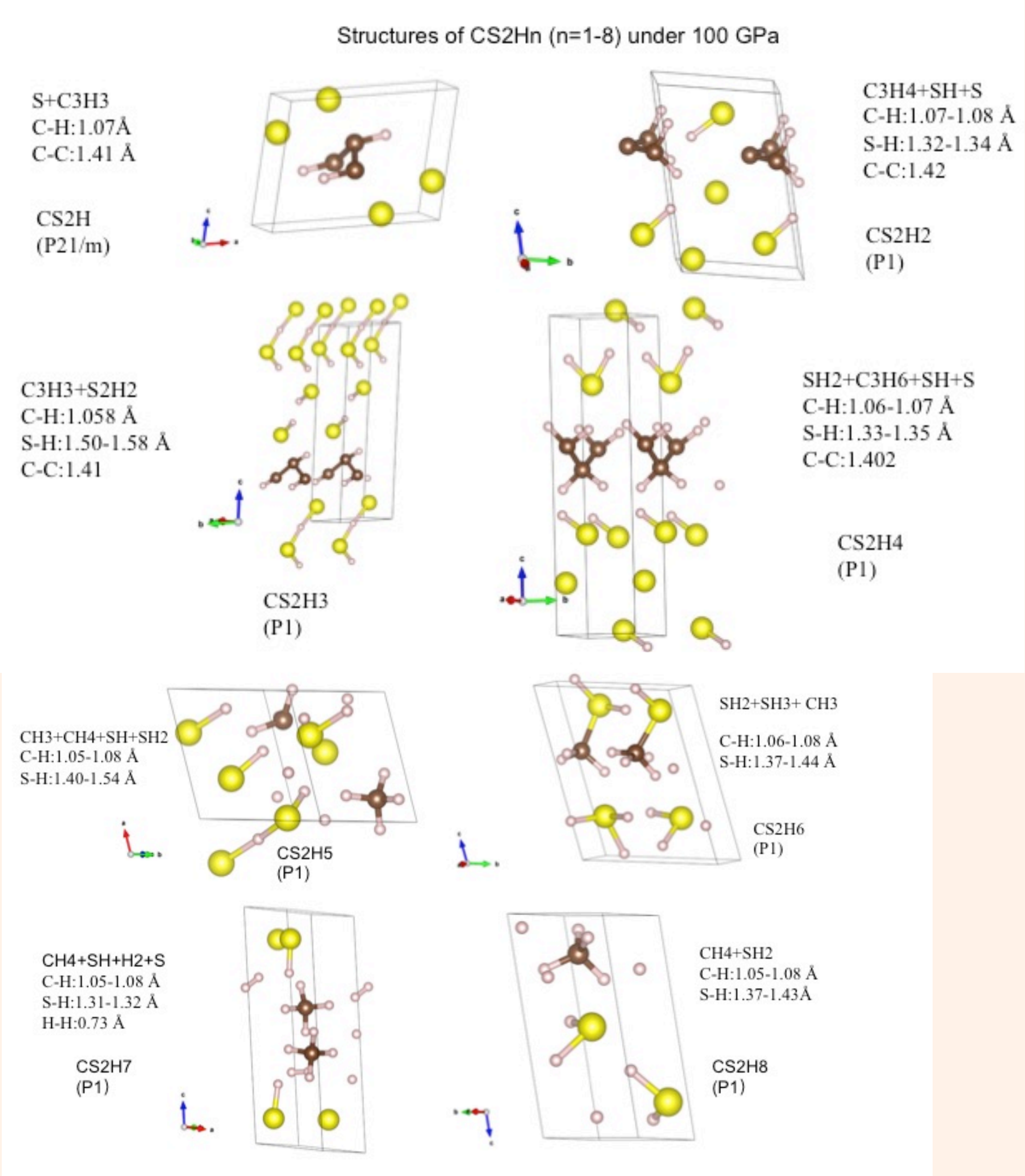
1 bar *stability*

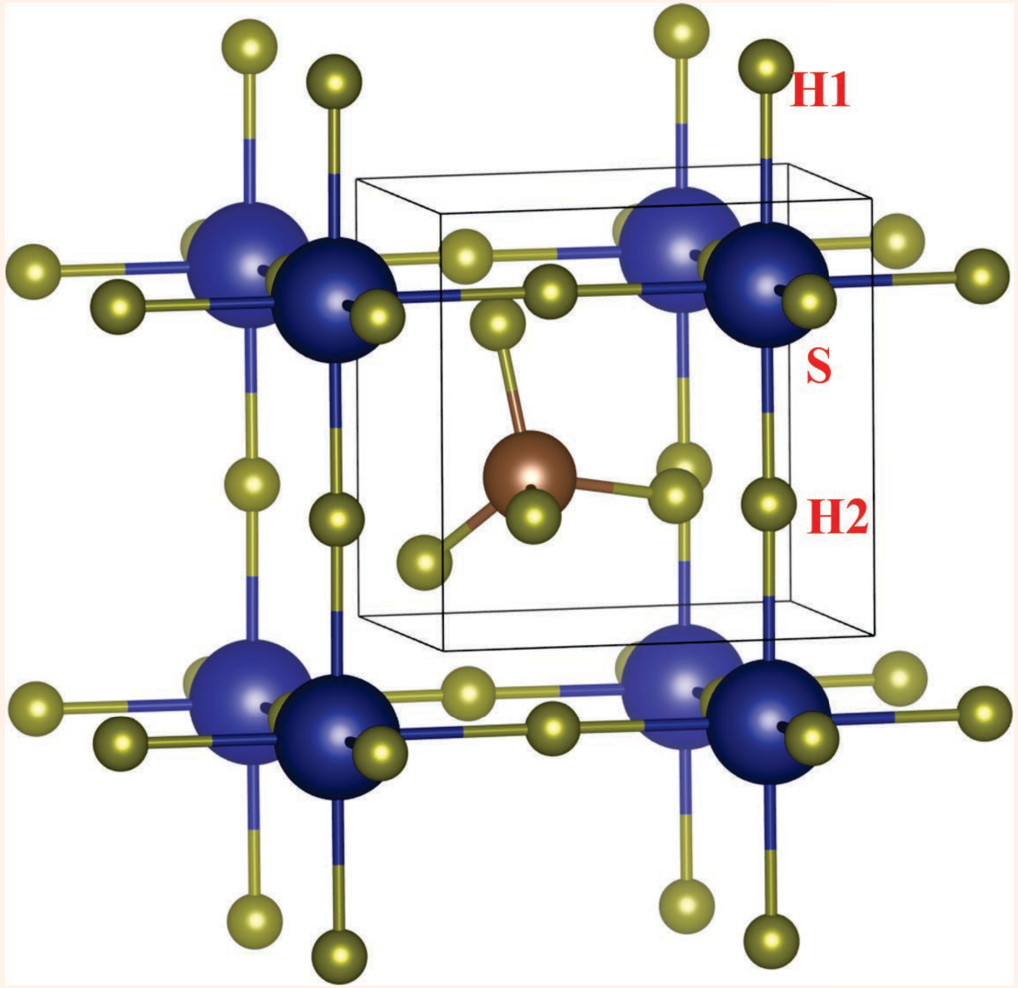
[Lu *et al., Phys. Rev. B* (2016)]

C-S-H



C-S-H Ternary: *Structure Search*

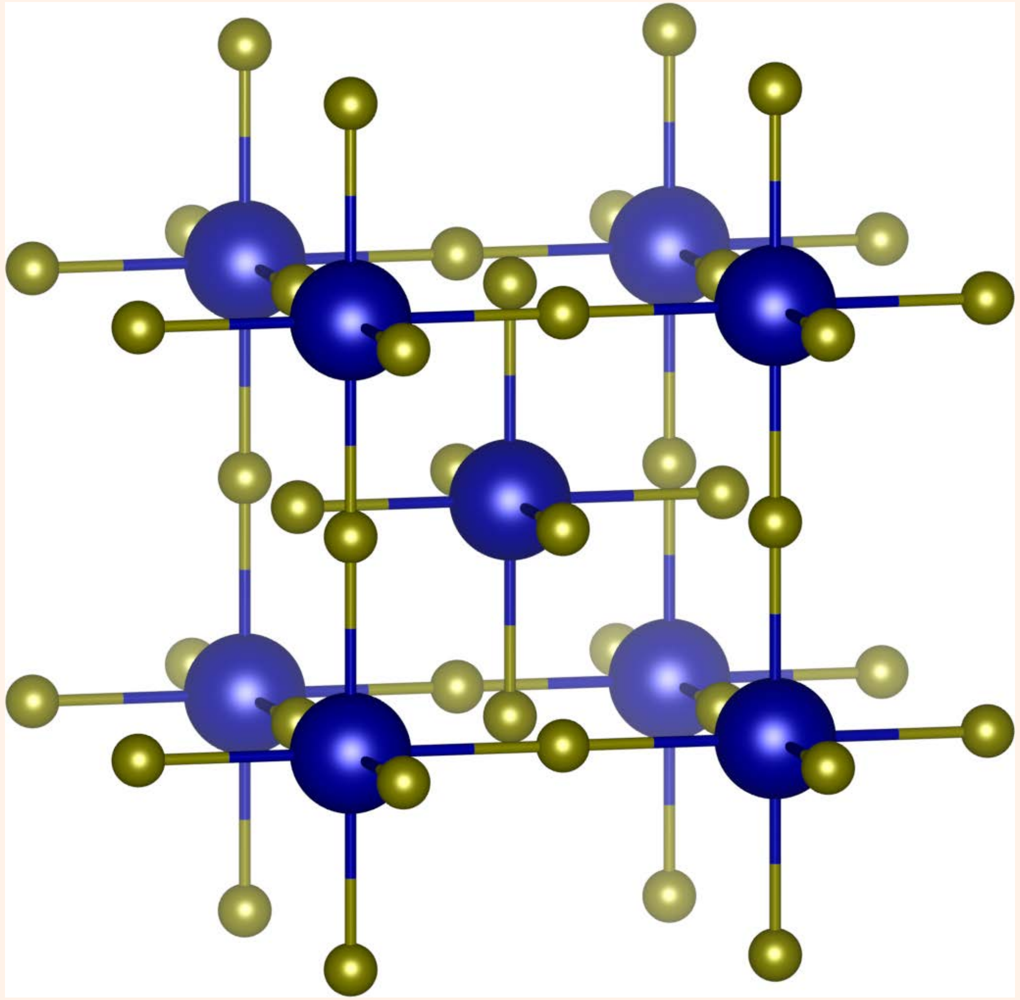




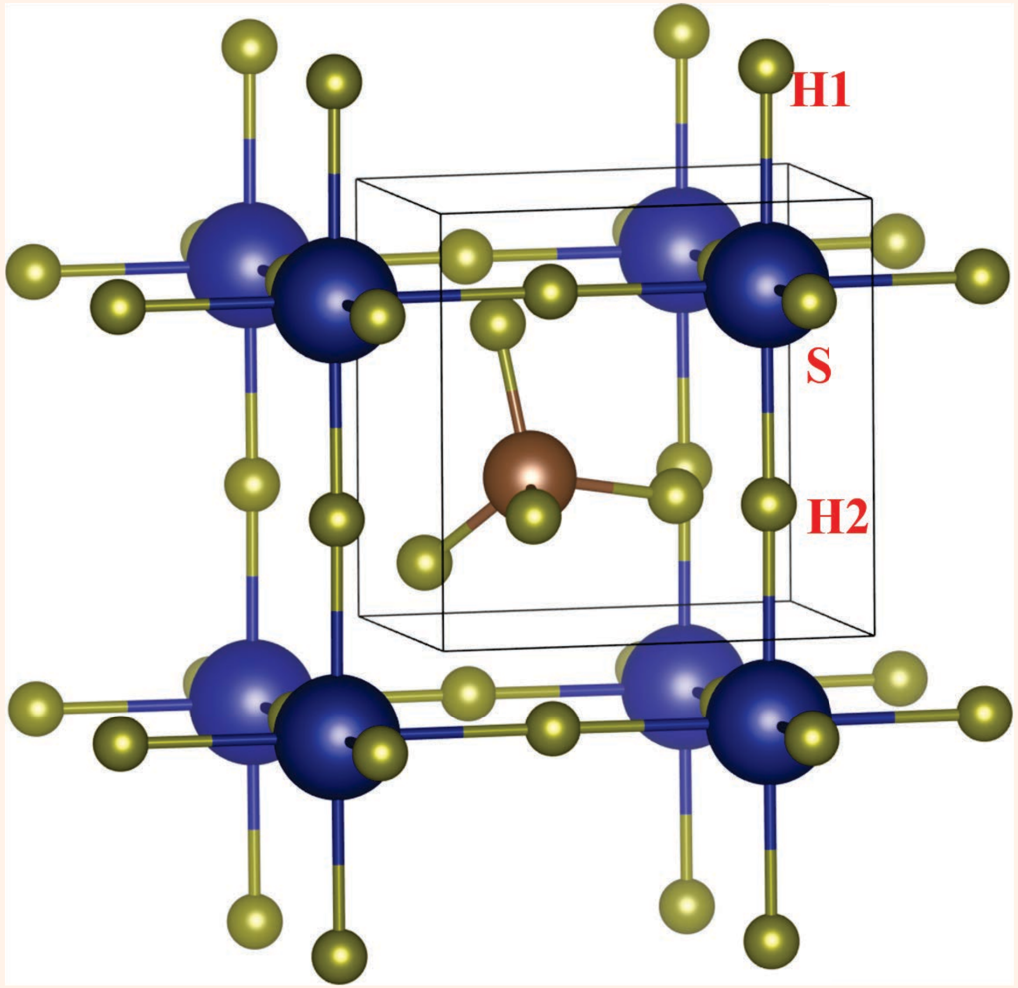
CH_4-H_3S (CSH_7)

Hydride Perovskites:

A New Class of High T_c Superconductors?



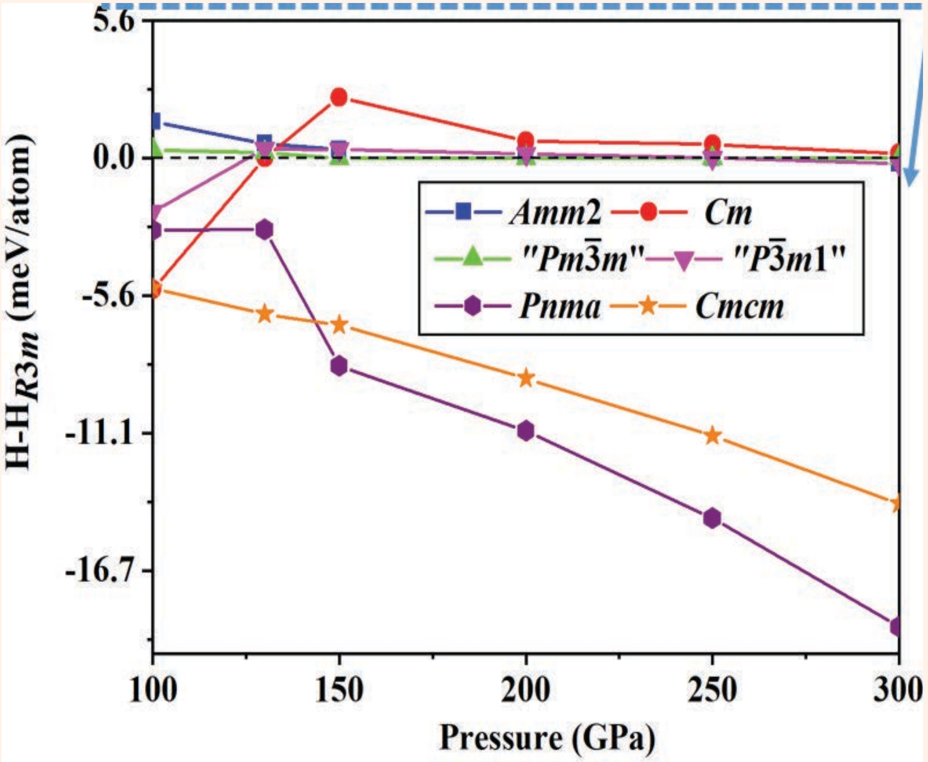
H_3S *Im3m*



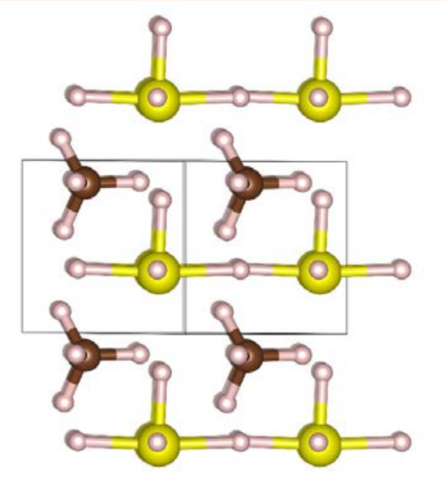
CH_4-H_3S (CSH_7) *R3m*

Hydride Perovskites:
A New Class of High T_c Superconductors?

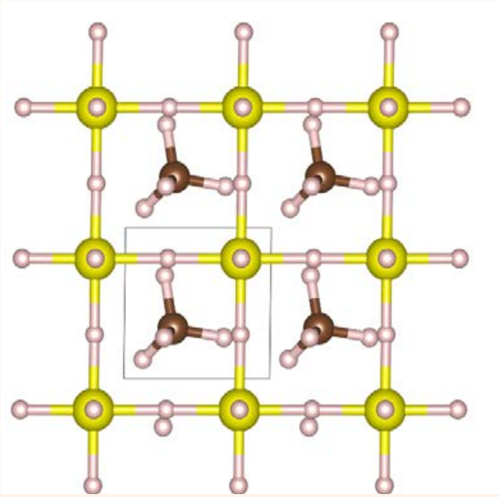
Enthalpy per formula as a function of pressure for CSH_7 structures relative to *R*3*m*



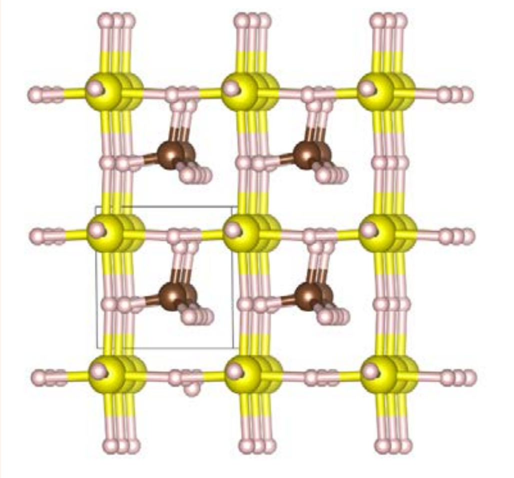
[Cui et al., *Phys. Rev. B,* in press]



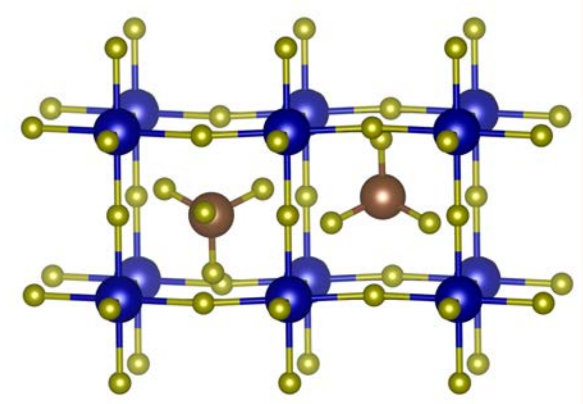
Cm



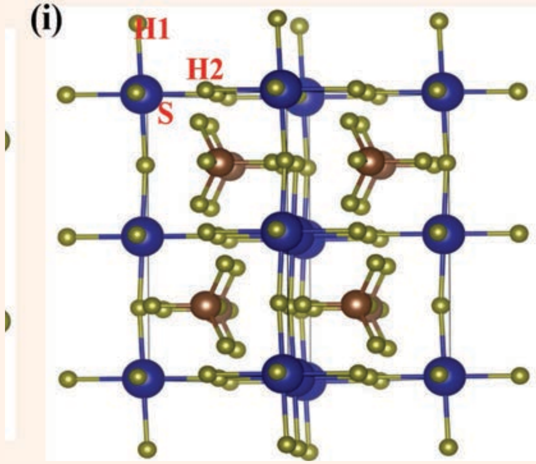
R3m



Amm2

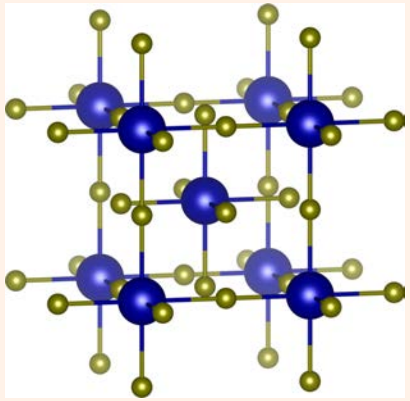


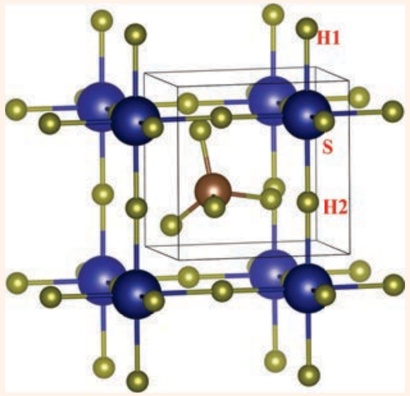
Cmca

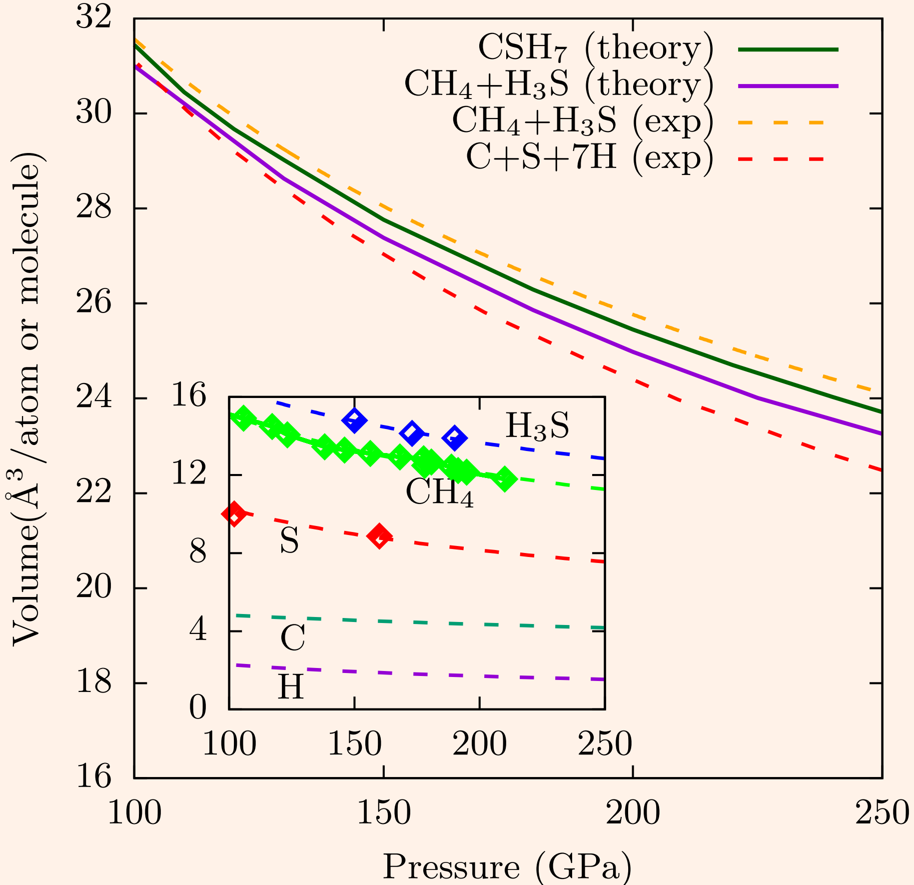


Pnma

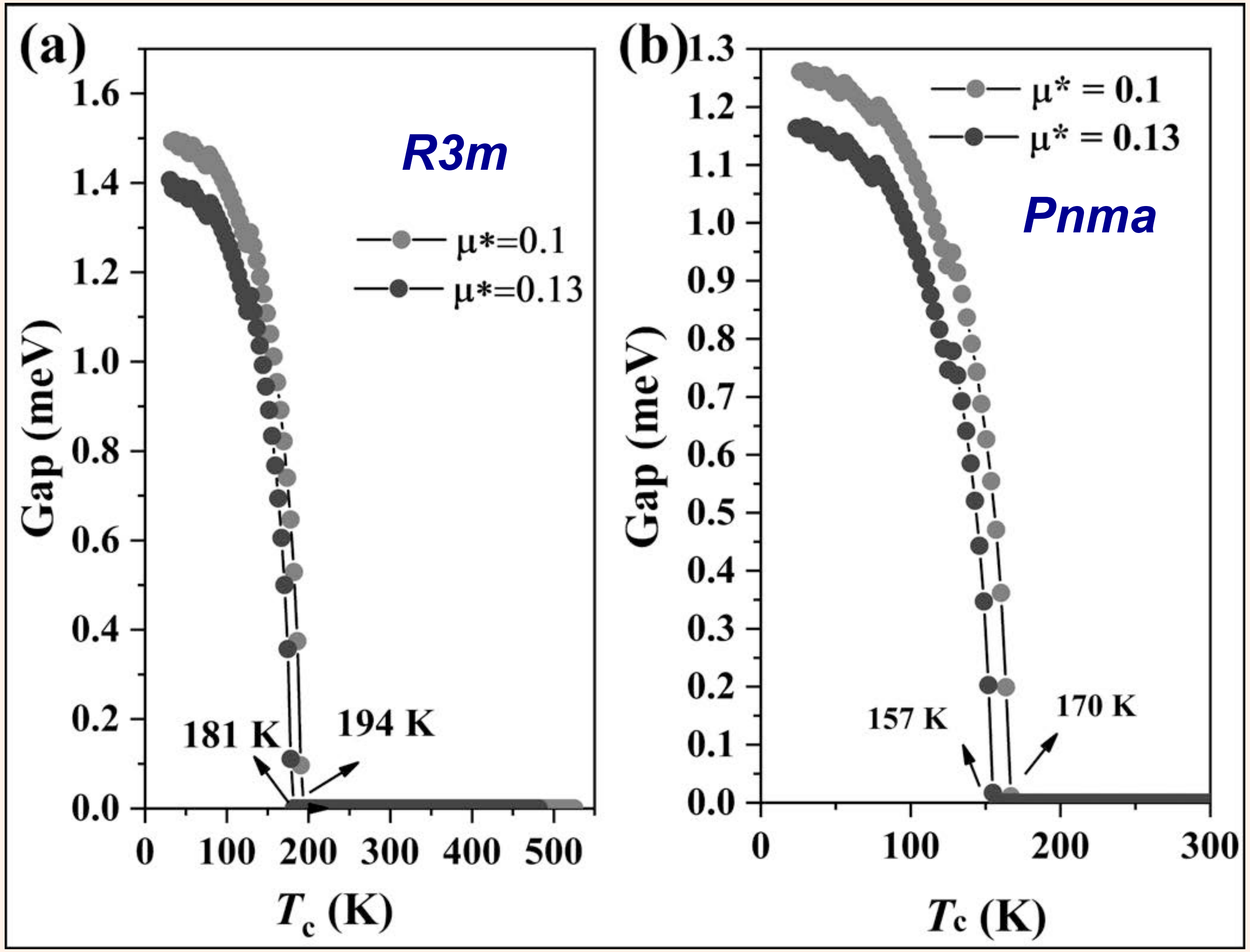
H_3S Hydride Perovskites







CH_4-H_3S (CSH_7) 150 GPa

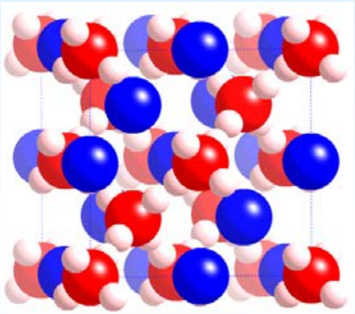


[Cui et al., *Phys. Rev. B,* in press]

From H-S to H-O:

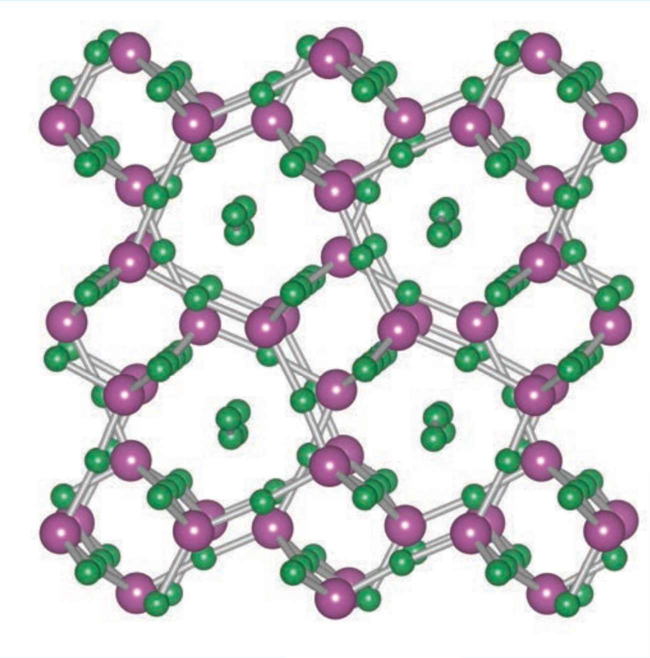
‘The Shape of Water’ Under Pressure

Structure Search / DFT Methods

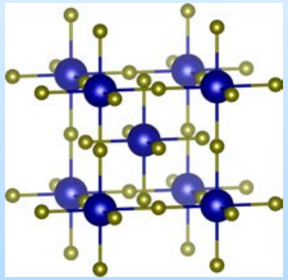


H_2O-H_2
(H_4O)

450 GPa

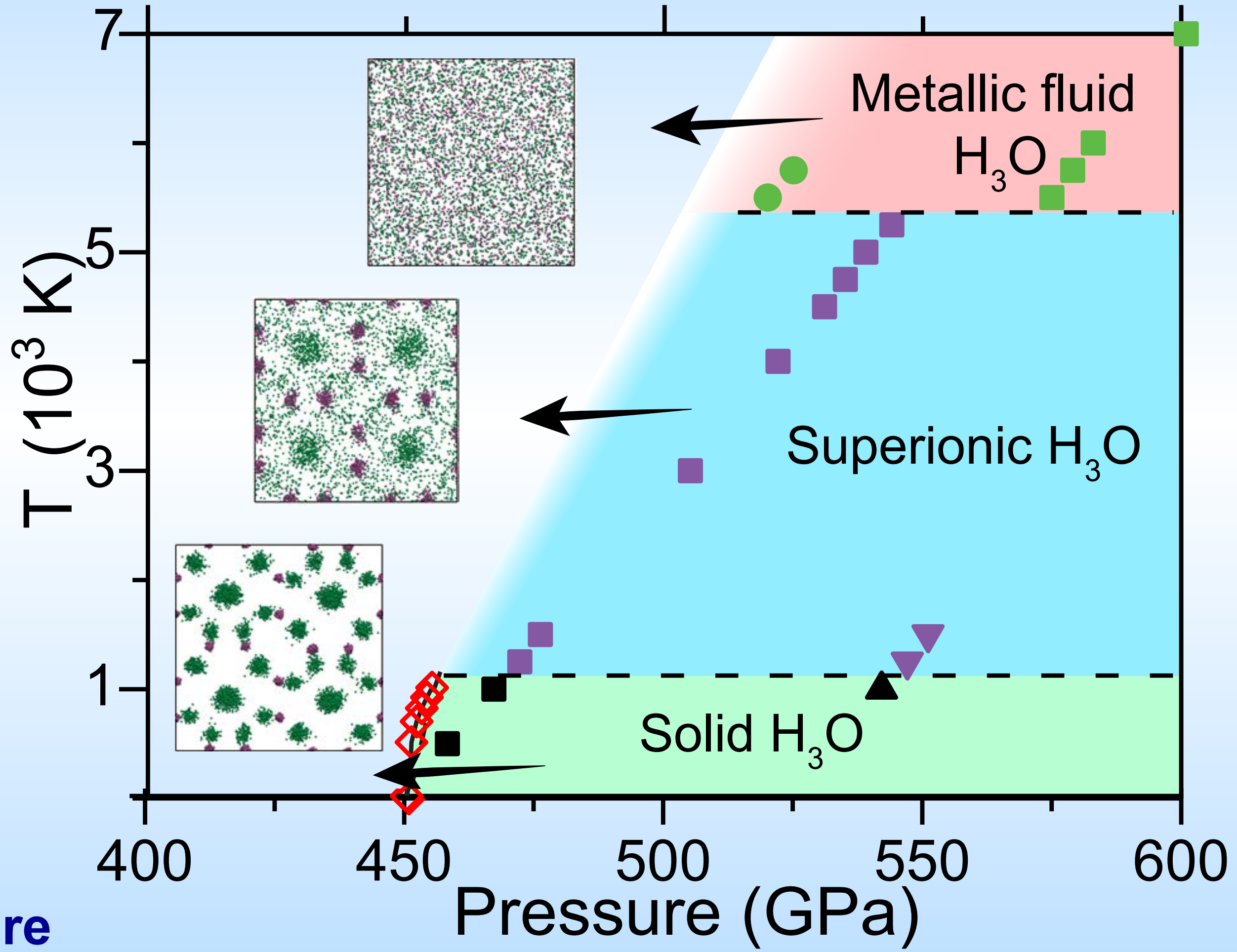


H_3O



H_3S

Ab initio MD

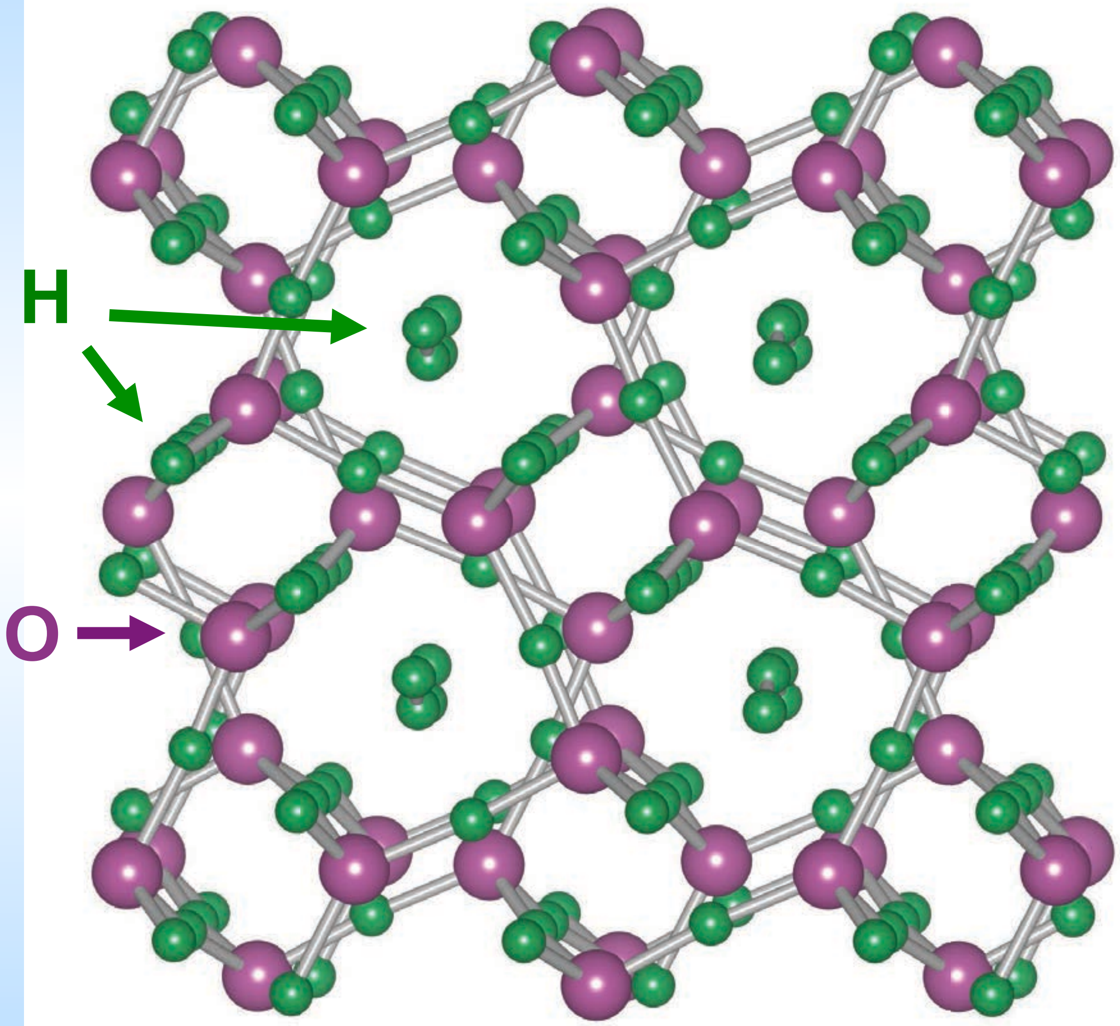


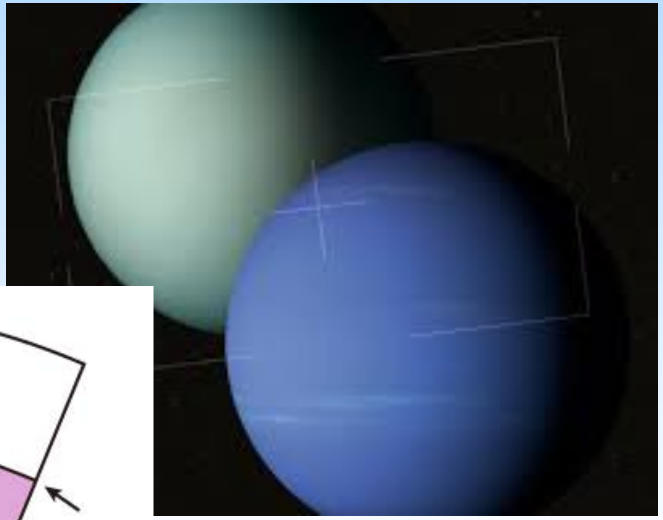
- *Cmca* clathrate-like structure
- “H_3S-type” *Im3m* stable >2 TPa
- Predicted superionic solid and fluid metal

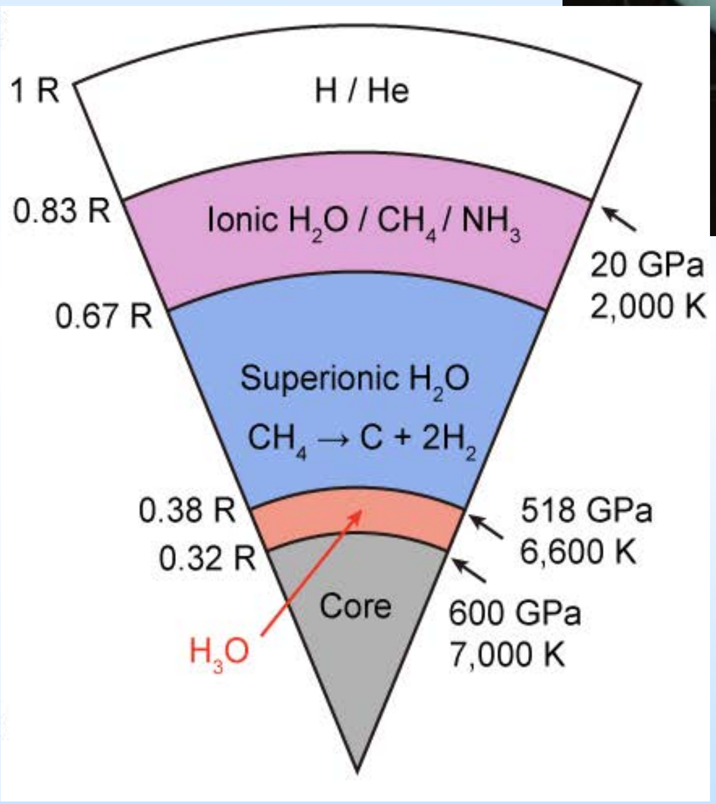
[Huang et al., *PNAS* (2020)]

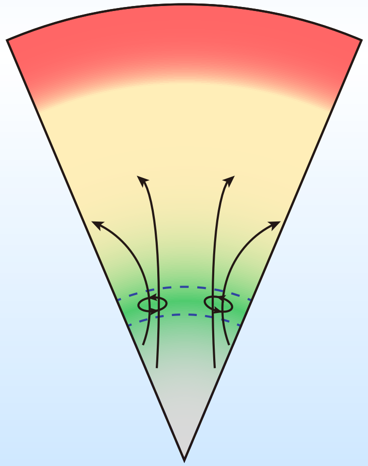
Extreme Hydrogen-rich Quantum Materials: H_3O

Structure Search / DFT Methods





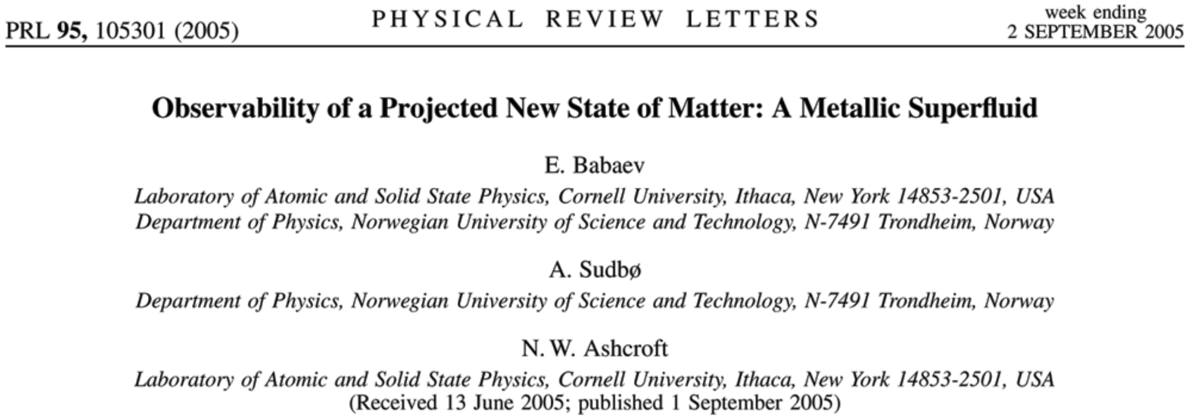




- **Explains anomalous magnetic fields: 'thin-shell' dynamos**

[Huang et al., *PNAS* (2020)]

Towards Hot Superconductivity/Superfluidity in Dense Hydrogen


PRL 95, 105301 (2005) PHYSICAL REVIEW LETTERS week ending 2 SEPTEMBER 2005

Observability of a Projected New State of Matter: A Metallic Superfluid

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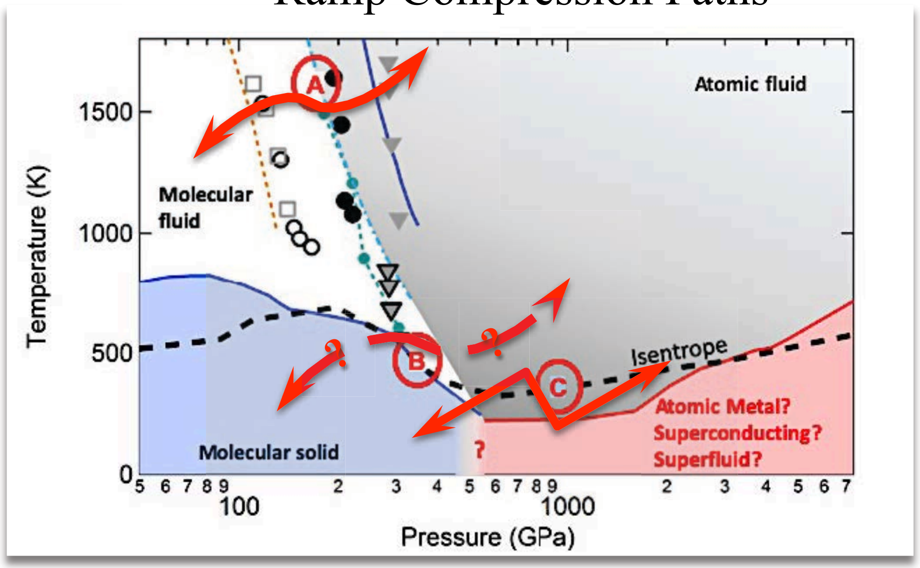
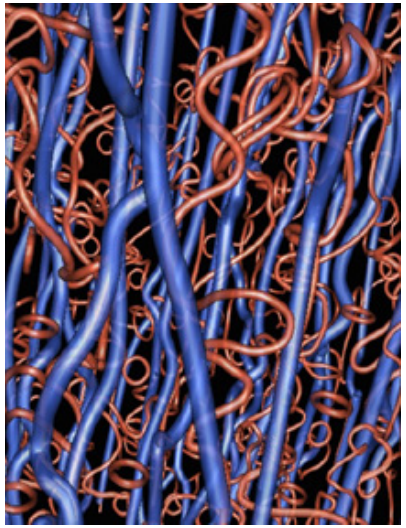
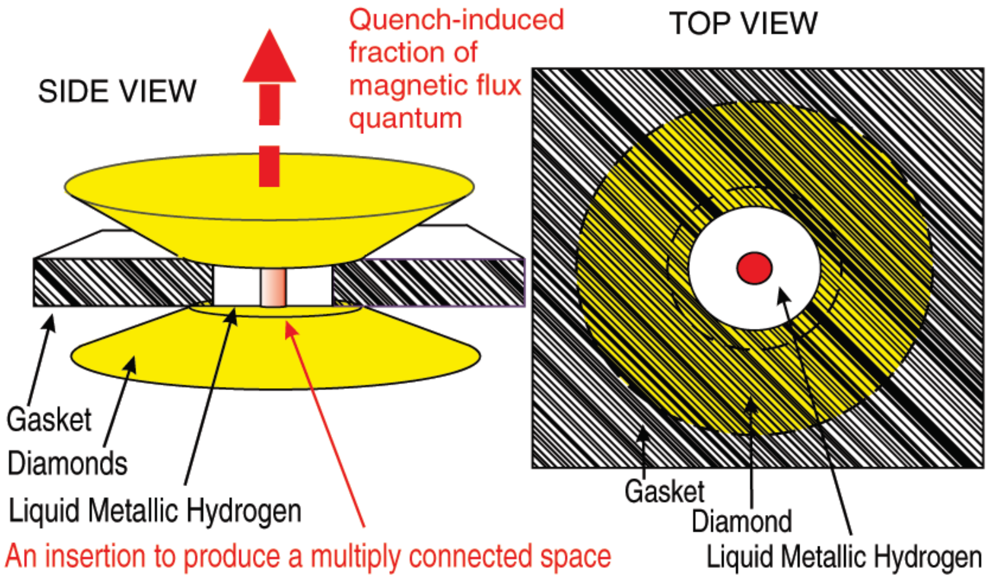
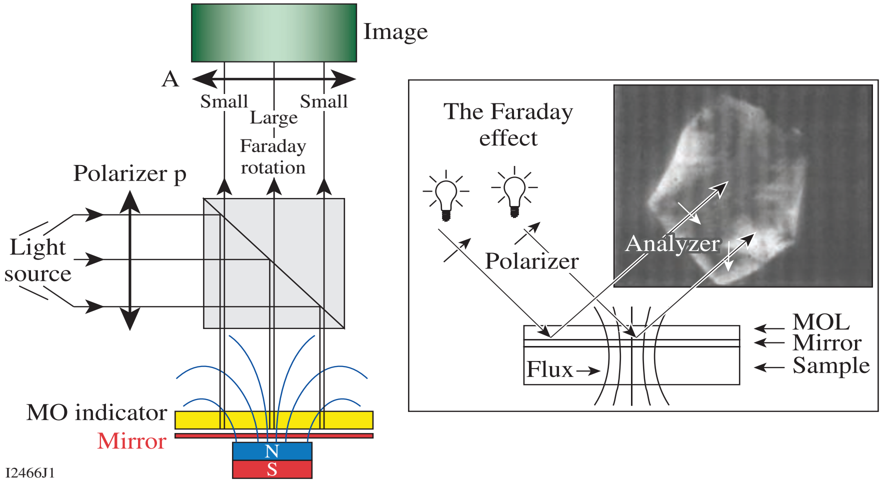
(Received 13 June 2005; published 1 September 2005)

Ramp Compression Paths



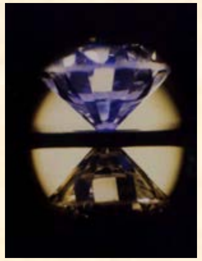




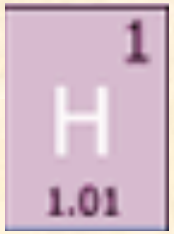


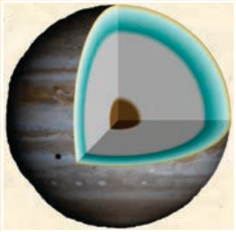
CONCLUSIONS AND OUTLOOK

1. **High pressure studies are revealing a variety of phenomena in quantum materials over a range of *P-T* conditions as a result of the close synergy between experiments and computation**

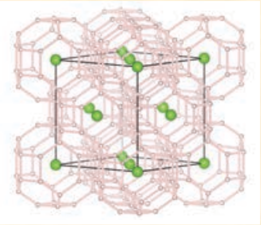


2. **Recent experiments on hydrogen provide evidence for a series of transitions to metallic phases at >300 GPa based on both static and dynamic compression, in good agreement with theory**





3. **Studies of hydrogen-rich simple hydrides reveal high T_c approaching room temperature, and new classes of novel phases continue to be found.**



ACKNOWLEDGEMENTS

Principal Collaborators

Maddury Somayazulu (ANL)
Muhtaer Ahart (UIC)
Zachary Geballe (Carnegie)
Hanyu Liu (Jilin)
Ravhi Kumar (UIC)
Ajay Mishra (BARC)
Maria Baldini (Fermilab)
Yue Meng (ANL)
Viktor Struzhkin (Carnegie)
Ivan Naumov (Howard)
N. W. Ashcroft (Cornell)
Roald Hoffmann (Cornell)

Yanming Ma (Jilin)
Wenwen Cui (JNU)
Zhenxian Liu (UIC)
Eric Rod (ANL)
Jesse Smith (ANL)
Rich Ferry (ANL)
Curtis Kenney-Benson (ANL)
Eva Zurek (Buffalo)
John Tse (Saskatoon)
Reini Boehler (ORNL)
Ronald Cohen (Carnegie)
Siyu Lu (Jilin)
Stan Tozer (FSU)
Peihao Huang (Jilin)

Financial Support

CDAC

THANK YOU!