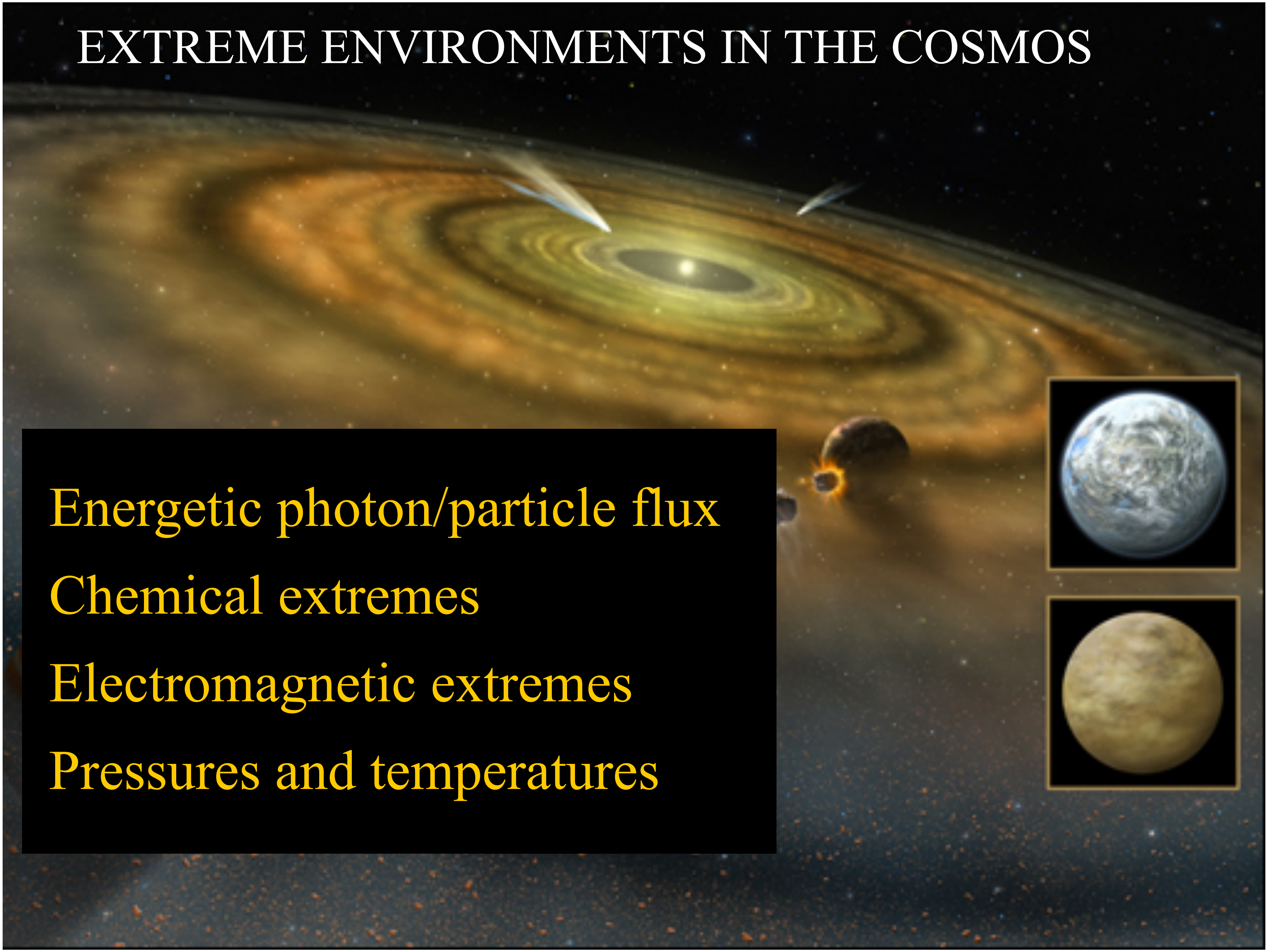
New World of Materials In Extreme Environments

Russell J. Hemley

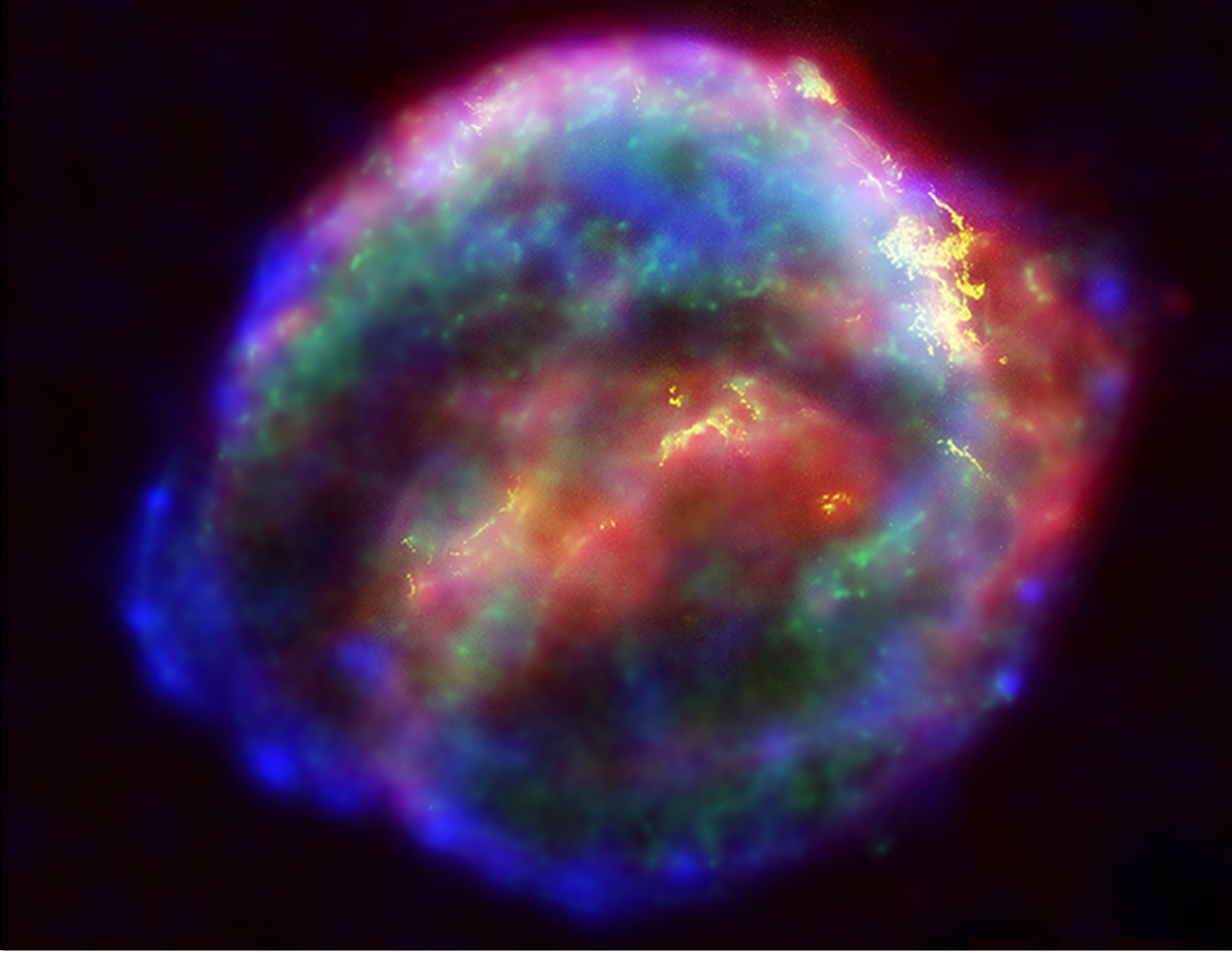
Geophysical Laboratory
Carnegie Institution of Washington
Washington, DC 20015

Lawrence Livermore National Laboratory
Livermore, CA 94550

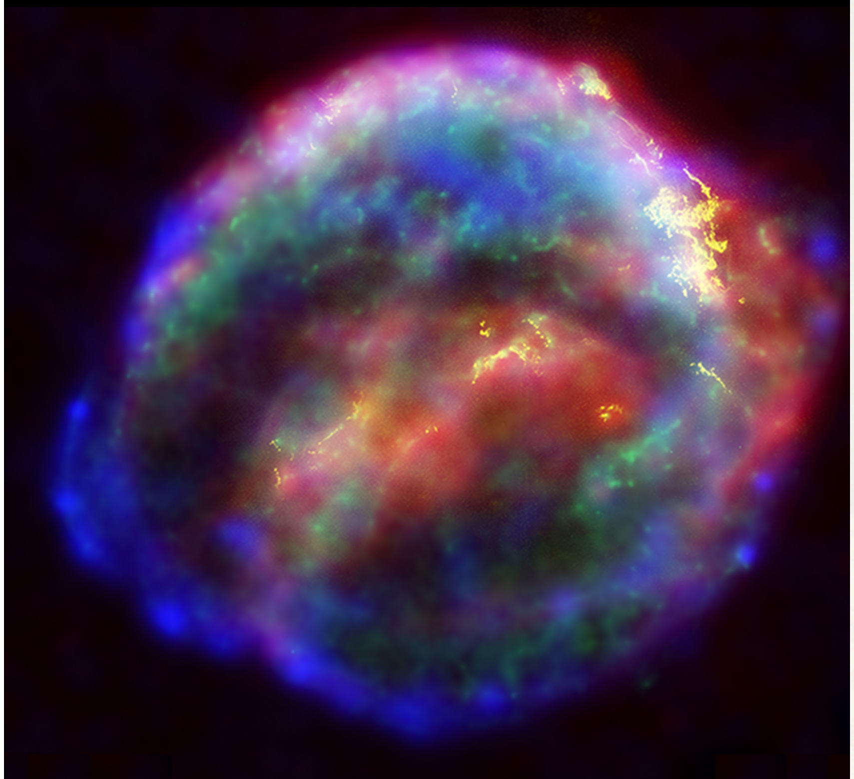
Physics Public Marker Lecture Apr. 6, 2016

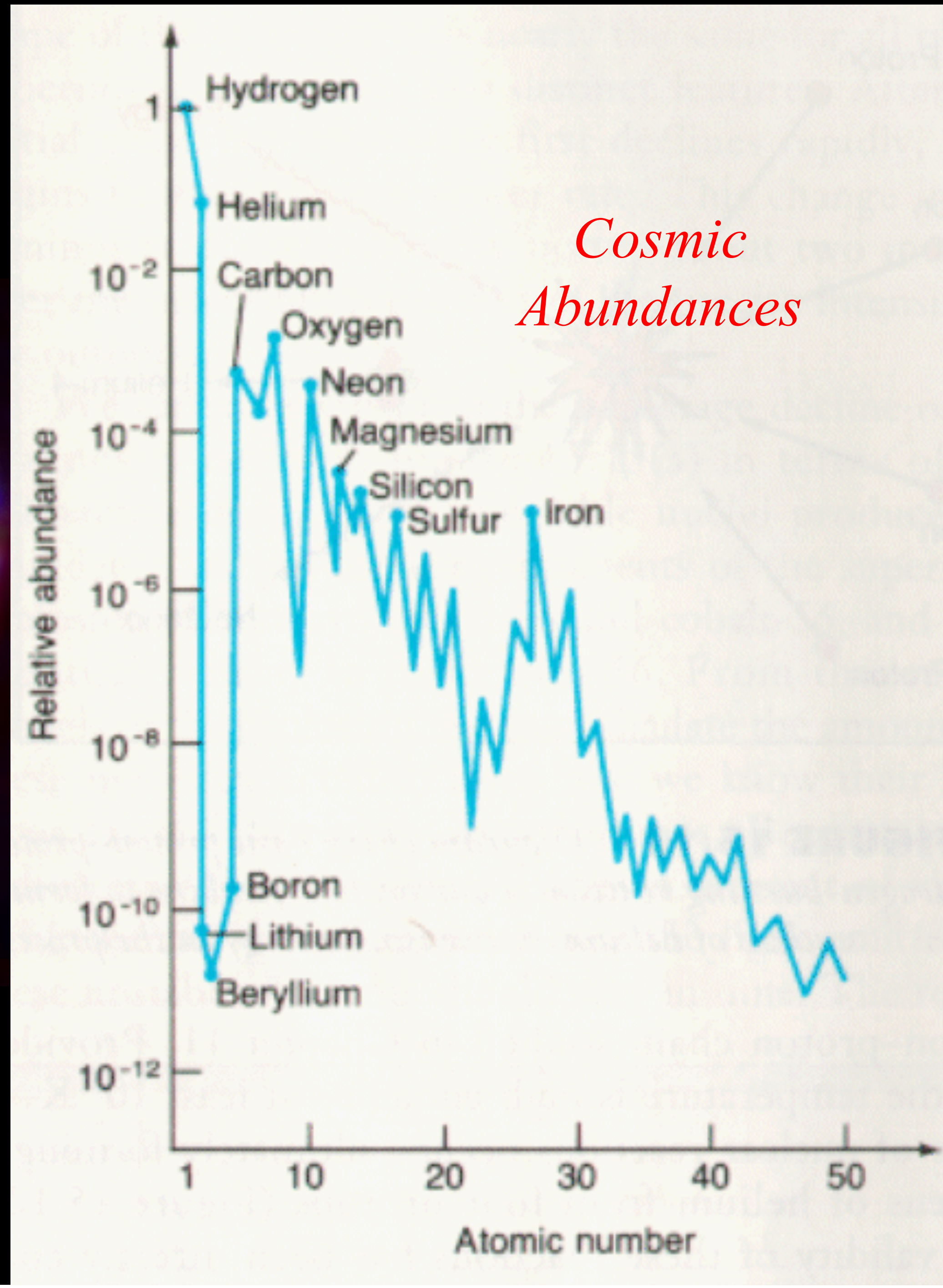

EXTREME ENVIRONMENTS IN THE COSMOS
Energetic photon/particle flux
Chemical extremes
Electromagnetic extremes
Pressures and temperatures

SUPERNOVAE AND NUCLEOSYNTHESIS

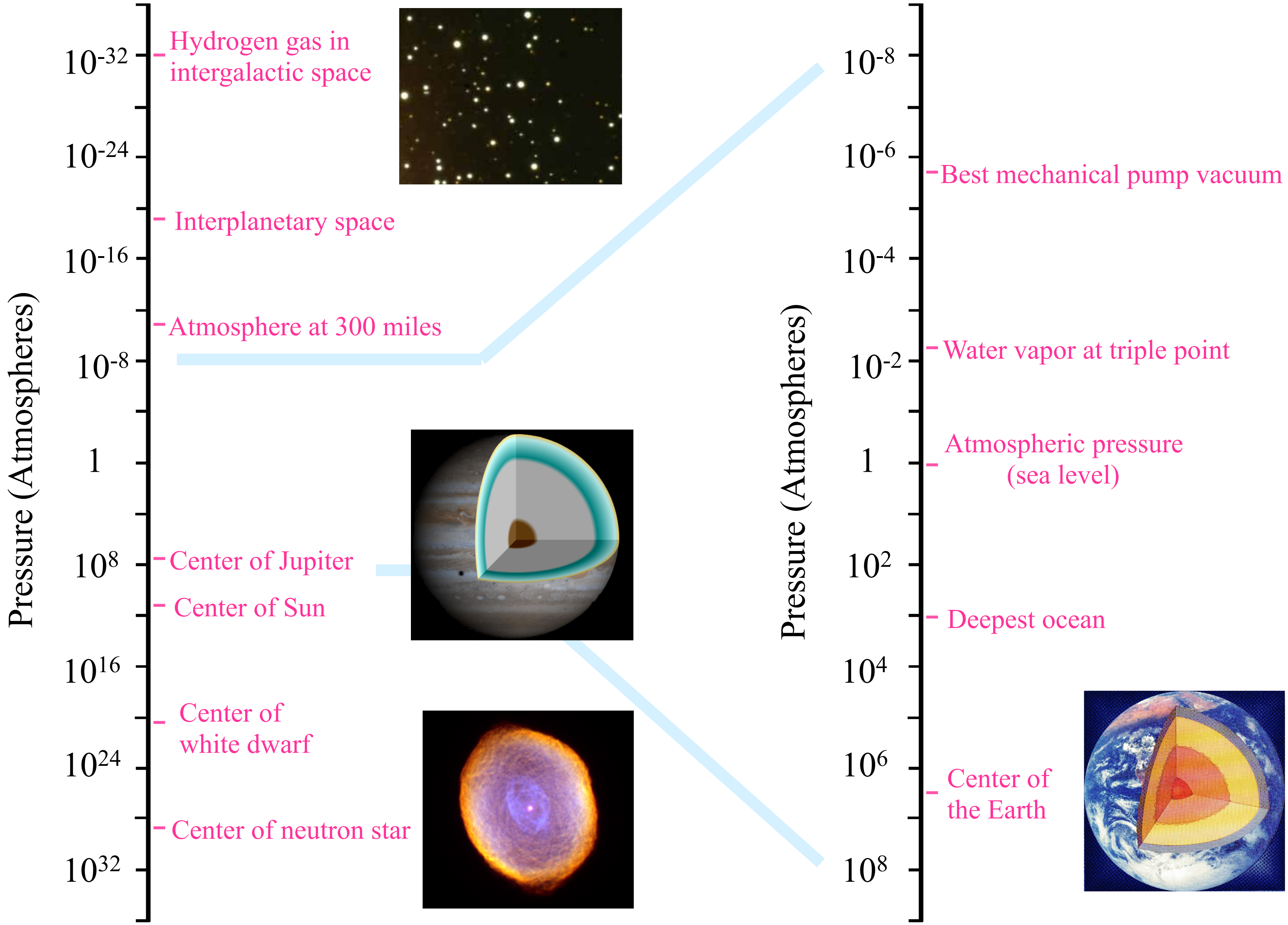


Cosmic Abundances

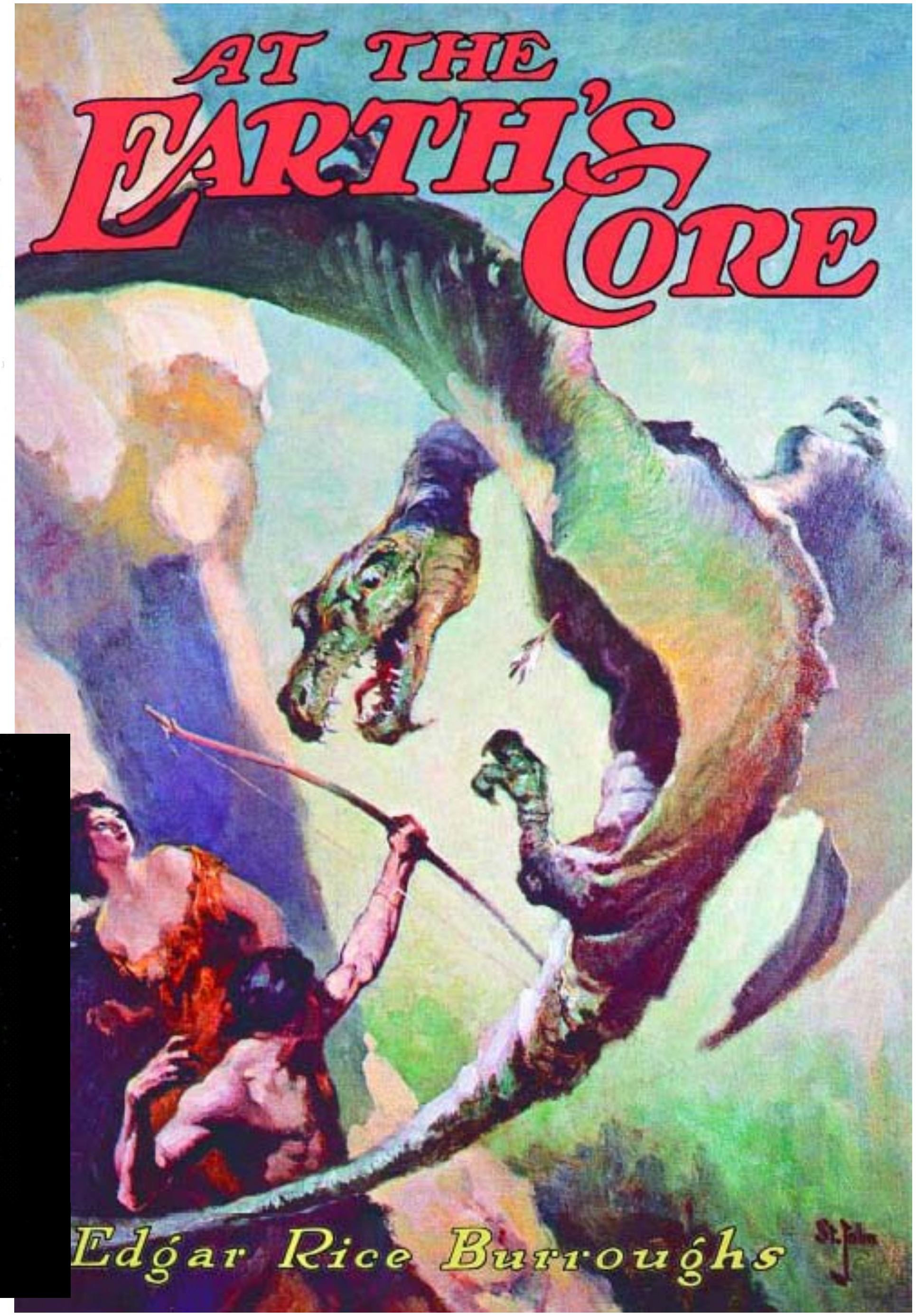


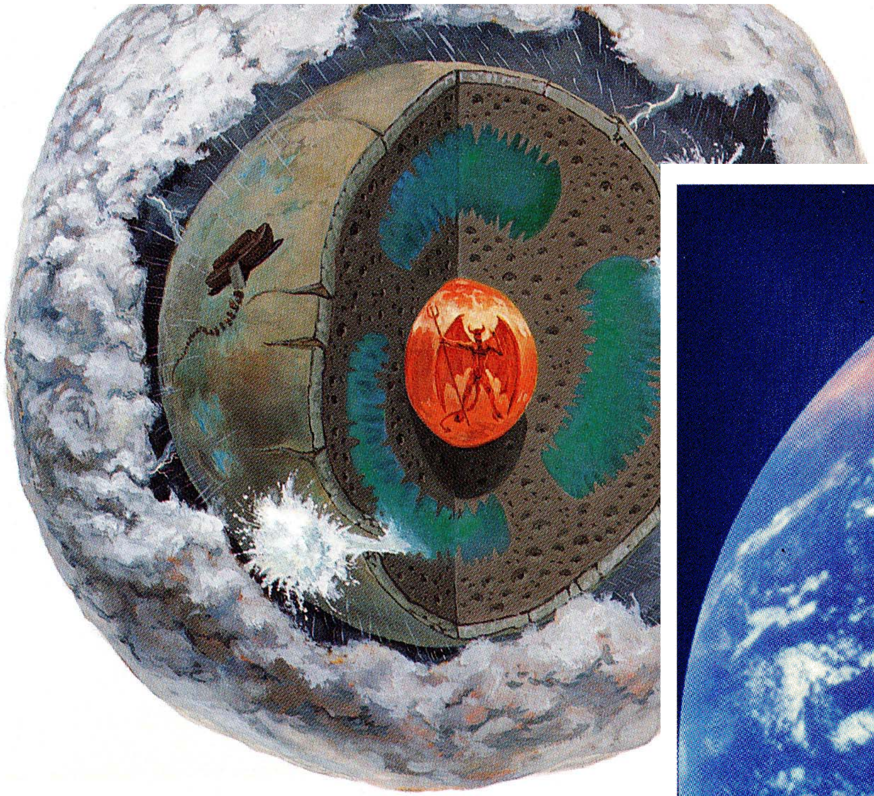


RANGE OF PRESSURE IN THE UNIVERSE

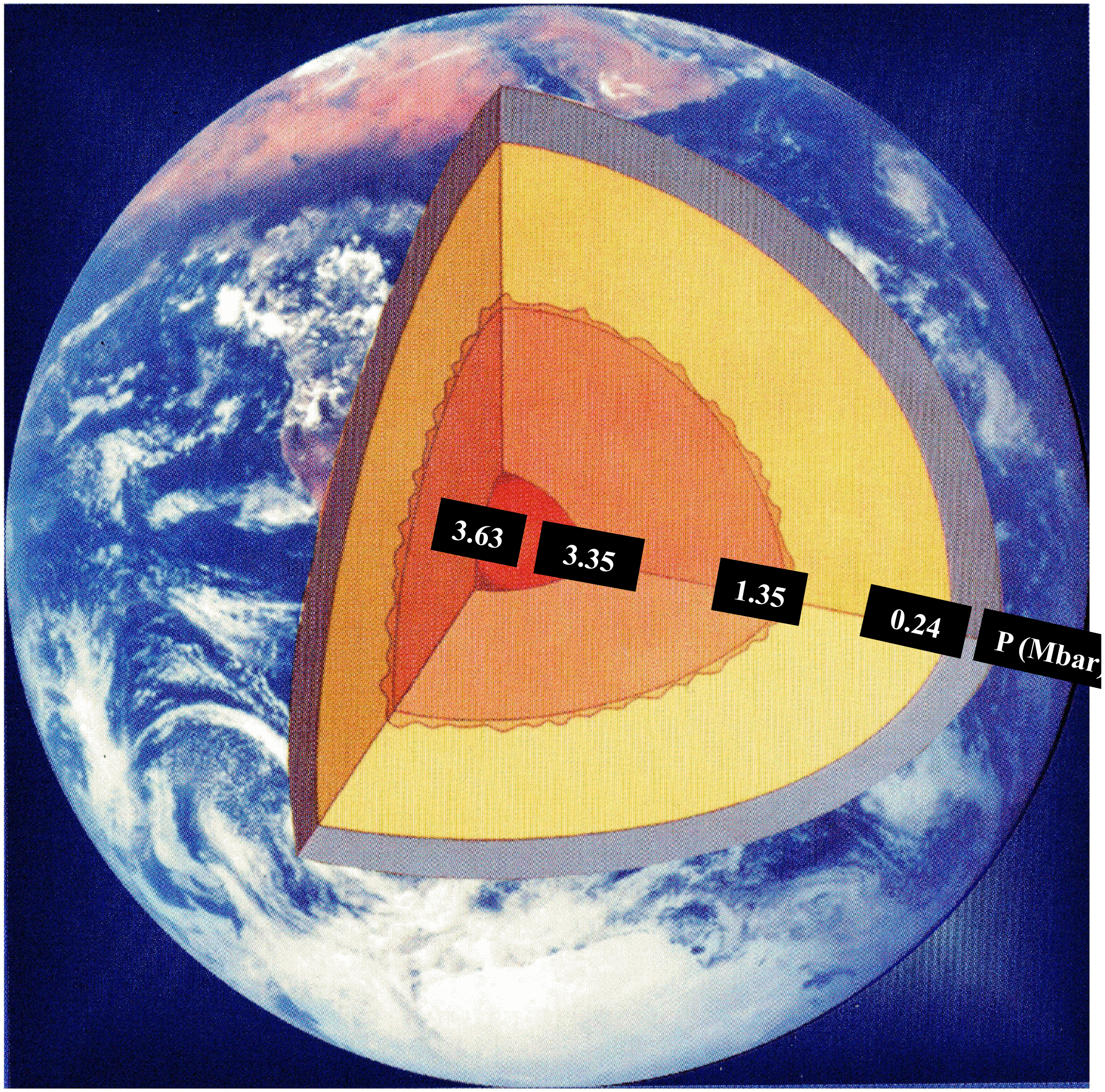


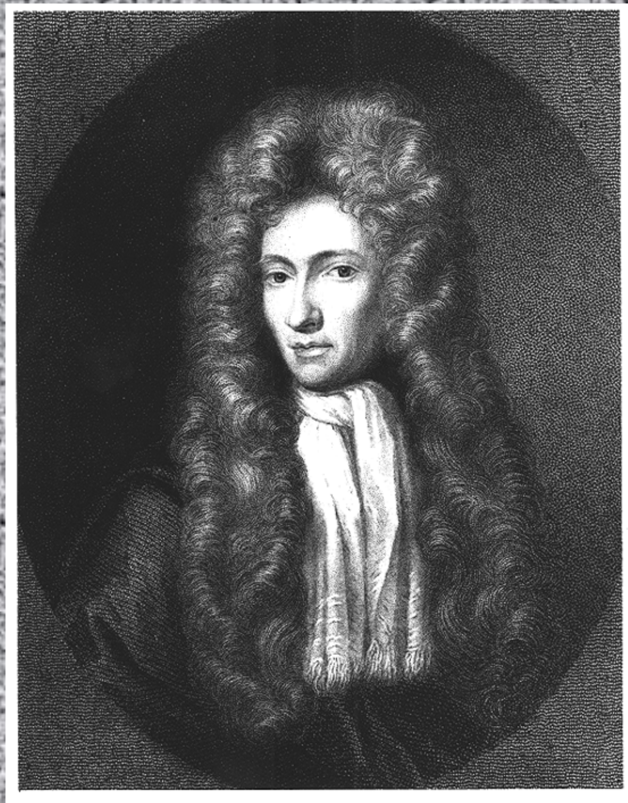

EARTH HAS A DEADLINE
THE CORE
THE ONLY WAY OUT IS IN


AT THE EARTH'S CORE
Edgar Rice Burroughs




EARTH HAS A DEA
THE CORE
THE ONLY WAY OUT IS I


3.63
3.35
1.35
0.24
P (Mbar)



Robert Boyle
1627-1691

EFFECTS OF PRESSURE ON GASES

Gas Laws: $P \times V$ = Constant

". . . perhaps the pressure of the air might have an interest in more phaenomena than men have hitherto thought."

"Touching the Spring of the Air"
New Experiments in Physics and Mechanics, XLIII

ESSAYES
OF
Natural Experiments

Made in the

ACADEMIE DEL CIMENTO,

Under the Protection of the

Most SERENE PRINCE

LEOPOLD of ***TUSCANY.***

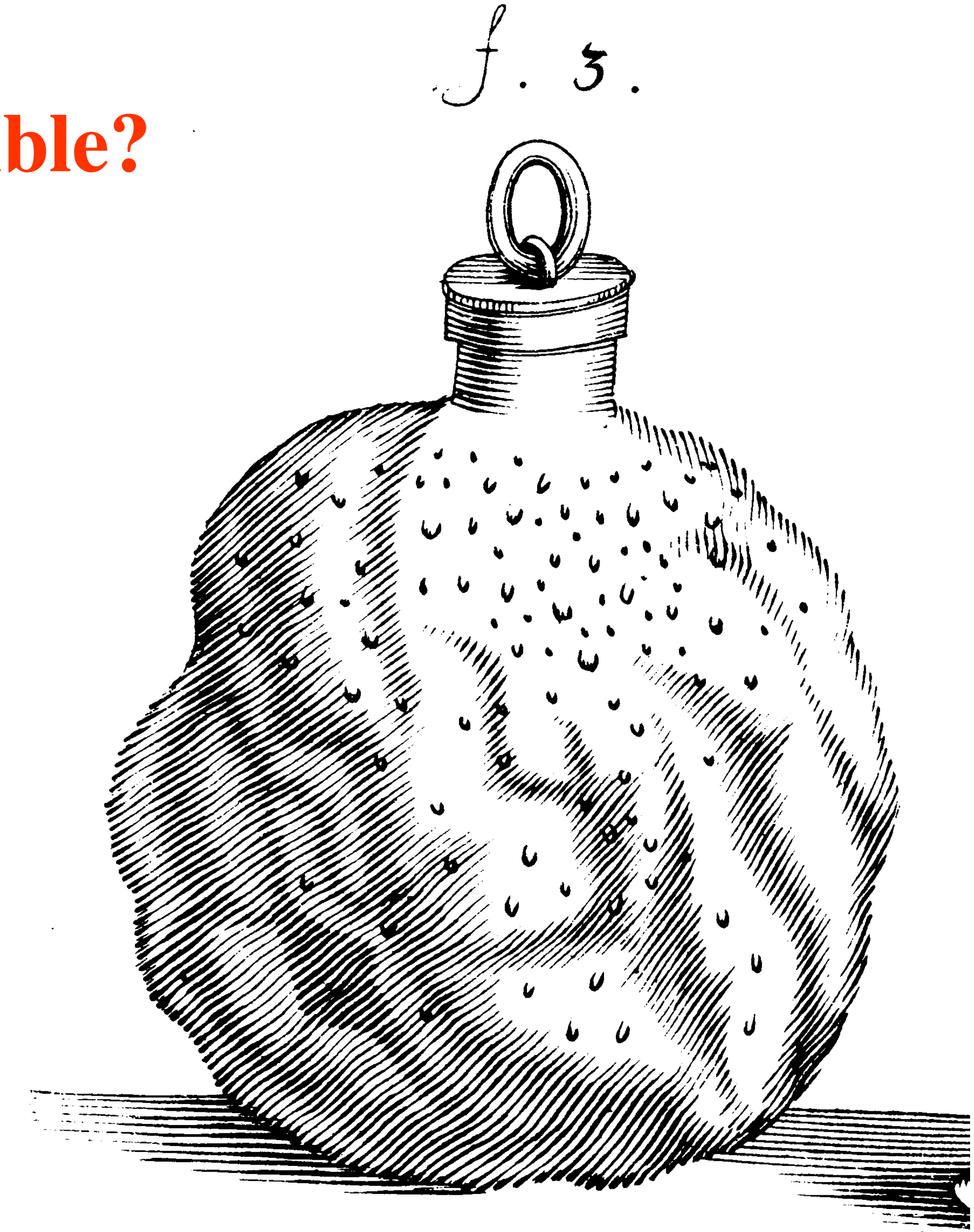
Written in Italian *by the Secretary of that* ACADEMY.

Englished by *RICHARD WALLER,* Fellow of the *Royal Society.*

LONDON,

Printed for *Benjamin Alsop* at the *Angel* and *Bible* in the *Poultrey,* over-against the *Church.* 1684.

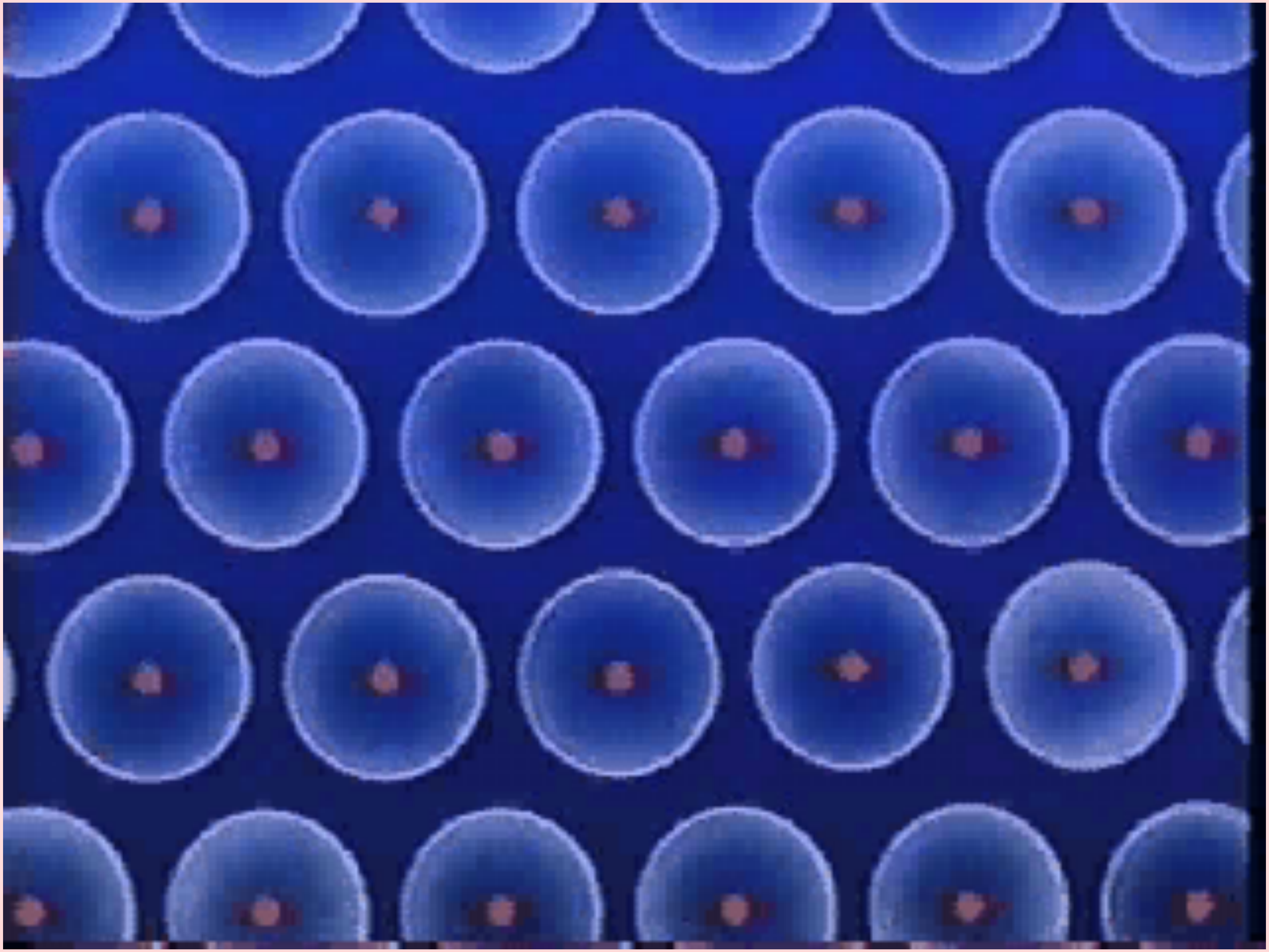
Is Water Compressible?



Compressing Atoms

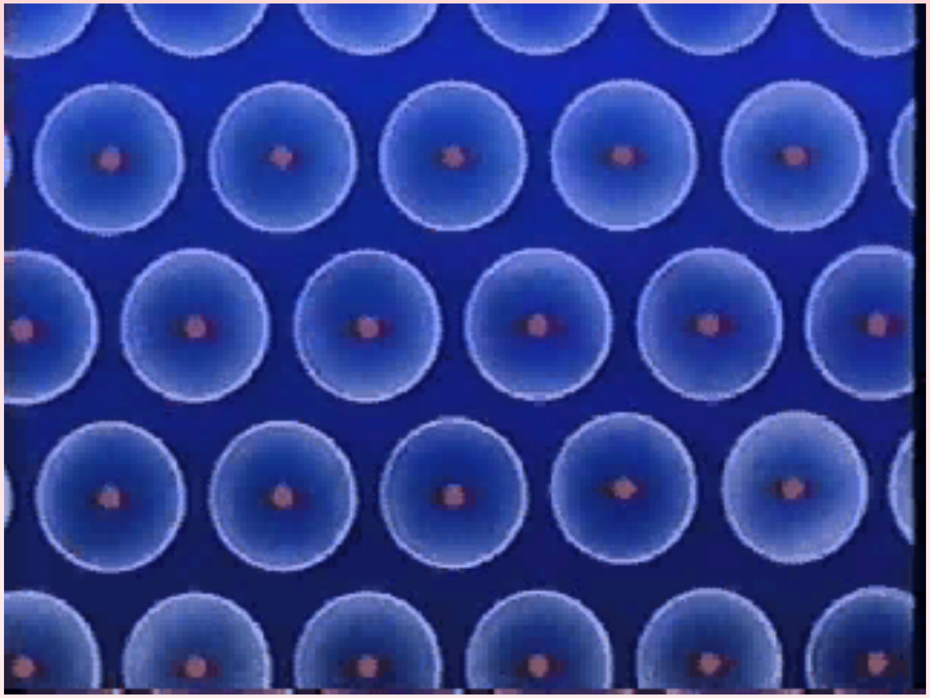
Fort Mercer, NJ

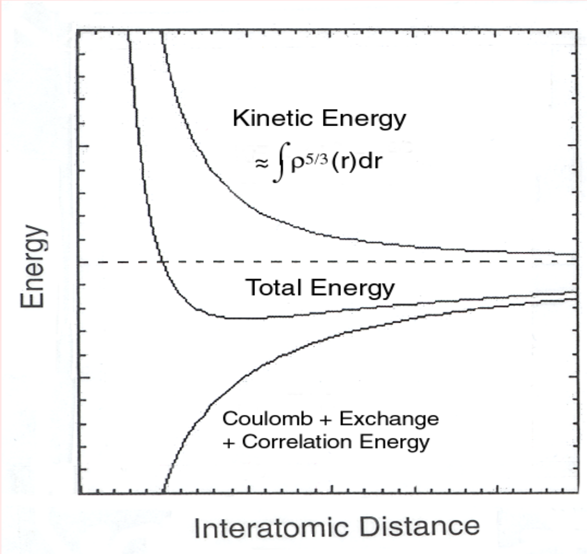
Compressing Atoms

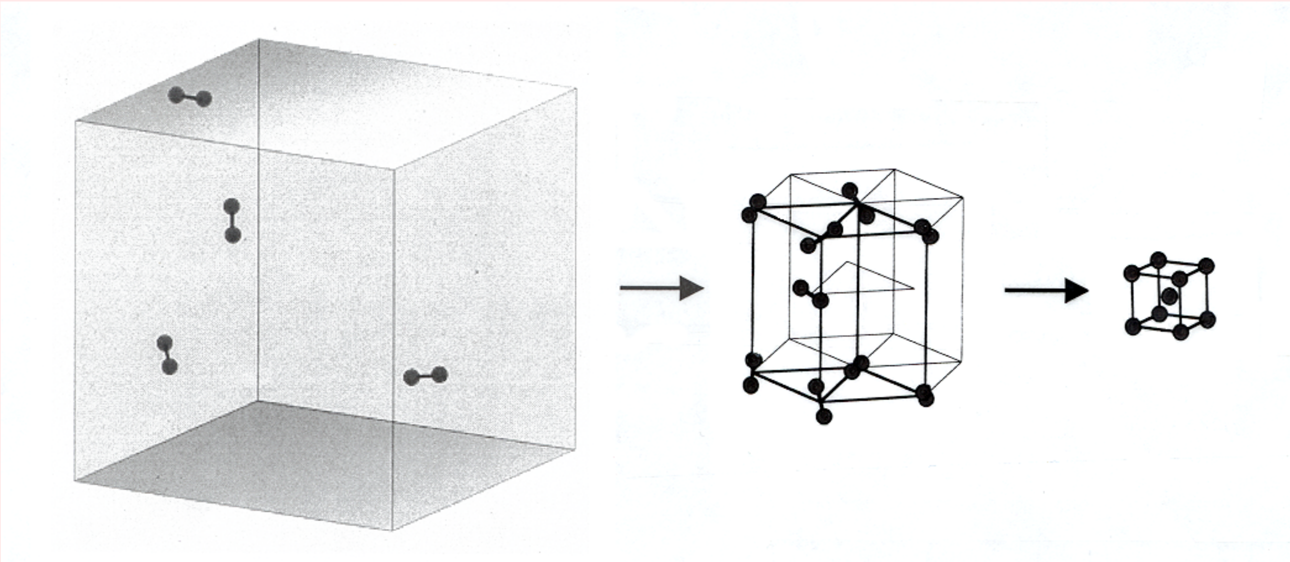


[Fowler, *Mon. Not. R. Soc. Astron. Soc.* (1926); Bridgman, *Phys. Rev.* (1927)]

Compressing Atoms and Molecules

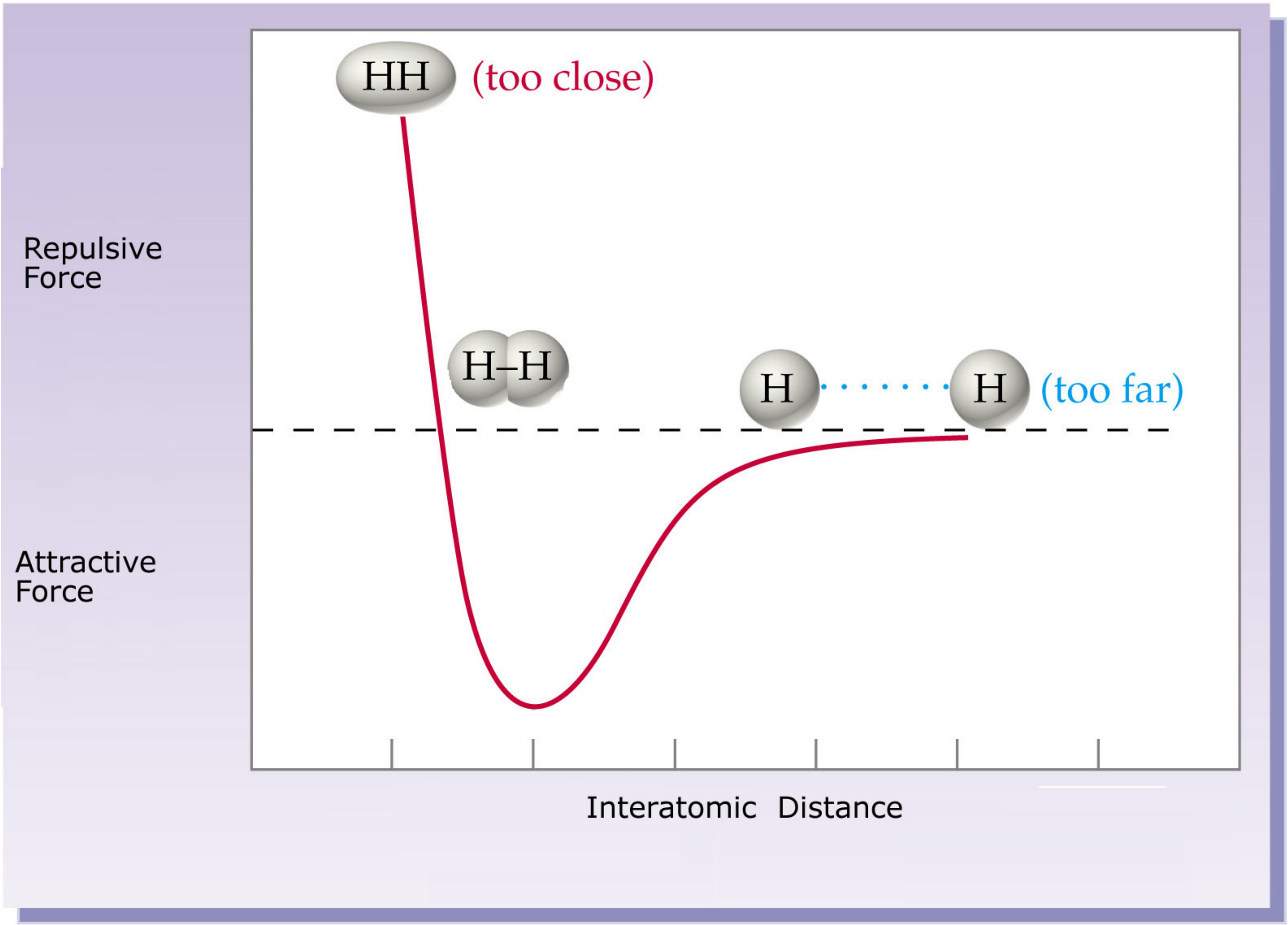




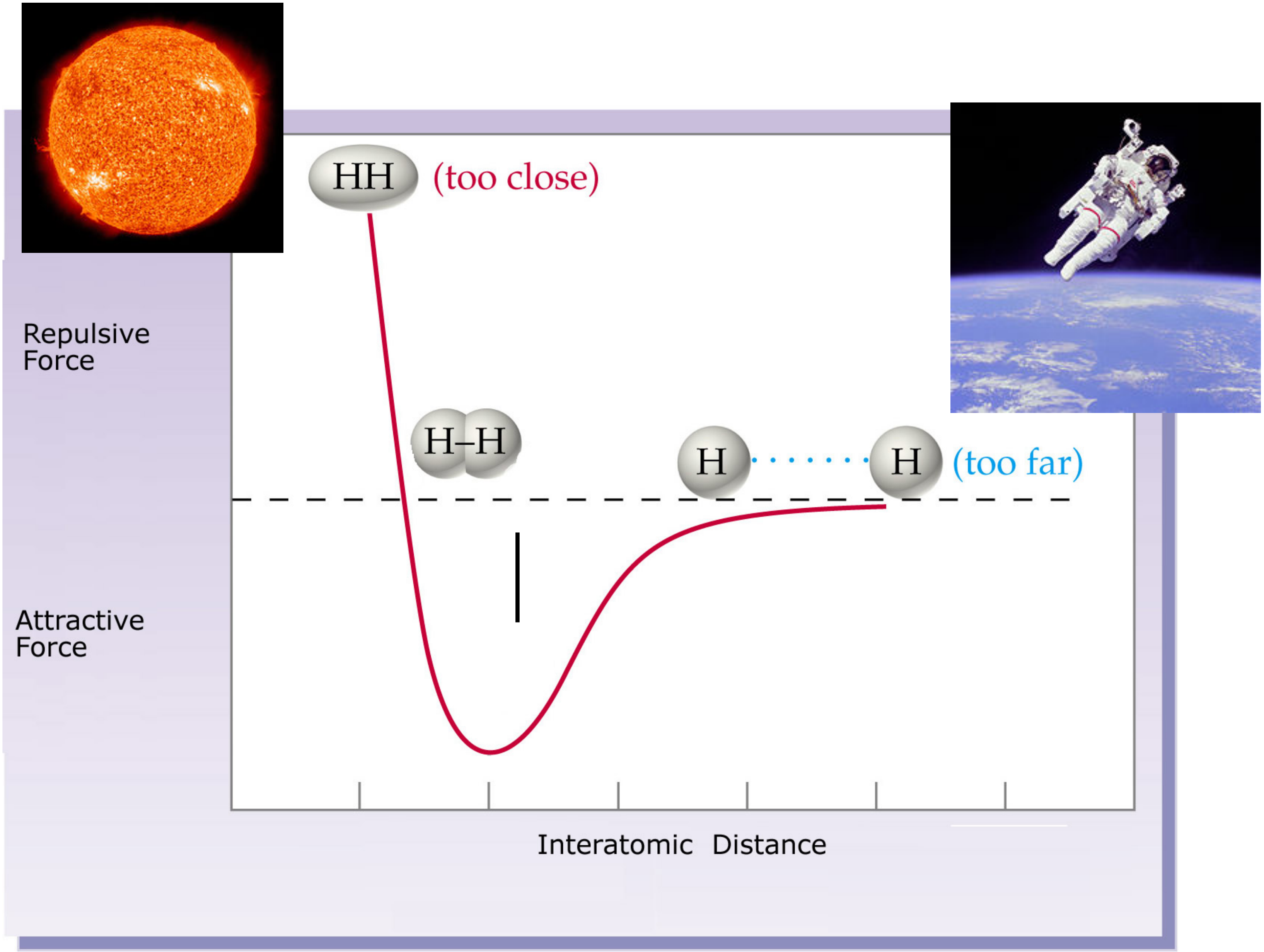


Ultimate state of molecules: "Metals" or "Valence Lattices"

[Bernal (1926); footnote in Wigner & Huntington, *J. Chem. Phys*. (1935)]



What happens when we bring atoms close together ?



What happens when we bring atoms close together ?

PRESSURE (→)

PRESSURE (↓)

Periodic Table of the Elements

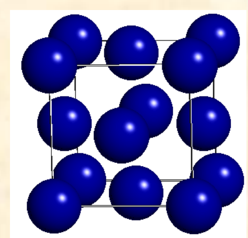
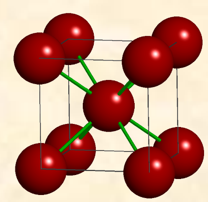
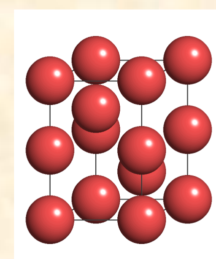
1 1A	2 2A	3	4	5	6	7	8	9	10	11	12	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La* 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226	89 Ac† (227)	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

Alkali metals; Alkaline earth metals (2A); Transition metals (3–12); Halogens (17, 7A); Noble gases (18, 8A); metals ← → nonmetals

	58	59	60	61	62	63	64	65	66	67	68	69	70	71
*Lanthanides	Ce 140.1	Pr 140.9	Nd 144.2	Pm (145)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 167.3	Tm 168.9	Yb 173.0	Lu 175.0

	90	91	92	93	94	95	96	97	98	99	100	101	102	103
†Actinides	Th 232.0	Pa (231)	U 238.0	Np (237)	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (260)

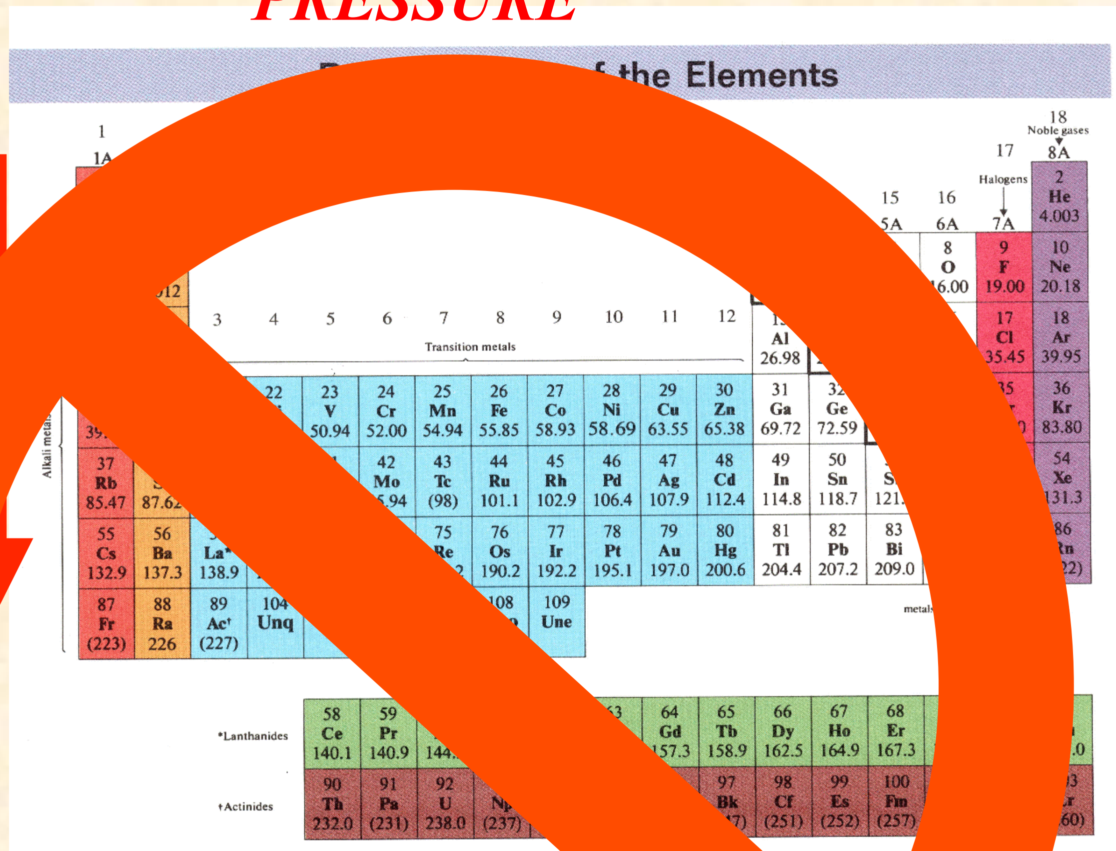
- **Filling of *s, p, d,* … orbitals**
- **Simple structures**

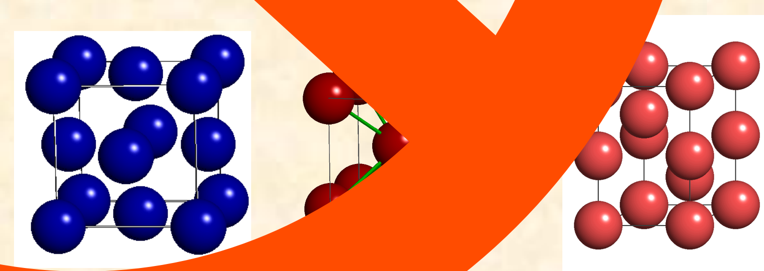
Under Pressure

- **Orbital hybridization (*e.g.*, *s*→*d*)**
- **Complex structures/electronic structure**

PRESSURE



- **Filling of s … orbitals**
- **Simple stru**



Under Pressure

- **Orbital hybridiza**
- **Complex structures/electronic structure**

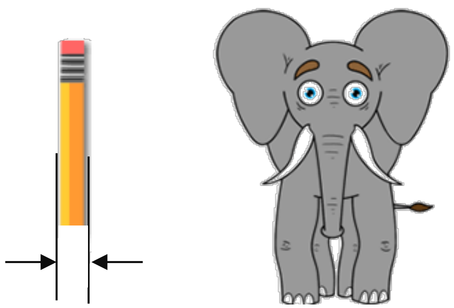
$P = F / A$

[*after* T. Strobel]

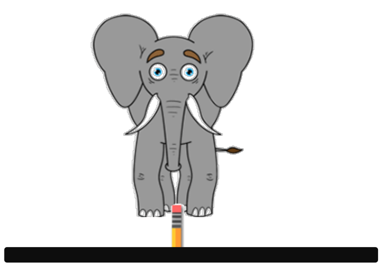
50 kg (110 lbs) woman on 12 mm heel (1/2") = 43 atm (630 psi)

Units: *atm, bar, Pa, psi, Torr, mmHg, inH$_2$O*

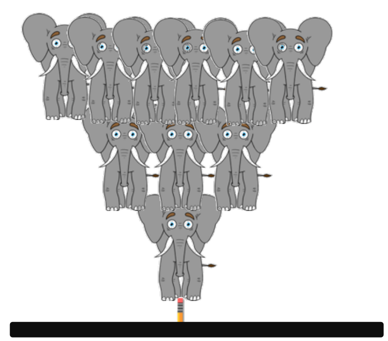
10^3 atm ≈ kbar
10^6 atm ≈ Mbar
10 kbar = 1 GPa
1 Mbar = 100 GPa



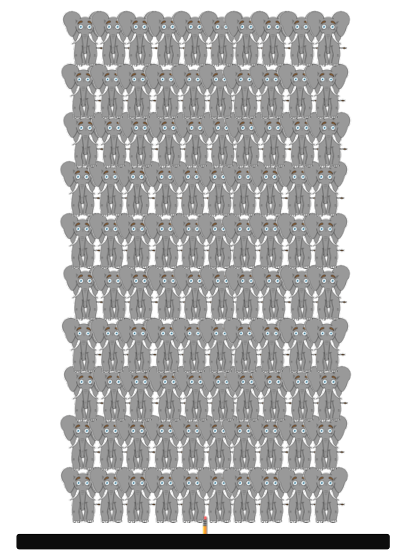
8 mm (1/3")   5,000 kg (11,000 lb)



1 GPa =
1 Elephant per pencil =10,000 atm



10 GPa =
10 Elephant per pencil =100,000 atm

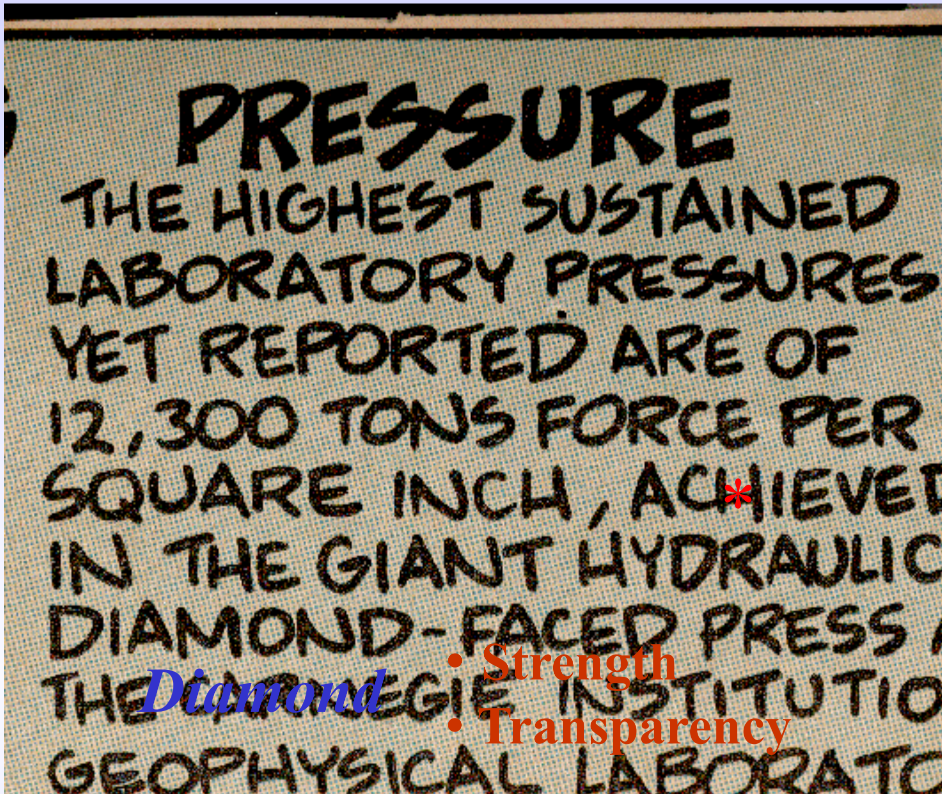


100 GPa =
100 Elephant per pencil =1,000,000 atm

50,000 ton press
(140 ft)

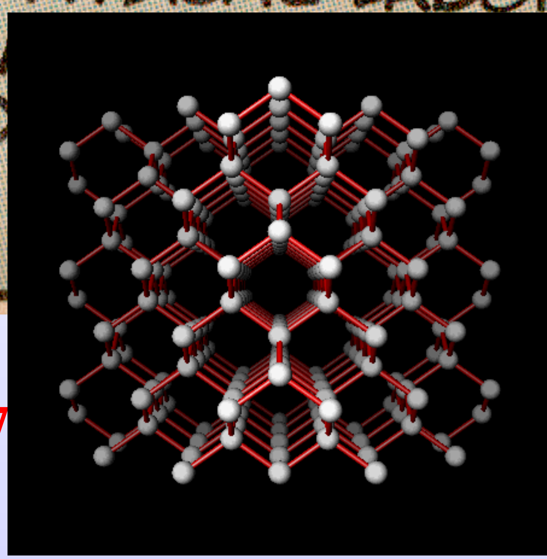
Institute of High
Pressure Physics

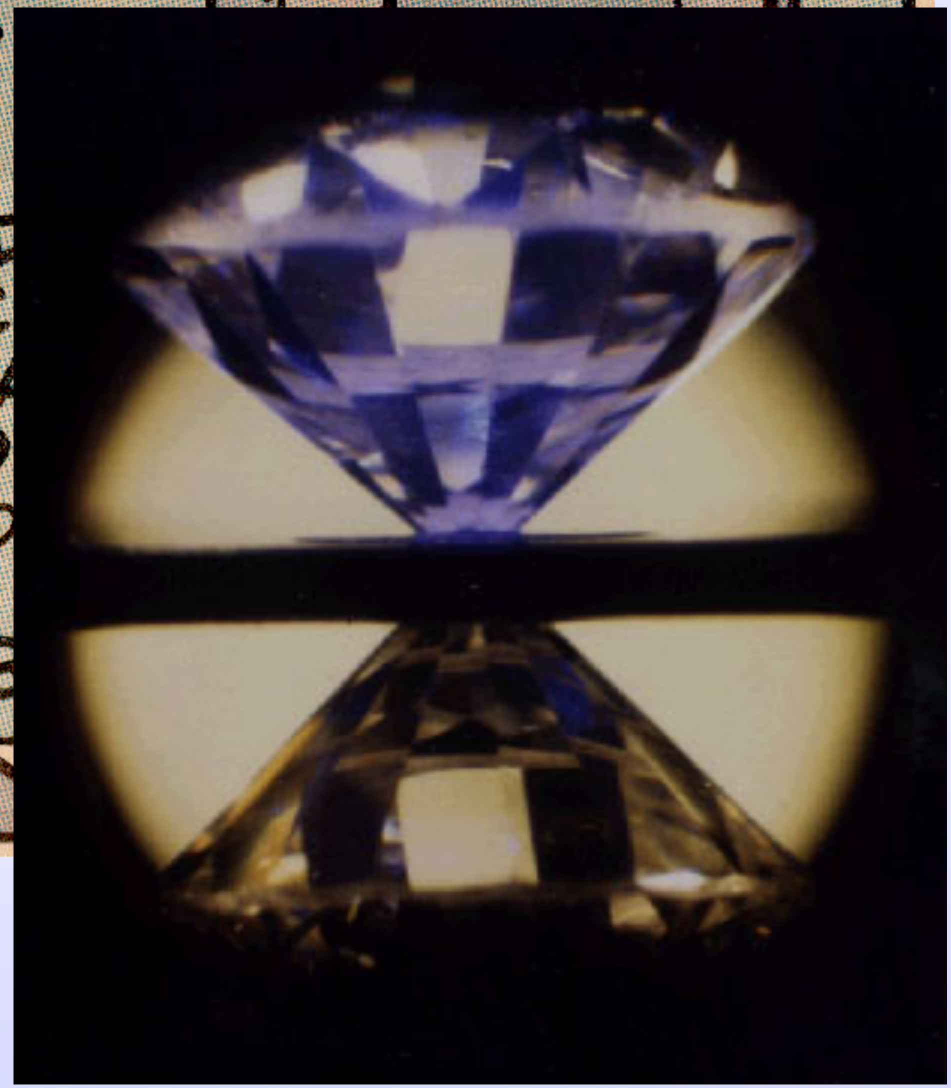
Troitsk, Russia



Diamond

- Strength
- Transparency

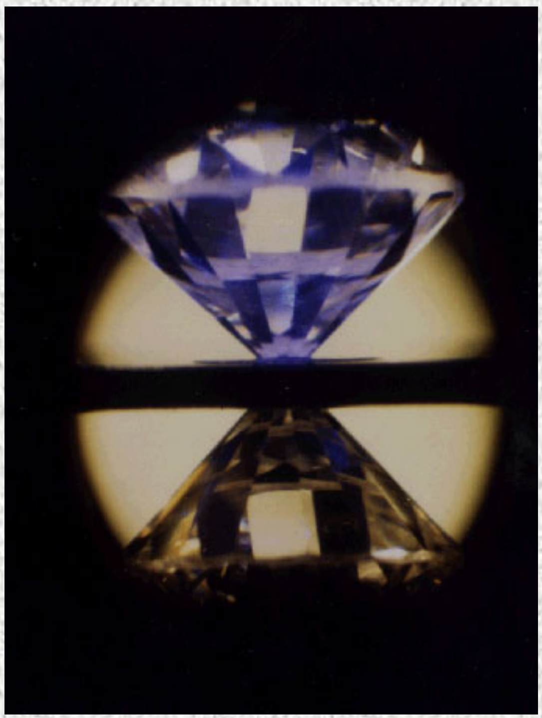


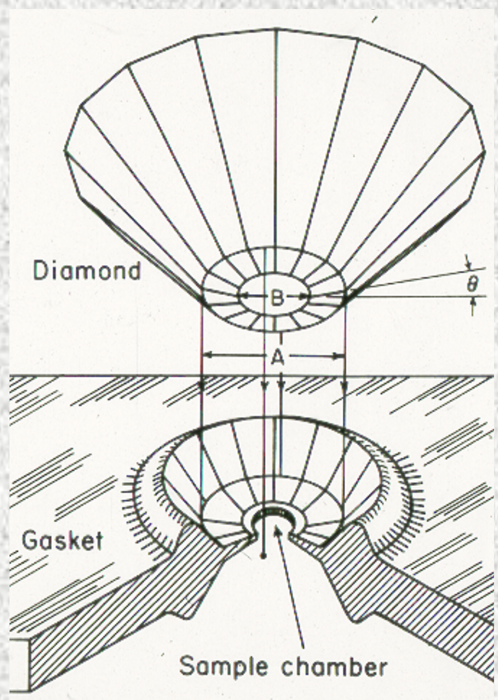


* 1.7 ... res

Generating Extreme Pressures in the Laboratory

Static

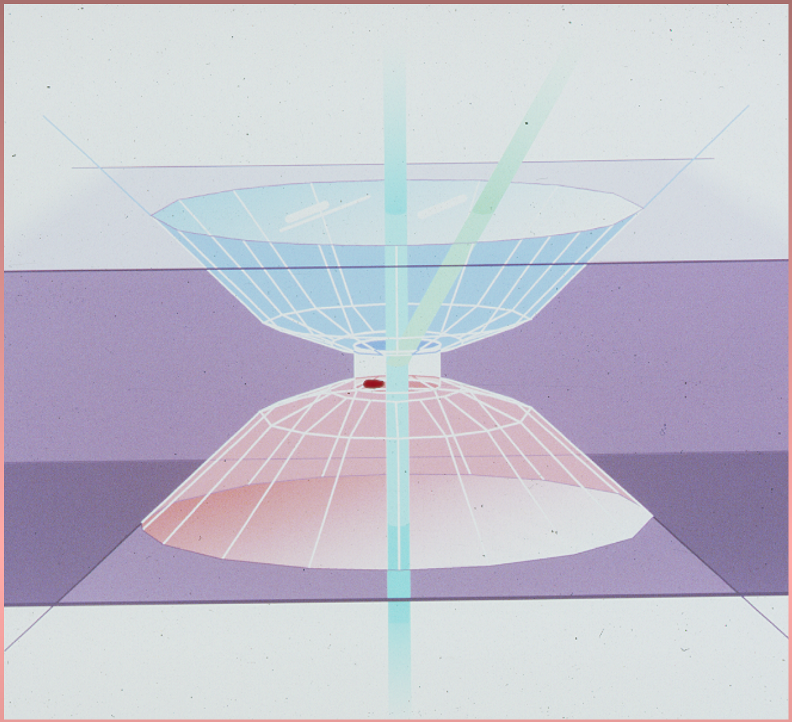




>100's GPa (~0.5 TPa)

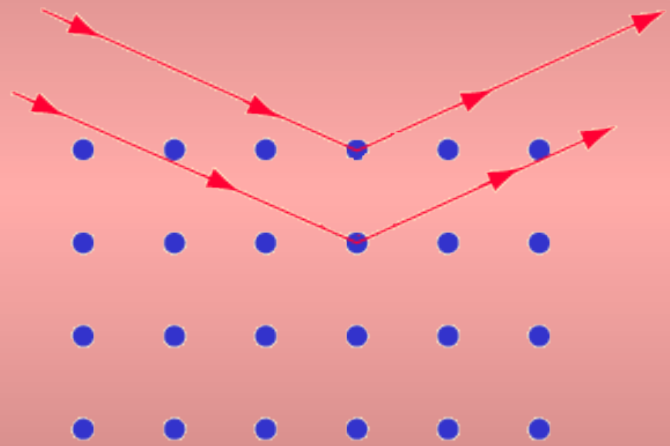
~ eV energies – valence electrons

Spectroscopies

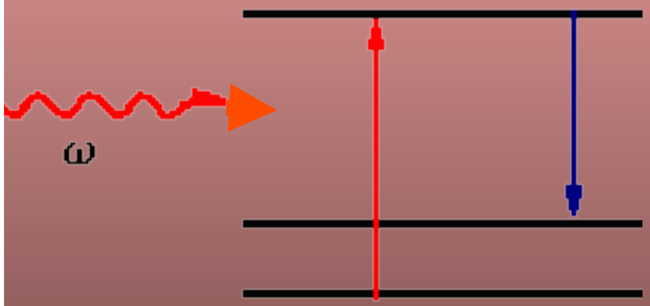


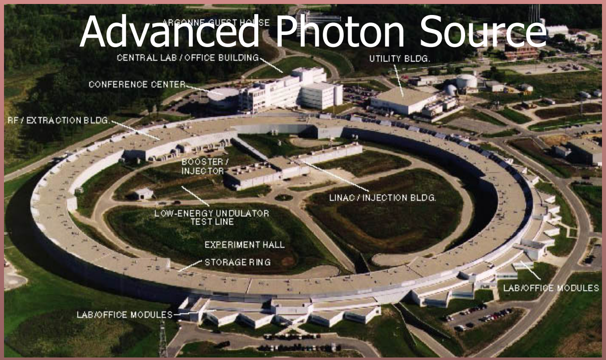
Absorption/emission

Diffraction/Scattering



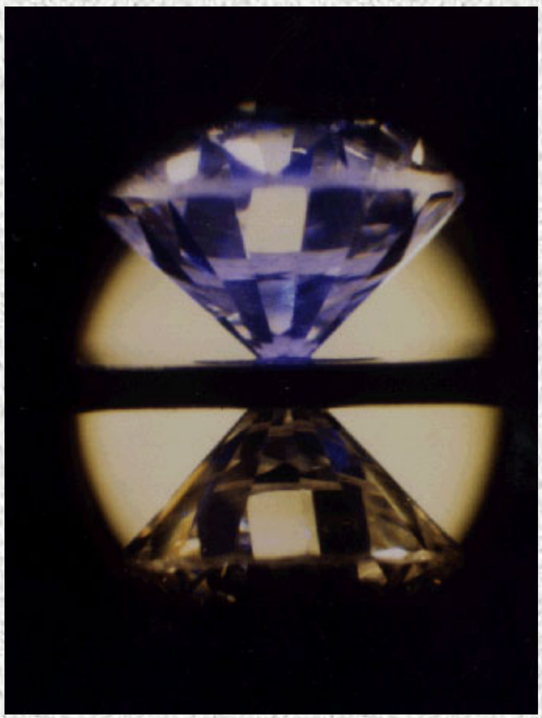
Inelastic Scattering

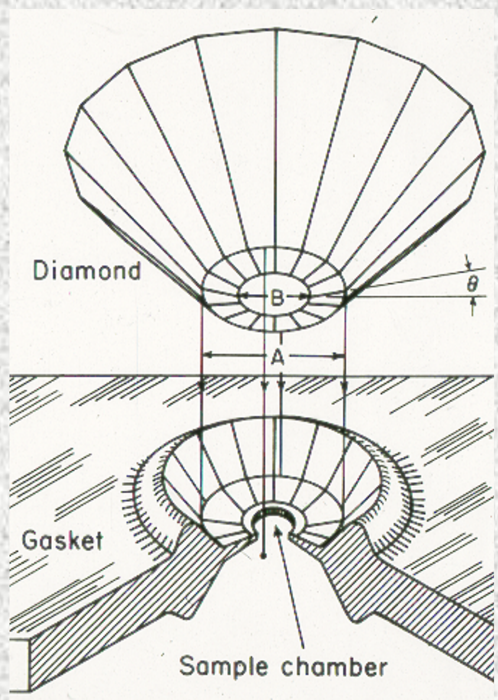




Generating Extreme Pressures in the Laboratory

Static

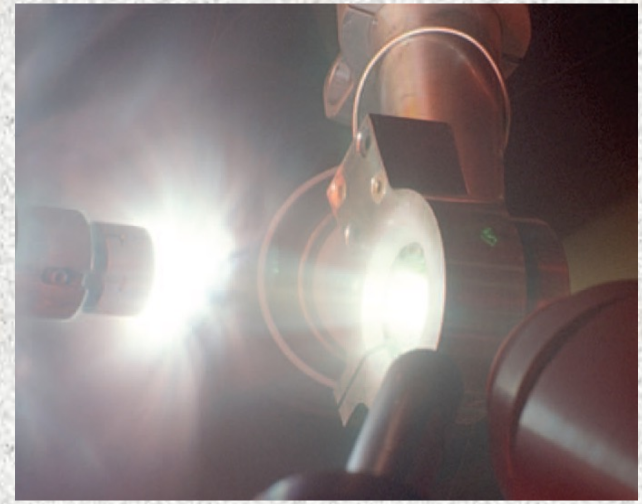




>100's GPa (~0.5 TPa)

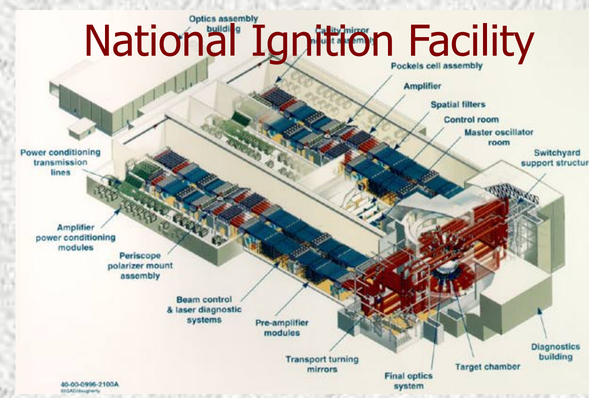
~ eV energies – valence electrons

Dynamic



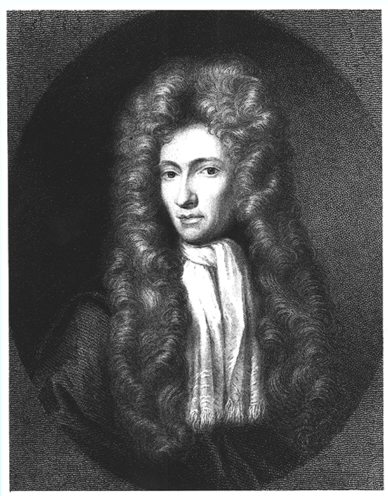
>100's Mbars (1 Gbar)

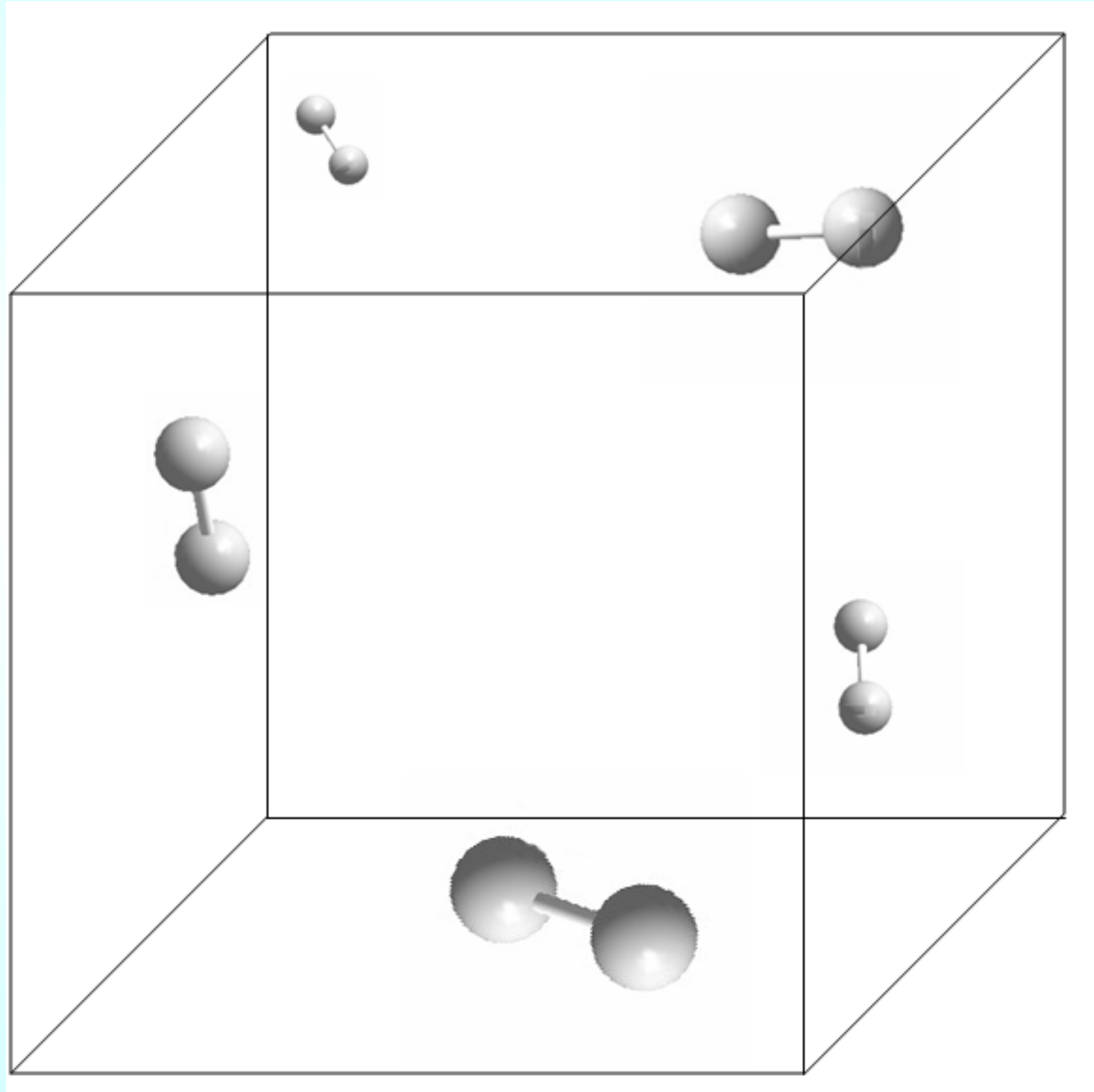
~ keV energies – core electrons



Touching the Spring of the Air

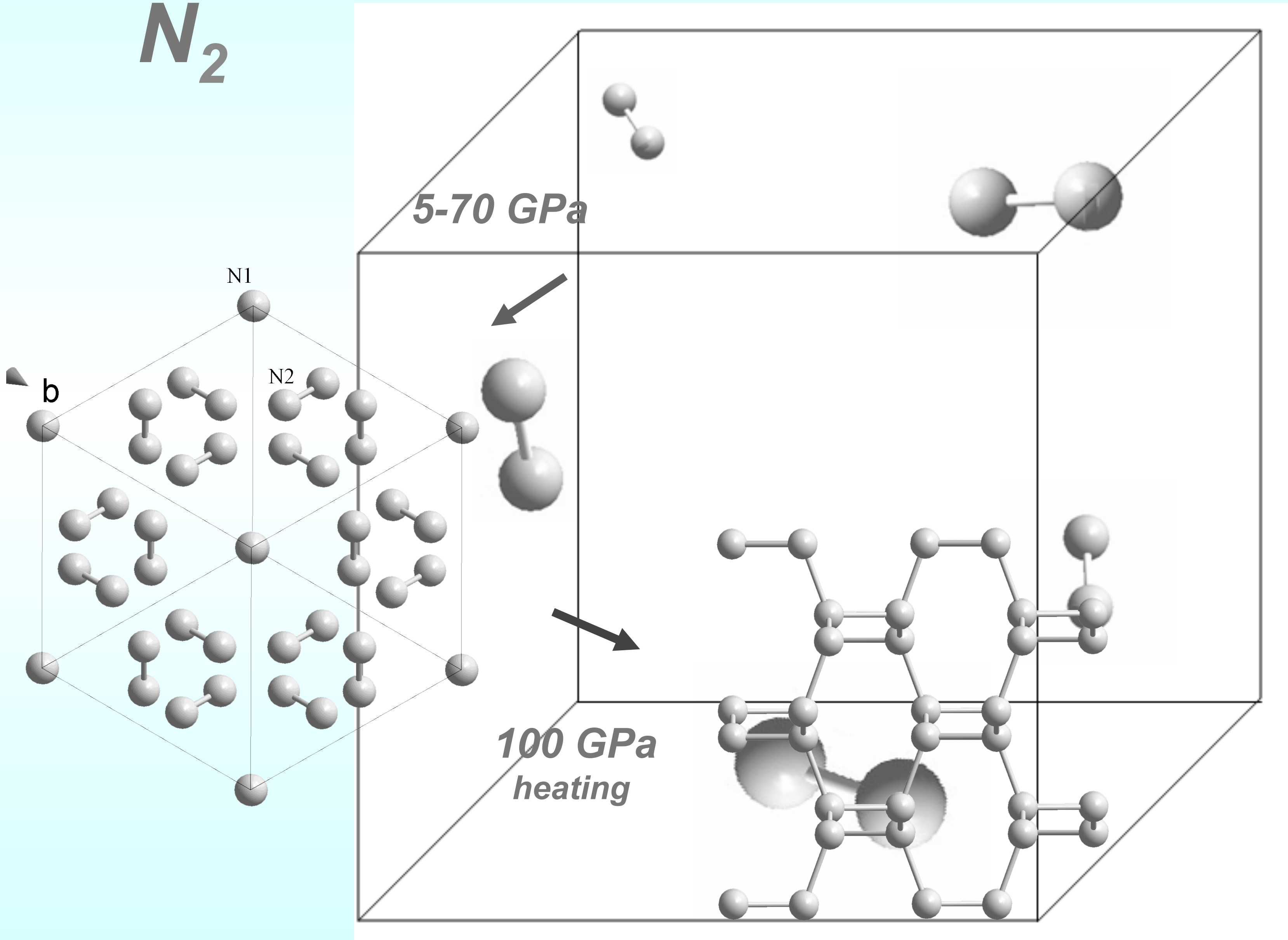
N_2



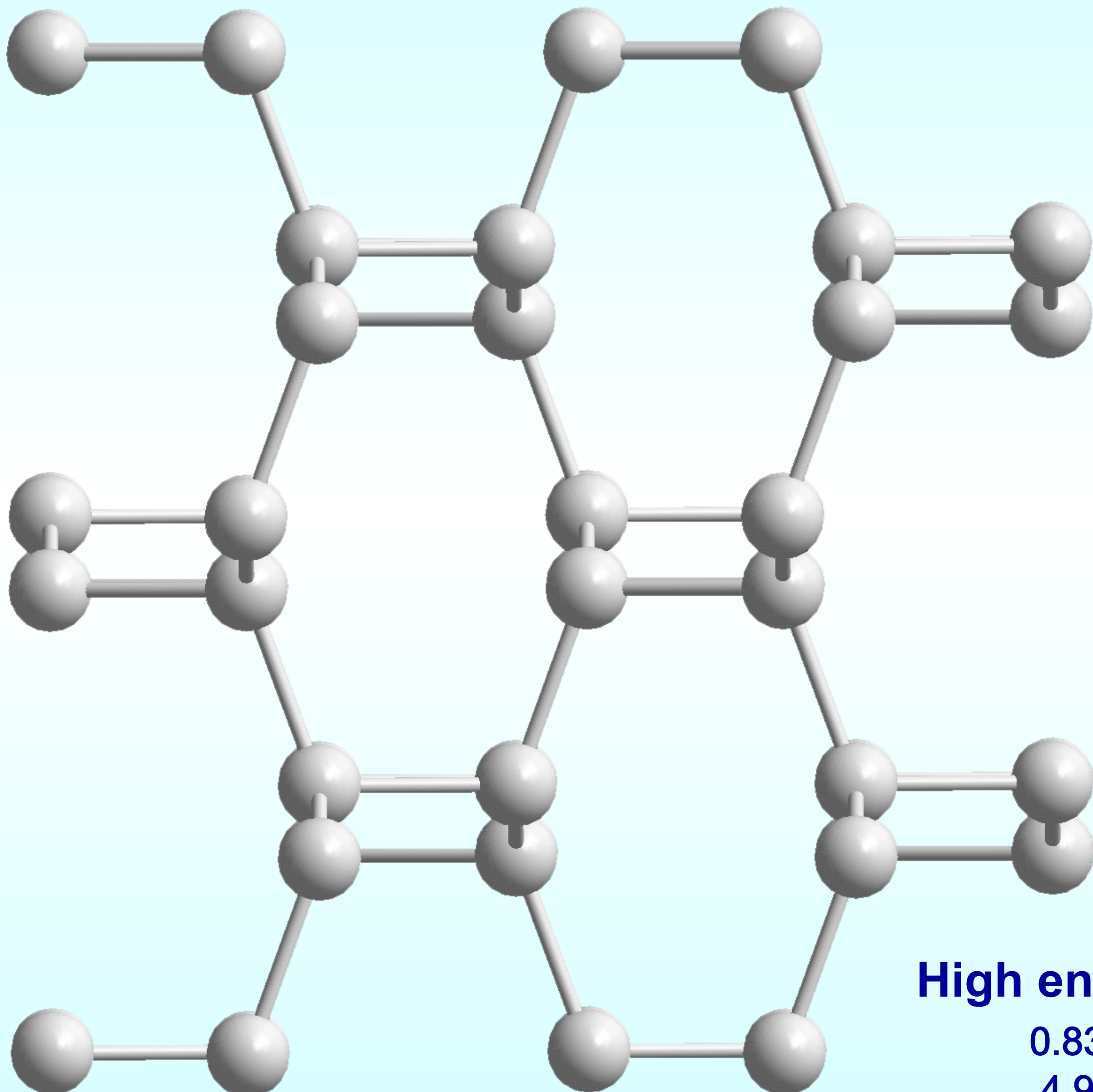


Touching the Spring of the Air

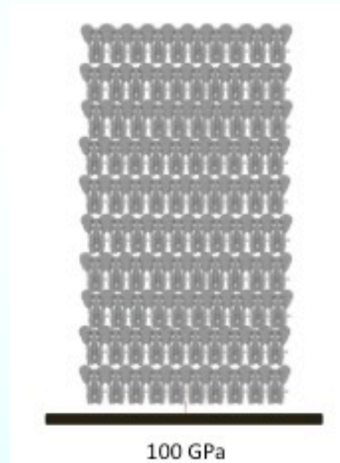
N_2



Touching the Spring of the Air

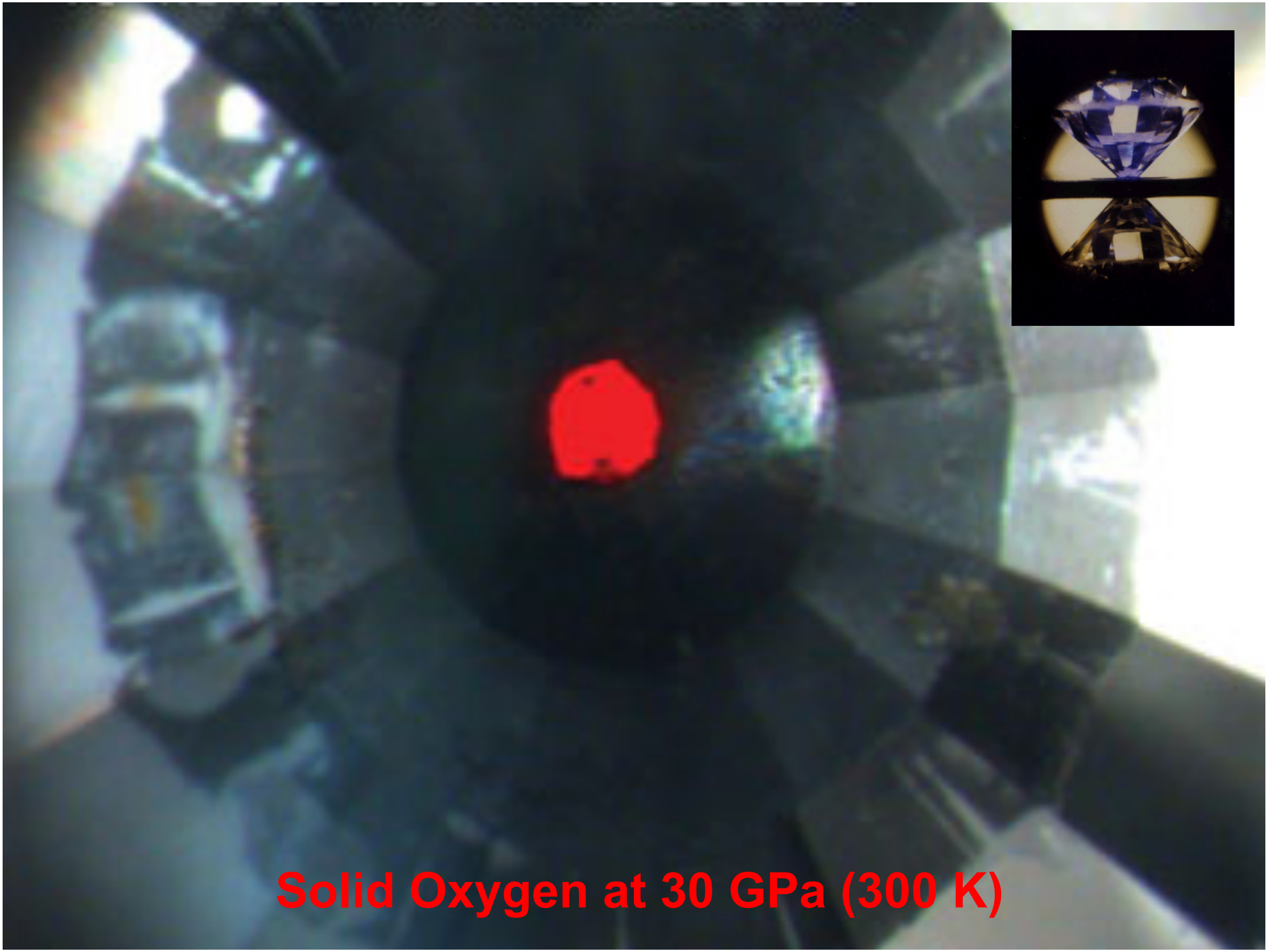


[Eremets et al., *Nature Materials* (2004); *J. Chem. Phys.* (2004)]



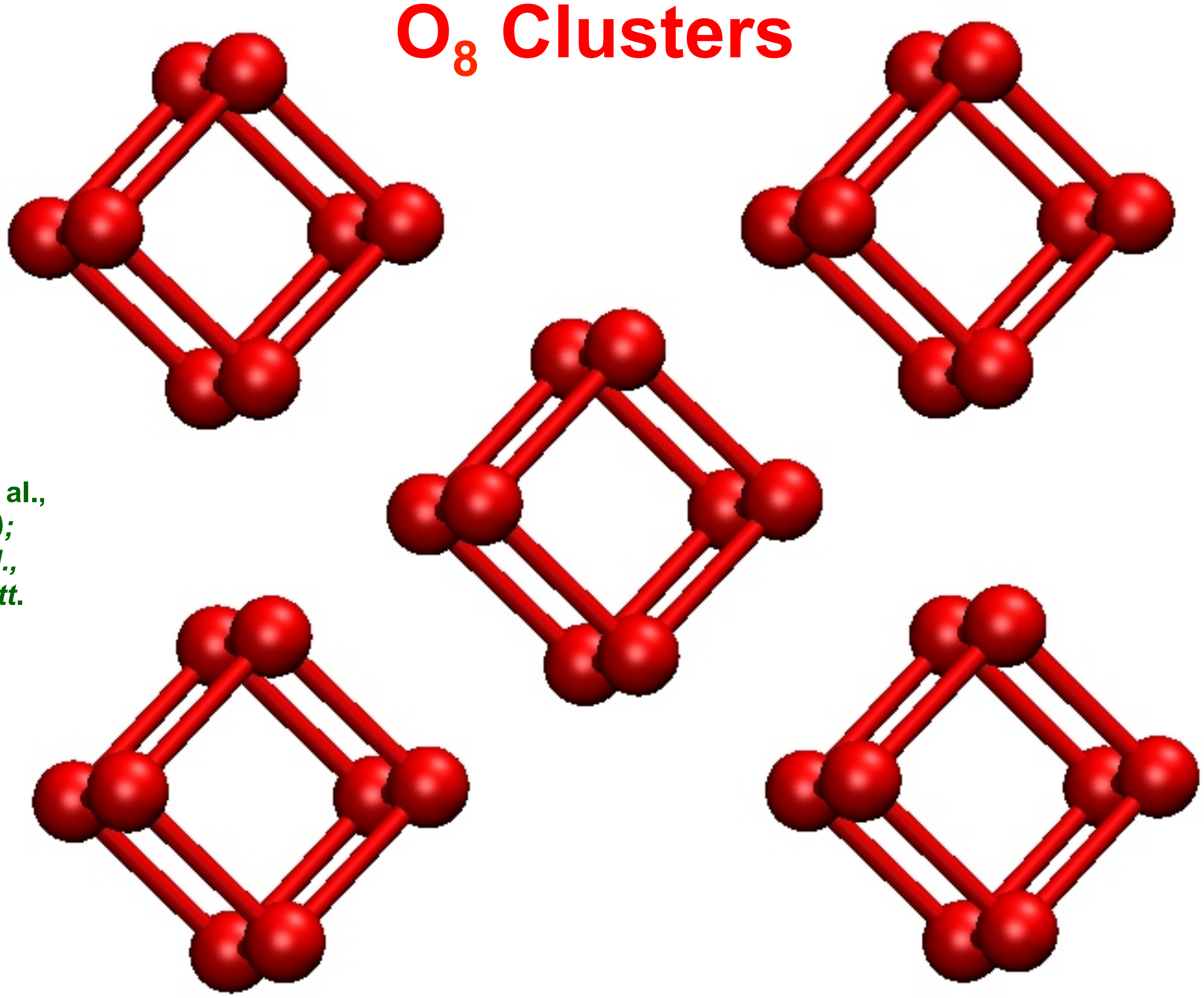
High energy density material

0.83 eV/atom (single bond)
4.94 eV/atom (triple bond)


Solid Oxygen at 30 GPa (300 K)

Touching the Spring of the Air

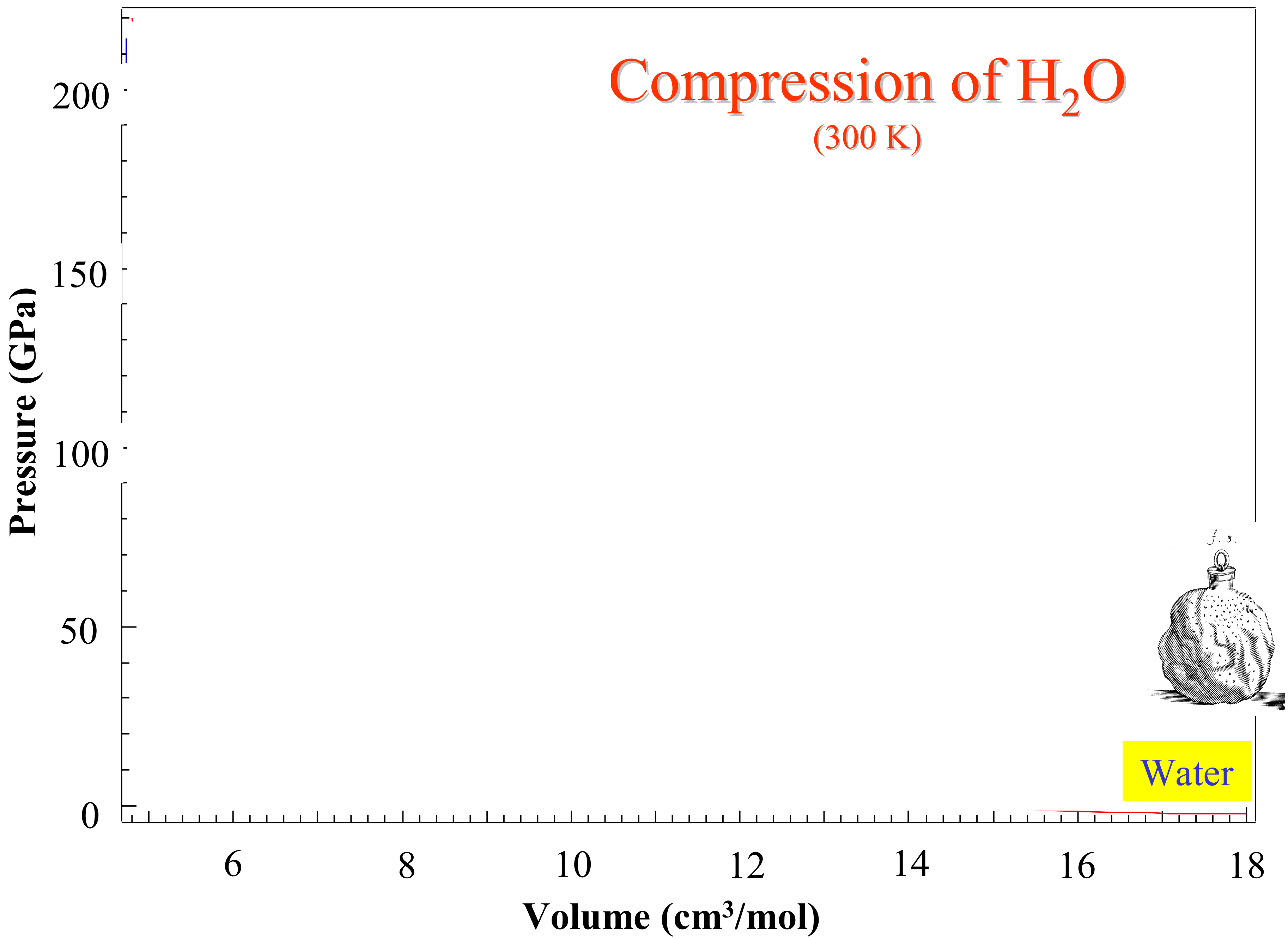
O_8 Clusters



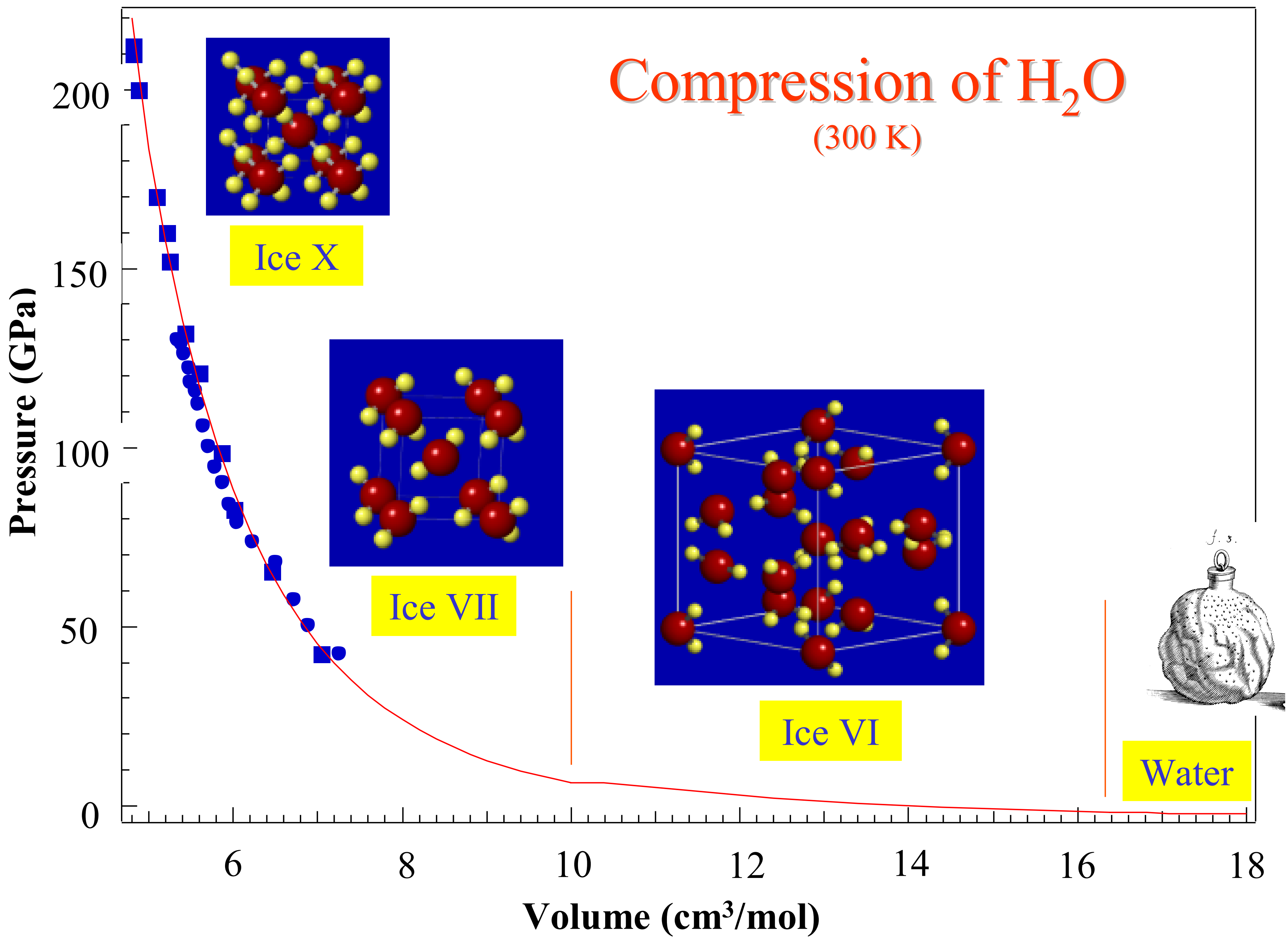
[Lundegaard et al., *Nature* (2006); Fujihishi *et al., Phys. Rev. Lett*. (2006)]

Solid Oxygen at 30 GPa (300 K)

H_2O

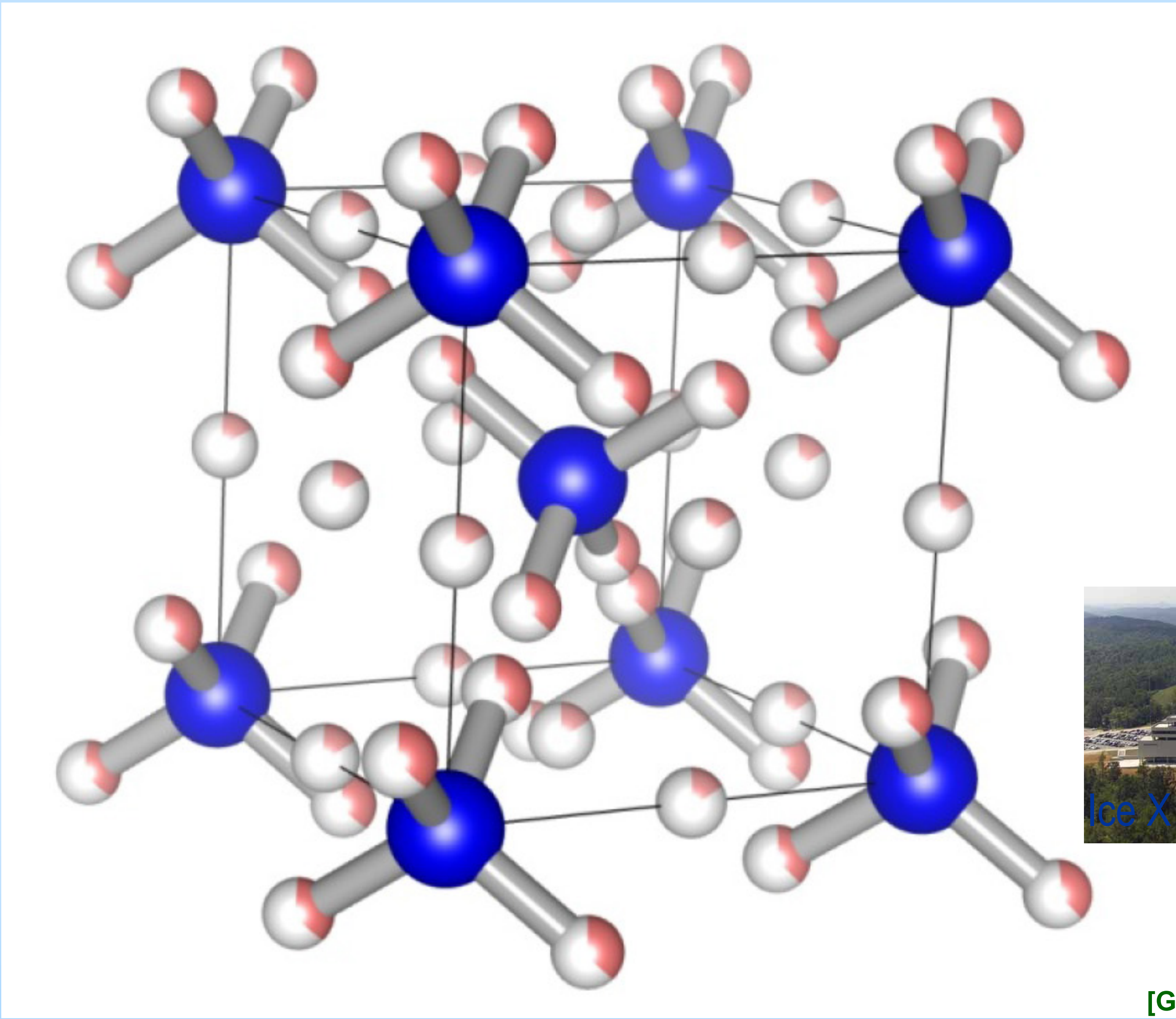


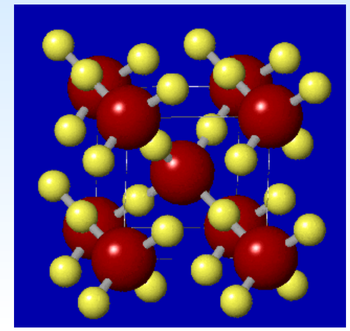
Compression of H2O
(300 K)
Pressure (GPa)
200
150
100
50
0
Volume (cm3/mol)
6
8
10
12
14
16
18
Water



Compression of H_2O
(300 K)
Ice X
Ice VII
Ice VI
Water
Pressure (GPa)
Volume (cm^3/mol)
0
50
100
150
200
6
8
10
12
14
16
18

‘Water’ at 100 GPa (1 Mbar)

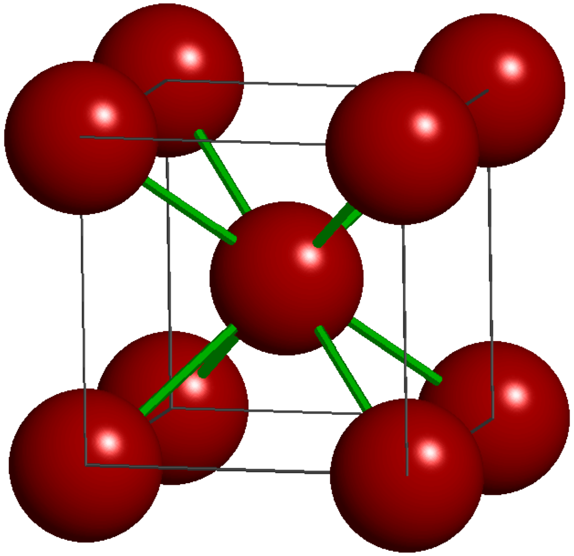




Spallation Neutron Source (ORNL)

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

The Simple Metals?



Body Centered Cubic (BCC)

MAY 15, 1933 PHYSICAL REVIEW VOLUME 43

On the Constitution of Metallic Sodium

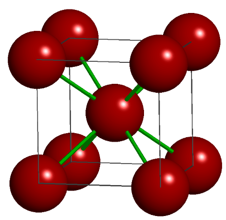
E. WIGNER AND F. SEITZ, *Department of Physics, Princeton University*

(Received March 18, 1933)

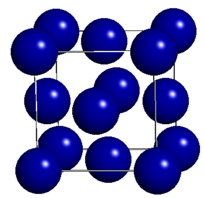
The Simple Metals?

[Gregoryanz et al., *Science* (2008)]

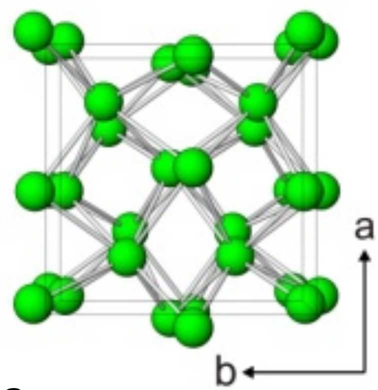
BCC



FCC

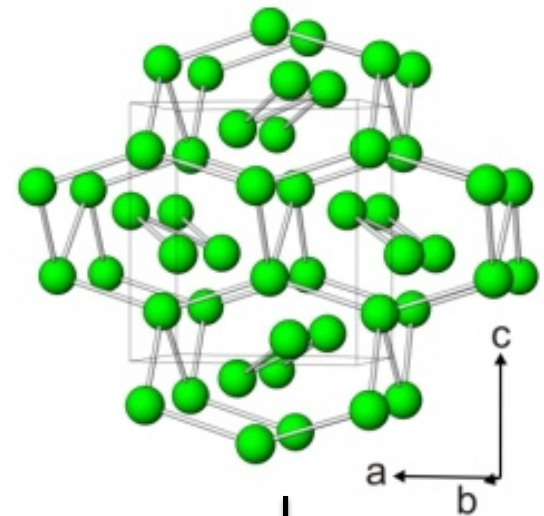


cI16



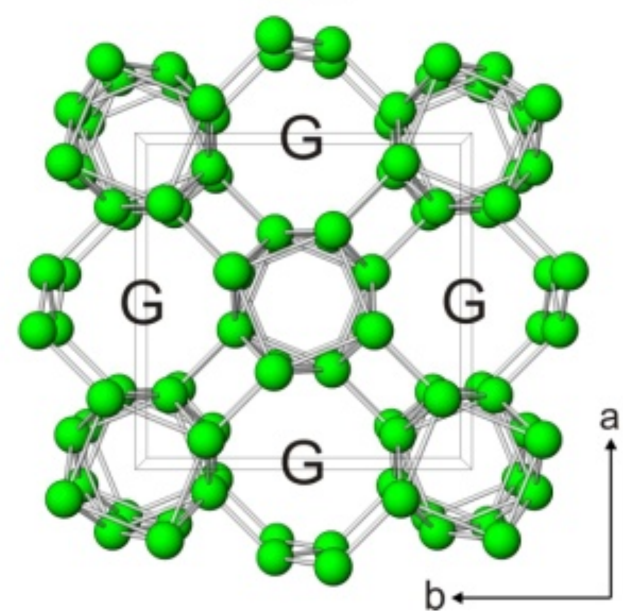
>100 GPa

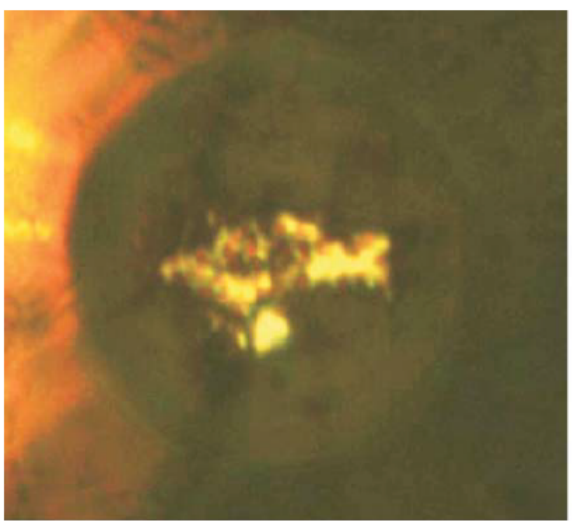
oP8



[Wigner & Seitz, *Phys. Rev.* (1933)]

tI19





199 GPa

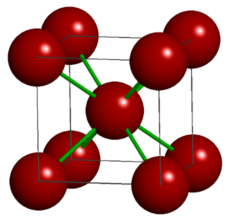
[Ma et al., *Nature* (2009)]

- **>11 Phases in Na**
- **Na melts <300 K**
- **Transparent**
  >200 GPa!

The Simple Metals?

[Gregoryanz et al., *Science* (2008)]

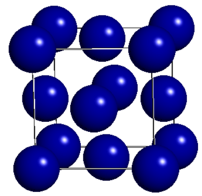
BCC



[Wigner & Seitz, *Phys. Rev.* (1933)]

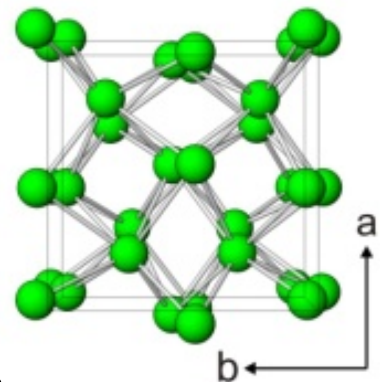
→

FCC



→

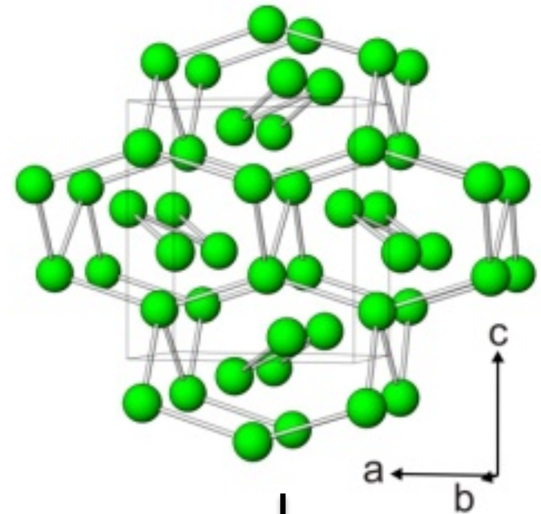
cI16



>100 GPa

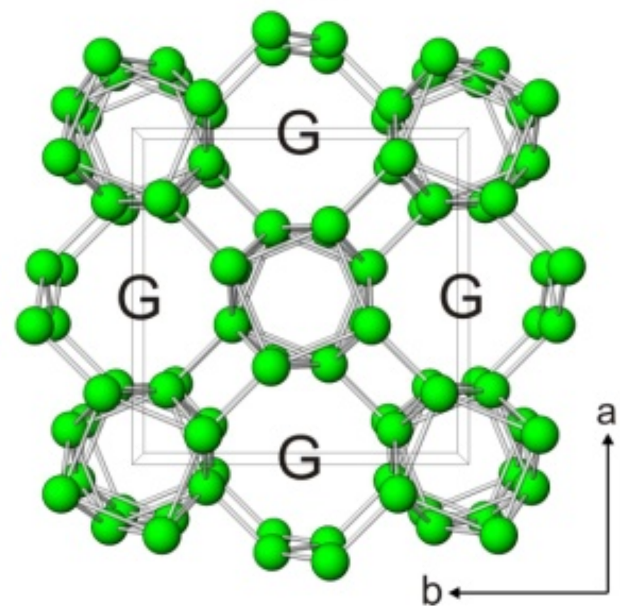
→

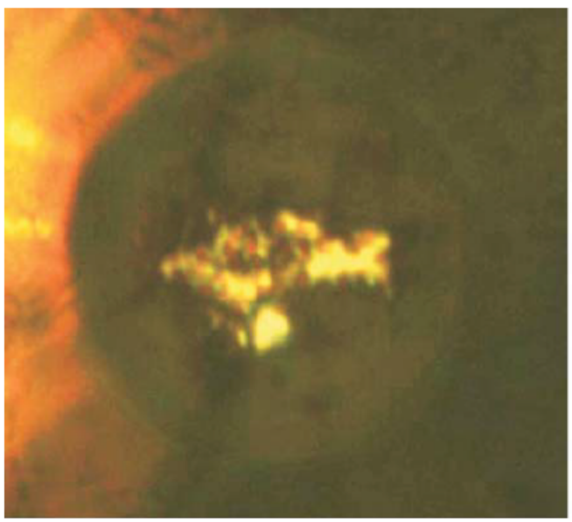
oP8



↓

tI19





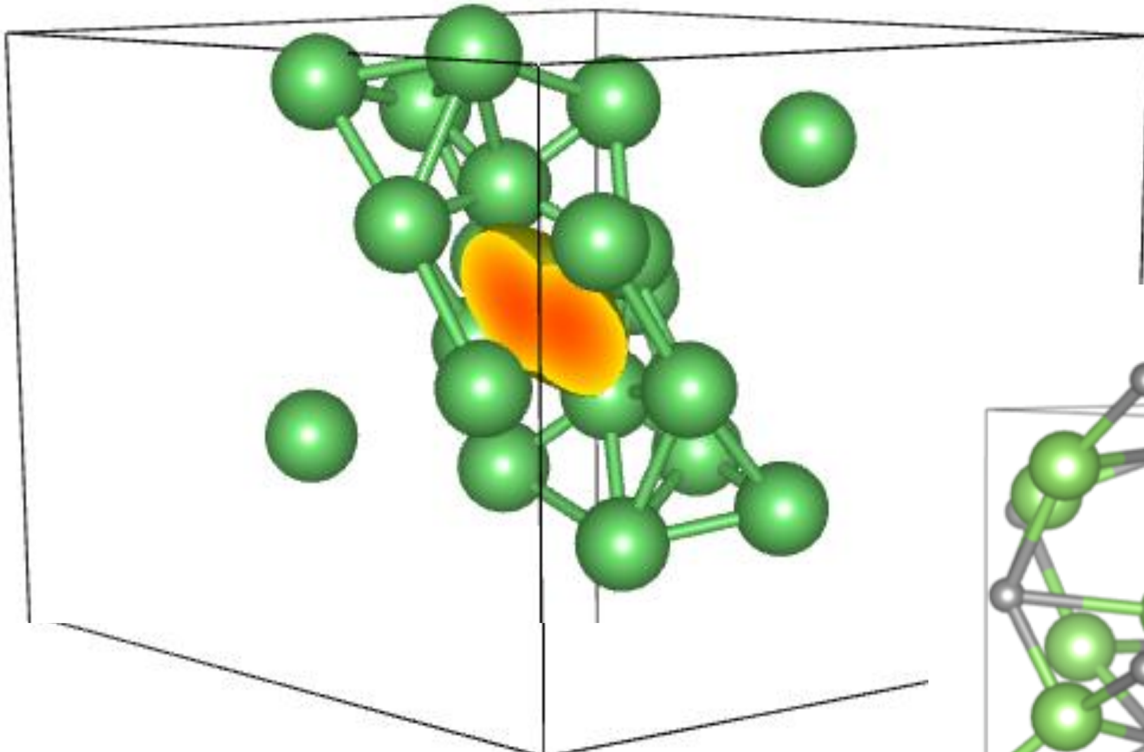
199 GPa

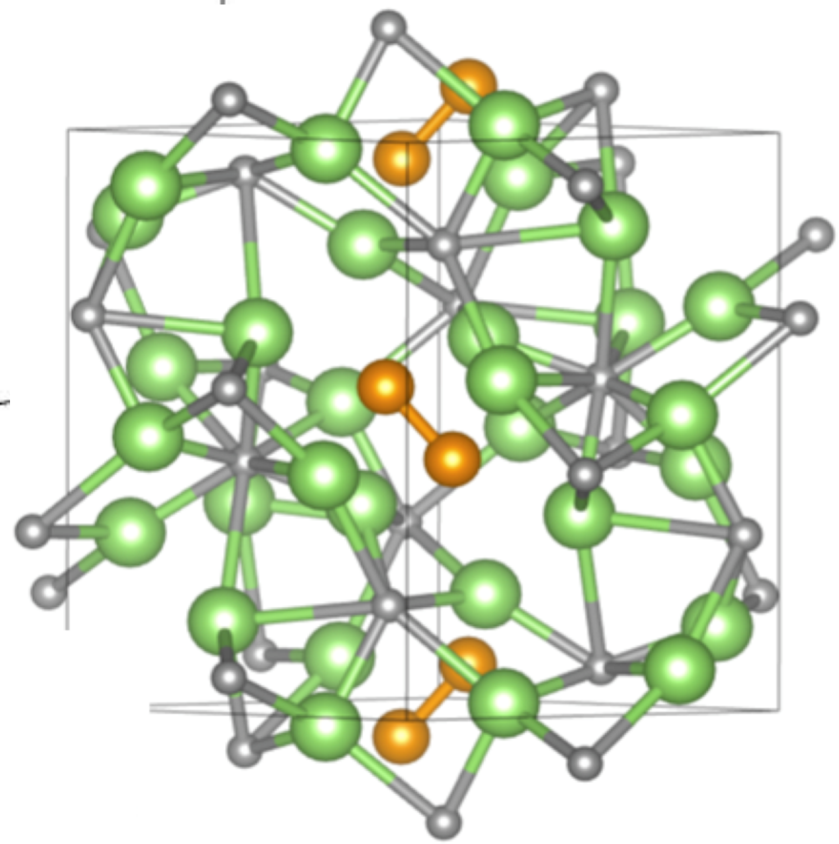
[Ma et al., *Nature* (2009)]

- **>11 Phases in Na**
- **Na melts <300 K**
- **Transparent >200 GPa!**

Bonding 'without nuclei'

The Simple Metals?





Bonding
'without nuclei'

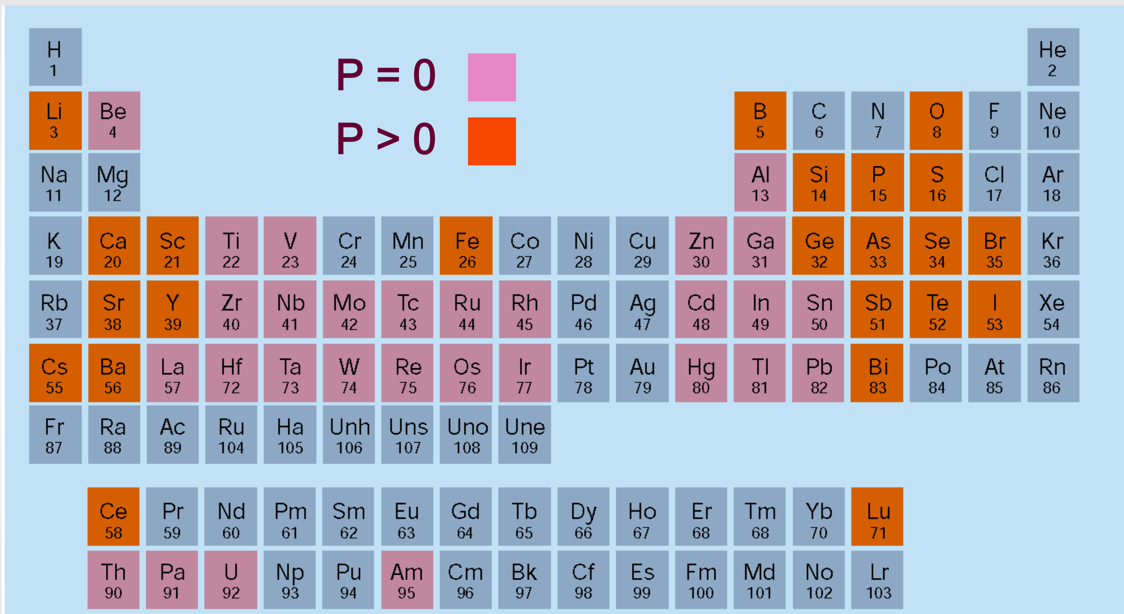
'Quasimolecules'
in Lithium (80 GPa)

[Miao, Naumov, Hoffmann, & Hemley, *submitted*]

Superconductivity

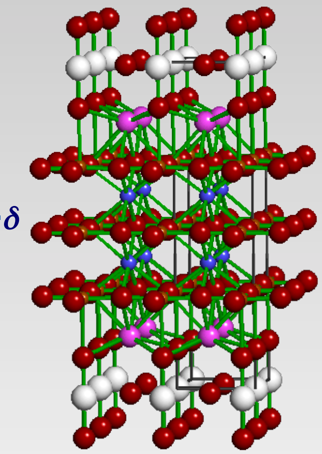
SUPERCONDUCTING ELEMENTS

23 produced under pressure; e.g., O, S, B, Fe, Li, Ca



$HgBa_2Ca_2Cu_3O_{8+\delta}$

T_c = 164 K at 30 GPa)

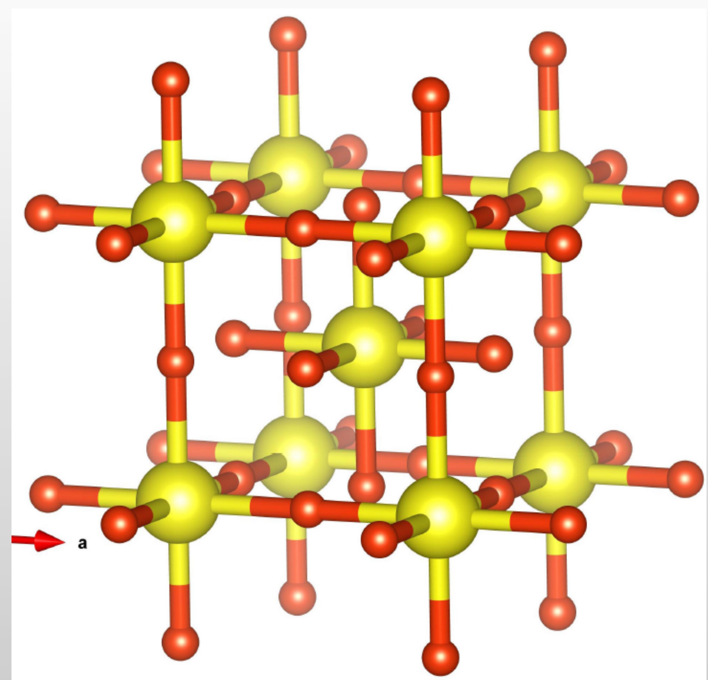


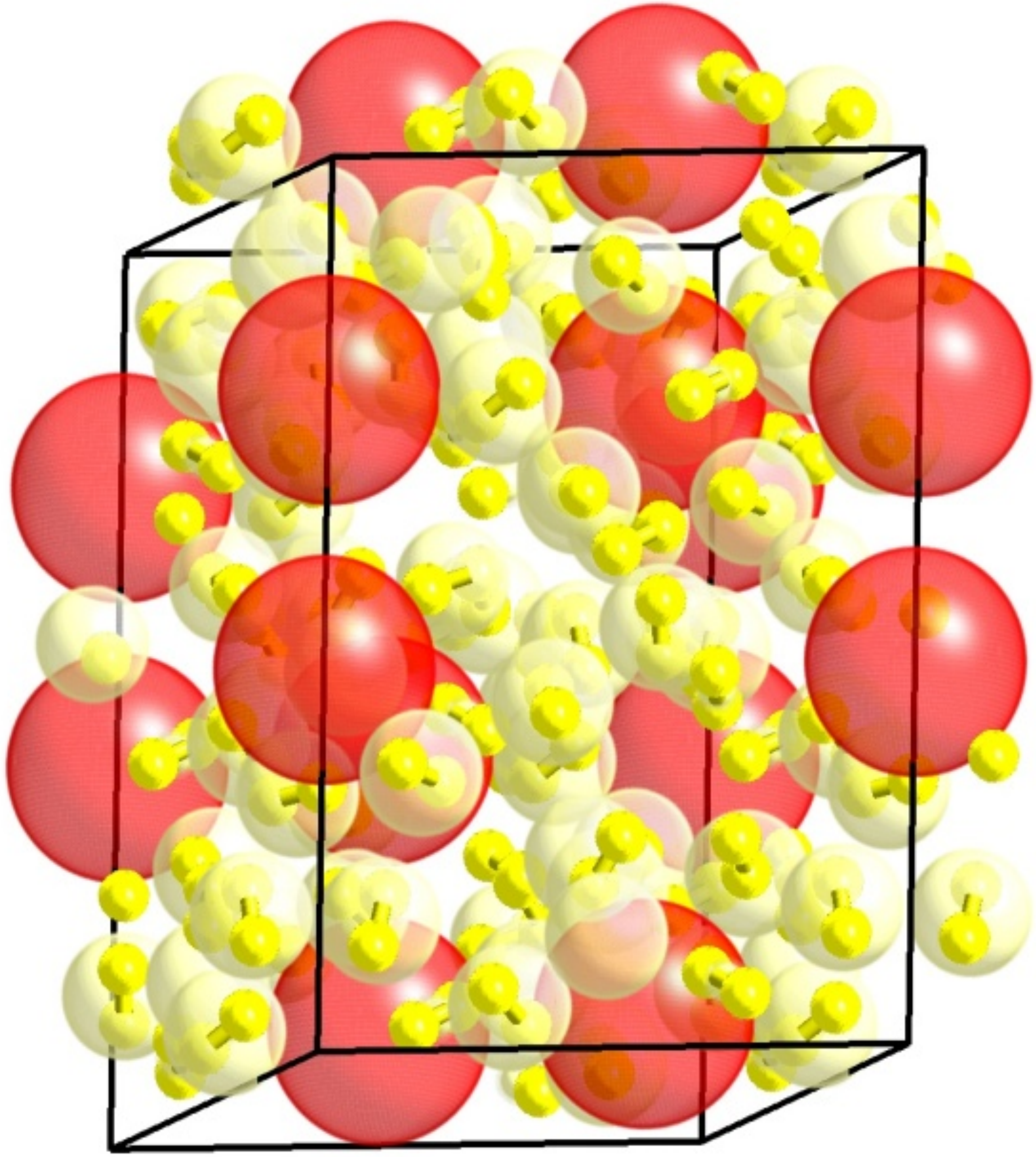
[Gao *et al.*, (1994); Lokshin *et al.* (2002)]

'H_3S'

T_c = 203 K at 200 GPa

[Drozdov et al., *Nature* (2015)]



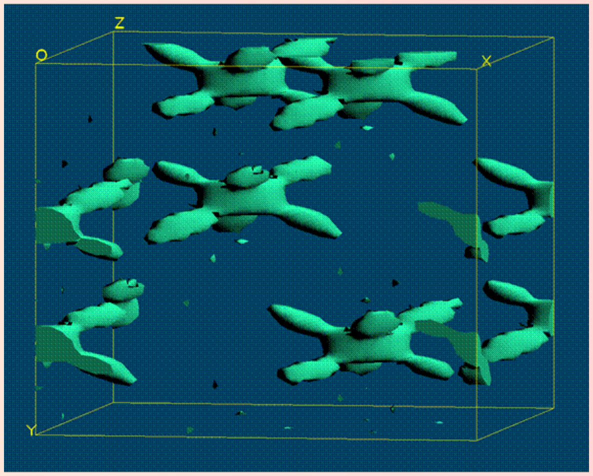


Novel Compounds

Elements from Noble to Ignoble

$Xe(H_2)_8$

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



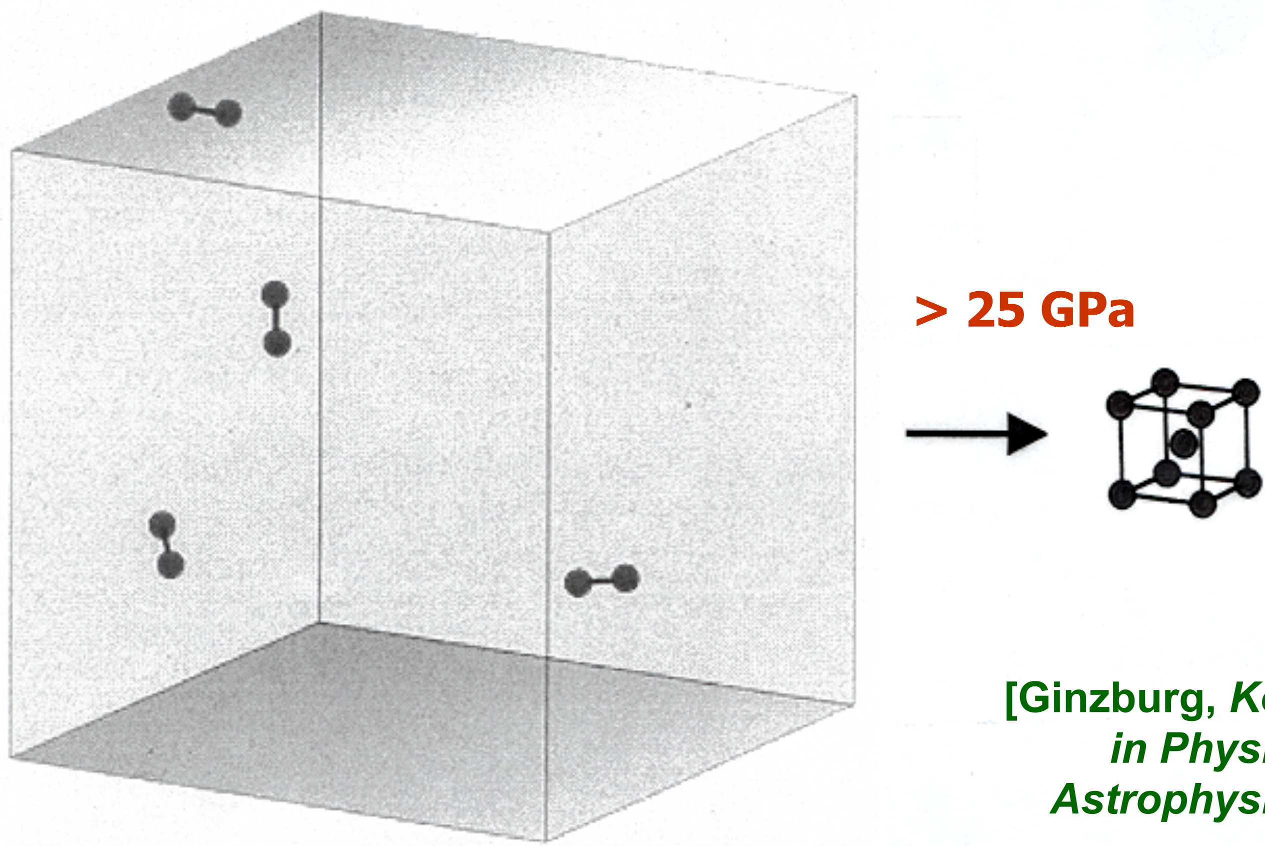
Xe ‘bonding’ with H_2

DECEMBER, 1935 JOURNAL OF CHEMICAL PHYSICS VOLUME 3

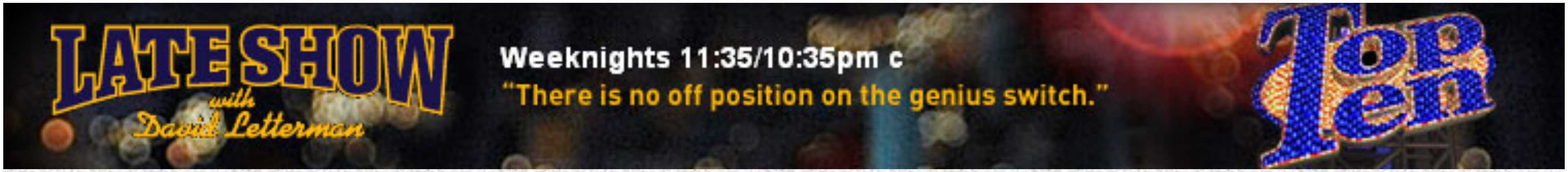
On the Possibility of a Metallic Modification of Hydrogen

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

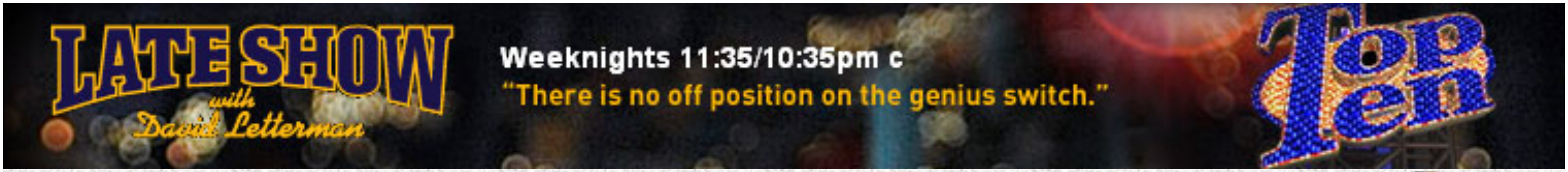
(Received October 14, 1935)



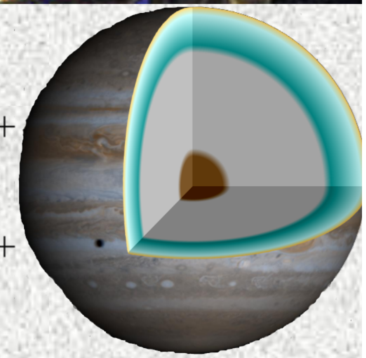
[Ginzburg, *Key Problems in Physics and Astrophysics* (1982)]



WHY HYDROGEN IS INTERESTING

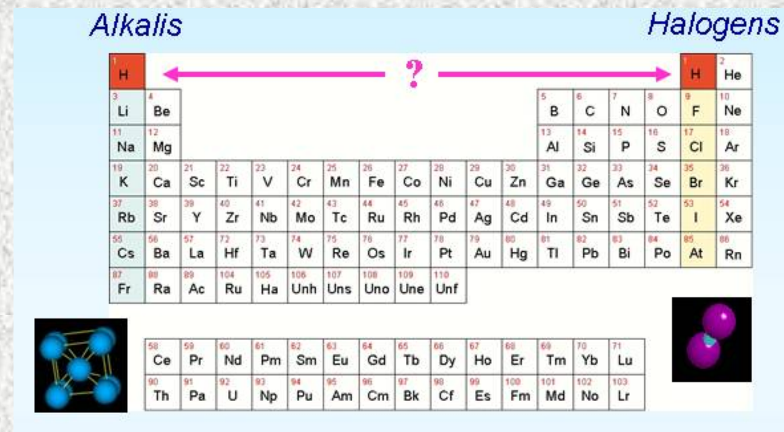


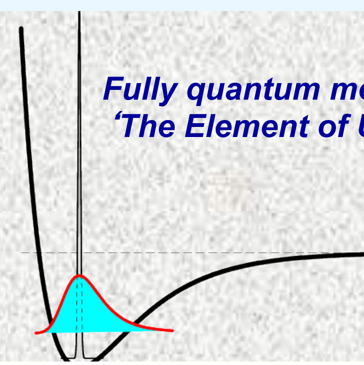
WHY HYDROGEN IS INTERESTING



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

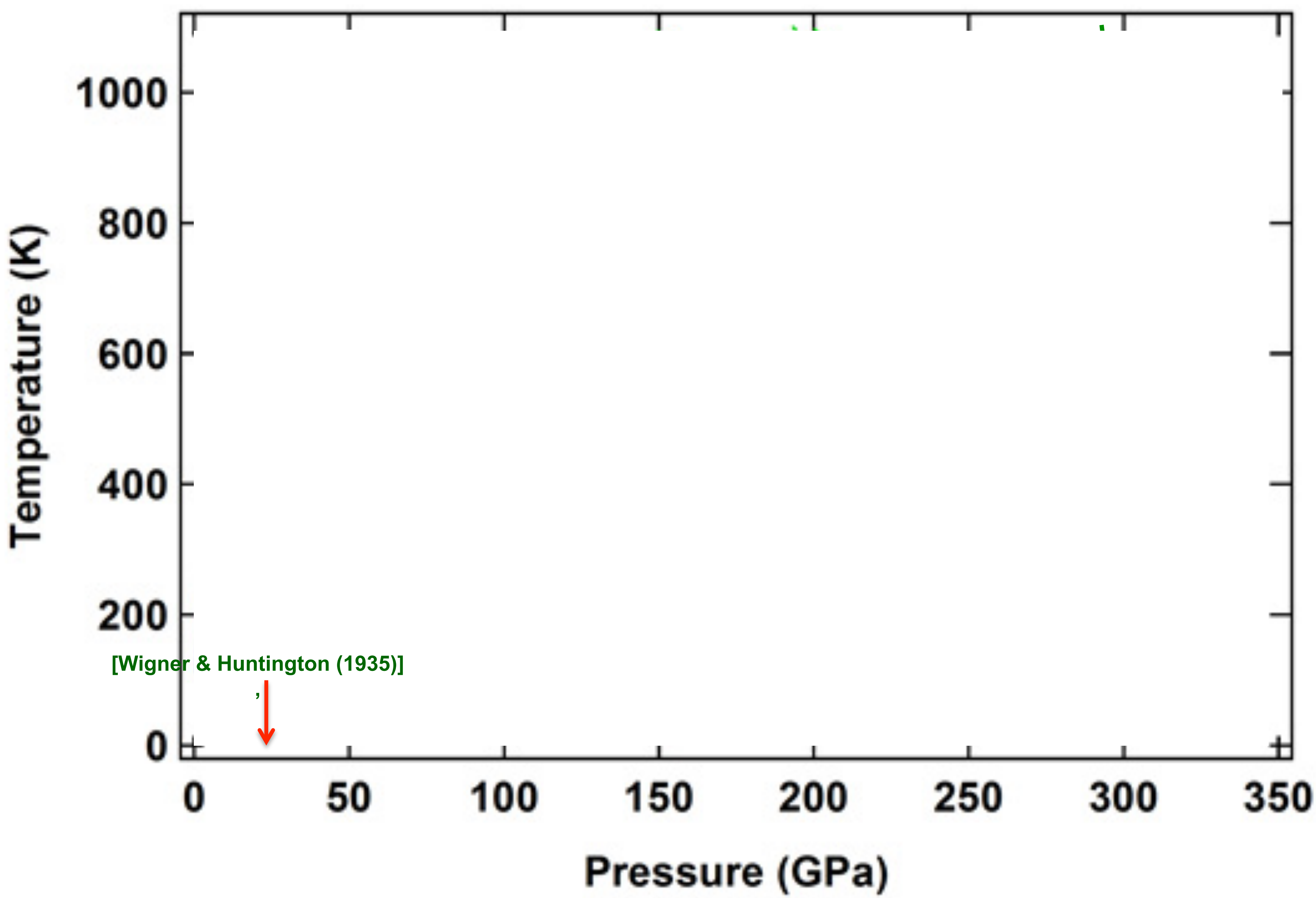
1. Tests of fundamental theory
2. Most abundant element
3. Very strong covalent bond
4. Chemical dichotomy
5. R-T superconductor?
6. Fluid ground state?
7. Superconducting/superfluid?
8. Energetic material (35 x TNT)
9. Path to inertial confinement fusion
10. Drives high *P-T* technique develop.





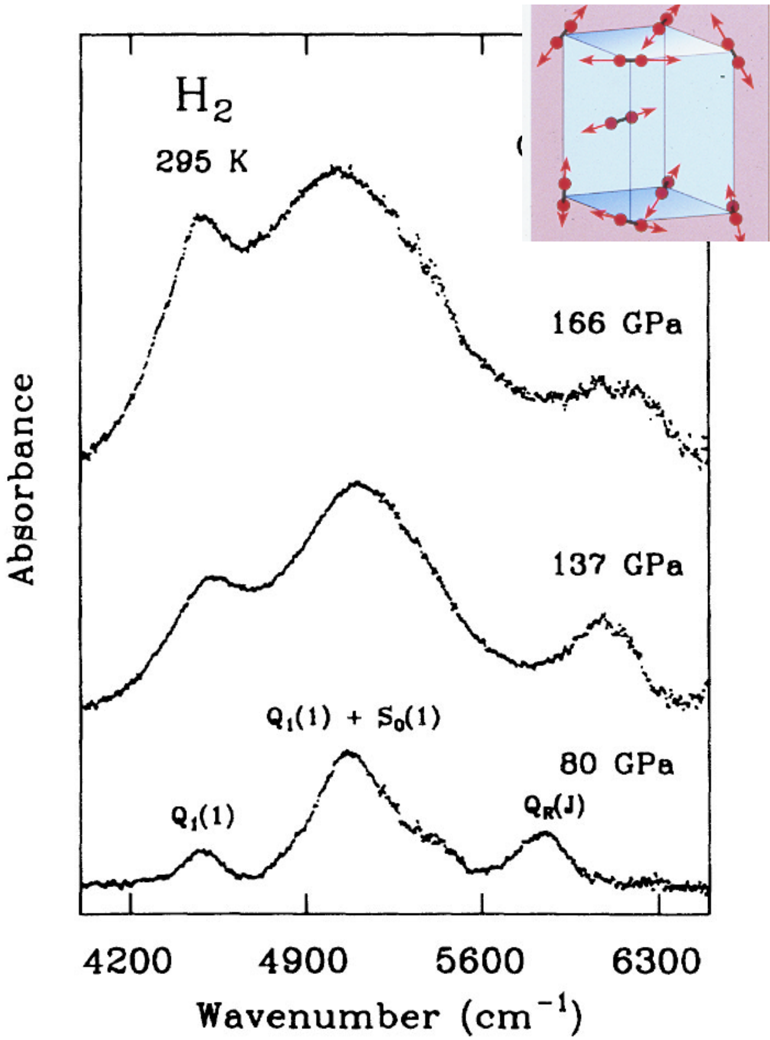
Fully quantum mechanical system: 'The Element of Uncertainty'

Hydrogen Phase Diagram



High-Pressure Vibrational Spectra

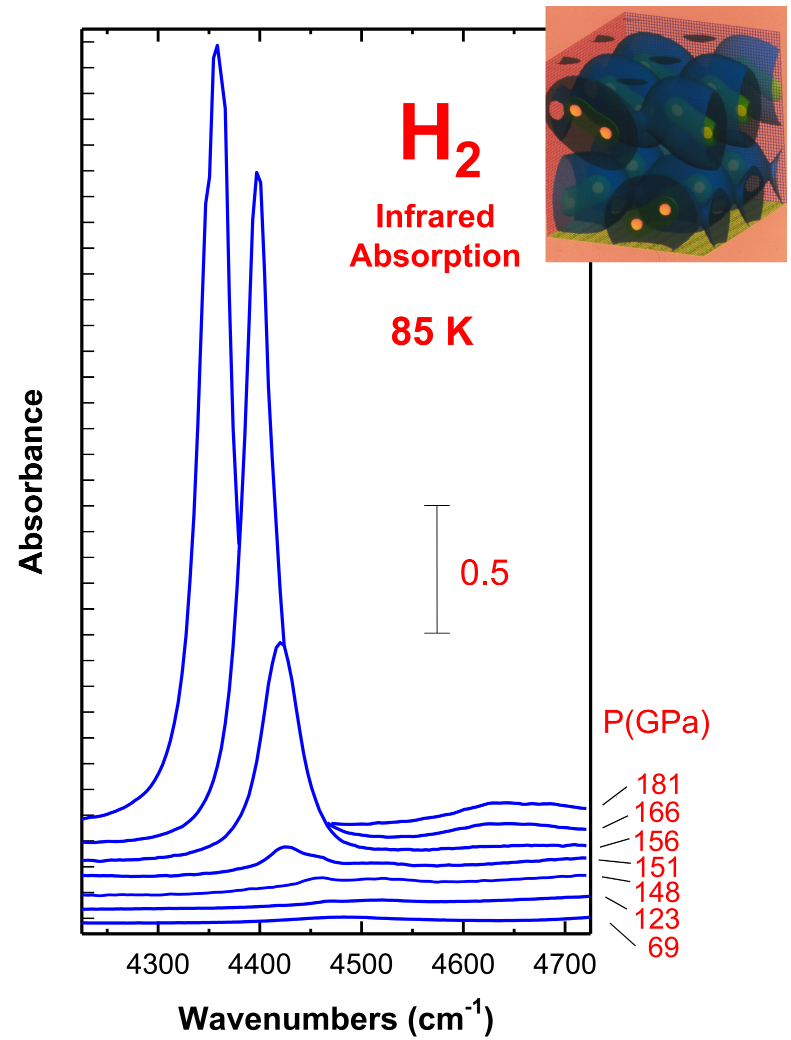
‘Collision-induced’



[Hanfland *et al. Phys. Rev. Lett.* (1992)

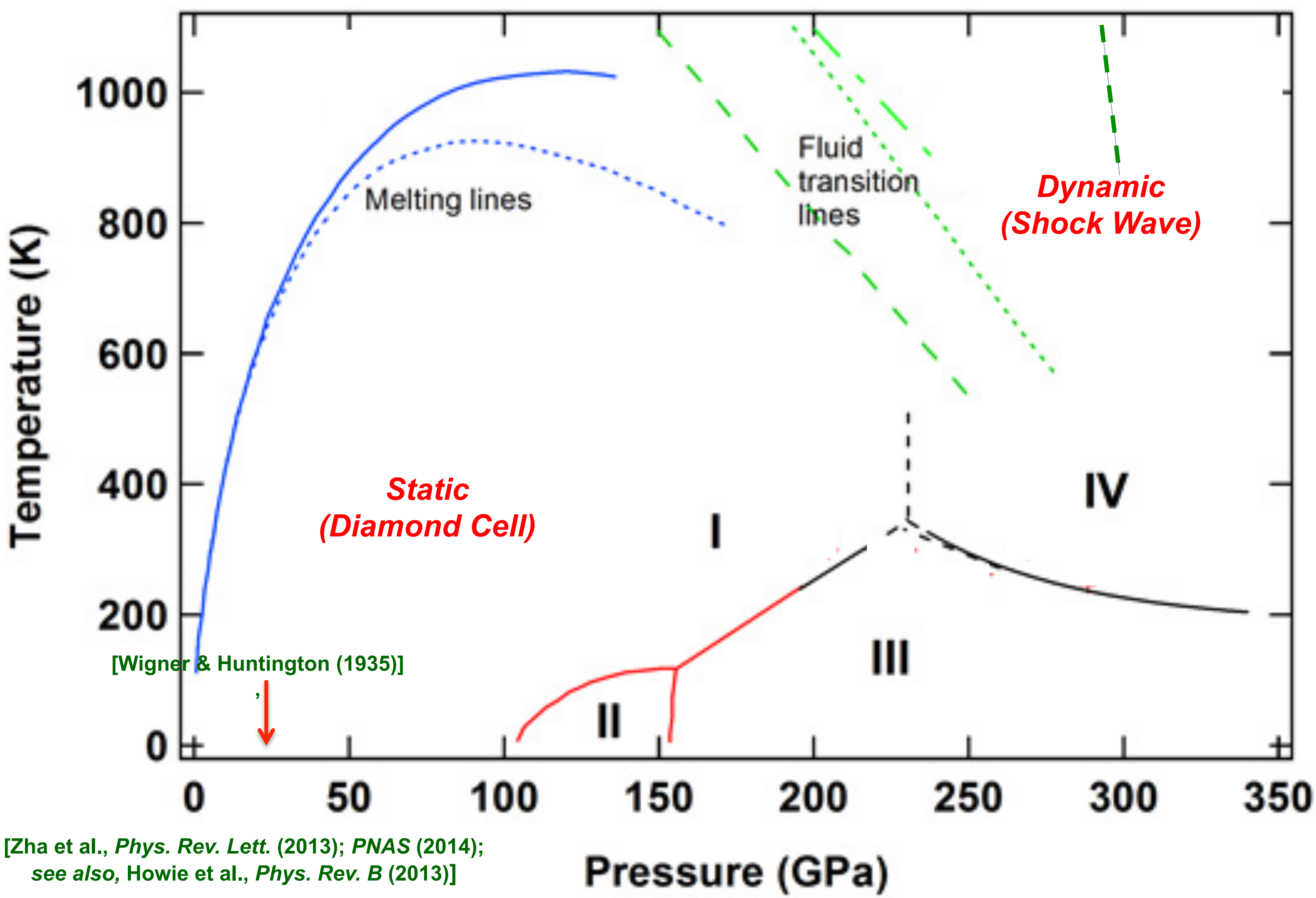
$I \sim \rho^3 \sim 1/r^6$

Dipole allowed: *Phase Transition*



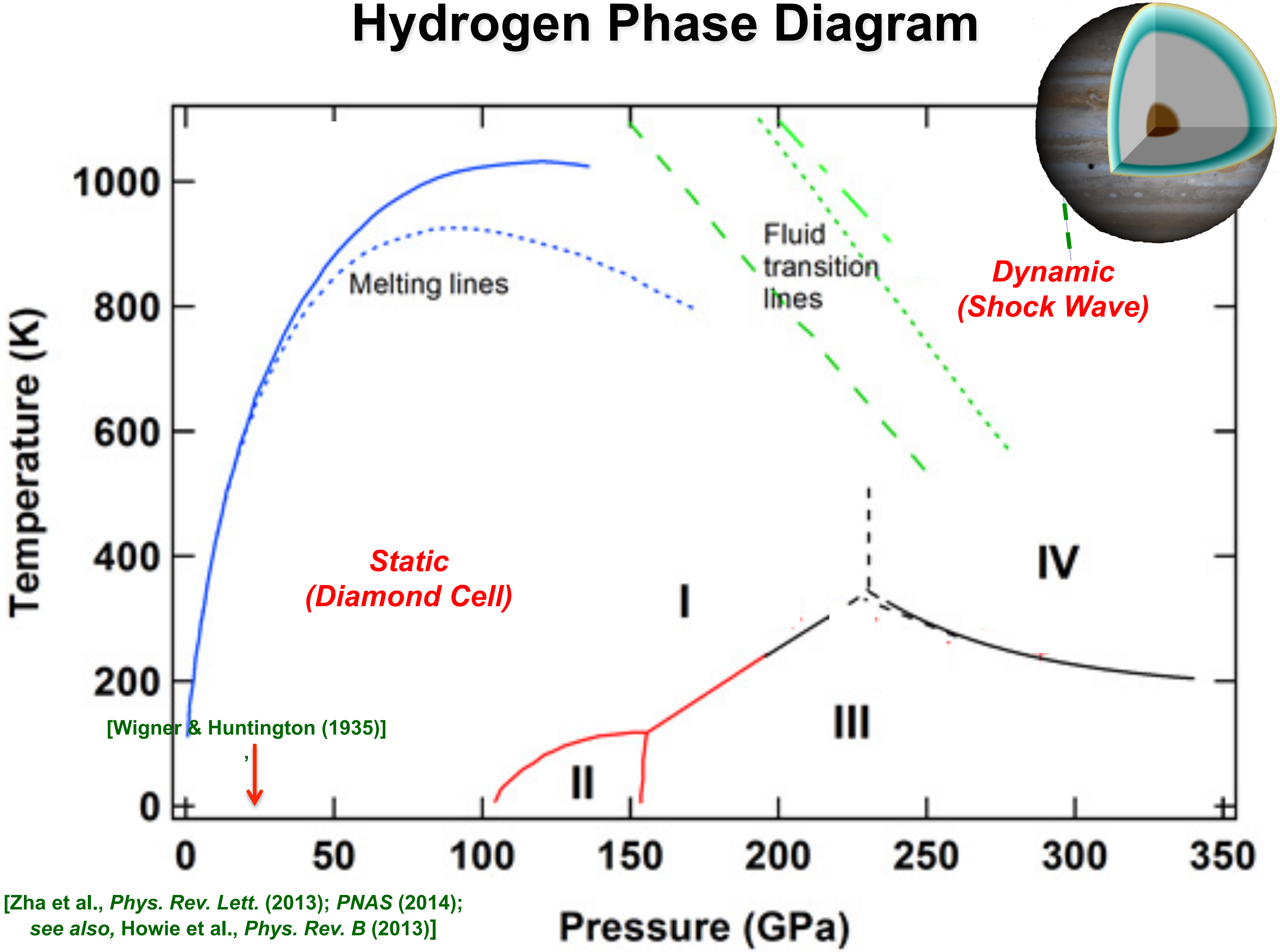
[Hanfland *et al. Phys. Rev. Lett.* (1993);
Hemley et al., *Nature* (1994);
Chen *et al. Phys. Rev. Lett.* 1995)]

Hydrogen Phase Diagram



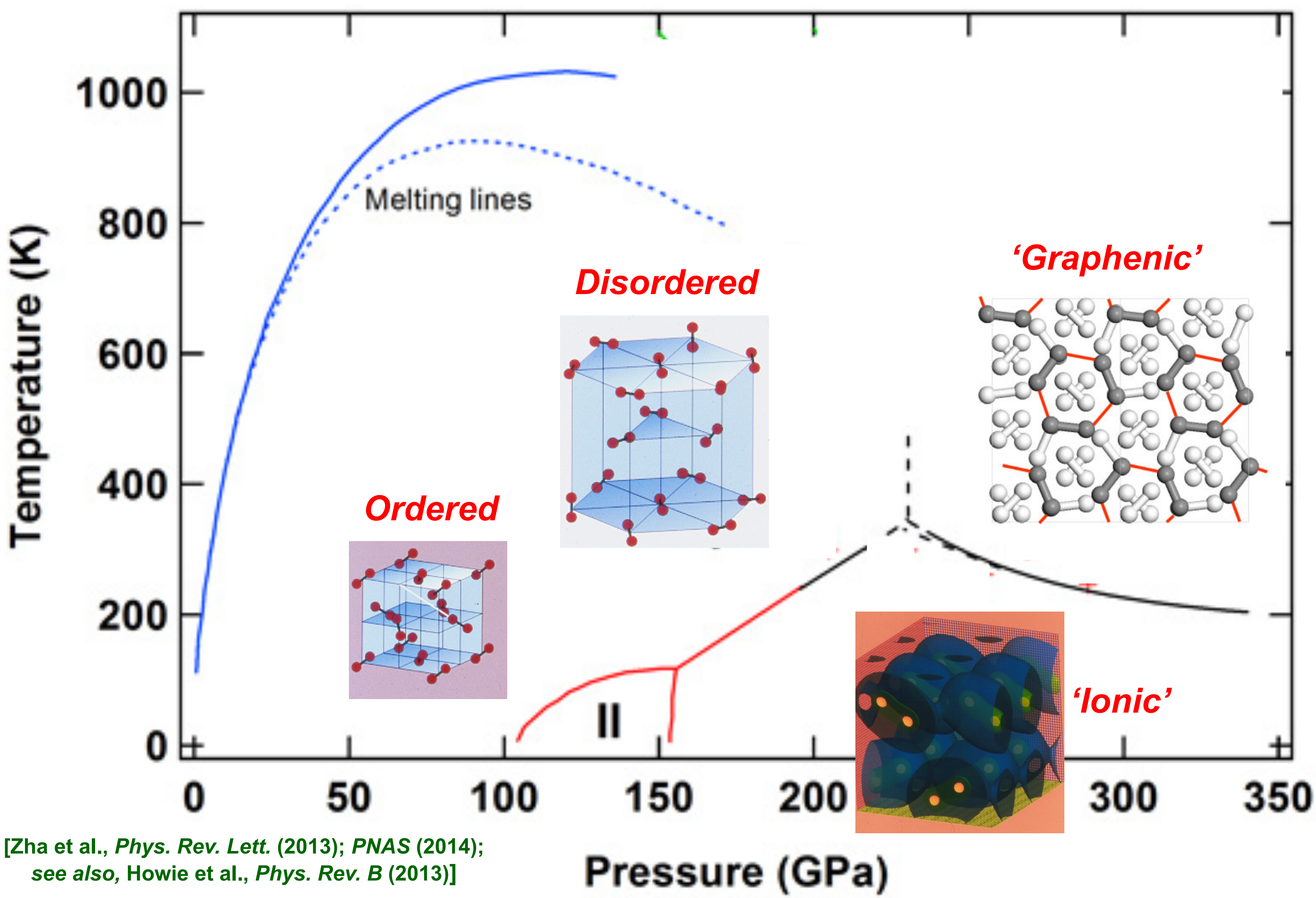
[Zha et al., *Phys. Rev. Lett.* (2013); *PNAS* (2014);
see also, Howie et al., *Phys. Rev. B* (2013)]

Hydrogen Phase Diagram



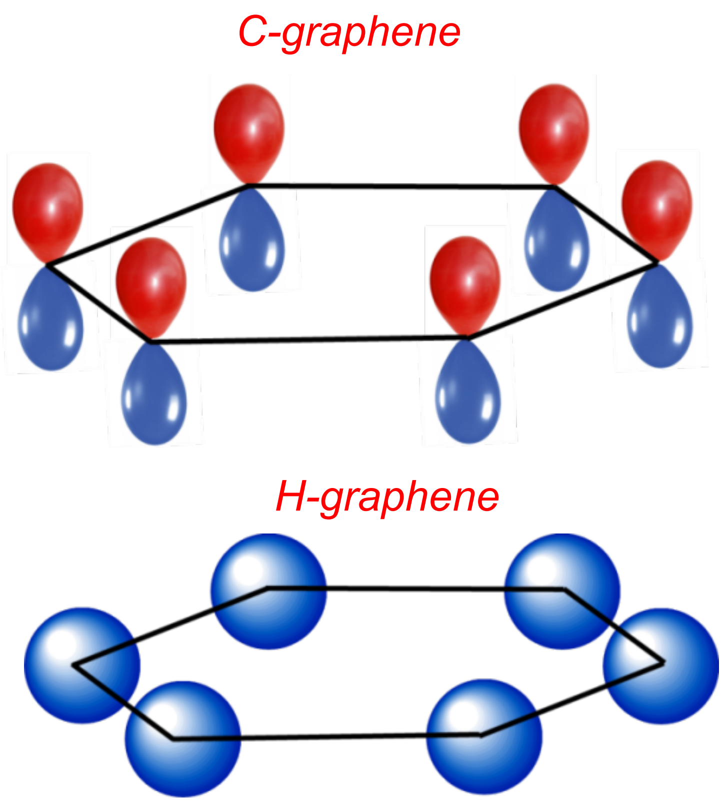
[Zha et al., *Phys. Rev. Lett.* (2013); *PNAS* (2014); *see also,* Howie et al., *Phys. Rev. B* (2013)]

Hydrogen Phase Diagram



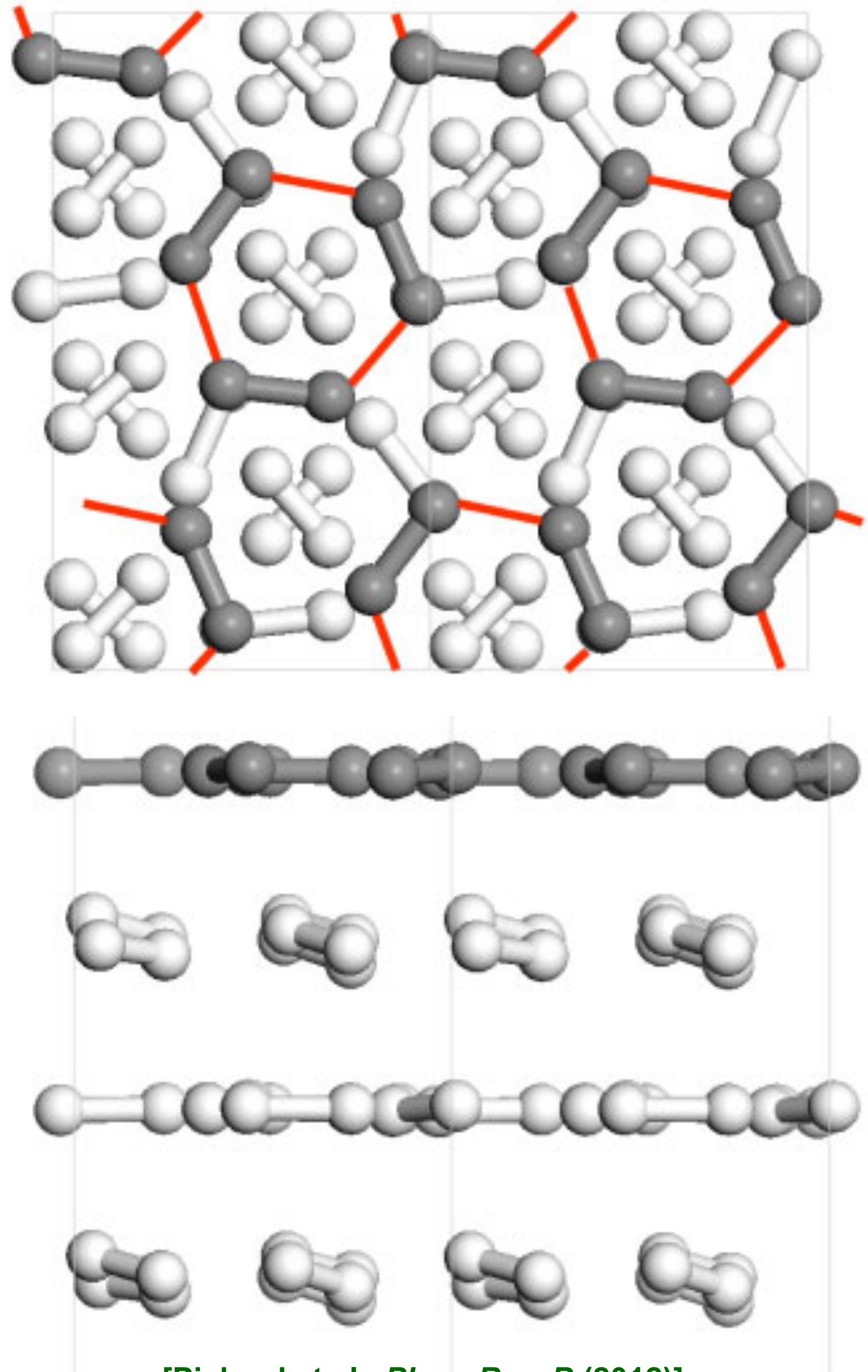
[Zha et al., *Phys. Rev. Lett.* (2013); *PNAS* (2014);
see also, Howie et al., *Phys. Rev. B* (2013)]

Phase IV is a graphene-based layer structure



H_6 'aromatic cluster'

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

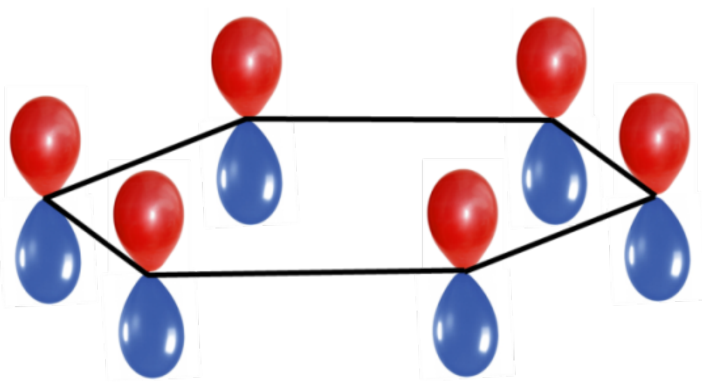


[Pickard et al., *Phys. Rev. B* (2012)]

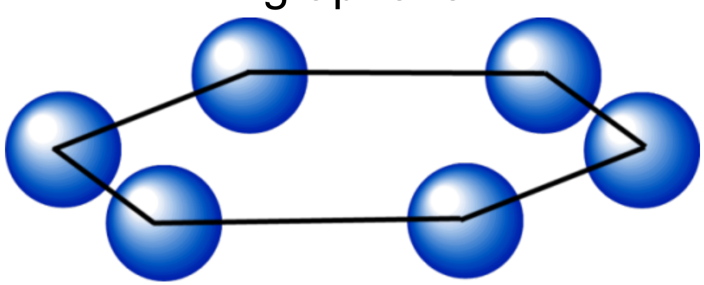
Graphene-based layer structures for dense hydrogen

[Cohen, Naumov & Hemley, *PNAS* (2013)]

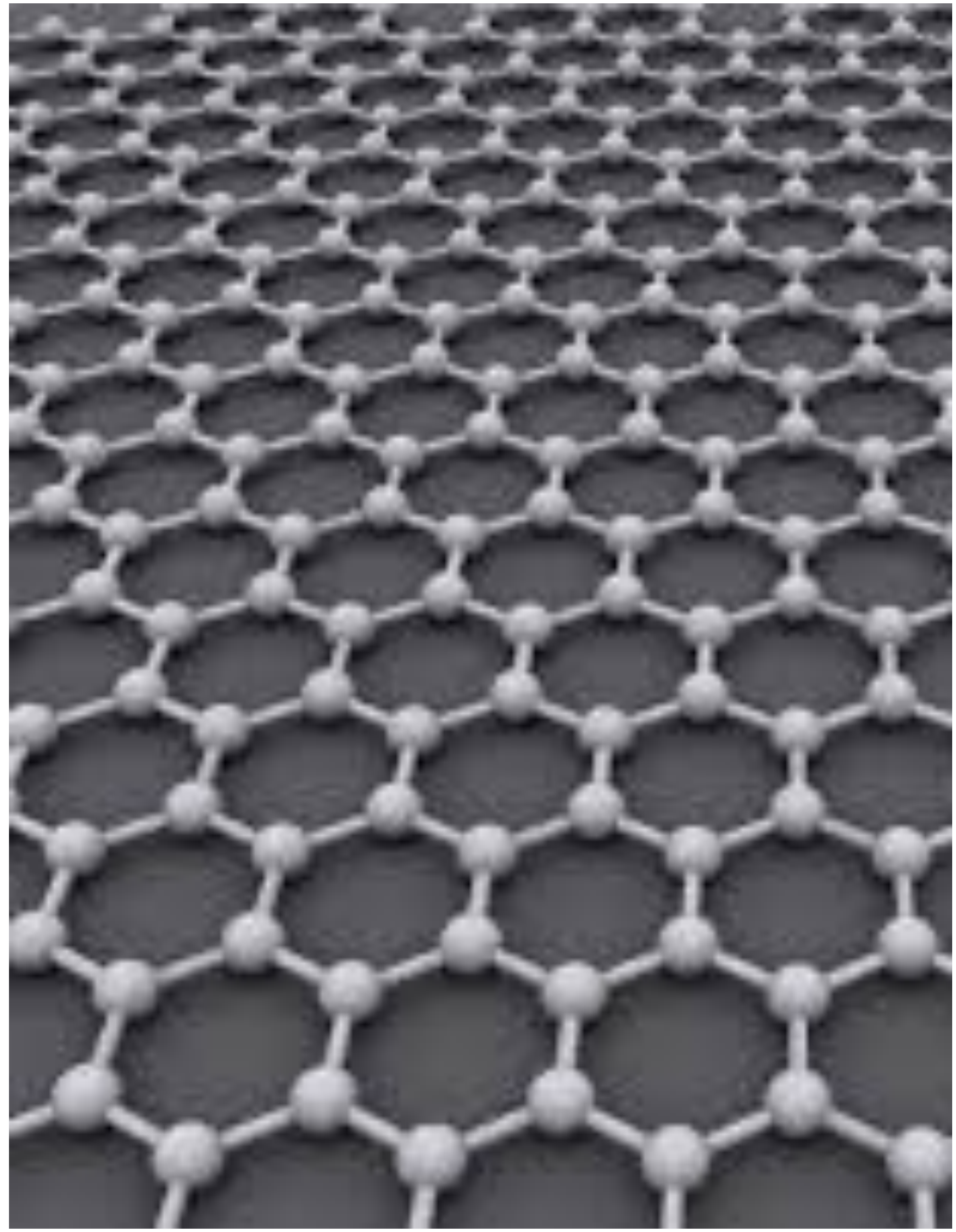
C-graphene



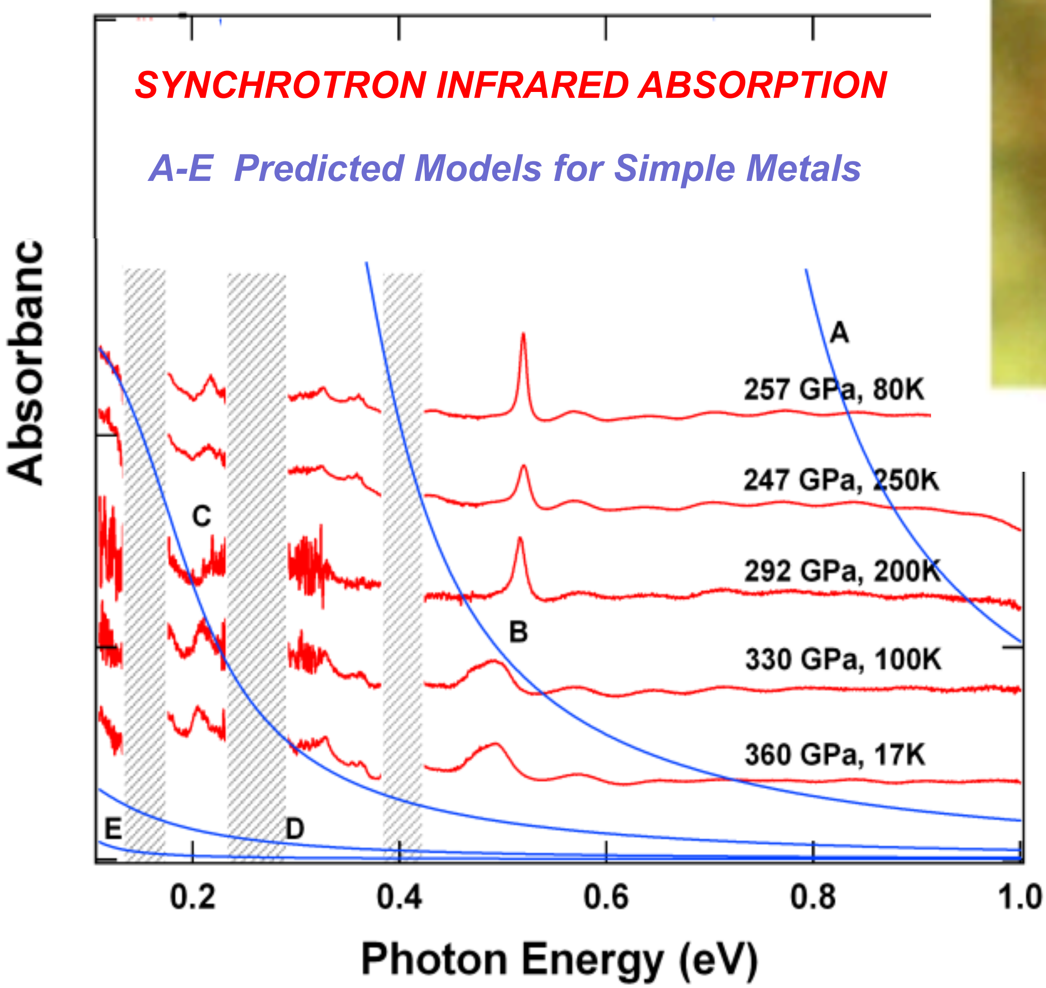
H-graphene

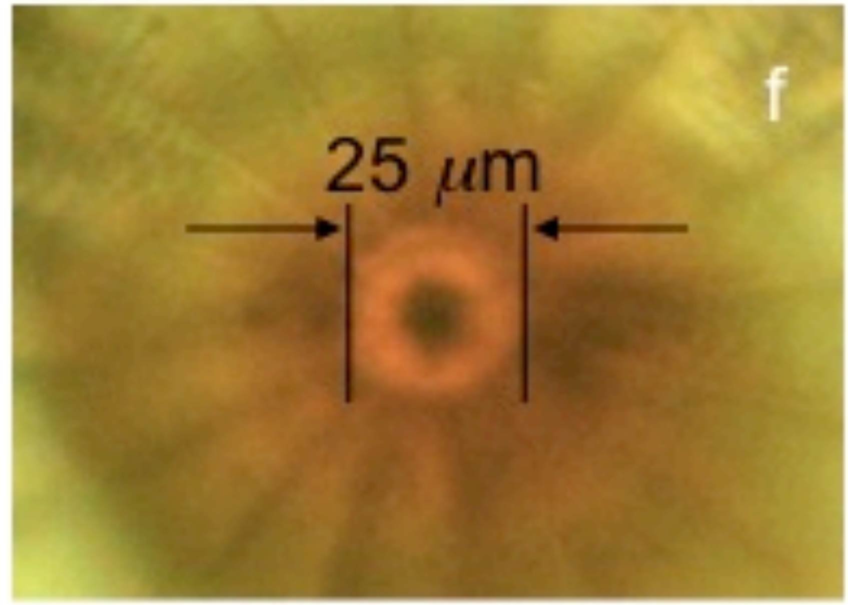


H_6 'aromatic cluster'



Is hydrogen metallic at these *P-T* conditions?





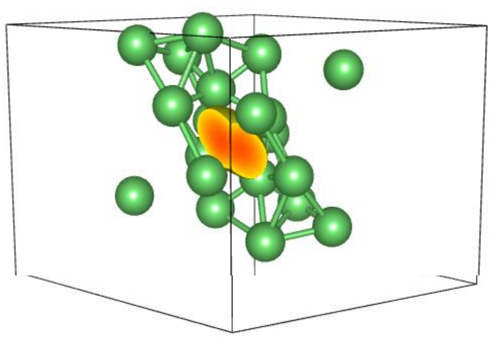
360 GPa, 100 K

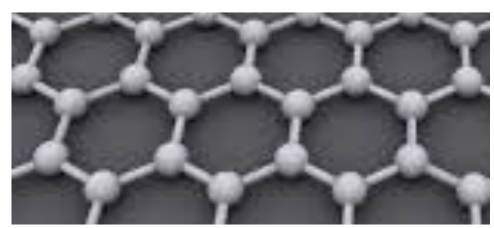
- **Like graphite (not 'alkali' metals)!**
- **Borderline of semi-conductor-semimetal**

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

New View of Solid Metallic Hydrogen

New View of Solid Metallic Hydrogen





Predicted
superconducting
superfluid
ultradense
hydrogen
(400 GPa)

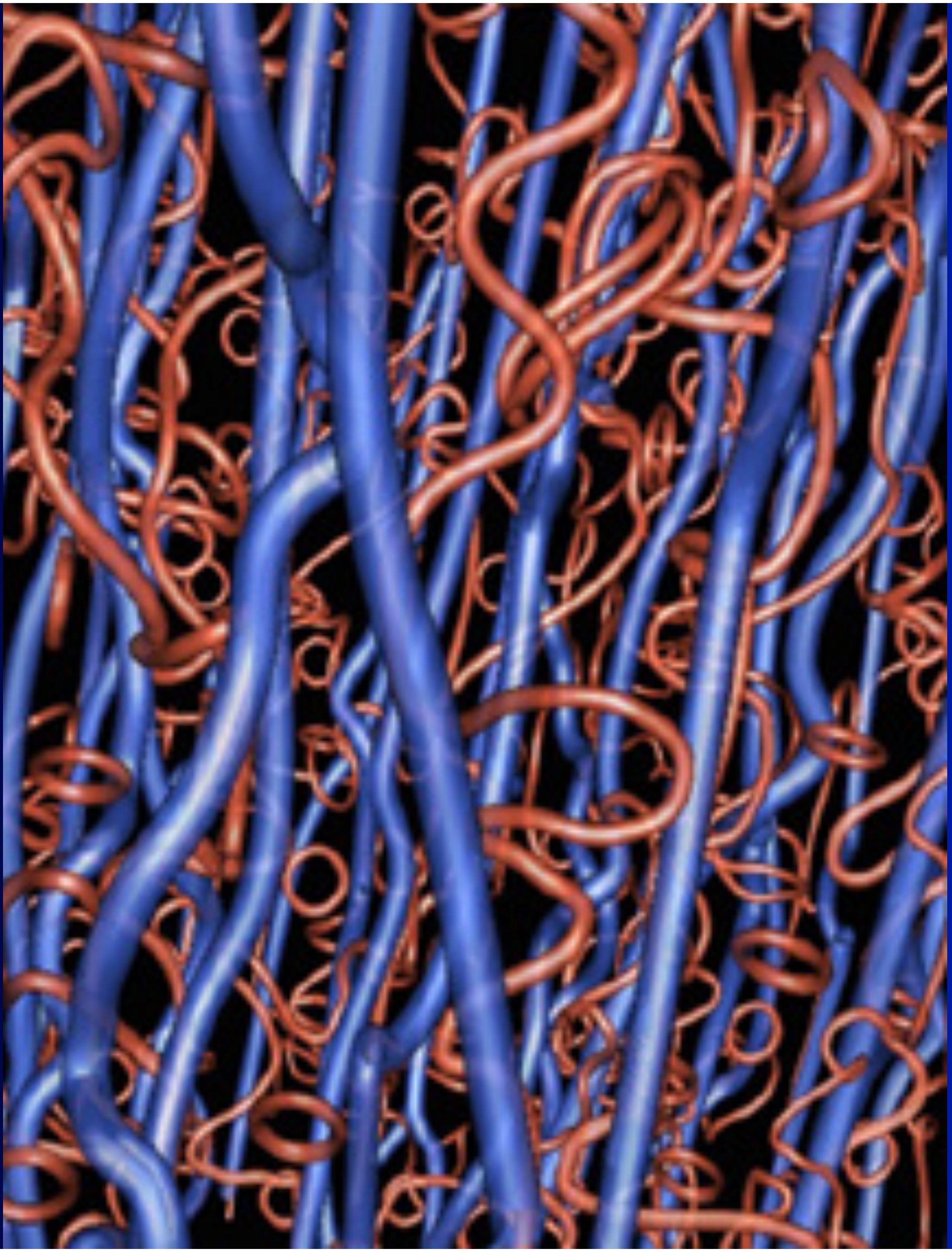
[Babaev *et al.*,
Phys. Rev. Lett.
(2008)]

Predicted superconducting superfluid ultradense hydrogen (400 GPa)

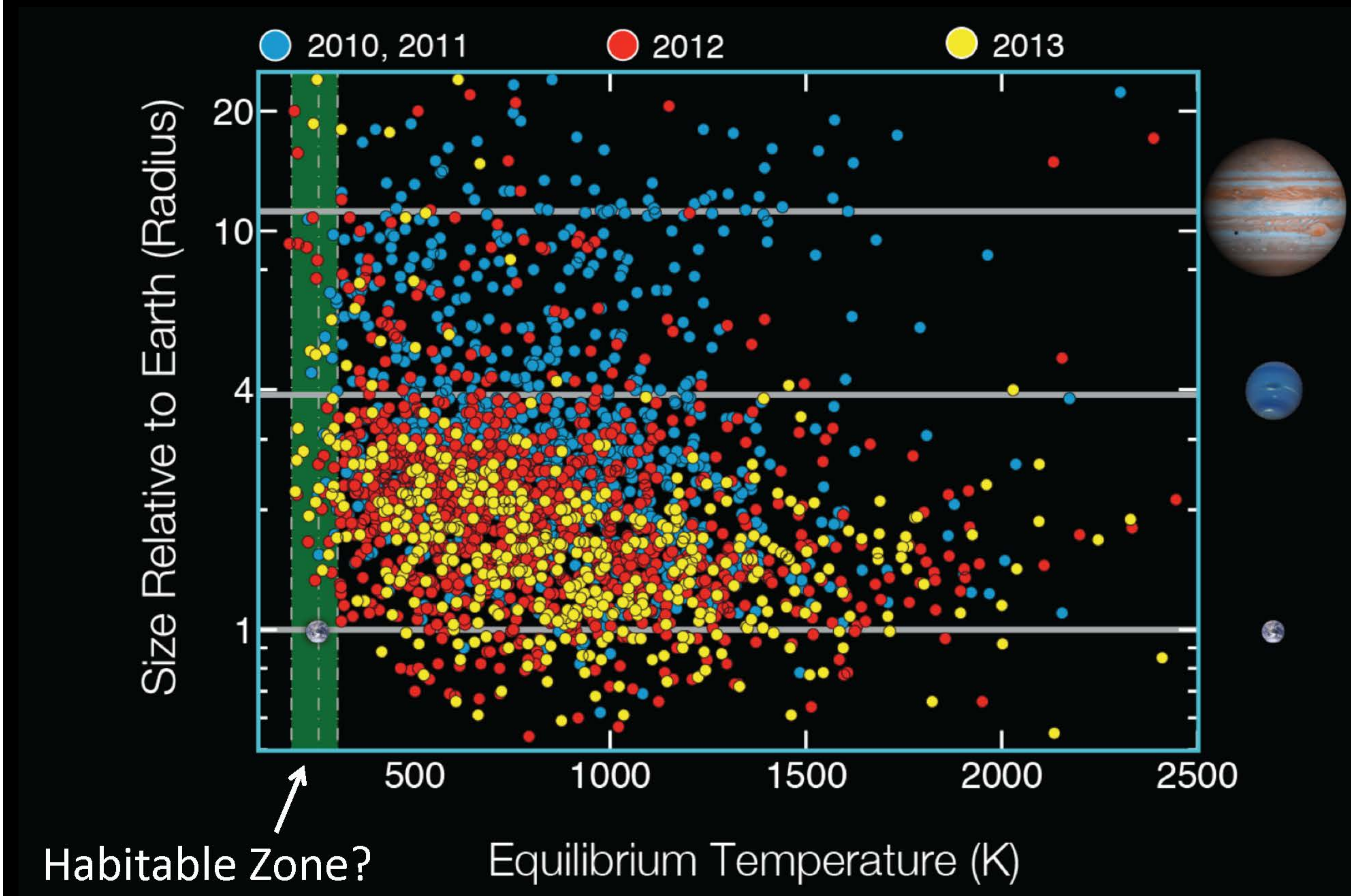
[Babaev *et al.*, *Phys. Rev. Lett.* (2008)]

MAGNETIC VORTICES

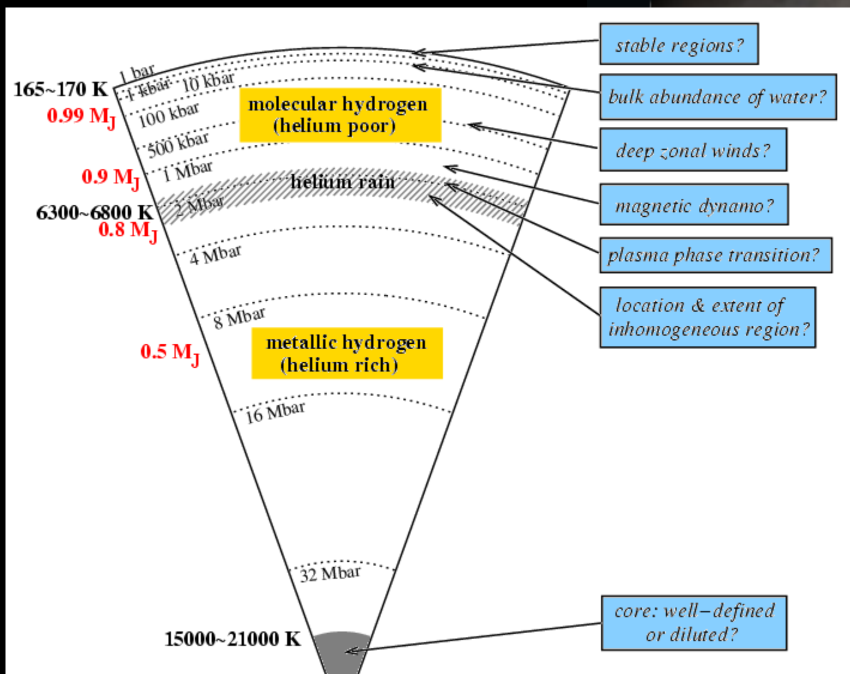
[Abrikosov, *J.E.T.P.* (1964)]



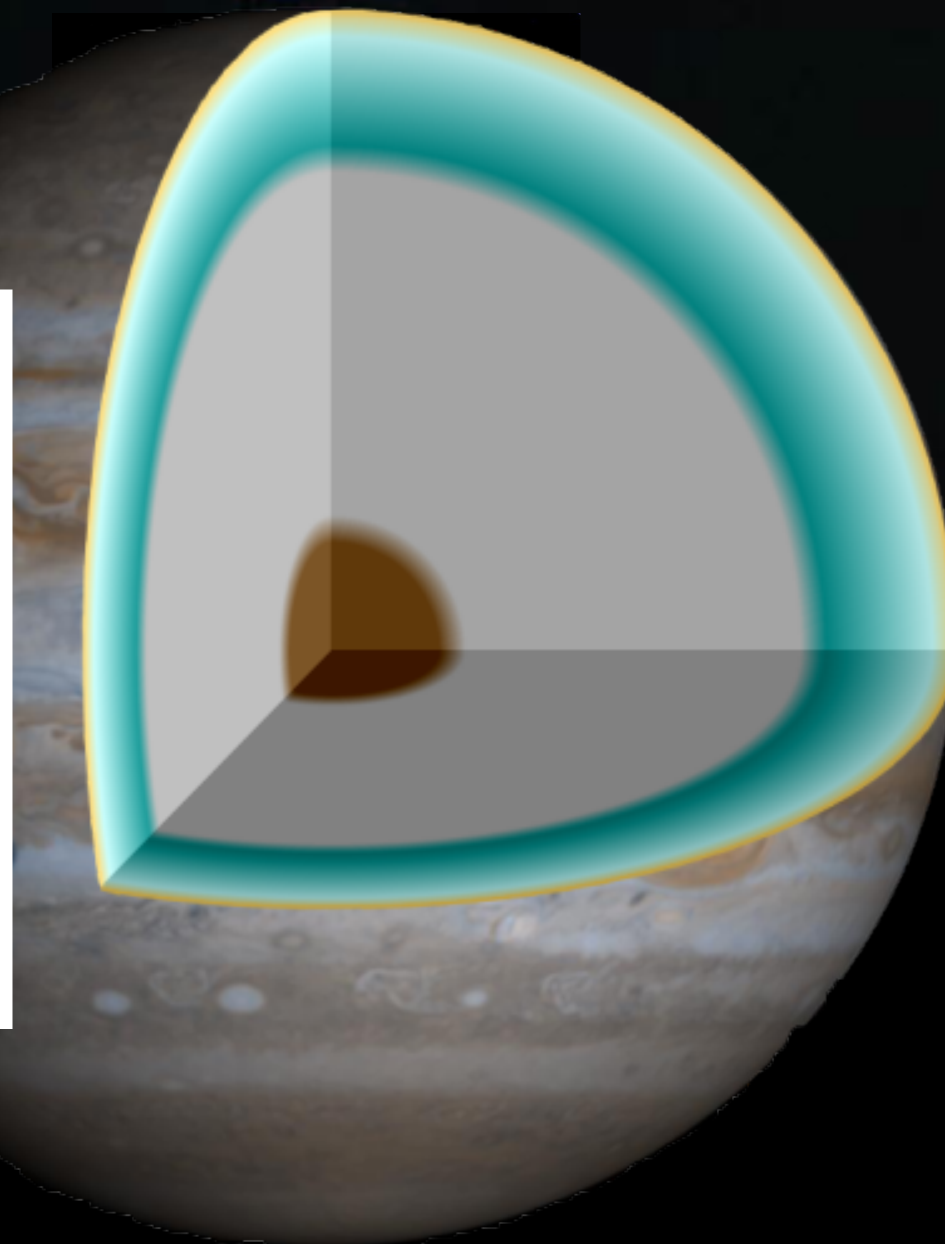
$>10^3$ Extrasolar Planets



Jupiter



[Guillot *et al.* (2002)]



Juno Mission to Jupiter

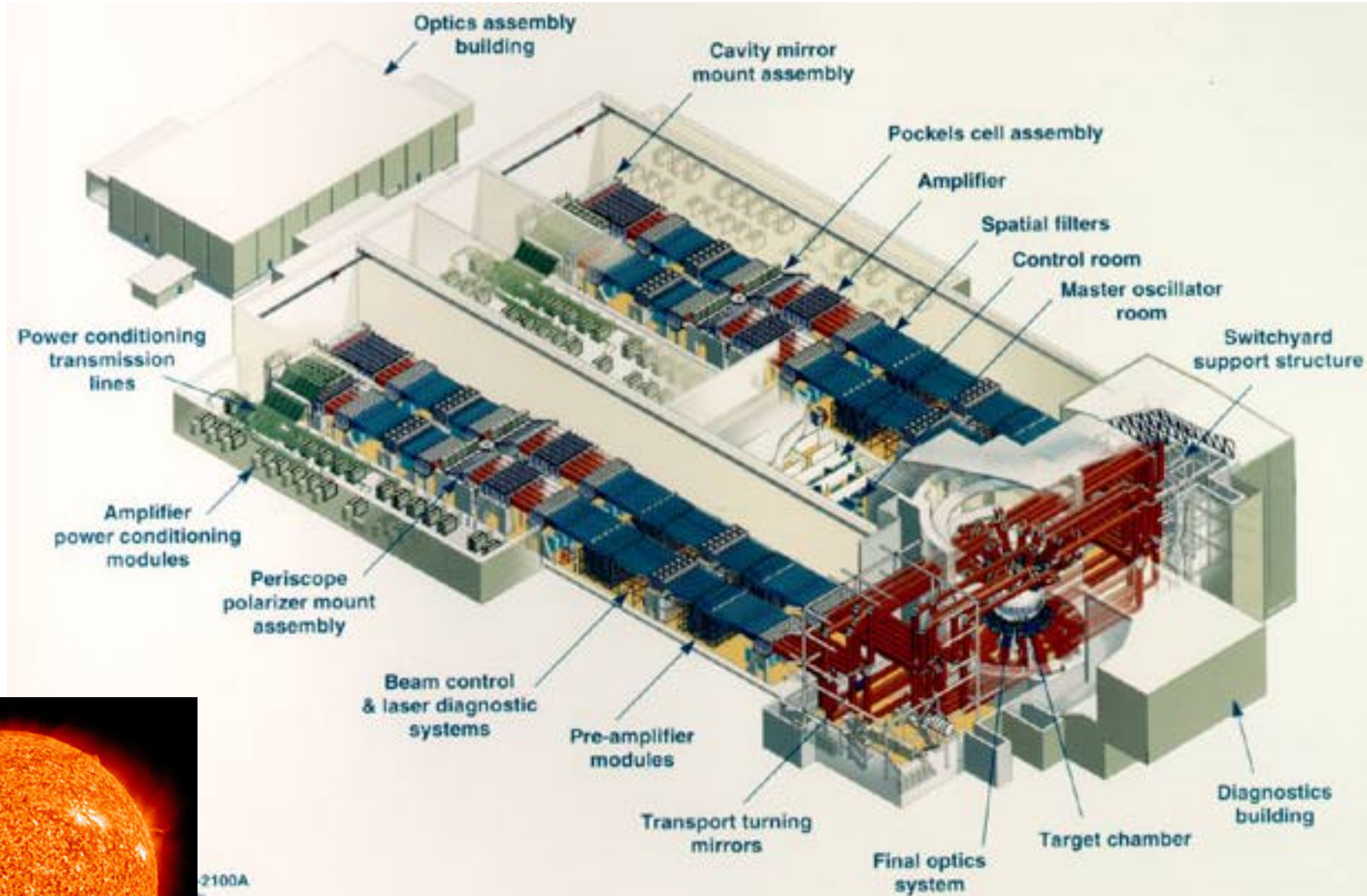
August 5, 2011 Launch

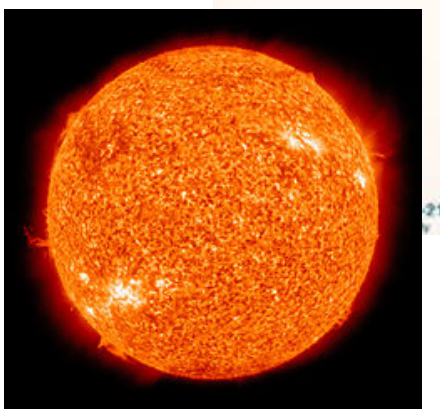
July14, 2016 Arrival

Mission Goals

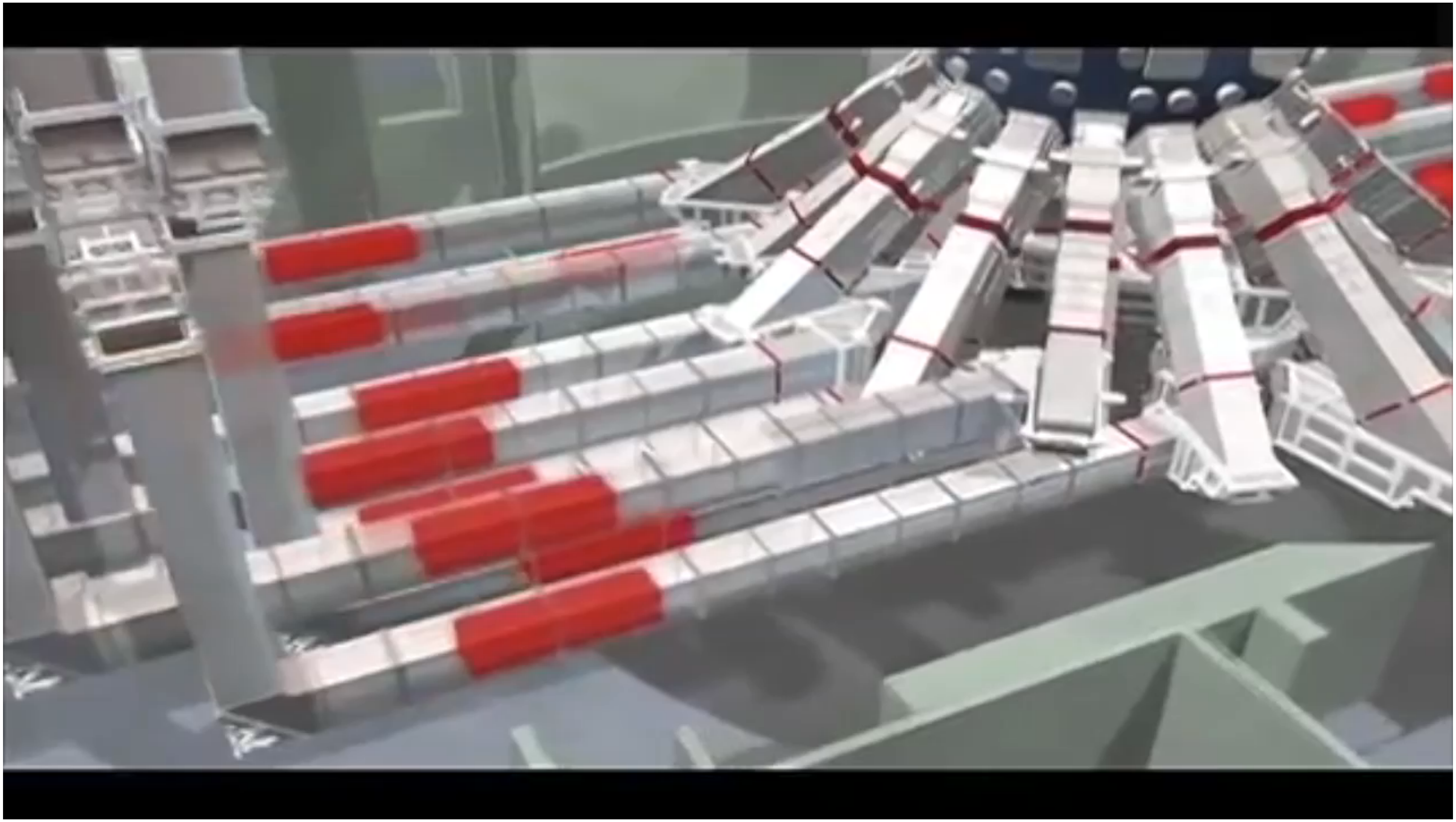
- *Origin and evolution?*
- *Composition (e.g., H_2O)?*
- *Gravity / magnetic fields?*
- *Internal structure?*
- *Size and existence of a core?*

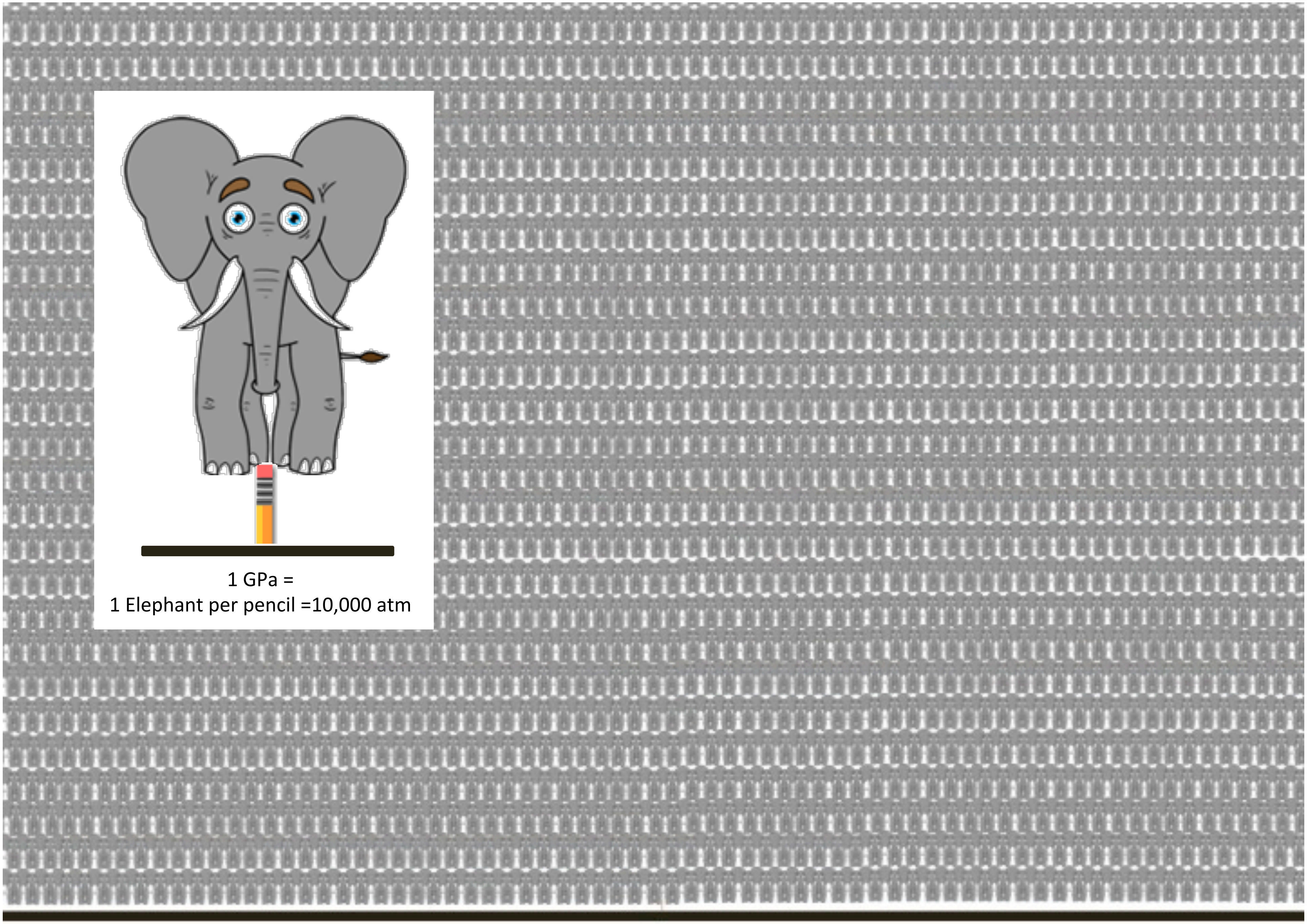
National Ignition Facility





National Ignition Facility

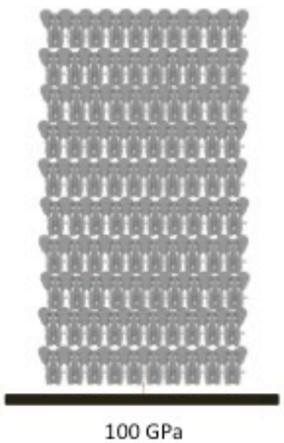




1 Gbar =
100,000 Elephants per pencil =1,000,000,000 atm

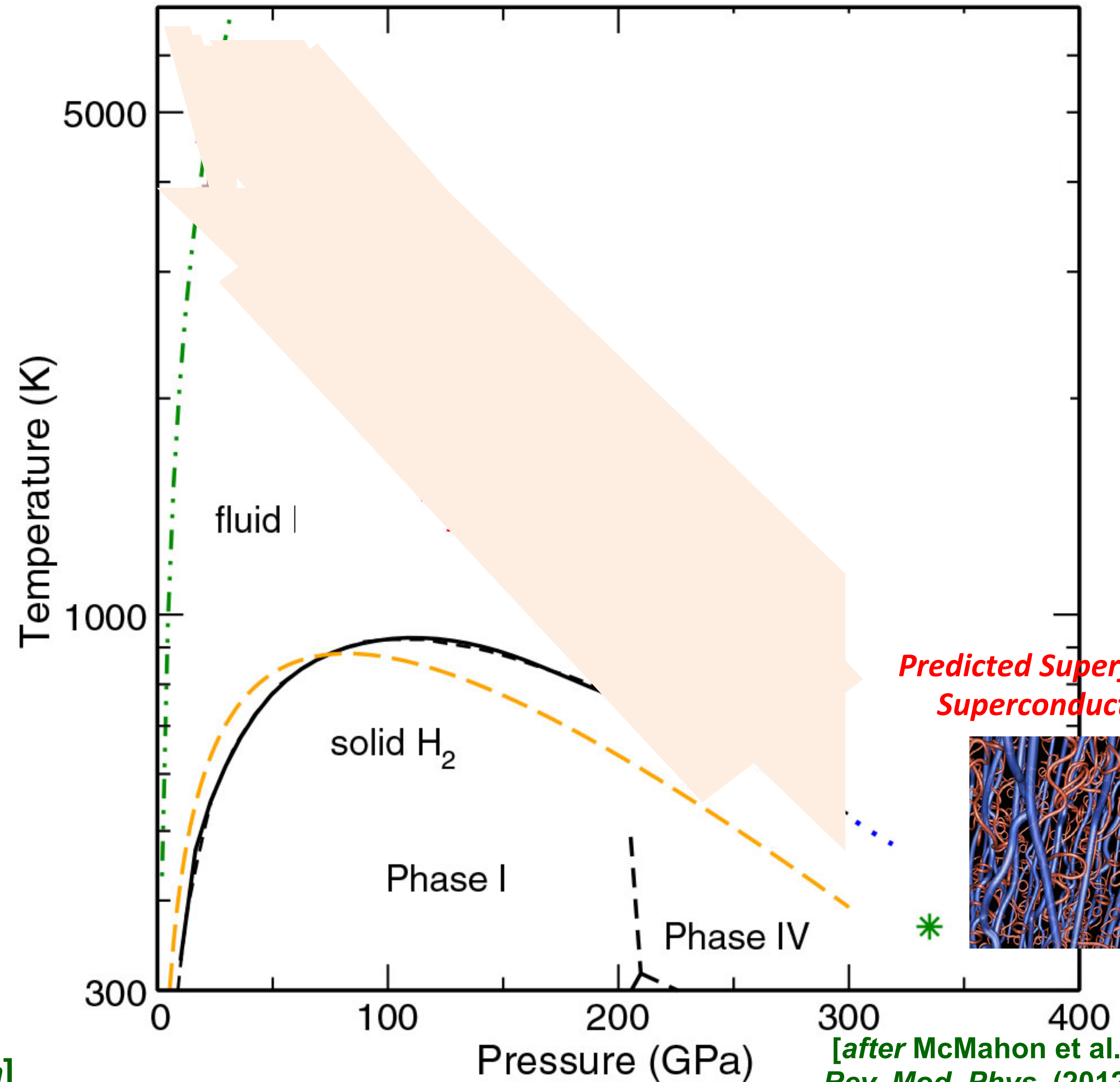
High *P-T* Transition in Fluid Hydrogen

DYNAMIC COMPRESSION



Conductivity of dense fluid hydrogen:
depth of magnetic field generation?

[Jeanloz & Hemley (PIs),
***NIF Discovery Science Campaign*]**

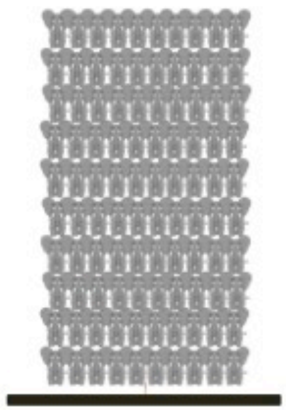


Predicted Superfluid Superconductor

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

High *P-T* Transition in Fluid Hydrogen

DYNAMIC COMPRESSION



Conductivity of dense fluid hydrogen:
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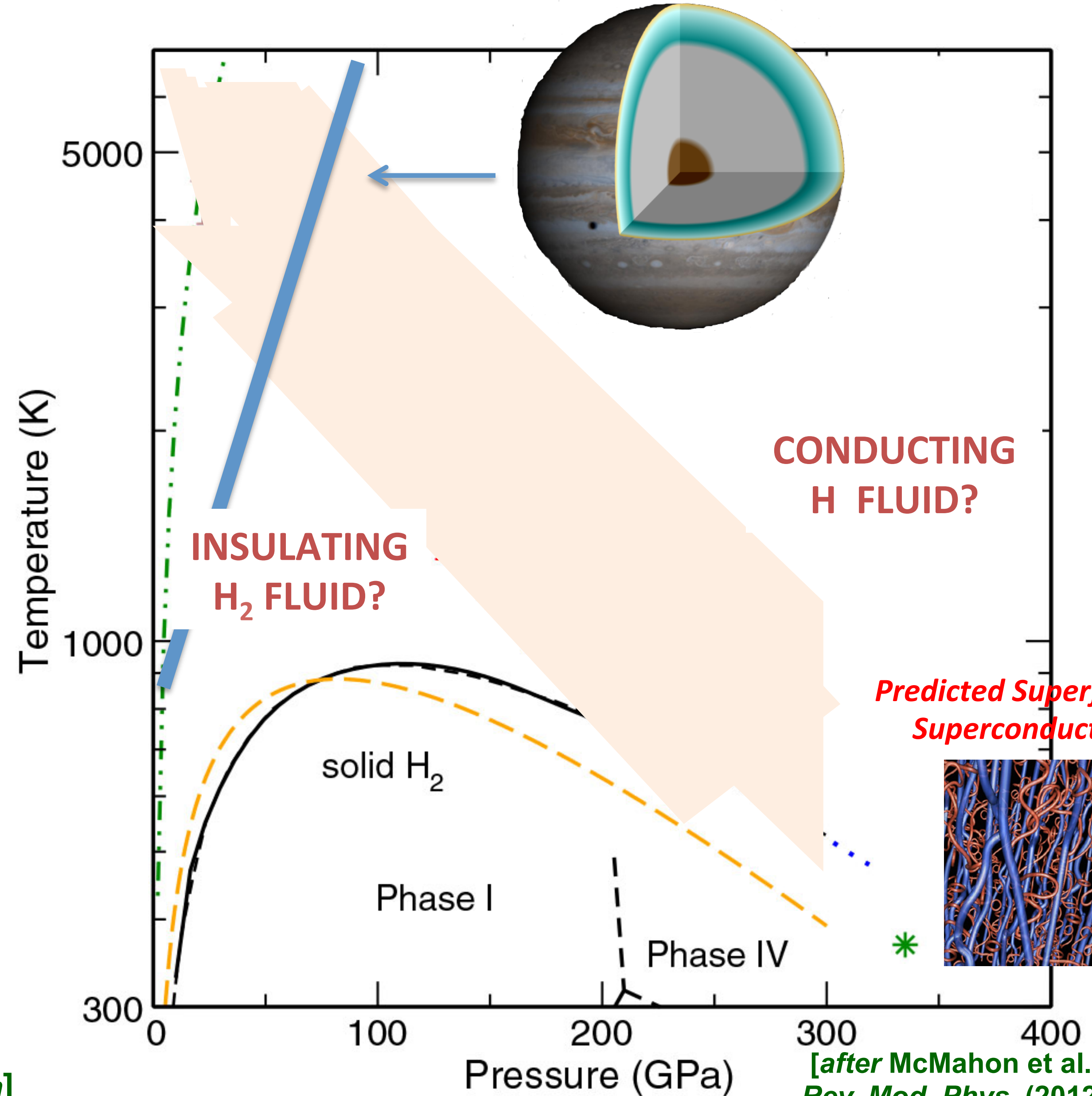
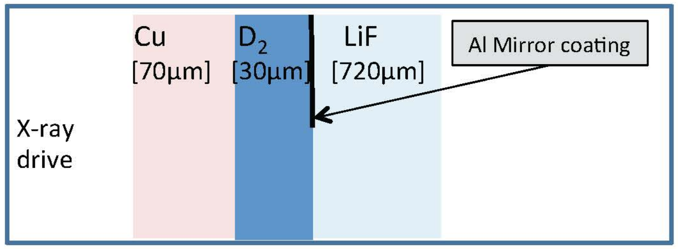


[*after* McMahon et al.,
Rev. Mod. Phys. (2012)]

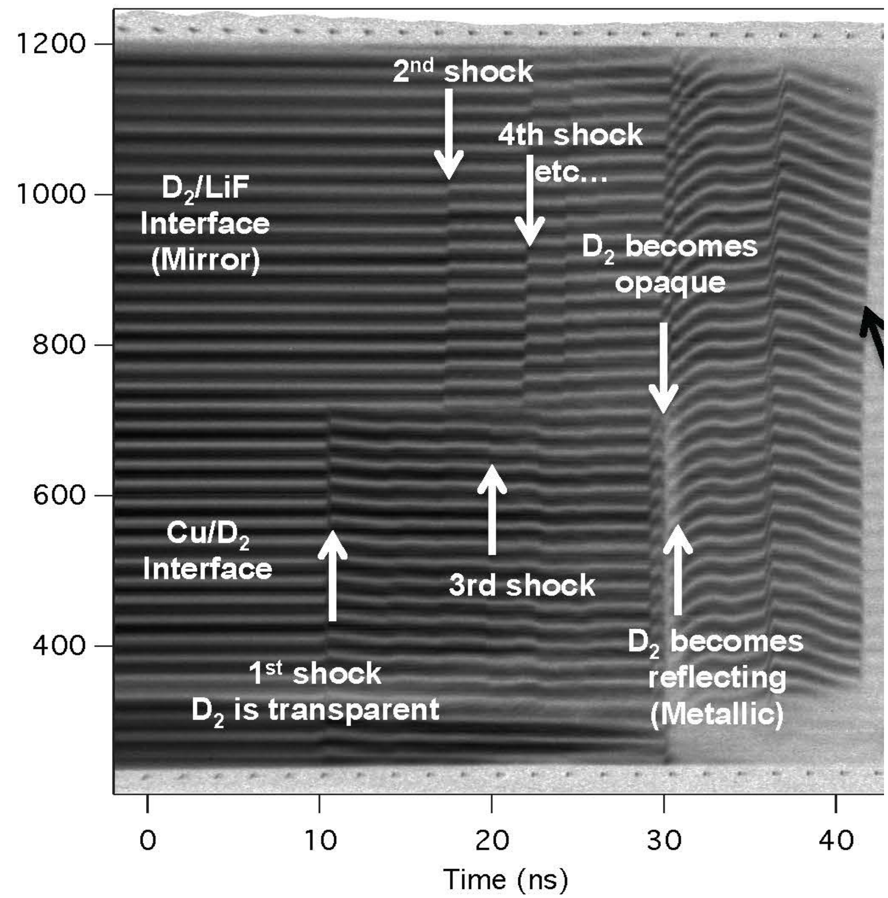
High *P-T* Transition in Fluid Hydrogen

Laser Pulse

Sample Geometry



Optical/Velocity (VISAR) Data

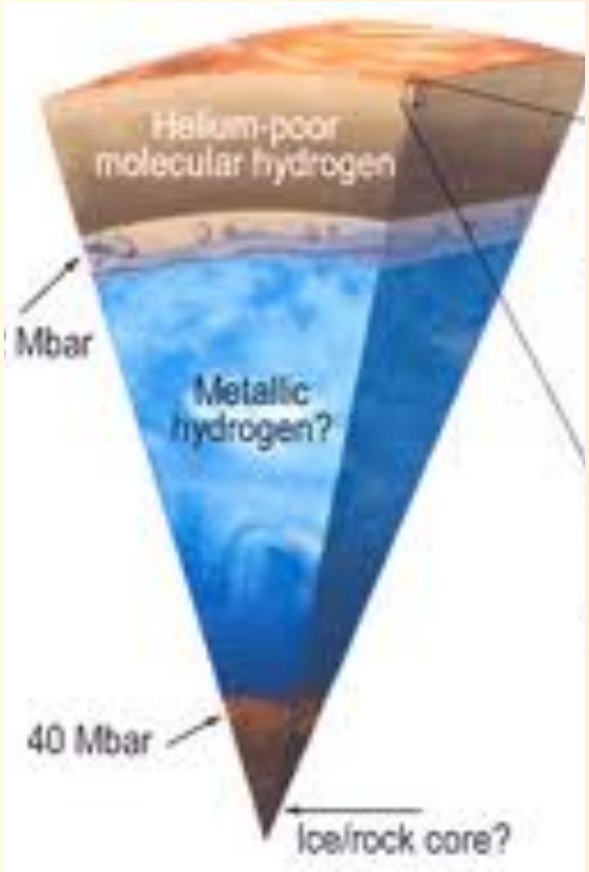


Onset of reflectivity near 200 GPa

H_2 → H

[Jeanloz & Hemley (PIs),
NIF Discovery Science Campaign]

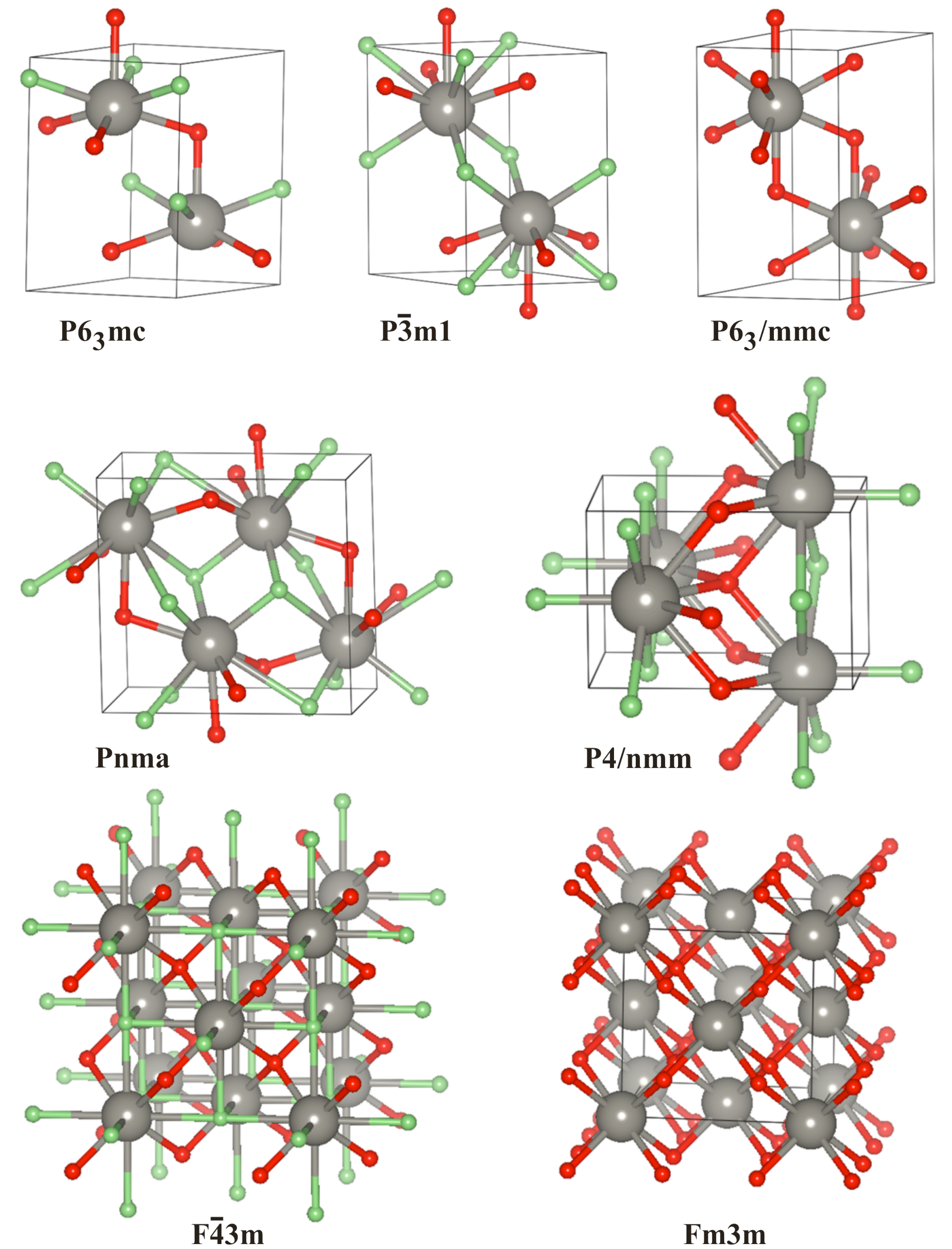
Size and Existence of the Jovian Core?



- ***Extreme reactivity of hydrogen will 'erode' the core***

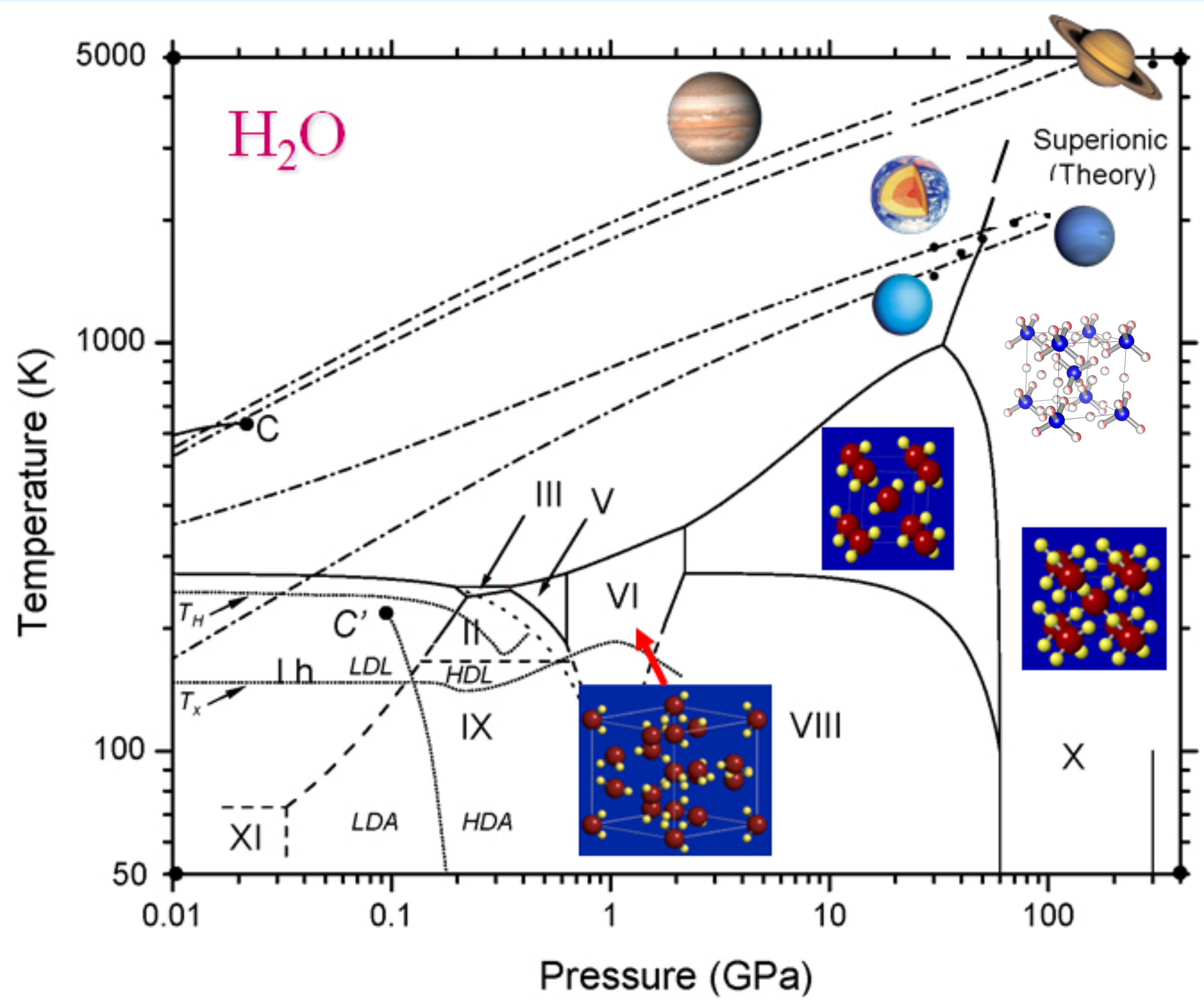
Hydriding of inert metals: *Re, Ir, Pt, W*

Structures of WH_n

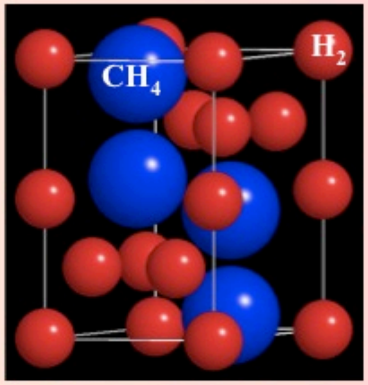


[Zaleski-Eigierd et al., *Phys. Rev. B* (2012)]

Complexity of Water



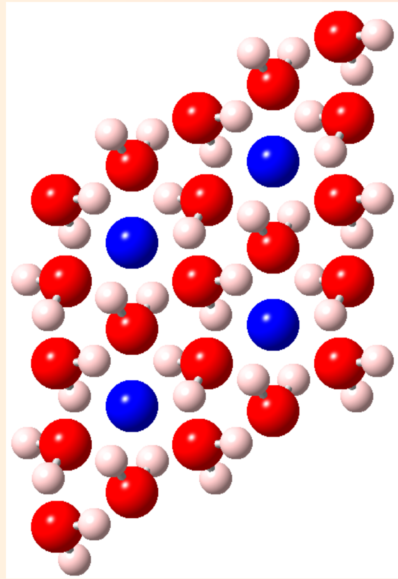
Novel Molecular Compounds



$CH_4(H_2)_4$

33.4 wt% H_2

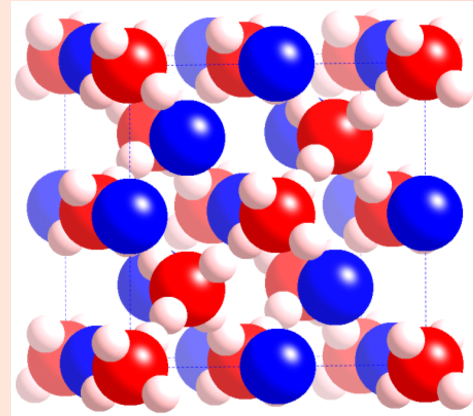
[Somayazulu *et al., Science* (1996);
W. Mao *et al. Chem. Phys. Lett.* (2005)]



$(H_2O)_2H_2$

α-quartz-type

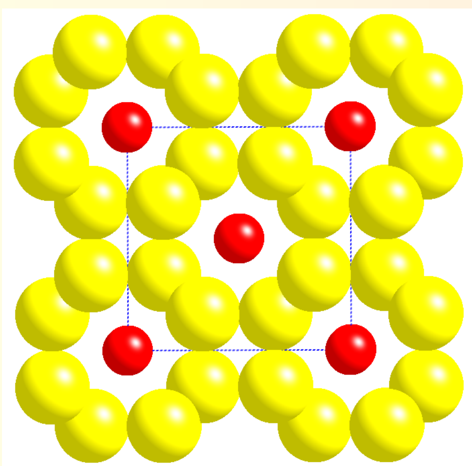
[Strobel et al., *J. Phys. Chem.* (2011)]



H_2O-H_2

11.3 wt% H_2

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



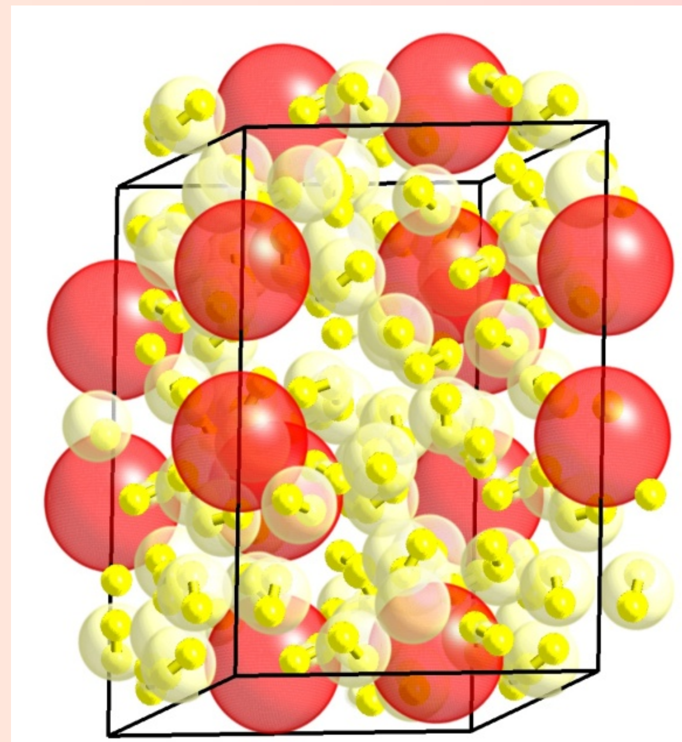
$(H_2S)_2H_2$

Al_2Cu type

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

➢ ***PRECURSOR TO HIGH T_c 'H_3S'***
T_c = 203 K

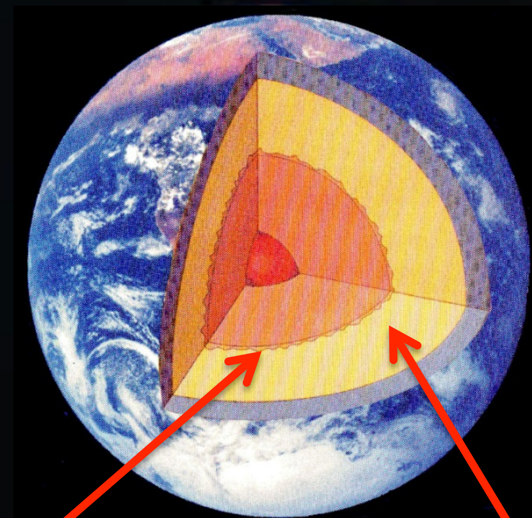
[Drozdov et al., *Nature.* (2015)]



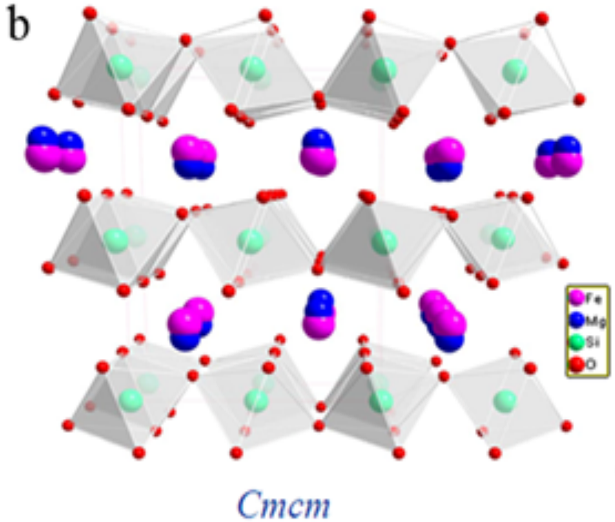
$Xe(H_2)_8$

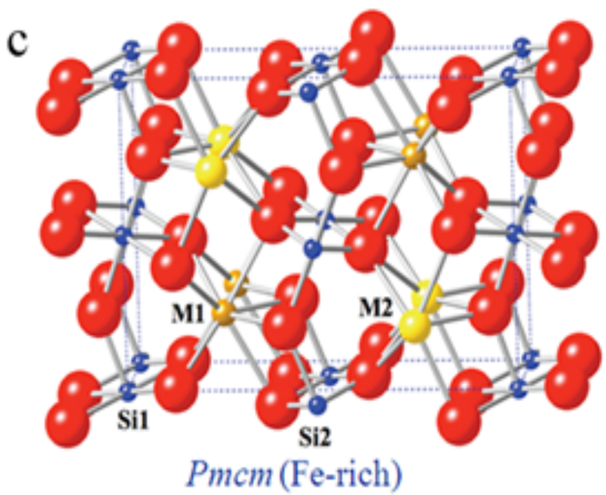
[Somayazulu et al., *Nature Chem.* (2009)]

Return to Earth



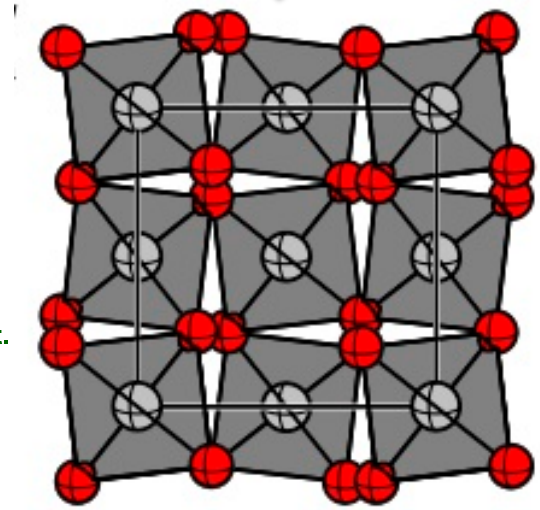
New dense silicates



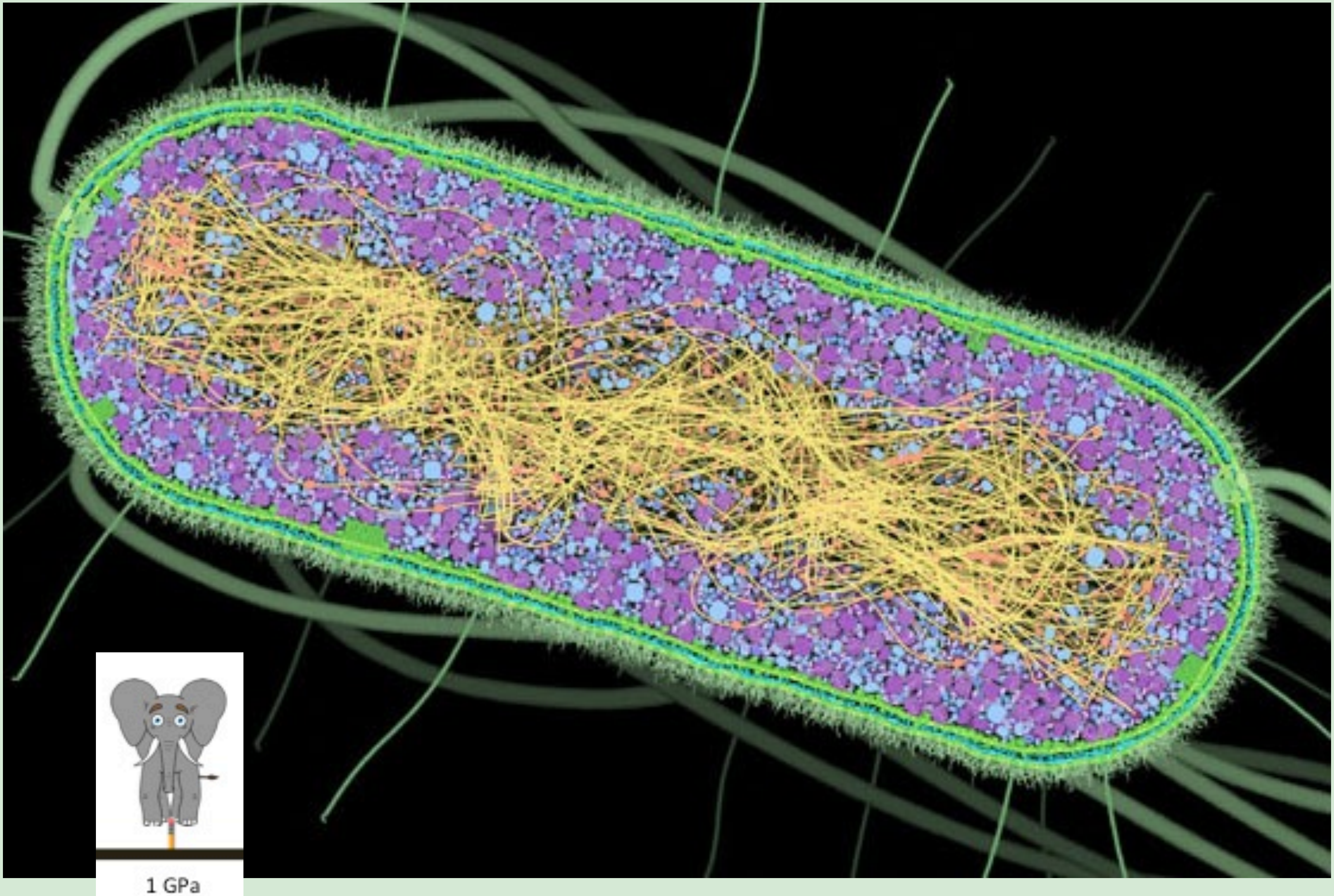


CO_2

[Santoro et al. *PNAS* (*2012*]]; Datchi et al., Phys. Rev. Lett. (2012)



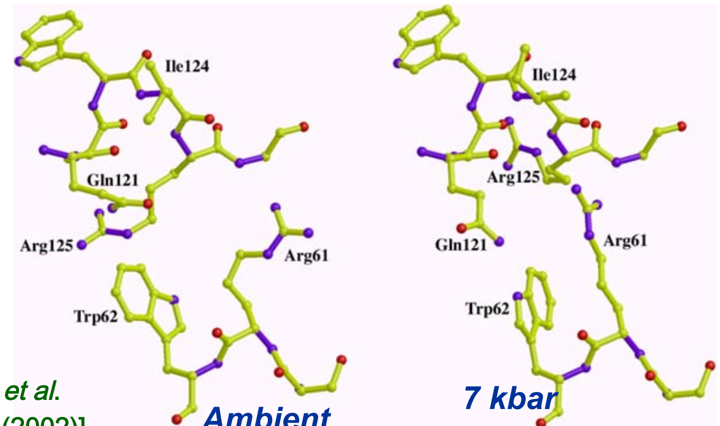
Biology at Extremes



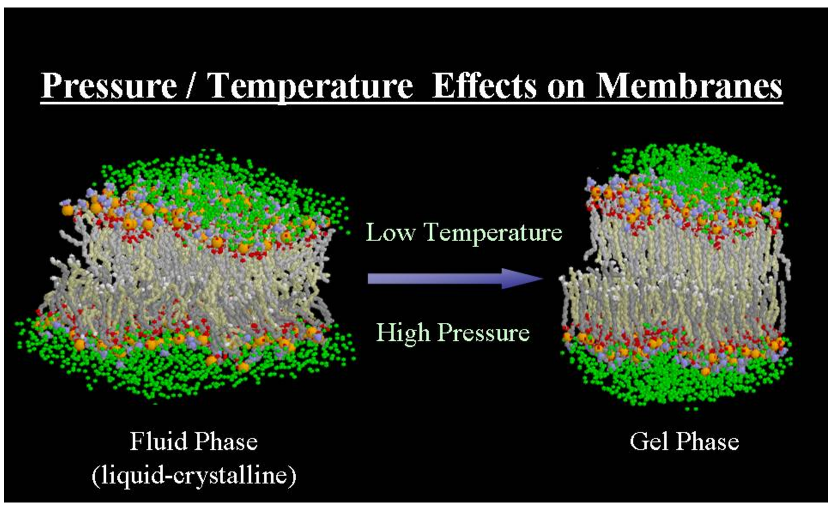
Biology at Extremes

Structure-function in biological systems

Lysozyme

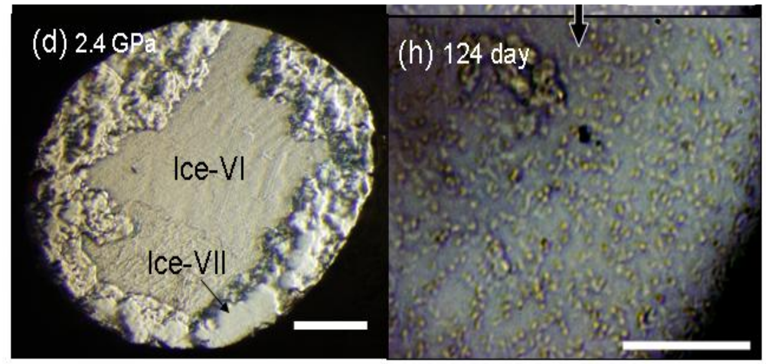


[Fourme *et al.*
. *Mol. Bio.* (2002)]



Microbial viability to >25 kbar

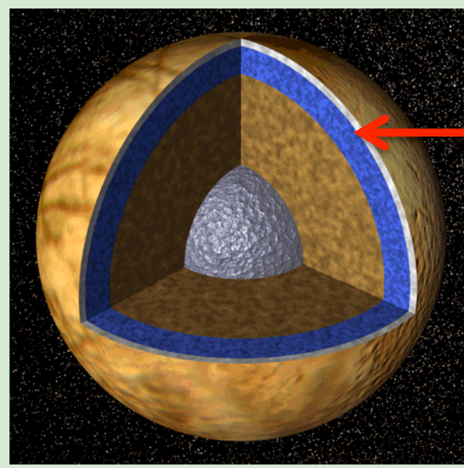
Direct observations



[Sharma *et al.*, *Science* (2002);

Pressure-induced directed evolution

[Vanlint *et al.*, *mBio* (2011)]

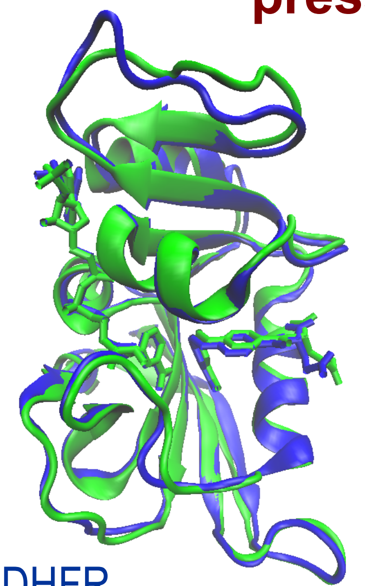


~100 km deep ocean of Europa

Biology at Extremes

DEEP CARBON OBSERVATORY

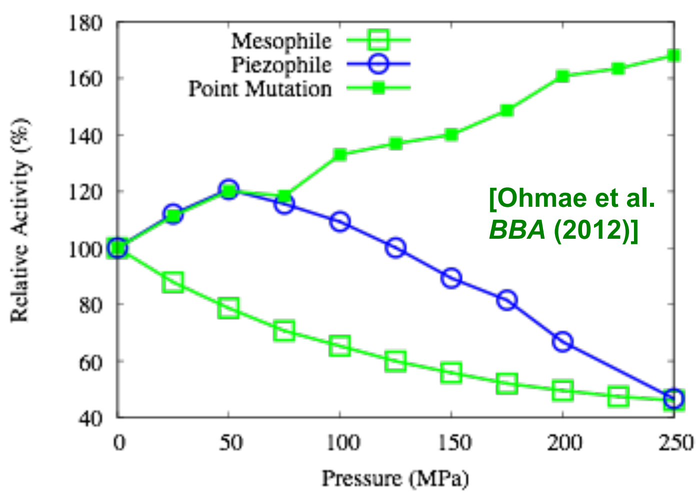
Protein dynamics under pressure



How can simulations inform structure-function relations at high pressures?

DHFR

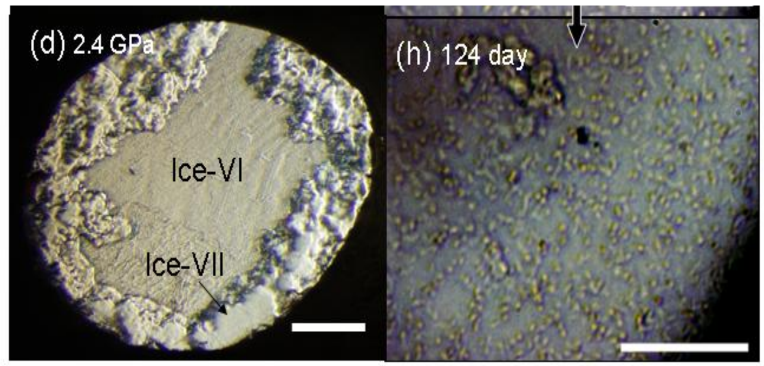
[Rodgers et al. In preparation]



[Ohmae et al. *BBA* (2012)]

Microbial viability to >25 kbar

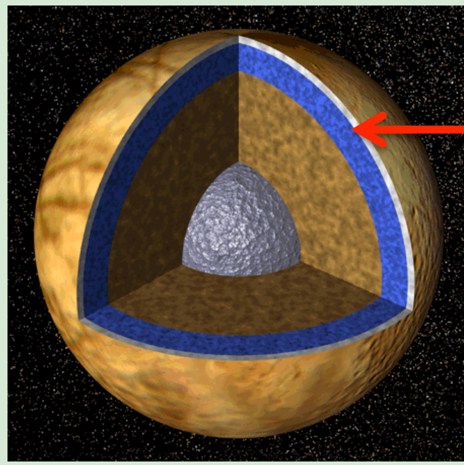
Direct observations



[Sharma *et al.*, *Science* (2002);

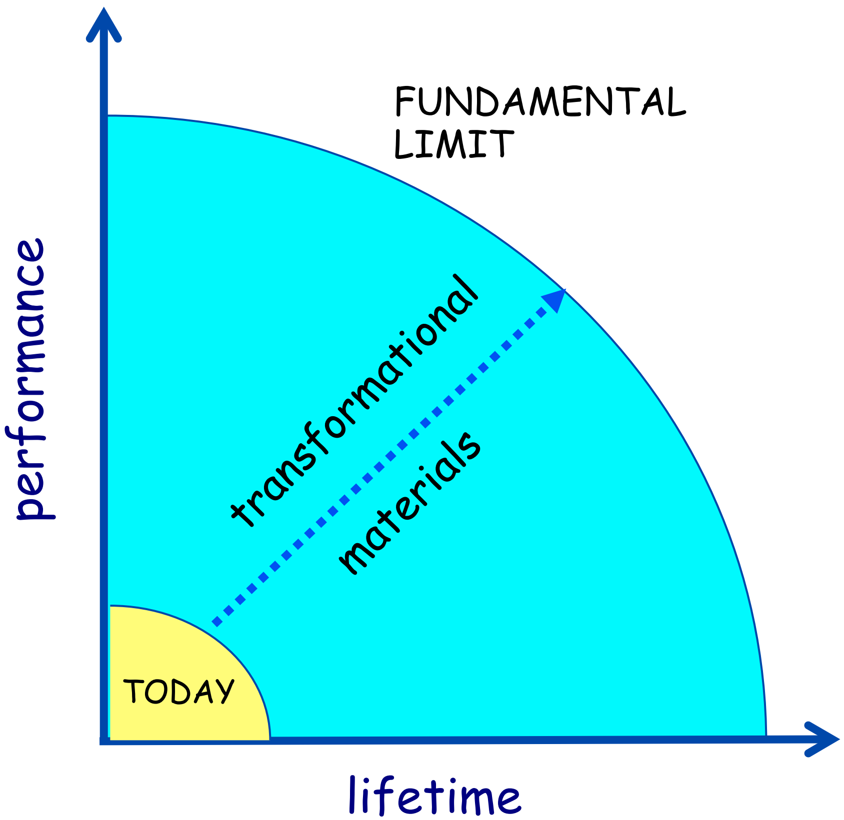
Pressure-induced directed evolution

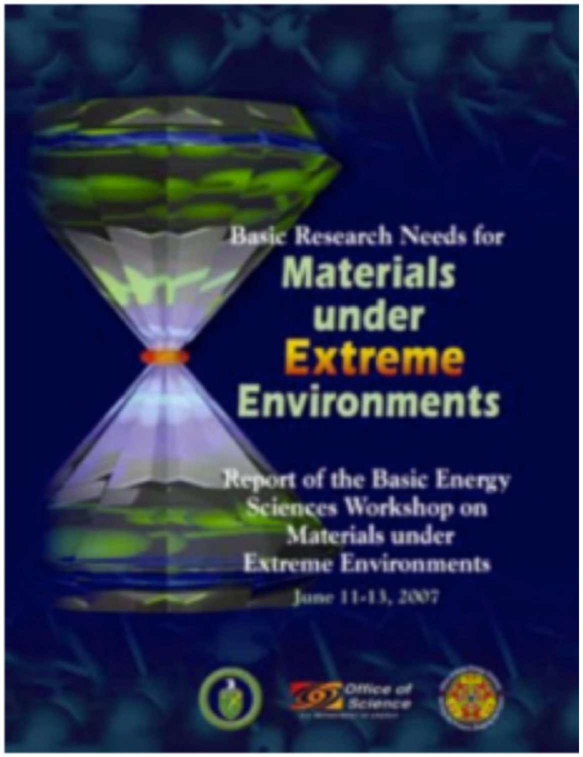
[Vanlint *et al.*, *mBio* (2011)]



~100 km deep ocean of Europa

Implications for New Materials

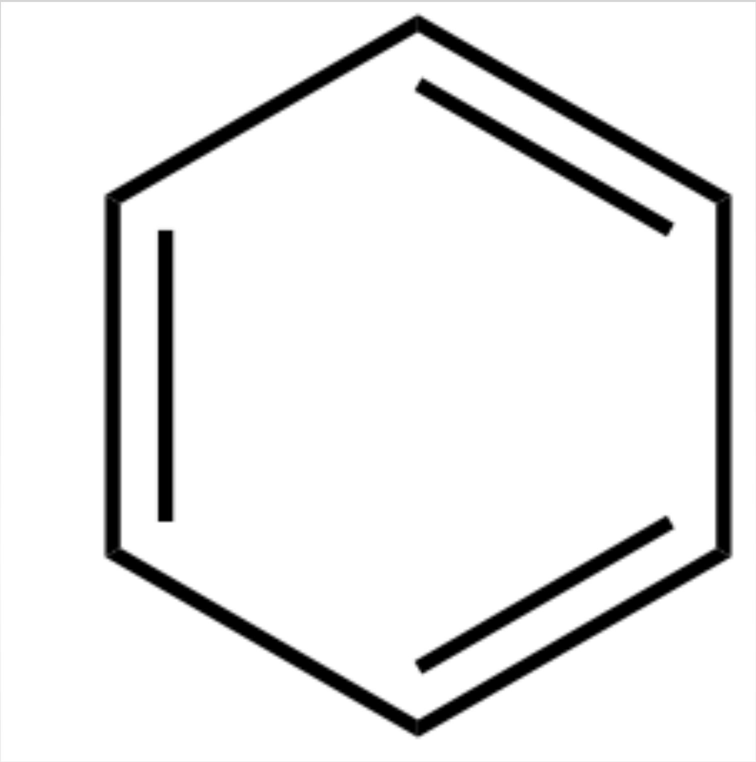


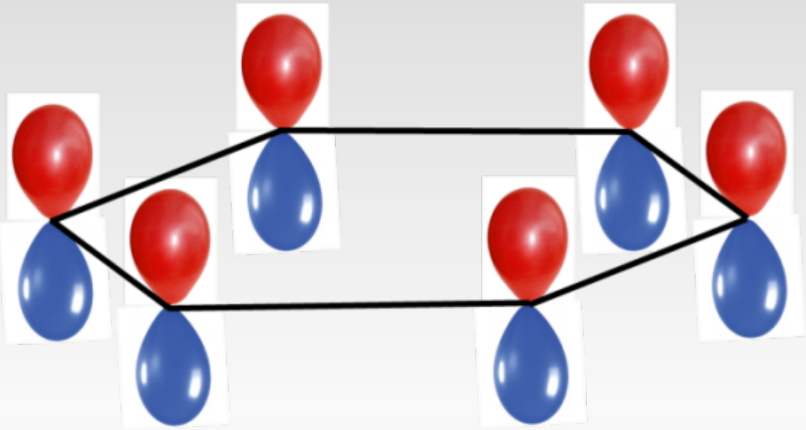


Basic Research Needs Report (2007)

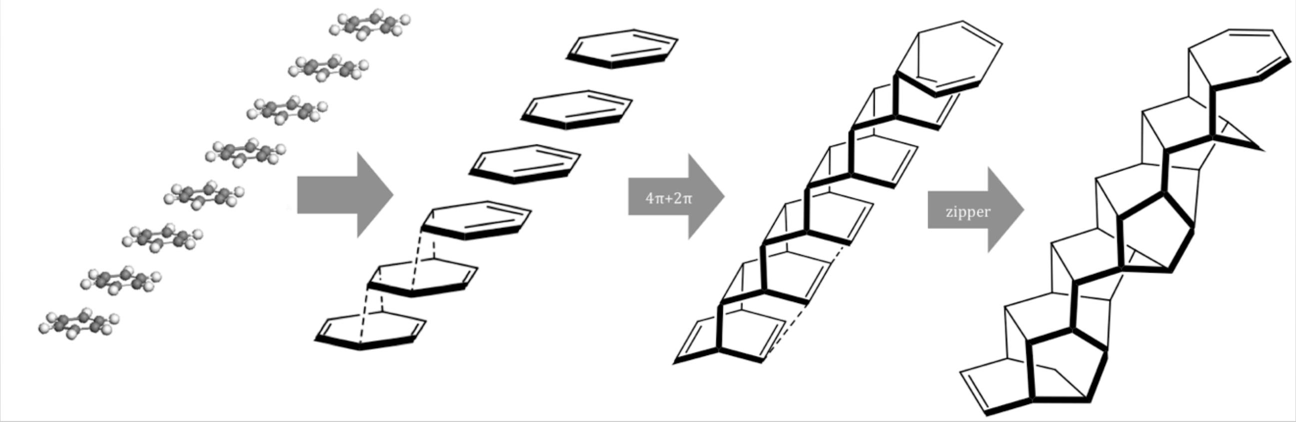
Can we use these techniques to design, discover and synthesize new technological materials?

Implications for New Materials

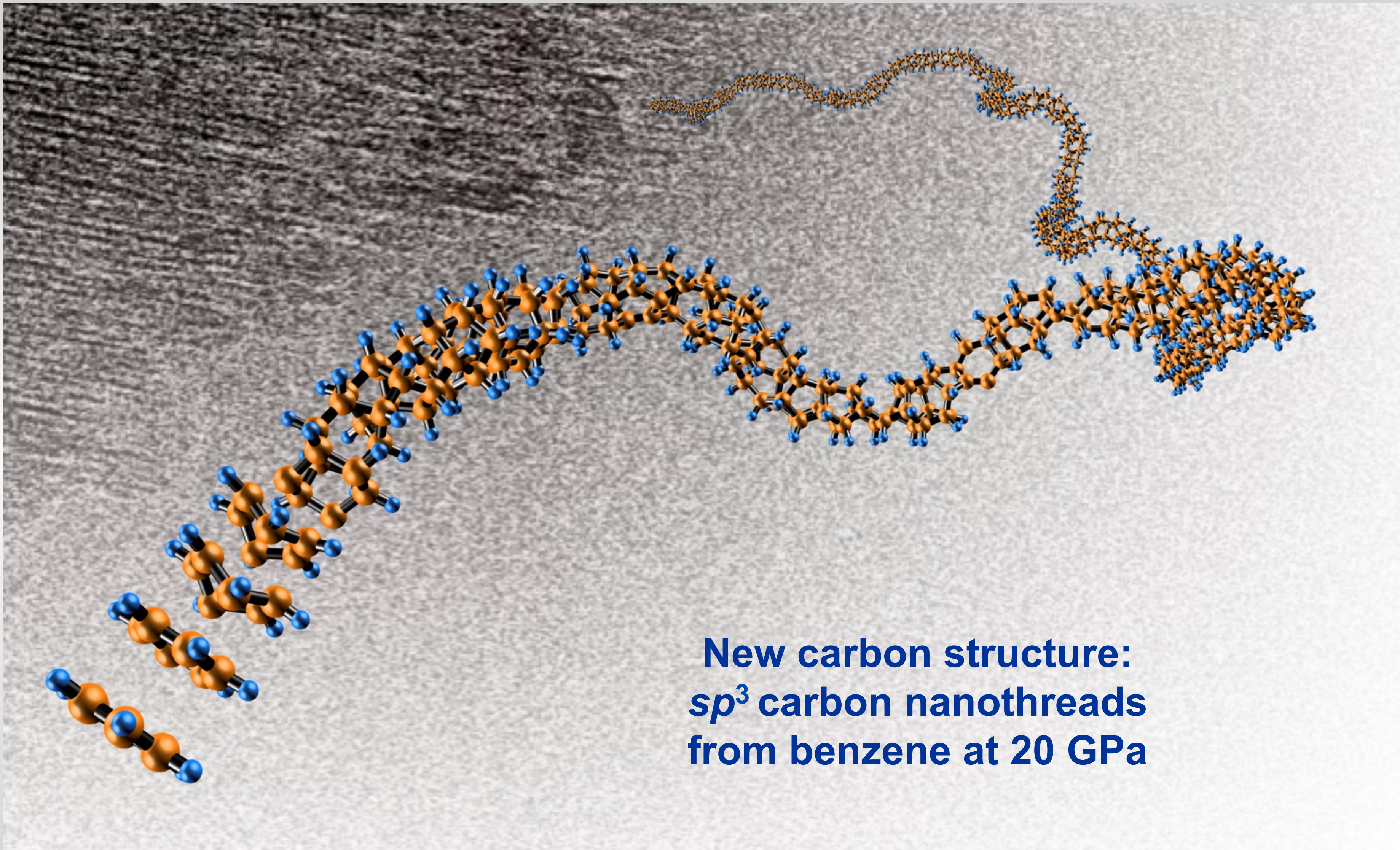




[Fitzgibbons et al., *Nature Mater*. (2014)]



Implications for New Materials

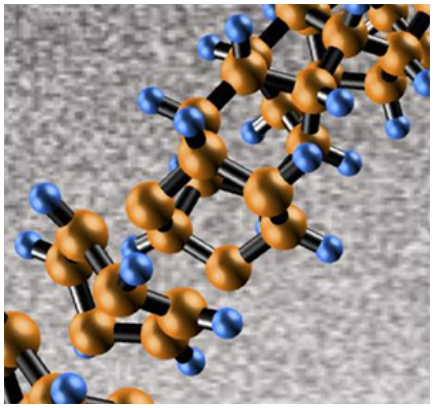


[Fitzgibbons et al., *Nature Mater*. (2014)]

New Technological Materials

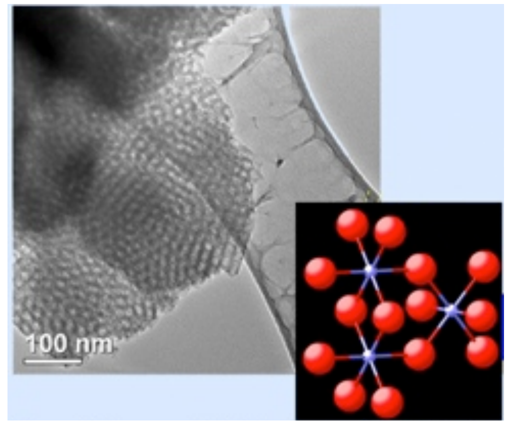
Energy Frontier Research Center

1. Discovery of sp^3 carbon nanothreads



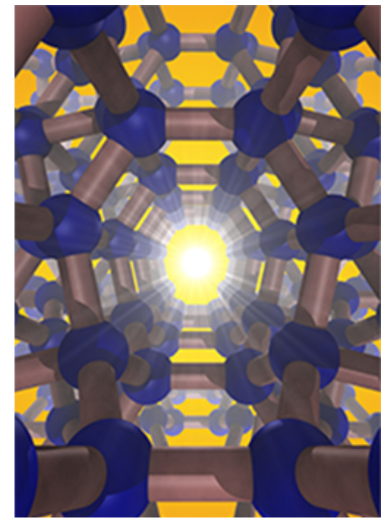
[Fitzgibbons et al., *Nature Mater.* 14, 43 (2014)]

2. Mesoporous 'dense' crystalline silica



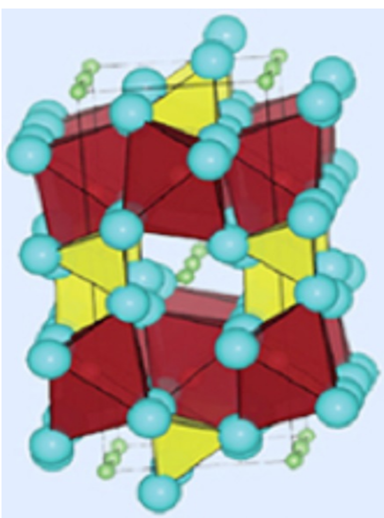
[Stagno et al., *Phys. Chem. Minerals* (2015)]

3. New allotrope of silicon: Si_{24}

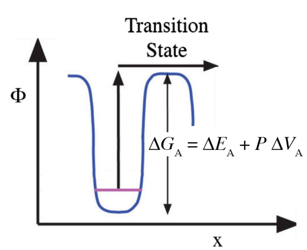


Direct Band Gap

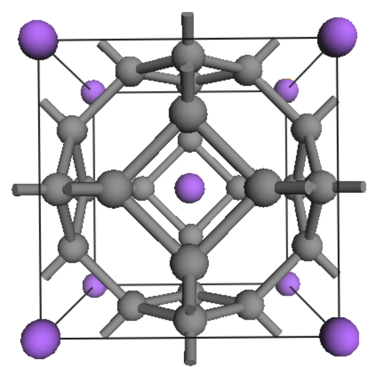
[Kim et al., *Nature Mater.* (2015)]



4. Li ion mobility in battery anodes



[Tracy et al., *Phys. Rev. B* (2014)]



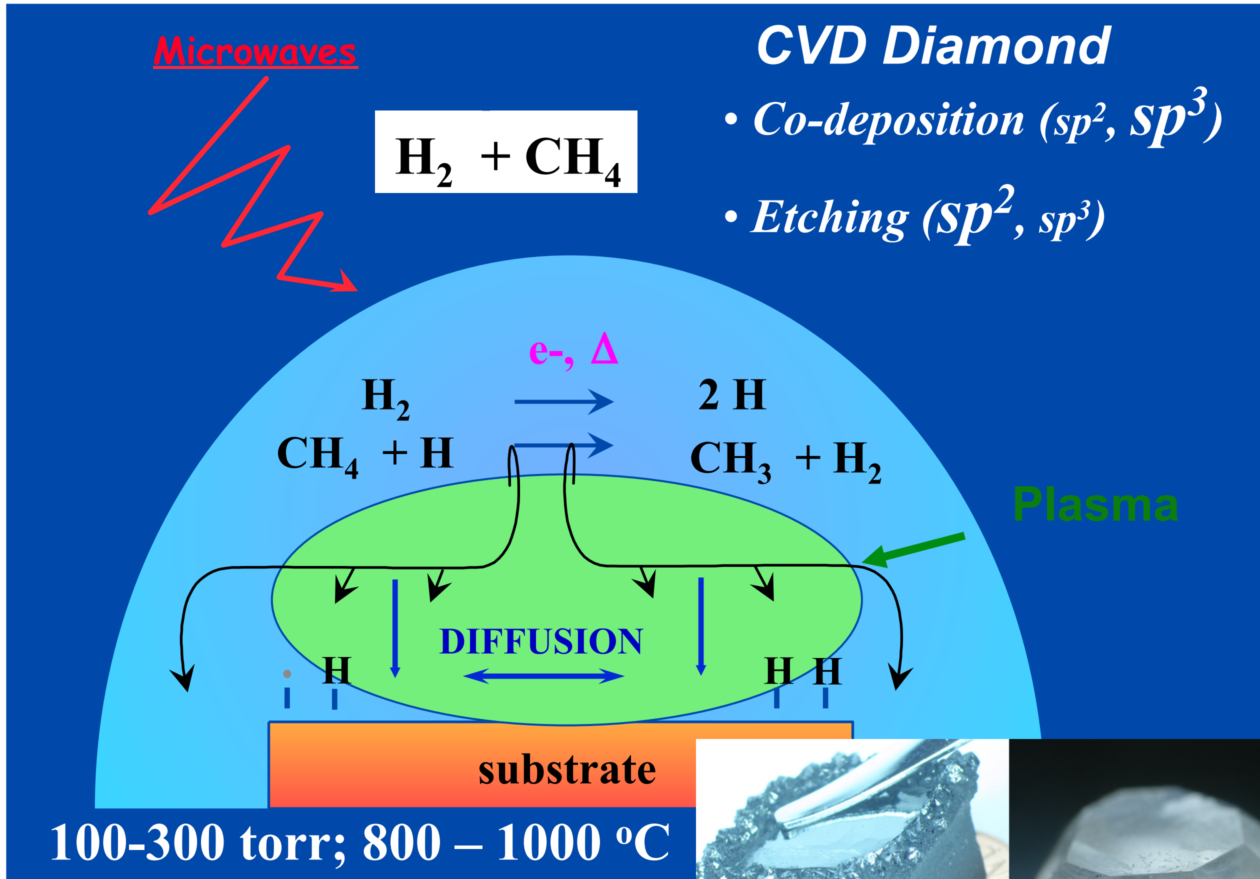
NaC_6 $T_c > 100$ K

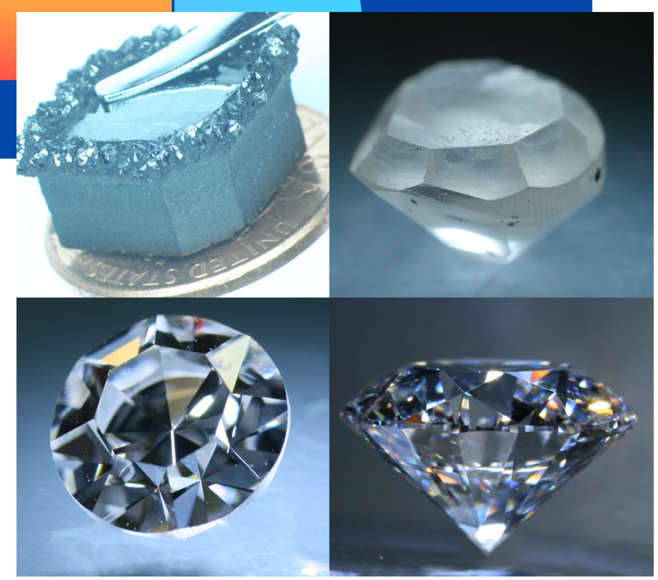
5. Predicted high T_c superconductivity in dense carbides

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

Alternative Routes to Synthesis of Novel Phases

Diamond Synthesis
General Electric, Co.
(1954)





- Limited in size and quality from Nature and conventional synthesis
- Optimized properties: strength, toughness, doping

[Liang *et al.*, *Superhard Materials* (2013)]

CONCLUSIONS AND OUTLOOK

1. **High pressure is opening a new world of materials**

2. **New predictive models are needed to understand the bonding and other phenomena in these regimes**

3. **These findings provide new insights into materials under 'normal' conditions**

4. **The implications span the sciences, from astrophysics to biology**

5. **There is the prospect for the creation of new useful materials using these techniques**

ACKNOWLEDGEMENTS

Collaborators

CARNEGIE INSTITUTION

Ivan Naumov	Ronald E. Cohen
M. Somayazulu	Ho-kwang Mao
Viktor Struzhkin	Muhetaer Aihaiti
Timothy Strobel	Alexander Goncharov
Zhenxian Liu	Changsheng Zha
Reini Boehler	Yufei Meng
Yingwei Fei	Stephen Gramsch
Guoyin Shen	Jocelyn Rodgers

OTHER INSTITUTIONS

John Badding (Penn State)
Vincent Crespi (Penn State)
Nasim Alem (Penn State)
K. Landsktron (Lehigh)
E. Gregoryanz (Edinburgh)
B. Fultz (Caltech)
Anurag Sharma (Boston)
Neil Ashcroft (Cornell)
Roald Hoffman (Cornell)
Maosheng Maio (UCS Northridge
Raymond Jeanloz (UCB)
G. W. Collins (LLNL)
Toshiko ichiye (Georgetown)
Tianshu Li (George Washington)

Financial Support

DOE/NNSA, DOE/OS/BES, A. P. Sloan Foundation, NSF, Carnegie Institution


2.4 carat CVD
[Meng et al., *NDNC* (2009)]
0.3 carat
natural
Carnegie Institution