Hydrogen Rich Solids
as source of
Quantum Spin Liquids &
High Tc Superconductivity

ICTP Workshop on Current Trends in Magnetism

School of Physics
Jawaharlal Nehru University
New Delhi

The Institute of Mathematical Sciences
Chennai

G. Baskaran

8-13, January 2015

Acknowledgement

wakeup call on 2nd Dec 2014 from
V P S Awana (NPL) &
Mukul Laad (Matscience)

Science and Engineering Research Board (SERB, India) for a
SERB Distinguished Fellowship

Perimeter Institute for Theoretical Physics (Waterloo, Canada) for a
Distinguished Visiting Research Chair

About *Institute of Mathematical Sciences*

http://www.imsc.res.in

60 faculy
100 Ph.D. students
20 PDF's
10 visitors

Research in
- *Theoretical Physics*
- *Pure Mathematics*
- *Computer Science*

autonamous Institute, aided by DAE,

similar to IISc, Bangalore TIFR, Bombay

Summer Program for B.Sc., B.E. students before their last year

JEST - a national leve exam to become JRF at IMSc and several other similar Institutions in India

Why spin liquids ?

Metallic Hydrogen – some history

My new proposal – Molecular singlets to Resonating Singlets

Molecular solid to Fermi liquid metal transition via Mott insulator phase

Pressure induced Frustration and

Emergence of Quantum Spin Liquids in solid Hydrogen

H-rich Solids – Silane, H_2S ...

H_2S under Pressure - Superconductivity at 190 K ?

Quantum spin liquid phase in solid H_2S at high pressures

Self doping and RVB Theory of Superconductivity

Why do we crave for spin liquids ?

Quantum spin liquids display
rich structures than anticipated
Quantum Entanglement Organization (GB)

Compared to
Superfluids and superconductors

Many quantum phases and new notions/ideas

Emergent Z2, U(1) and SU(2) gauge fields

Quantum order, topological entanglement

novel topological excitations

Spinon, pseudo fermi surfaces
Holon, gauge bosons
Majorana fermion, Fibonaci anyon ..

.

Symmetry Protected Topological (SPT) phases
classification
Slave particles (partons)
Projective symmetry groups

Connections to Chern-Simon, topological field theories

Unexpected connection to New Mathematics
create new mathematics

Cohomology theory, Tensor Category theory
Ricci flow (Premi's talk) ...

Quantum Spin Liquids are
abode of
High Tc and Unconventional Superconductivity
and a variety of phases

All known high Tc superconductors have
deep connection to
Quantum spin liquids
(GB, unpublished)

Techonological application ?

Spinonics

(A Jafari, GB 2002)

Metallic Hydrogen

Huntington-Wigner (1935)

Solid Hydrogen will become a metal at ~ 25 GPa

Ashcroft (1968)

Metallic Hydrogen - a room temperature superconductor

Phonon mediated superconductivity and high Deby Temperature

Planetary interiors - Jupitor, Mercury ..

Metallic core

Spin liquid shells ?

(similar to superfluidity in neutron stars ..)

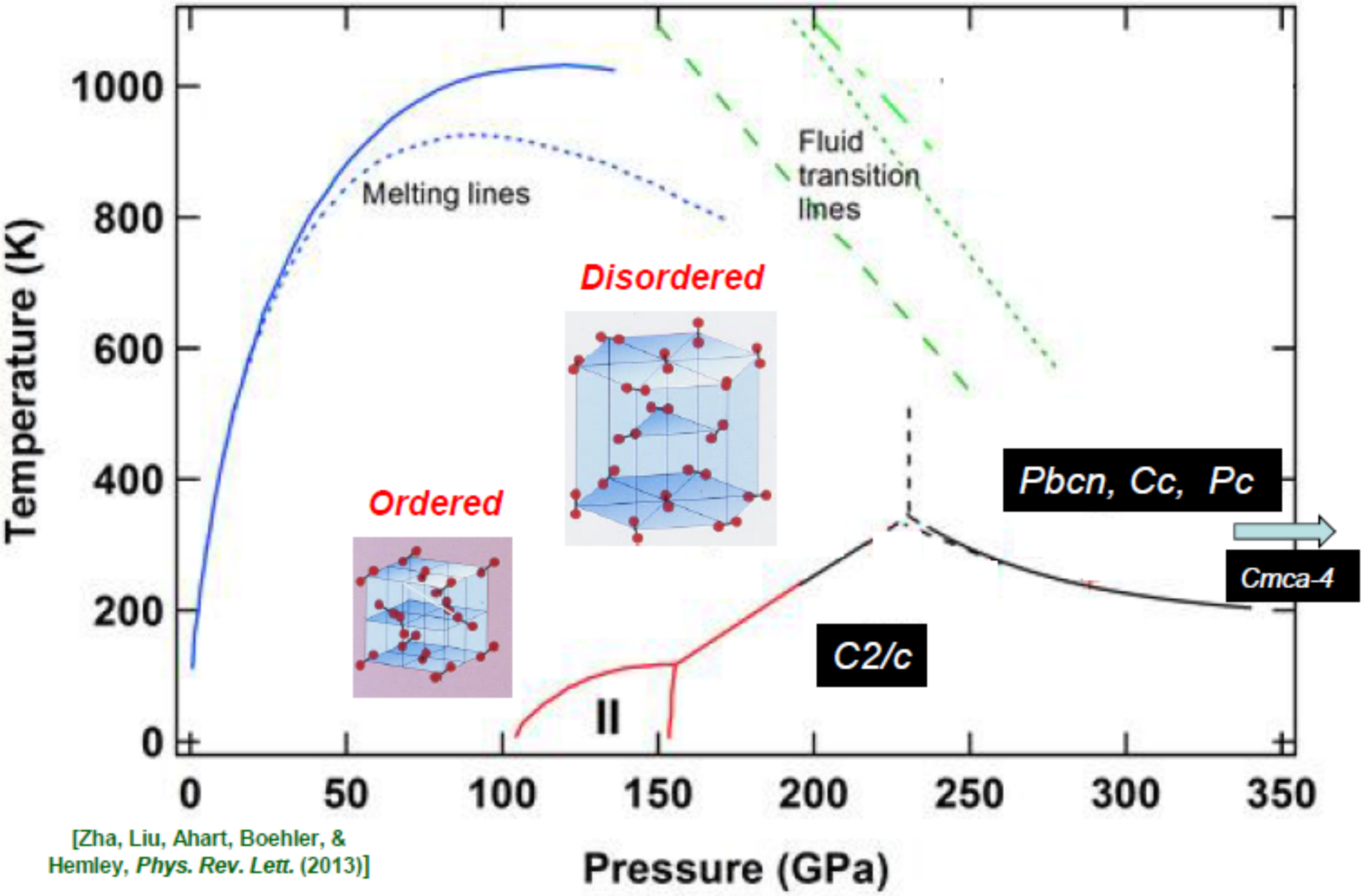
But solid Hydrogen resists metallization even at 300 GPa

It seems to exhibit a variety of

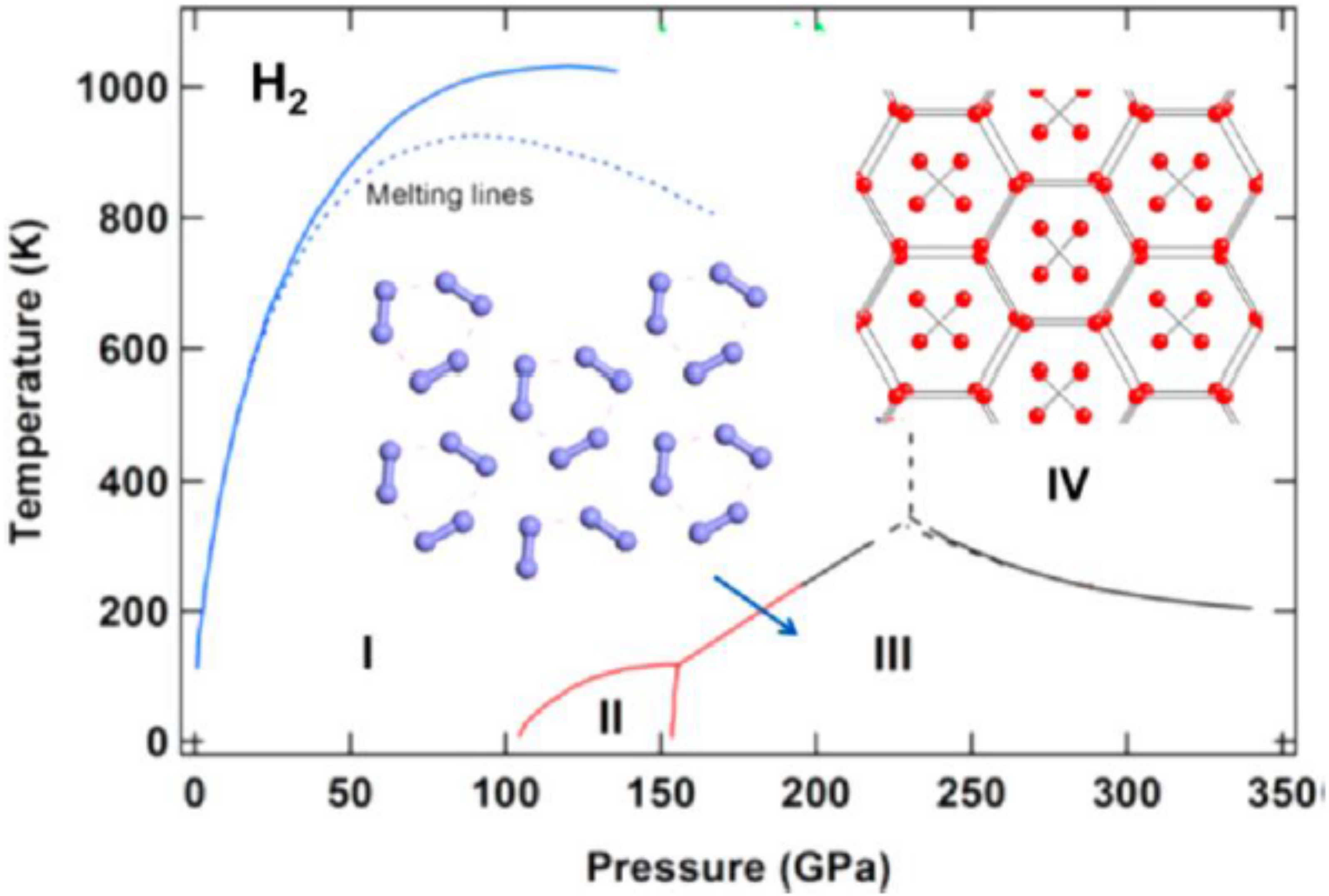
complex insulating structures

on the route to metalization

both in experiment and theory



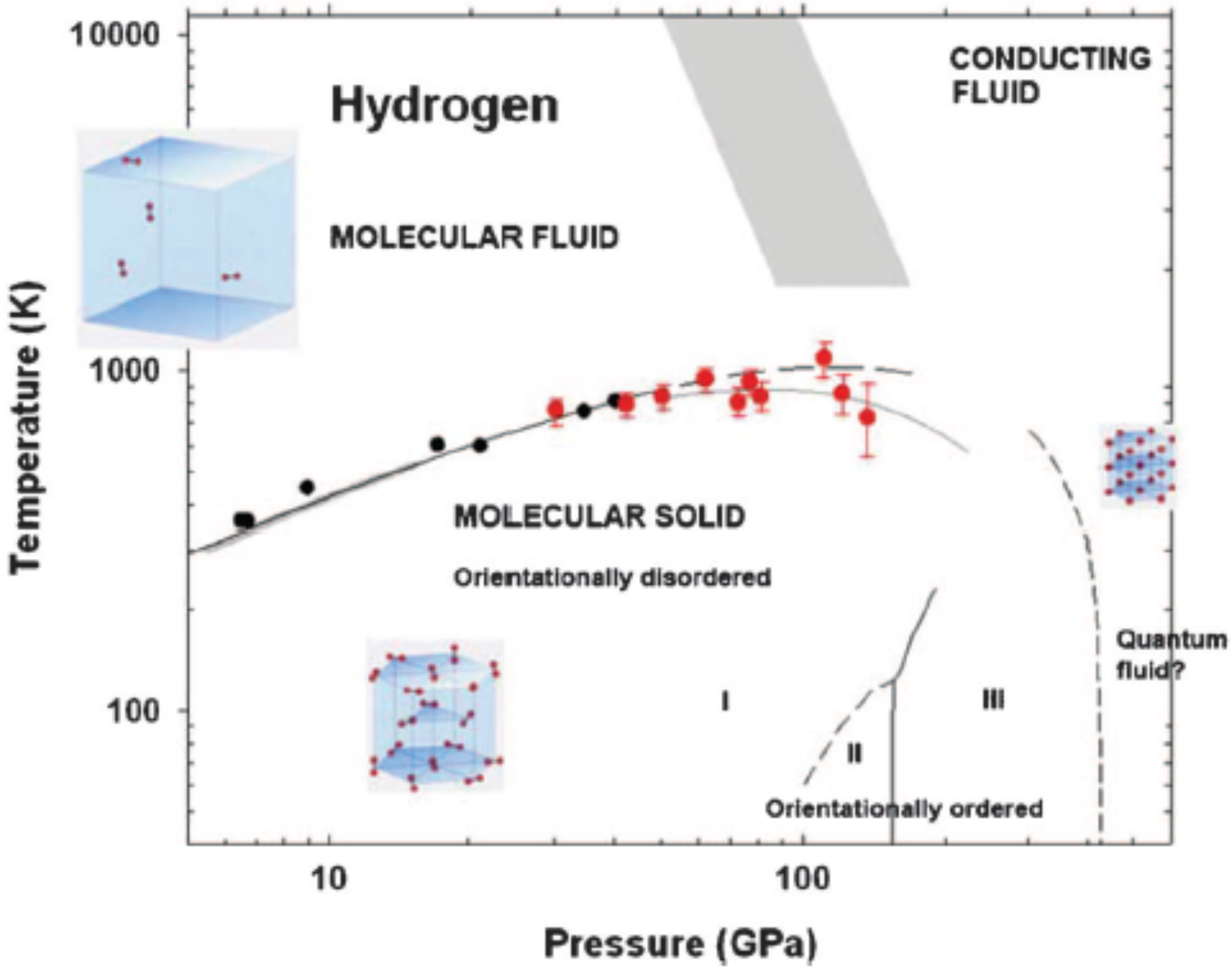
[Zha, Liu, Ahart, Boehler, & Hemley, *Phys. Rev. Lett.* (2013)]



Naumov & Hemley, *Accts. Chem. Res.*, 47(12), 3551 (2014)

Vanessa Labet,[1,a)] Paulina Gonzalez-Morelos,[1] Roald Hoffmann,[1,b)] and N. W. Ashcroft

J. Chem. Phys. **136**, 074501 (2012)



We need a Guiding Hypothesis

At extremely high pressure a natural tendency will be to form an electron gas, obey Pauli principle and form a Fermi sea.

This results in increase in kinetic energy of electron.

In the presence of coulomb repulsion the system will try to maximize exchange and correlation energy and look for reorganization of fermi sea at local and global leval.

In other words a simple fermi sea or a filled band is not an optimal many body state.

Mott localization resulting in electron pairing, at the level of covalent bond formation or pairing in k-space could help .

A Guiding Hypothesis GB 2005

pressure ↓

Molecular Solid

Lower dimensional Mott Insulator + molecular solid

Internal charge transfer and doped Mott Insulator

Jellium Metal

Contrast it with Wigner-Huntington (1936) hypothesis

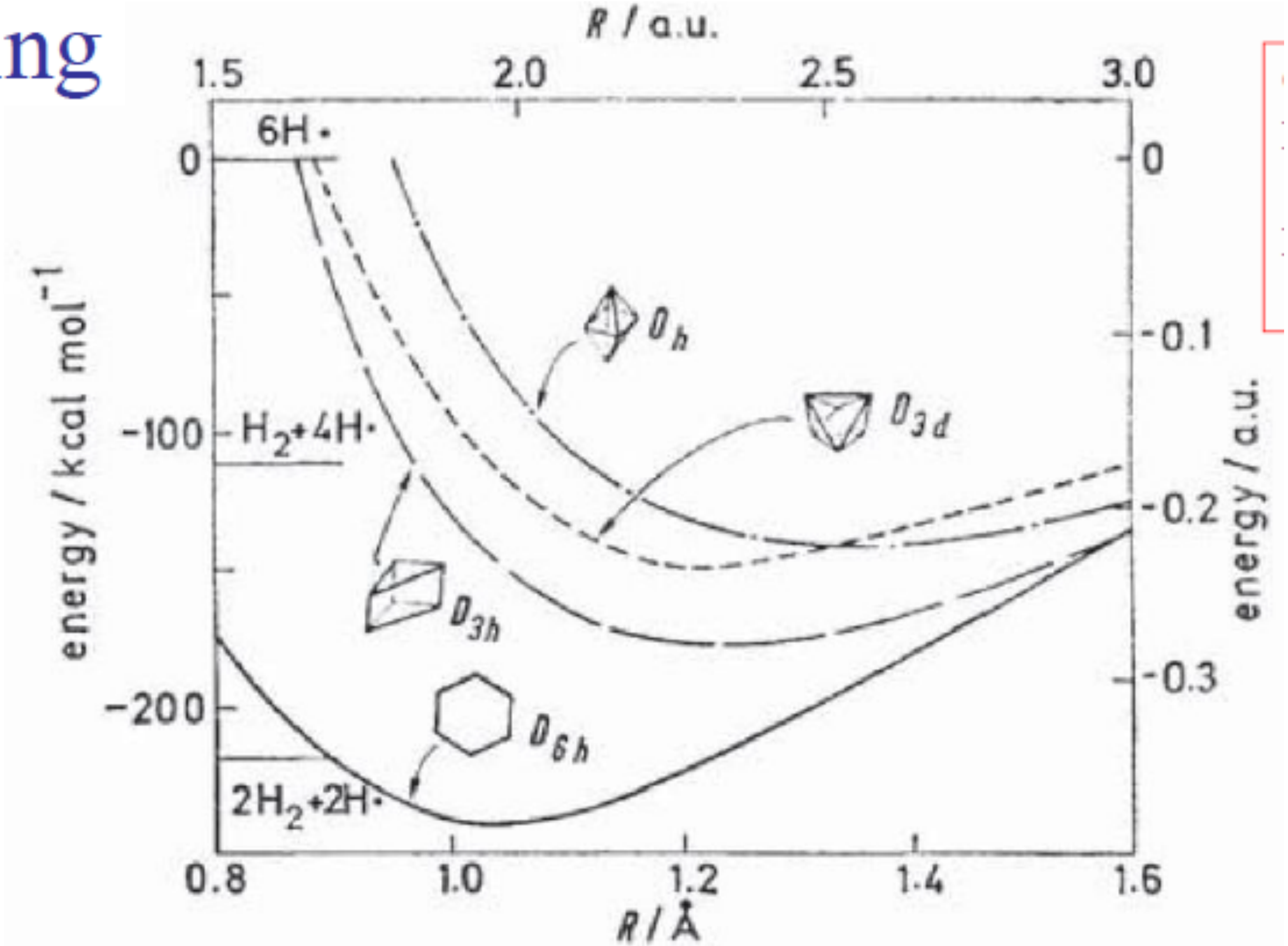
Band Insulator → Jellium Metal

(Wigner did not have the advantage of knowing Mott insulator !)

Band insulator → excitonic insulator → metal

Molecular solid → Mott insulaor → metal GB2015

H_6 ring



D. A. Dixon et al. *Faraday Discuss. Chem. Soc.*, **62**, 110 (1977).

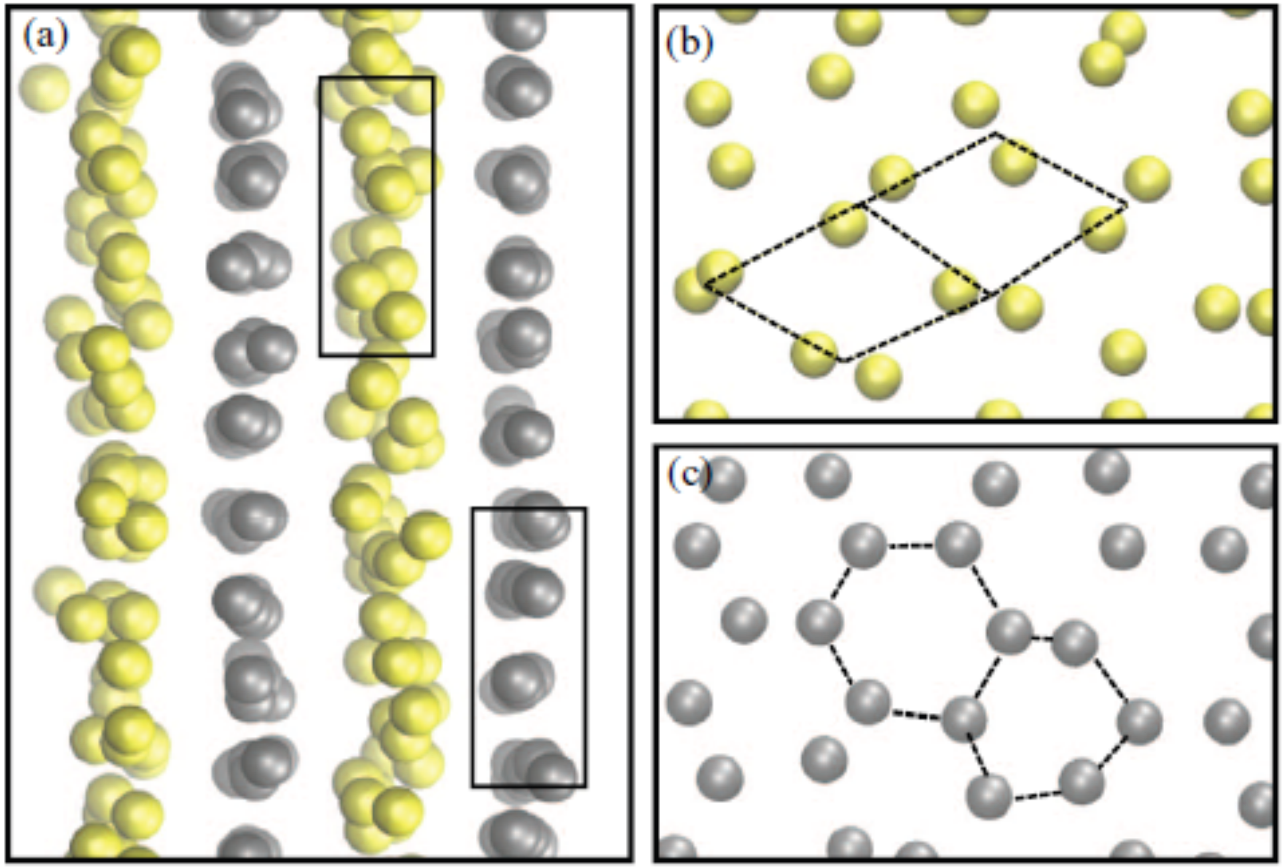
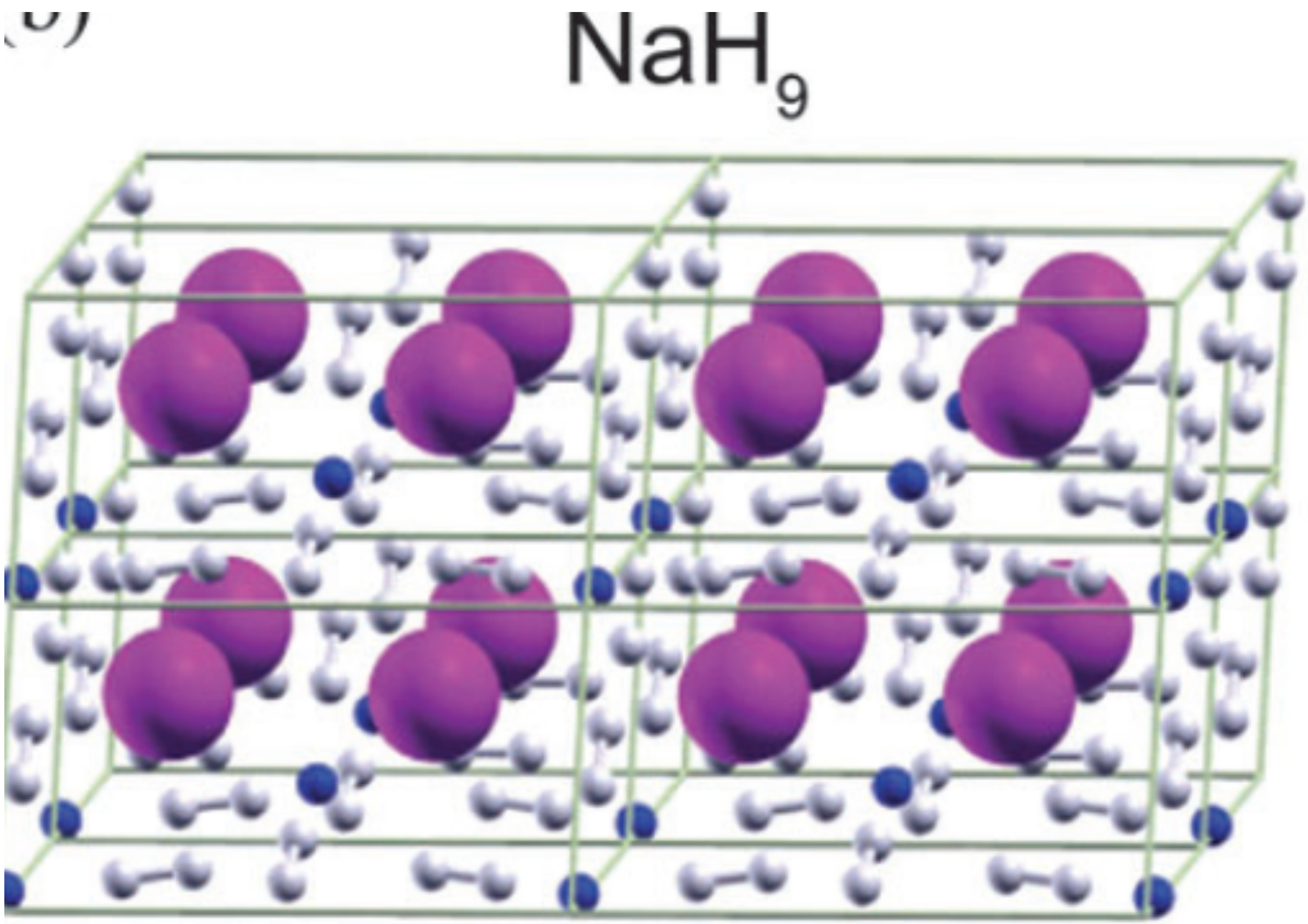


FIG. 1. Snapshots of the *ab initio* MD simulations for the mixed molecular phase. Panel (a) shows the sideview of the simulation cell. Panel (b) shows the topview of the strong molecular layer, as indicated yellow balls in panel (a). Panel (c) shows the topview of the weak molecular layer, as indicated by balls in gray in panel (a). The dashed lines are guide lines for the tetrahedral and honeycomb structures.

Eva Zurek*[a] and Wojciech Grochala
Phys. Chem. Chem. Phys., 2015, **17**, 2917–2934



Where is the Spin Liquid in solid hydrogen ?

Molecular solid H2 is a valence bond solid

Part of the valence bonds start resonating
locally and gain resonance energy

with increasing pressure this resonance percolates
through formation of
1 or 2 dimensional structures

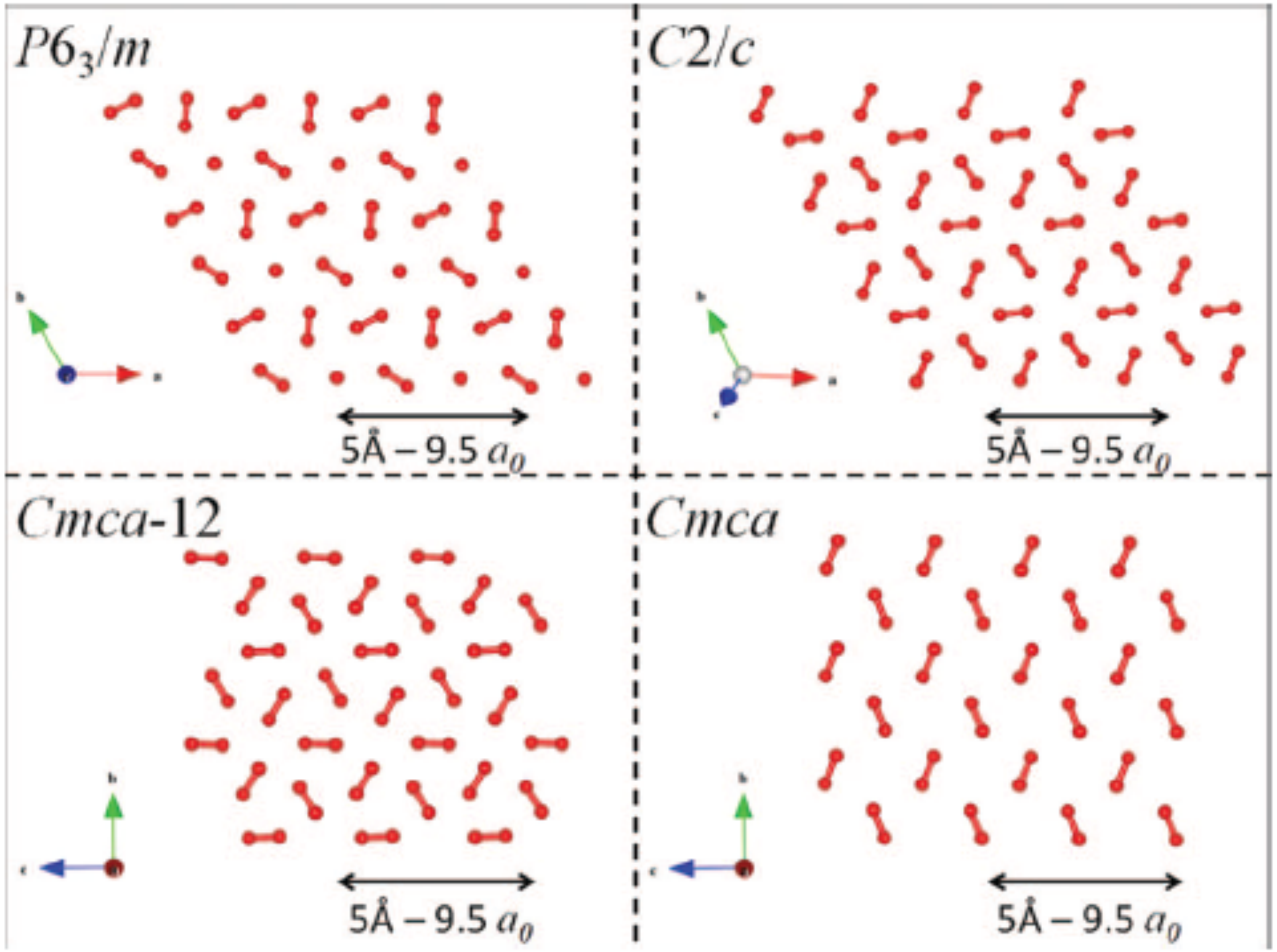
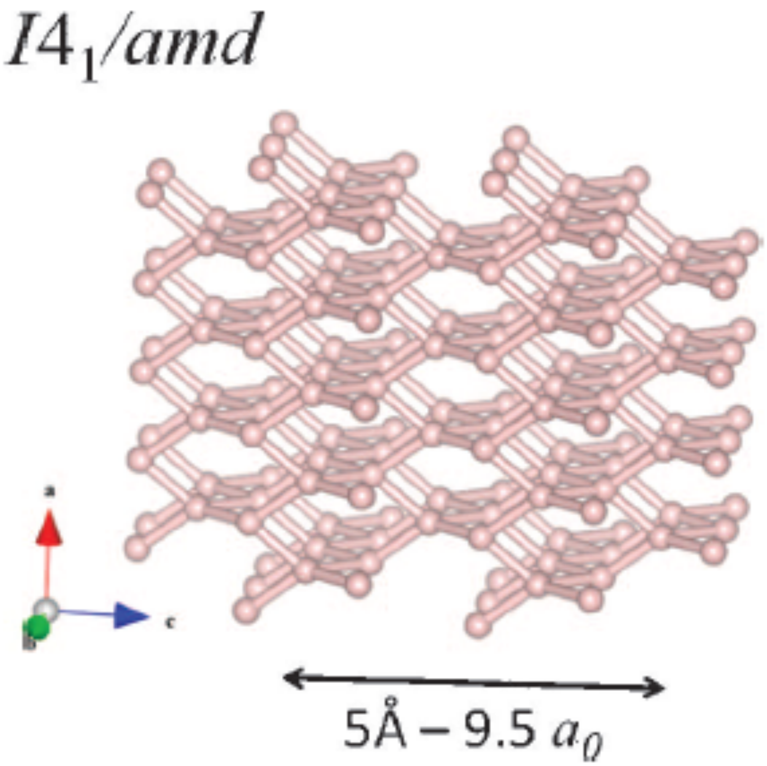
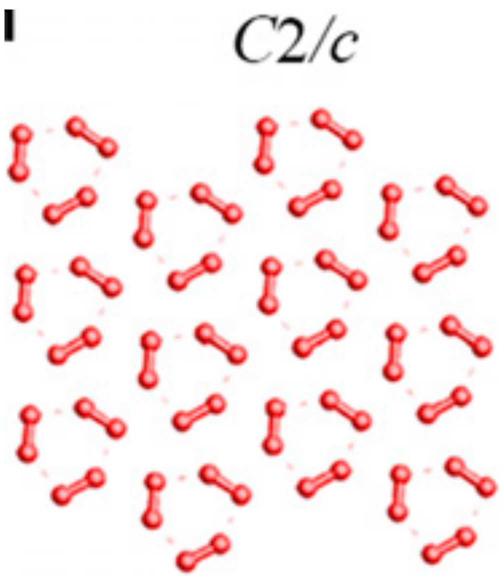
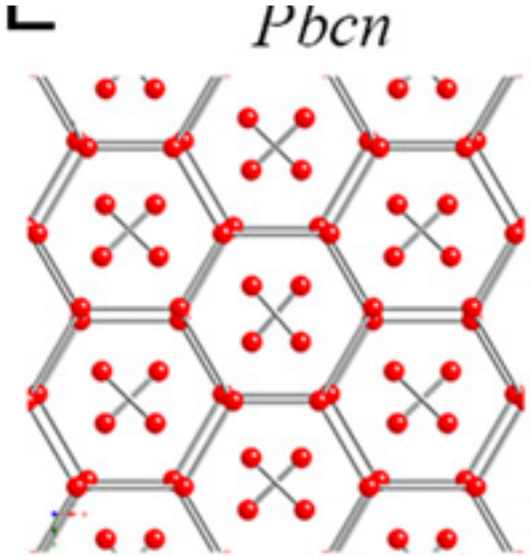


FIG. 3. A layer of the $P6_3/m$, $C2/c$, C*mca*-12, and *Cmca* structures at $P = 300$ GPa ($r_s = 1.33$—relative compression of 12.6). In the $P6_3/m$, *Cmca*-12, and *Cmca* structures the layers are arranged in an ABA fashion; in the $C2/c$ structure they are arranged in an ABCDA fashion.


$I4_1/amd$
a
c
b
5Å – 9.5 a_0



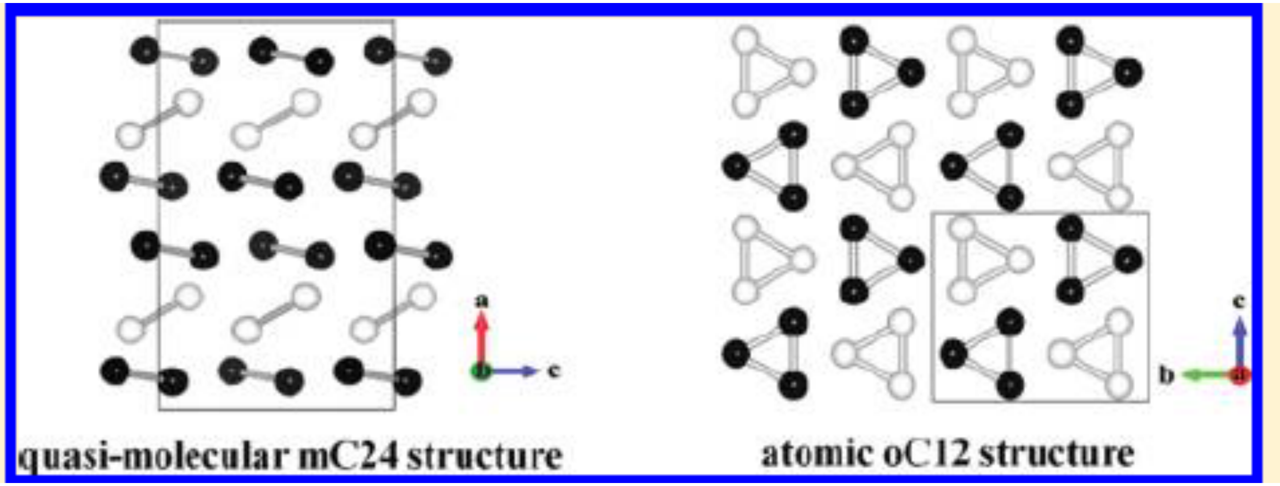
C2/c

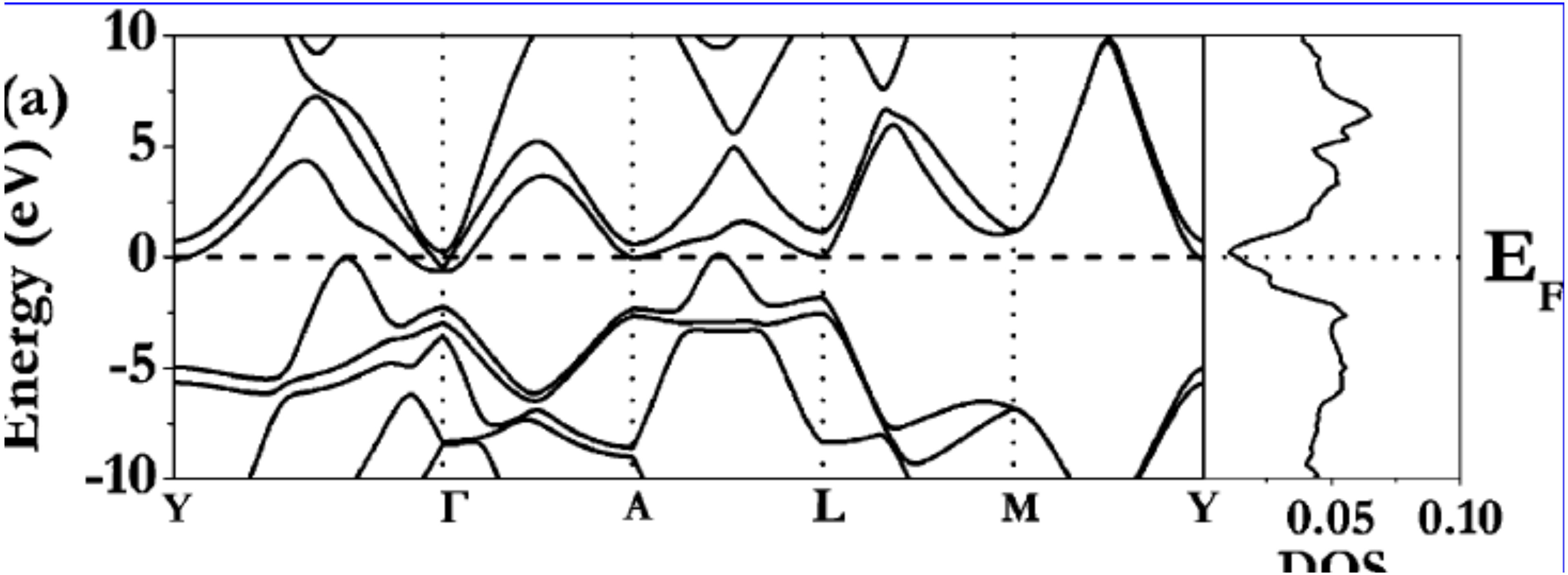


Pbcn

Hanyu Liu, Hui Wang, and Yanming Ma

J. Phys. Chem. C 2012, 116, 9221−9226





Metallic Hydrides

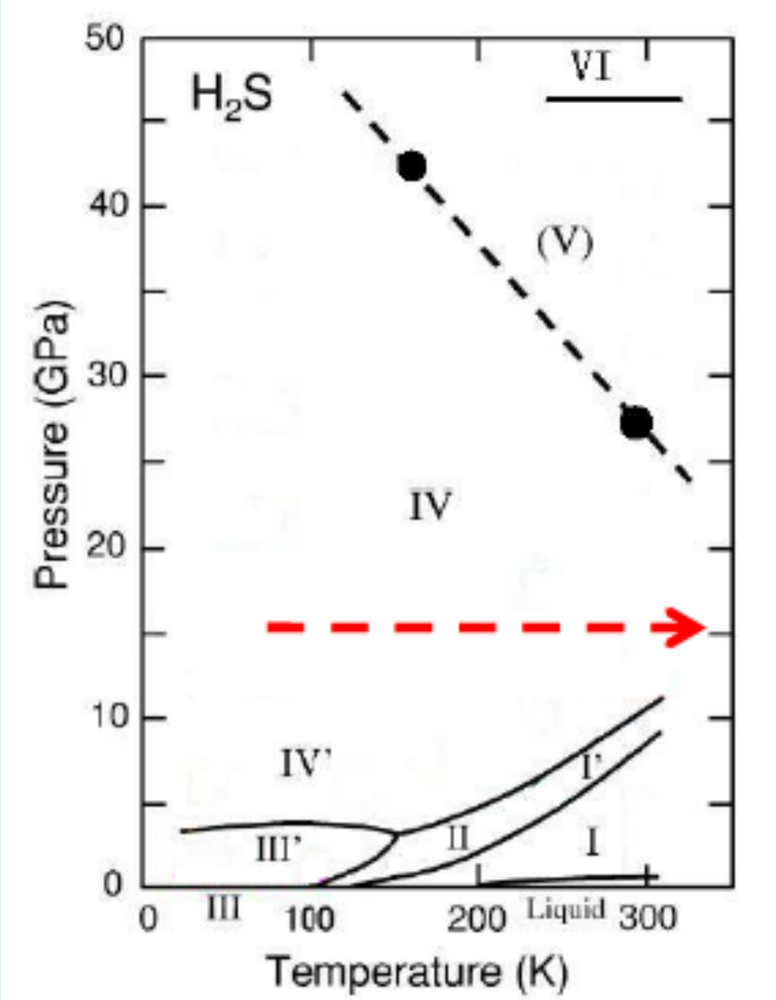
PdH_x , NiH_x …
Hydrogen storage materials
Molecular Solid Silane, SiH_4

Molecular Solid H_2S

similar to ice (H_2O) but with
weaker sulfur-hydrogen bond

XRay structural studies

Even at a pressure of a few GPa
there is dissociation and direct
sulfur-sulfur bond formation
as helical chain -S-S-S-S-S-
position of H atoms not known



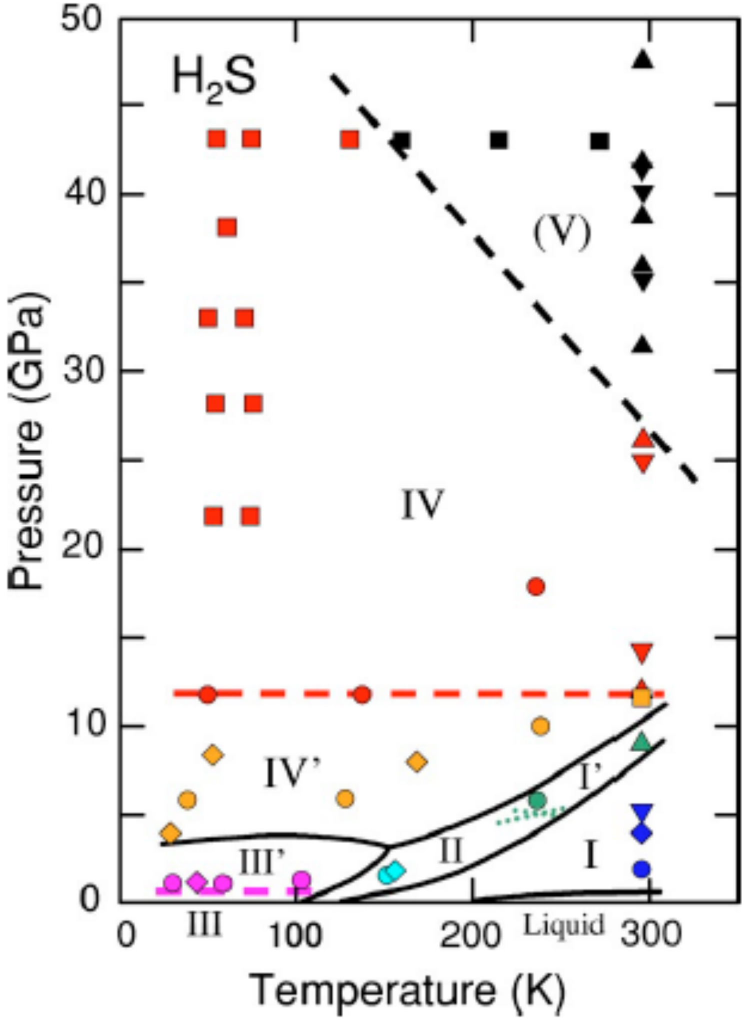
Phase diagram of H_2S

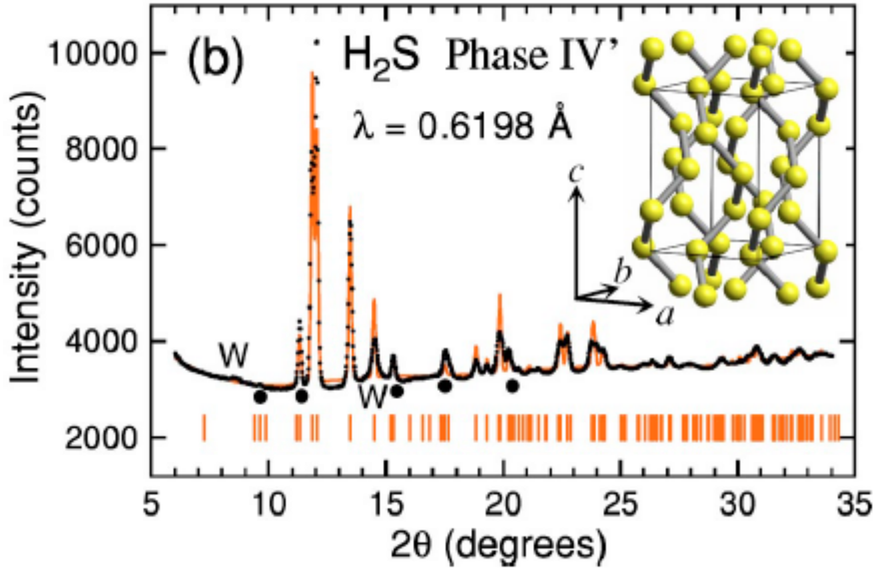
Fujihisa, et al. (2004) PRB 69:214102

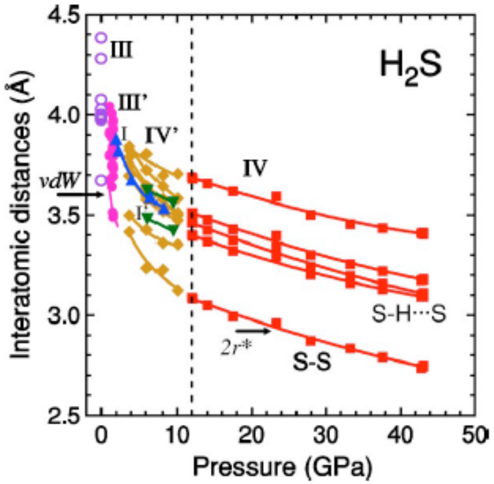
PHYSICAL REVIEW B **69**, 214102 (2004)

Molecular dissociation and two low-temperature high-pressure phases of H_2S

Hiroshi Fujihisa,[1] Hiroshi Yamawaki,[1] Mami Sakashita,[1] Atsuko Nakayama,[2] Takahiro Yamada,[1] and Katsutoshi Aoki[3]



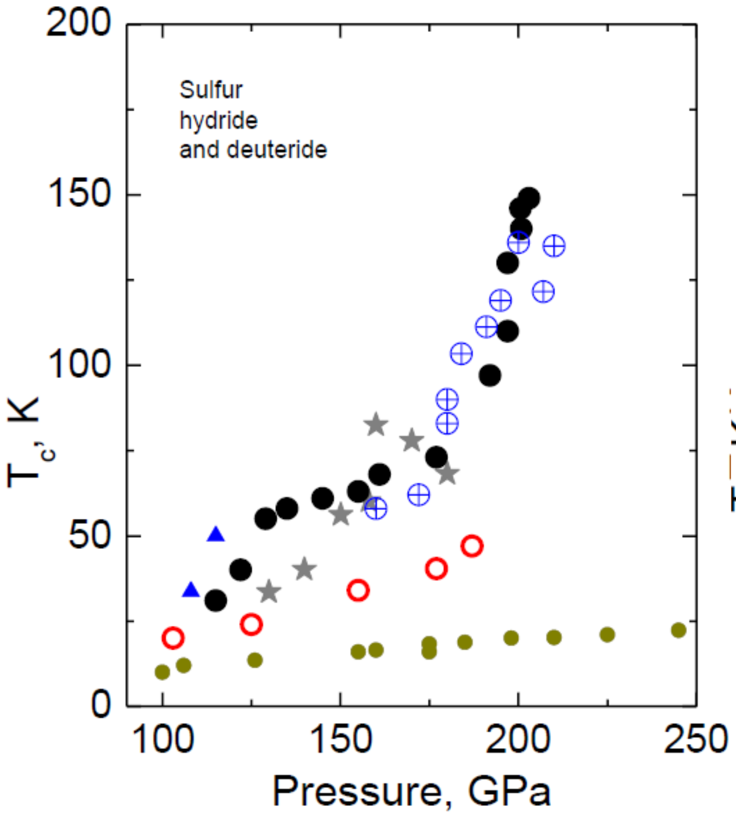


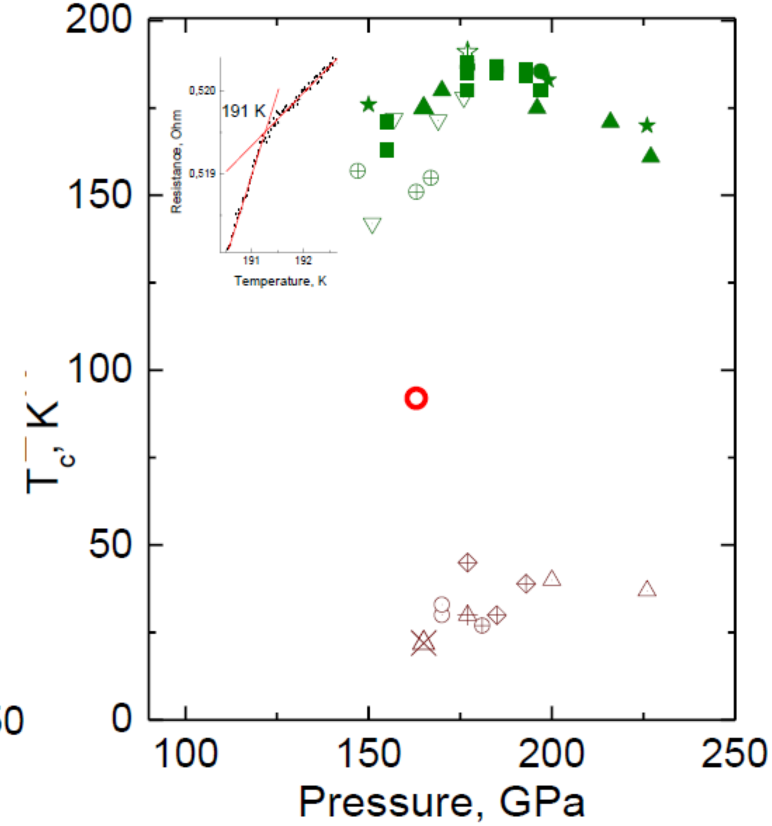


Conventional superconductivity at 190 K at high pressures

A.P. Drozdov, M. I. Eremets, I. A. Troyan
Max-Planck Institut fur Chemie, Chemistry and Physics at High Pressures Group
Postfach 3060, 55020 Mainz, Germany

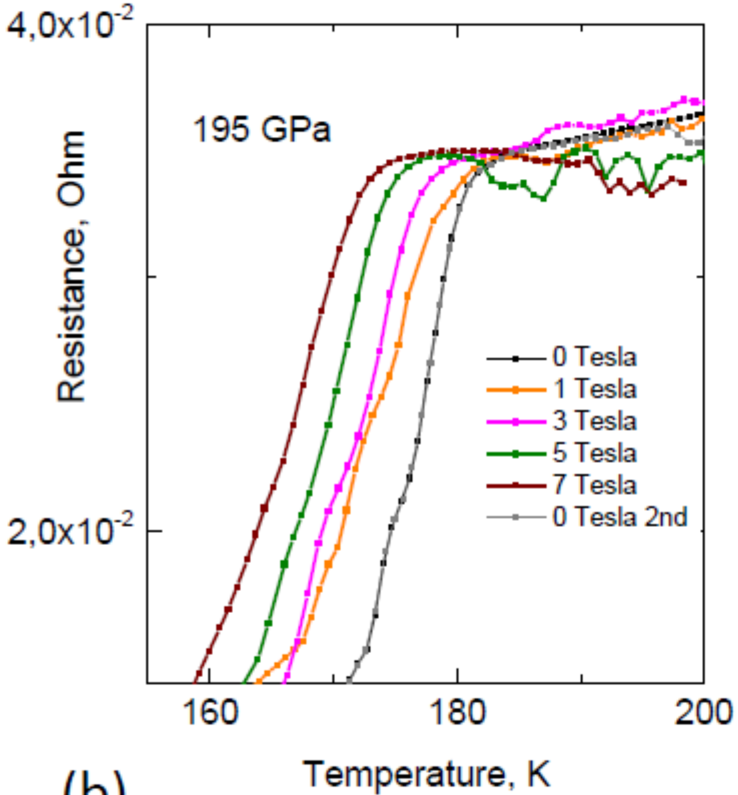
arXiv:1412.0460



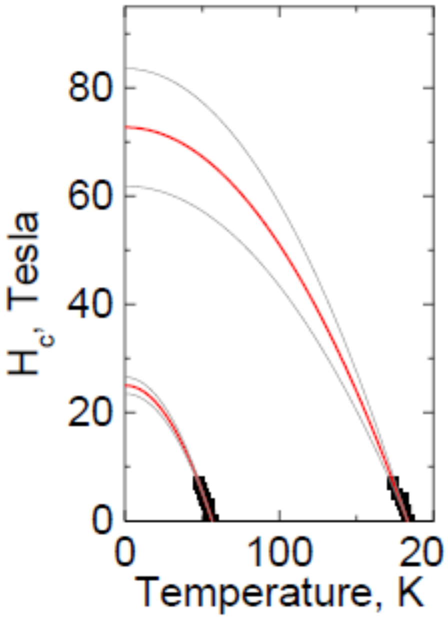


Isotope Effect

uperconducting Dome


4,0x10-2
2,0x10-2
195 GPa
Resistance, Ohm
0 Tesla
1 Tesla
3 Tesla
5 Tesla
7 Tesla
0 Tesla 2nd
160
180
200
Temperature, K

(b)


80
60
40
20
0
H c', Tesla
0
100
20
Temperature, K

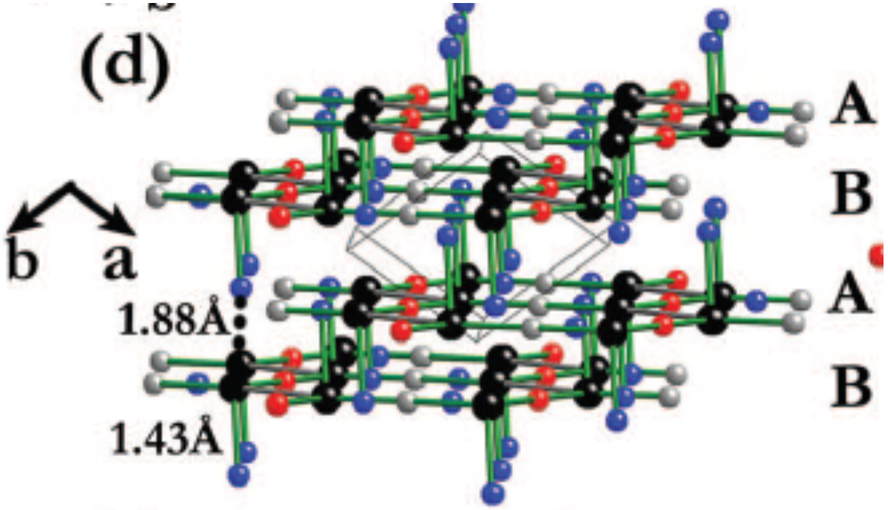
(c)

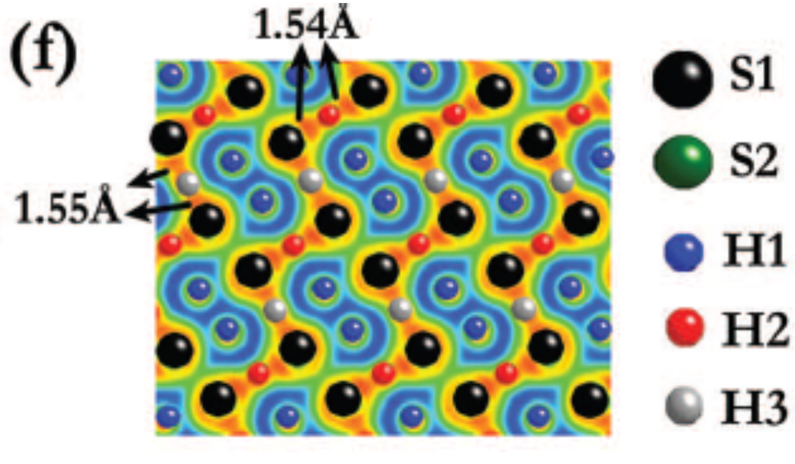
The metallization and superconductivity of dense hydrogen sulfide

Yinwei Li, Jian Hao, Hanyu Liu, Yanling Li, and Yanming Ma

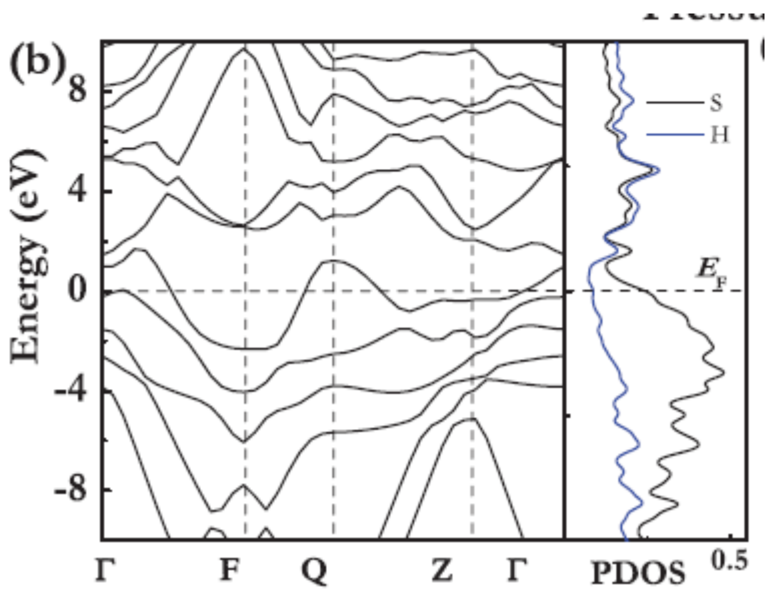
The Journal of Chemical Physics **140**, 174712 (2014)

LDA Calculation
for H_2S



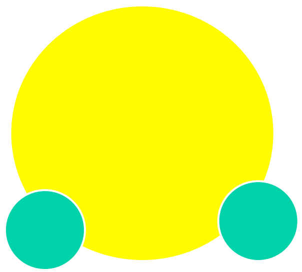


valence electron
localization function
in (110) plane



Model building

Crystal structure, band structure ?
phenomenology ? isotope effect, superconducting dome
quantum chemistry, solid state chemistry H_2S



Covalent radius of S atom ~ 1.6 Au
Covalent radius of H atom ~ 0.37 Au

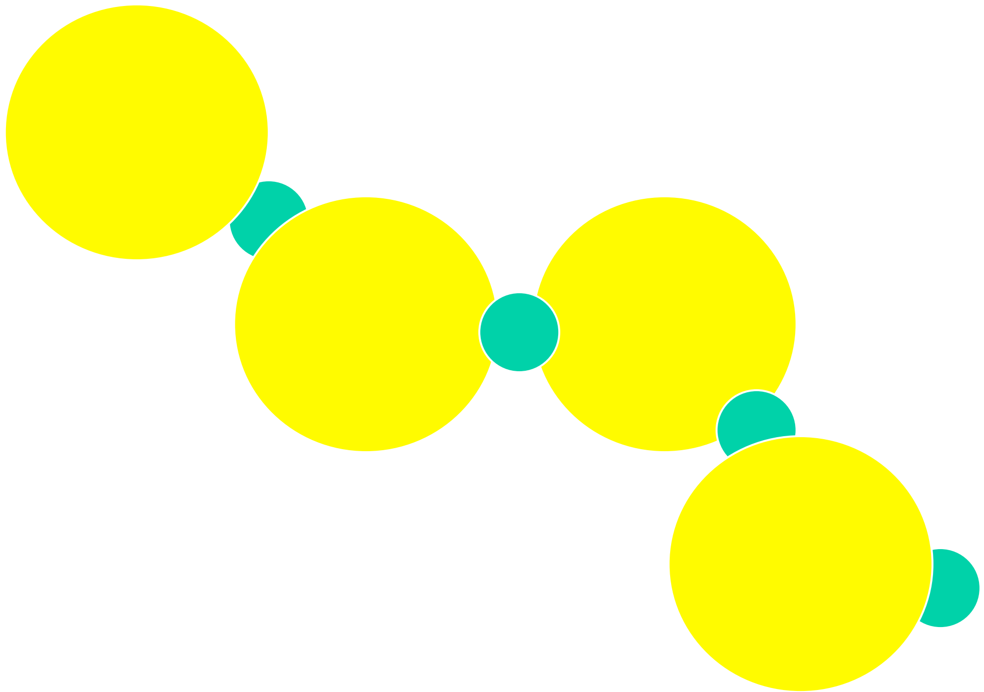
Ionization energy of H atom is high, 13.4 eV

Sulfur, to fill its 3p shell has a tendency to form single bonds with neighbors –S- and form helical chains (similar to Se, Te)

Atomic hydrogen has to find its optimal position, in the presence of space filling sulfur atoms and hybridize with sulfur orbitals

H-H separation is large and direct H-H bonding is not possible

Trapping of hydrogen atom between S atoms and
Gain hybridization energy, resulting in superexchange



Atomic Hydrogen network hypothesis

H_2S molecule looses its molecular identity

A fraction of H in the unit cell regains its atomic identity

From now on the situation is similar to cuprates

tJ Model

Preformed neutral singlet pairs, doping the Mott insulator, charged singlet pairs

Weakly interacting chains, interchain pair tunneling …

Mean field theory

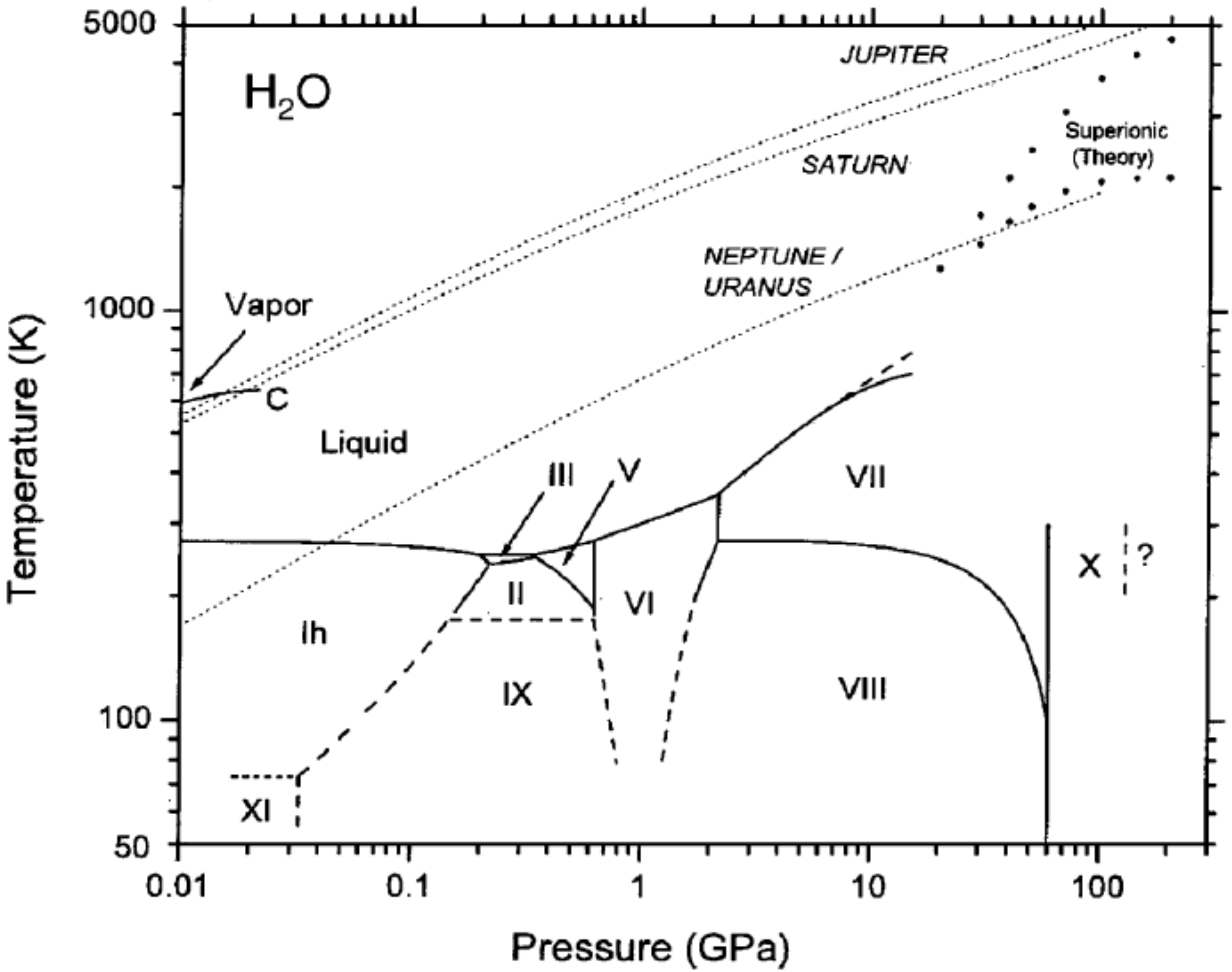
Estimates of t and J and Tc

Predictions:

Hope for higher Tc ~ 300 K in other hydrides
Quantum magnetism (spin liquid)
Pseudogap phase
Look at other hydrides for similar Tc’s …

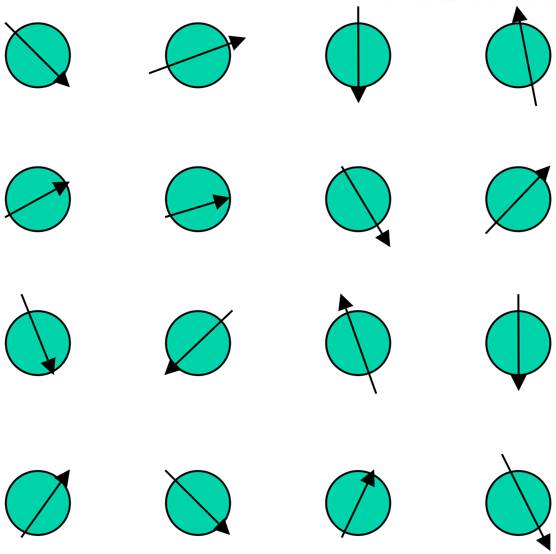
Converting Water into Quantum Spin Liquid ?

GB 2015

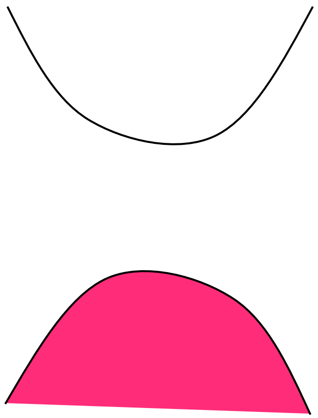


H2O
JUPITER
SATURN
NEPTUNE / URANUS
Superionic (Theory)
Vapor
C
Liquid
III
V
VII
II
VI
Ih
IX
VIII
X
?
XI
5000
1000
100
50
0.01
0.1
1
10
100
Temperature (K)
Pressure (GPa)

Mott Insulator



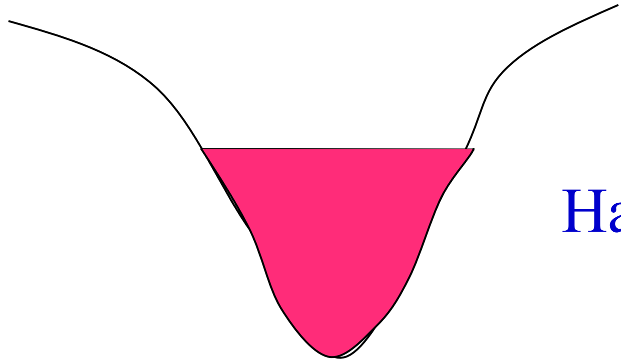
$a >> a_B$



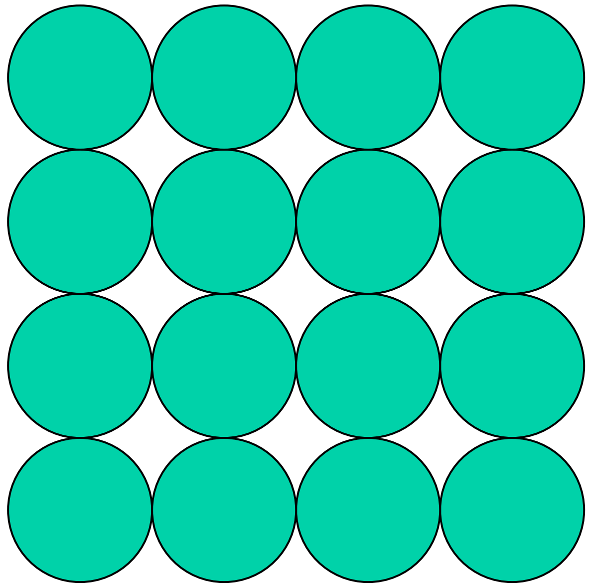
upper Hubbard band

lower Hubbard band

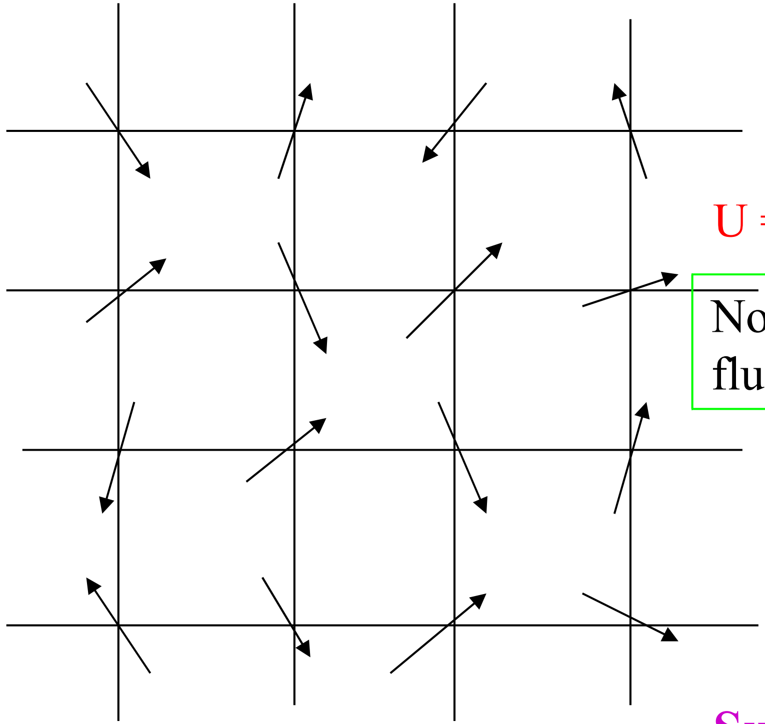
Metal



Half filled band



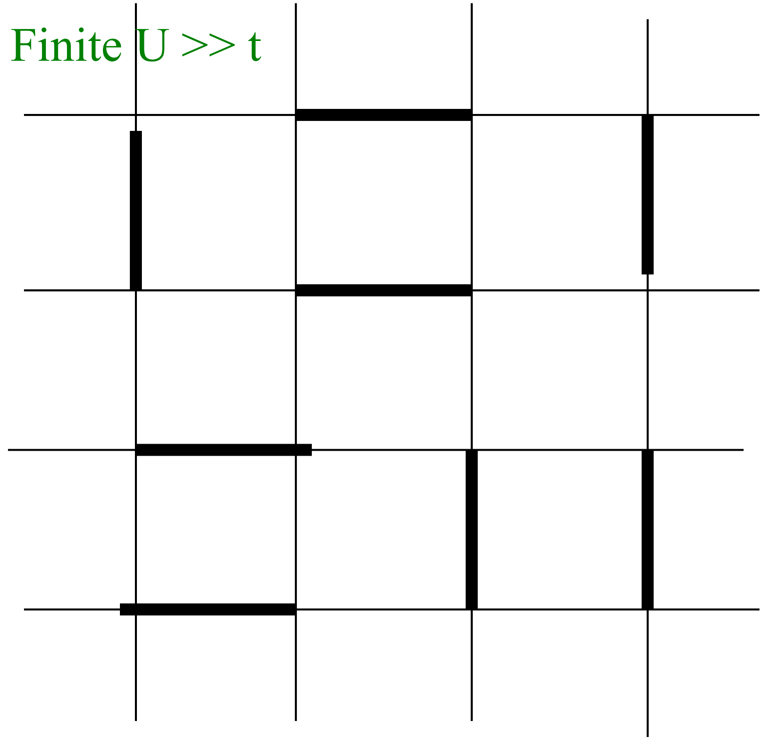
$a \sim a_B$



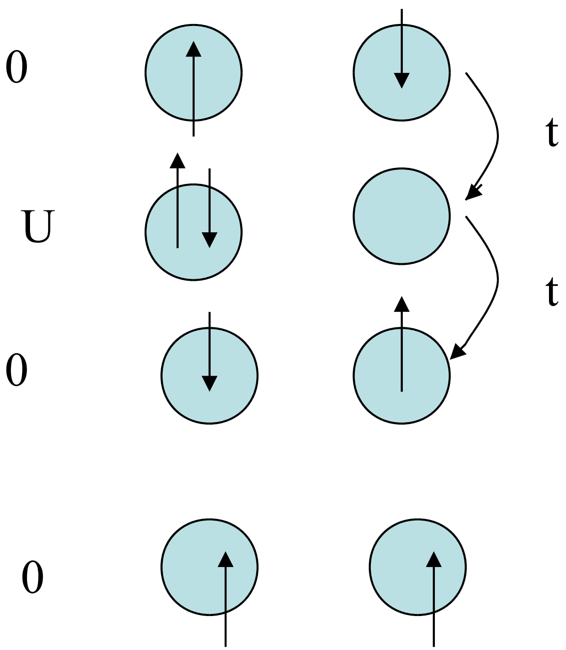
U = infinity

No quantum fluctuations

Finite U >> t



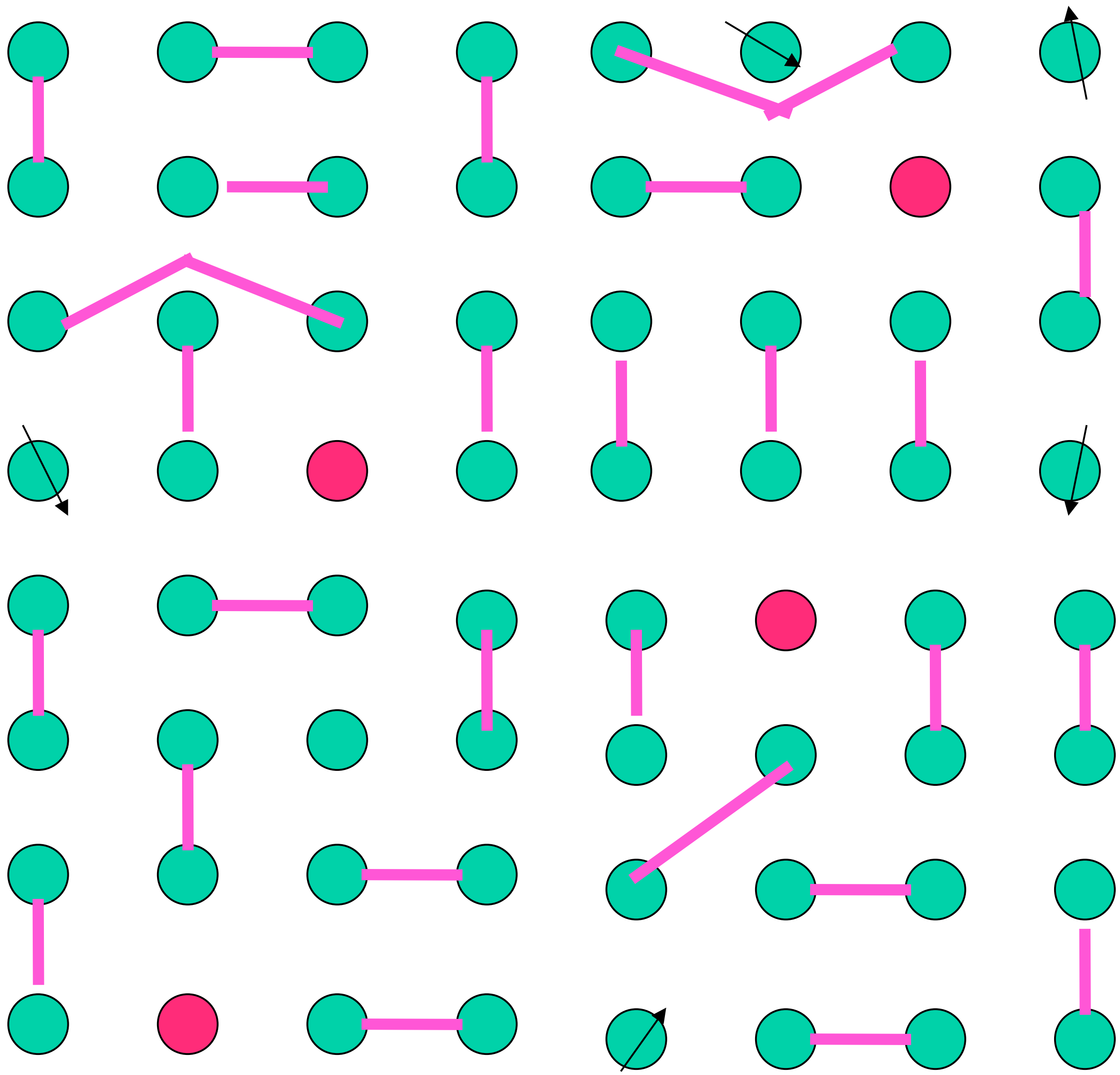
Superexchange or Kinetic exchange process



Energy gain = $J = \dfrac{-4t^2}{U}$

$= \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$

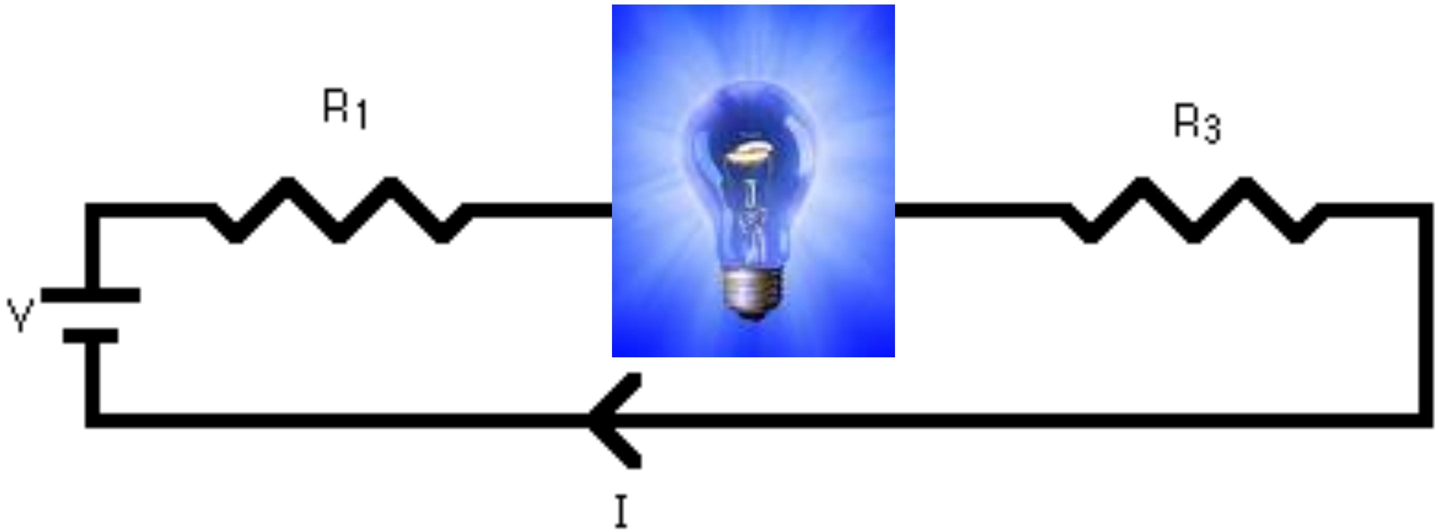
Energy gain = 0



Acknowledgement

P W Anderson
(Noble Prize in Physics 1978)

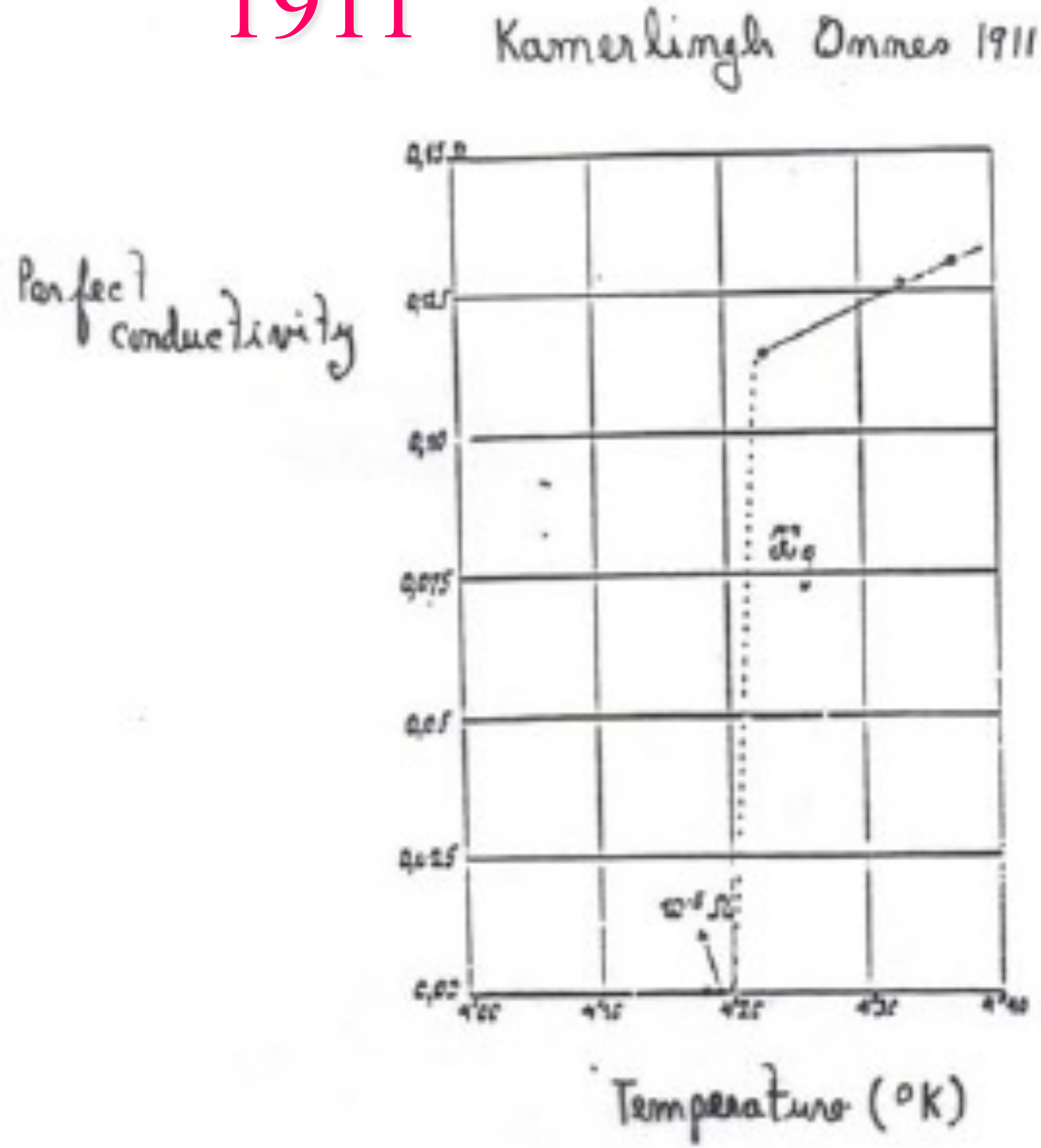
his insights and collaboration has been valuable to me in the superconductivity Game, since 1984


R1
R3
V
I

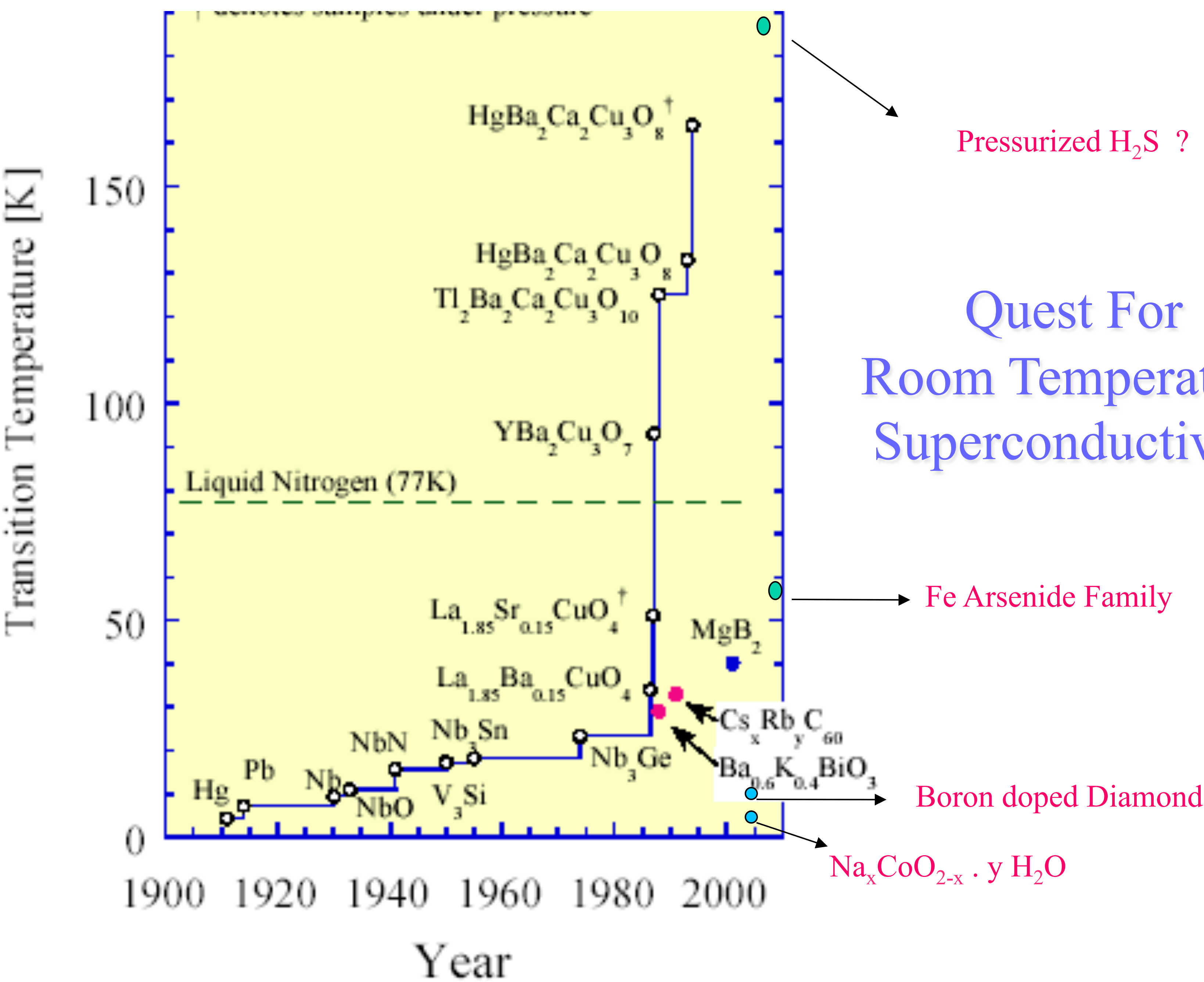
Heike Kamerlingh Onnes

Nobel Prize 1913

1911



Source: Carrington



Quest For Room Temperature Superconductivity

Source: Carrington

Search For Room Temperature Superconductivity

Early theoretical suggestions … Excitonic Mechanism, Phonon Mechanism
Theoretical Constraints
on phonon mechanism … 30 K limit on maximum Tc ? (Anderson-Cohen)

Metallic Hydrogen … Possibility of Room Temperature SC (Ashcroft)

A silent revolution in ceramics by Bednorz and Muller 1986
– discovery of cuprate superconductors
Maximum Tc ~ 164 K in trilayer cuprate

MgB_2
Fullerites
FeAs superconductors
… ?

Pressurized H_2S, a Tc ~ 190 K ?

Electron-phonon interaction mechanism

(Frohlich, Bardeen, ….)

The best electron phonon superconductor is MgB_2 with a Tc ~ 39 K

The best electron-electron mechanism based superconductors
are cuprates

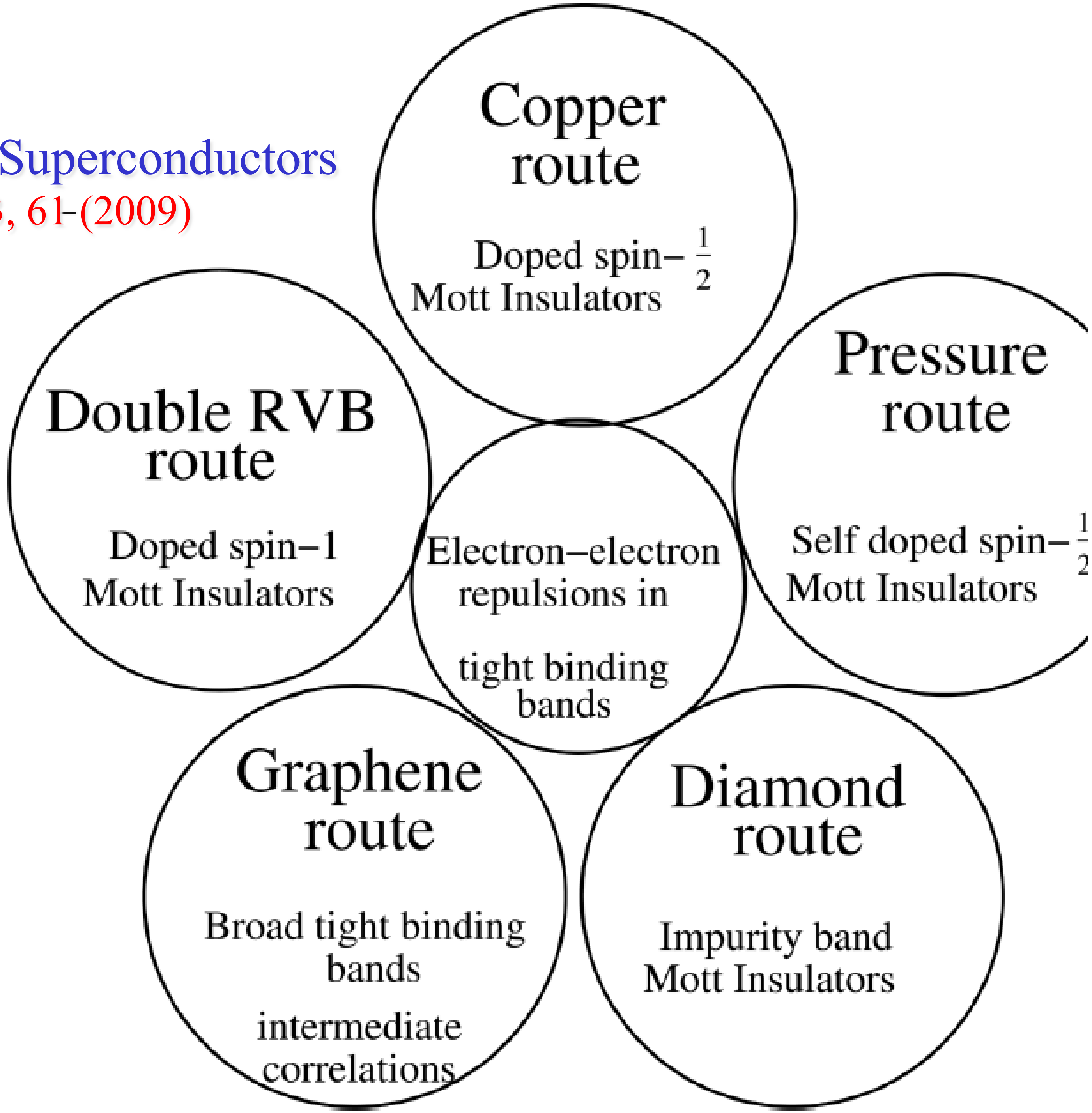
Fullerites, organics, FeAs and other superconductors seem
to be based on electron correlation effects.

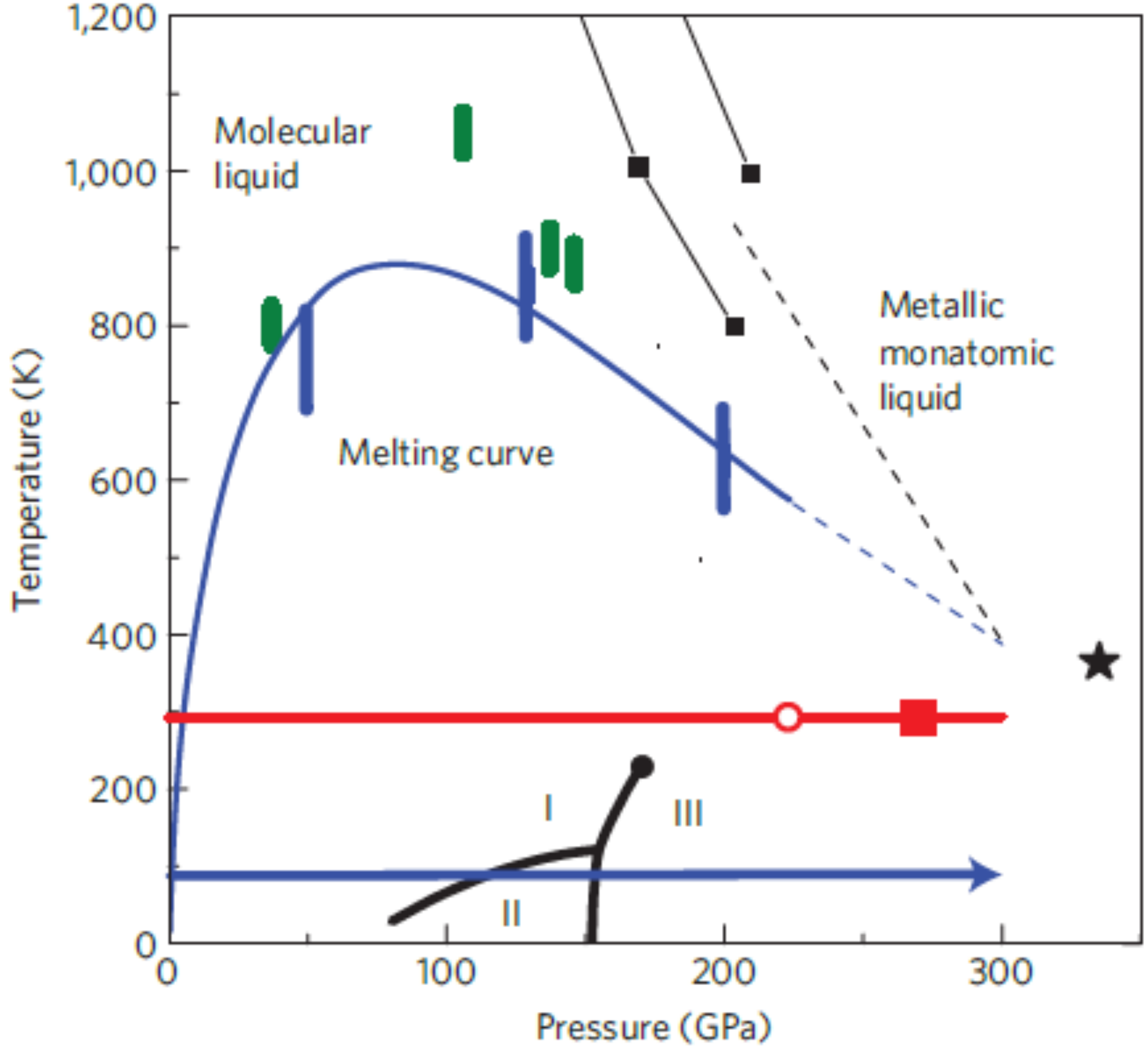
What limits the Tc ?

5-Fold Way to New Superconductors

G Baskaran, Pramana 73, 61-(2009)

available freely in the web





Eremets and Troyan, Nature Materials 2011

Molecular solid Hydrogen (H_2) under pressure

Metallization will take place around 25 GPa
Wigner and Huntington 1935

Metallic Hydrogen and possibility of room temperature superconductivity
based on phonon mechanism (High Debye frequency due to light weight of H atoms)
Ashcroft 1968

Exotic possibilities, including liquid hydrogen superconductor has been theoretically proposed.

Experimentally hydrogen solid has not been metallized even at a pressure of 300 GPa !
Many complex structural reorganization takes place. Even at these pressures a finite fraction of hydrogen tend to retain their molecular identity. Complete dissociation of molecular hydrogen does not seem to take place.

Diamond anvil experiment (eg. Arumugam's Lab), shock wave experiments