

New Findings in Simple Molecular Systems Under Pressure

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Geophysical Laboratory

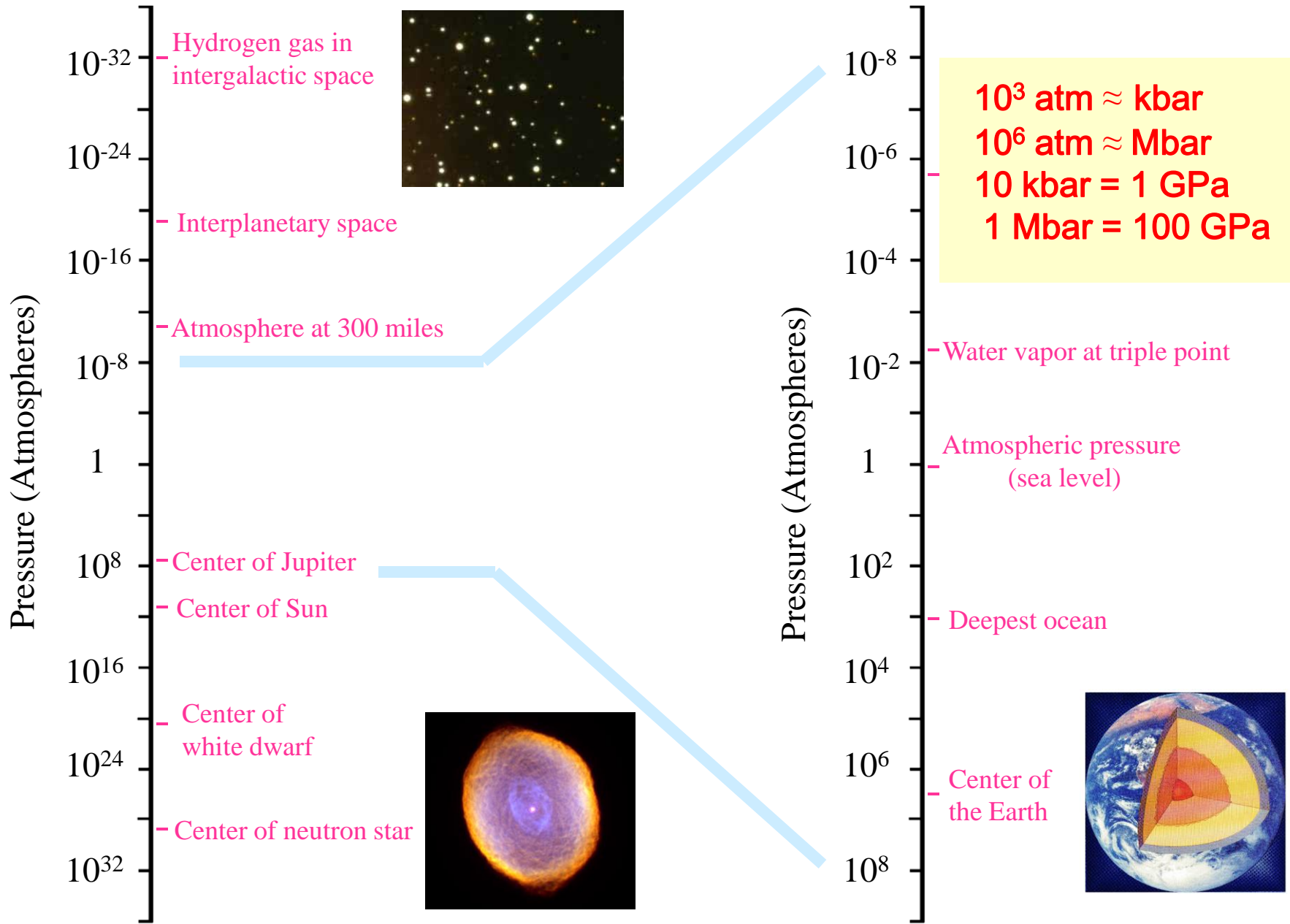
Carnegie Institution of Washington

Washington, DC

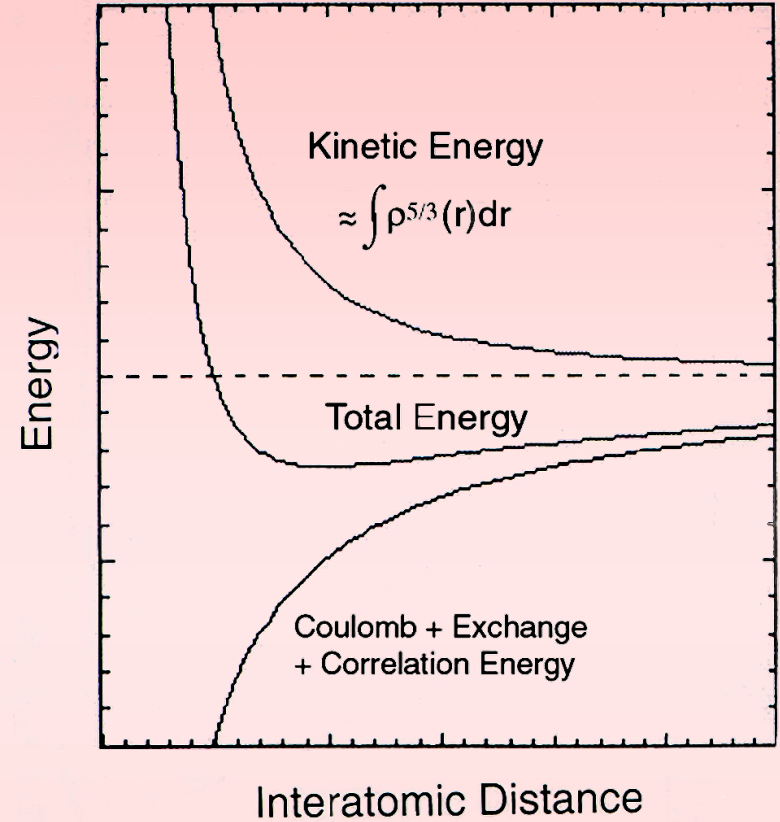
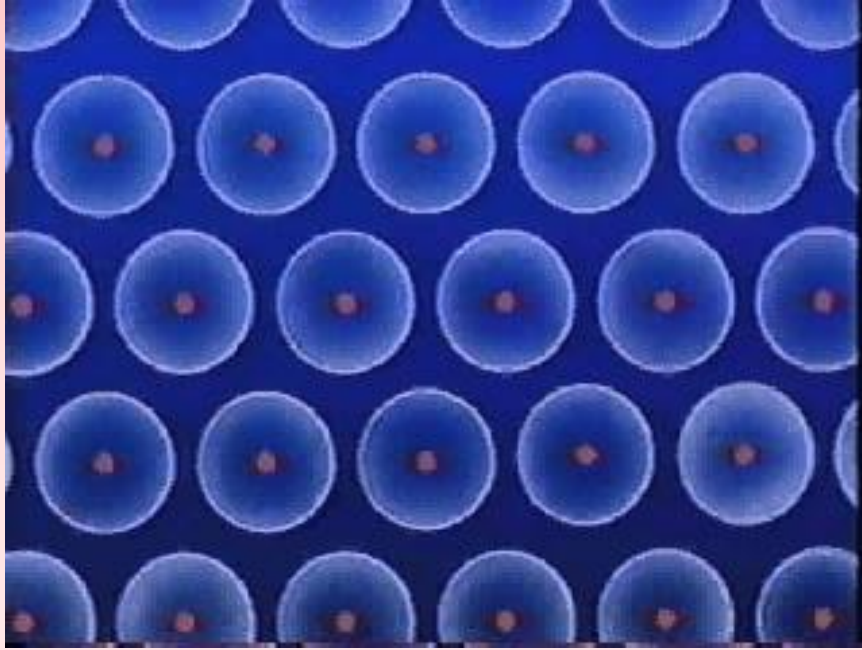


CC2010 "School for Young Scientists"
July 26, 2010

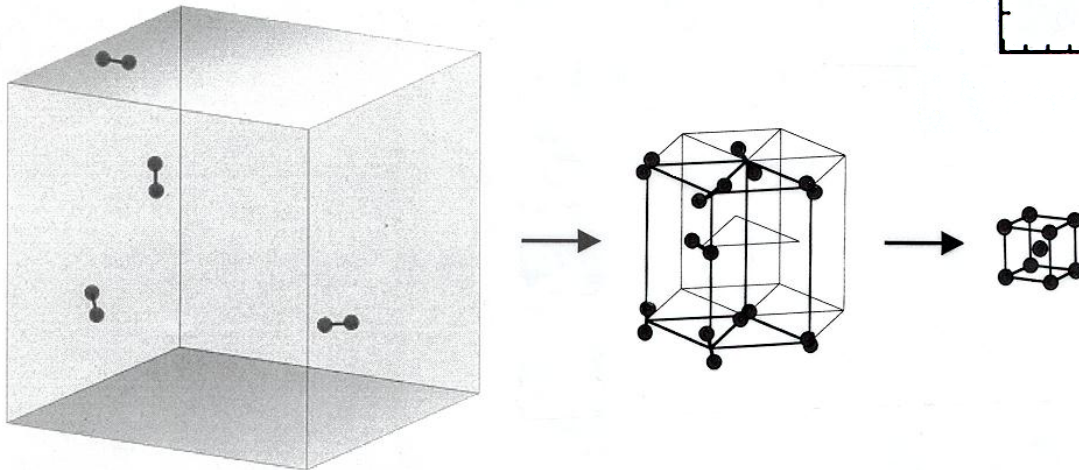
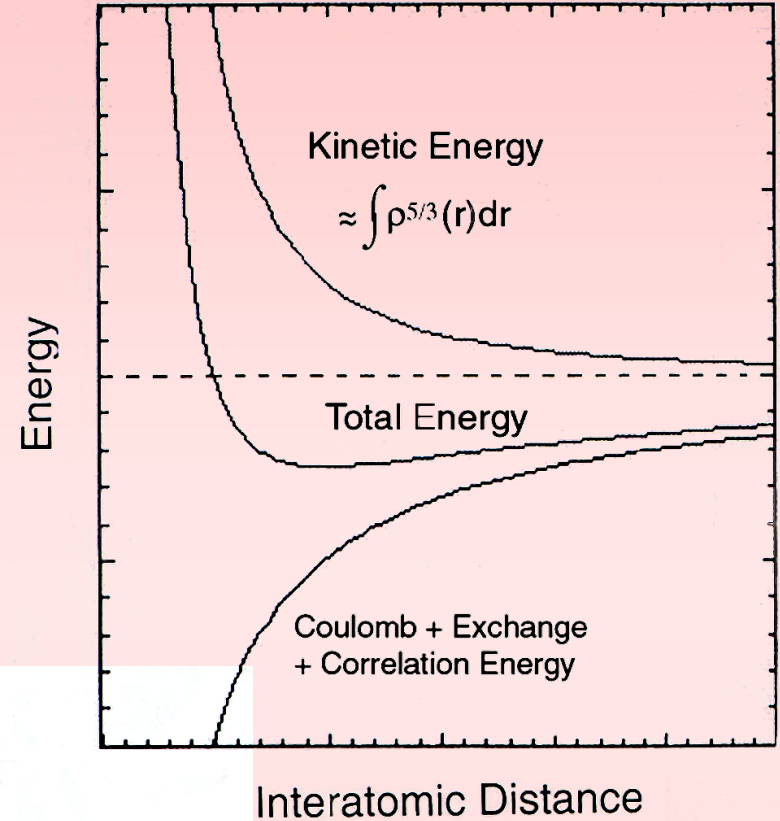
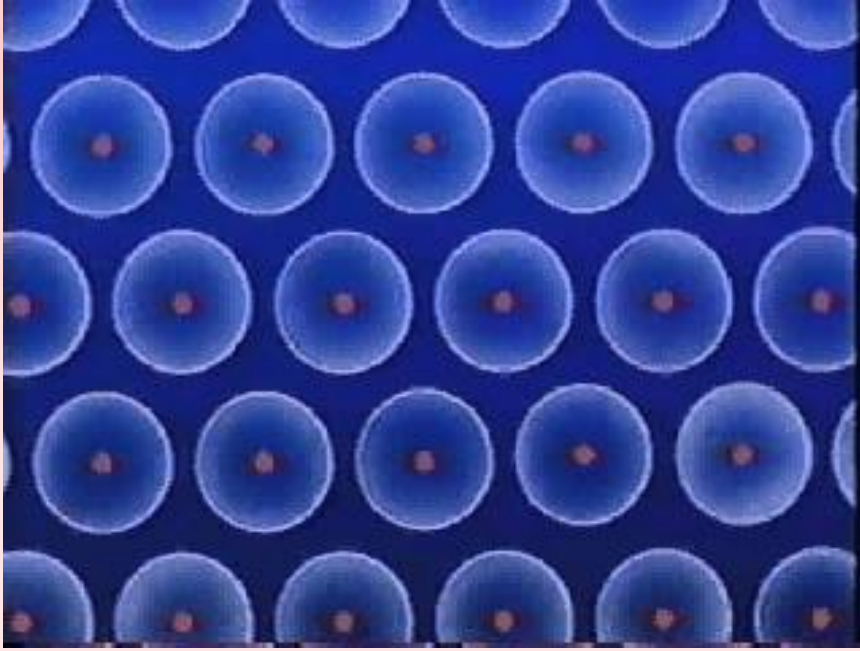
RANGE OF PRESSURE IN THE UNIVERSE



Compressing Atoms and Molecules



Compressing Atoms and Molecules

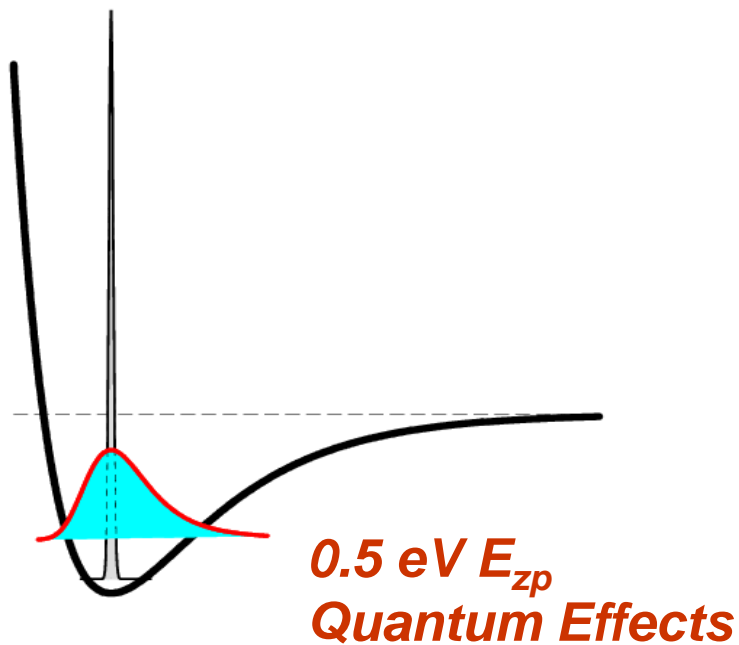
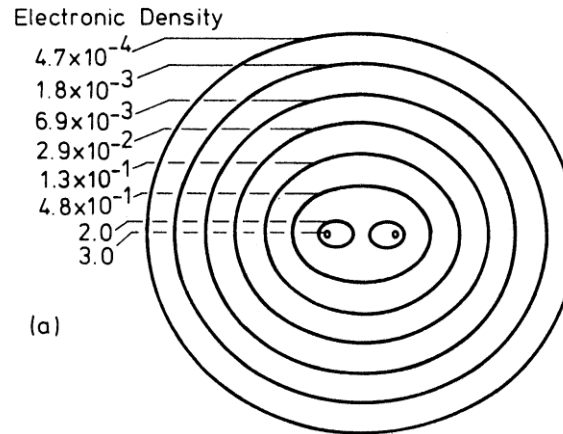


$$P = - \frac{\partial E}{\partial V}$$

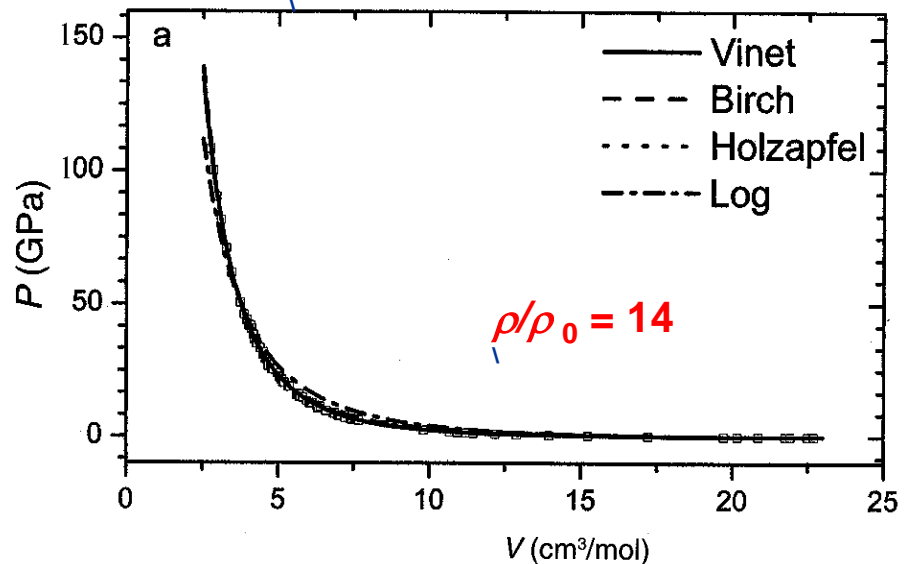
Simple Molecular Systems Under Pressure

HYDROGEN

- *Nearly spherical charge distribution p-H₂*
- *E_b = 4.5 eV*

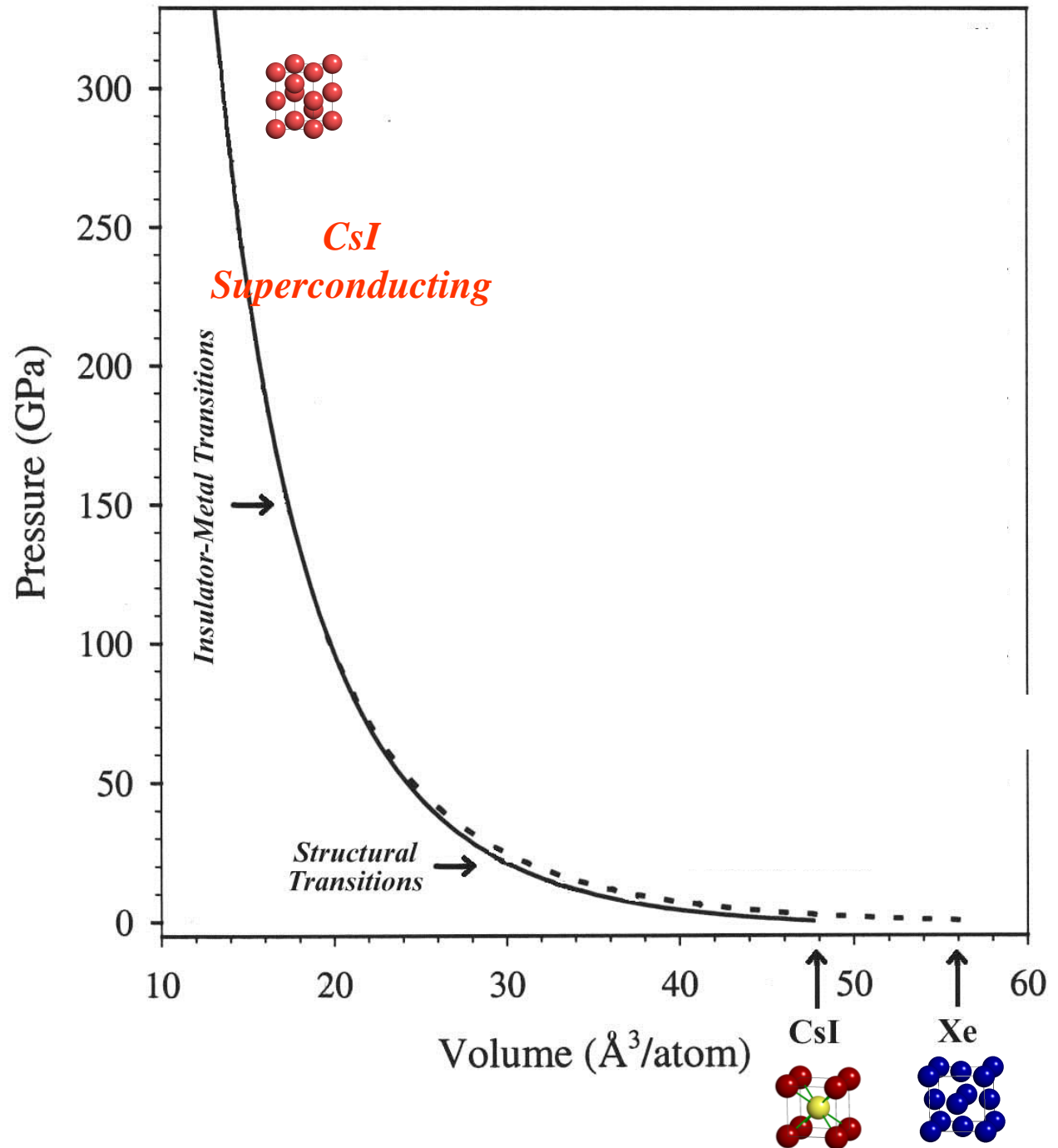


Compressibility



[Cohen et al. *Am. Mineral.* (2000)]

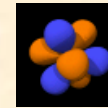
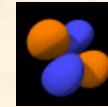
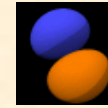
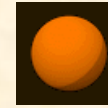
Free Energy Changes and Chemical Bonding



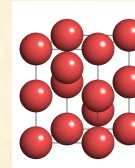
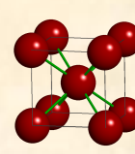
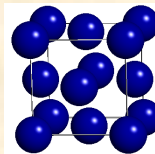
[Hemley and Ashcroft,
Physics Today (1998)]

Periodic Table of the Elements

1 1A		2 Alkaline earth metals 2A										3 Transition metals										4 Transition metals										5 Transition metals										6 Transition metals										7 Transition metals										8 Transition metals										9 Transition metals										10 Transition metals										11 Transition metals										12 Transition metals										13 3A										14 4A										15 5A										16 6A										17 Halogens 7A										18 Noble gases 8A																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
1 H 1.008		3 Li 6.941										4 Be 9.012										11 Na 22.99										12 Mg 24.31										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 101.1										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										58 Ce 140.1										59 Pr 140.9										60 Nd 144.2										61 Pm (145)										62 Sm 150.4										63 Eu 152.0										64 Gd 157.3										65 Tb 158.9										66 Dy 162.5										67 Ho 164.9										68 Er 167.3										69 Tm 168.9										70 Yb 173.0										71 Lu 175.0										90 Th 232.0										91 Pa (231)										92 U 238.0										93 Np (237)										94 Pu (244)										95 Am (243)										96 Cm (247)										97 Bk (247)										98 Cf (251)										99 Es (252)										100 Fm (257)										101 Md (258)										102 No (259)										103 Lr (260)									

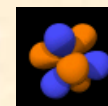
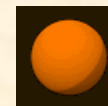


- Filling of s , p , d , ... orbitals
- Simple structures



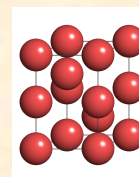
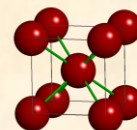
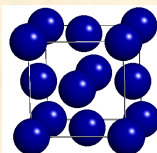
PRESSURE

PRESSURE

• Filling of s, p, d, \dots orbitals

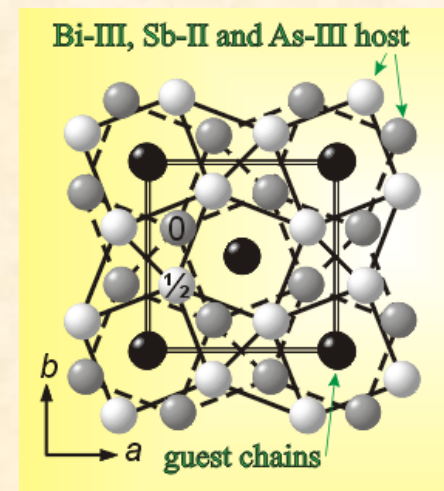
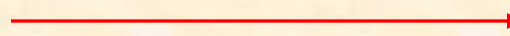
• Simple structures



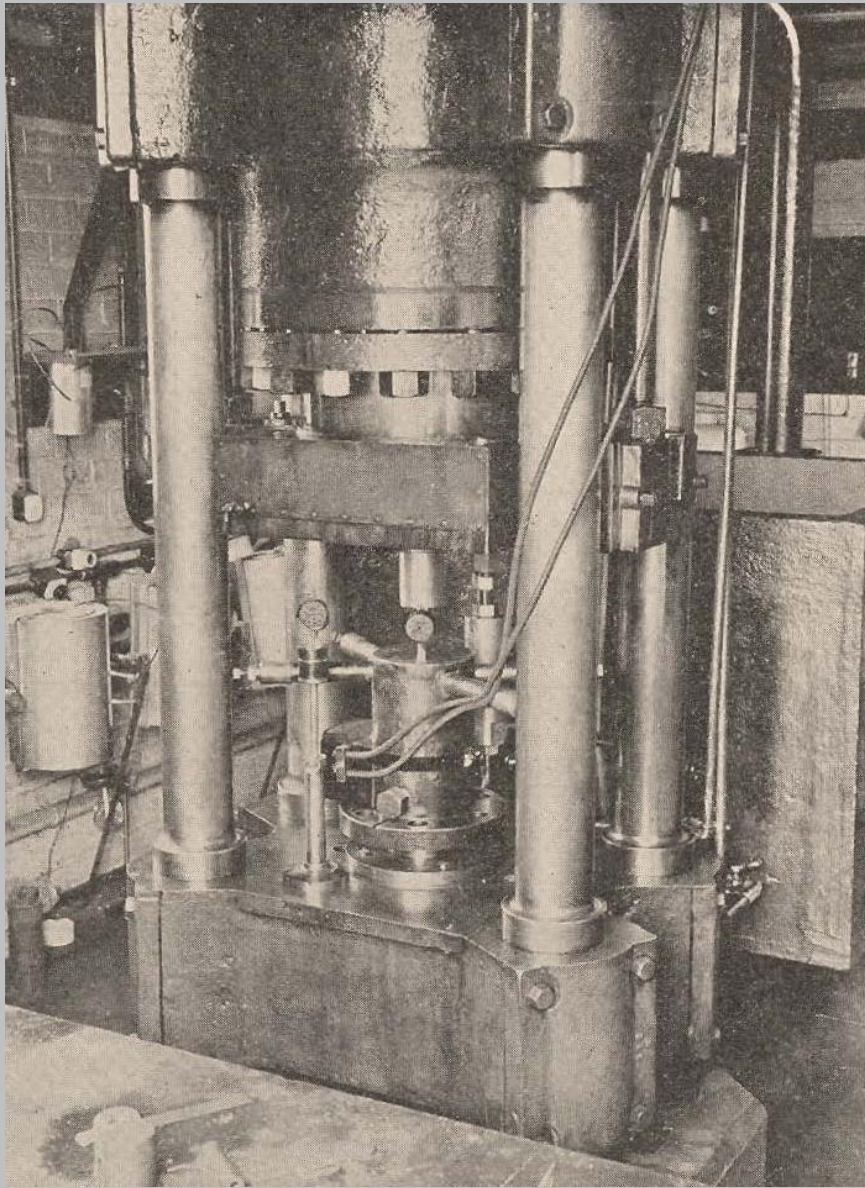
Under Pressure

• Orbital hybridization (e.g., $s \rightarrow d$)

• Complex structures



DIAMOND ANVIL CELL



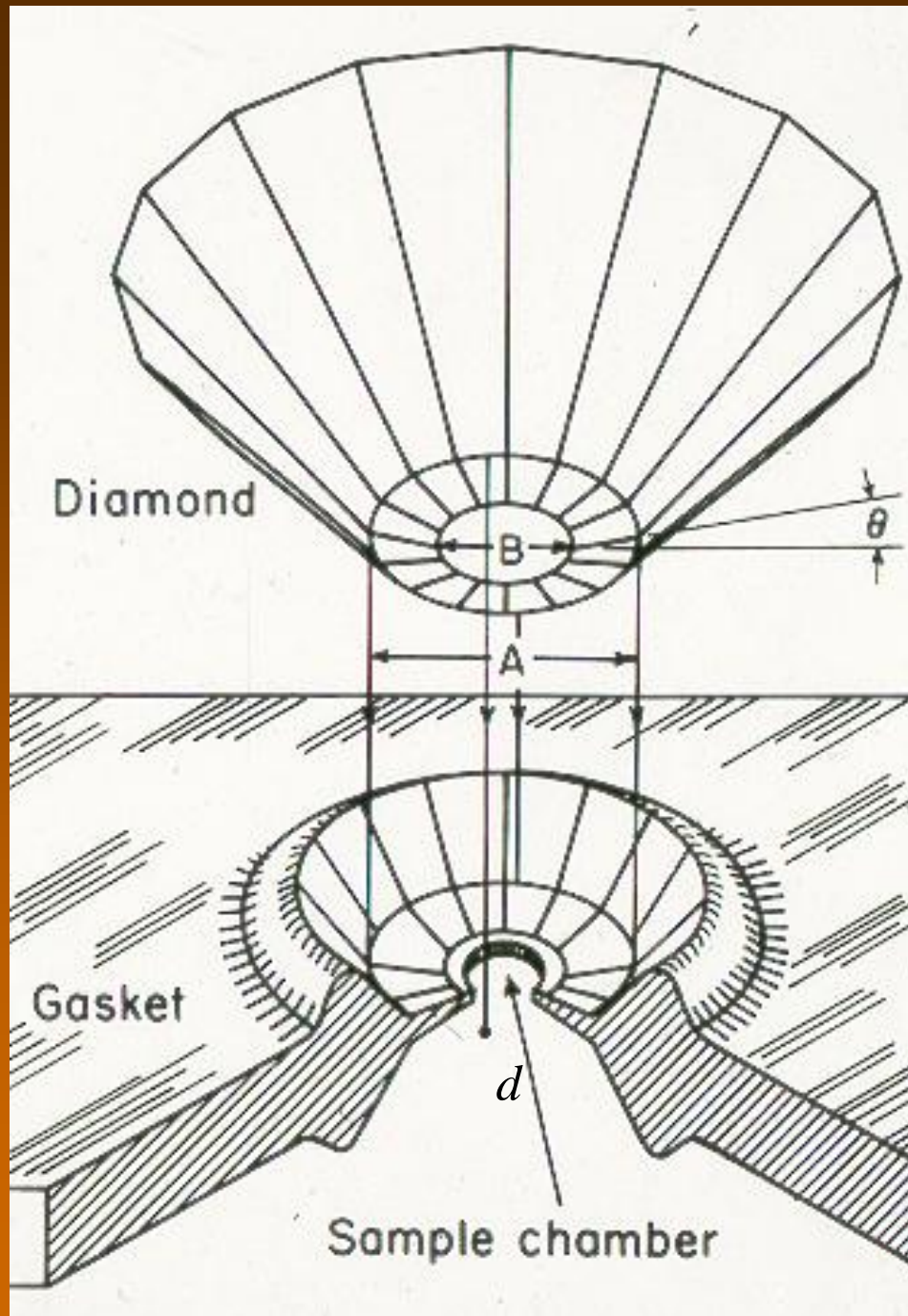
[E. D. Williamson, *J. Franklin Inst.* (1922)]



Diamond

- **Strength**
- **Transparency**

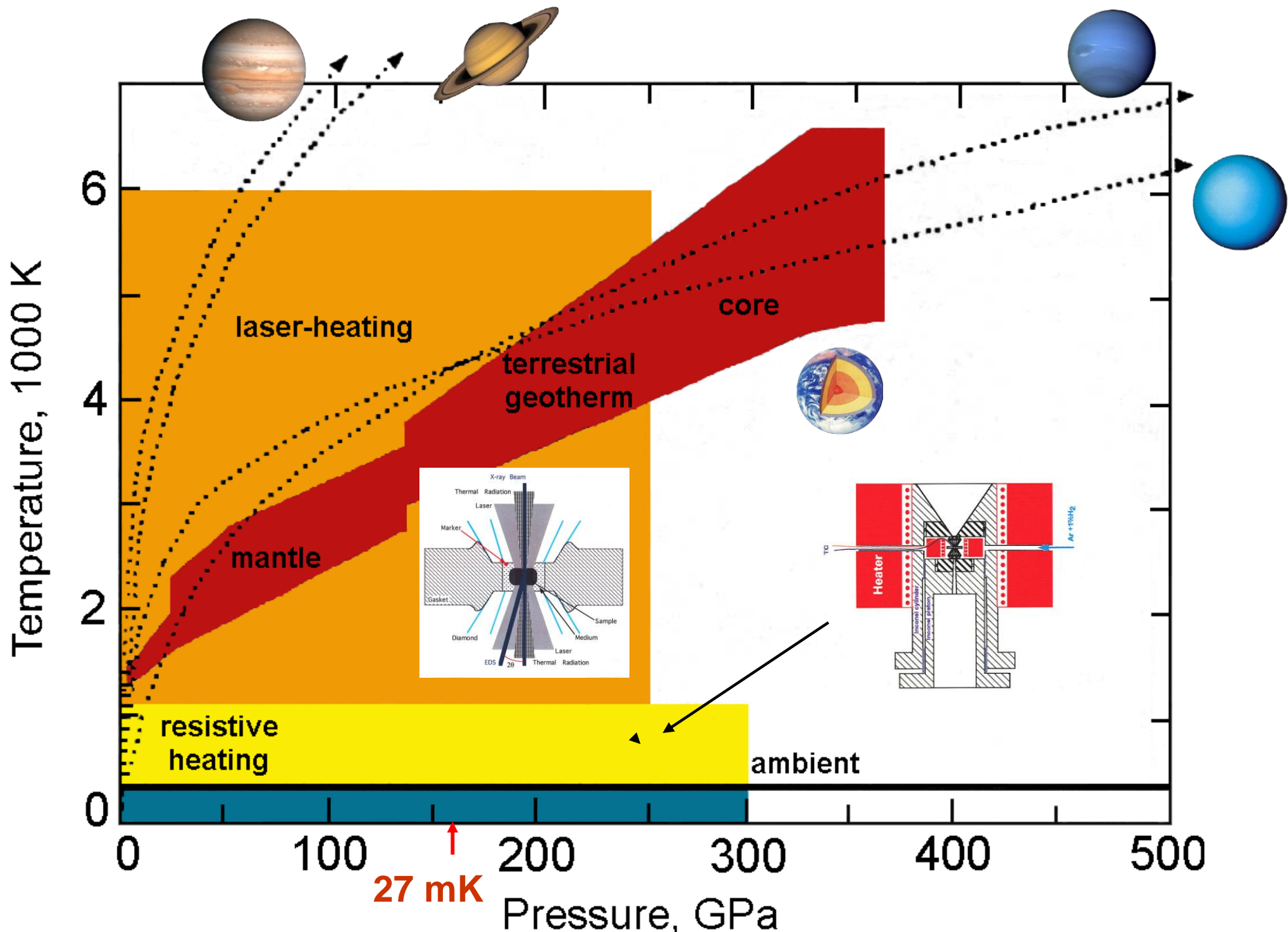
MEGABAR DIAMOND ANVIL CELL



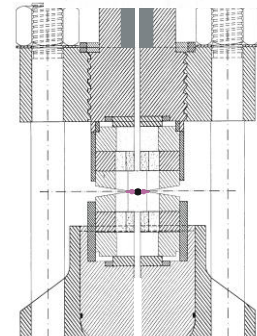
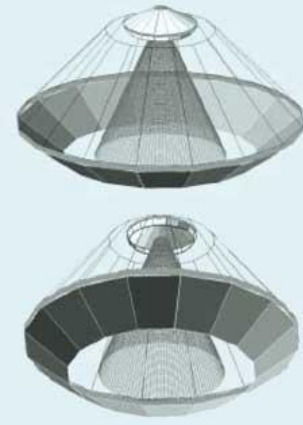
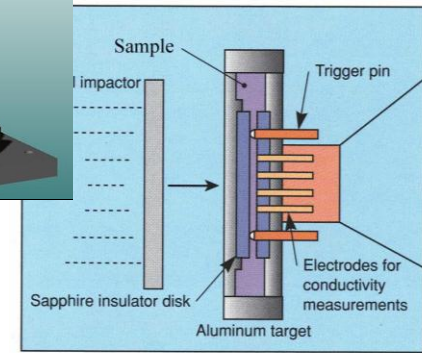
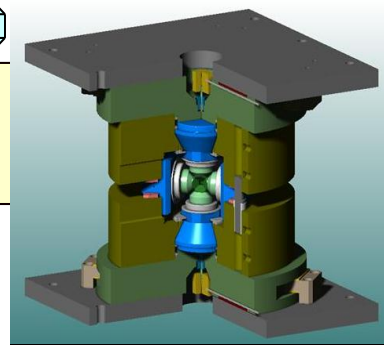
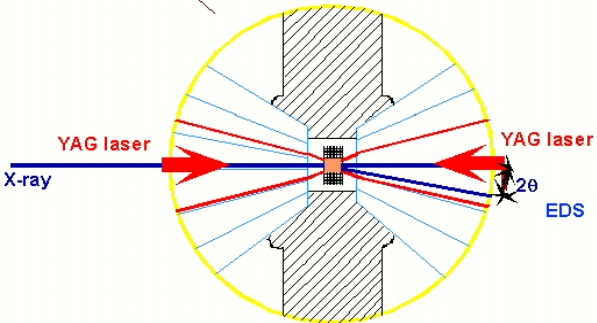
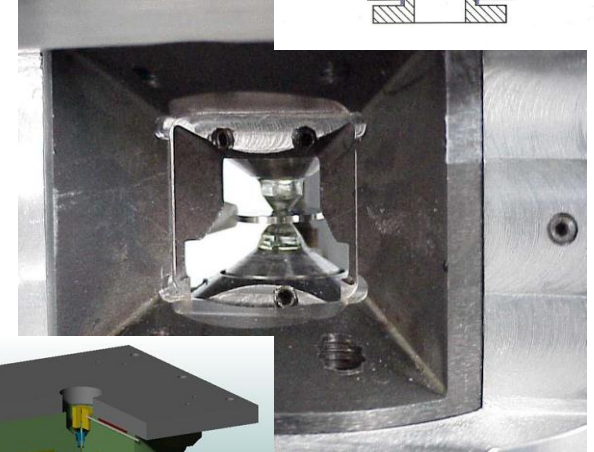
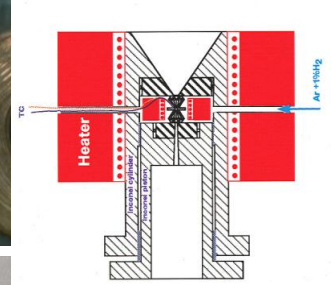
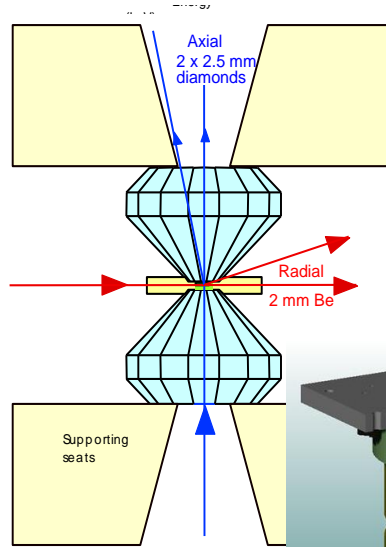
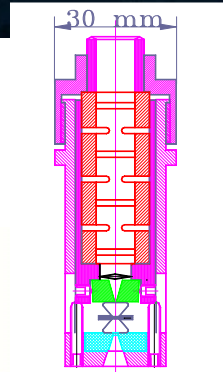
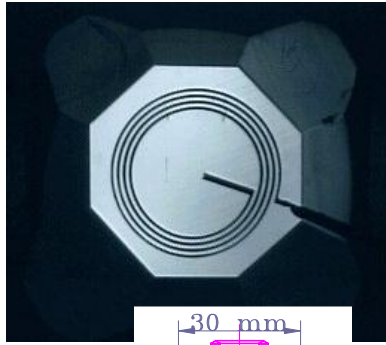
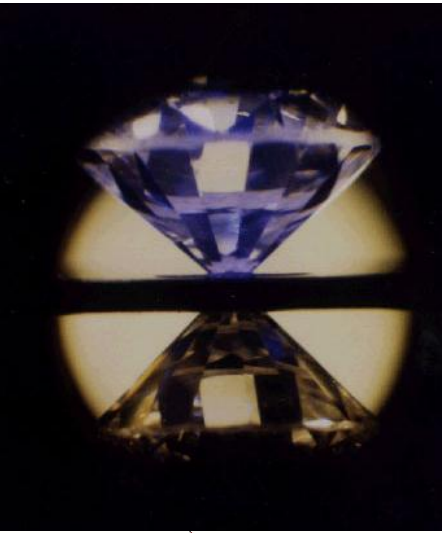
$$P = F/A$$

<i>P</i>	<i>d</i>	Volume
50 GPa	~200 μm	~10 nl (10 ⁻⁹ l)
200 GPa	~20 μm	~1 pl (10 ⁻¹² l)

EXTREME STATIC PRESSURES AND TEMPERATURES

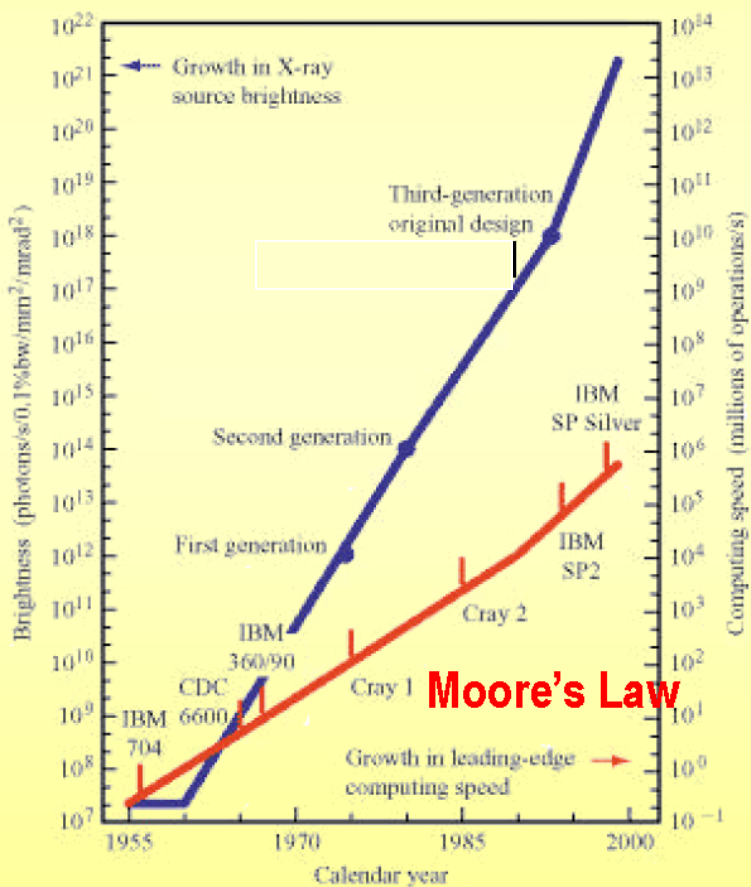


High-Pressure Technology: TOOLS FOR IN SITU MEASUREMENTS

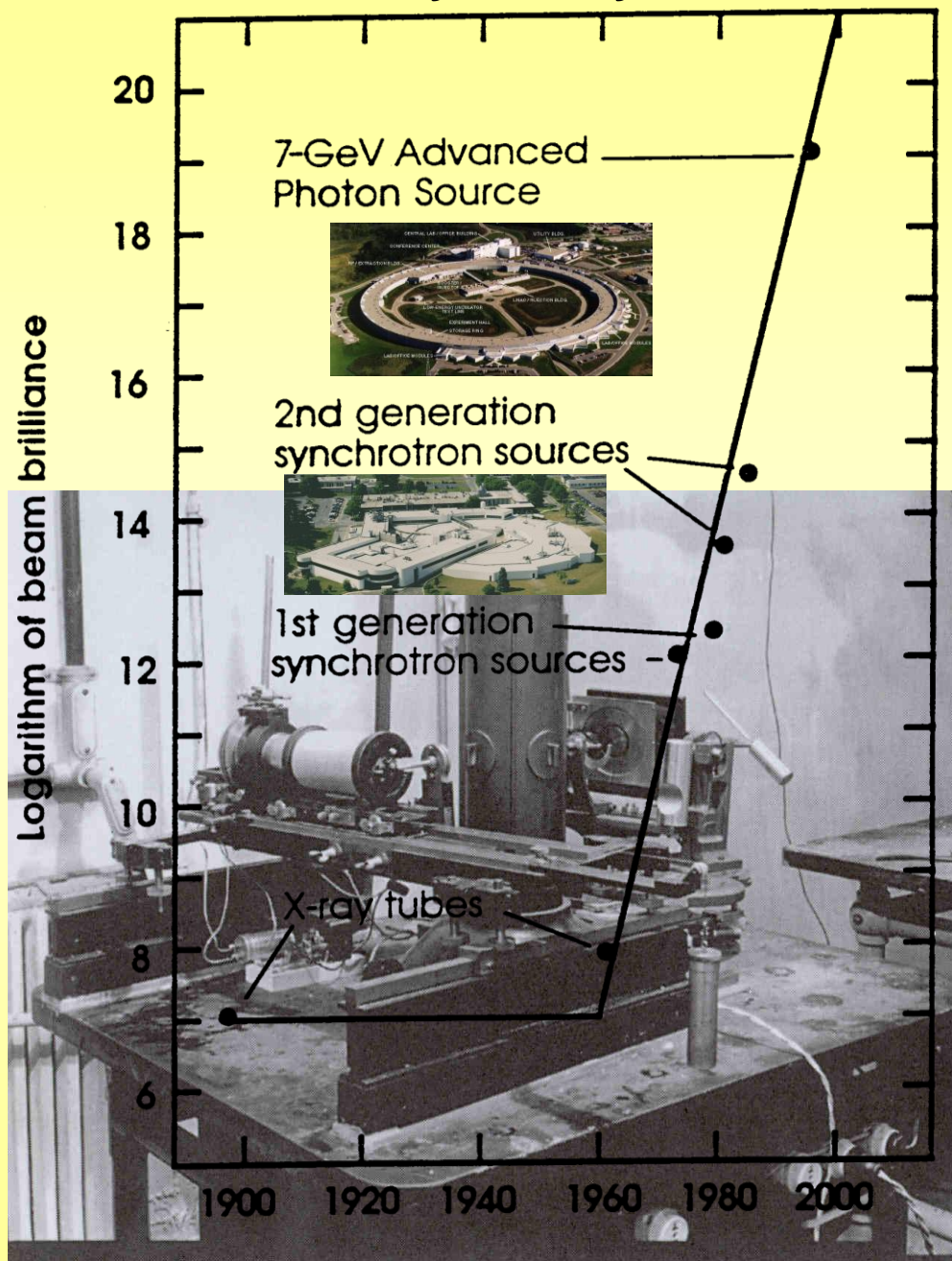


Evolution of Light Sources

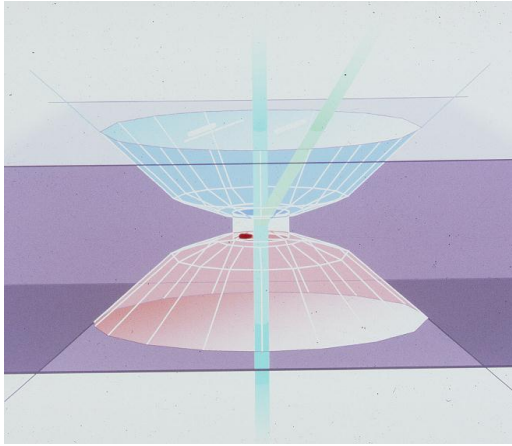
- X-ray to infrared (diffraction limited)



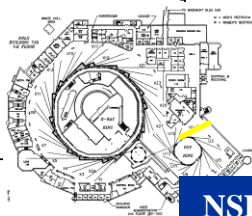
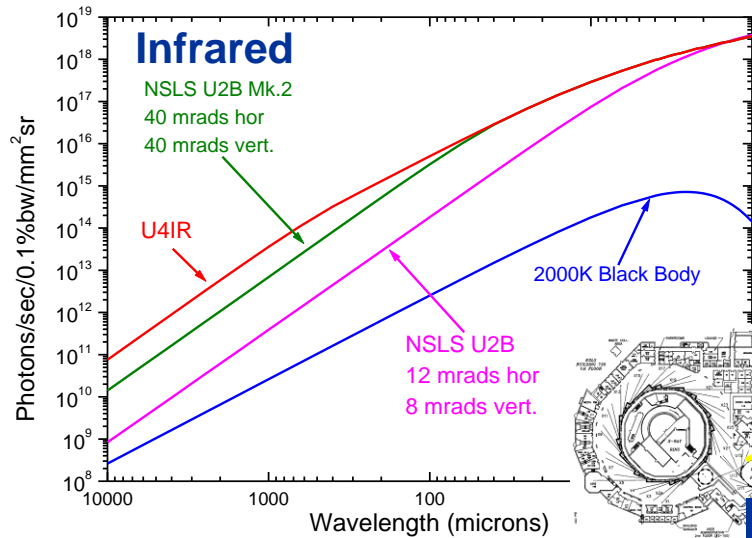
History of X-ray Sources



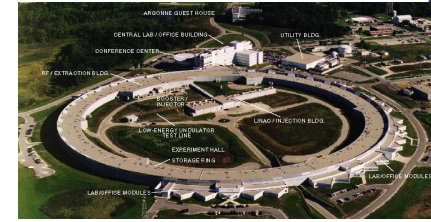
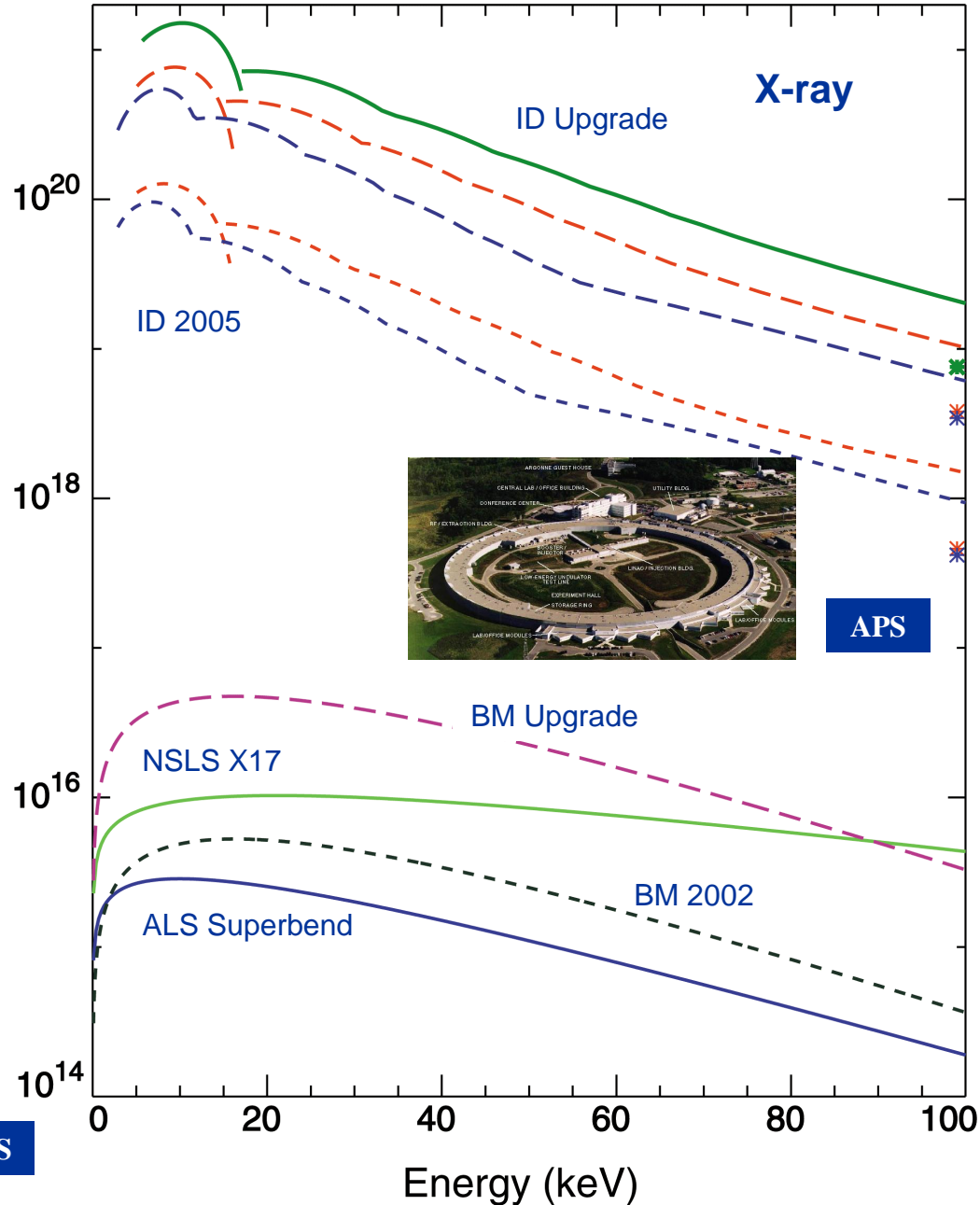
Need for High Brightness Microbeams



- X-ray focused to $< 1 \mu\text{m}$
- Infrared (diffraction limited)



On-Axis Brilliance ($\text{ph/s/mrad}^2/\text{mm}^2/0.1\%bw$)

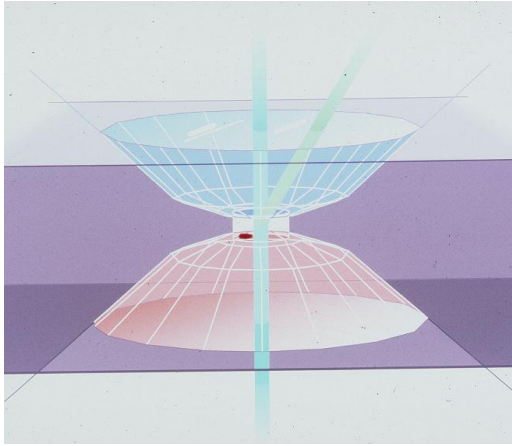


APS

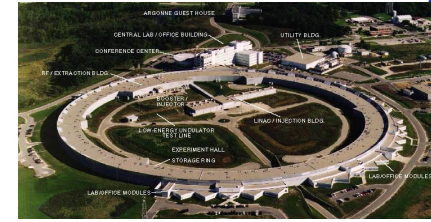
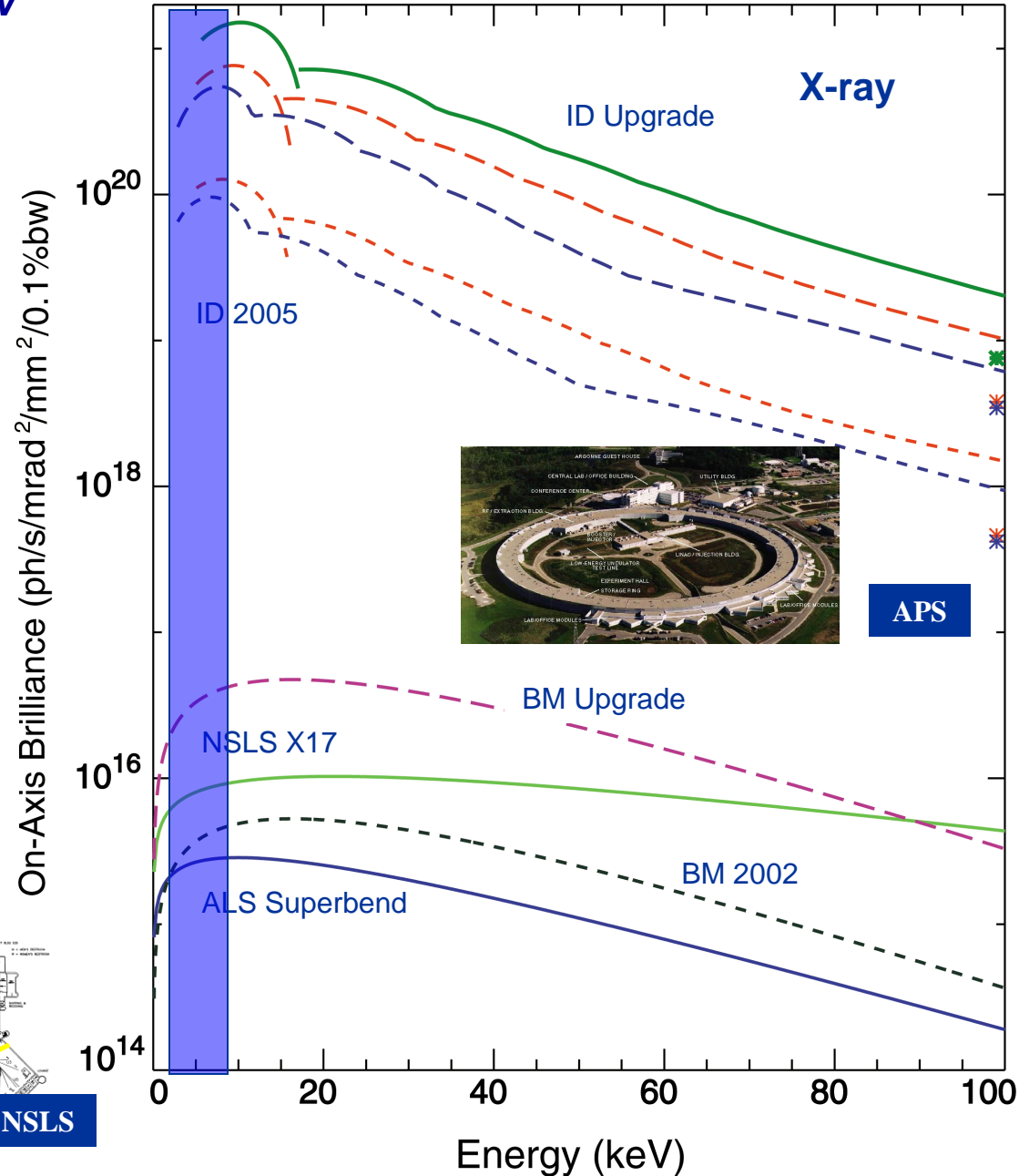
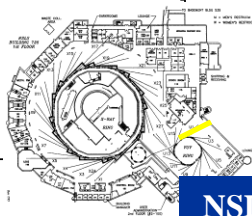
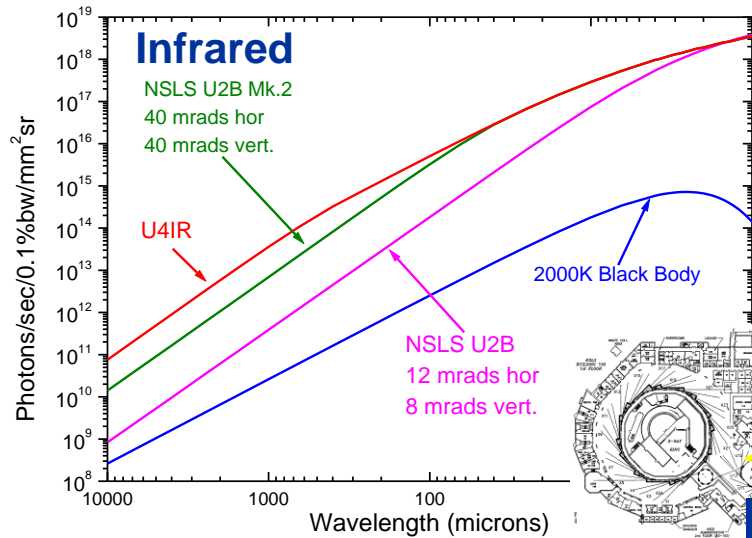
NSLS

Need for High Brightness Microbeams

Diamond opaque at >5 eV to ~ 10 keV



- X-ray focused to $< 1 \mu\text{m}$
- Infrared (diffraction limited)



HOW DO WE KNOW THE PRESSURE?

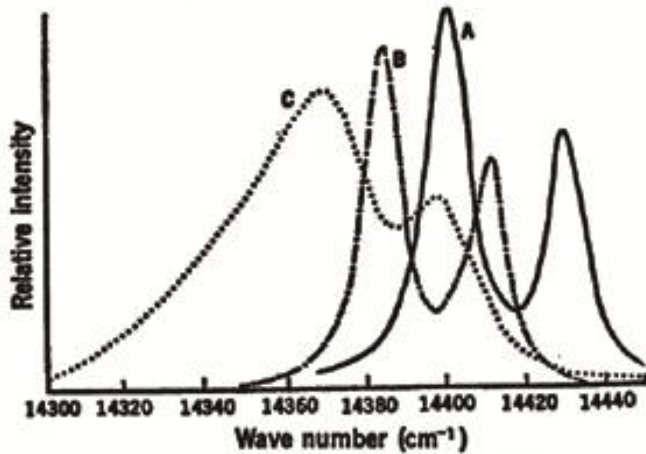


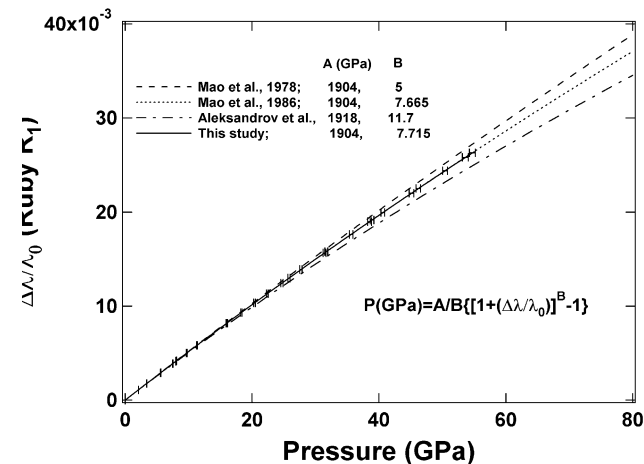
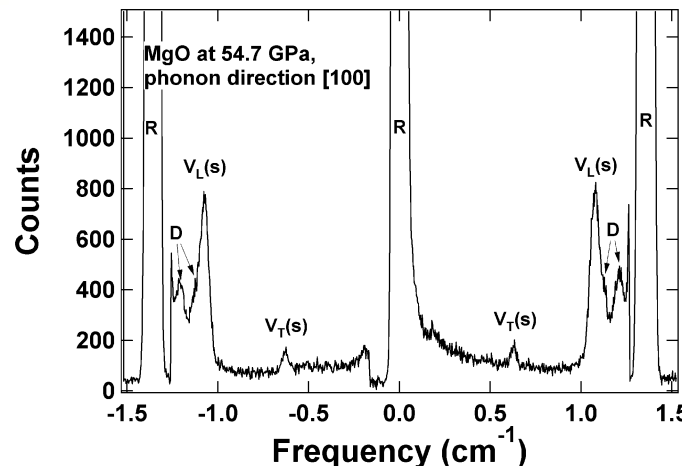
Fig. 1. The R-line luminescence spectra of a crystal of ruby in the diamond cell: curve A, ruby sample at ambient atmospheric pressure; curve B, ruby sample in a mixture of ices VI and VII at approximately 22.3 kbar; and curve C, ruby sample in a mixture of CCl₄ III and IV at an average pressure of 40 kbar (nonhydrostatic environment). (Peak heights are arbitrary.)

- Original ruby scale to 10 GPa produced in 1972 (NBS).
- Volume of metals from diffraction using shock-wave equations of state; pressure scales to >200 GPa in 1978 (Carnegie)
- Primary pressure scales measuring volume and bulk modulus in 2000.

Brillouin scattering combined with x-ray diffraction; confirms quasihydrostatic ruby scale (1%)

[Forman et al., *Science* (1972); Piermarini et al., *J. Appl. Phys.* (1975)].

[Zha et al., *Proc. Nat. Acad. Sci.* (2003)].



Brave New World Under Pressure

- **Novel transformations: solids, liquids, glasses**
- **Structures: unexpected complexity**
- **Molecules break down, but new ones form**
- **Novel electronic and magnetic phenomena**
- **New recoverable materials**
- **Materials basis for understanding planets**
- **Structure-function in biological systems**

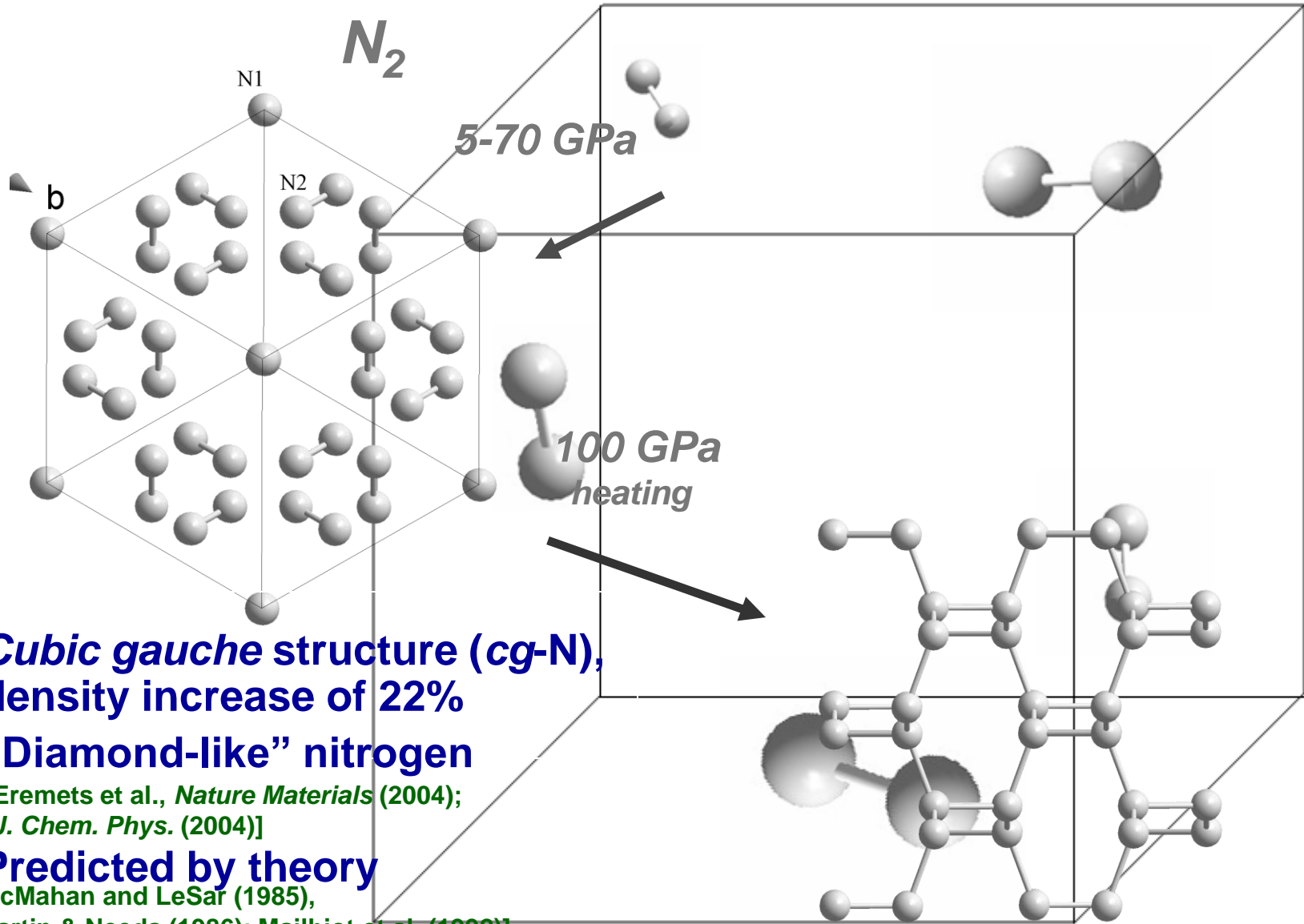
EXAMPLES:

1. 'Simple' diatomics
2. Dense hydrogen
3. Elemental metals
4. Polyatomic systems
5. Van der Waals compounds
6. Transforming carbon

THEMES

- *Surprising structures and bonding*
- *Novel transitions*
- *New techniques*
- *Theory and experiment*
- *Future developments*

'Simple' diatomics: high-pressure behavior of nitrogen



- **Cubic gauche structure (cg-N), density increase of 22%**

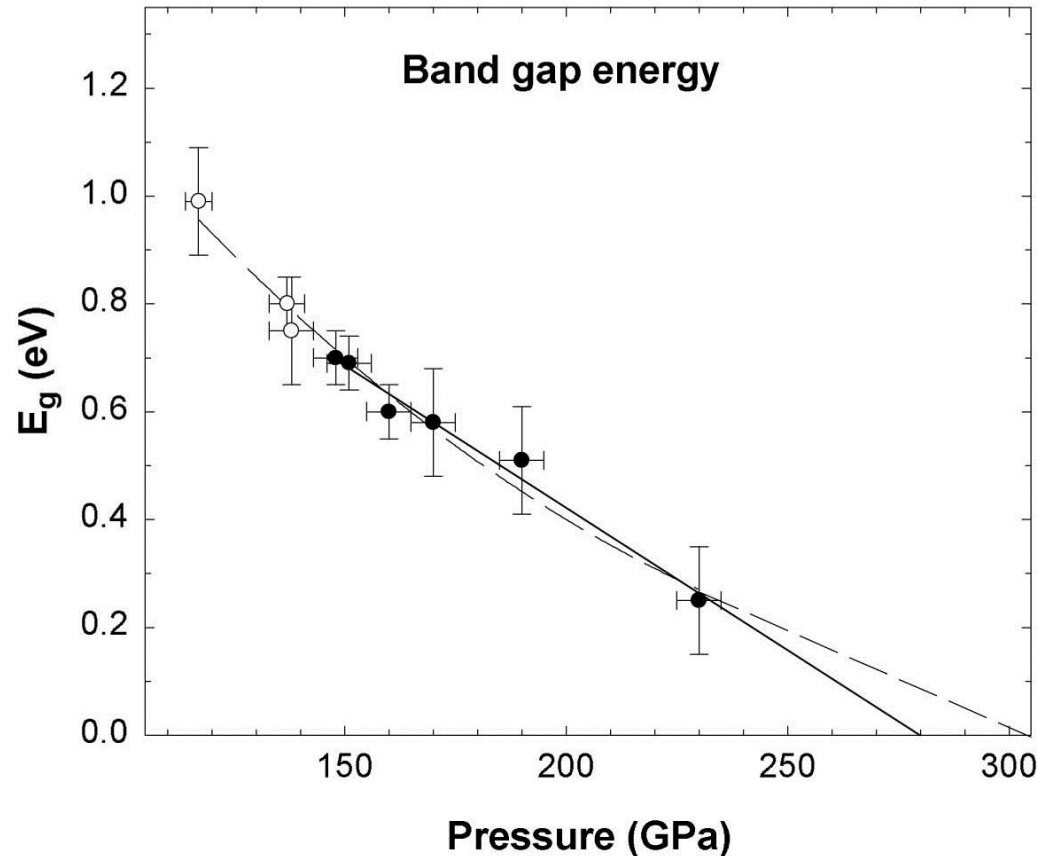
- **“Diamond-like” nitrogen**

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

- **Predicted by theory**

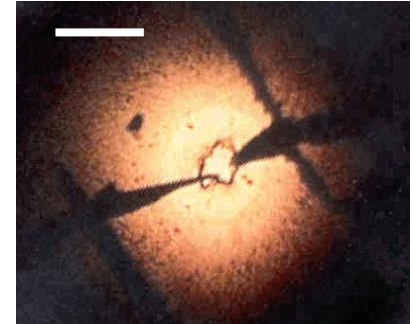
[McMahan and LeSar (1985),
Martin & Needs (1986); Mailhiot et al. (1992)]

Non-molecular 'polymeric nitrogen' is semiconducting above 230 GPa

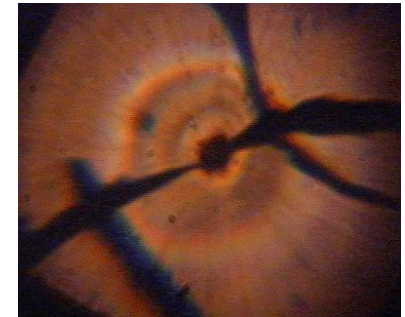


50 μm

75 GPa



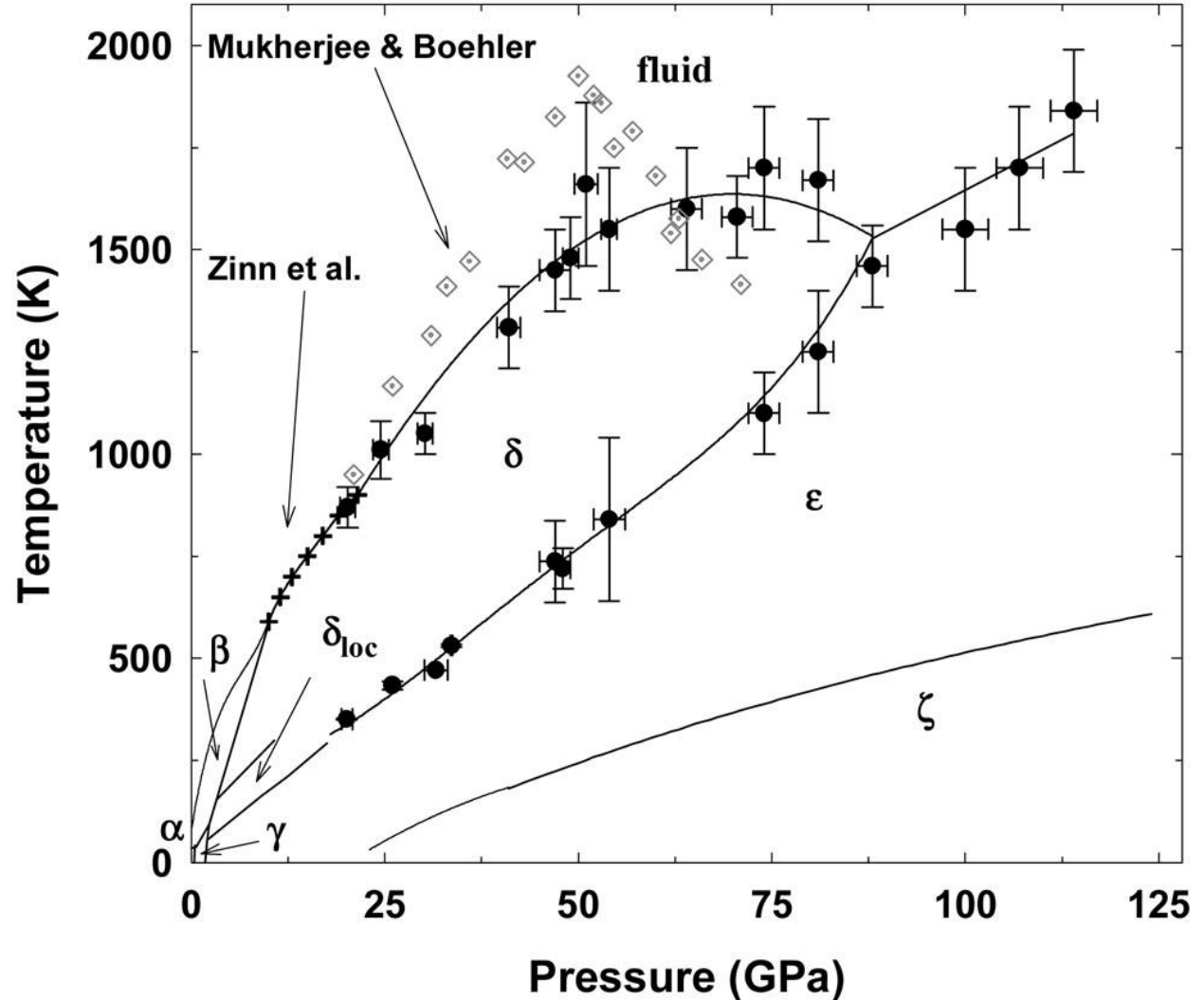
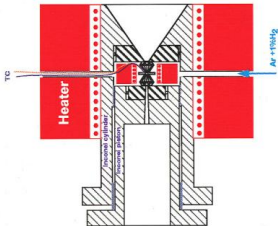
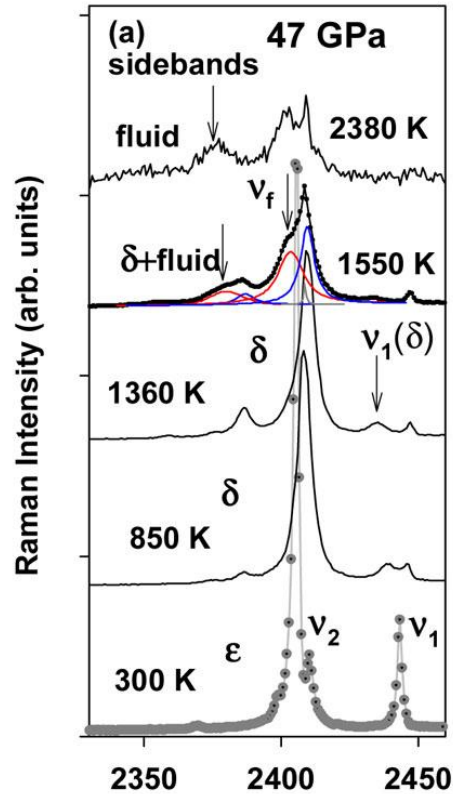
193 GPa



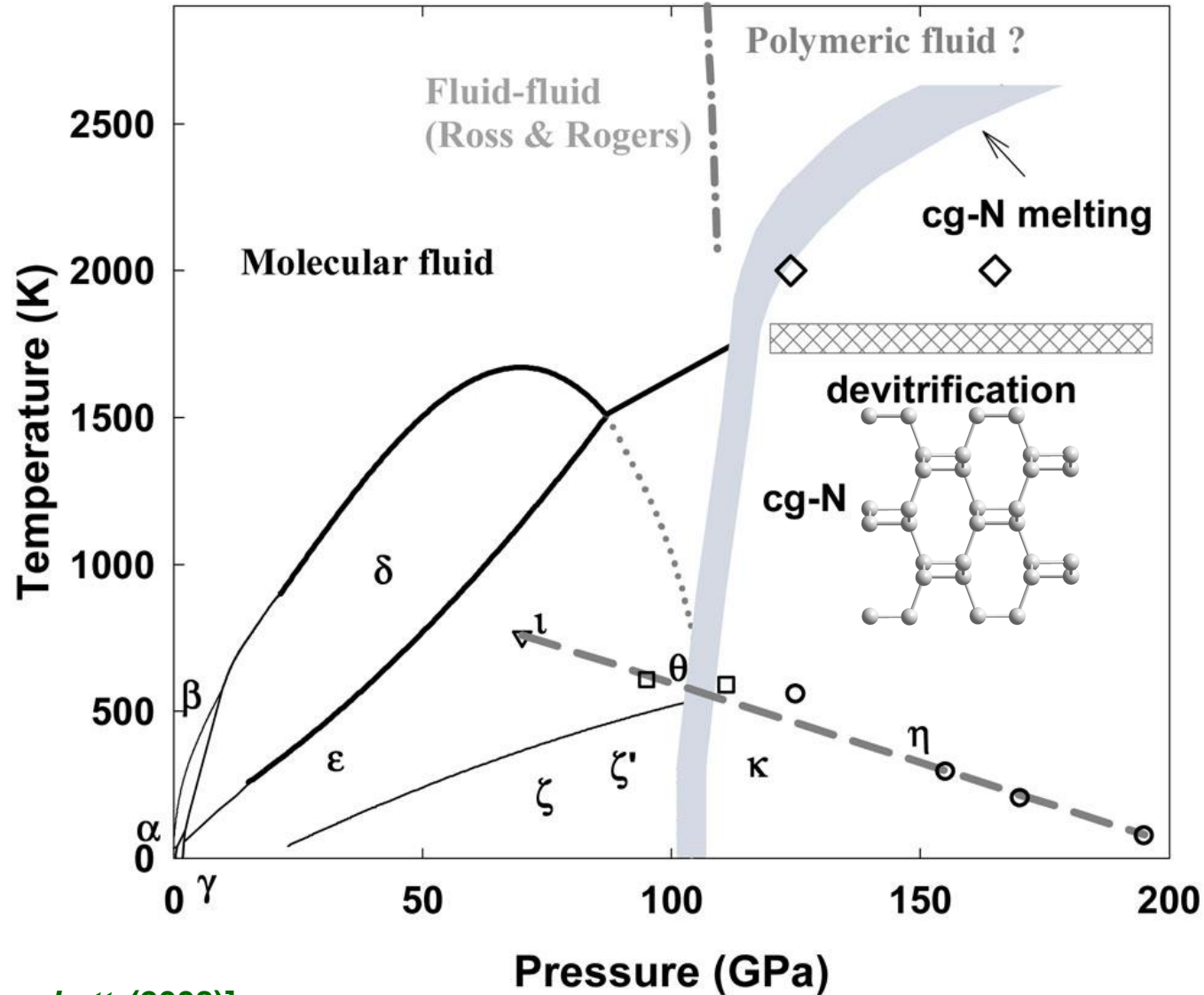
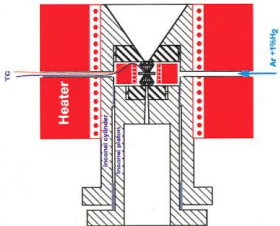
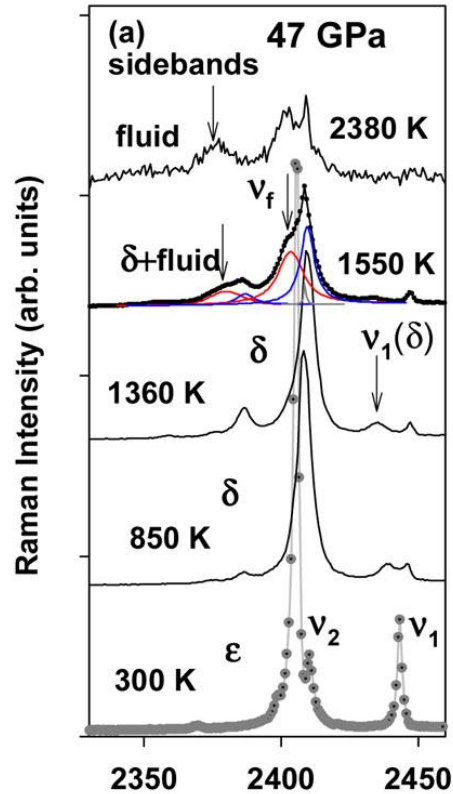
- Optical (IR) absorption and electrical conductivity
- Possible band gap closure at 270 GPa

[Goncharov *et al.*, *Phys. Rev. Lett.* (2000);
Eremets *et al.*, *Nature* (2001)]

New observations of the phase and reaction diagram of nitrogen

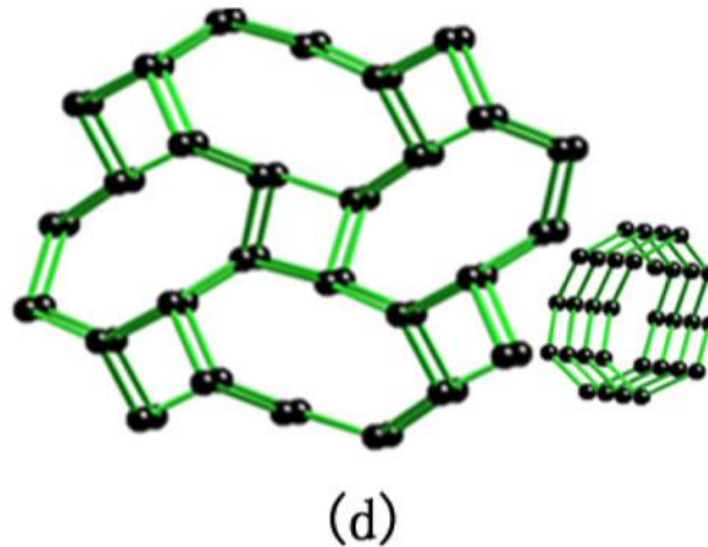
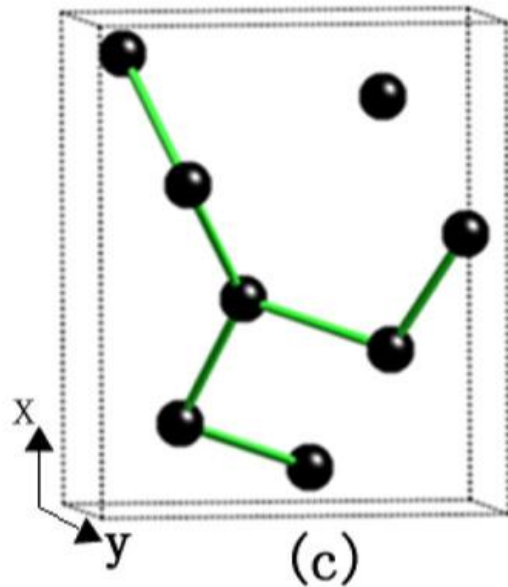
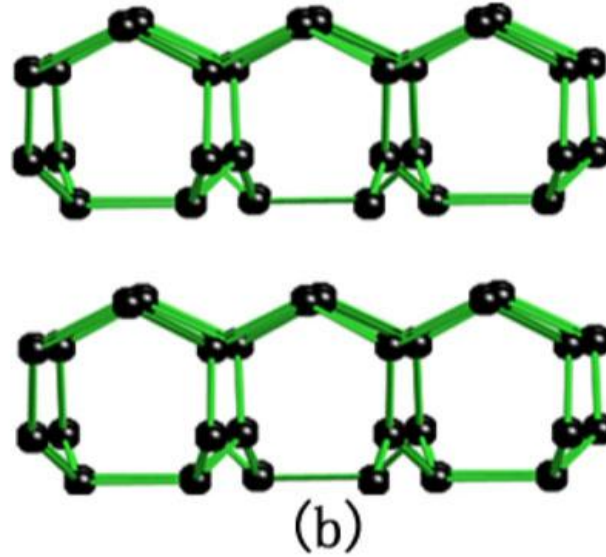
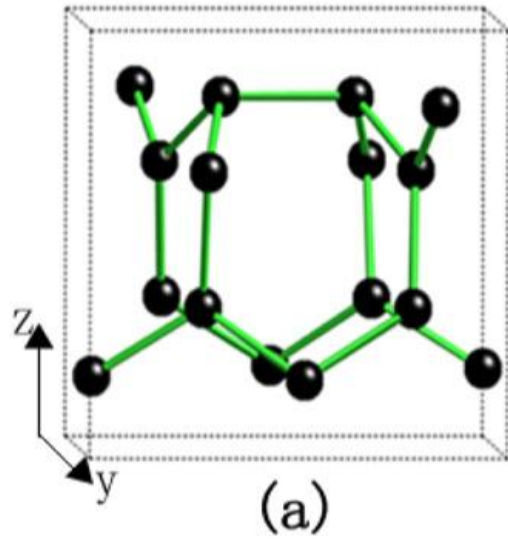


New observations of the phase and reaction diagram of nitrogen



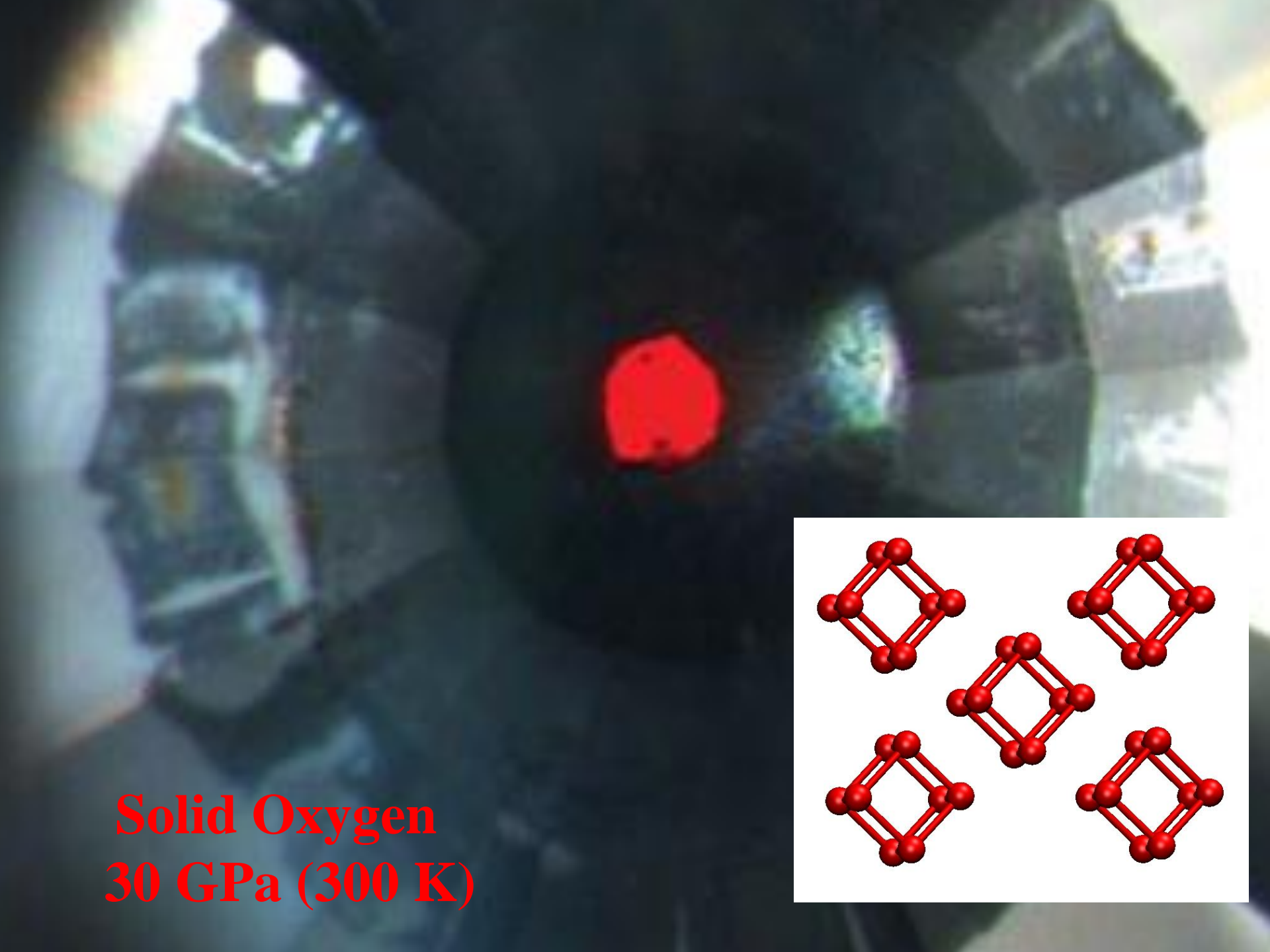
[Goncharov *et al.*, *Phys. Rev. Lett.* (2008)]

Theoretical predictions of higher pressure behavior of nitrogen

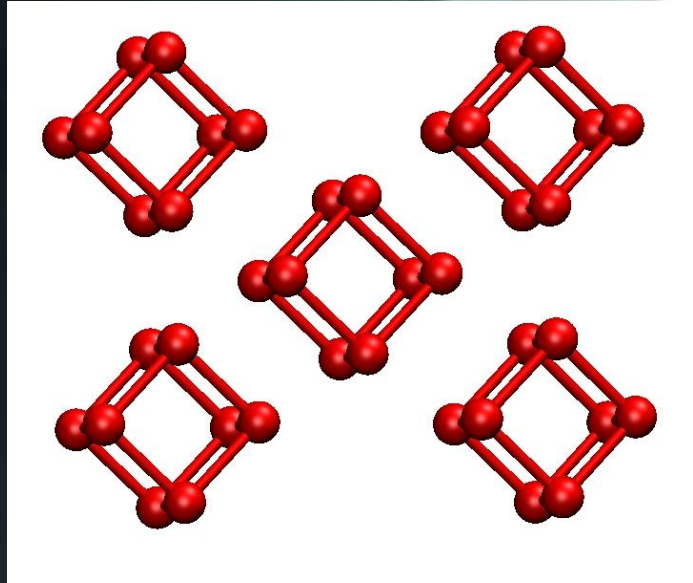


[Ma et al., *Phys. Rev. Lett.* (2009)]

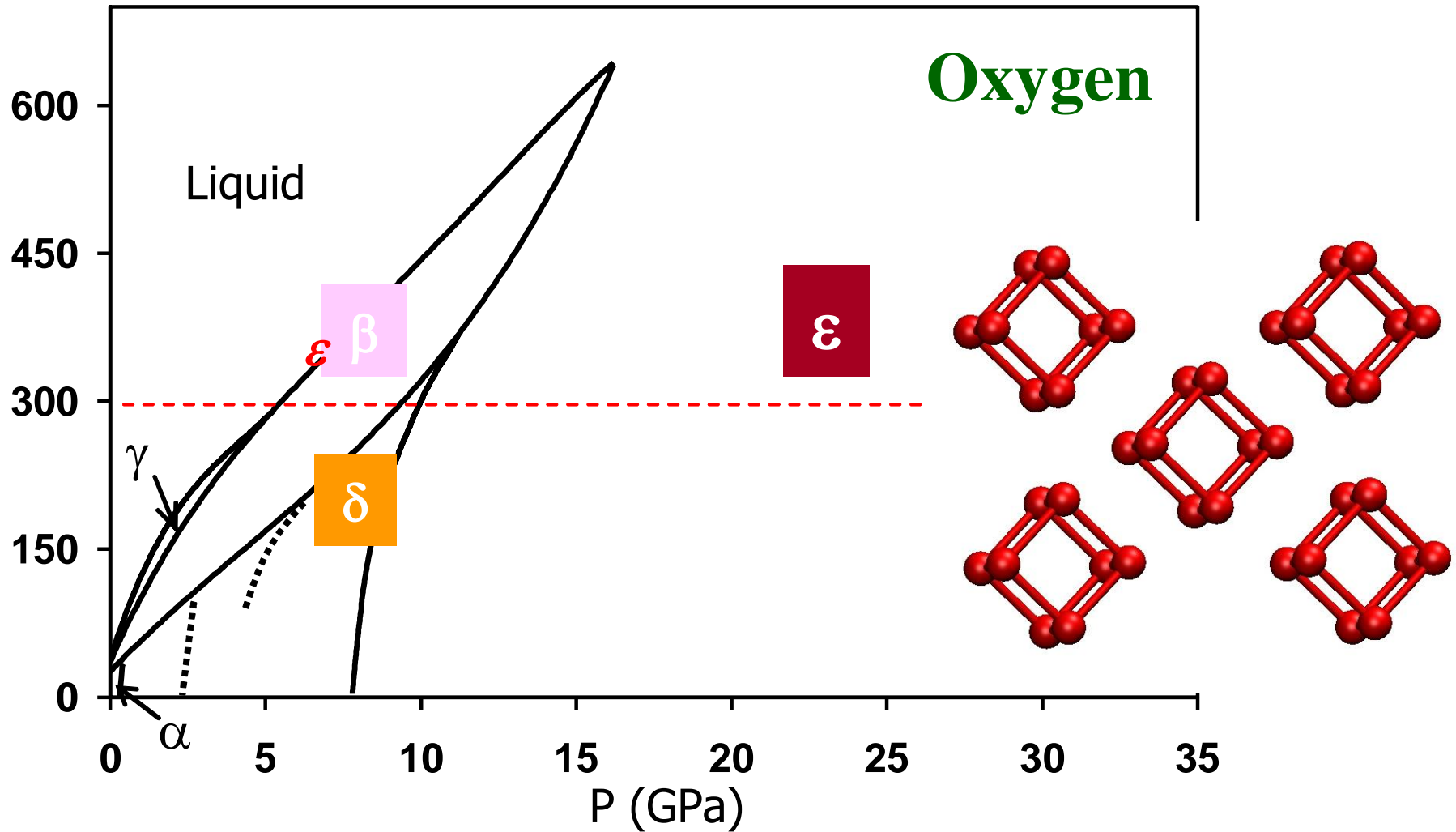
[see also, Bonev et al., *Phys. Rev. Lett.* (2008)]



Solid Oxygen
30 GPa (300 K)

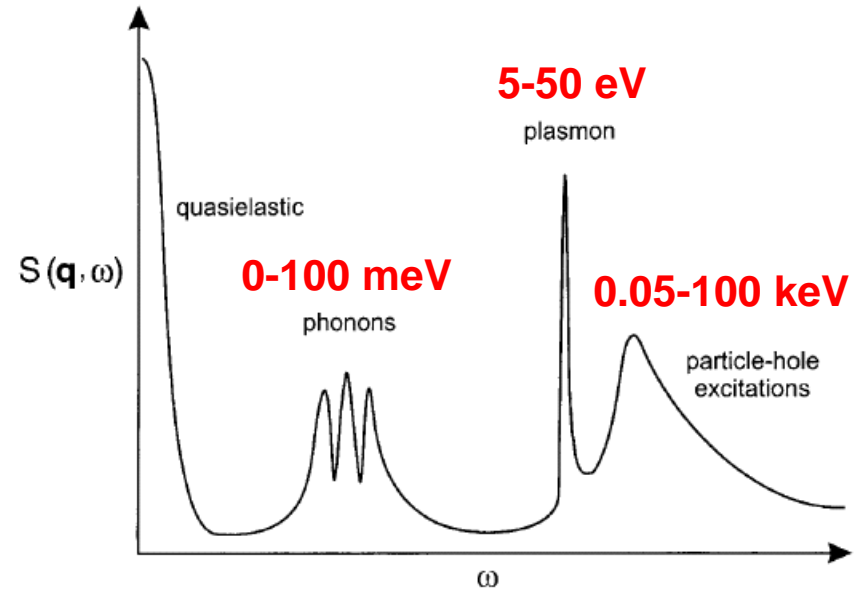
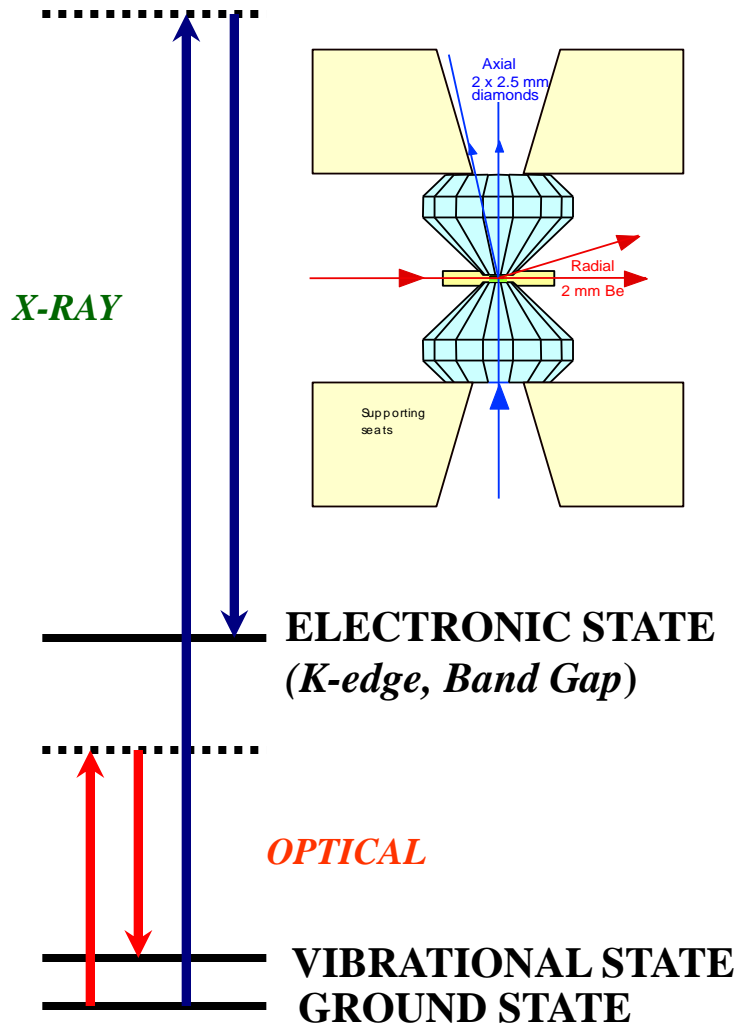


Origin of stability of ϵ -oxygen structure



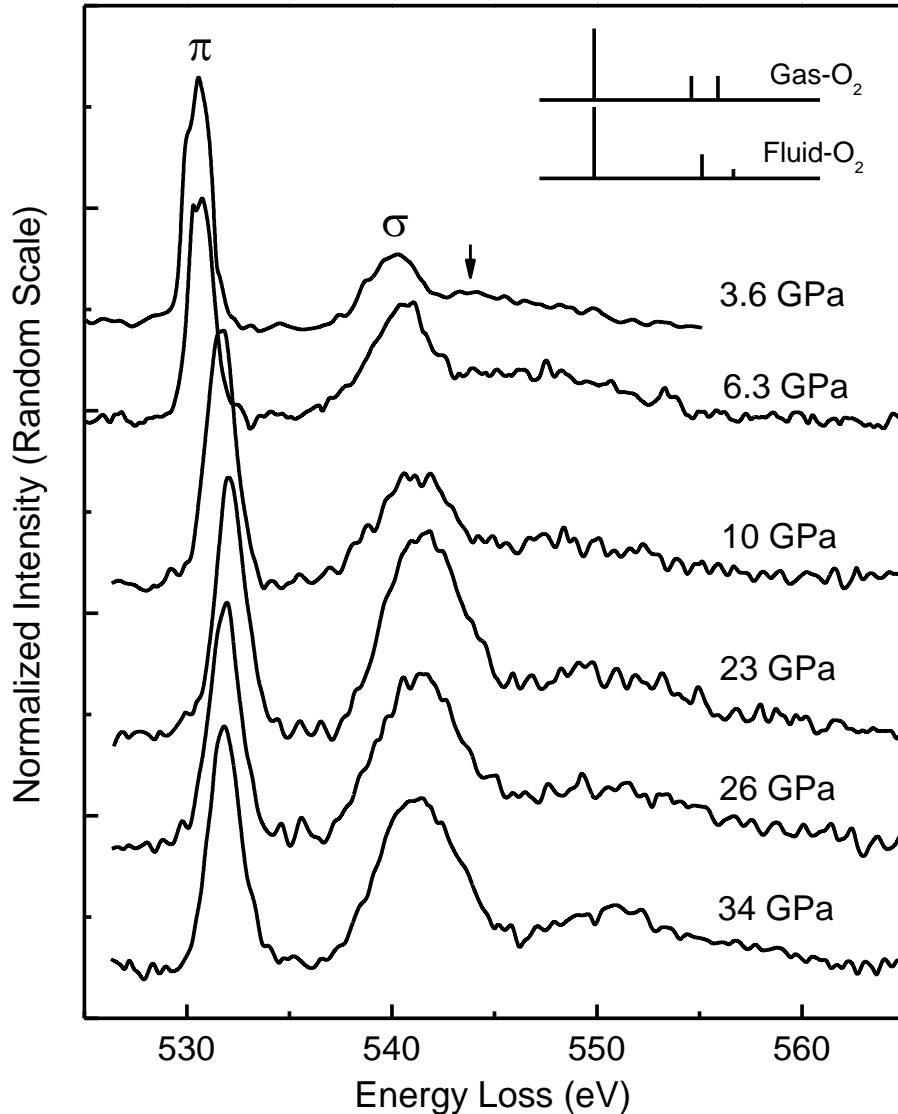
[Lundegaard et al., *Nature* (2006);
Fujihishi et al., *Phys. Rev. Lett.* (2006)]

Pressure dependence of bonding and electronic structure from inelastic x-ray scattering

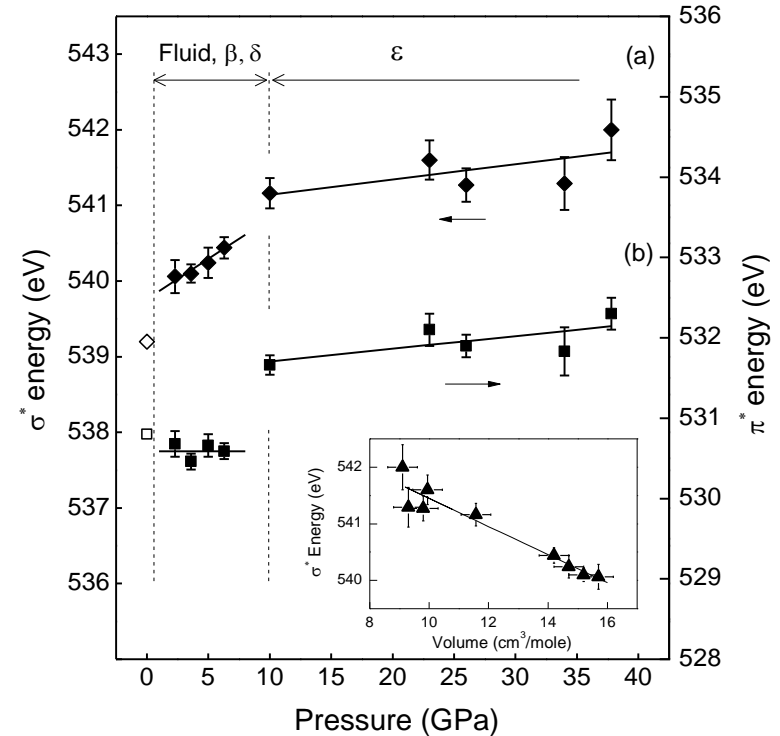


- **Diamond window**
opaque above 5 eV
- **Q dependence**
- **Scatter into excited states**

X-ray Raman reveals the origin of unusual bonding in dense oxygen



[Meng et al., *PNAS* (2008)]

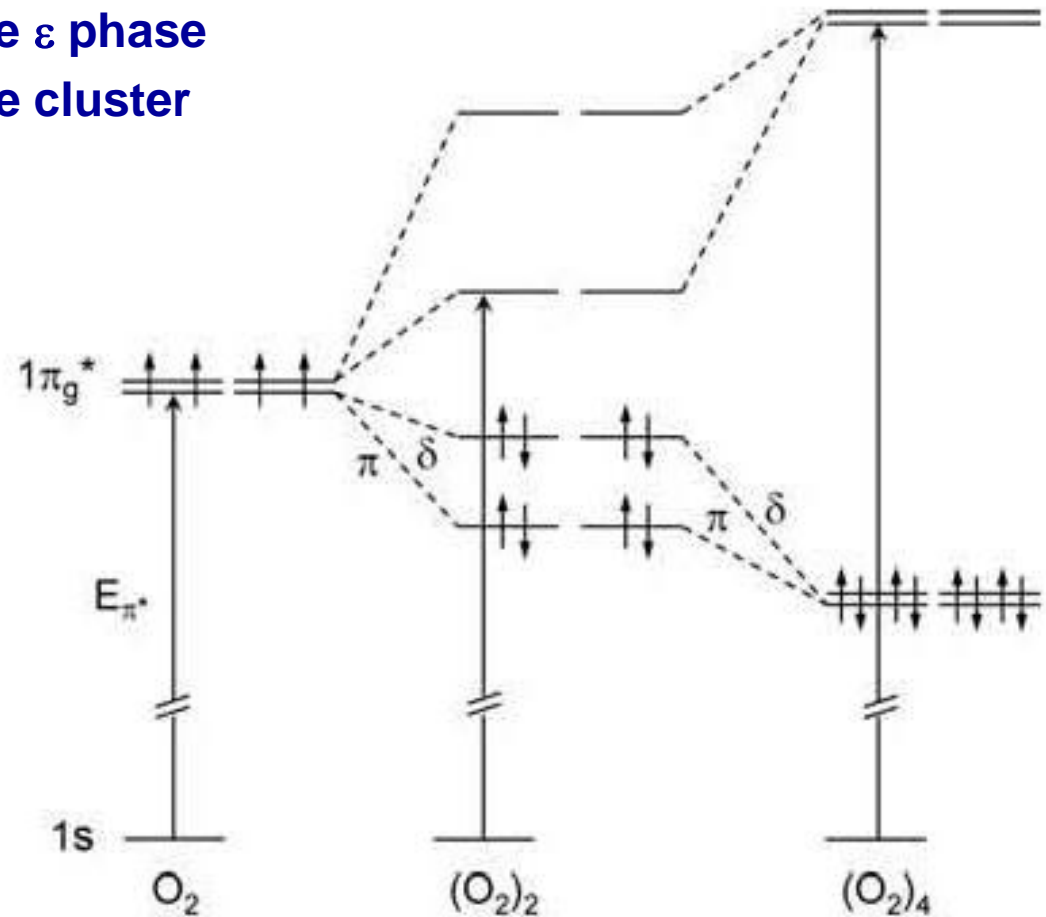
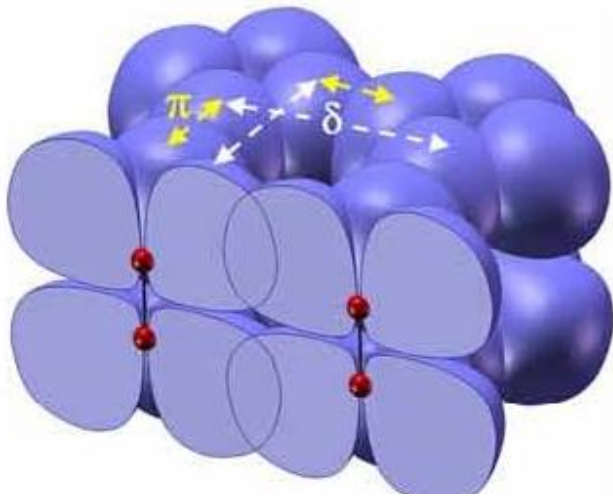


- **Molecules interact through half-filled $1\pi_g^*$ orbital in the low-pressure phases**

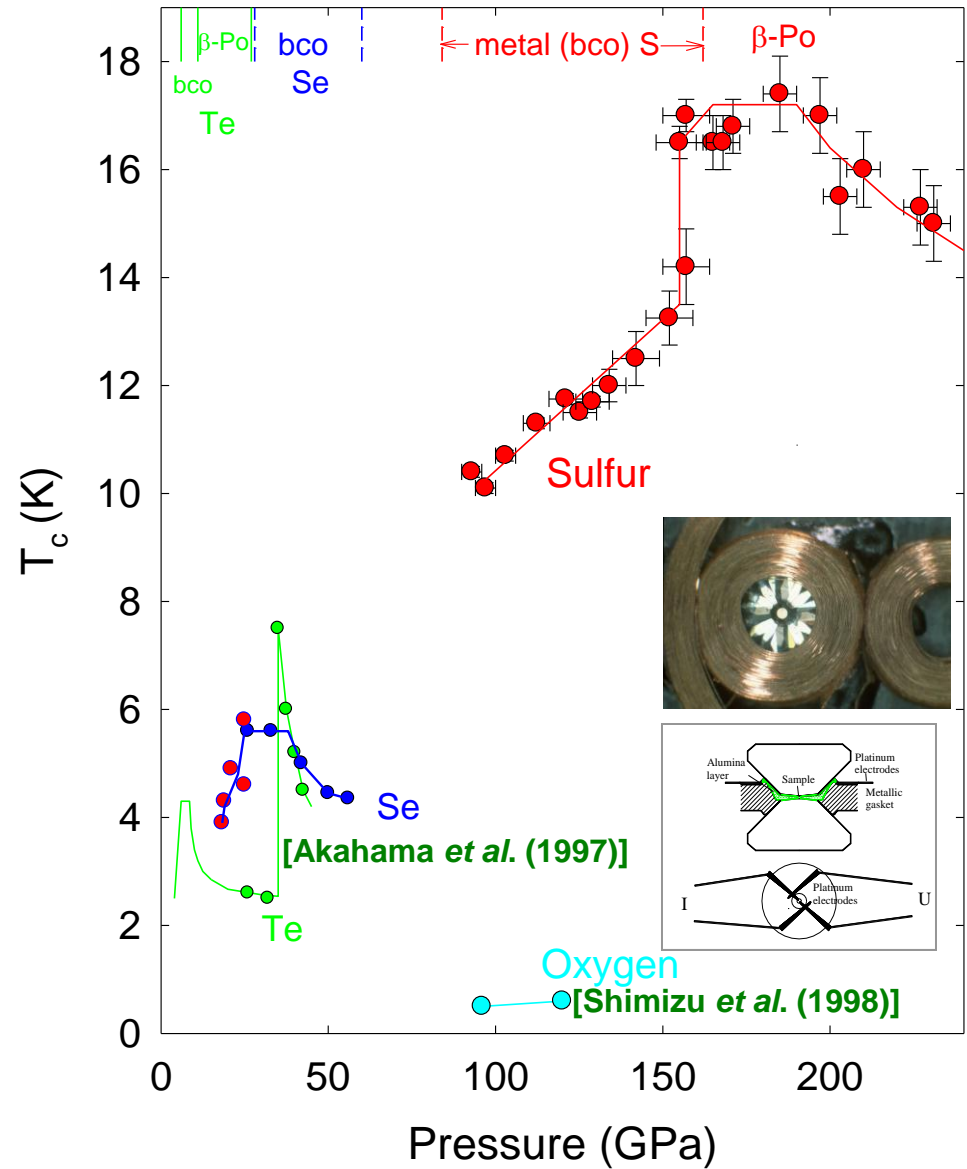
X-ray Raman reveals the origin of unusual bonding in dense oxygen



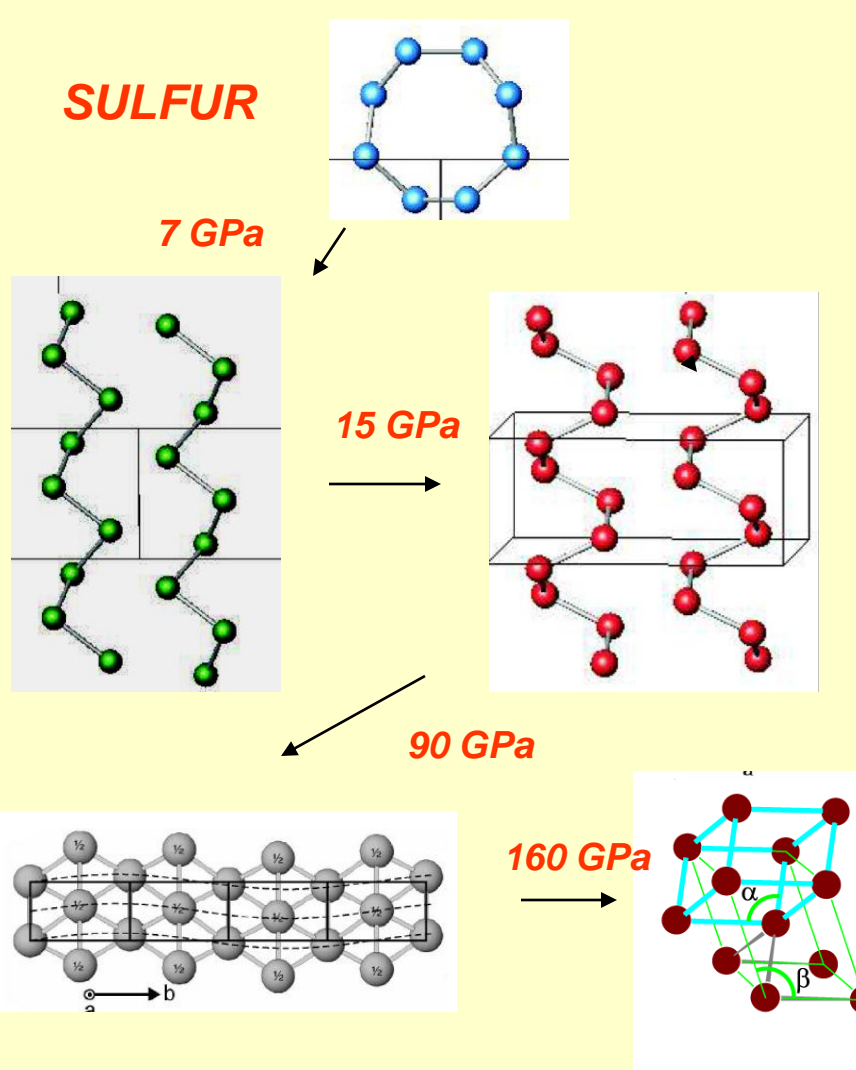
- Increasing orbital overlap with pressure
- Intermolecular π^* -bonding in $(\text{O}_2)_4$ cluster
- Closed-shell interactions in the ϵ phase
- Stabilization of a four-molecule cluster



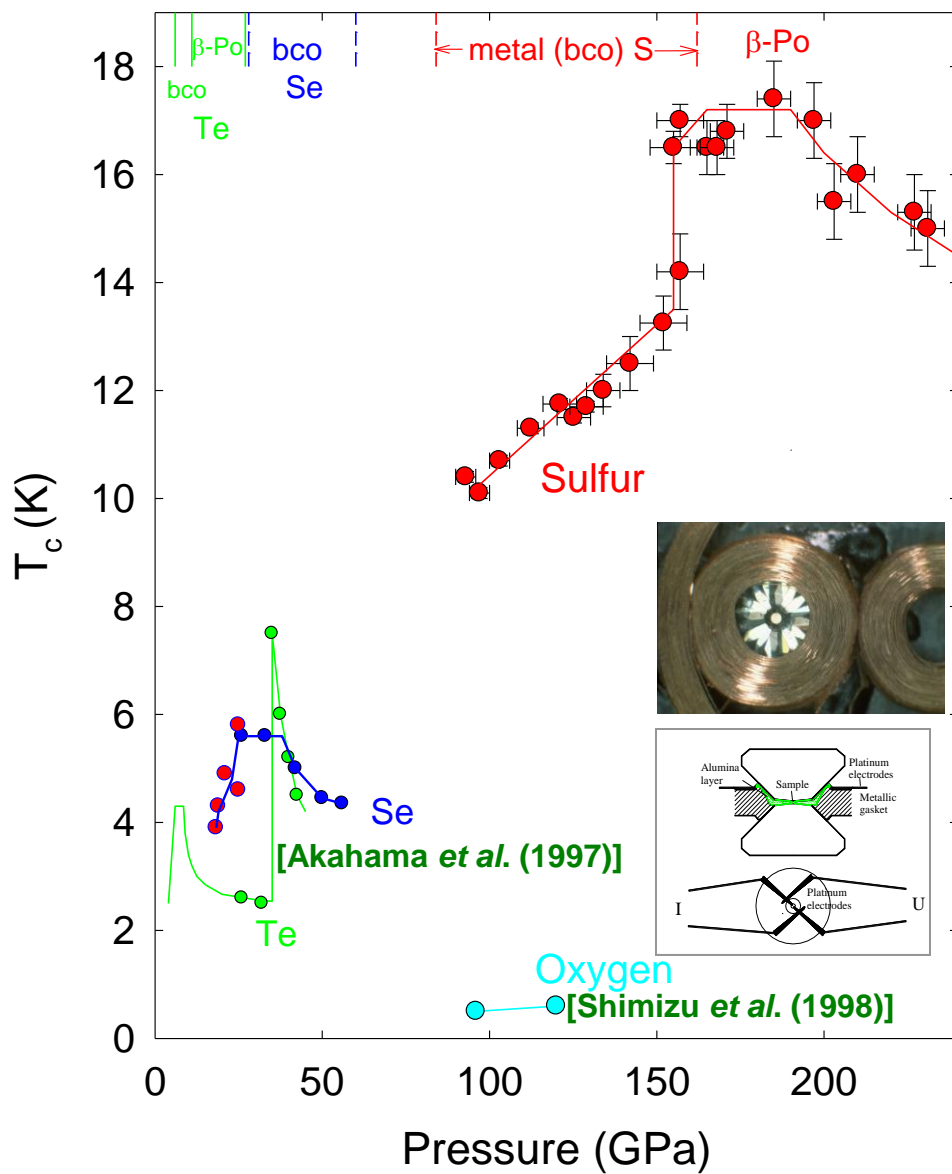
Structures and superconductivity in Group VI elements under pressure



Structures and superconductivity in Group VI elements under pressure



[Degtyareva *et al.*, *Nature Materials*, (2005)]
 [Fujihishi *et al.*, *Phys. Rev.* (2004)]



Hydrogen occupies a unique position in the Periodic Table

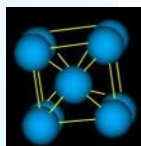
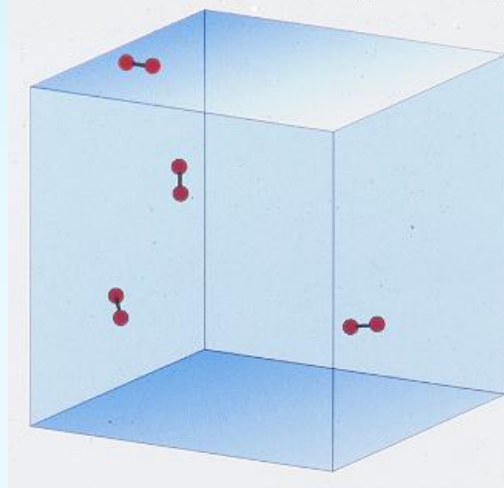


Discovered by Henry Cavendish in 1766

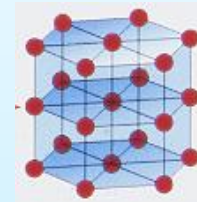
Alkalis

Halogens

1 H	← ? →																1 H	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104 Ru	105 Ha	106 Unh	107 Uns	108 Uno	109 Une	110 Unf									



58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



>25 GPa

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)

Any lattice in which the hydrogen atoms would be translationally identical (Bravais lattice) would have metallic properties. In the present paper the energy of a body-centered lattice of hydrogen is calculated as a function of the lattice constant. This energy is shown to assume its minimum value for a lattice constant which corresponds to a density many times higher than that of

the ordinary, molecular lattice of solid hydrogen. This minimum—though negative—is much higher than that of the molecular form. The body-centered modification of hydrogen cannot be obtained with the present pressures, nor can the other simple metallic lattices. The chances are better, perhaps, for intermediate, layer-like lattices.

Later predictions indicated even more exotic behavior of hydrogen at high density



• *Superconductivity*

VOLUME 21, NUMBER 26

PHYSICAL REVIEW LETTERS

23 DECEMBER 1968

METALLIC HYDROGEN: A HIGH-TEMPERATURE SUPERCONDUCTOR?

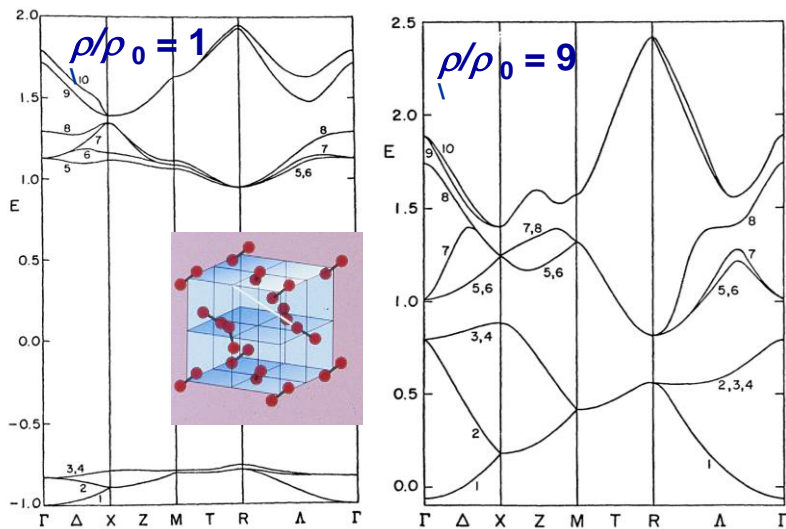
N. W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 3 May 1968)

Application of the BCS theory to the proposed metallic modification of hydrogen suggests that it will be a high-temperature superconductor. This prediction has interesting astrophysical consequences, as well as implications for the possible development of a superconductor for use at elevated temperatures.

• *Band overlap*

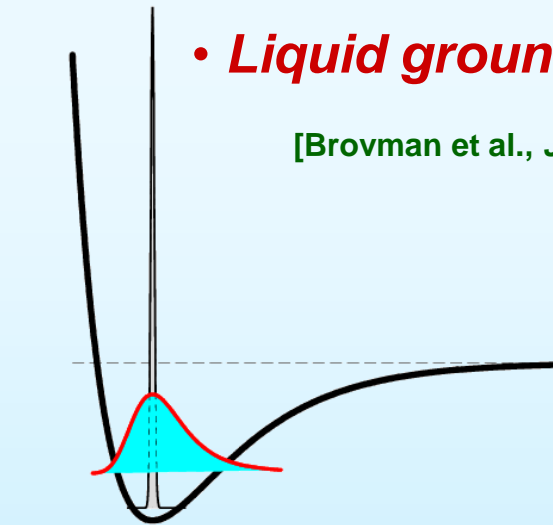


[Friedli & Ashcroft, *Phys. Rev. B* (1977);

[Ramaker et al., *Phys. Rev. Lett.* (1975)]

• *Liquid ground state*

[Brovman et al., *JETP* (1974)]

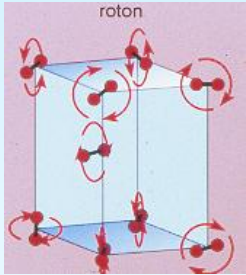


*Fully quantum mechanical system:
'The Element of Uncertainty'*

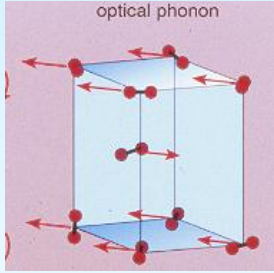
Vibrational spectroscopy has been an important probe of the high-pressure behavior of hydrogen



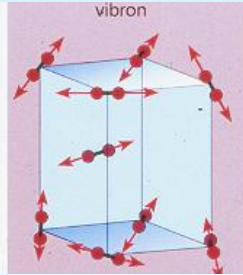
Rotons



Lattice Modes



Vibrons

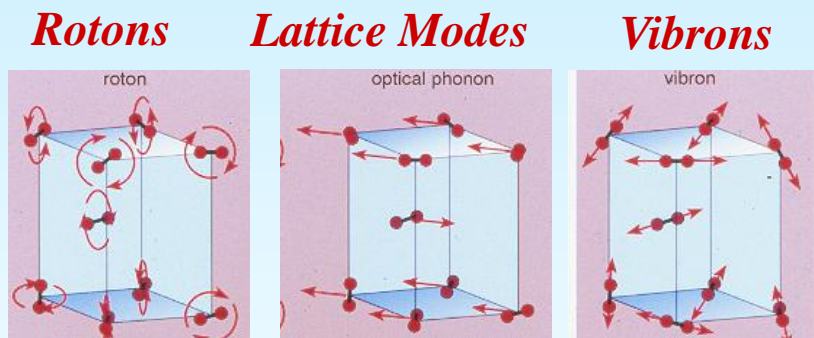


$S_0(J)$ $Q_{\Delta\nu}(J)$; e.g., $Q_1(1)$

PRESSURE EFFECTS

- Rotational ordering
- Molecular stability
- Molecular interactions

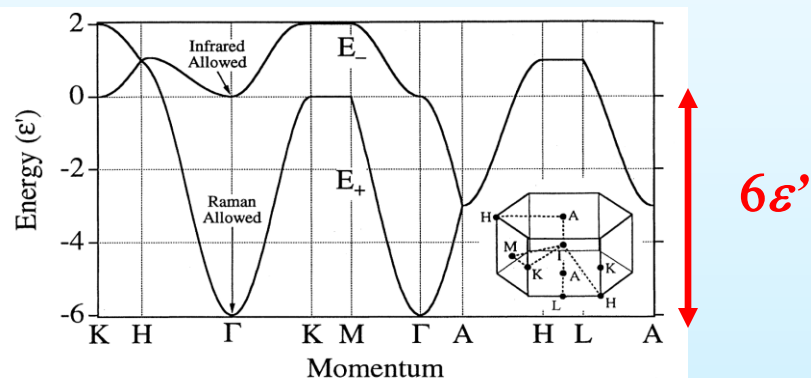
Vibrational spectroscopy has been an important probe of the high-pressure behavior of hydrogen



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PRESSURE EFFECTS

- Rotational ordering
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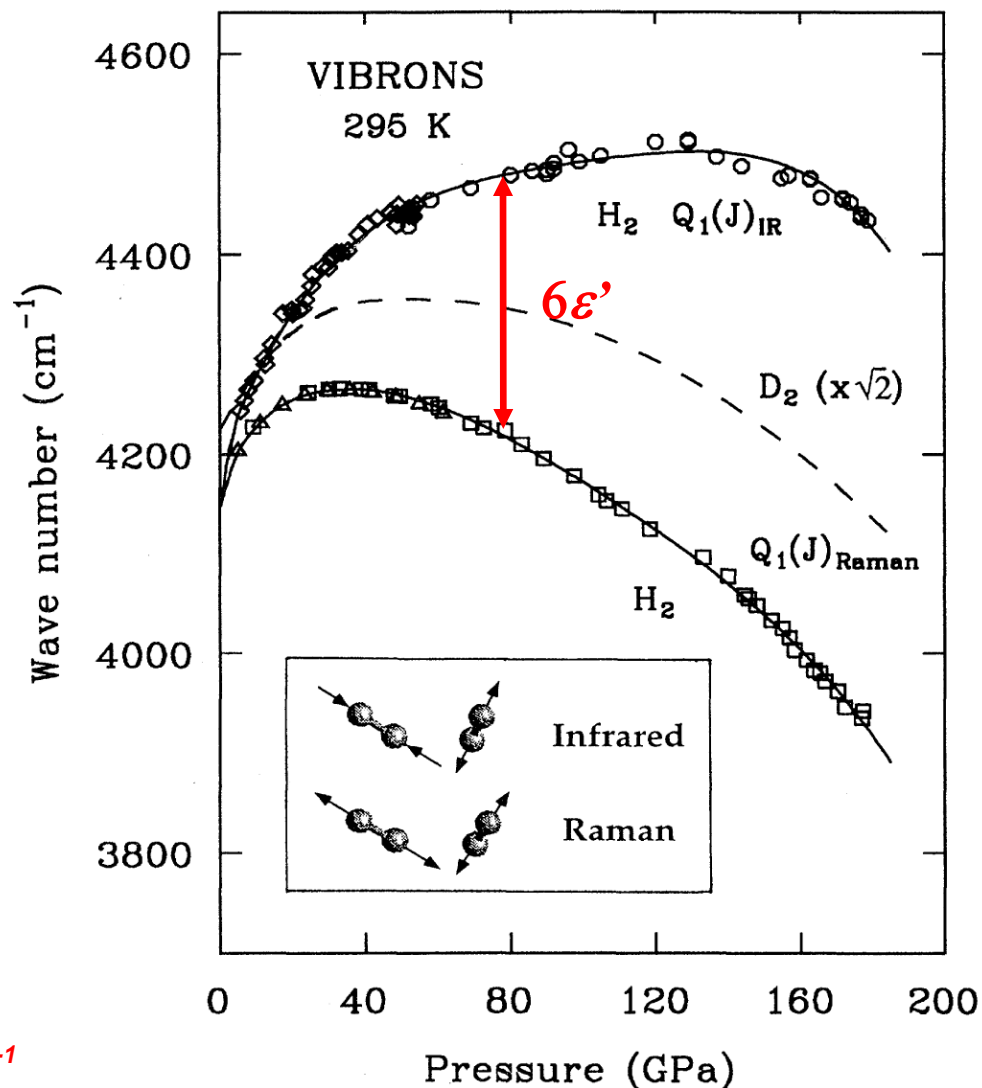


$$H_{JK} = \sum_m W'_m |m\rangle \langle m| - \frac{1}{2} \sum_{m,n \neq m} \epsilon'_{m,n} |m\rangle \langle n|$$

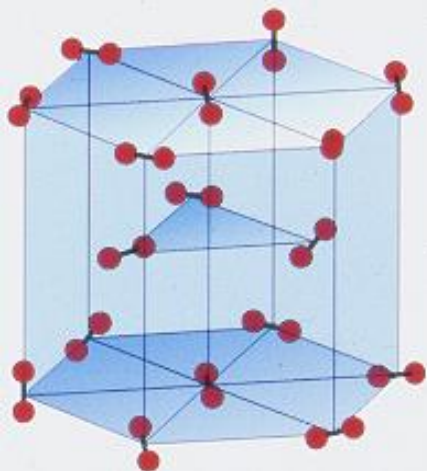
On-site term

Coupling
 $\sim 1/r^6$

$6\epsilon' = 3 \text{ cm}^{-1}$
(zero pressure)



Solid hydrogen at megabar pressures



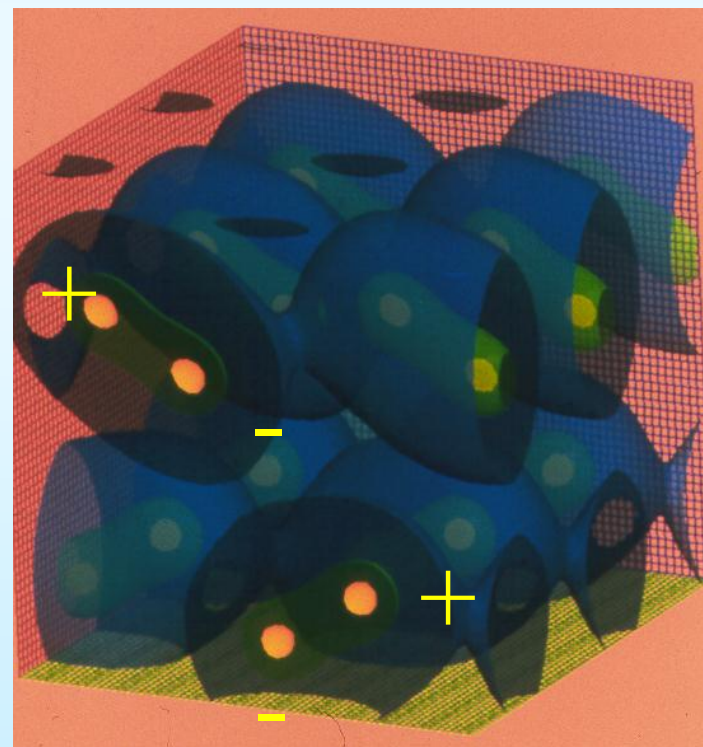
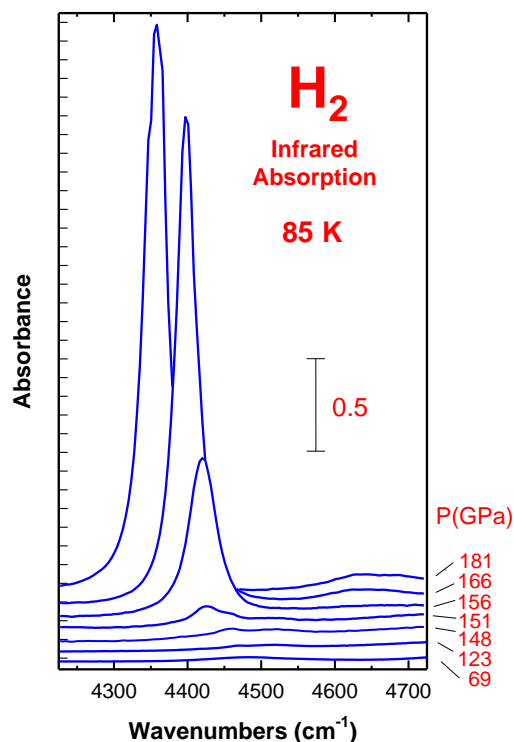
**High Pressure
Structure (Phase I)**

[Glazkov *et al.*, *JETP Lett.* (1988); Mao *et al.*, *Science* (1988); Loubeyre *et al.*, *Nature* (1996)]

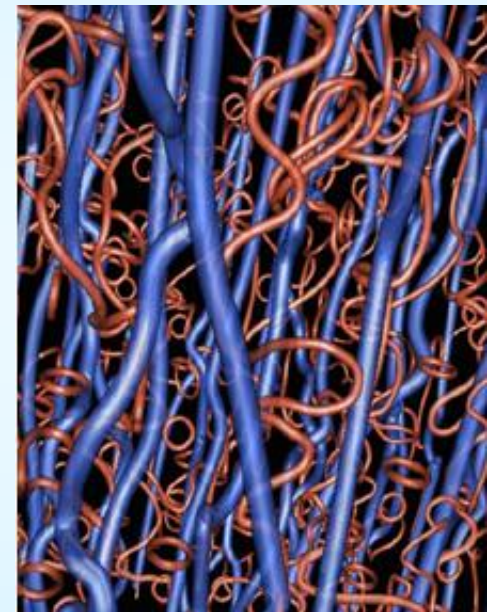
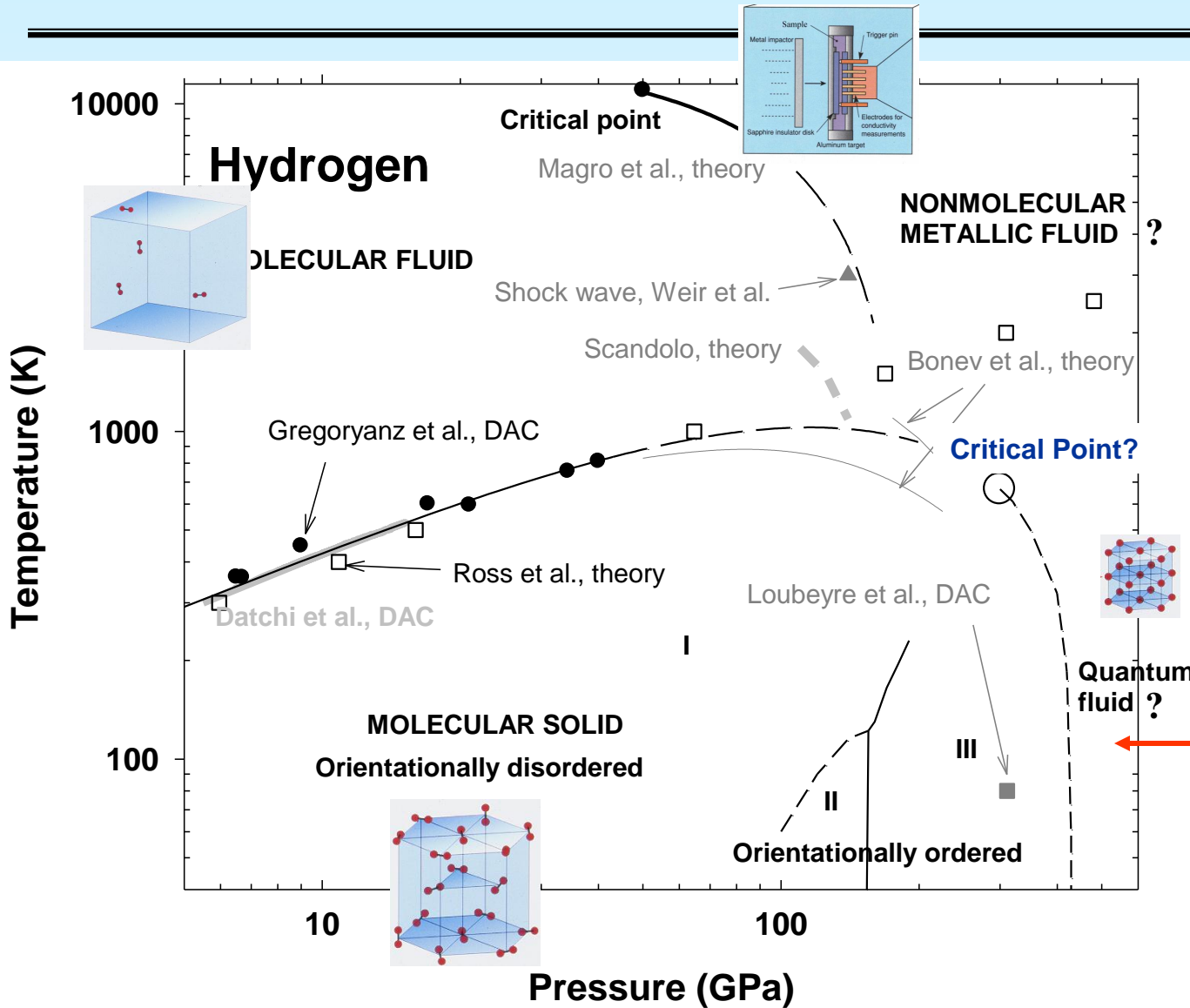
**“Ionic” charge-transfer
state forms at 150 GPa;
stable to >300 GPa**

[Hemley *et al.*, *Nature* (1994);
Goncharov *et al.*,
Proc. Nat. Acad. Sci. (2002);
Loubeyre *et al.*, *Nature* (2002)]

- Molecules stable to ~300 GPa in solid
- $\rho/\rho_0 \sim 14$ at 300 GPa from x-ray eos



Phase diagram of dense hydrogen

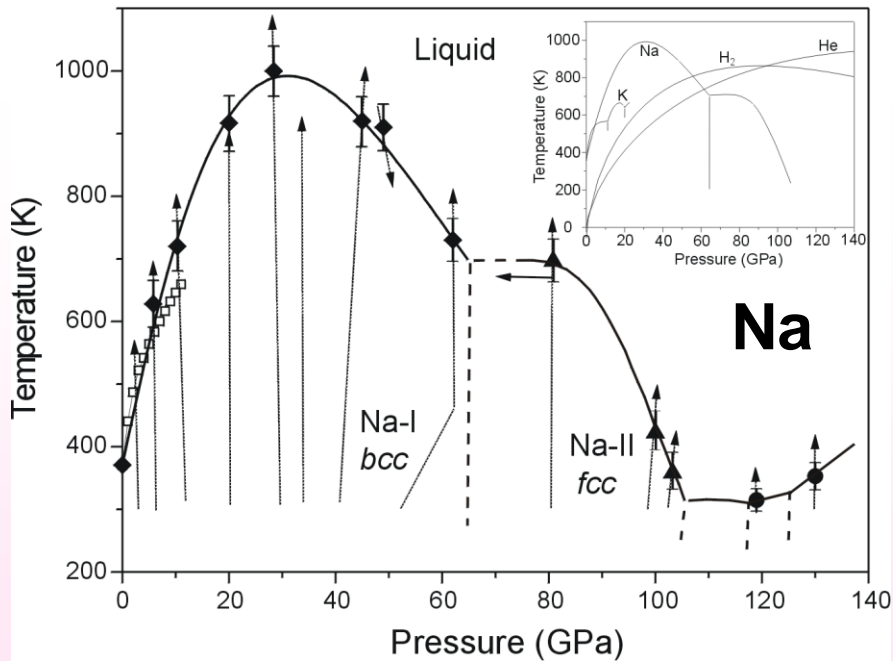


Combined superfluidity and superconductivity >400 GPa predicted

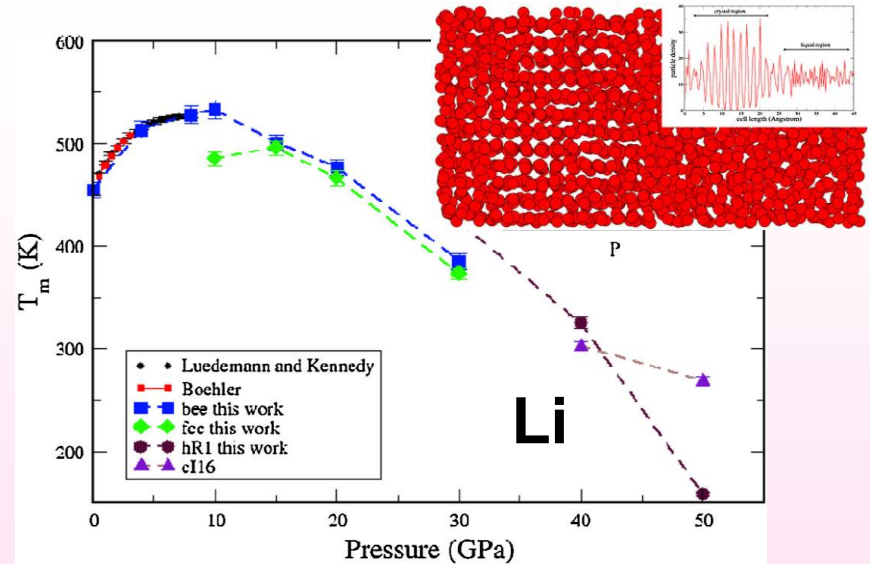
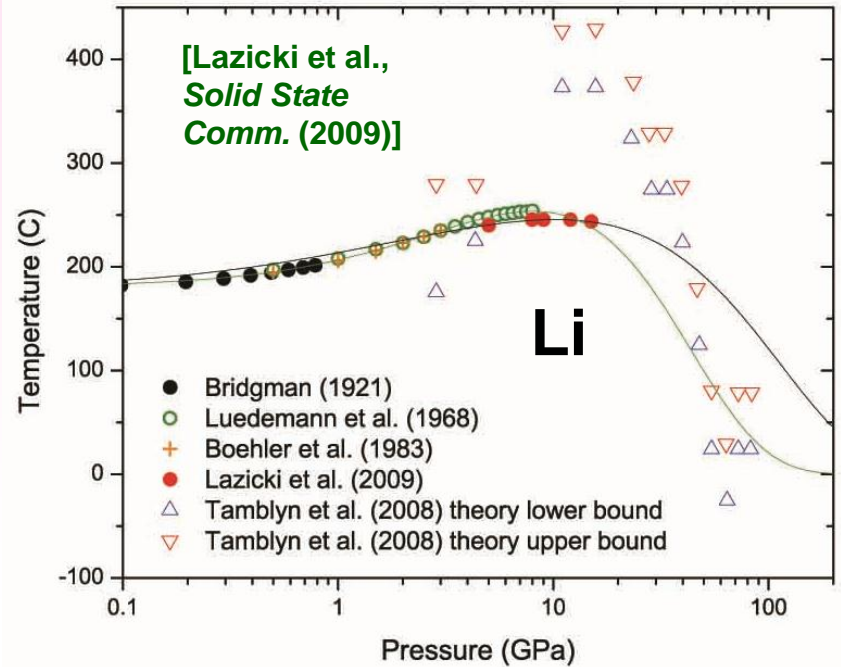
[Babaev et al., Phys. Rev. Lett. (2005)]

[Goncharov and Crowhurst, Phase Transitions (2007)]

Alkali metals at megabar pressures

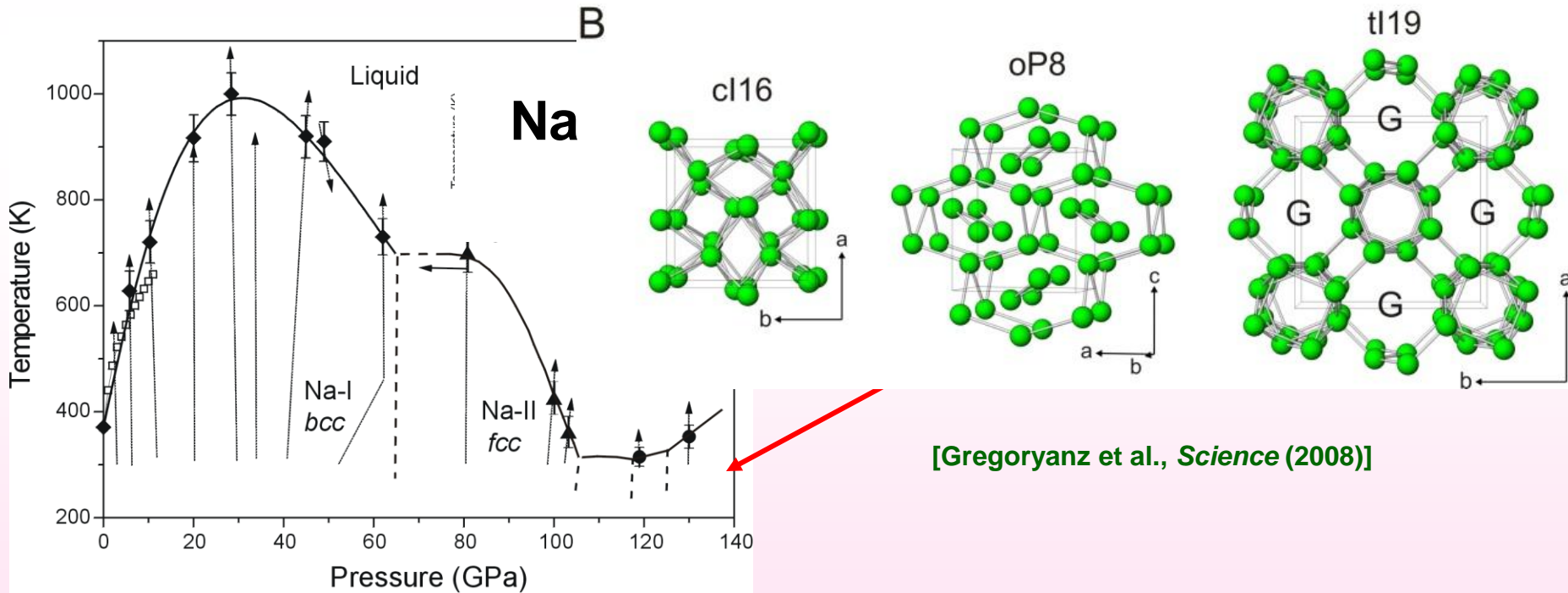
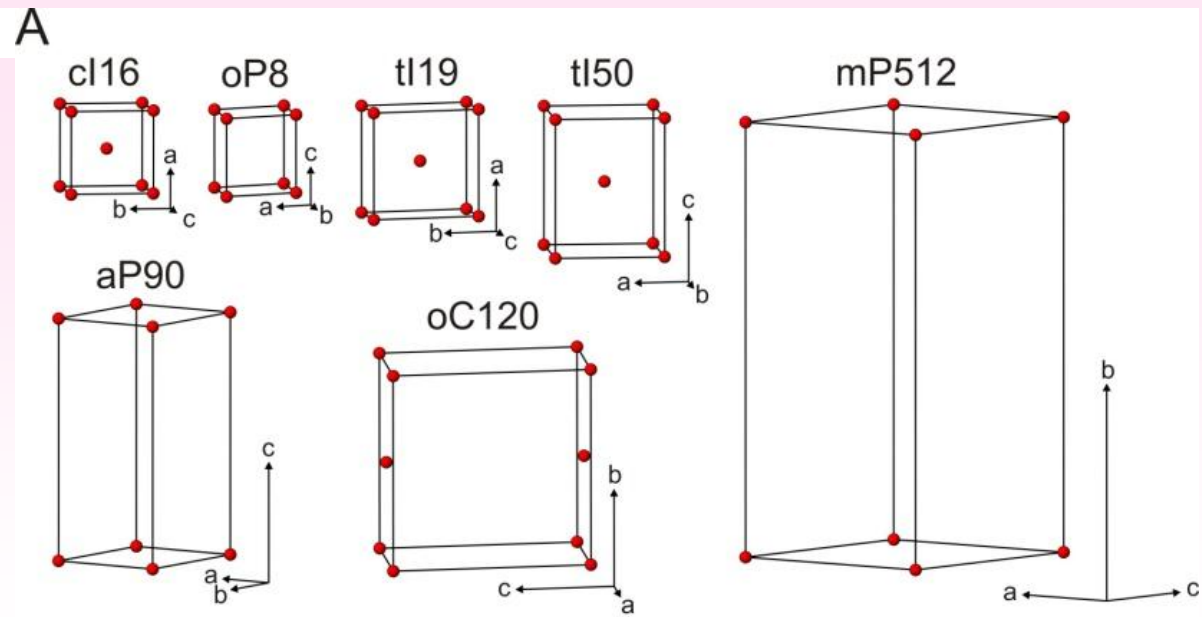


[Gregoryanz et al., *Phys. Rev. Lett.* (2005)]



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

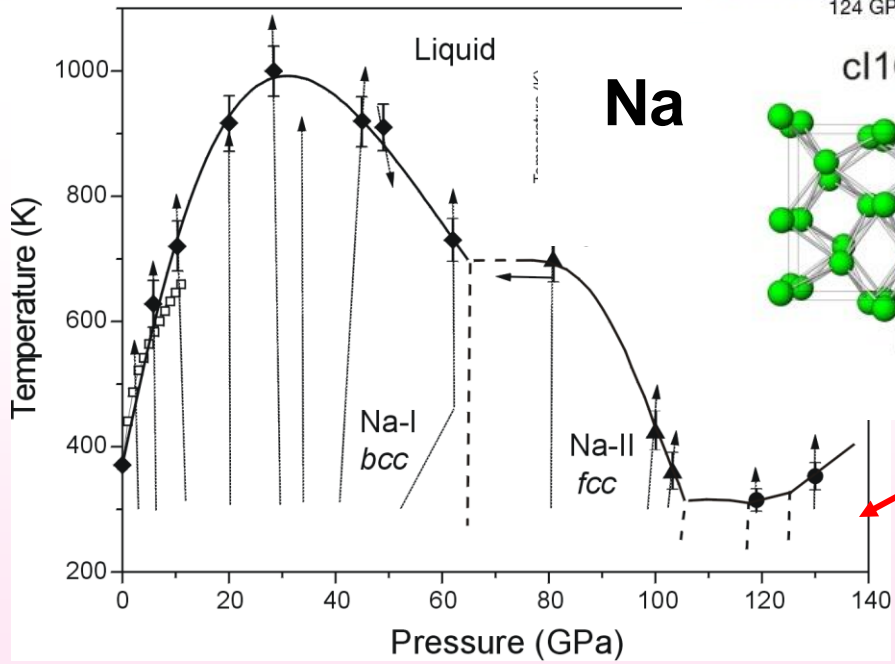
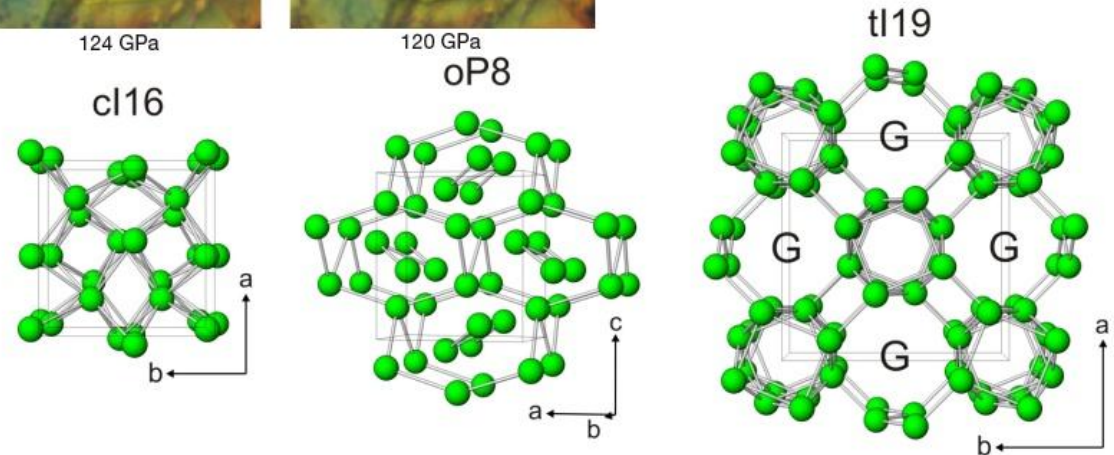
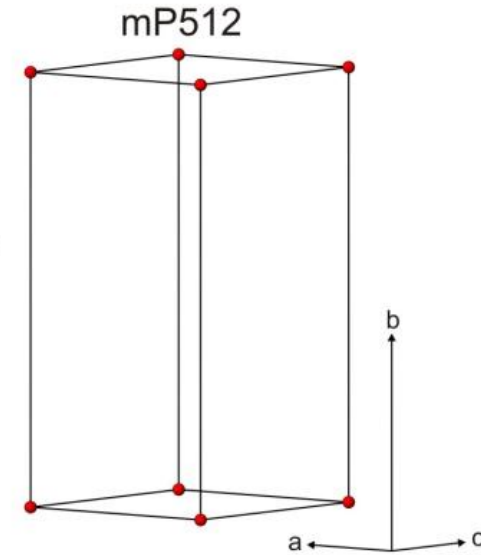
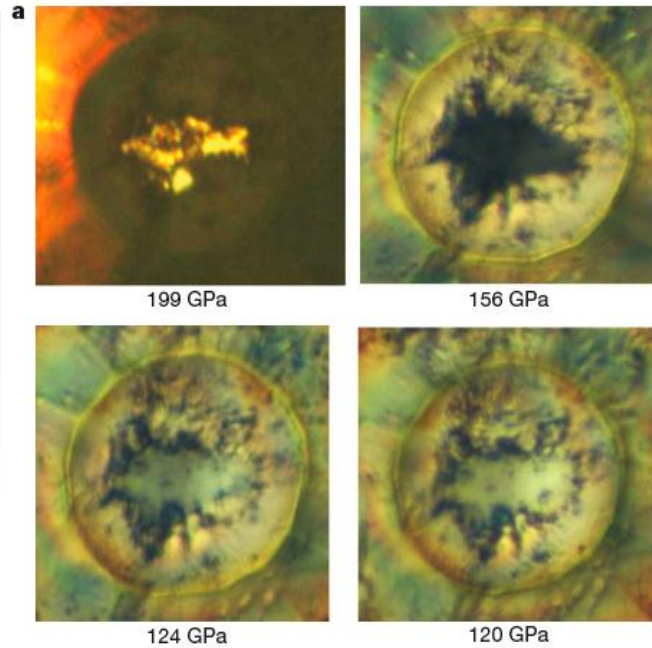
Alkali metals at megabar pressures



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

[Gregoryanz et al., *Phys. Rev. Lett.* (2005)]

Alkali metals at megabar pressures

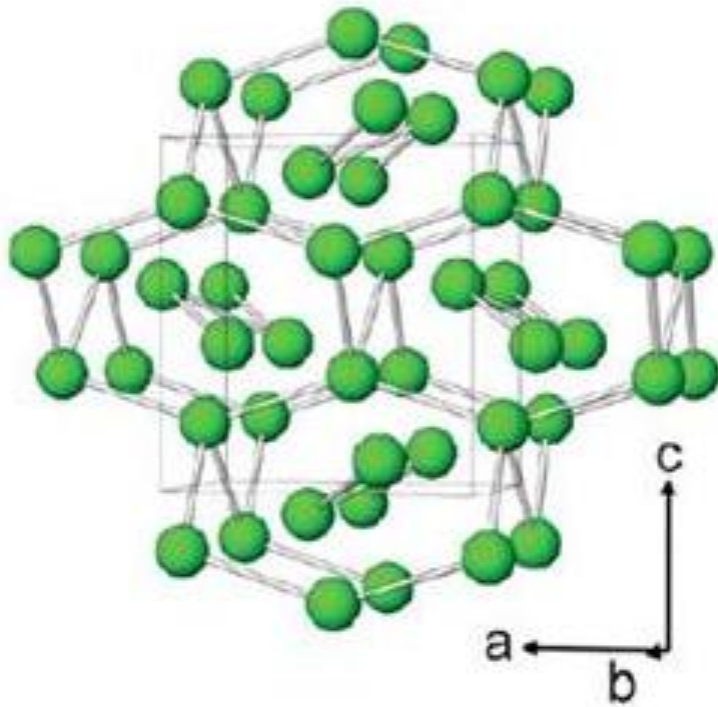


[Gregoryanz et al., *Phys. Rev. Lett.* (2005)]

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

**fcc - cl16 - tl19 - hP4 (transparent)
METAL TO INSULATOR TRANSITION!**

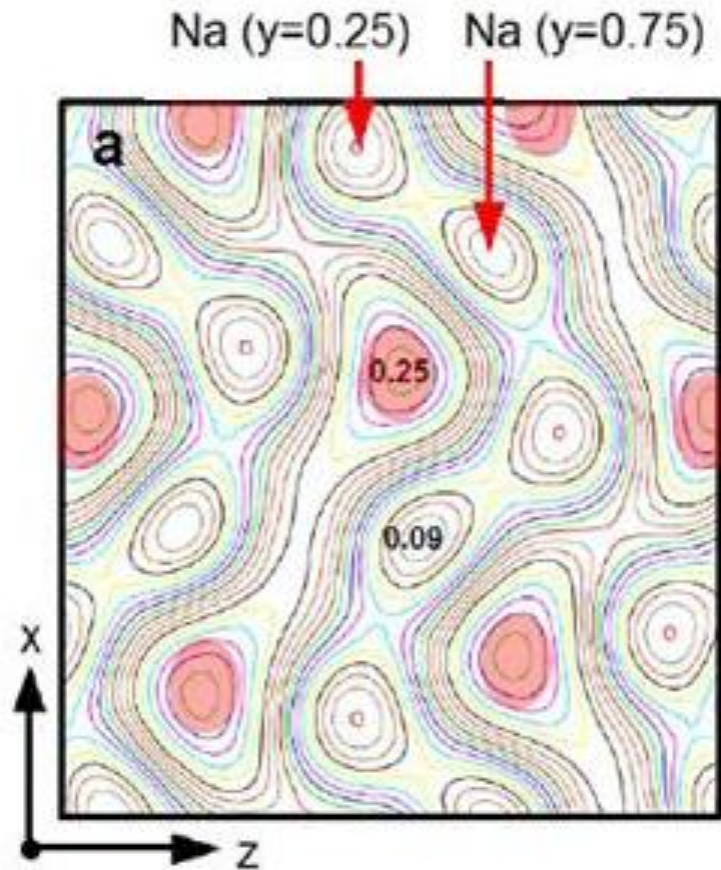
Origin of the phenomena: *interstitial charge densities*



[Lazicki et al., *PNAS* (2009);
see also, Ma et al., *Nature* (2009)]

“Dimerized” and insulating Li

[Neaton & Ashcroft, *Nature* (2002)]

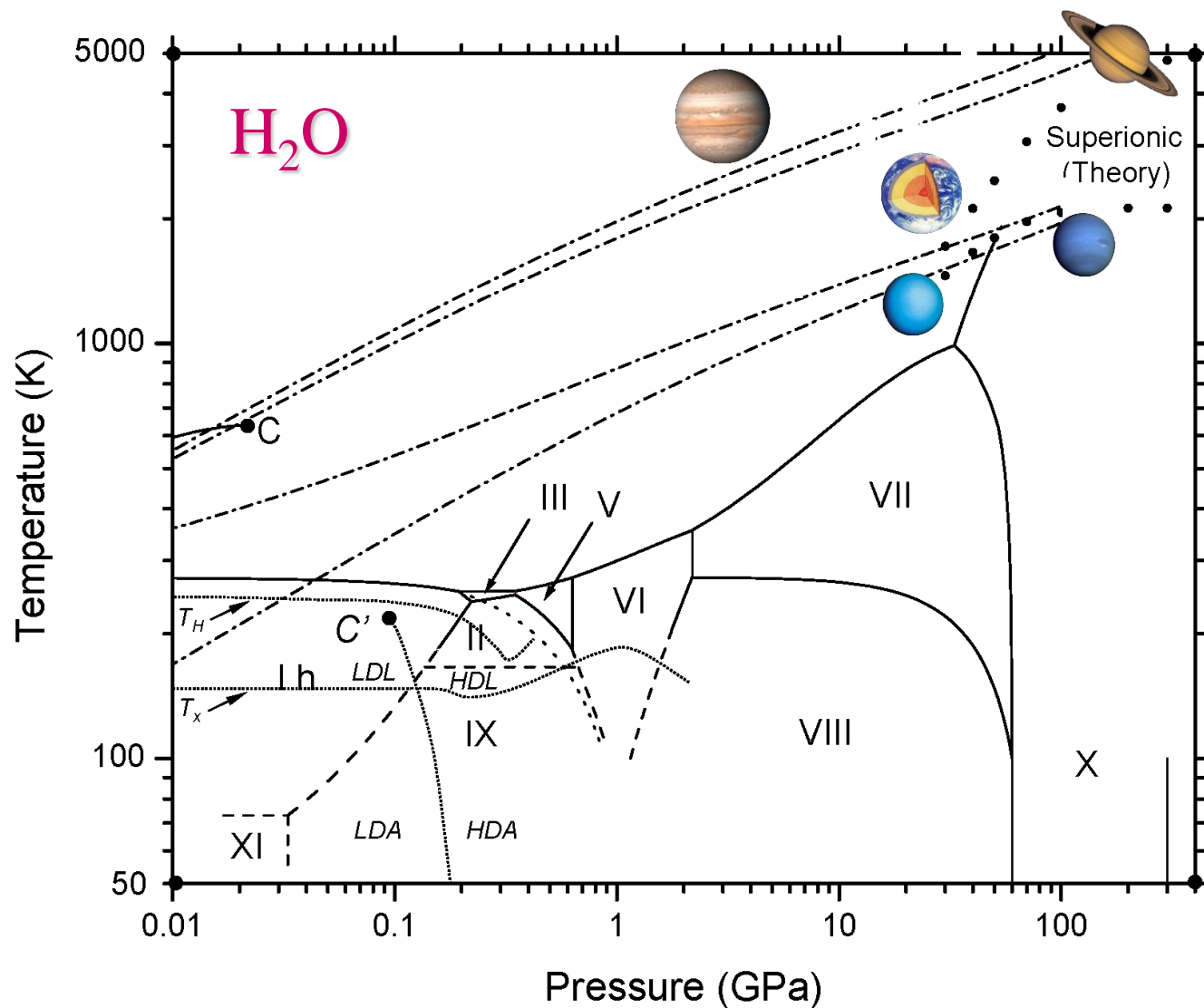


- *Altogether new bonding type*
- *“Re-entrant” molecular solid*
- *Other systems?*

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



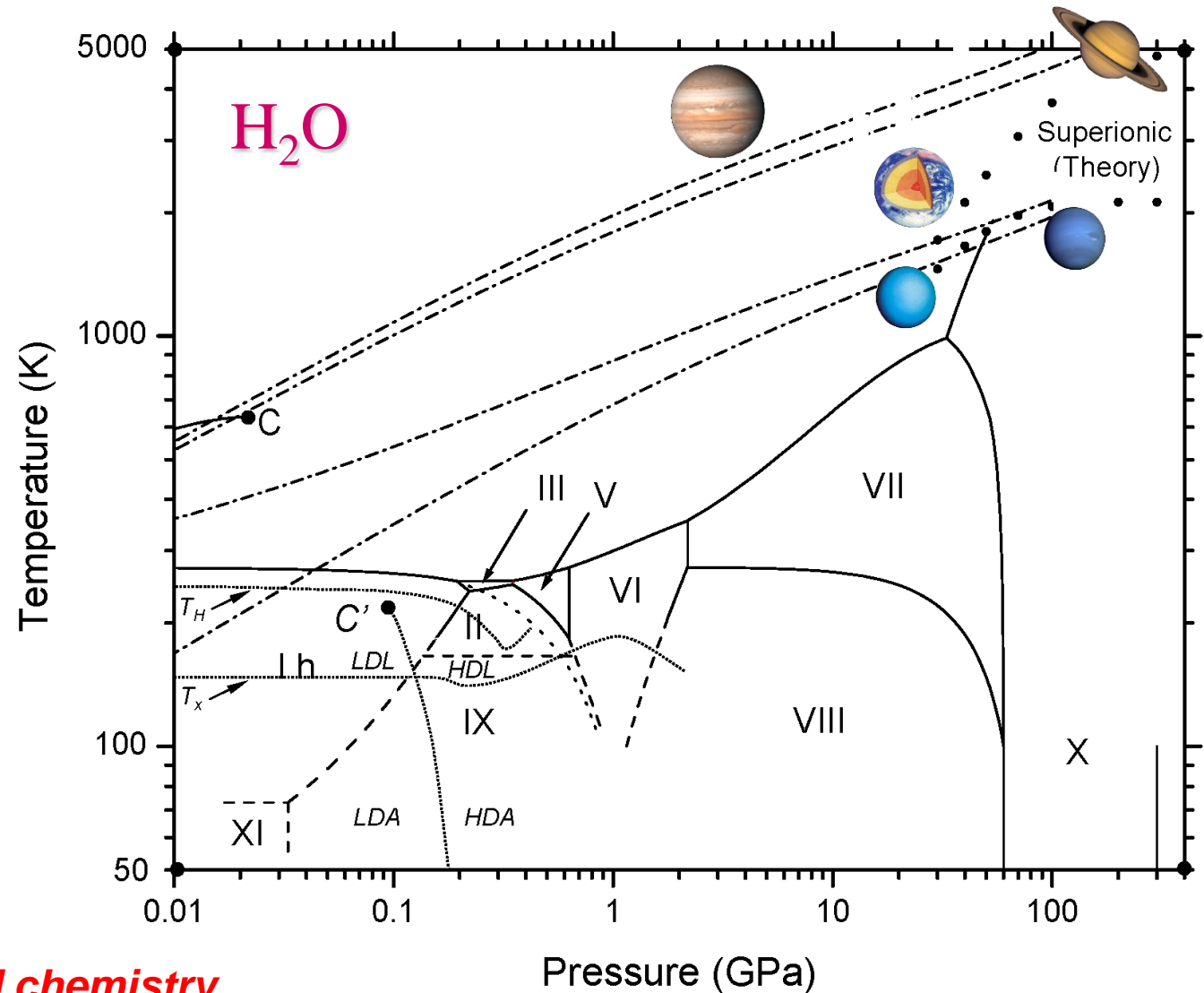
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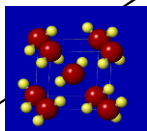
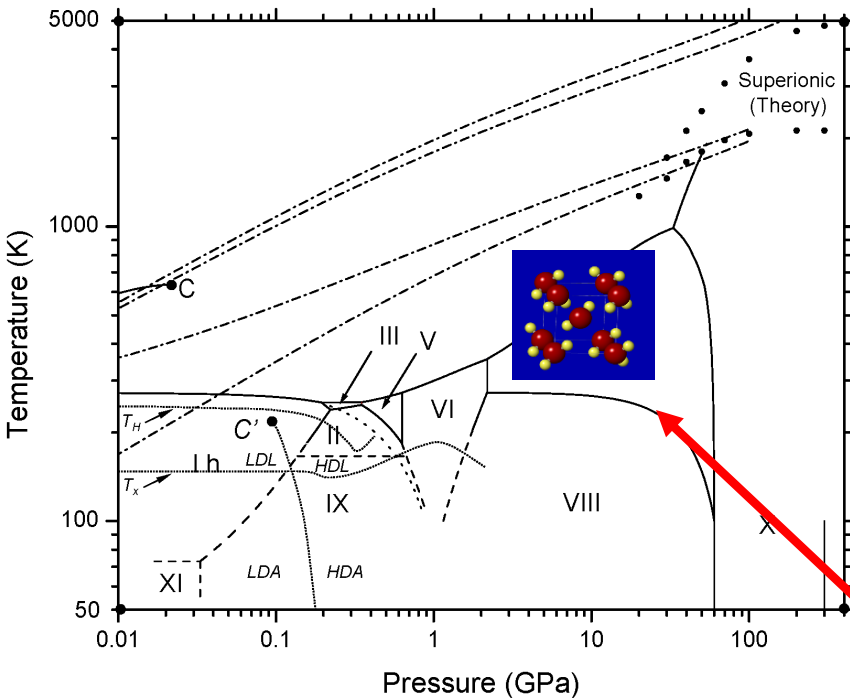


- ~20 stable and metastable phases
- Novel transitions
 - non-molecular
 - amorphization
 - liquid/liquid trans
- Nature of the hydrogen bond



- *Radiation-induced chemistry*
- *Higher pressure behavior*

Radiation-induced chemistry under pressure

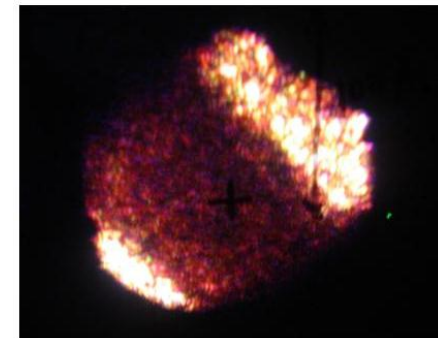


Similar breakdown of NH₃

NH₃ solid III
1.73 GPa

2 hours long exposure
to 9.6872 keV

2.42 GPa

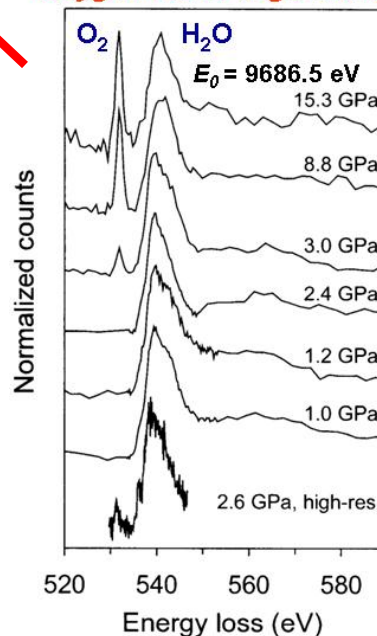


[W. Mao *et al.*, *Science* (2006)]

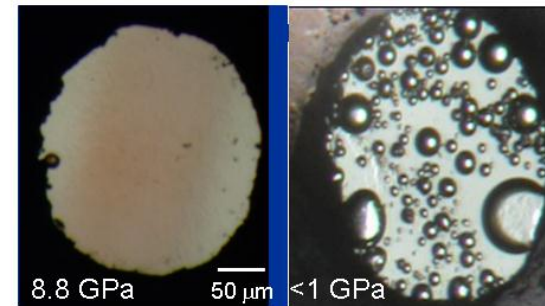
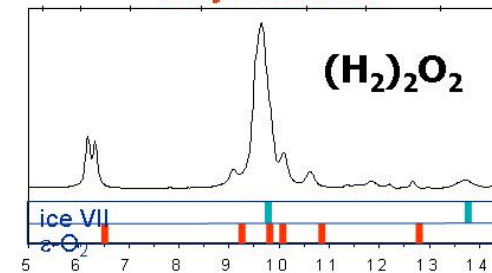
- Molecular alloy of H₂-O₂
- High-pressure van der Waals compound
- Metastable energetic material

➤ **High density excited-state chemistry**

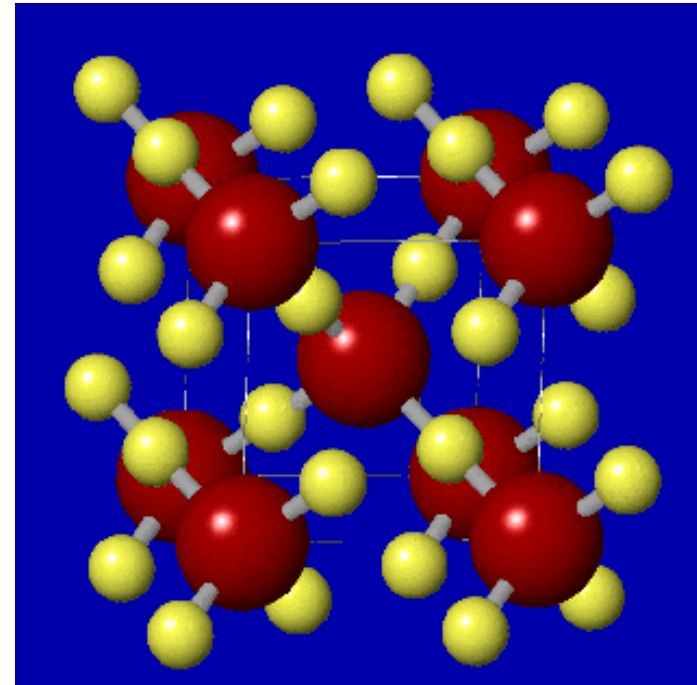
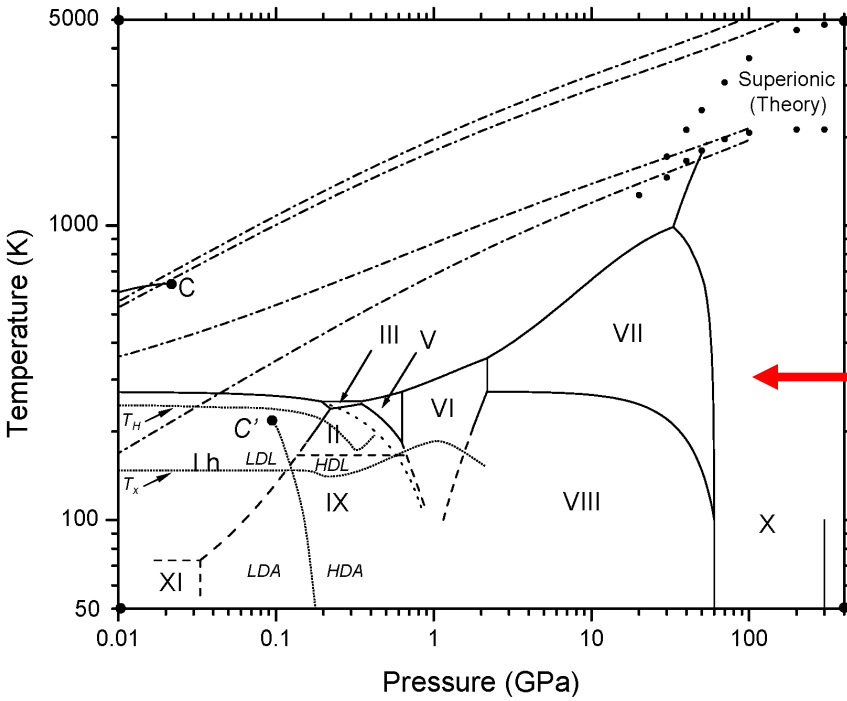
Oxygen IXS K-edge Raman



X-ray Diffraction

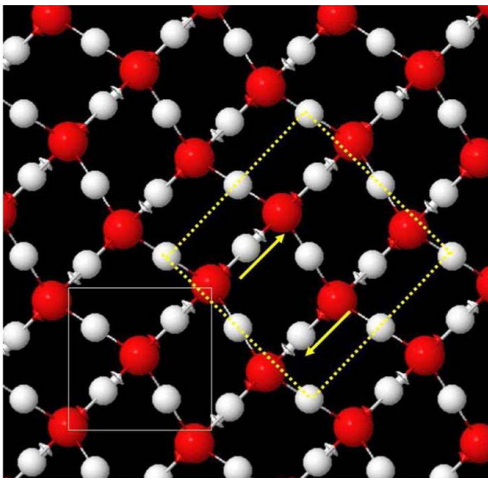


H₂O at multimegabar pressures



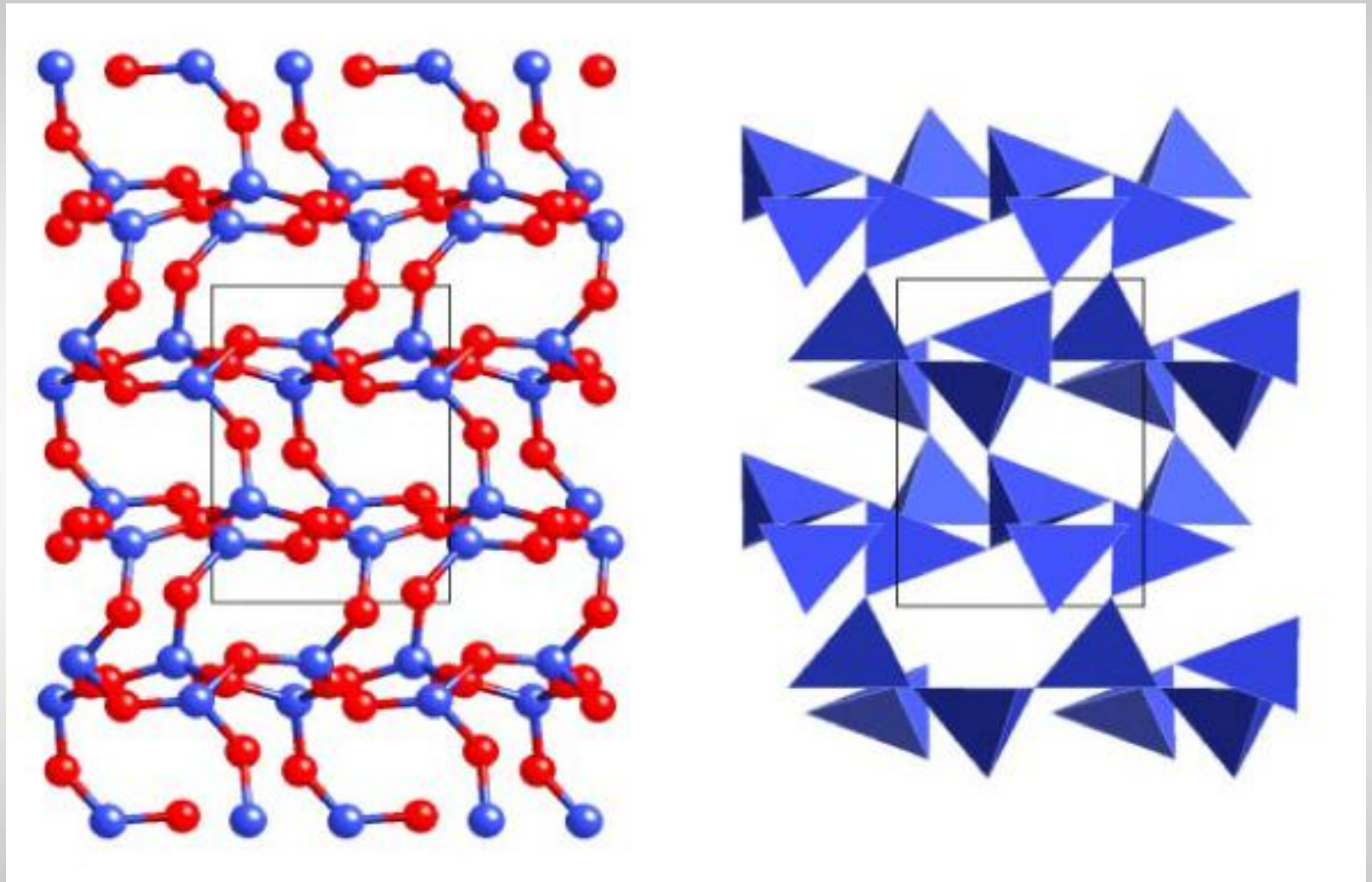
- Non-molecular ice X
- Ionic solid

[Goncharov *et al.*, *Science* (1996);
suggested by Kamb & Davis, *PNAS* (1964)]



- Post-ice X at 400 GPa predicted
- M-point phonon instability (ice X)
[Caracas, *Phys. Rev. Lett.* (2008)]

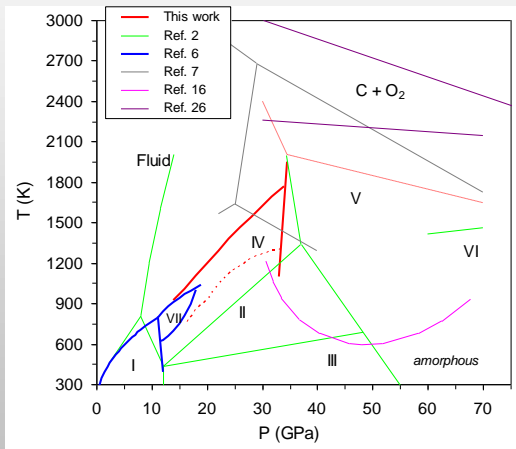
Novel high P - T transformations of CO_2



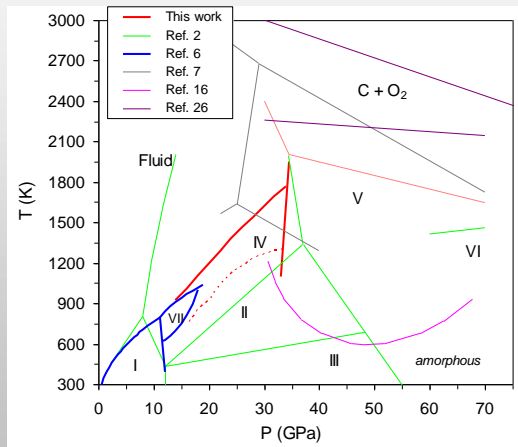
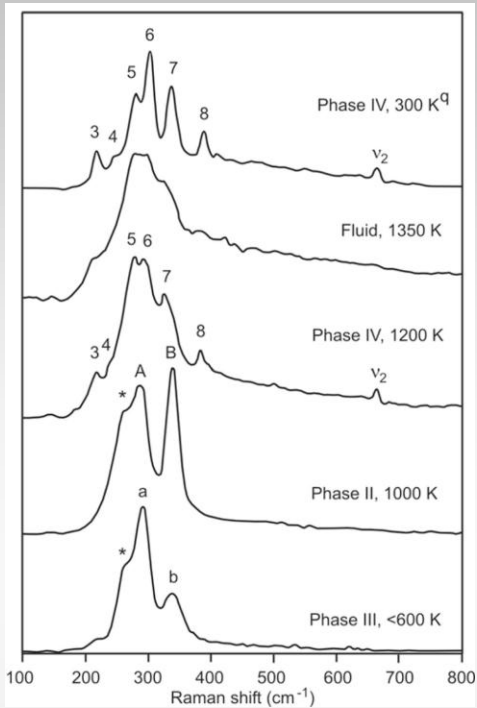
[Iota et al., *Science* (1999);
Lipp et al., *Nature Mat.* (2005)].

- CO_2 behaves like SiO_2 in lower mantle
- Phase diagram?

High P - T CO_2 melting and dissociation

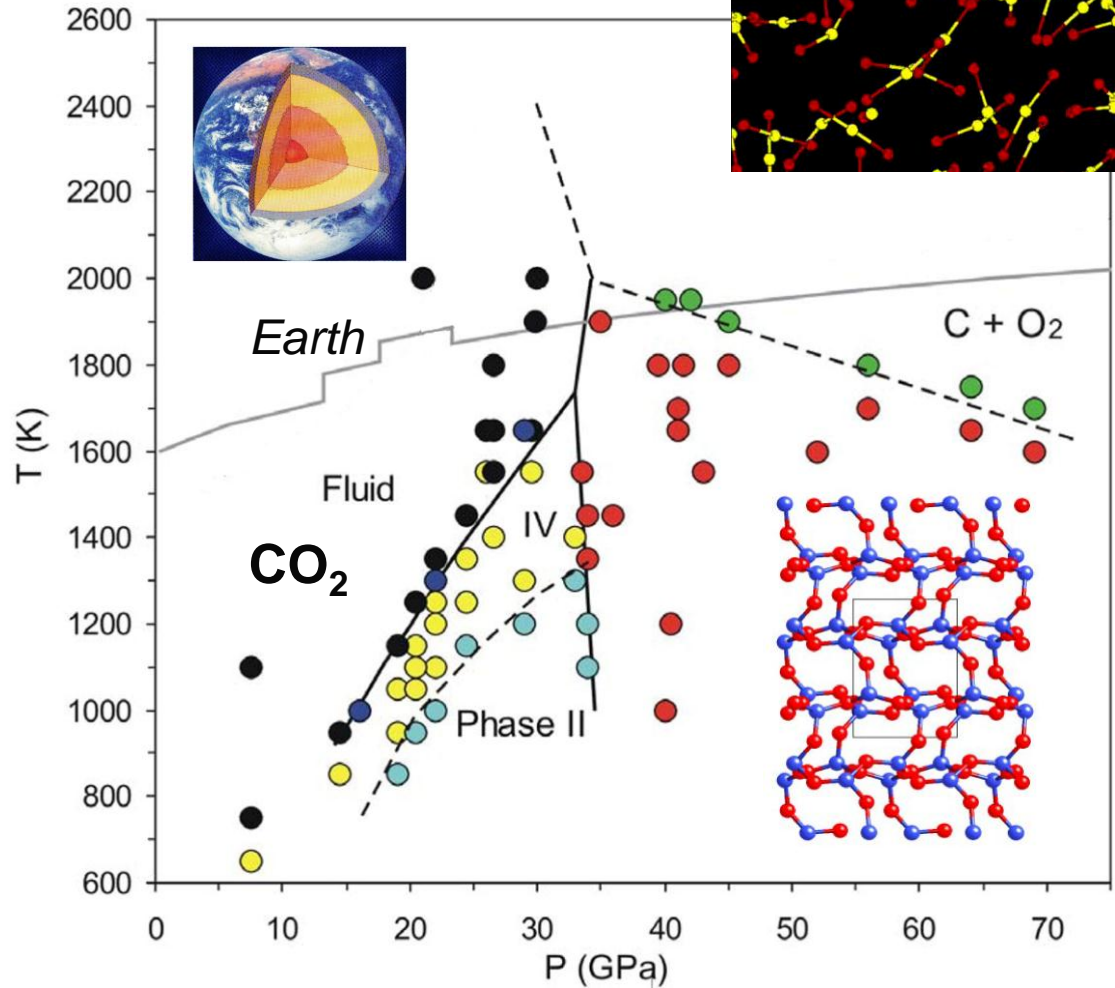
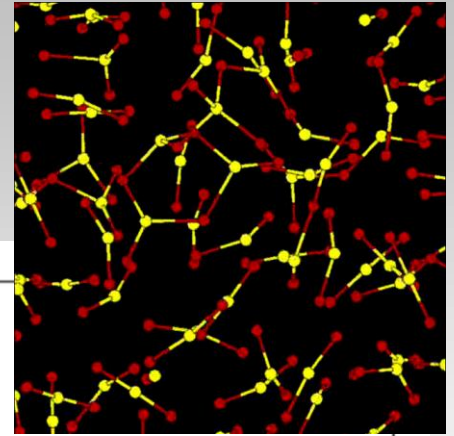


High P - T CO_2 melting and dissociation



THEORY

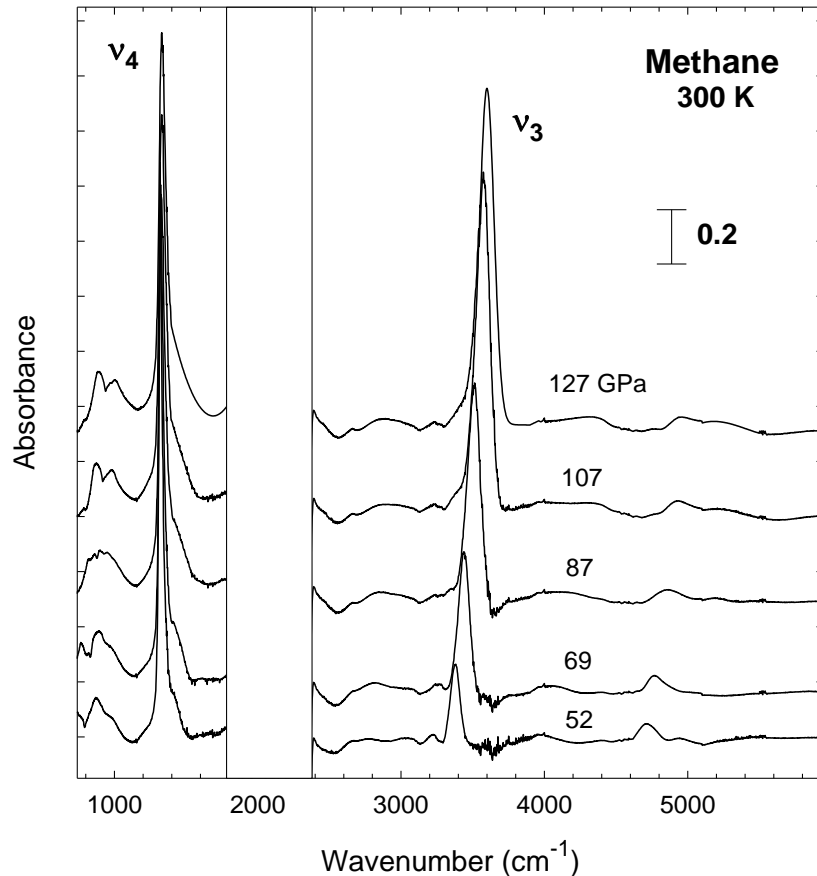
[Montoya et al., submitted]



[Litasov et al., submitted]

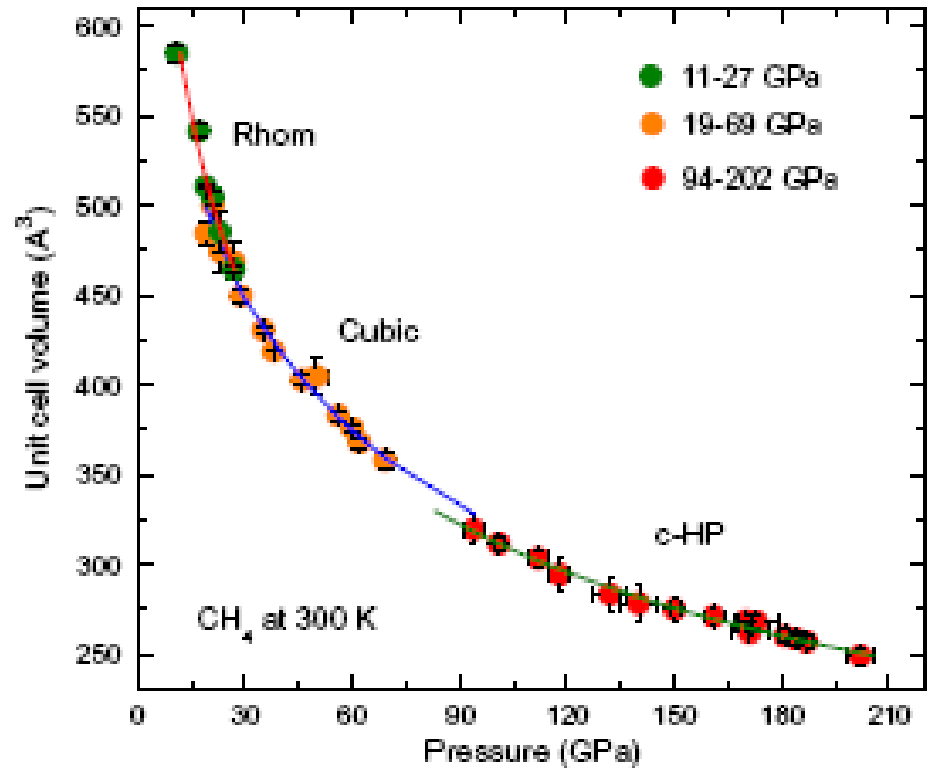
Methane is stable to megabar pressures at 300 K

Infrared



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

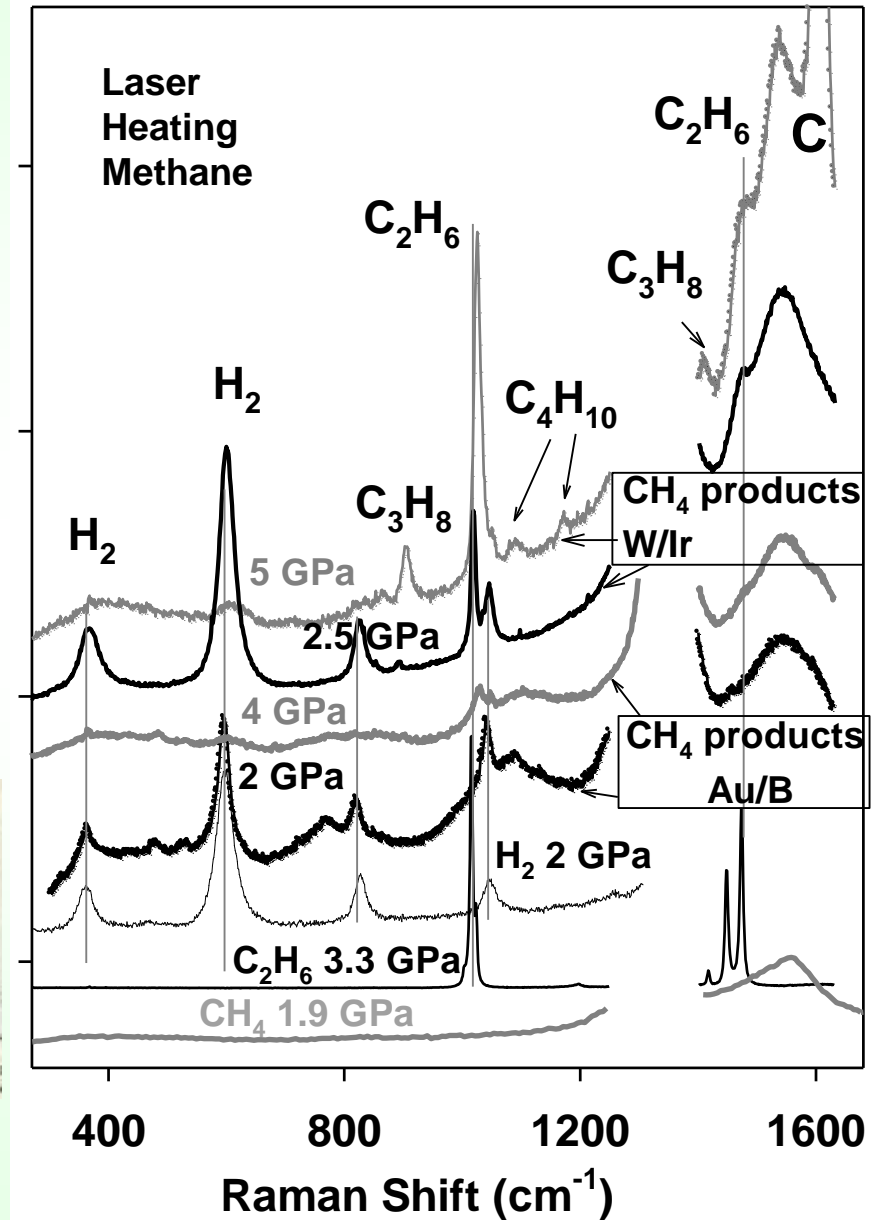
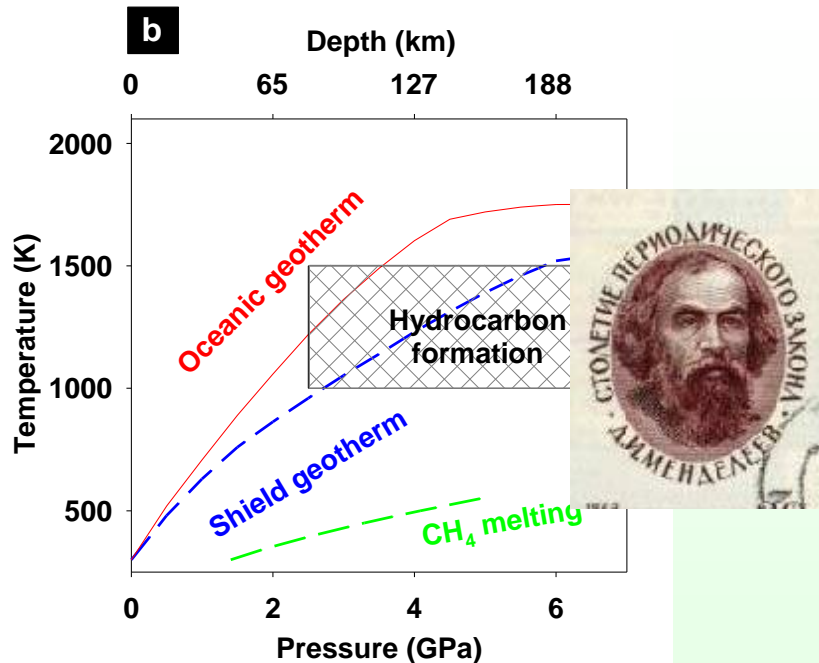
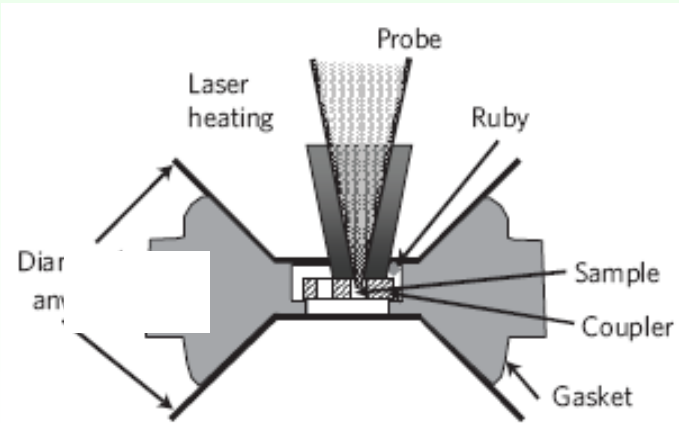
X-ray



[Sun *et al.*, *Chem. Phys. Lett.* (2009)]

- Large metastability
- Remains insulating
- Equilibrium phases?

Higher hydrocarbons are produced from laser heating pressurized methane



[Kolesnikov *et al.*, *Nature Geoscience* (2009)]

Metallization of Group IVA molecular hydrides?

VOLUME 92, NUMBER 18

PHYSICAL REVIEW LETTERS

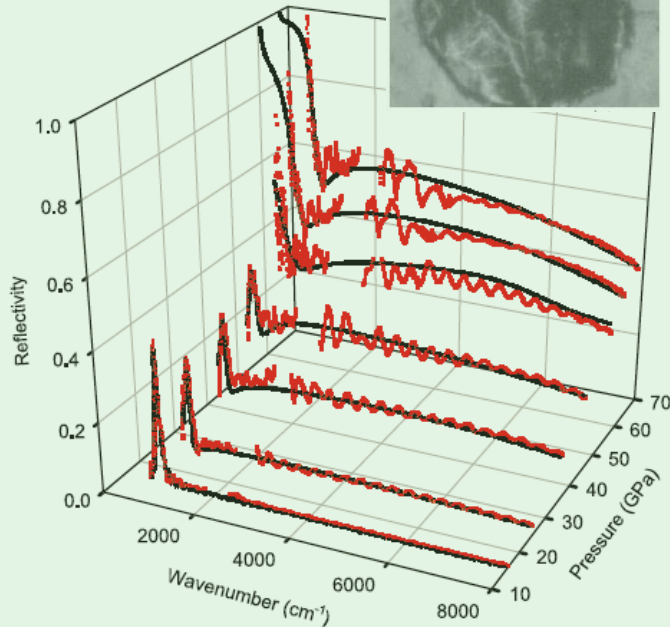
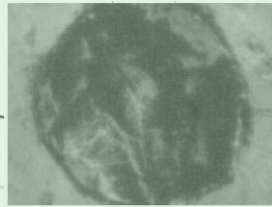
week ending
7 MAY 2004

Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

N.W. Ashcroft

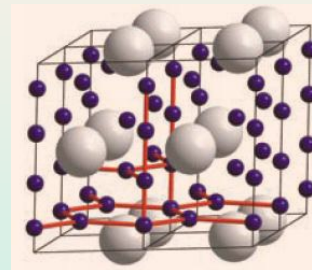
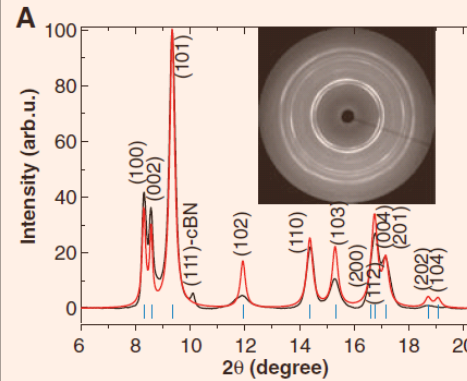
Infrared reflectivity indicates metallization of silane at 60 GPa.

Silane turns black and shiny >30 GPa



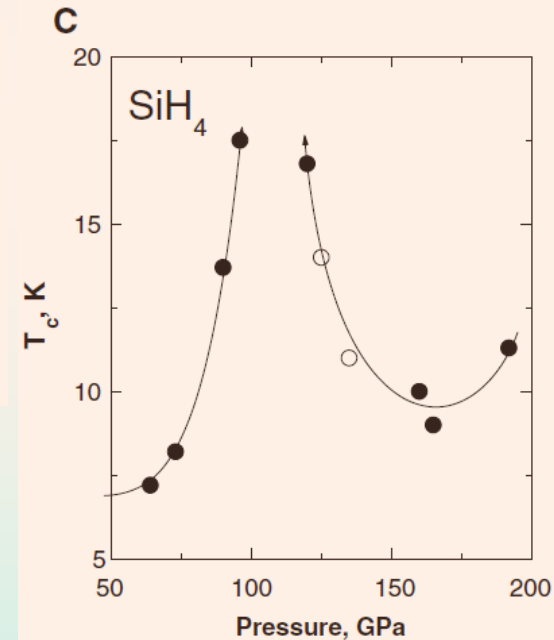
Chen *et al. Proc. Natl. Acad. Sci.* **105**, 211 (2008)

Metallization via electrical resistance at 50-65 GPa. Superconductivity : 17 K @ 100 GPa.



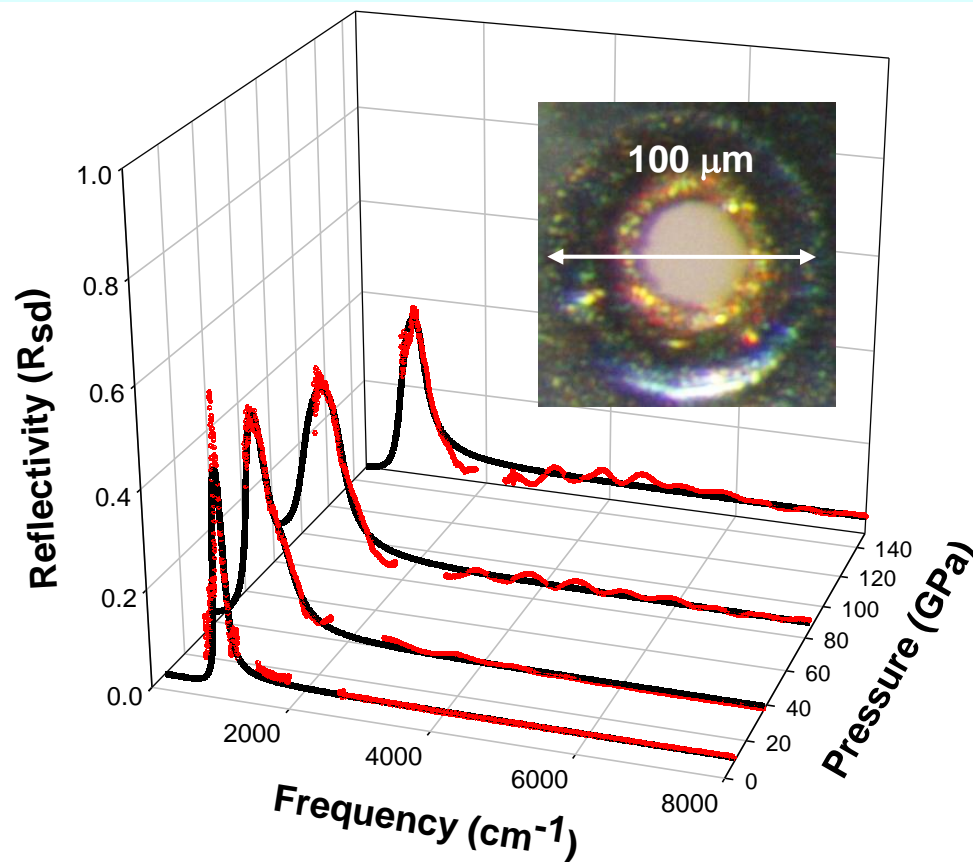
Metallic $P6_3$ Structure

Eremets *et al. Science* **319**, 1506 (2008)



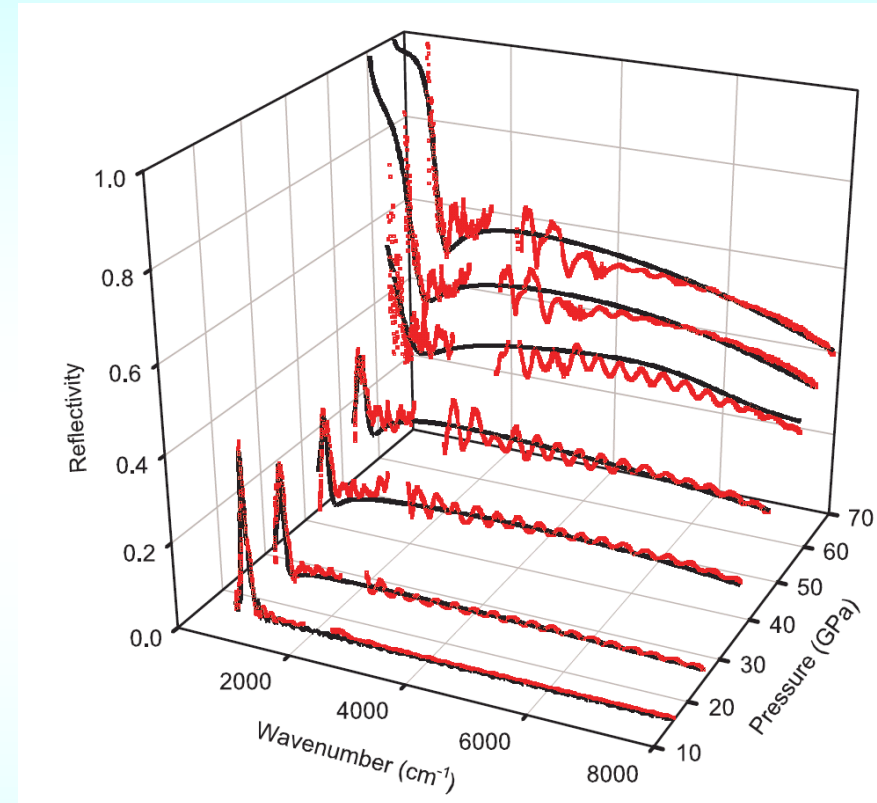
The metallization of silane has been revisited

Gold-lined gasket –
non-metallic behavior



[Strobel et al., to be published]

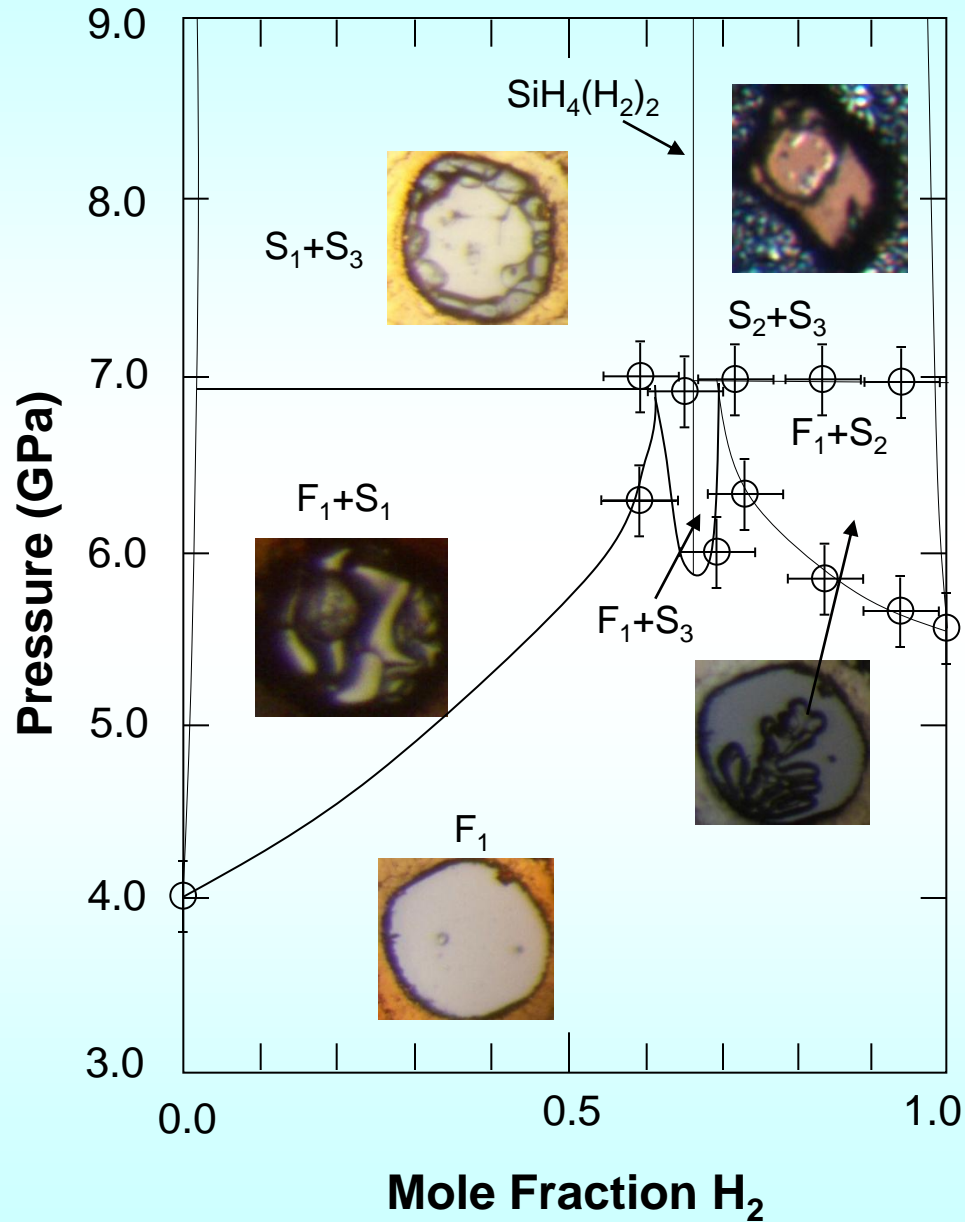
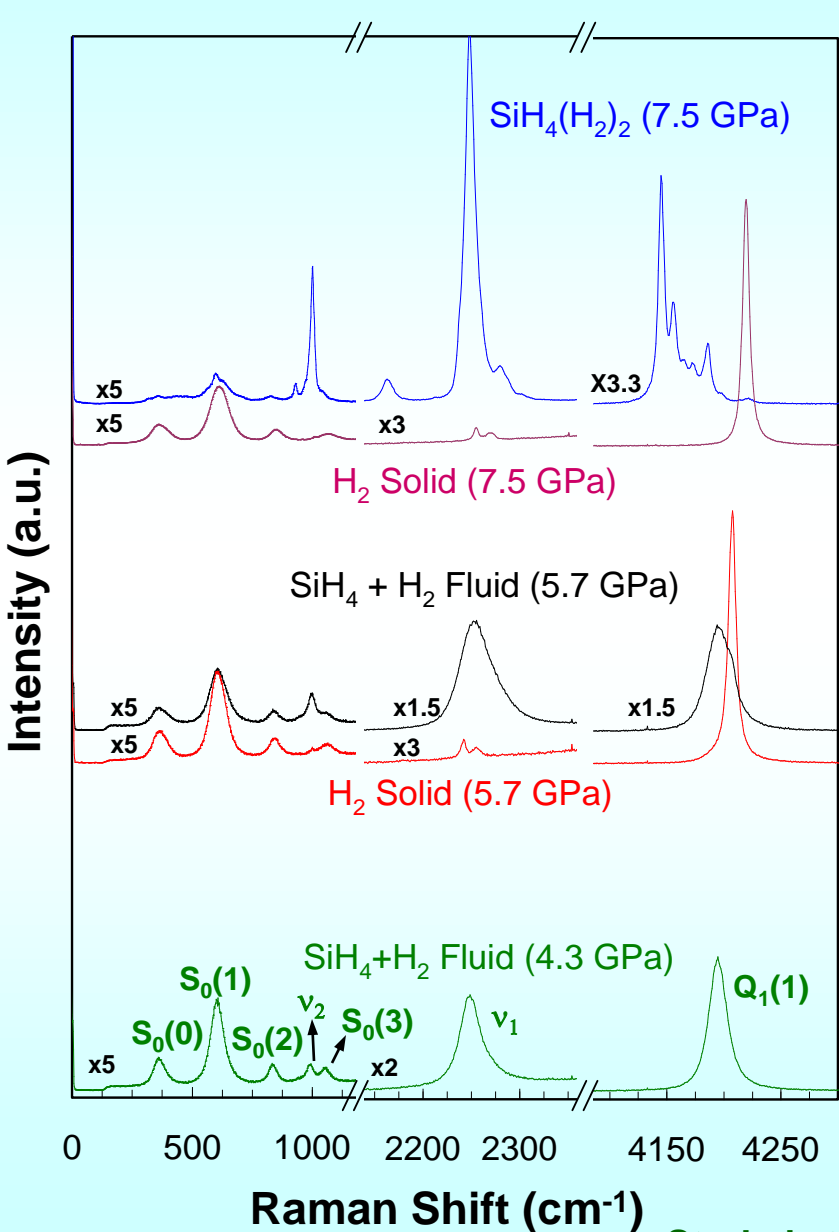
Rhenium gasket



Chen et al. *Proc. Natl. Acad. Sci.* **105**, 211 (2008)

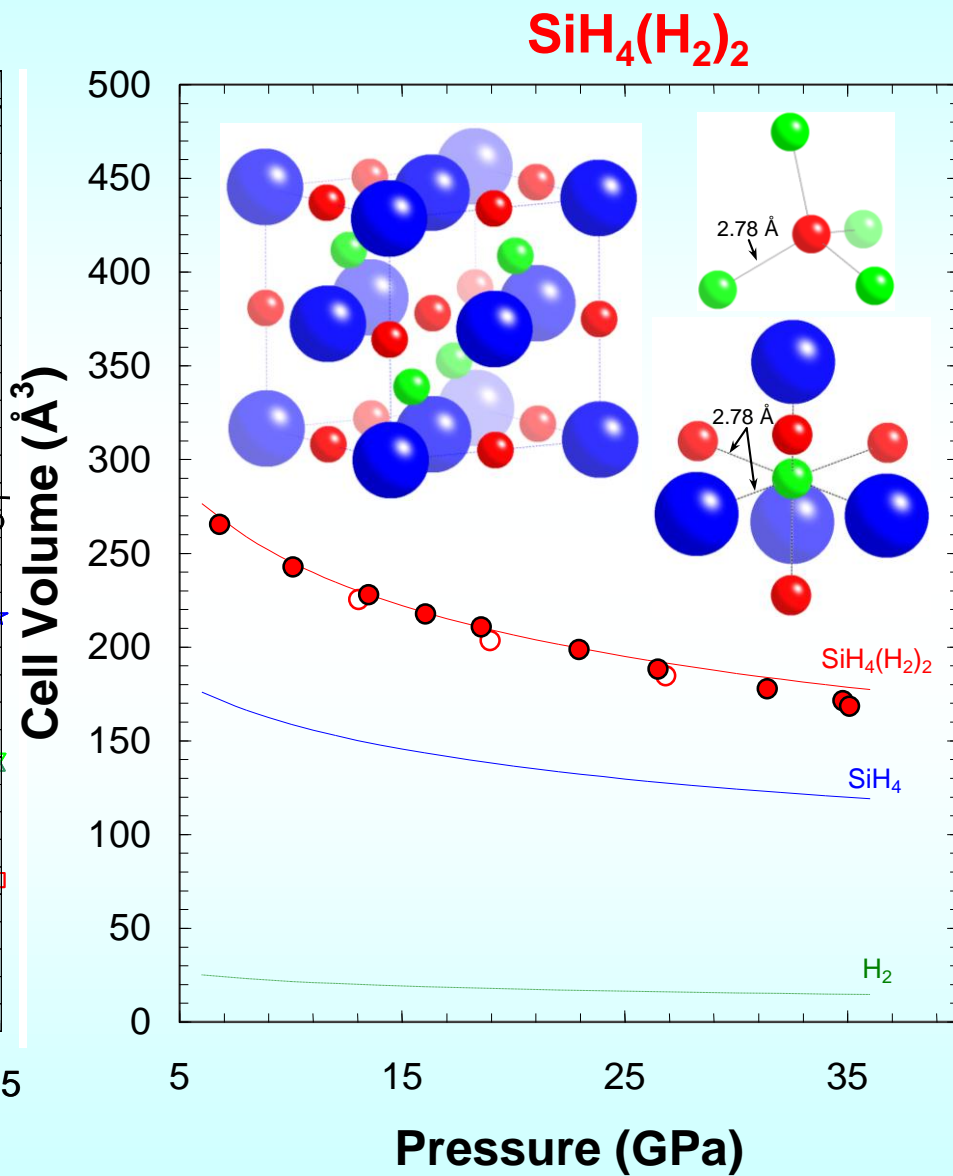
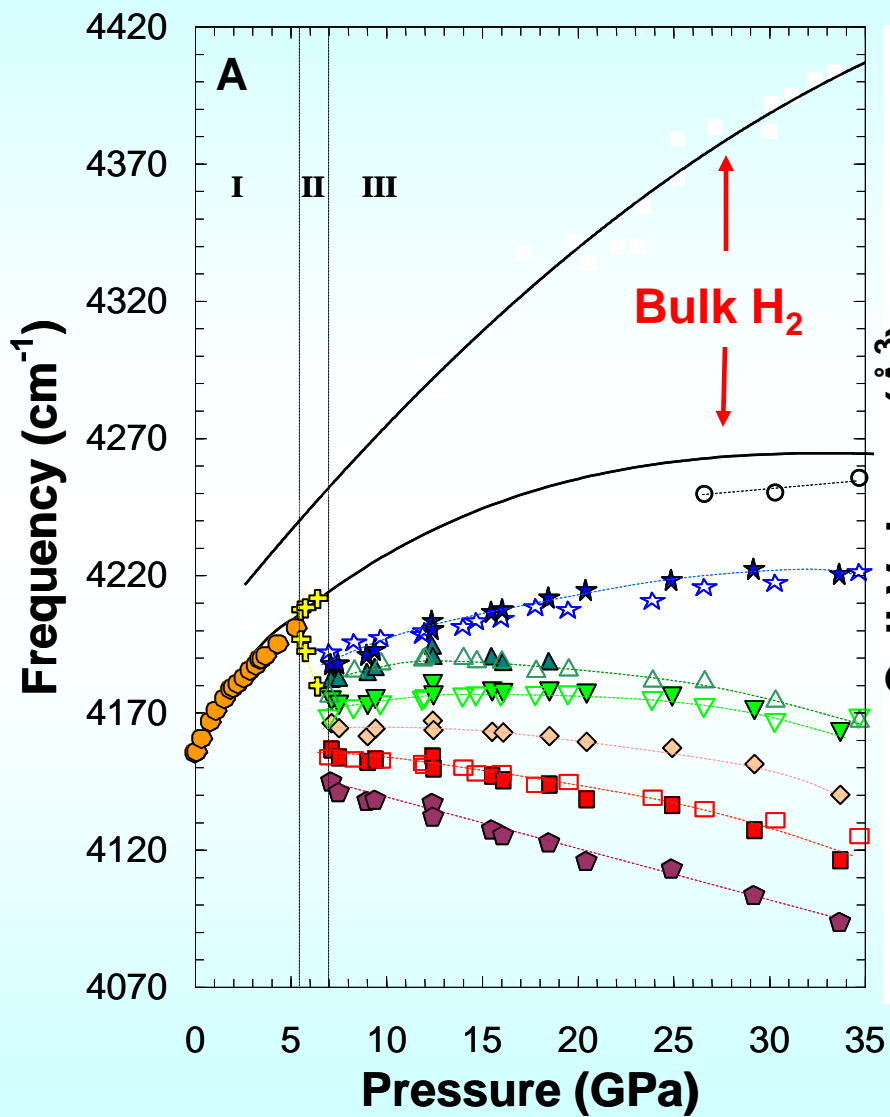
- Silane decomposes to metallic Si and amorphous Si:H above ~ 30 GPa.
- Previously reported metallization is likely related to a combination metal hydride formation and gasket/laser/x-ray catalyzed decomposition.
- Mixing SiH_4 with H_2 ? [see also, Degtyareva et al., *Solid State Comm.* (2009)]

The $\text{SiH}_4\text{-H}_2$ system exhibits rich high-pressure behavior



[Strobel et al. *Phys. Rev. Lett.* (2009)]

Novel interactions in $\text{SiH}_4\text{-H}_2$



[Strobel *et al.*, *Phys. Rev. Lett.* (2009)]

New hydrogen-xenon chemistry



VOLUME 50, NUMBER 17

PHYSICAL REVIEW LETTERS

25 APRIL 1983

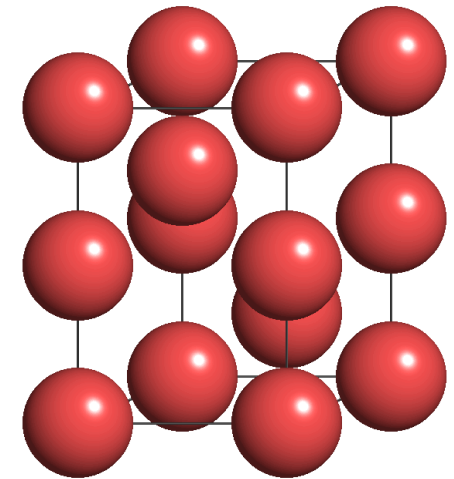
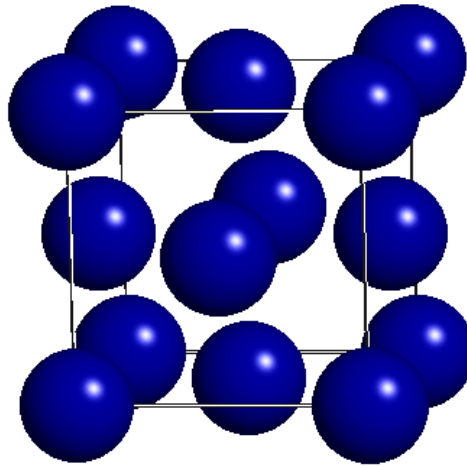
Approaches for Reducing the Insulator-Metal Transition Pressure in Hydrogen

A. E. Carlsson and N. W. Ashcroft

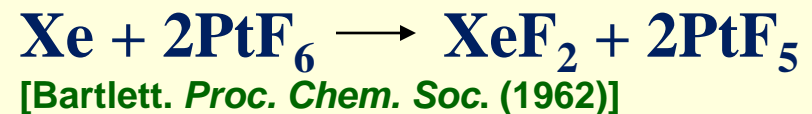
*Laboratory of Atomic and Solid State Physics and the Materials Science Center, Cornell University,
Ithaca, New York 14853
(Received 7 February 1983)*

**Xe fcc-hcp transition
then becomes metallic
at 140 GPa (300 K)**

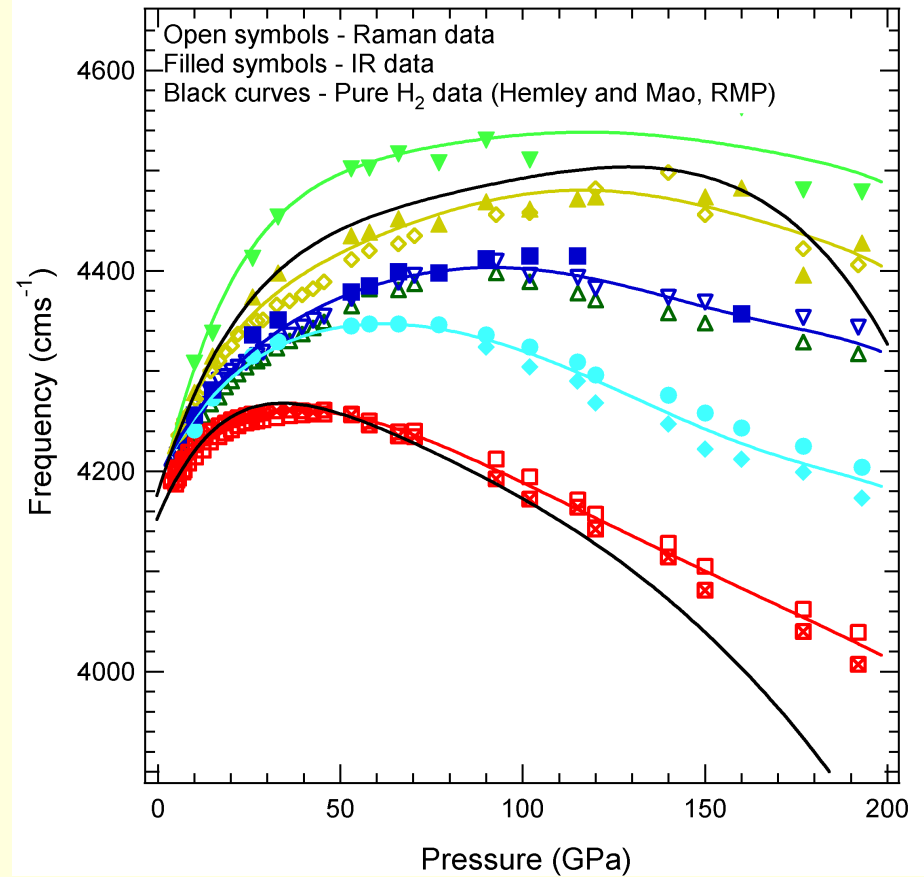
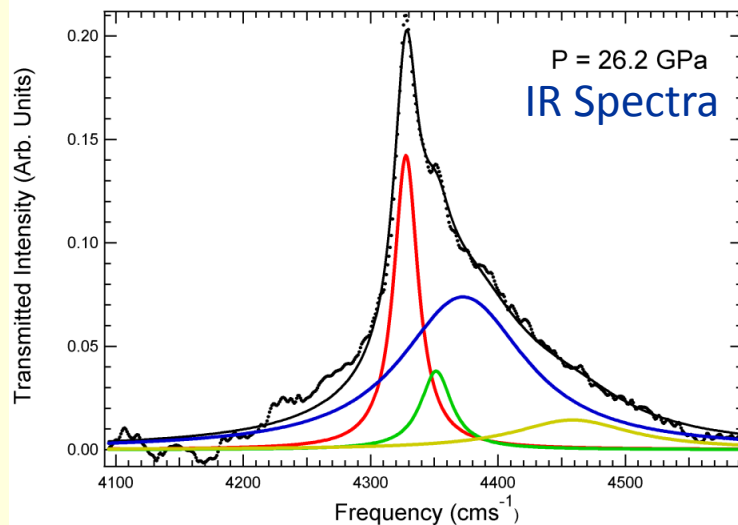
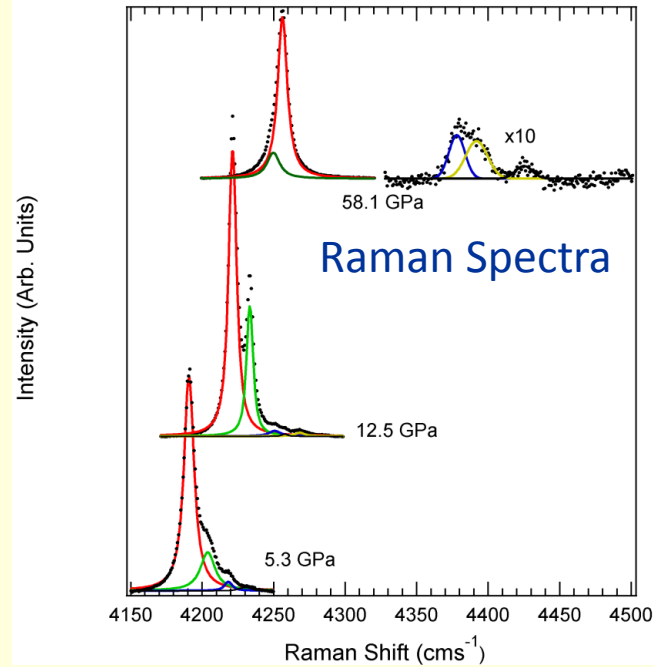
[Reichlin et al., *Phys. Rev. Lett.*
(1986); *ibid.*, Goettel et al. (1986);
Eremets et al., *ibid.* (2000)]



**Pressure-ionize Xe atoms in H₂?
Alloy stable?**

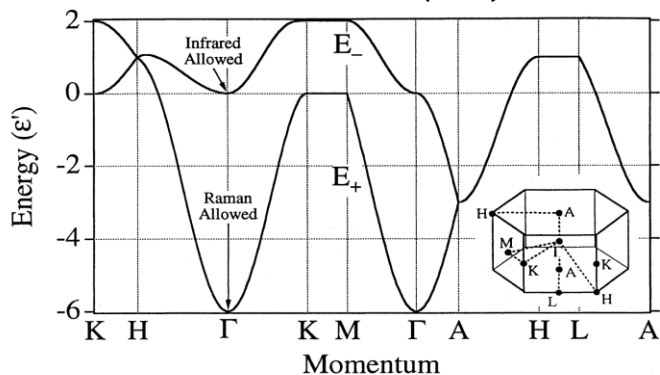
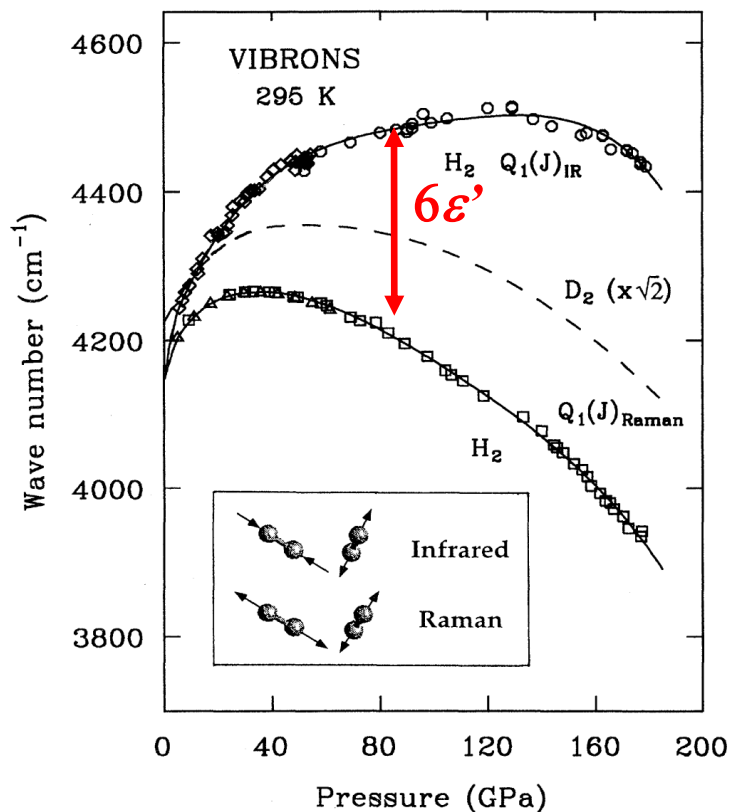


Vibrational spectroscopy of Xe-H₂ to 250 GPa

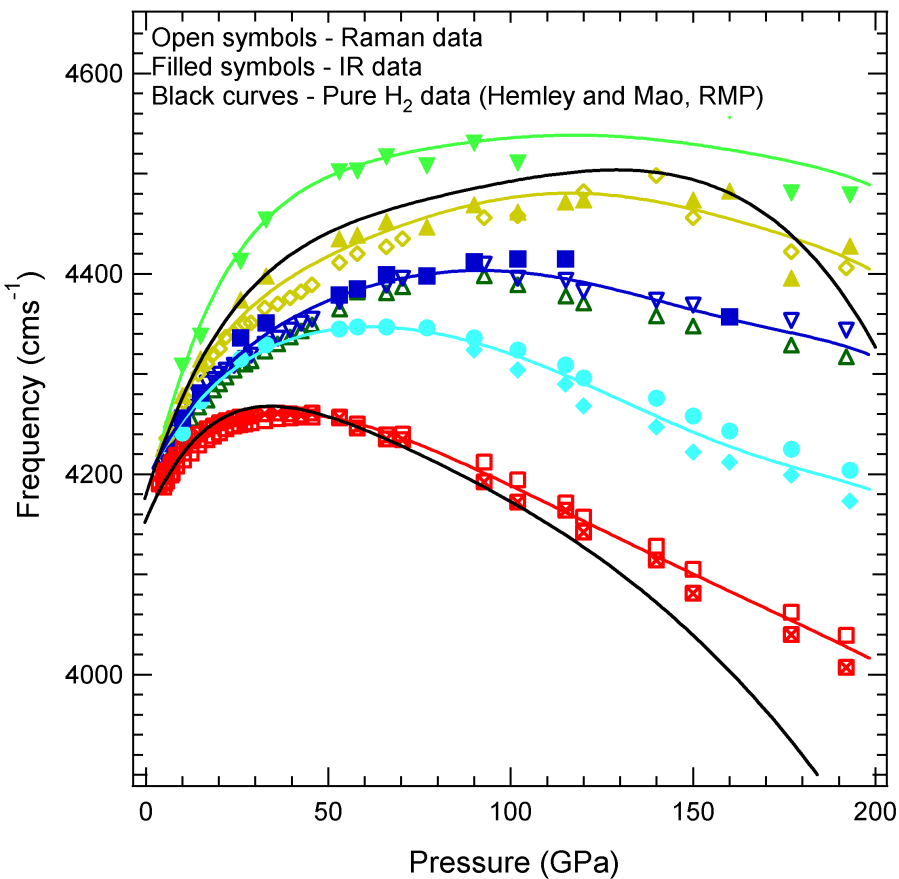


[Somayazulu et al.,
Nature Chem. (2010)]

Vibrational spectroscopy of Xe-H₂ to 250 GPa



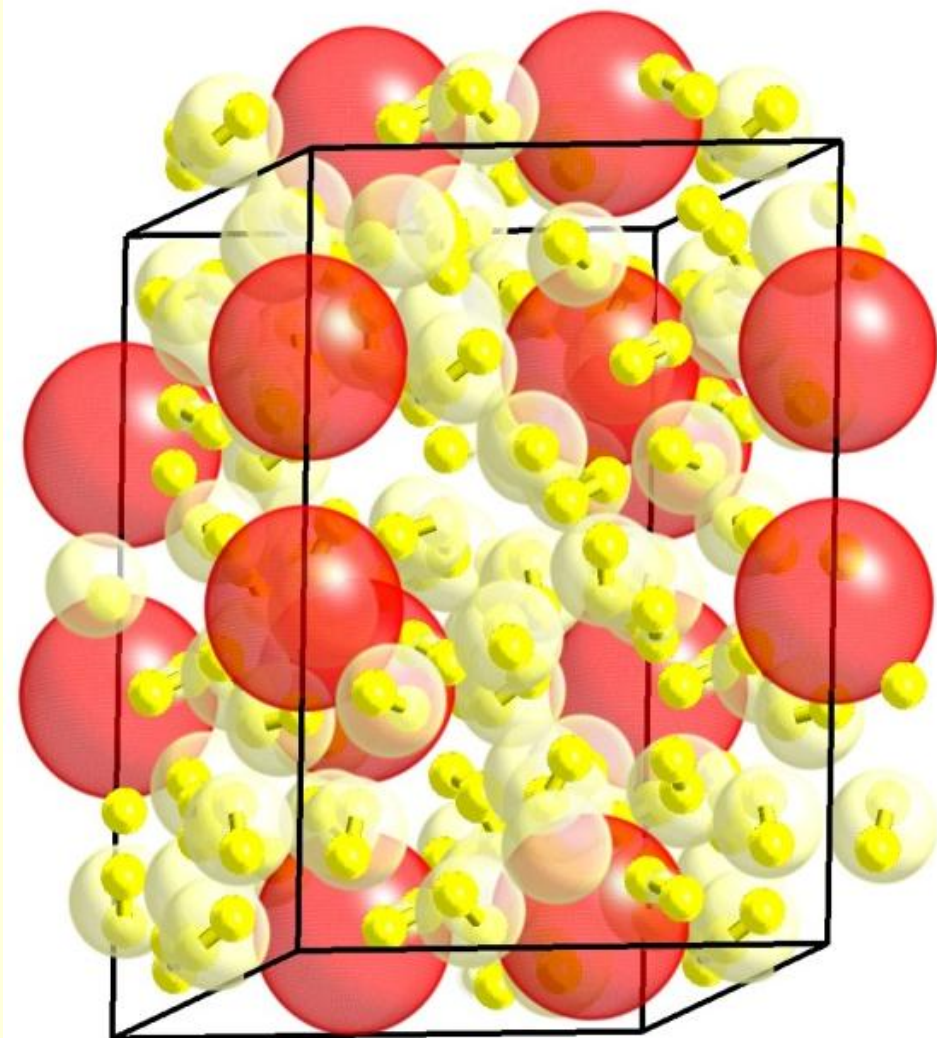
$6\epsilon'$



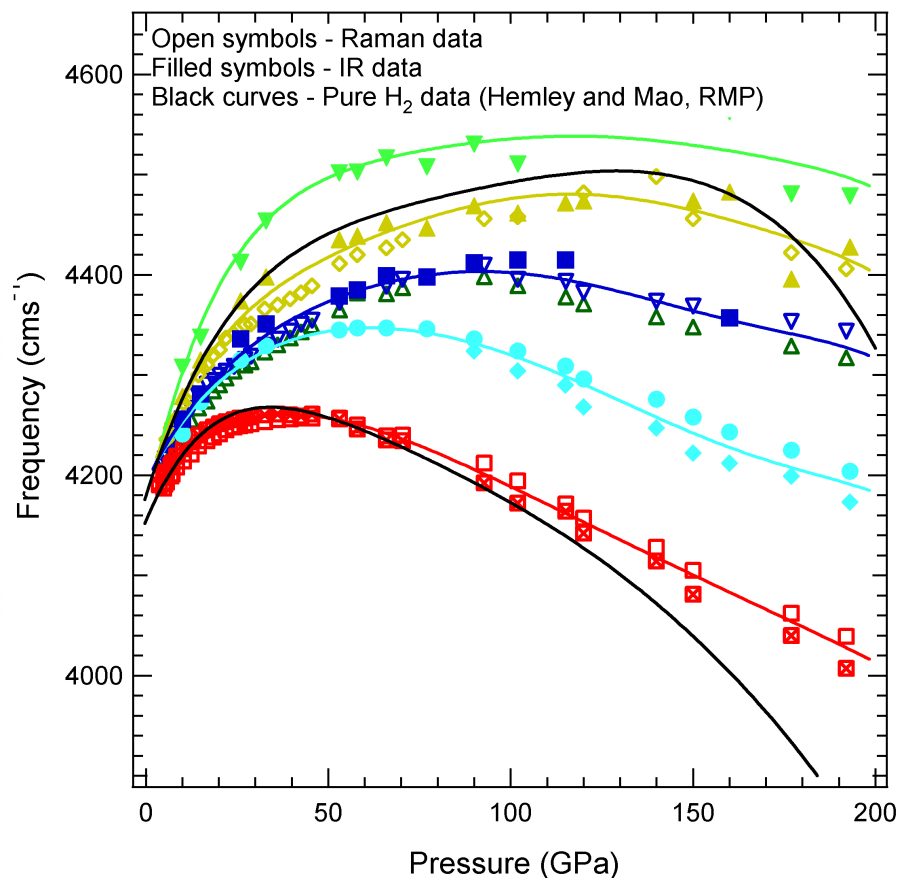
Vibrational
Coupling
Pure H₂

[Somayazulu et al.,
Nature Chem. (2010)]

Structure and stability of Xe-H₂

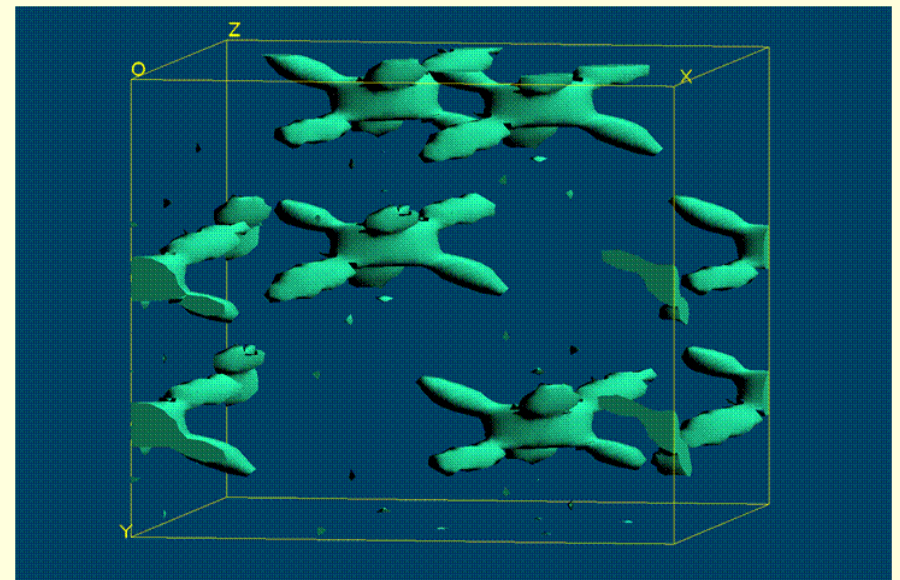
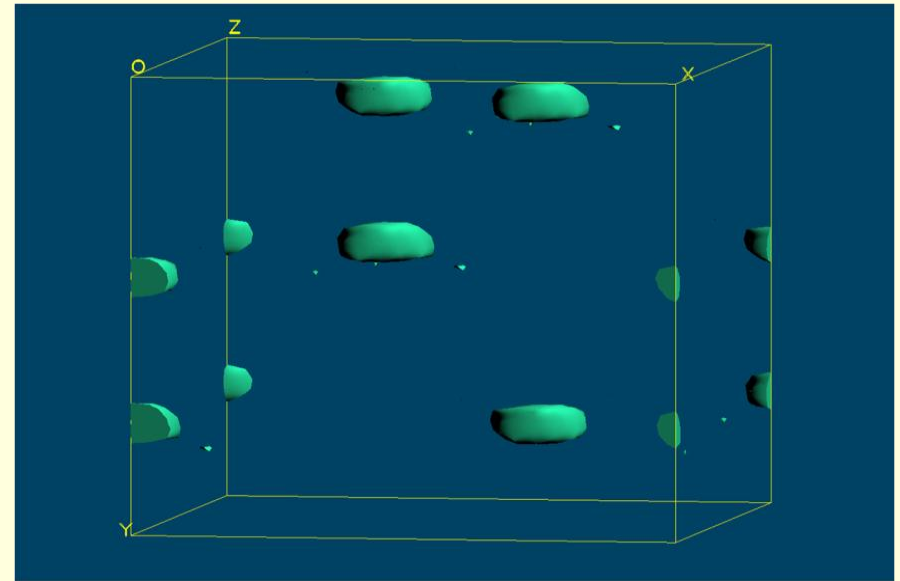
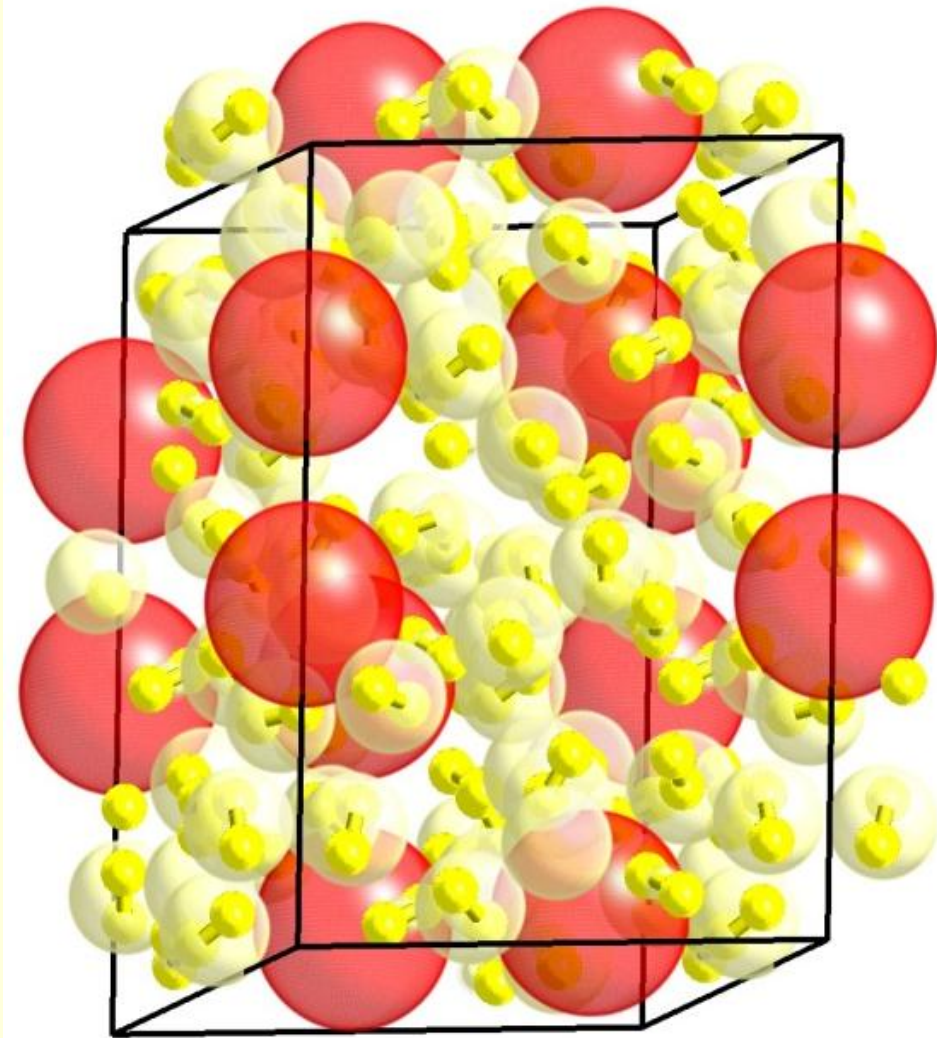


[Somayazulu et al., *Nature Chem.* (2010)]



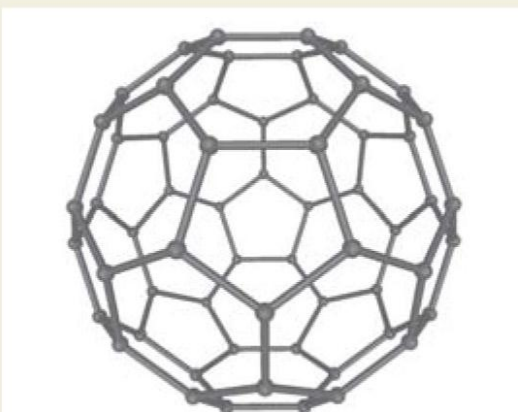
- **Stoichiometry: Xe(H₂)₇**
- **H₂ molecules intact to 250 GPa**
- **Not metallic at 250 GPa (300 K)**
- **Potential hydrogen storage material**

Structure refinement reveals electron density spread into hydrogen

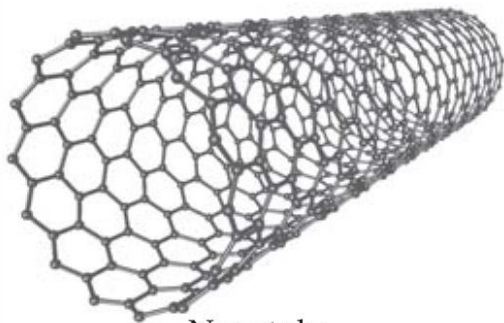


[Somayazulu et al., *Nature Chem.* (2010)]

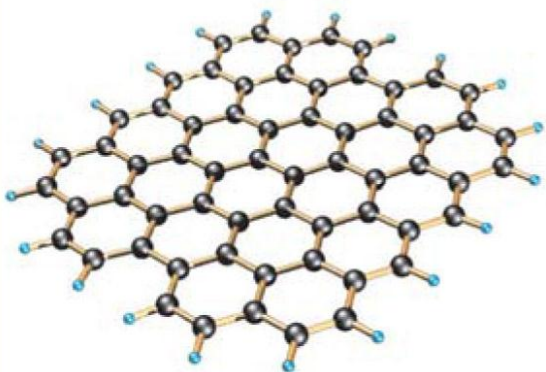
Rich polymorphism of carbon: *stable and metastable phases*



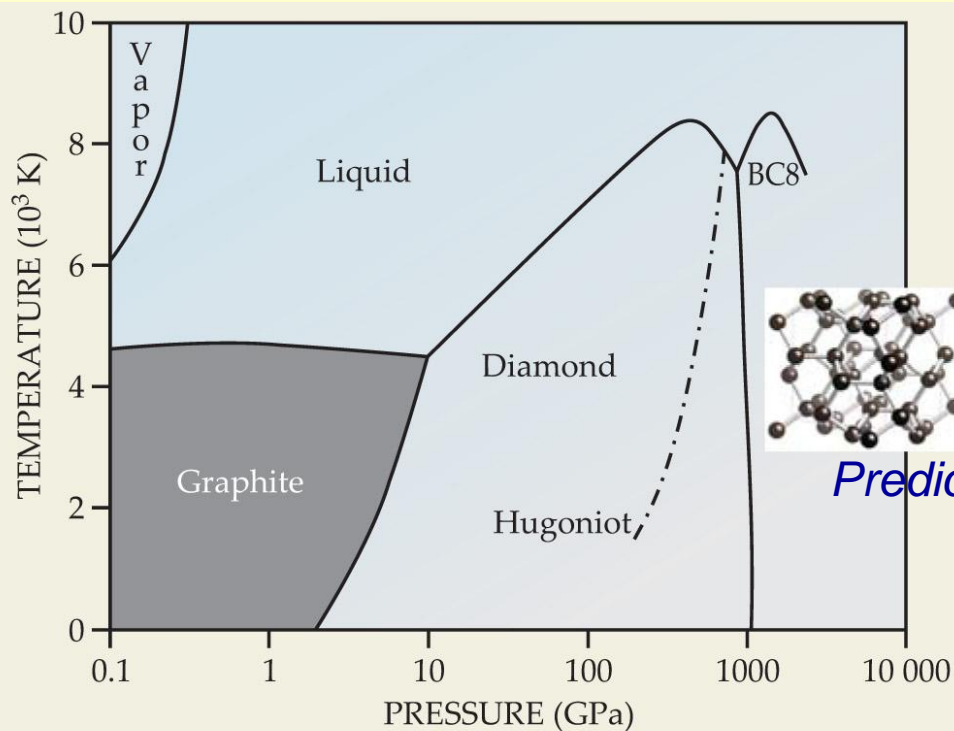
Fullerene



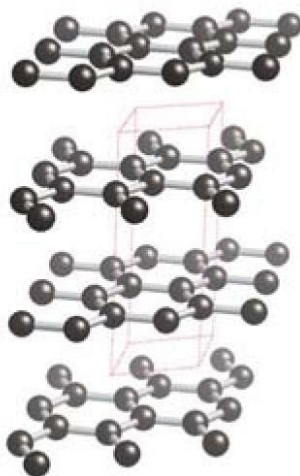
Nanotube



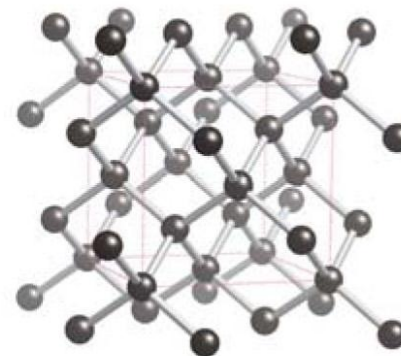
Graphene



Predicted



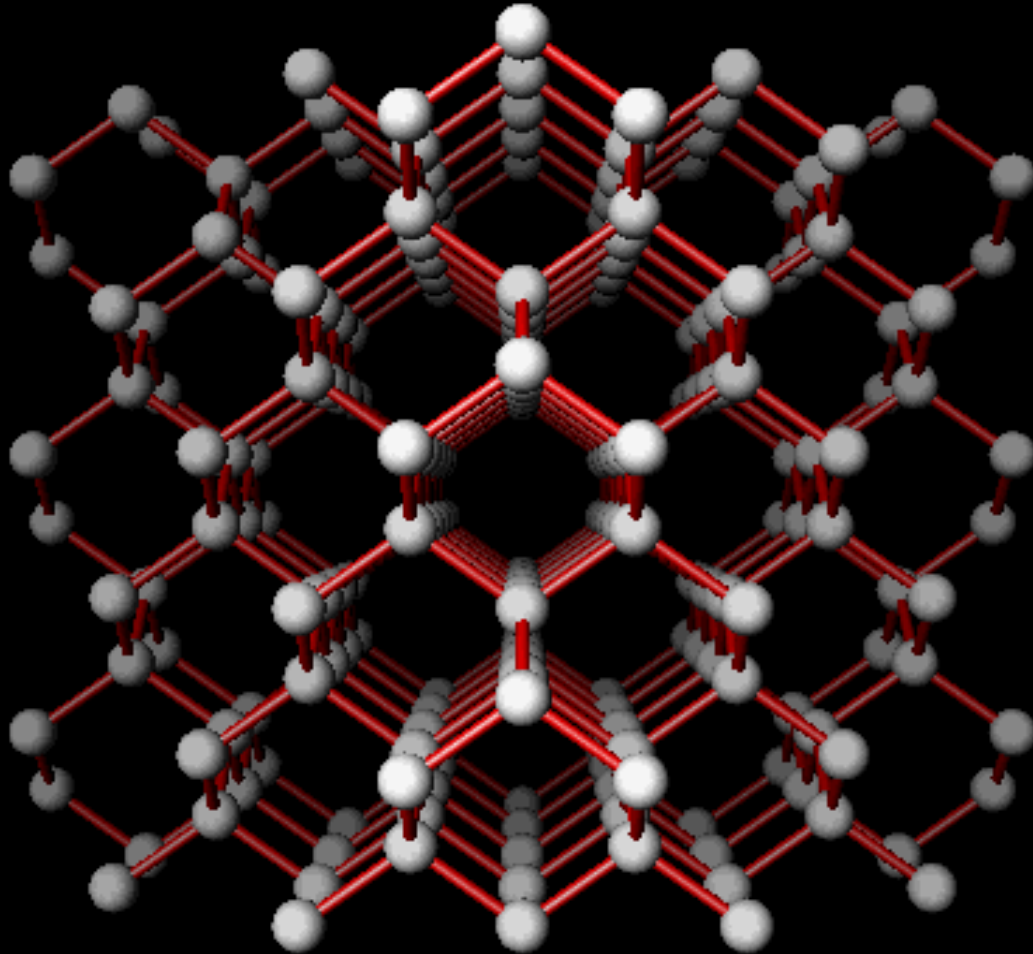
Graphite



Diamond

[Hemley, Crabtree & Buchanan, *Physics Today* (2009)]

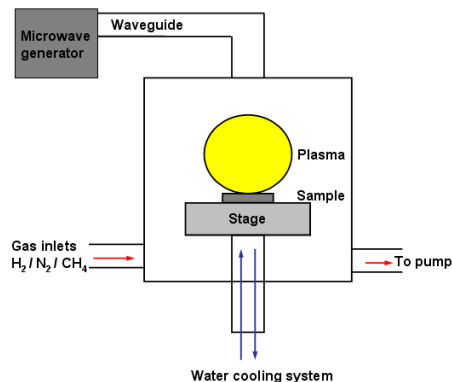
Diamond has unique physical properties:
ultimate material for extreme conditions



- High hardness/strength
- Transparency
- Low friction
- Low adhesion
- High thermal conductivity
- Low thermal expansion
- High refractive index
- Chemical inertness
- Biocompatibility
- Radiation hardness
- Electrical insulator
- Electronic properties

CVD techniques have enabled a new diamond technology

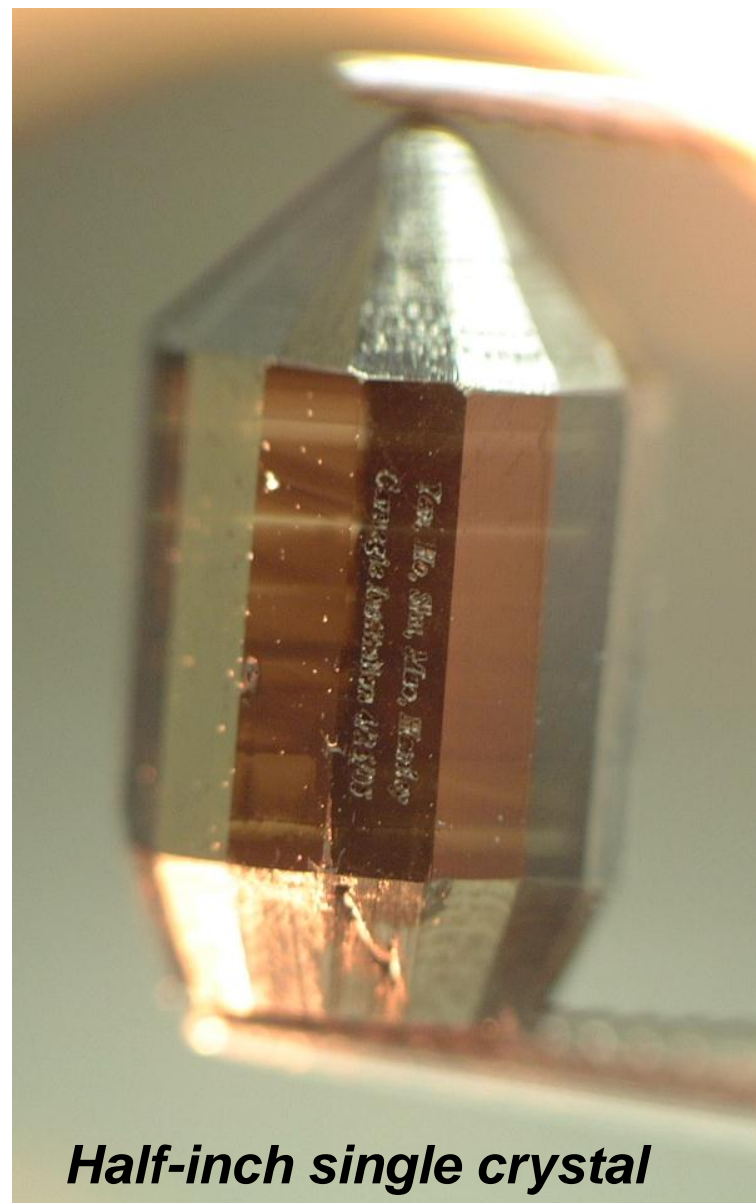
Synthesis of diamond General Electric, Co. (1954)



Microwave Plasma Chemical Vapor Deposition (CVD)

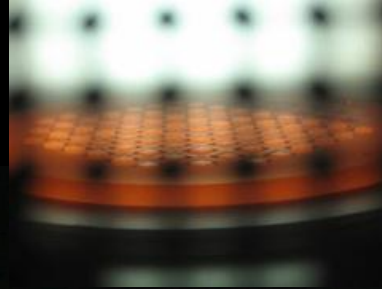
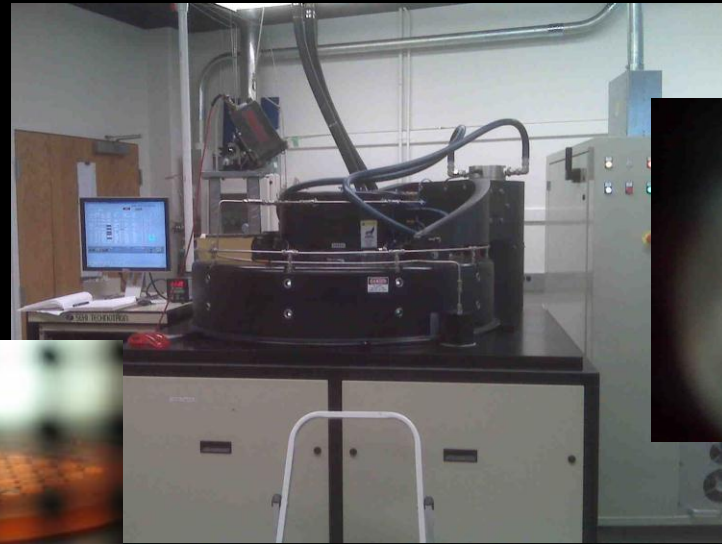


[Ho et al., *Industrial
Diamond Rev.* (2006)]



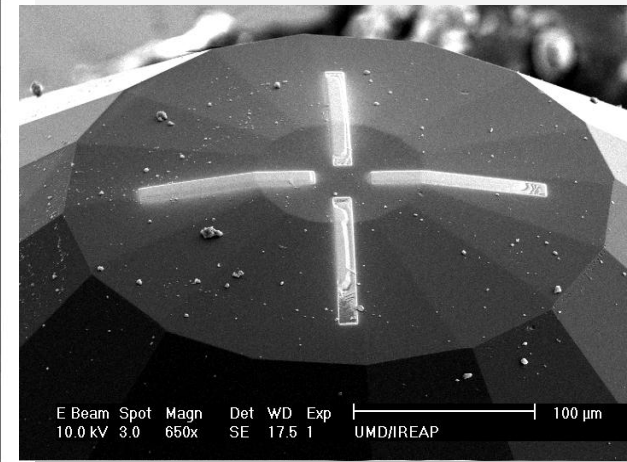
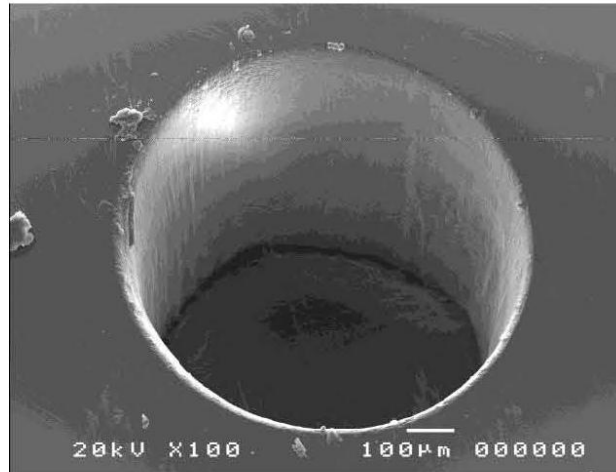
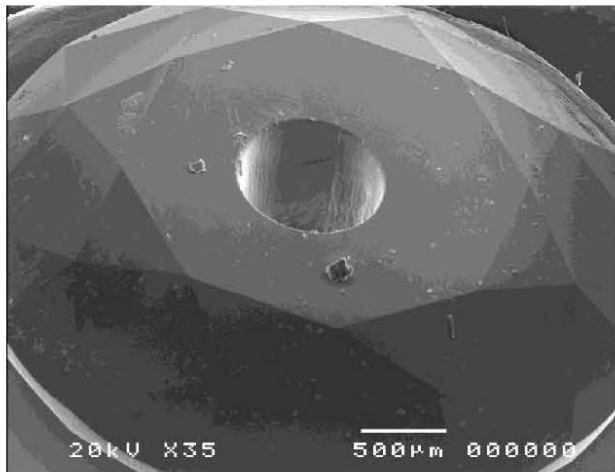
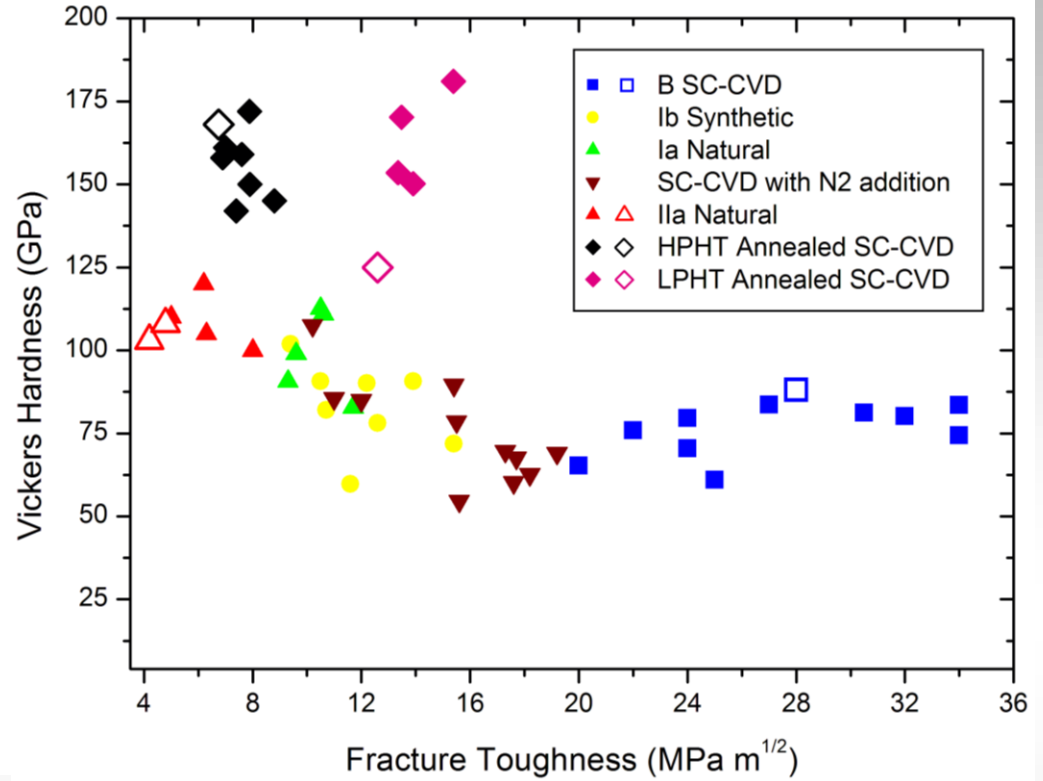
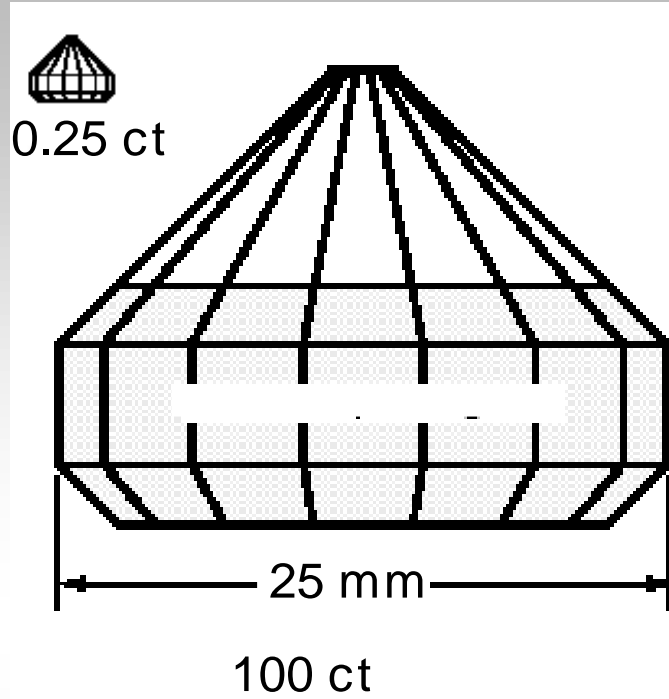
Half-inch single crystal

Single Crystal Diamond from Chemical Vapor Deposition

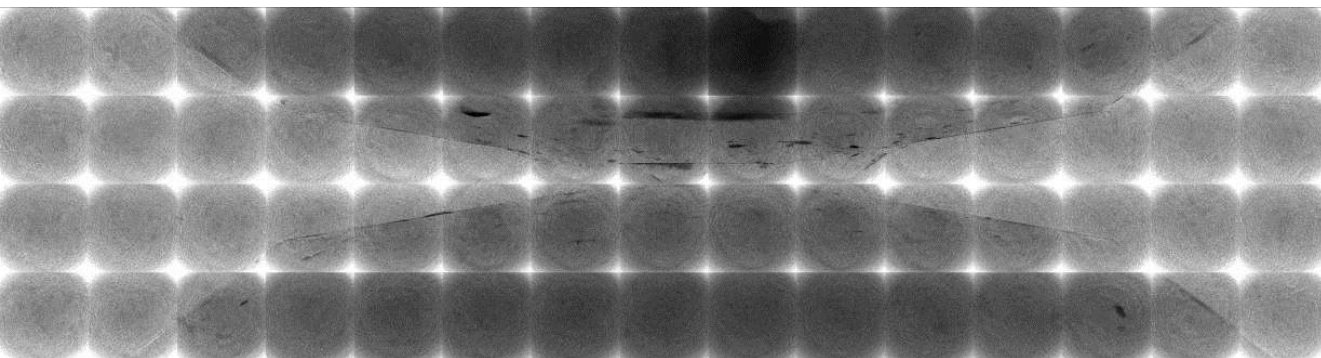


[Meng et al., PNAS (2008)]

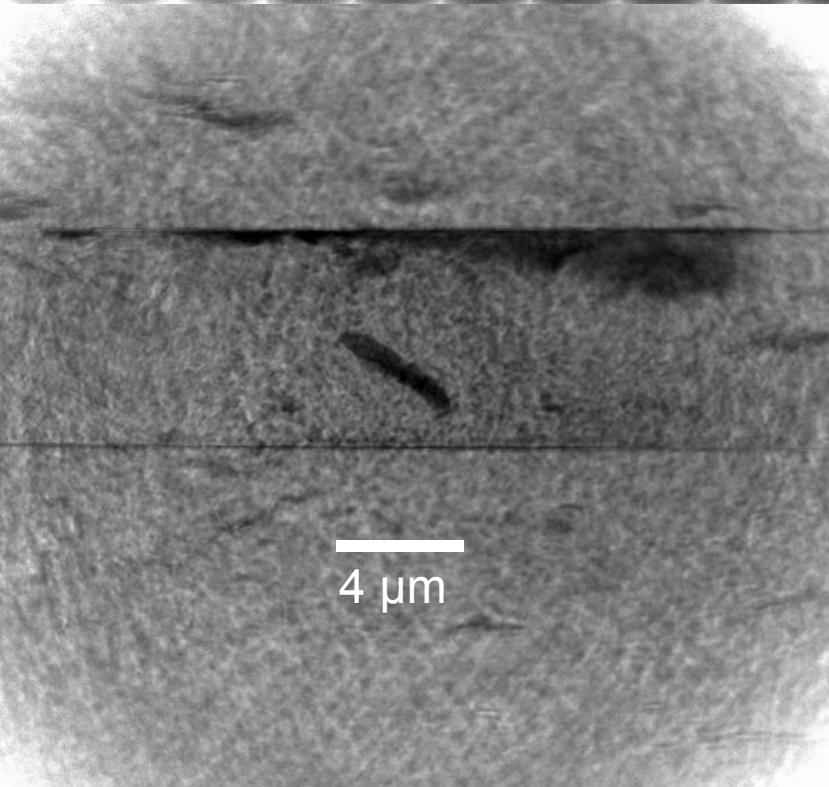
Next generation CVD diamond technology for high pressure



Using nanobeams to measure anvil nanostrains and optimize pressure

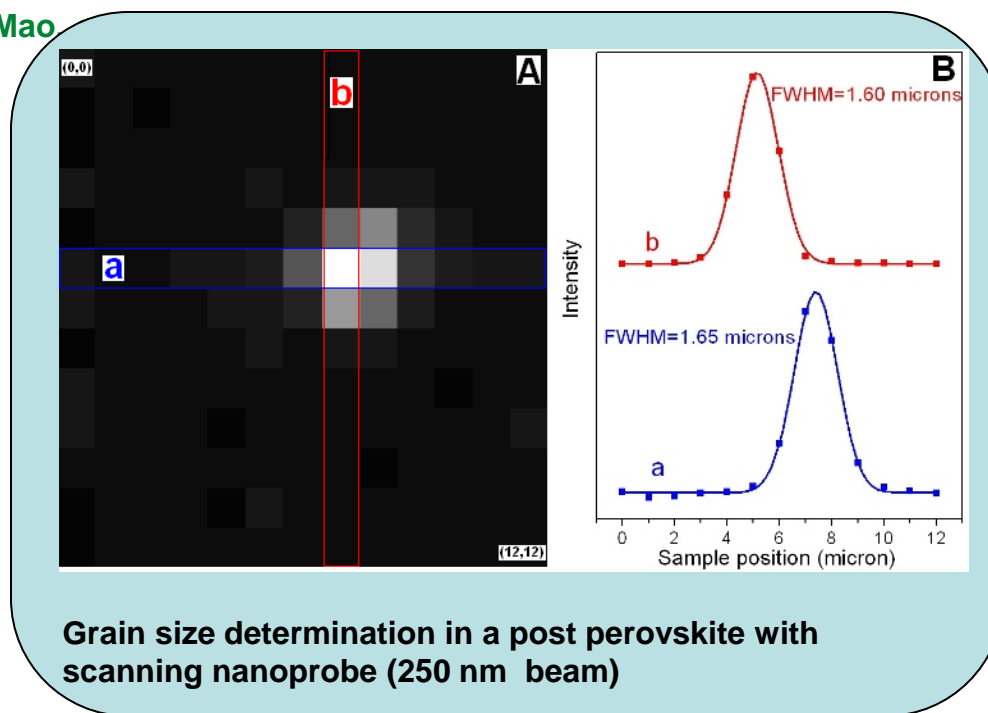


First submicron megabar x-ray measurements



30 nm resolution

[W. Mao]



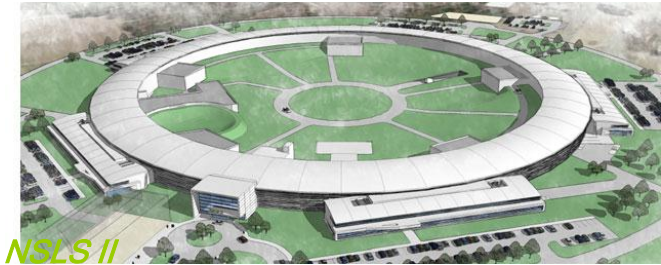
Xradia nanoscope with 30 nm resolution

SSRL Beamline 6-2

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

New generations of large facilities are coming on line

X-ray Sources



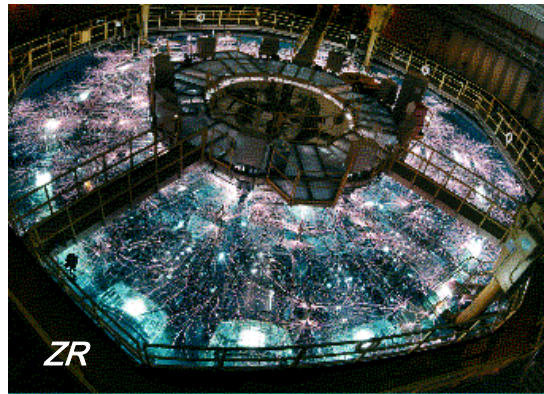
- *Higher brightness synch.*
- *Dynamic compression*
- *Energy Recovery Linacs*
- *Fourth Generation Sync.*

Neutron Sources



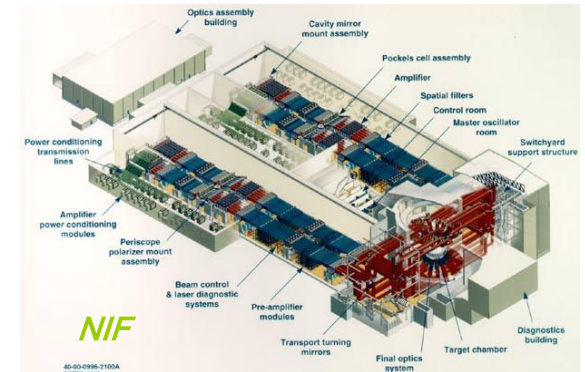
- *Dedicated beamlines*
- *>100 GPa neutron scattering*

Pulsed Power



- *Ultrahigh P-T conditions*
- *New diagnostics*
- *Static/dynamic*

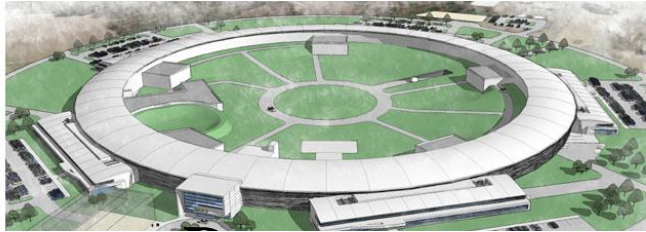
Laser Sources



- *10 Mbar-Gbar pressures*
- *New diagnostics*
- *Static/dynamic*

New generations of large facilities are coming on line

X-ray Sources



Neutron Sources



➤ ***New inelastic scattering in new domains***

➤ ***Time dependent (<ps-scale) diffraction/imaging***

➤ ***Heterogeneous/complex assemblages: nm-diffraction***

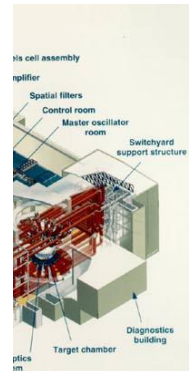
➤ ***Interfaces/grain boundaries***

➤ ***New domains of P-T-t***

Pulsed Power

- μ
- Λ
- ***Static/dynamic***

ing



ns

- ***Static/dynamic***

CONCLUSIONS AND PERSPECTIVES

- 1. Exploring materials under extreme conditions is deepening our understanding of chemistry at a fundamental level.**
- 2. Unexpected structures and bonding schemes are emerging through a combination of experiment and theory.**
- 3. 'Simple' molecular and elemental systems provide a useful starting point for developing this new understanding.**
- 4. Progress continues as a result of continued development of new techniques and materials.**



ACKNOWLEDGEMENTS

Collaborators

CARNEGIE INSTITUTION

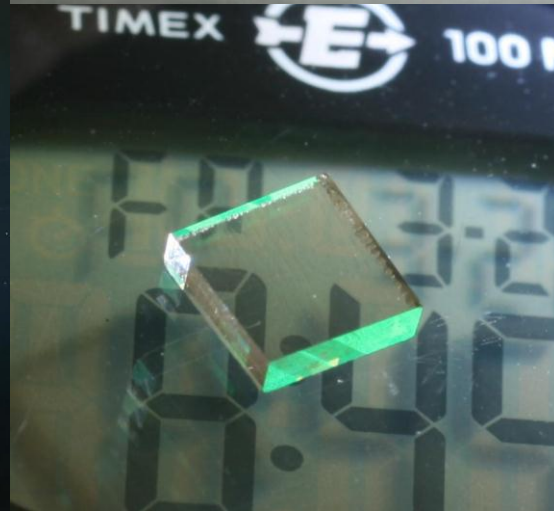
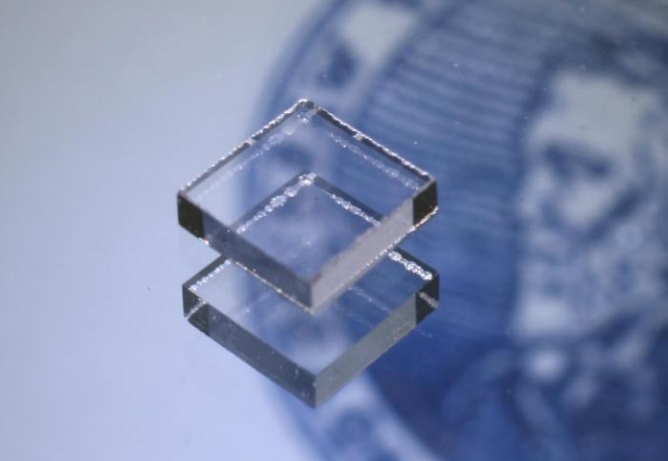
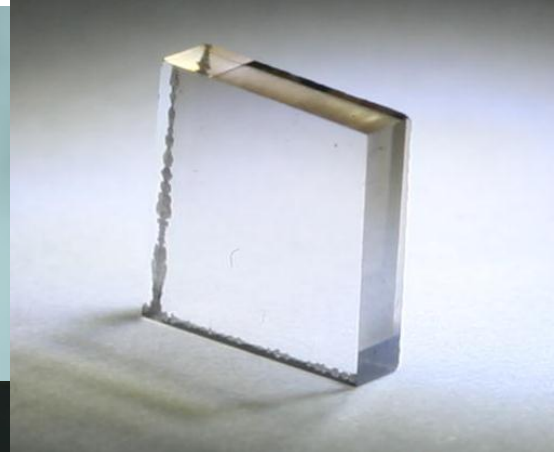
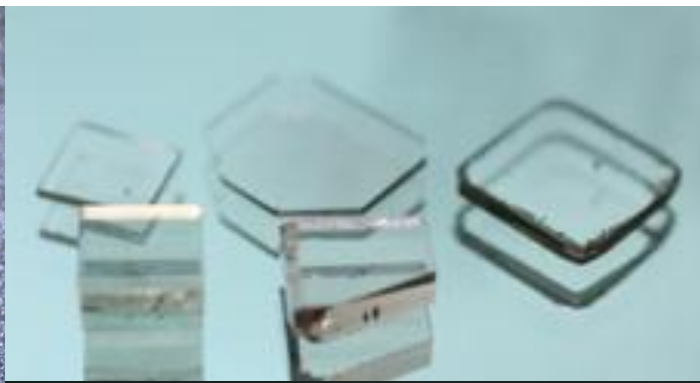
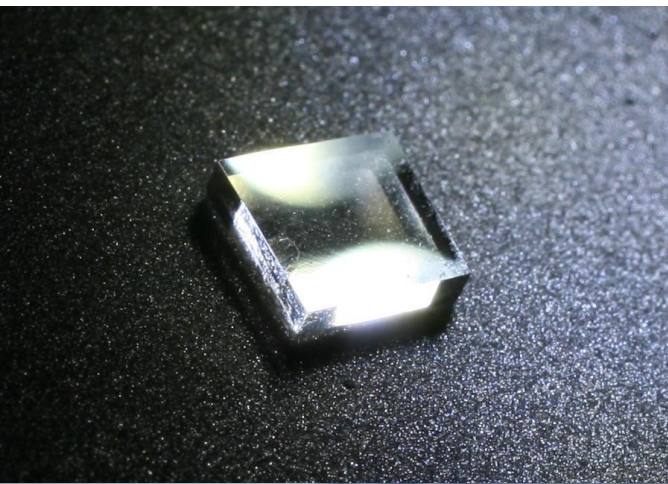
Ho-kwang Mao	Alexander Goncharov
Viktor Struzhkin	Ronald E. Cohen
Chih-shue Yan	M. Somayazulu
Changsheng Zha	Timothy Stobel
Joe Lai	Robert Hazen
Yufei Meng	Yingwei Fei
Yingwei Fei	Stephen Gramsch
Jinfu Shu	Qi Liang
Zhenxian Liu	Yue Meng
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Anurag Sharma	Patrick Griffin
Yang Ding	Amy Lazicki
P. Ganesh	S. Krasnicki

OTHER INSTITUTIONS

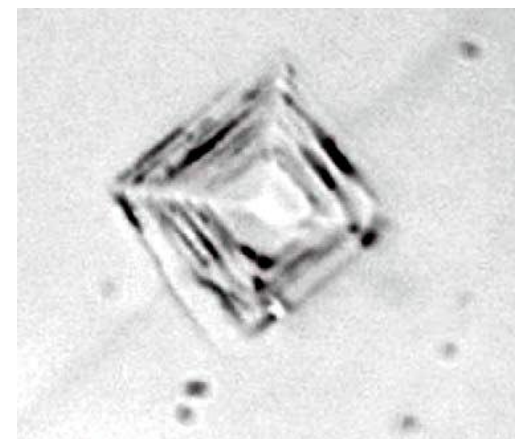
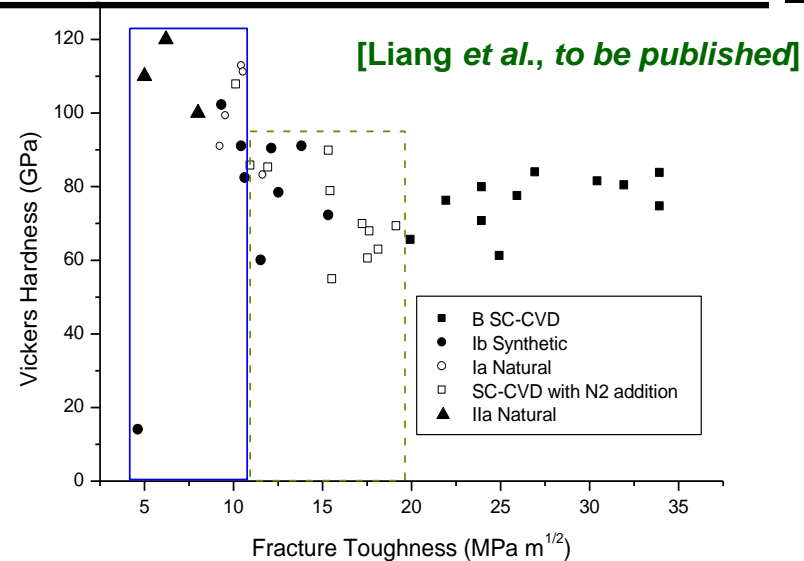
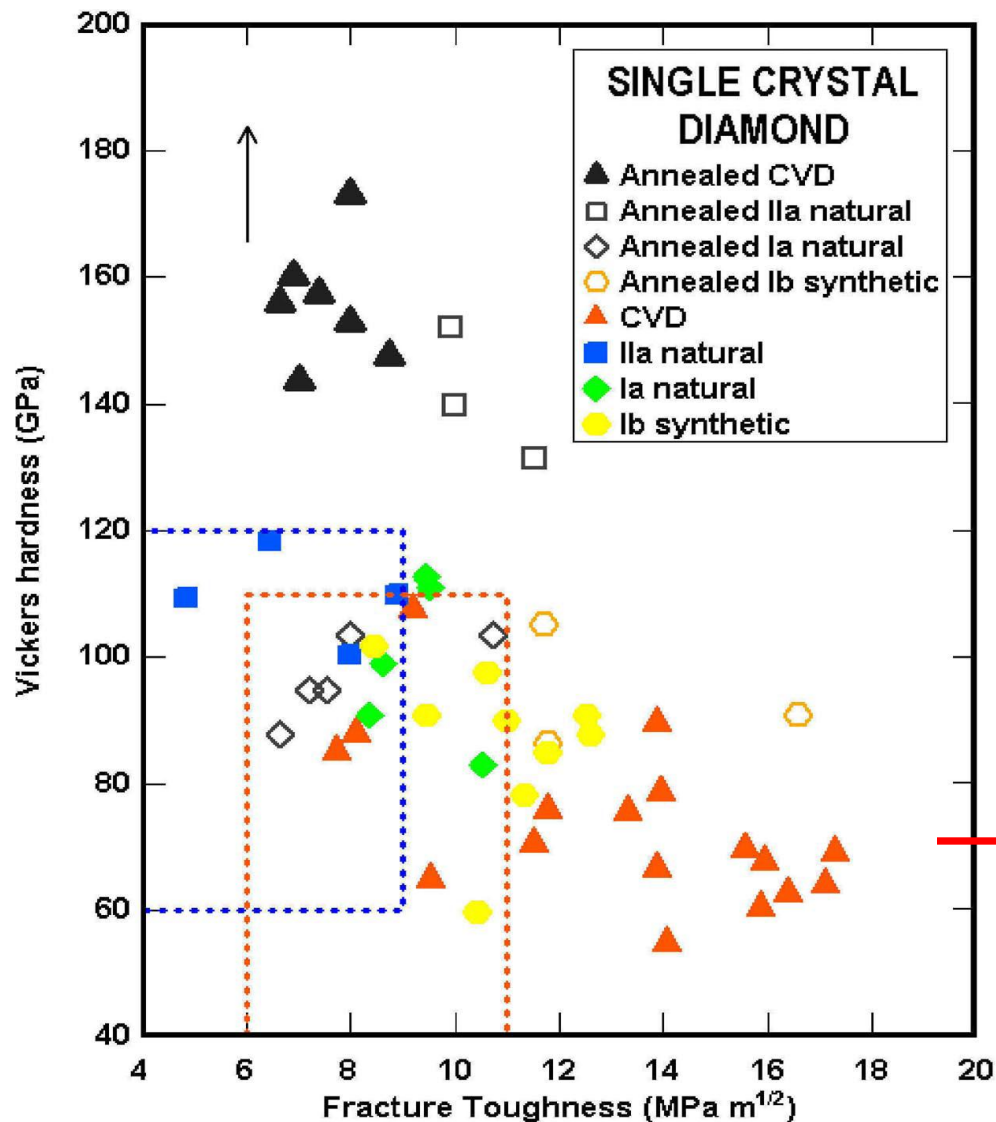
Pierre Toledano (Ameins)
K. Litasov (Tohoku)
(Chi-chang Kao (BNL)
Przemek Dera (GSECARS)
Jennifer Ciezak (ARL)
Tim Jenkins (NIST)
E. Gregoryanz (Edinburgh)
Mikhail Eremets (Mainz)
Wendy Mao (Stanford)
Yusheng Zhao (LANL)
Nick Sobolev (Novosibirsk)
G. Zou (Jilin)
Eric Shirley (NIST)
Paul Loubreyre (CEA)
Raymond Jeanloz (Berkeley)
G. W. Collins (Livermore)

Financial Support

DOE/NNSA/SSAAP
DOE/OS/BES
NSF, Carnegie Institution

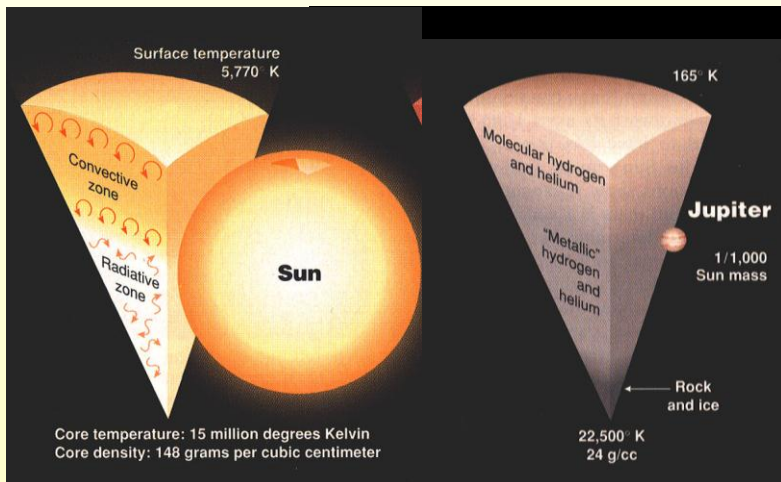
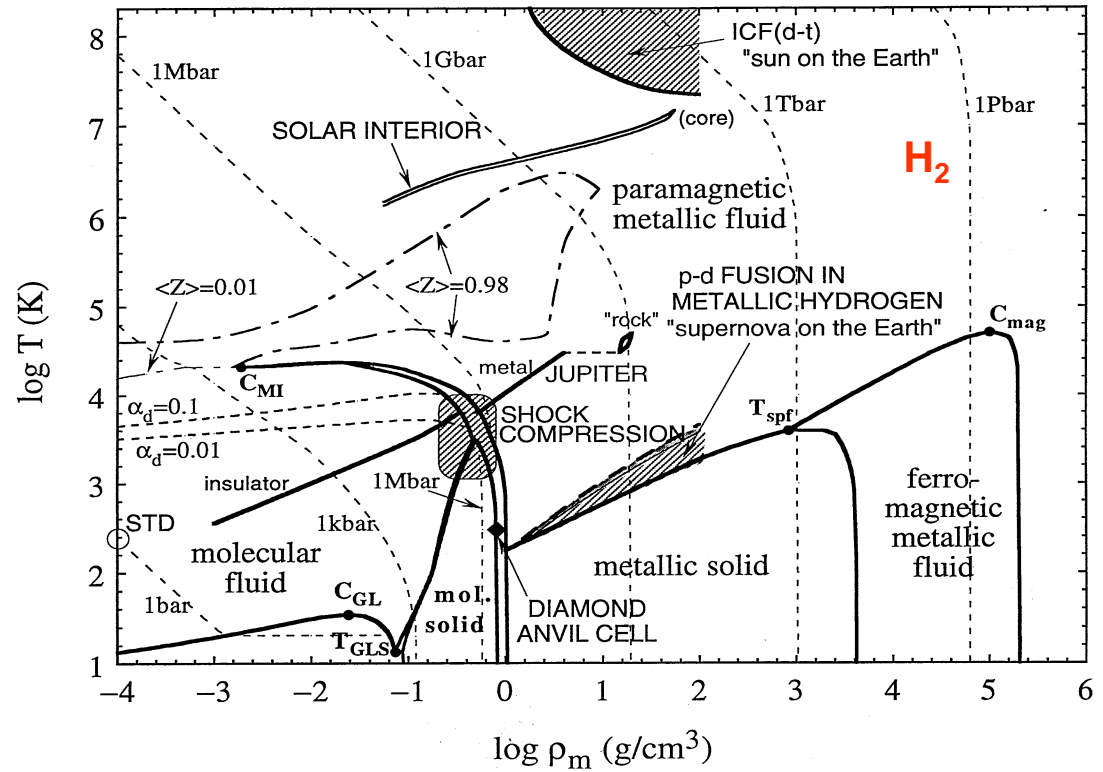


The mechanical properties can be tuned over a range of hardness and toughness

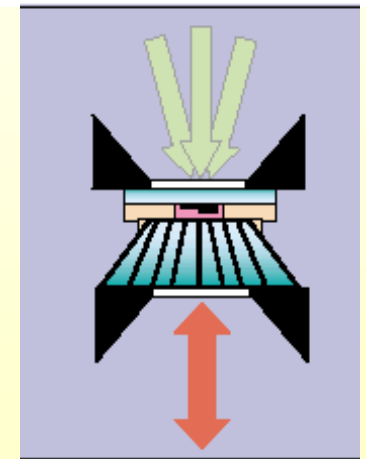


Ultratough Diamond:
 No crack propagation
 $K_{Ic} > 30 \text{ MPa m}^{1/2}$

Uncharted Territory Beyond Conventional Materials Physics



- Combined static/dynamic compression
- Ultra-fast diagnostics



[Loubeyre et al., *High Pres. Res.* (2004)]