New superconductors

waiting for room-temperature (?)

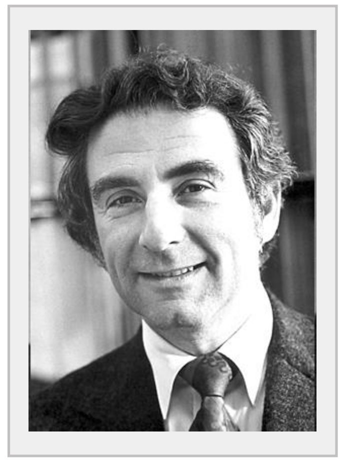
Prof. G. Profeta

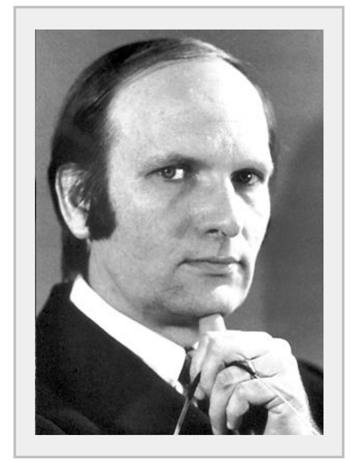
University of L’Aquila and SPIN-CNR

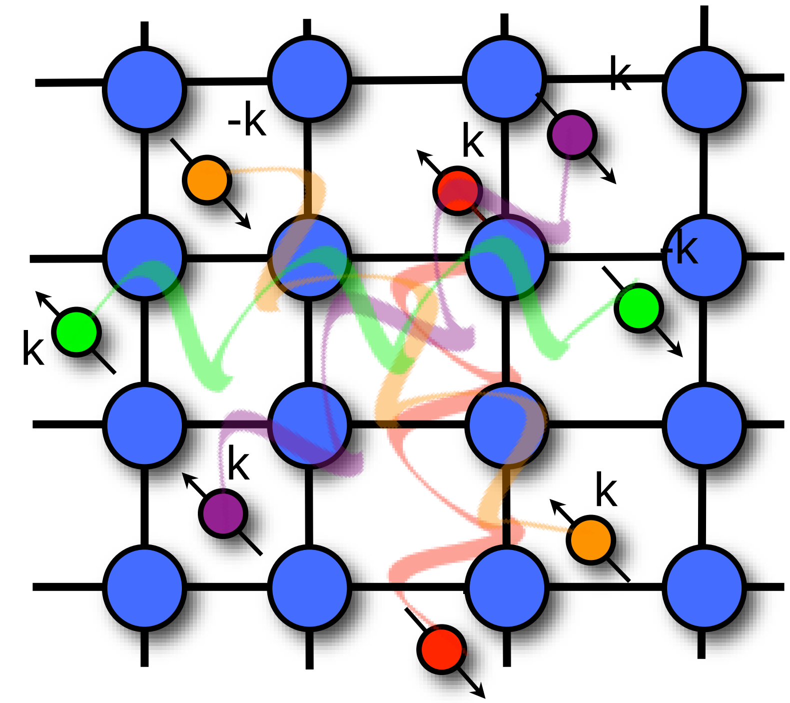
Department of Physical and Chemical Sciences

Theory of Superconductivity*

J. Bardeen, L. N. Cooper,† and J. R. Schrieffer‡
Department of Physics, University of Illinois, Urbana, Illinois
(Received July 8, 1957)

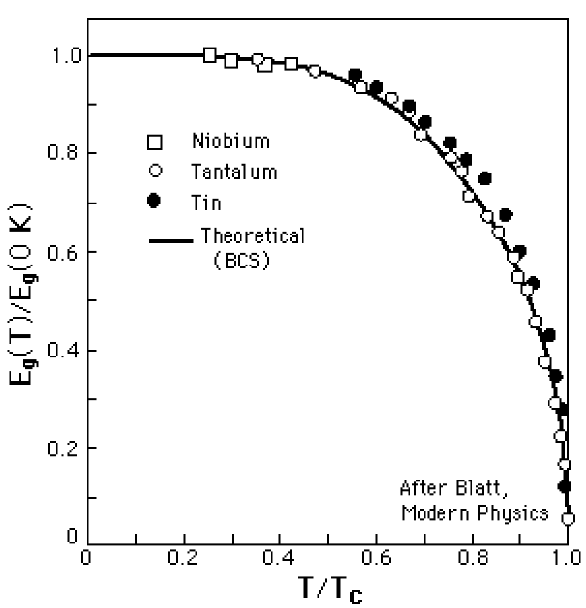




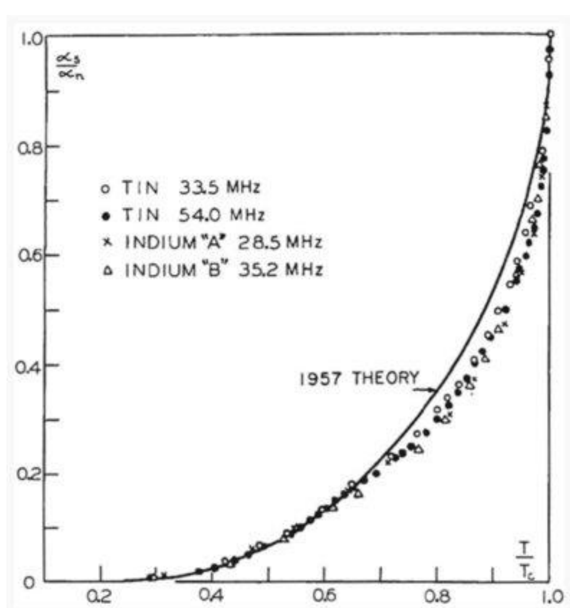


$$\Psi_N(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)=\mathcal{A}\psi(\mathbf{r}_1,\mathbf{r}_2)\psi(\mathbf{r}_3,\mathbf{r}_4)\cdots\psi(\mathbf{r}_{N-1},\mathbf{r}_N)(1\uparrow)(2\downarrow)(3\uparrow)(4\downarrow)\cdots(N-1\uparrow)(N\downarrow).$$

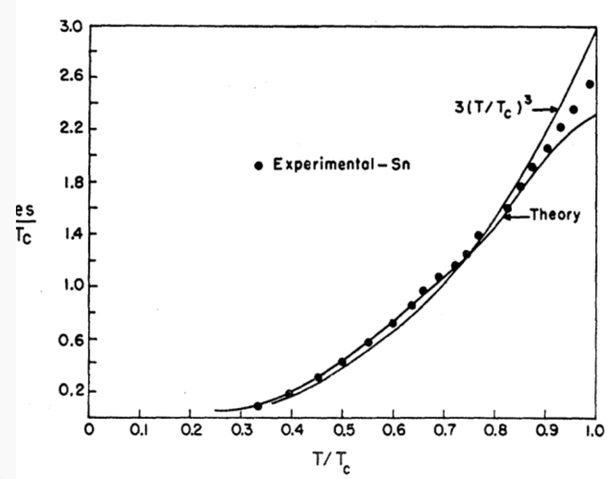
Gap



Ultrasonic attenuation



Specific heat



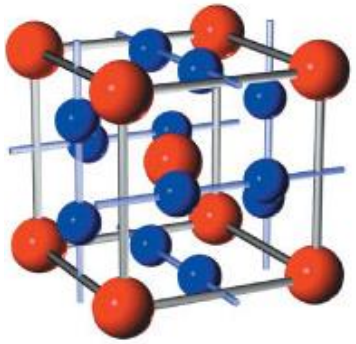
$$\Delta(0)=1.76k_BT_c$$

$$\frac{\Delta(T)}{\Delta(0)}=1.74\left(1-\frac{T}{T_c}\right)^{\frac{1}{2}}$$

$$T_c^{BCS}=\omega_D e^{-\frac{1}{\lambda}}$$

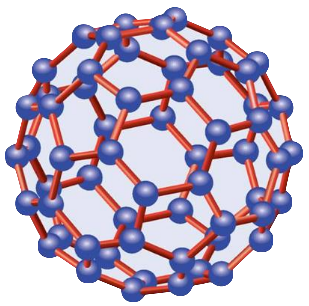
First-principles theory of superconductivity

1958 : Migdal solved the electron-phonon coupling via MBPT

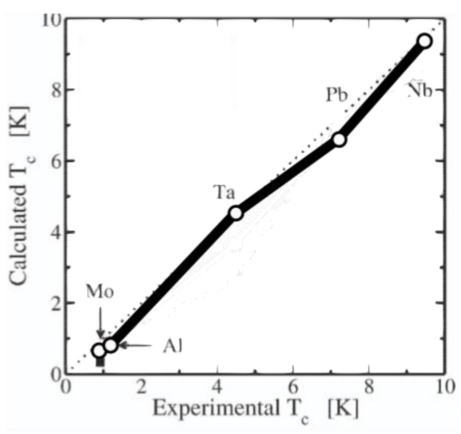


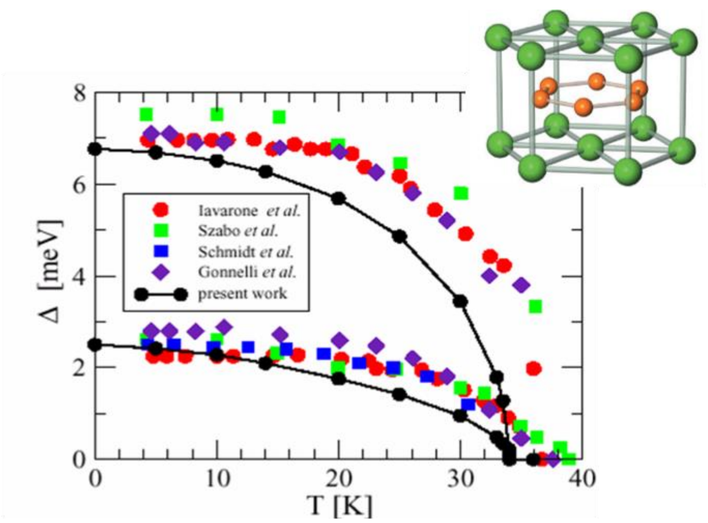
1960 : Eliashberg considered the pair condensation in presence of electron-phonon coupling.

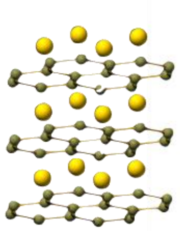
1964 : Hohenberg – Kohn formulated the Density Functional Theory

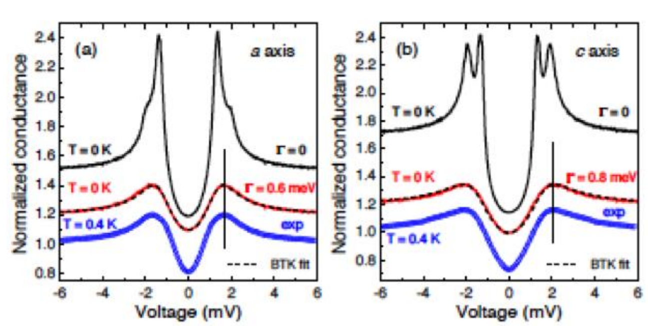


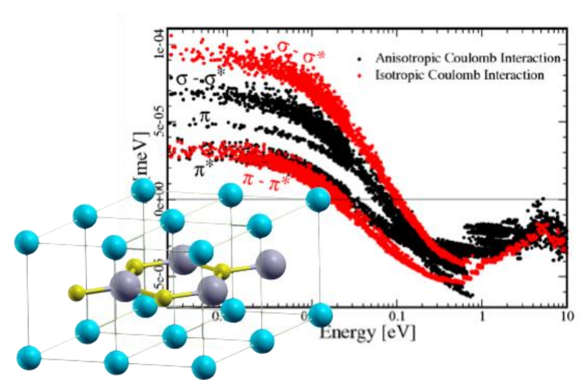
2005 : SuperConducting-Density Functional Theory

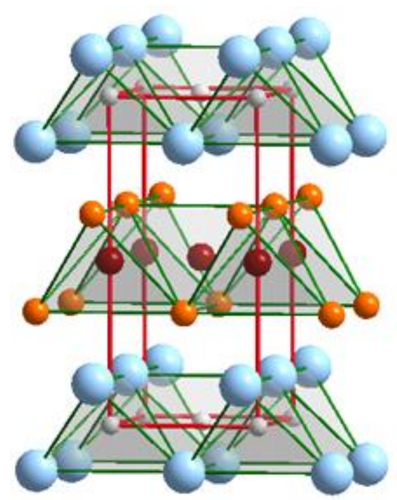












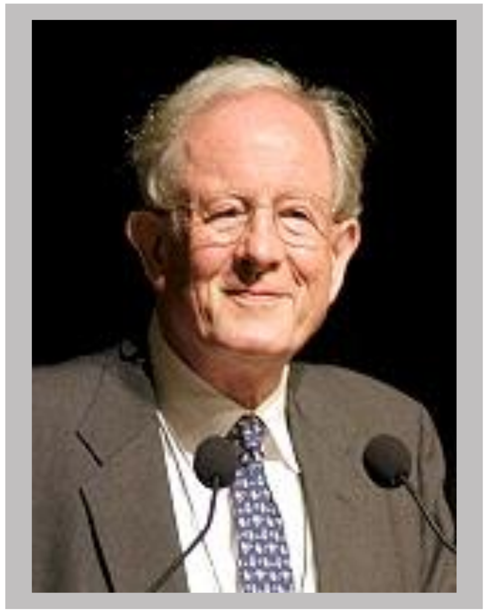
A new era for superconductivity

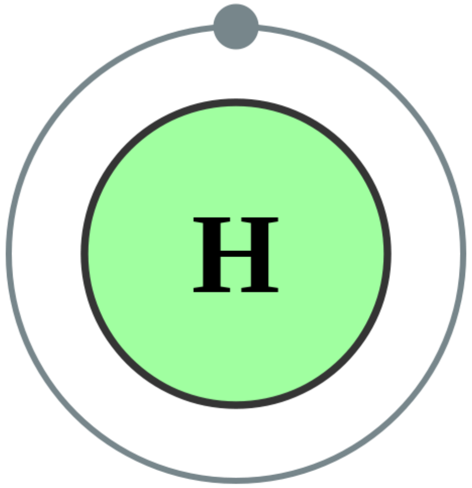
Can we predict a superconducting material?

Can we predict Tc?

Which is the material with the highest Tc?

Neil Ashcroft's idea





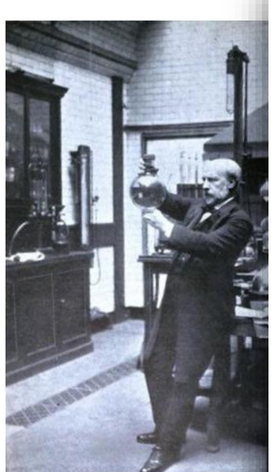
Small ionic mass guarantees large phonon frequencies

Lack of electronic core screening the el-ph

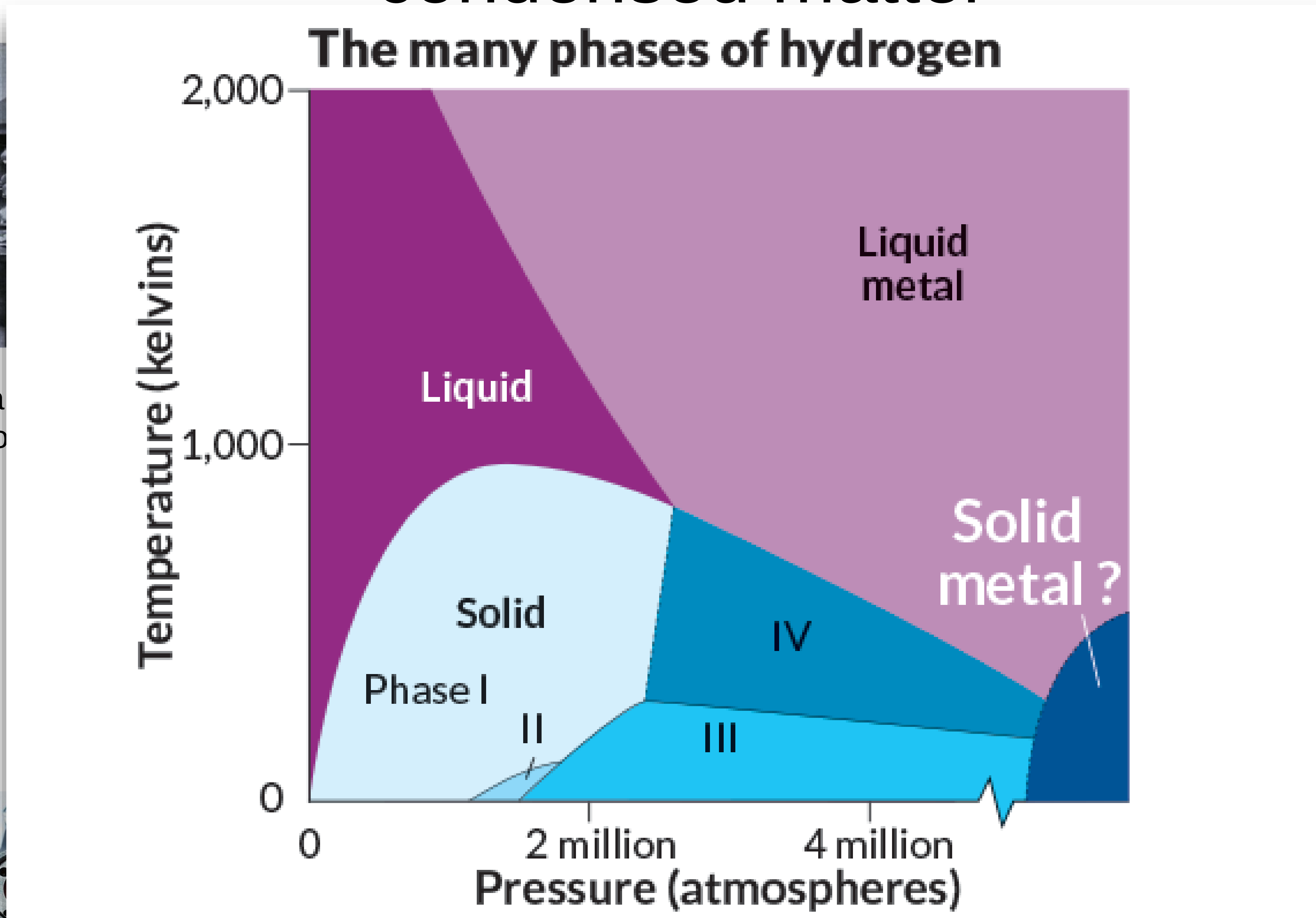
Wide bands under pressure reduce Coulomb interaction

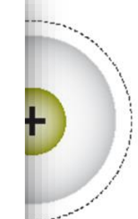
$$T_c^{BCS} = \omega_D e^{-\frac{1}{\lambda}}$$

Metallic hydrogen: The holy grail of condensed matter



1899: Dewa
produces so
hydrogen





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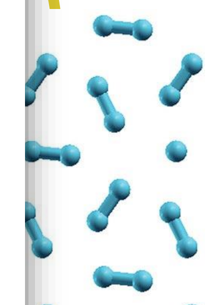
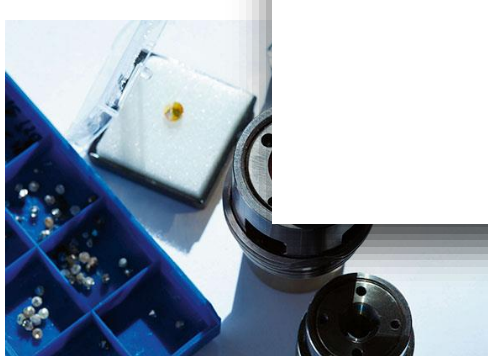
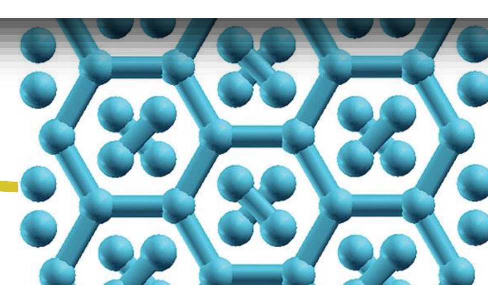


se III

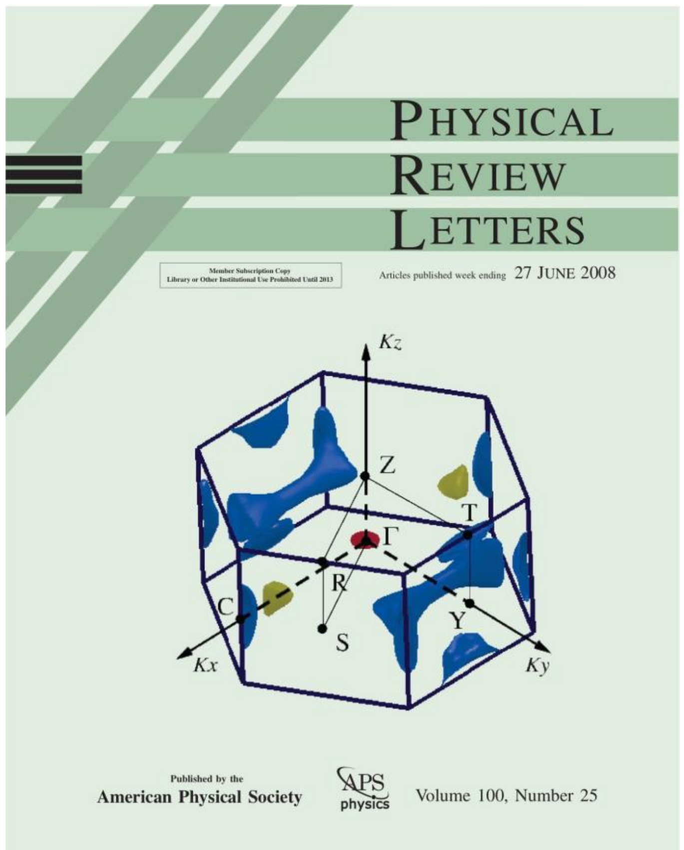


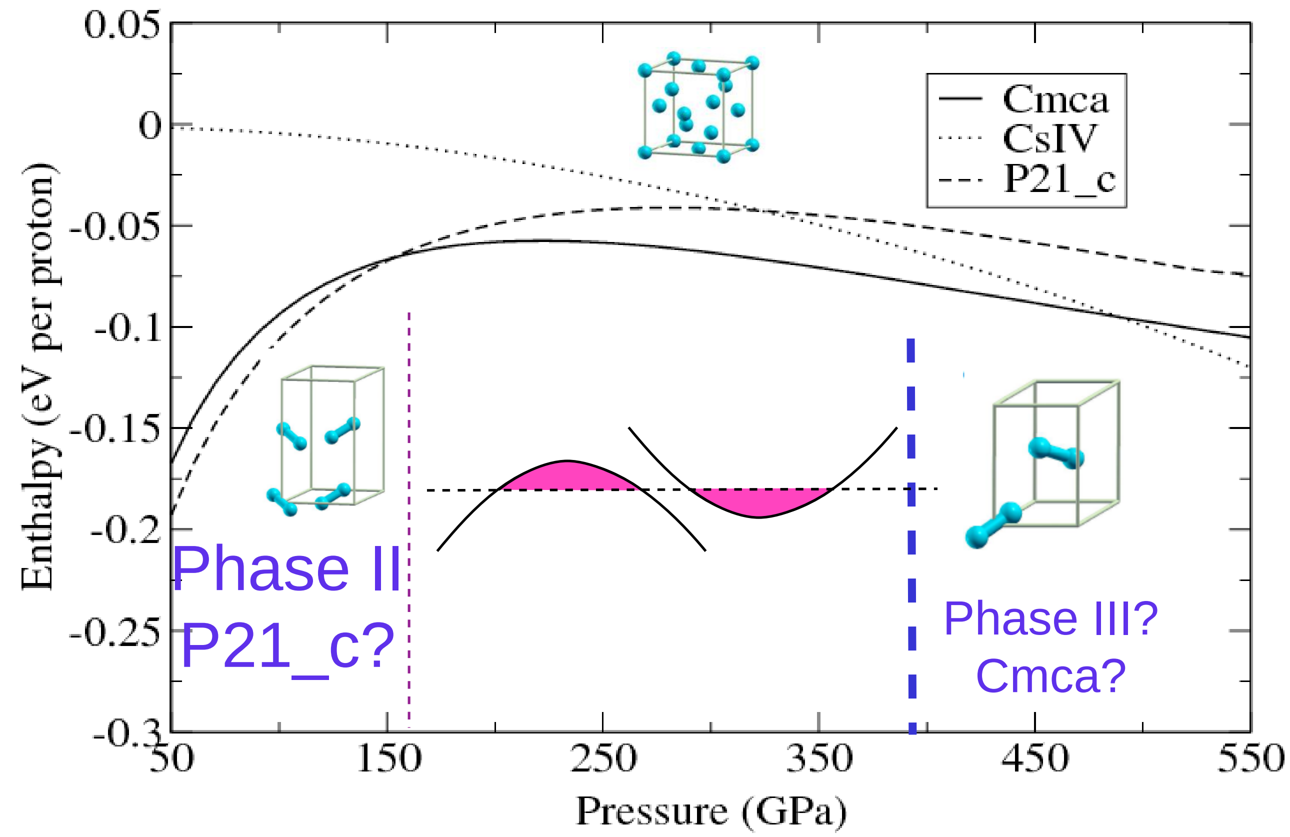


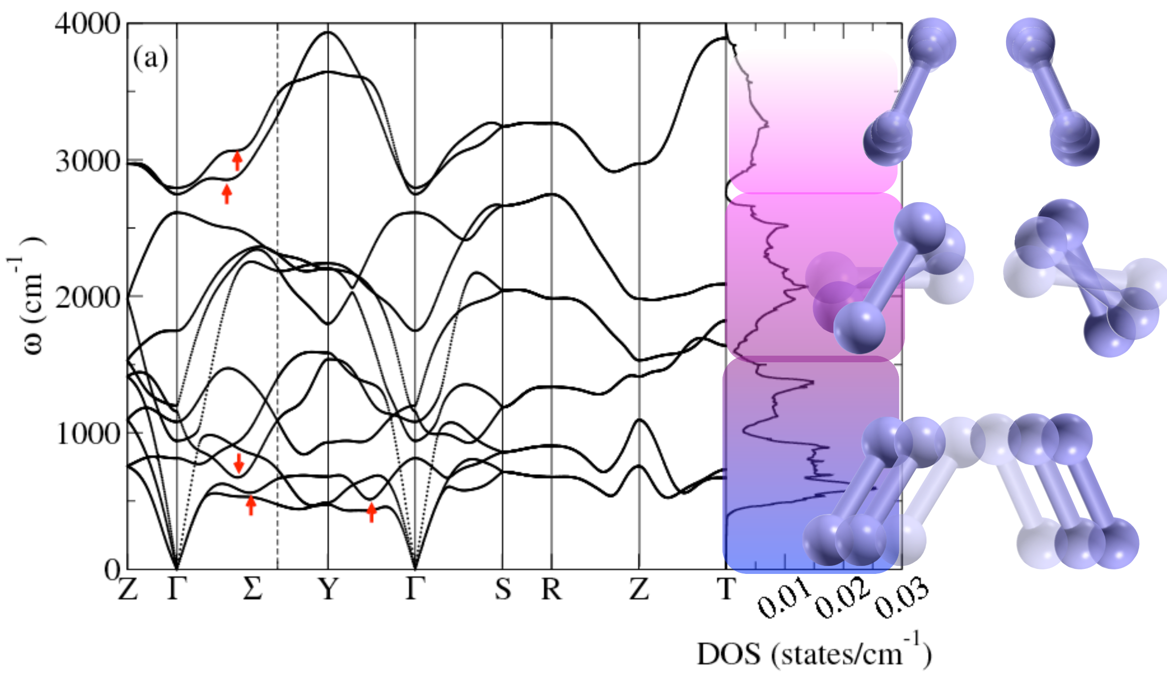
2016: 400 GPa
Claims of different phases

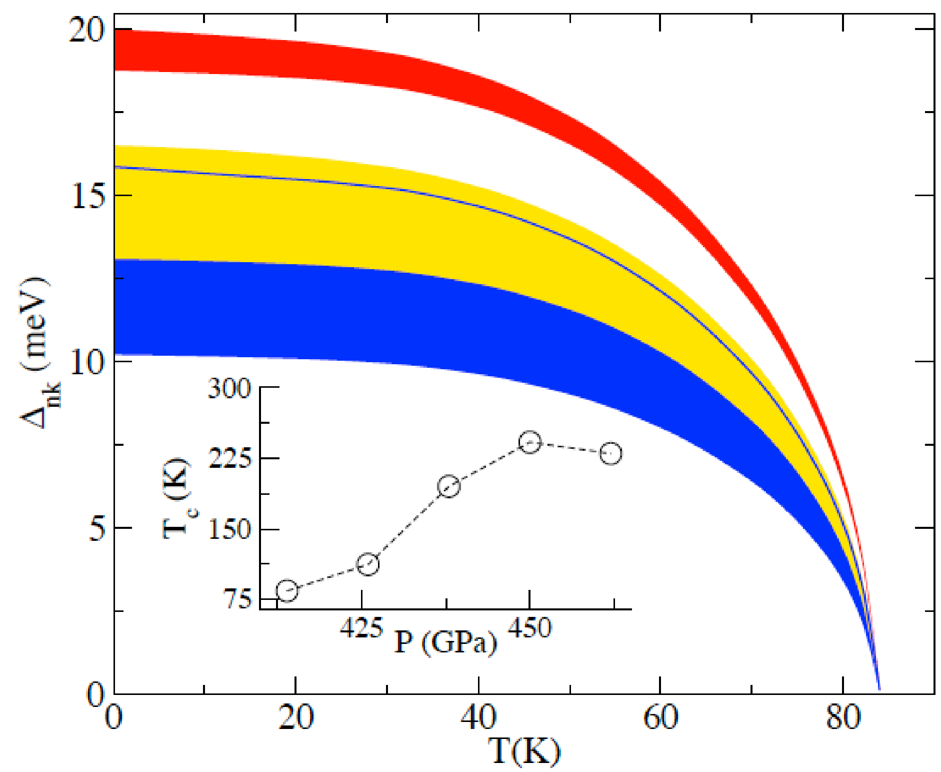
1996: Nellis produces liquid metallic hydrogen (140 GPa and 3000K)

Superconducting phase

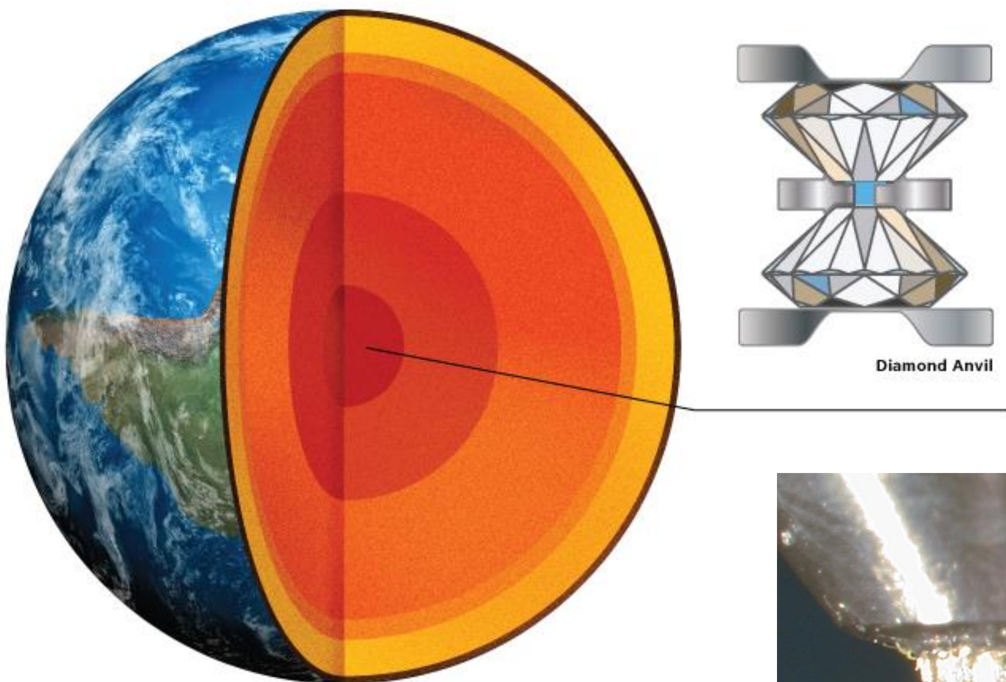






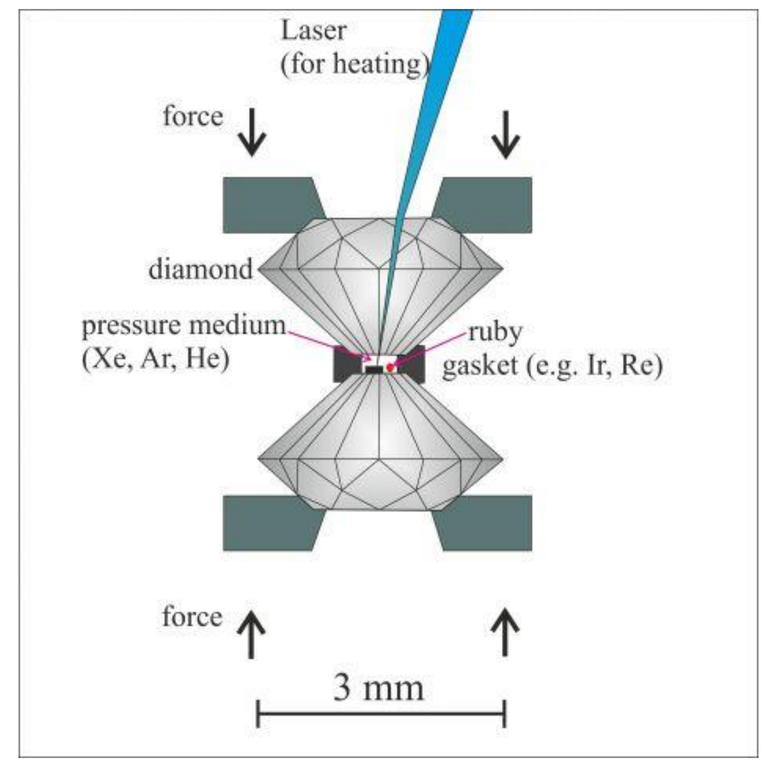


Hydrogen metallization: P > 450 GPa



Modern anvil cell reaches 350 GPa

Pressure in the inner core of earth is about 330 GPa!



Waiting for new and better technologies?
or re-think about the problem?

Lesson 1: chemical pressure

VOLUME 92, NUMBER 18 PHYSICAL REVIEW LETTERS week ending 7 MAY 2004

Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

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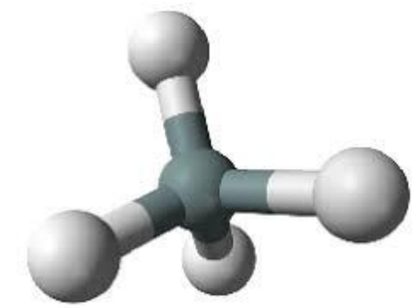
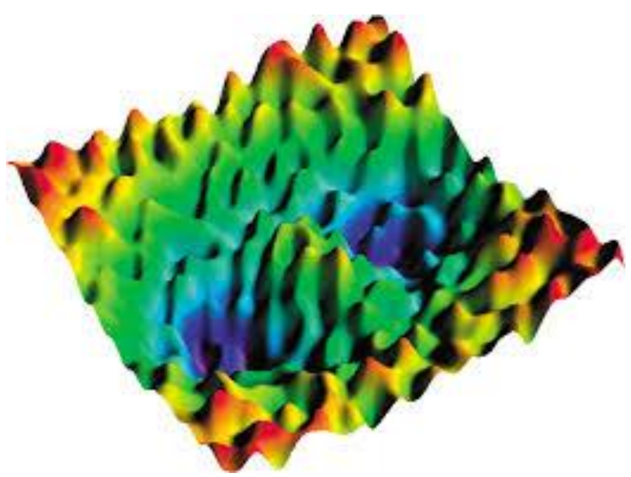
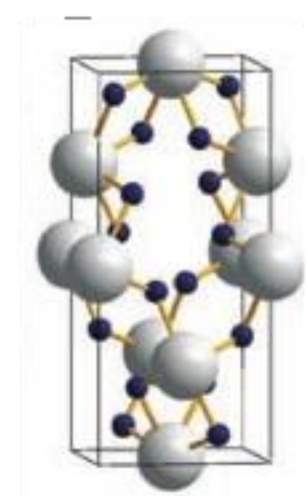
Donostia International Physics Center, San Sebastian, Spain
(Received 29 December 2003; published 6 May 2004)

The arguments suggesting that metallic hydrogen, either as a monatomic or paired metal, should be a candidate for high temperature superconductivity are shown to apply with comparable weight to alloys of metallic hydrogen where hydrogen is a dominant constituent, for example, in the dense group IVa hydrides. The attainment of metallic states should be well within current capabilities of diamond anvil cells, but at pressures considerably lower than may be necessary for hydrogen.





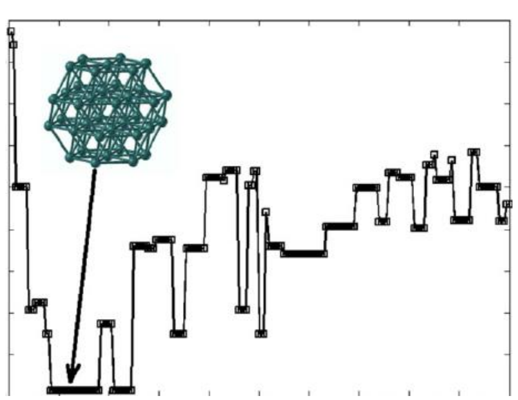


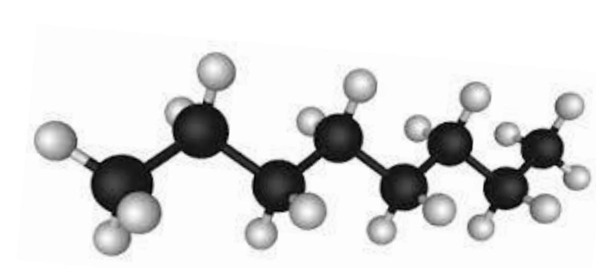
Superconductivity in Hydrogen Dominant Materials: Silane

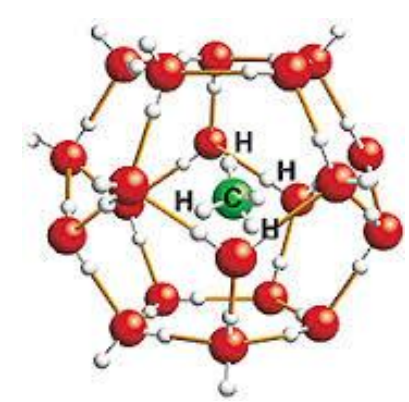
M. I. Eremets,[1*] I. A. Trojan,[1†] S. A. Medvedev,[1] J. S. Tse,[2] Y. Yao[2]

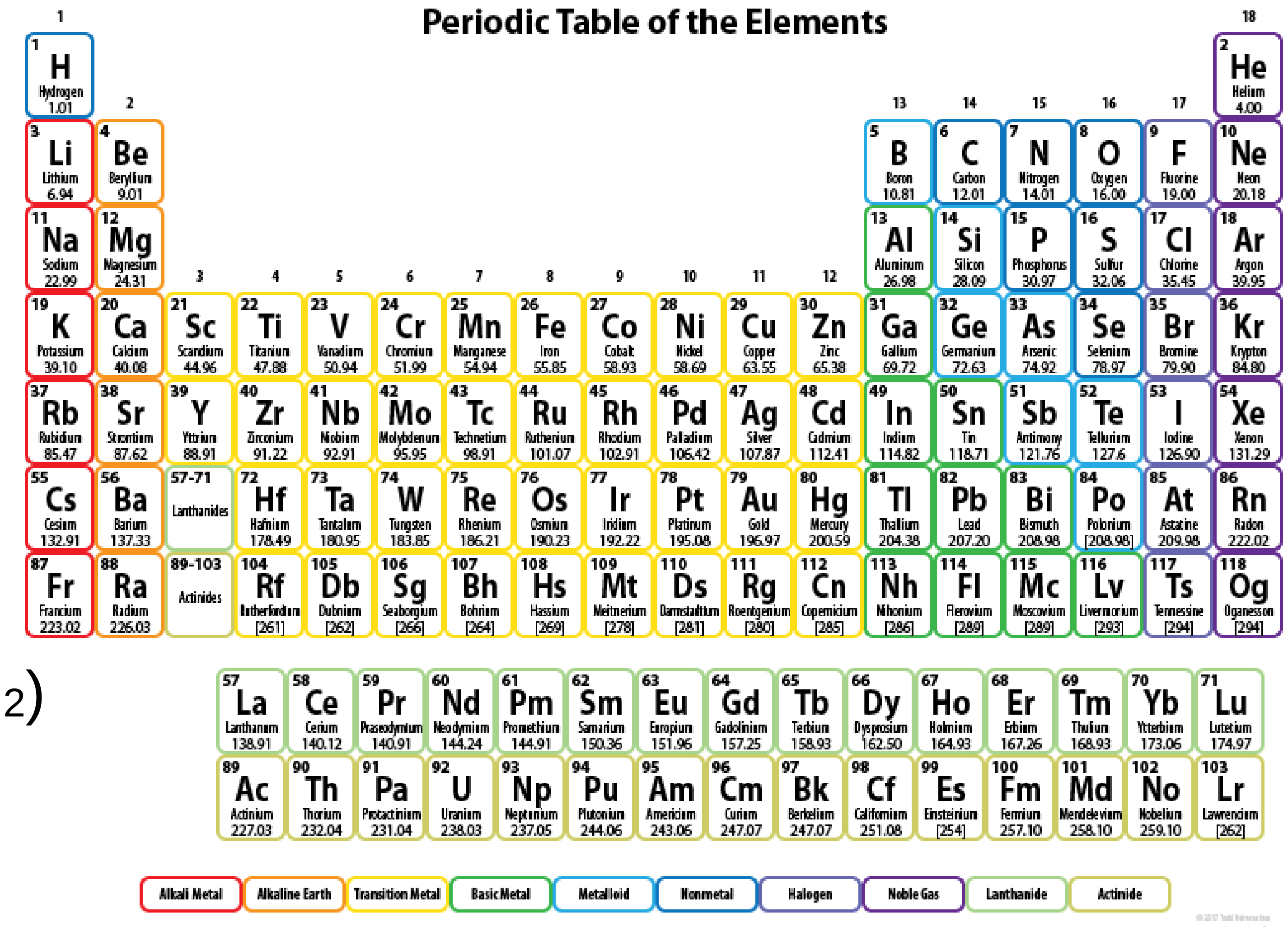
The metallization of hydrogen directly would require pressure in excess of 400 gigapascals (GPa), out of the reach of present experimental techniques. The dense group IVa hydrides attract considerable attention because hydrogen in these compounds is chemically precompressed and a metallic state is expected to be achievable at experimentally accessible pressures. We report the transformation of insulating molecular silane to a metal at 50 GPa, becoming superconducting at a transition temperature of T_c = 17 kelvin at 96 and 120 GPa. The metallic phase has a hexagonal close-packed structure with a high density of atomic hydrogen, creating a three-dimensional conducting network. These experimental findings support the idea of modeling metallic hydrogen with hydrogen-rich alloy.

Lesson 2: find the right crystal structure









SiH_4, GeH_4, KH_6

GaH_3, GeH_3, Si_2H_6

CaH_6, $SiH_4(H_2)$

$GeH_4(H_2)$

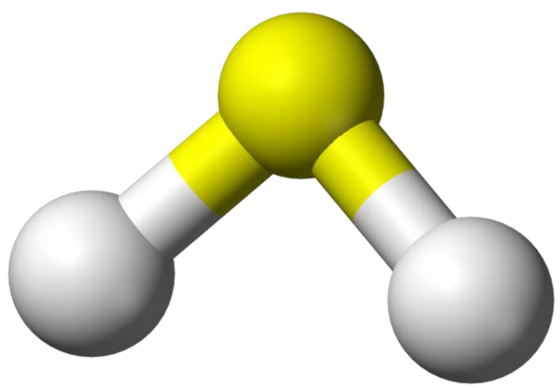
were **predicted** to metallize (from 100 to 250 GPa)

and (some of them) **superconduct** at “high temperatures”(80-230 K)

but superconductivity was measured only (?) in

PdH (10 K, 1972), SiH_4 (17 K, 2008) and $BaReH_9$ (7 K, 2015)

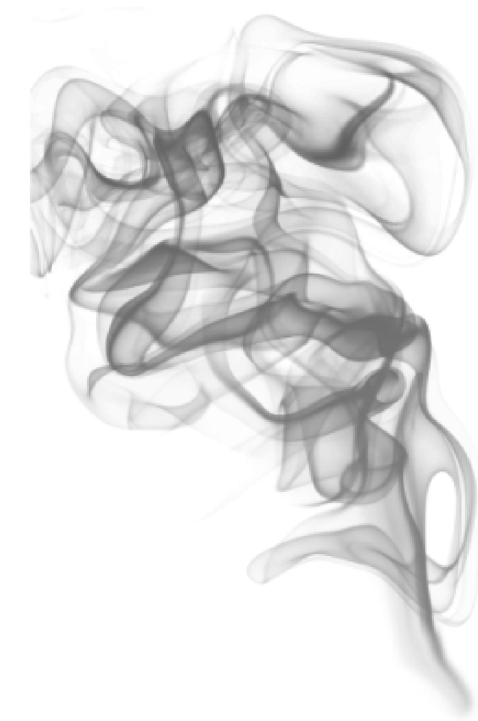
Hydrogen sulfide



Discovered in 1777

It is a colorless gas with the characteristic foul odor of rotten eggs.

It is very poisonous, corrosive, and flammable, explosive



Solid hydrogen sulfide (H_2S) has not previously been considered a superconductor because, upon metallization under pressure, it was believed to dissociate into its constituent elements.

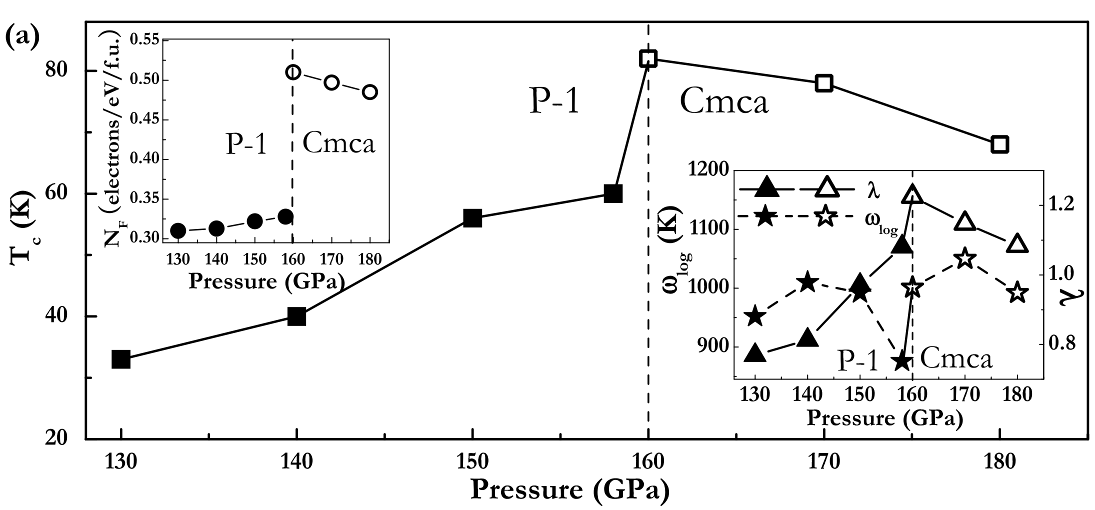
THE JOURNAL OF CHEMICAL PHYSICS **140**, 174712 (2014)

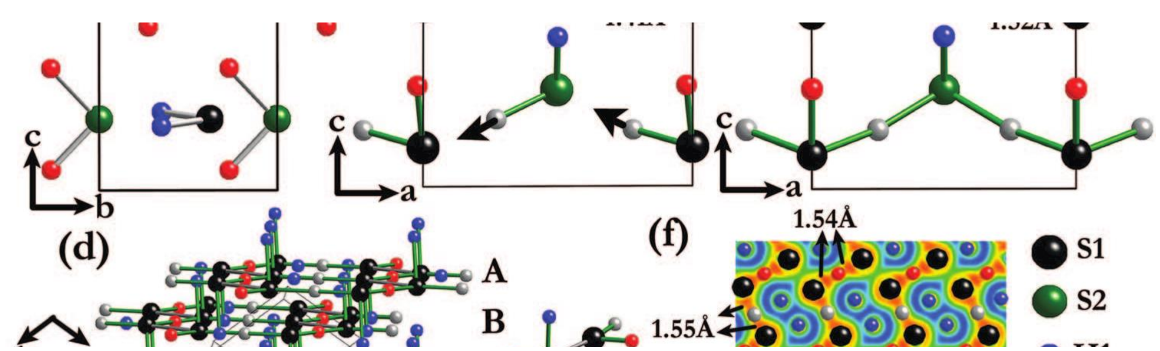
The metallization and superconductivity of dense hydrogen sulfide

Yinwei Li,[1,a)] Jian Hao,[1] Hanyu Liu,[2] Yanling Li,[1] and Yanming Ma[3,b)]
[1]*School of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, People's Republic of China*
[2]*Department of Physics and Engineering Physics, University of Saskatchewan, Saskatchewan S7N 5E2, Canada*
[3]*State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China*

(Received 20 March 2014; accepted 18 April 2014; published online 7 May 2014)

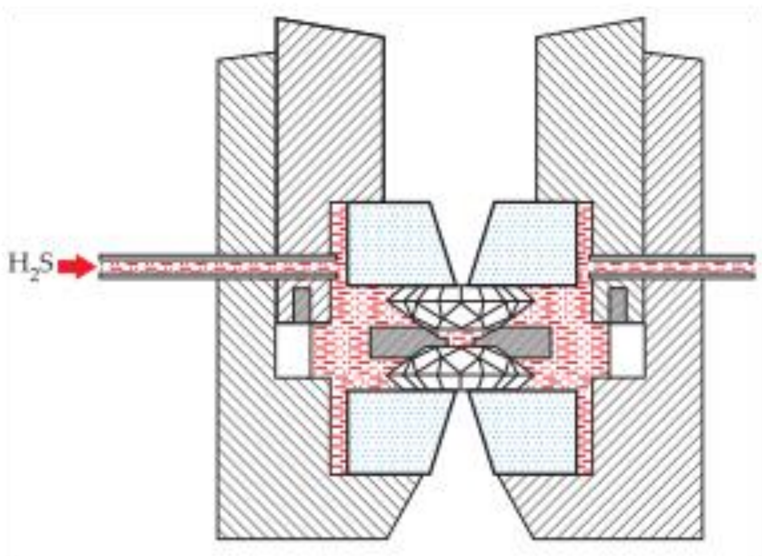
Metallization of H_2S

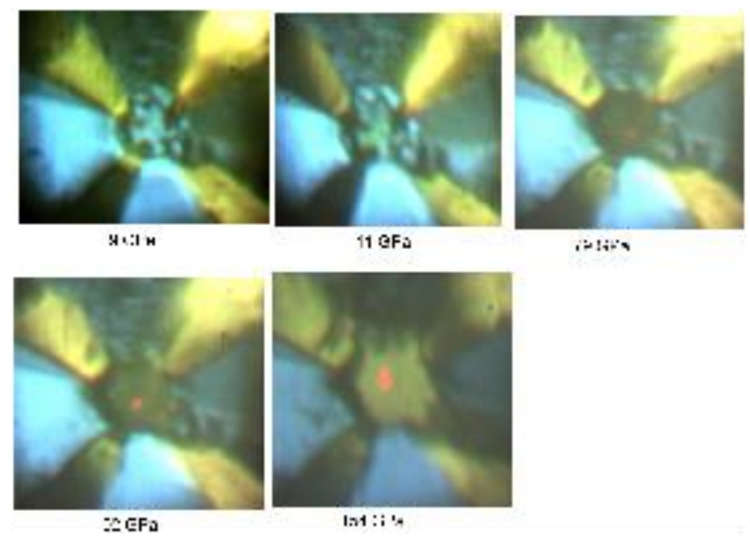


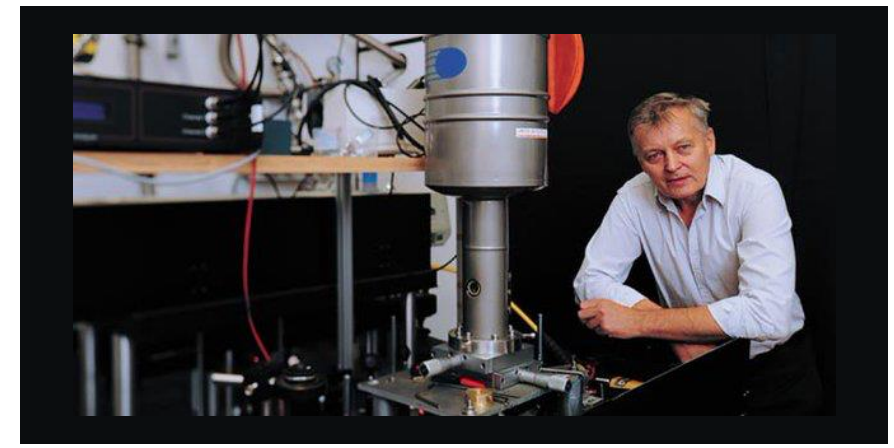


Eremets's experiment

Max-Planck-Institut fur Chemie (Mainz), Germany.



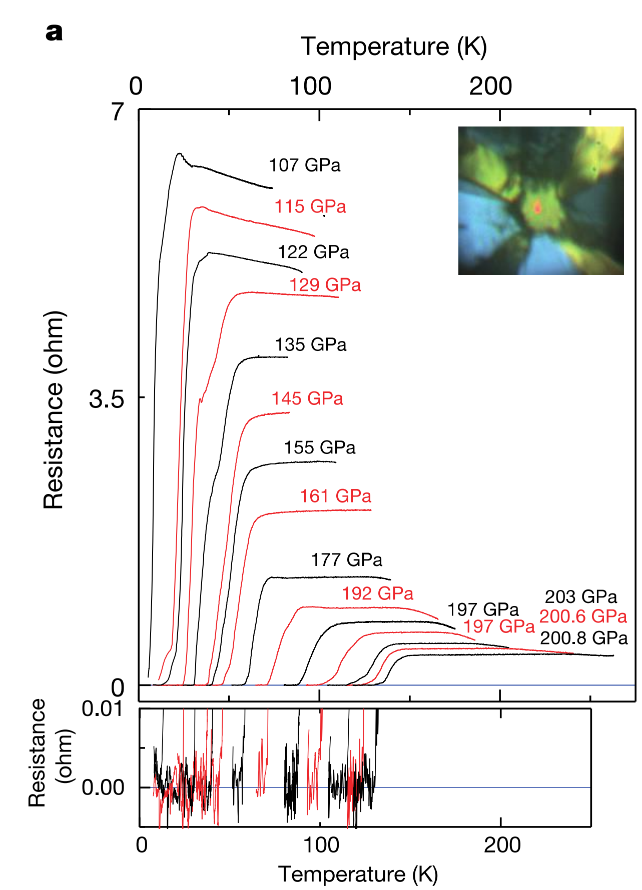


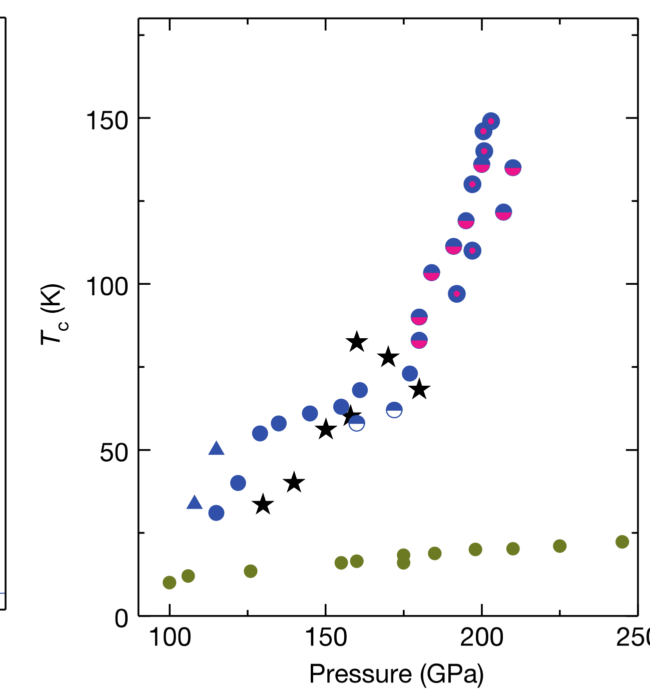


SQUEEZING SULFUR HYDRIDE in a diamond anvil cell.

The cell is first cooled to 200 K, then hydrogen sulfide (H_2S) gas is sent into the cell through a capillary.

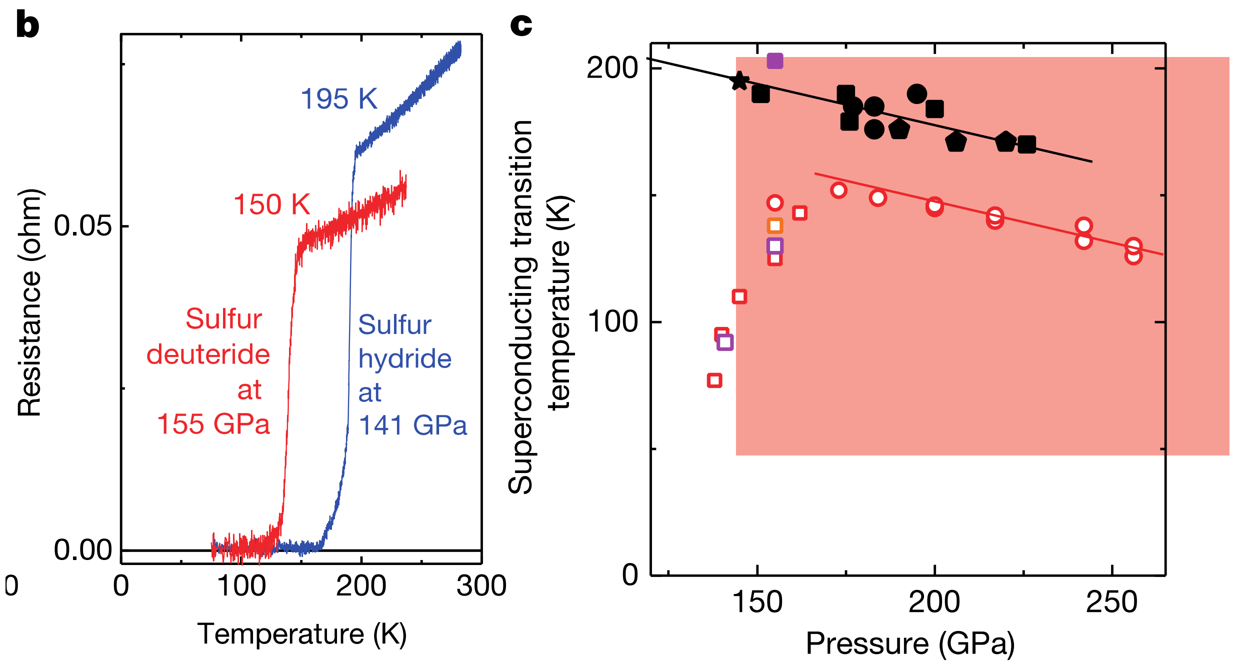
Inside the cell, H_2S liquefies; only then pressure is applied



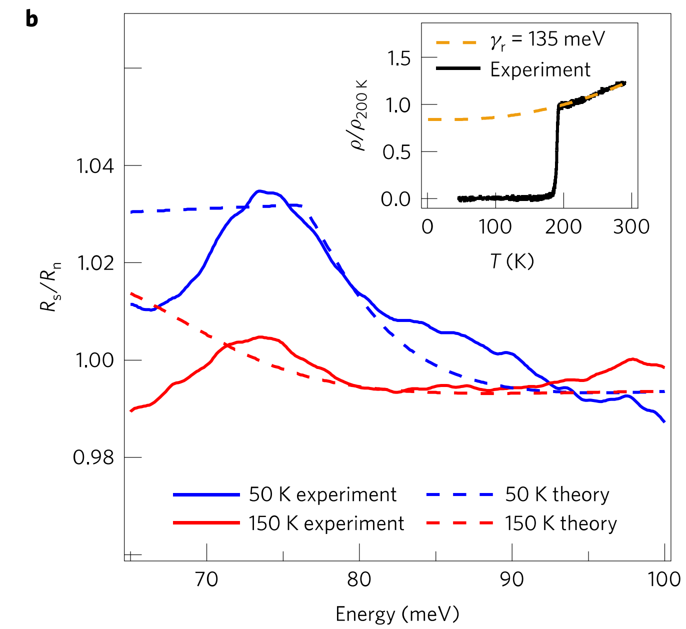


200K (-73 ºC) superconductivity?

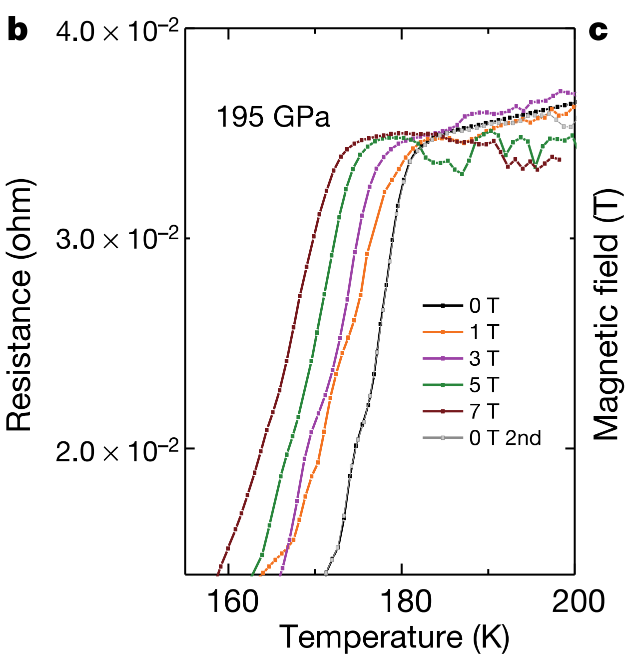
Isotope effect
(phonons are involved)

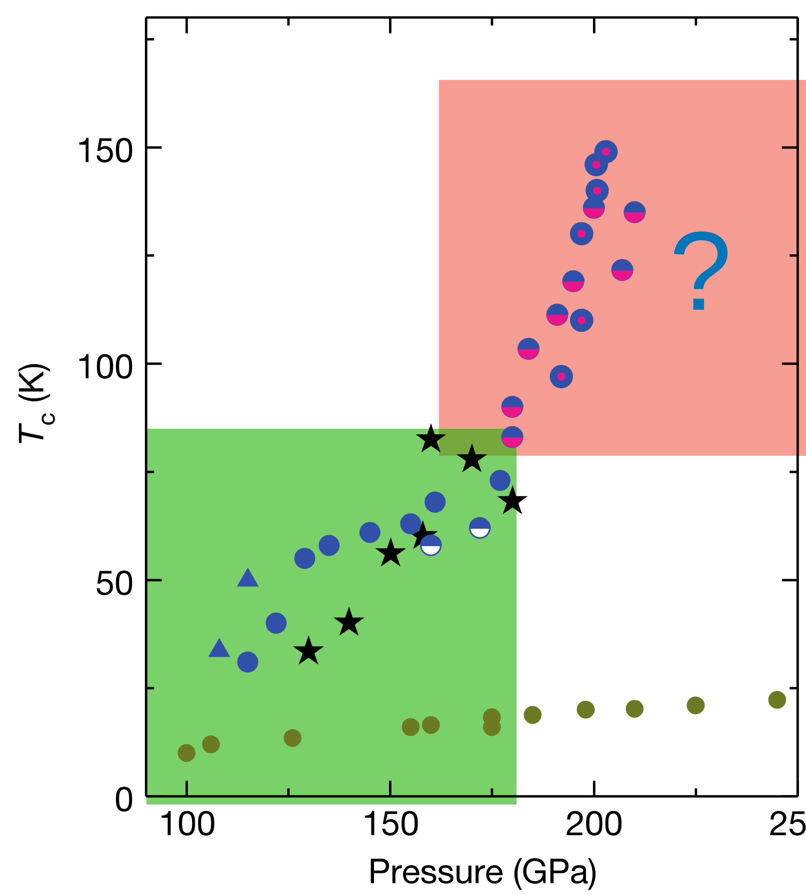


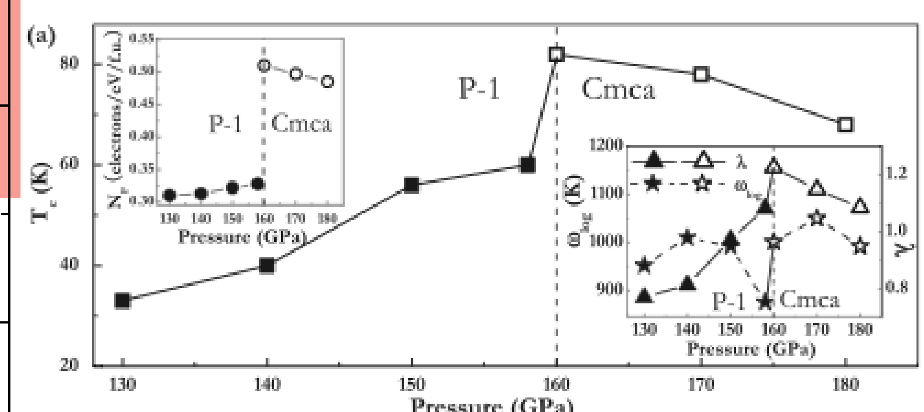
Electronic energy gap



Meissner effect
(Magnetic field)

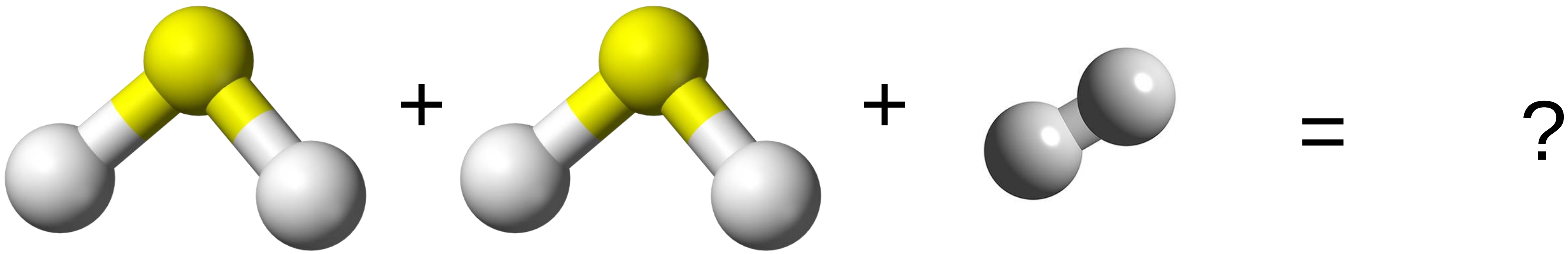




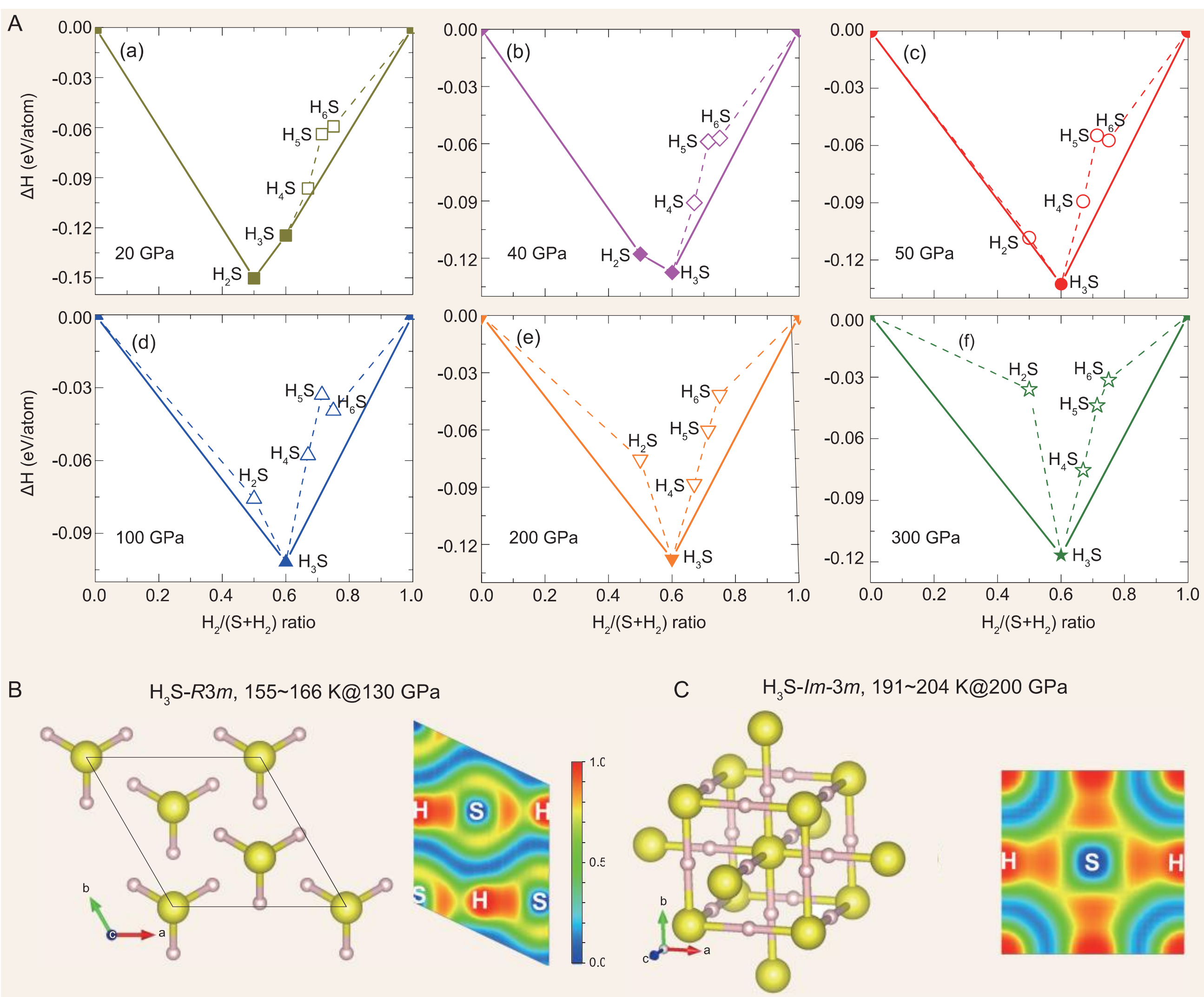


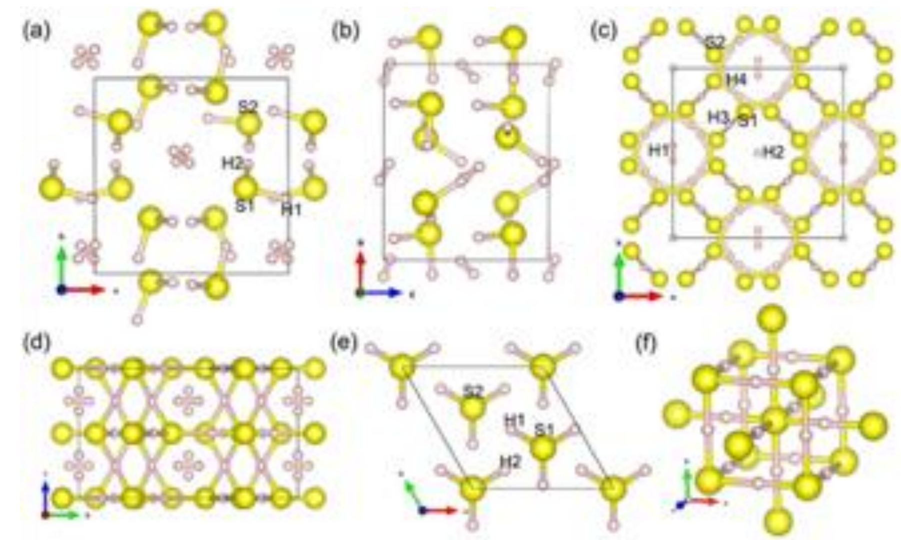
Lesson 3: New chemistry

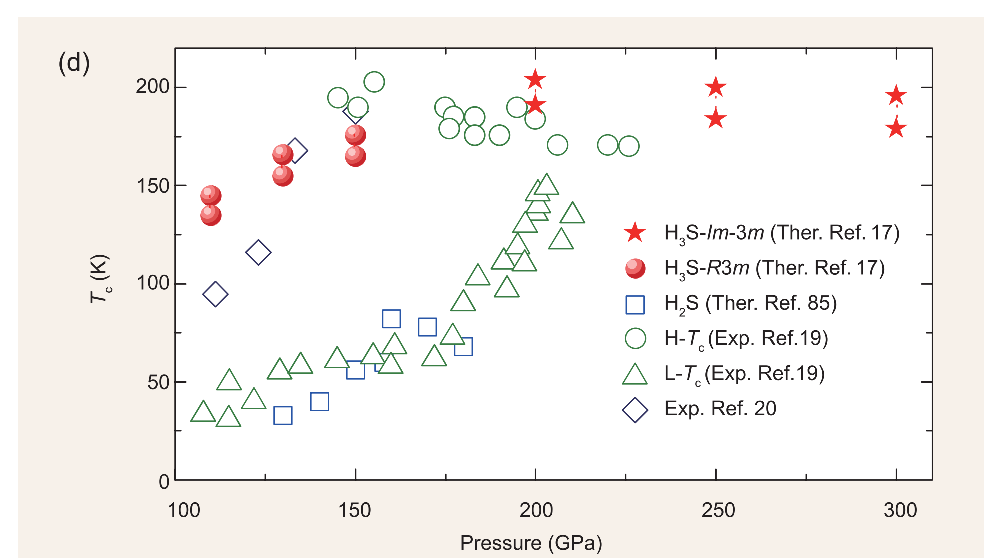
Duan et al. (2014)



Maxwell plot





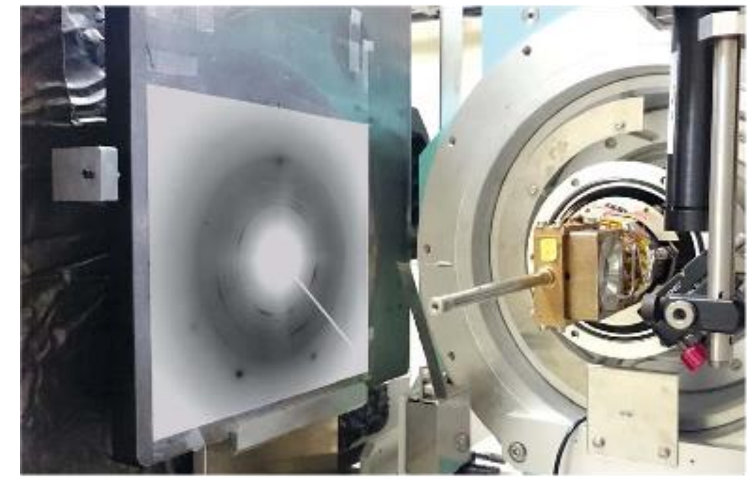


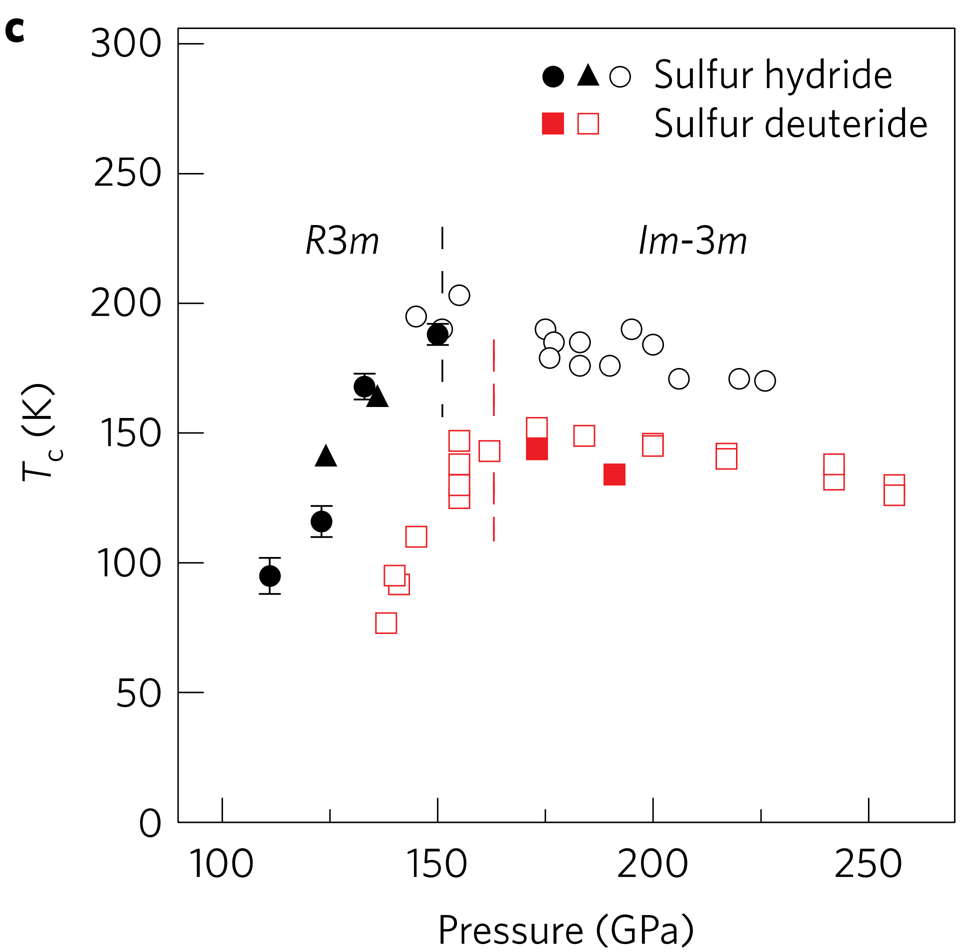
It is true

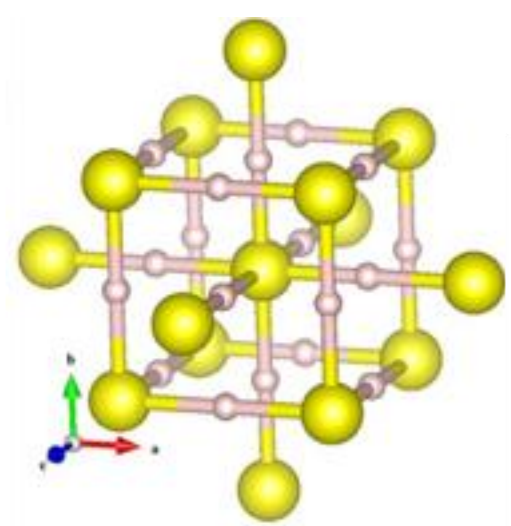
nature physics
LETTERS
PUBLISHED ONLINE: 9 MAY 2016 | DOI: 10.1038/NPHYS3760

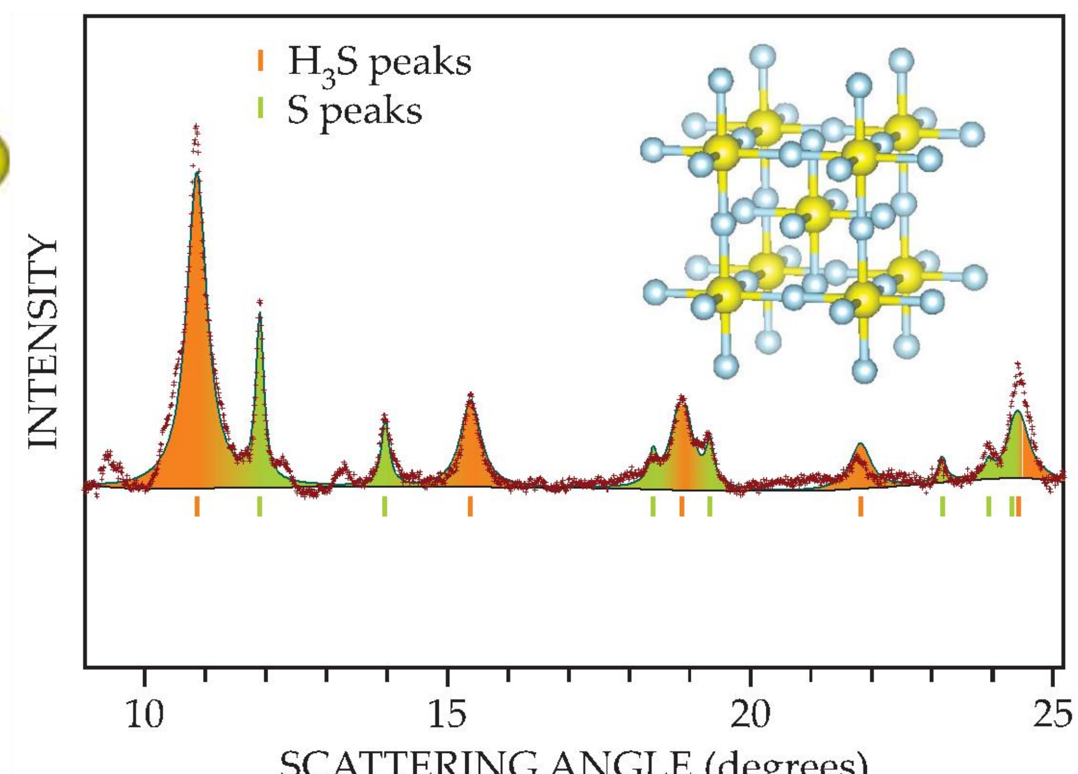
Crystal structure of the superconducting phase of sulfur hydride

Mari Einaga[1*†], Masafumi Sakata[1], Takahiro Ishikawa[1], Katsuya Shimizu[1†], Mikhail I. Eremets[2†], Alexander P. Drozdov[2], Ivan A. Troyan[2], Naohisa Hirao[3] and Yasuo Ohishi[3]

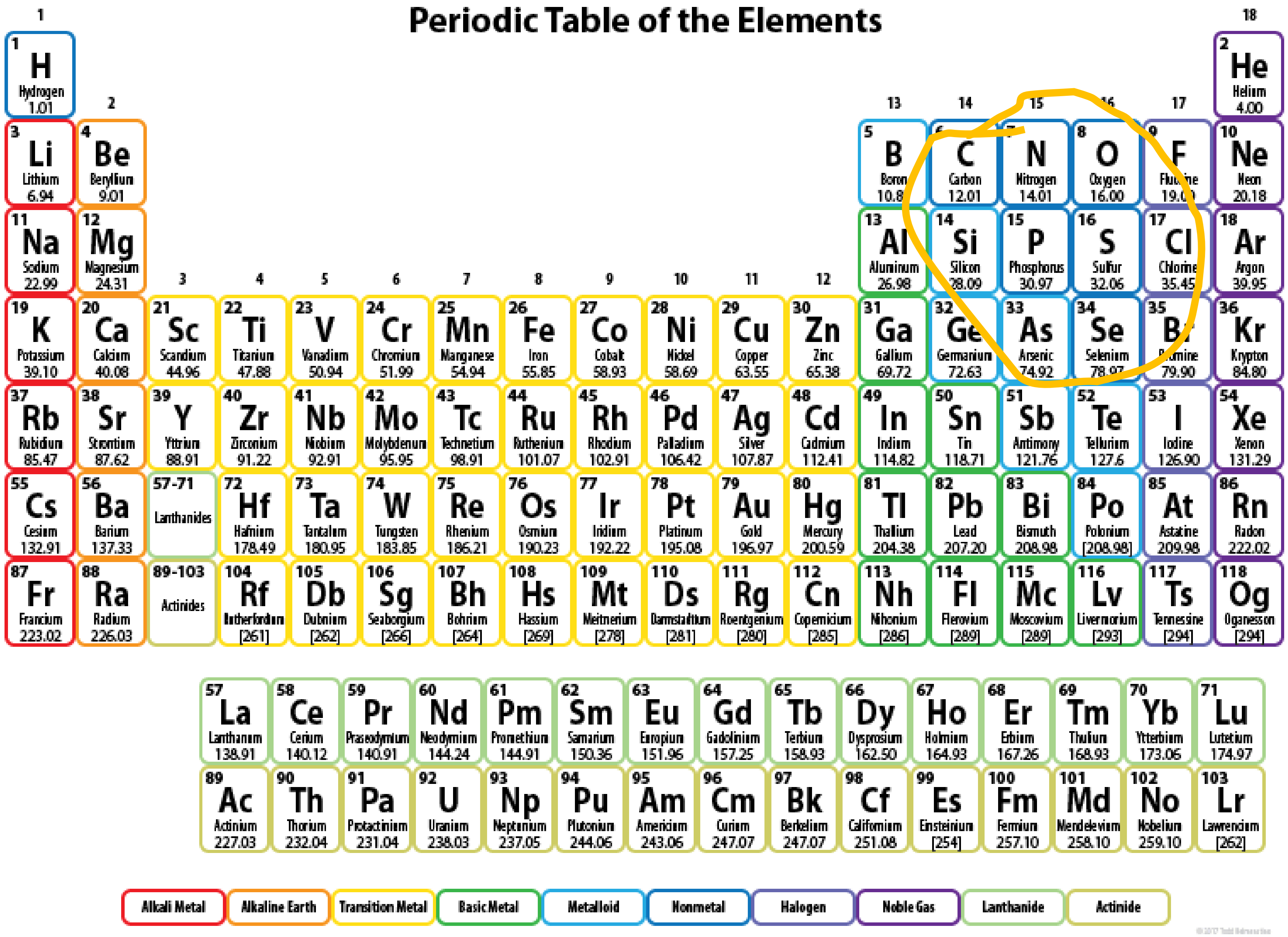








Is H_2S (H_3S) an isolated example?



Superconducting phosphines (PH_3)

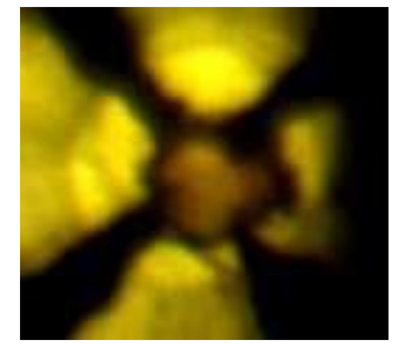
It is a colorless, flammable, toxic gas and odorless.

Superconductivity above 100 K in PH_3 at high pressures

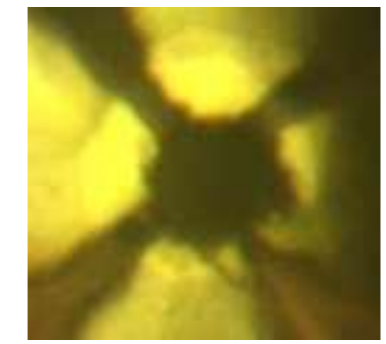
A. P. Drozdov, M. I. Eremets and I. A. Troyan

Max-Planck Institut fur Chemie, Hahn-Meitner Weg 1,55128, Mainz, Germany

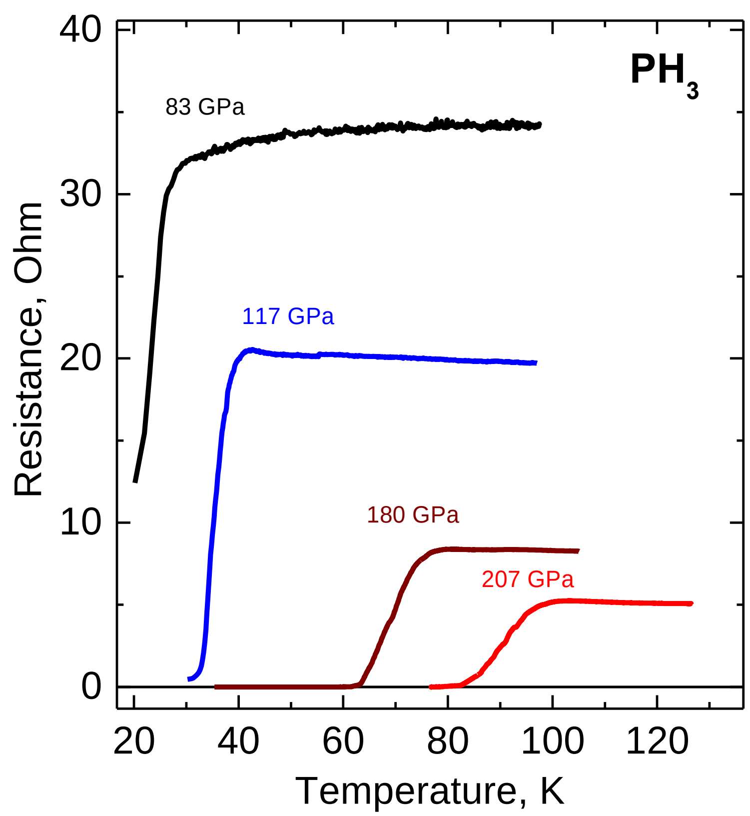
Following the recent discovery of very high temperature conventional superconductivity in sulfur hydride (critical temperature T_c of 203 K, Ref[1]) we searched for superconductivity in other hydrides and found that a covalent hydride phosphine (PH_3) also exhibits a high T_c >100 K at pressure P > 200 GPa as determined from four-probe electrical measurements.



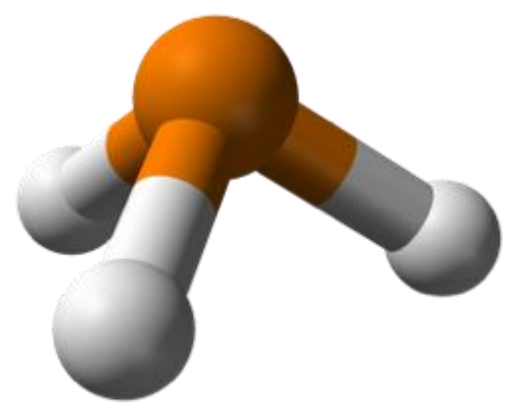
a. Clamped at 20 GPa, 180 K

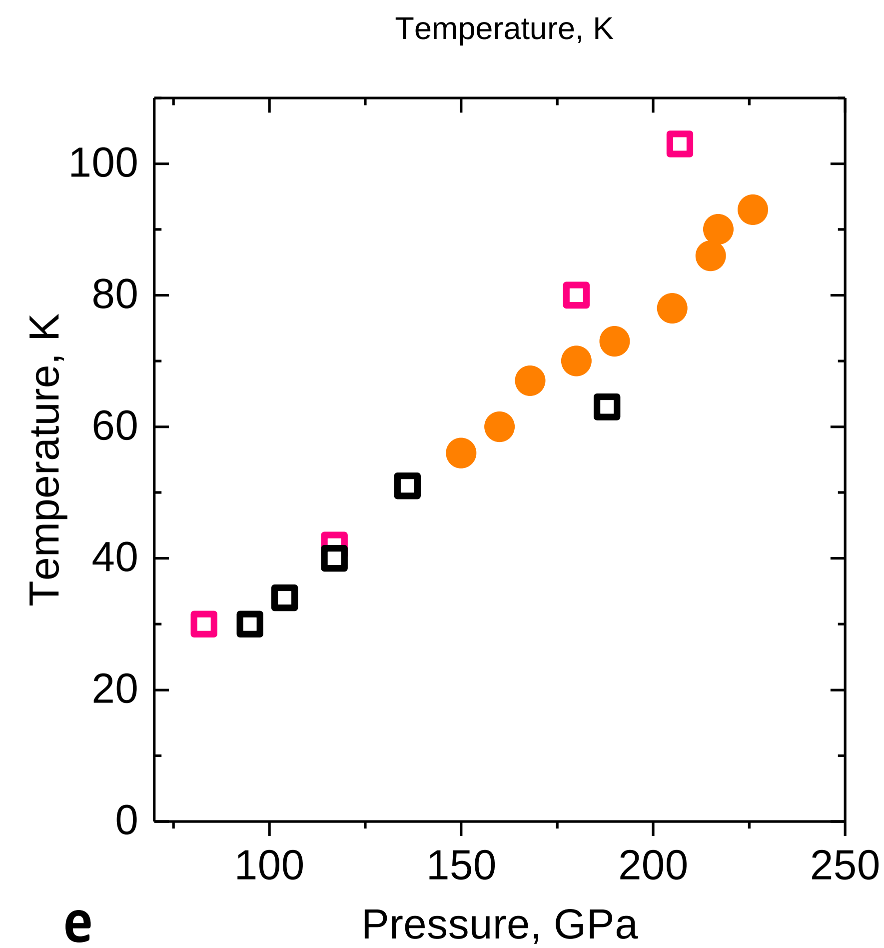


b. 46 GPa, 191 K



a

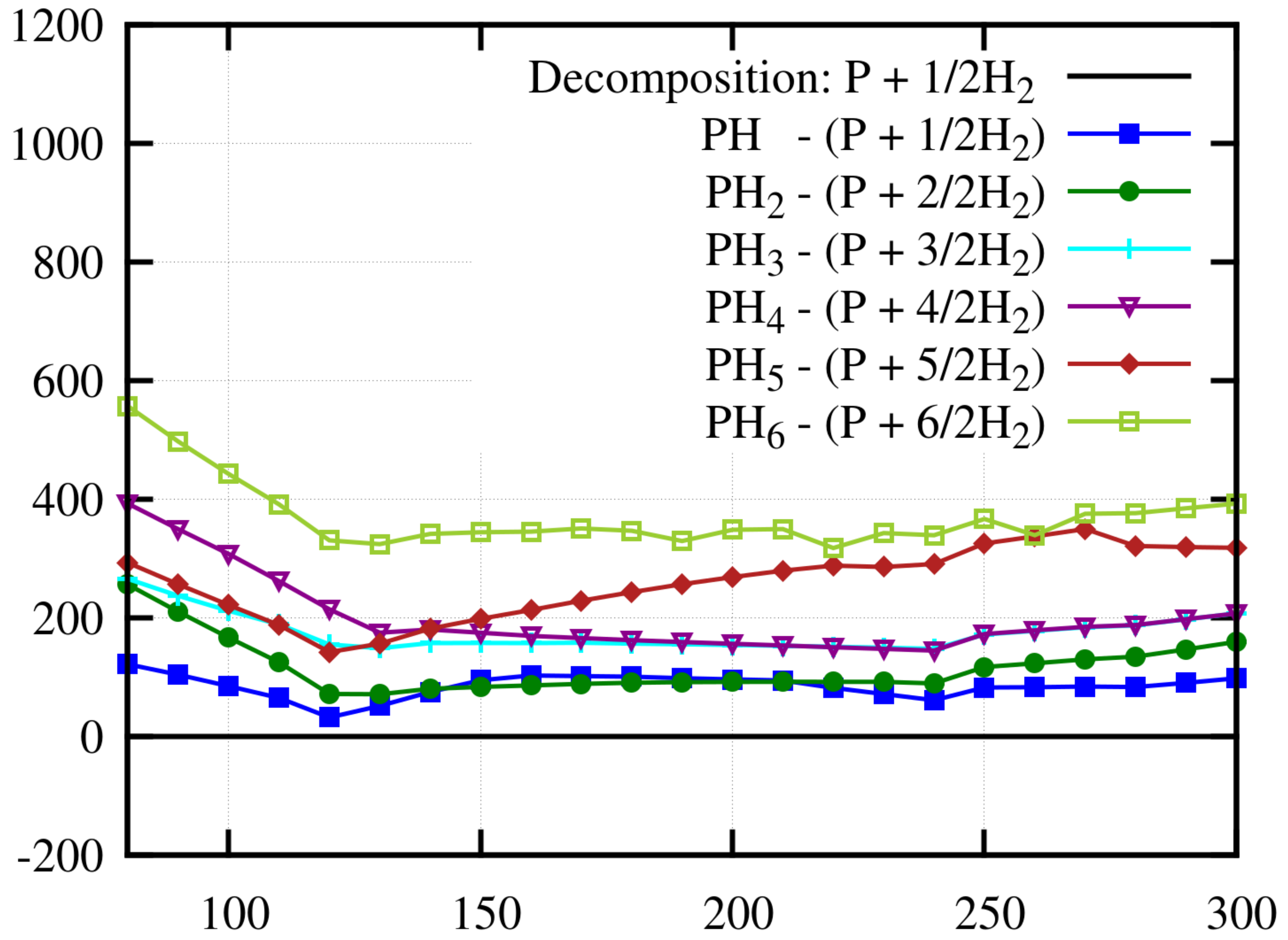




e

Which is the stable crystal structure?

Enthalpy
w.r.t.
to decomposition
to pure constituents



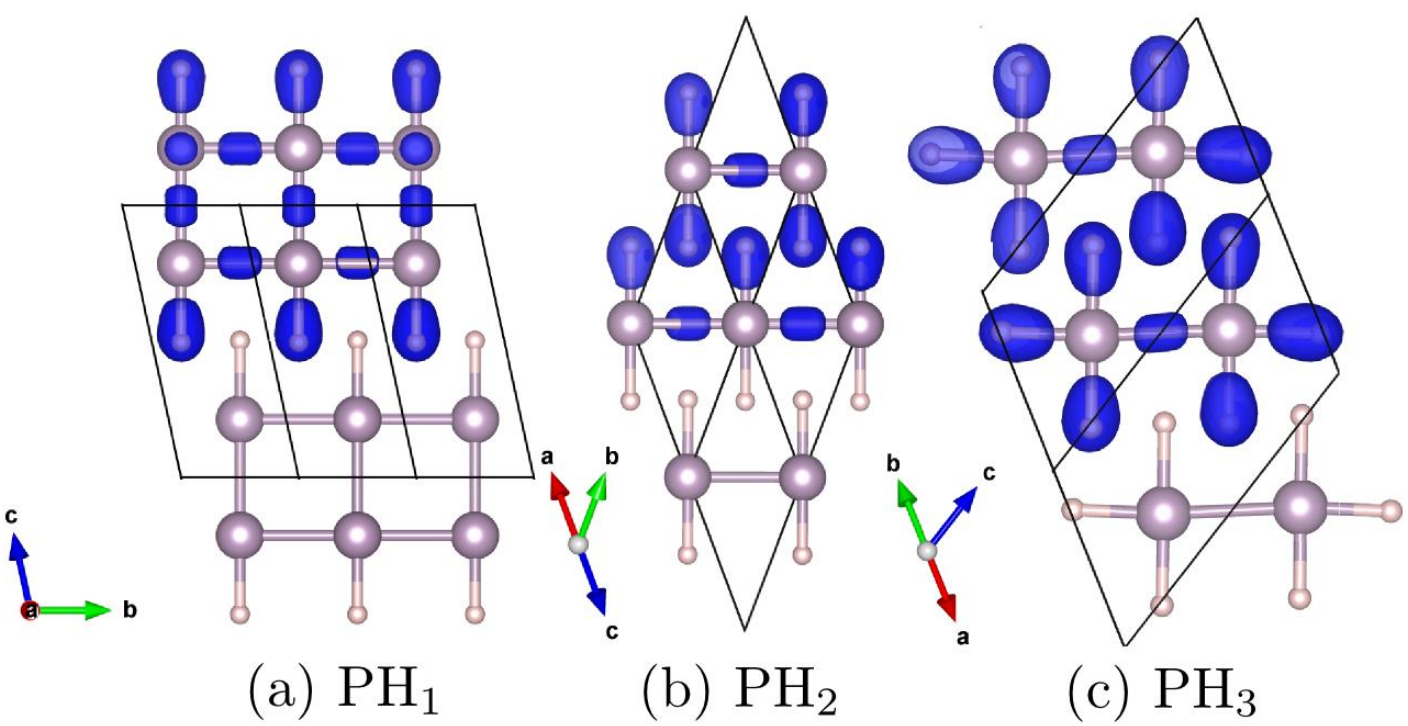
Pressure (GPa)

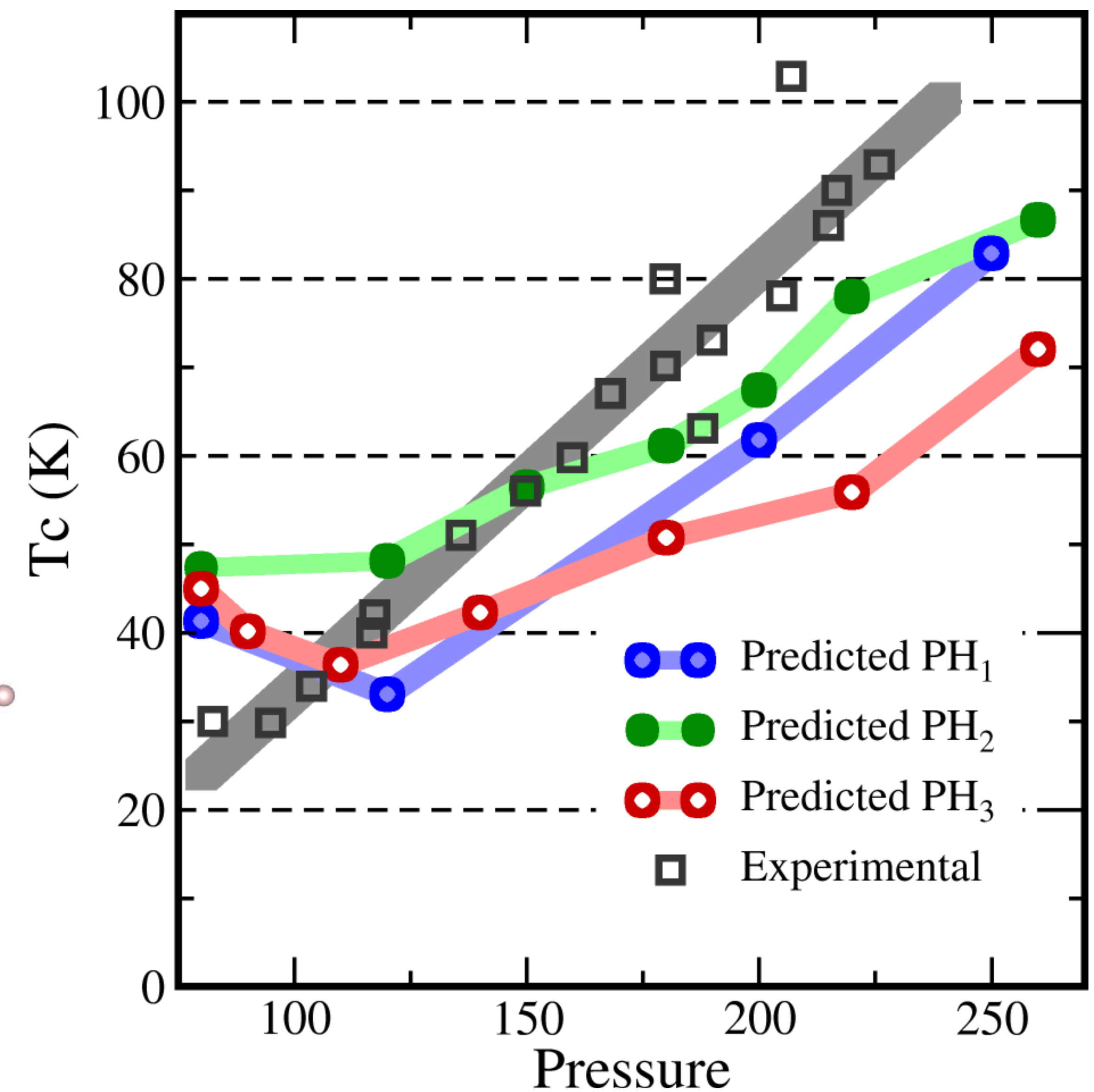
All phases are metastable with respect to elemental decomposition

Superconductivity by metastability

Hypotesis:
Possible non equilibrium process and/or non-hydrostatic effects can stabilize the lowest energy phases (PH and PH_2)

PH_3 decomposes at high P

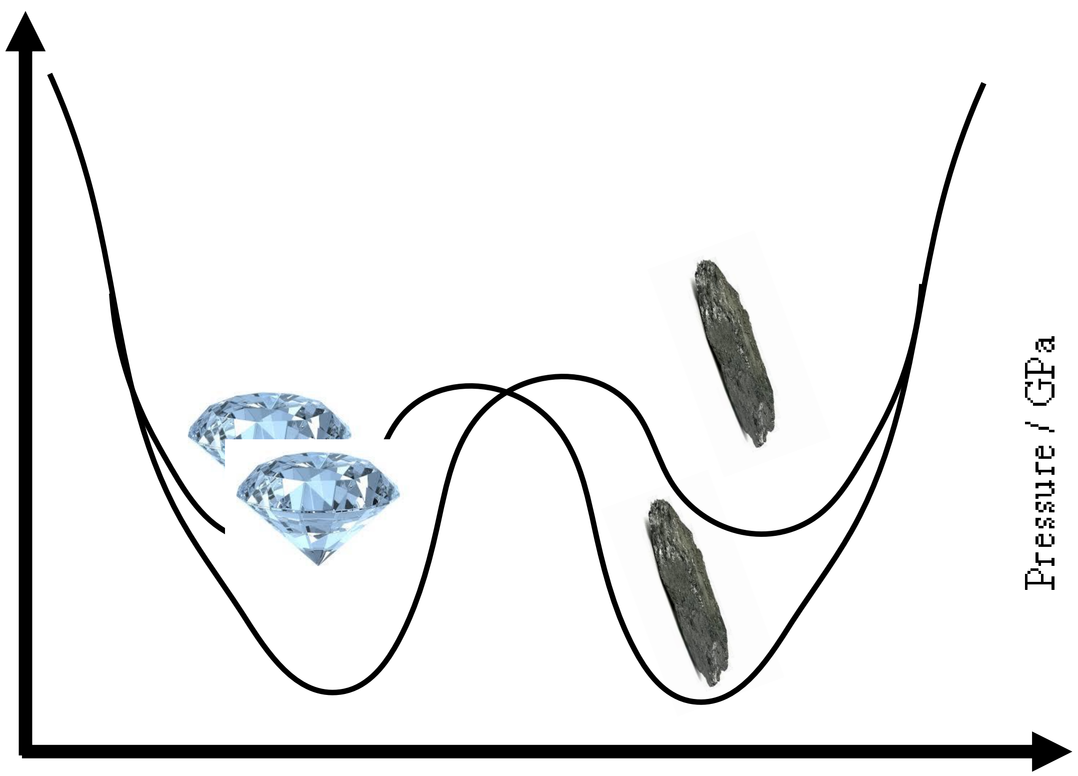




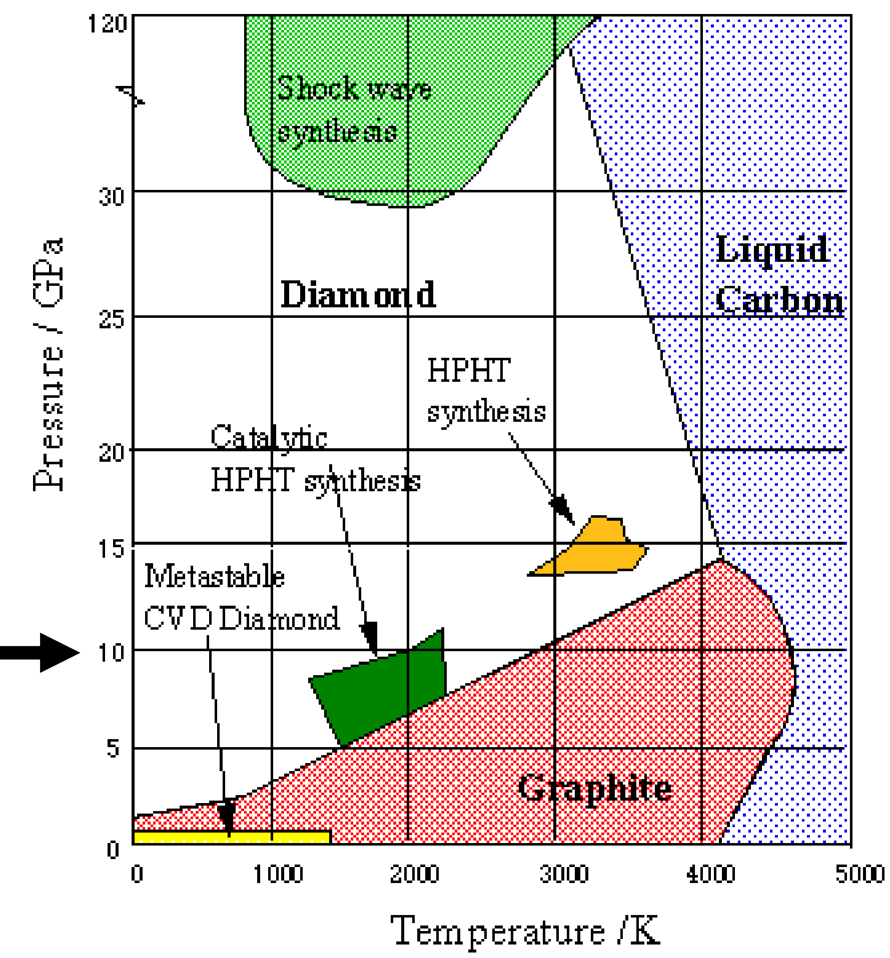
PH2 seems to be the best candidate (?)

Lesson 4: Metastability, a new possibility

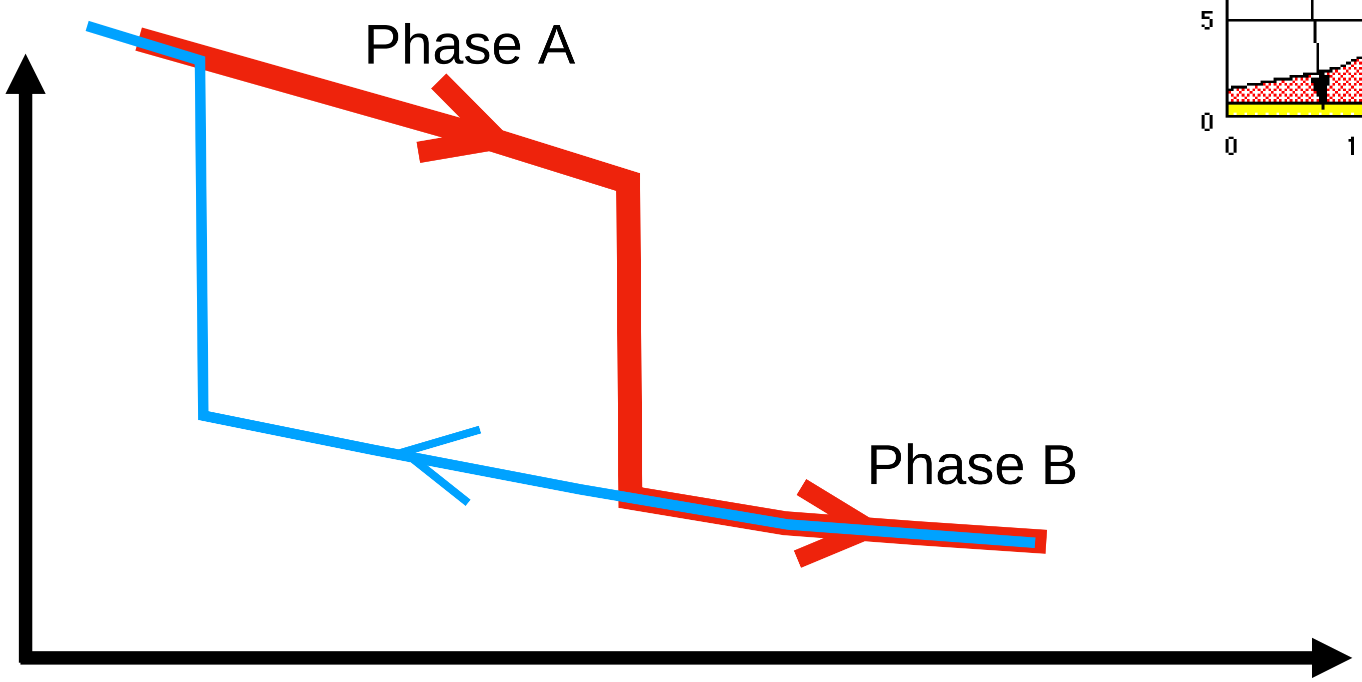
Energy



Diamond
is more stable
than graphite
above 1 GPa



Volume



Pressure

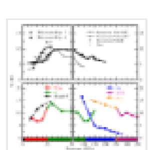
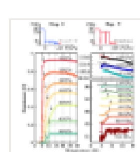
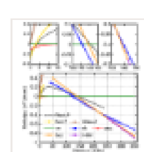
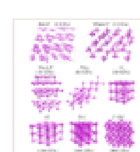
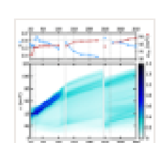
Interplay between structure and superconductivity: Metastable phases of phosphorus under pressure

José A. Flores-Livas, Antonio Sanna, Alexander P. Drozdov, Lilia Boeri, Gianni Profeta, Mikhail Eremets, and Stefan Goedecker

Phys. Rev. Materials **1**, 024802 – Published 20 July 2017

ABSTRACT

Pressure-induced superconductivity and structural phase transitions in phosphorus (P) are studied by resistivity measurements under pressures up to 170 GPa and by fully *ab initio* crystal structure exploration and superconductivity calculations up to 350 GPa. Two distinct superconducting transition temperature (T_C) vs pressure (P) trends at low pressure have been reported more than 30 years ago, and we are able to devise a consistent explanation founded on thermodynamically metastable phases of black phosphorus. Our experimental and theoretical results form a single, consistent picture which not only provides a clear understanding of elemental P under pressure but also sheds light on the longstanding and unsolved *anomalous* superconductivity trends. Moreover, at higher pressures we predict a similar scenario of multiple metastable structures which coexist beyond their thermodynamical stability range. We observe that all the metastable structures systematically exhibit larger transition temperatures than the ground-state structures, indicating that the exploration of metastable phases represents a promising route to design materials with improved superconducting properties.

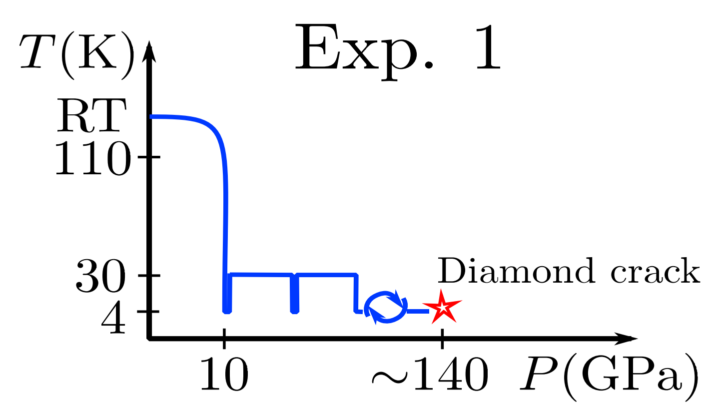






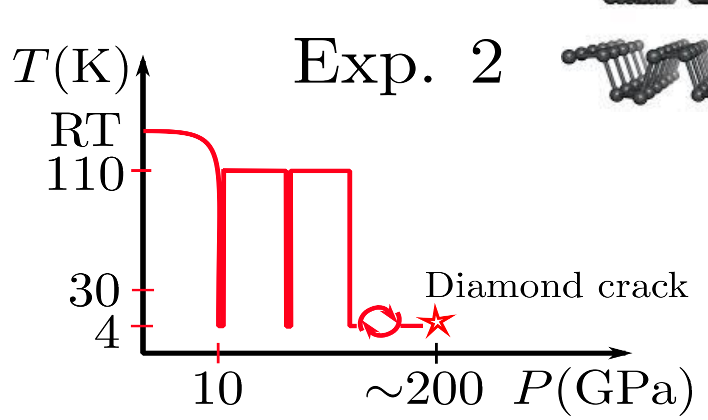
Issue

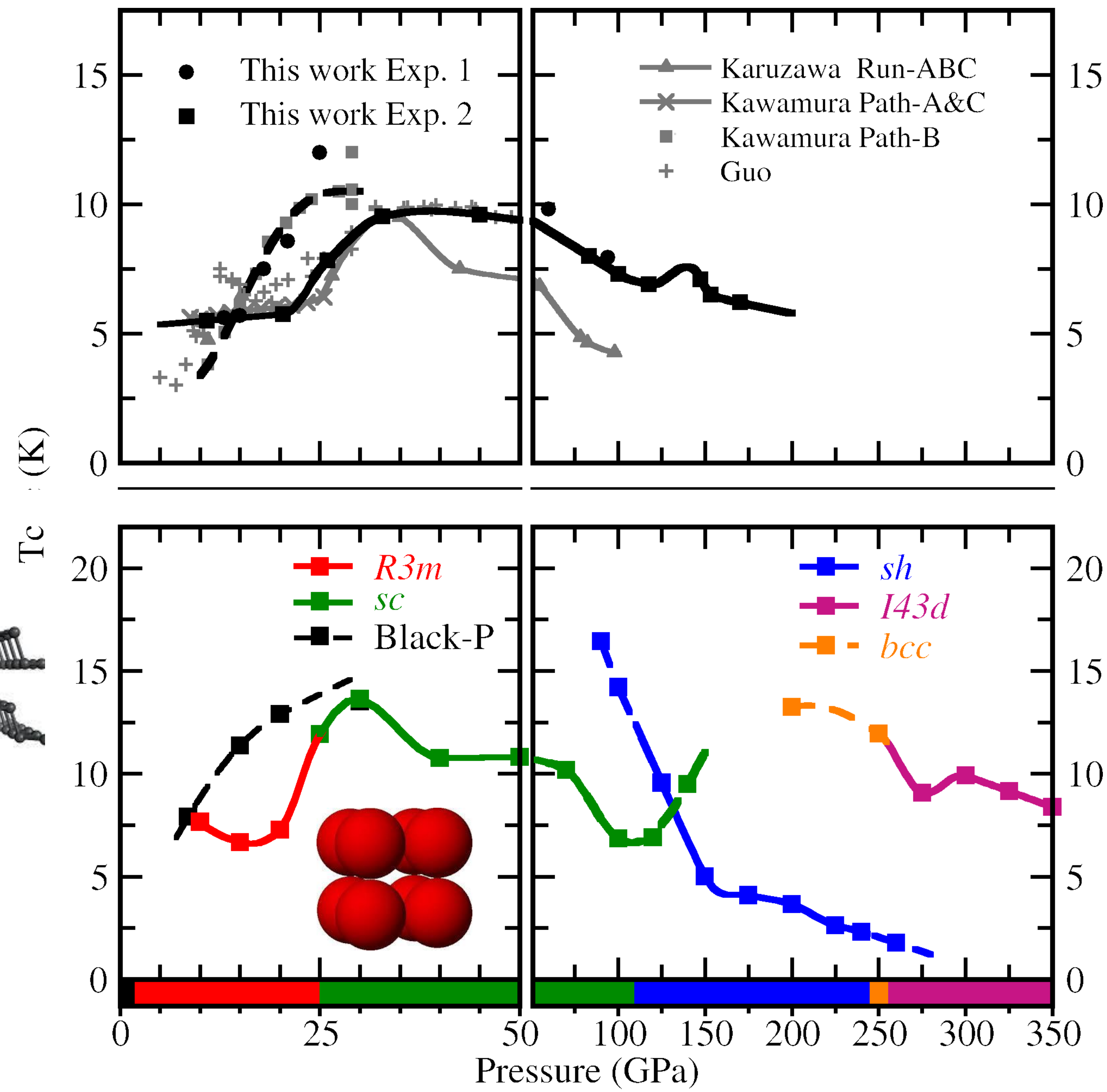
Vol. 1, Iss. 2 — July 2017

Phosphorus superconducting phase diagram

old problem new solution







Superconductivity in palladium hydride and deuteride at 52–61 kelvin

H. M. Syed, T. J. Gould, C. J. Webb and E. MacA. Gray*

Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan 4111, Brisbane, Australia

Superconductivity of barium-VI synthesized via compression at low temperatures

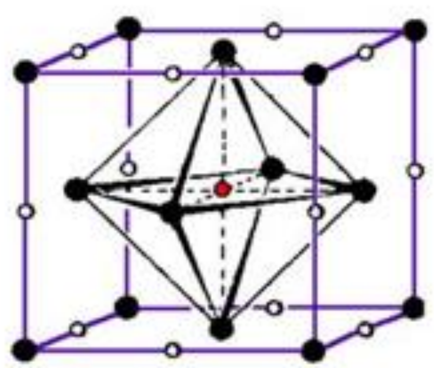
D. E. Jackson,[1] D. VanGennep,[1] Y. K. Vohra,[2] S. T. Weir,[3] and J. J. Hamlin[1,ò]

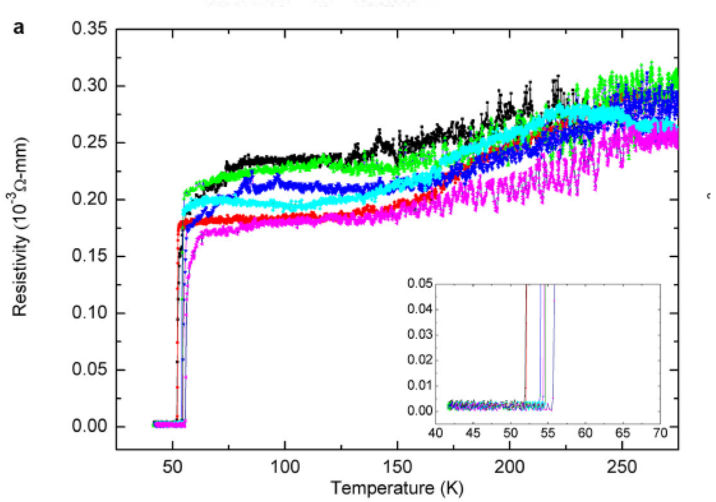
[1]*Department of Physics, University of Florida, Gainesville, FL 32611*

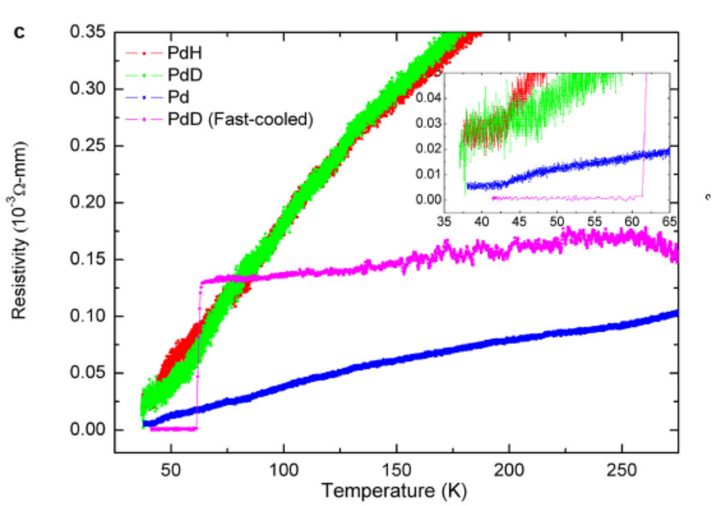
[2]*Department of Physics, University of Alabama at Birmingham, Birmingham, AL, 35294*

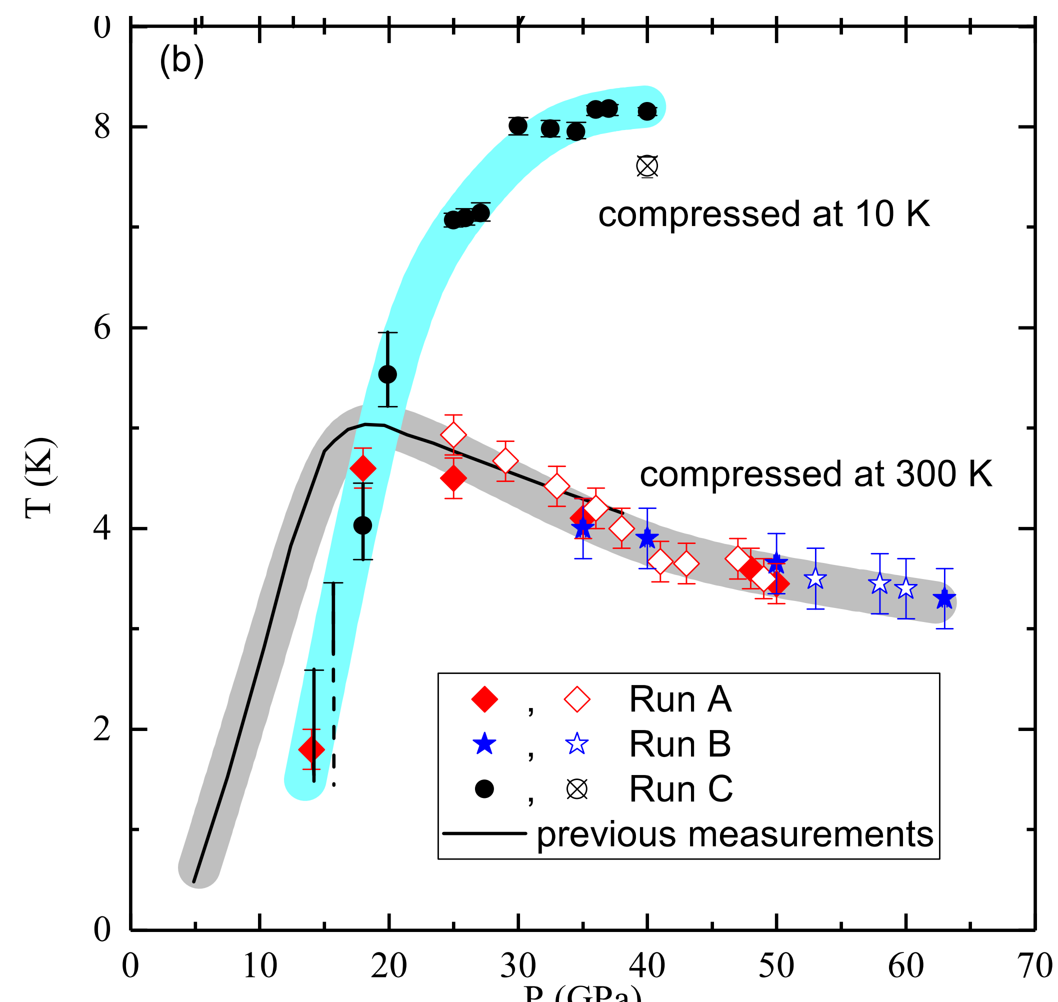
[3]*Physics Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA*

(Dated: July 20, 2017)





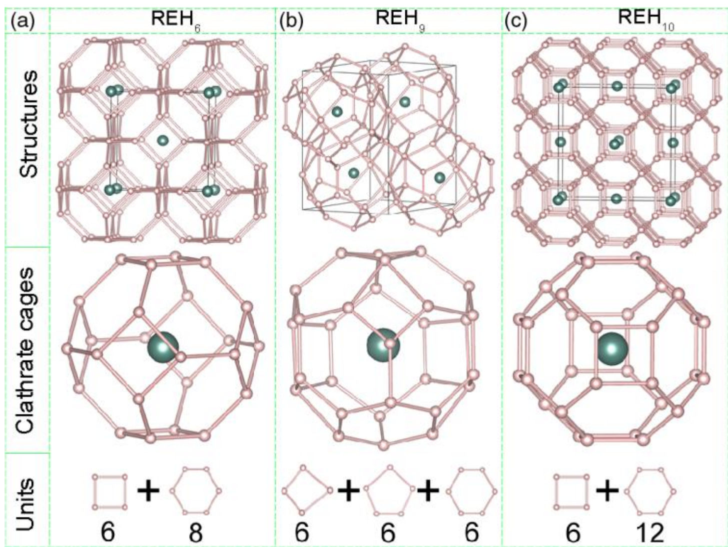


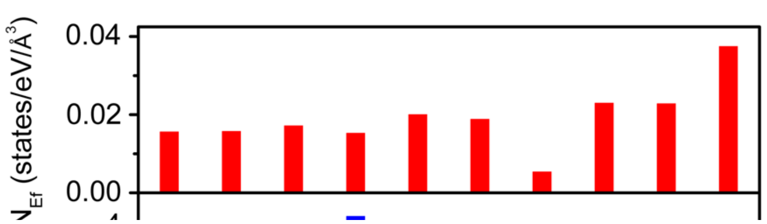


PRL 119, 107001 (2017) PHYSICAL REVIEW LETTERS week ending 8 SEPTEMBER 2017

Hydrogen Clathrate Structures in Rare Earth Hydrides at High Pressures: Possible Route to Room-Temperature Superconductivity

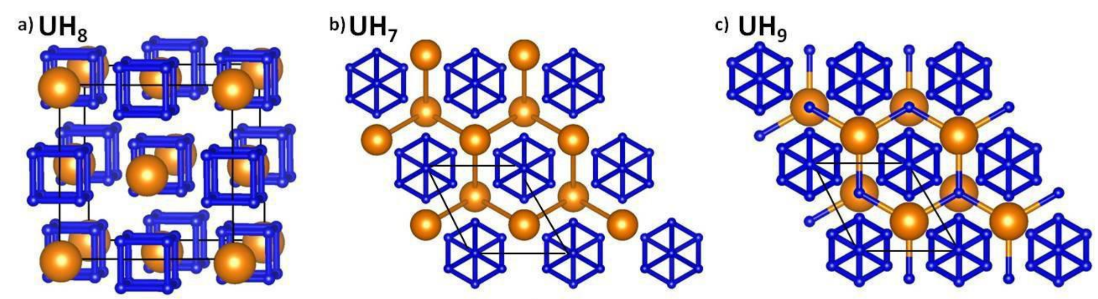
Feng Peng,[1,2,3] Ying Sun,[3] Chris J. Pickard,[4] Richard J. Needs,[5] Qiang Wu,[6] and Yanming Ma[3,7,*]

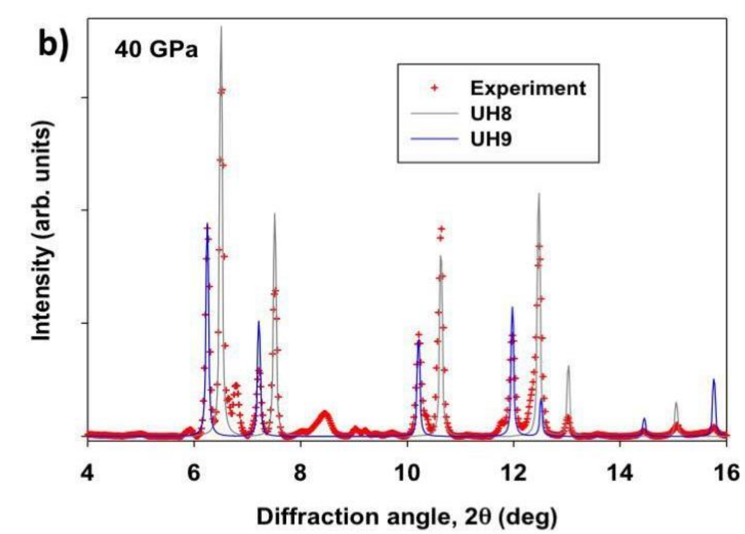




High-temperature superconductivity of uranium hydrides at near-ambient conditions.

Ivan A. Kruglov[1,2], Alexander G. Kvashnin[3,2], Alexander F. Goncharov[4,5], Artem R. Oganov[3,6,2,1]
Sergey Lobanov[4,7], Nicholas Holtgrewe[4,8], & Alexey V. Yanilkin[1,2]





pressure release at ambient conditions **stabilizes** the metastable UH8 phase with a (still predicted) Tc=193 K

Lesson 1: chemical pressure

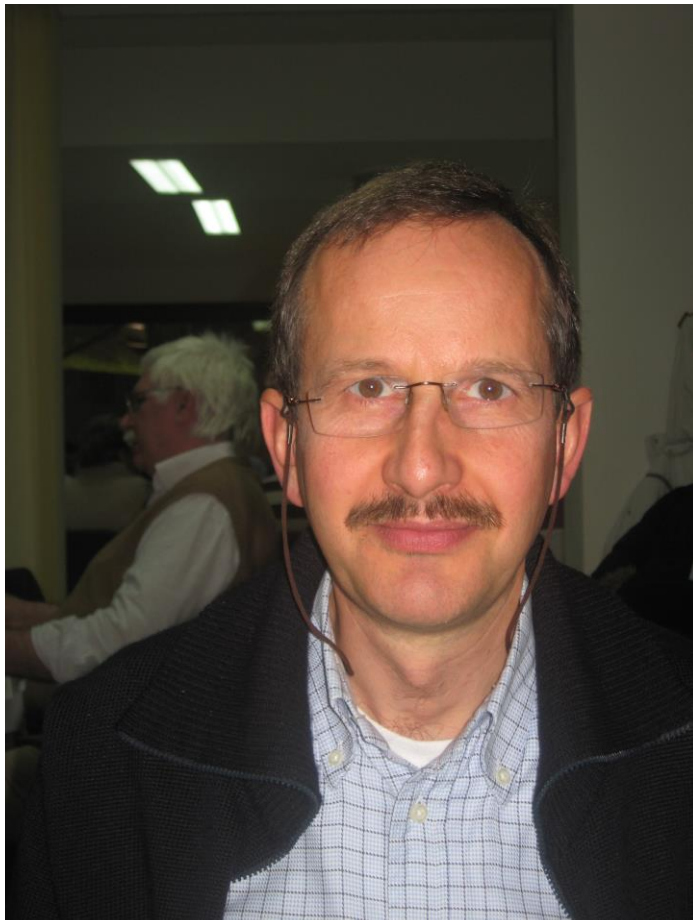
Lesson 2: find the right crystal structure

Lesson 3: new stoichiometry

Lesson 4: metastability

Thank you
for the attention

In memory of Prof. Sandro Massidda



PHYSICS LETTERS A 8 June 1987

ELECTRONIC STRUCTURE AND PROPERTIES OF $YBa_2Cu_3O_{7-\delta}$

S. MASSIDDA, Jaejun YU, A.J. FREEMAN
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, IL 60201, USA

and

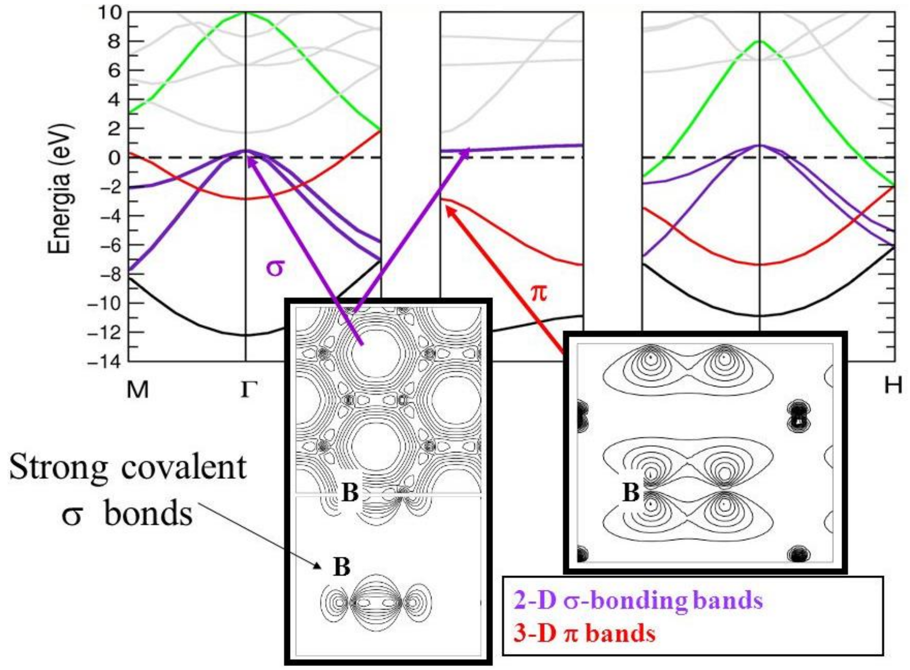
D.D. KOELLING
Materials Science and Technology Division, Argonne National Laboratory, Argonne, IL 60201, USA

Received 23 April 1987; accepted for publication 1 May 1987
Communicated by J.I. Budnick

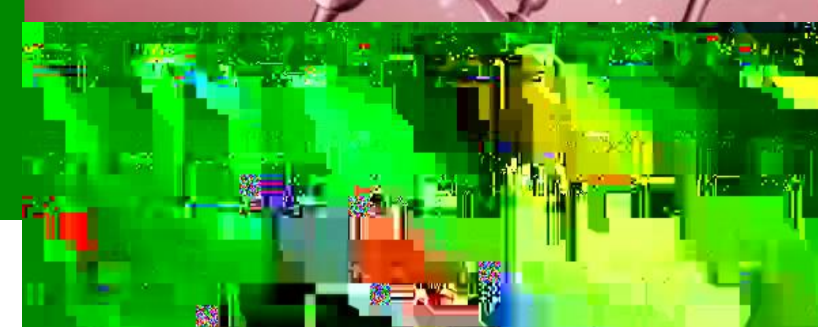
The electronic structure of the high T_c superconductor, $YBa_2Cu_3O_{7-\delta}$, determined from highly precise all-electron local density calculations yields a relatively simple highly 2D electronic band structure consisting of two 2D Cu2–O and two 1D Cu1–O bands (one almost empty and one almost full at $\delta = 0$, becoming full at $\delta \geqslant 0.1$) near E_F. Detailed features (multi-peaks) of the density of states (DOS) are correlated with the band structure of the 36 Cu–O band complex. Surprising features include: (i) the low DOS at E_F, especially for $\delta \geqslant 0.1$ which is much longer than that in $La_{2-x}Sr_xCuO_4$ – in agreement with experiment – and (ii) a relatively large magnetic Stoner factor.

The discovery of superconductivity above 90 K by Chu and collaborators [1] in Y–Ba–Cu–O compounds has generated experimental and theoretical excitement on an unprecedented scale. Recently, the superconducting phase was found [2] to be $YBa_2Cu_3O_{7-\delta}$ and its structure determined by neu-

This paper presents detailed high resolution results on the electronic band structure and density of states derived properties as obtained from highly precise state-of-the-art local density calculations [5]. These results demonstrate the close relation of the band structure to the structural arrangements of the con-



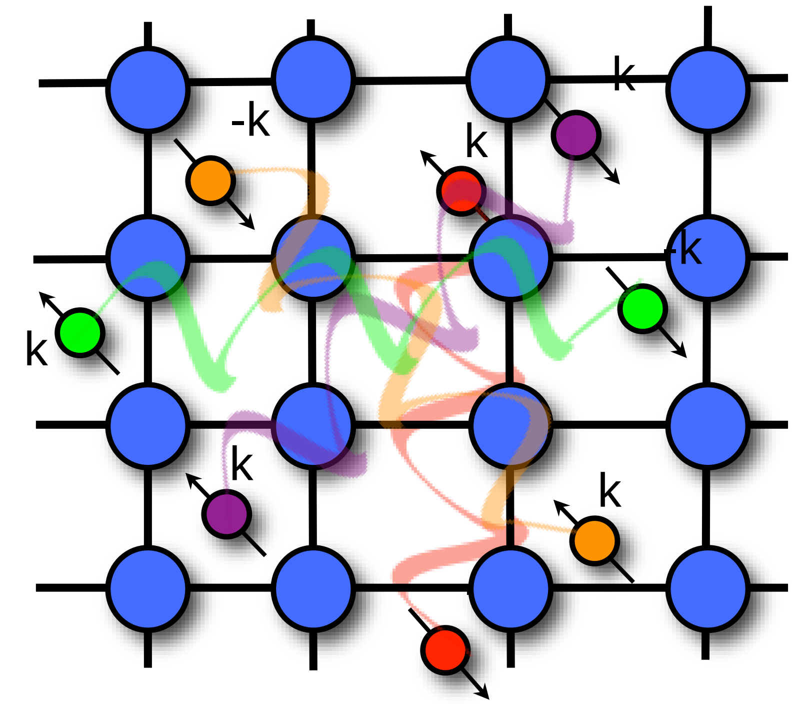
Are we close to room temperature supercondutivity?



Thank you
for the attention

Some Pros and Cons of BCS

- First Theory of superconductivity
- Explains many experimental evidences
- Guided the search of new materials
- Relates Tc to normal-state properties in a very simple formula



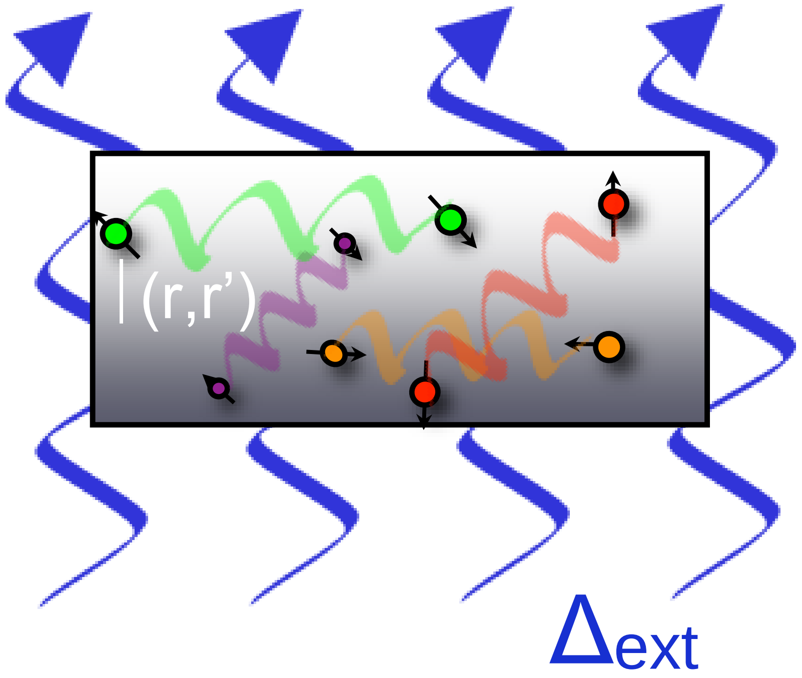
$$T_c^{BCS} = \omega_D e^{-\frac{1}{\lambda}}$$

- No Coulomb repulsion
- Weak coupling theory
- The true "e-ph" interaction is *time dependent*
- Quasiparticles have finite-lifetime
- T_c formula is simple, but wrong....

SuperConducting Density Functional Theory (2005)

$$\hat{H} = \hat{T}^{\mathrm{e}} + \hat{T}^{\mathrm{n}} + \hat{U}^{\mathrm{en}} + \hat{U}^{\mathrm{ee}} + \hat{V}^{\mathrm{e}}_{\mathrm{ext}} + \hat{V}^{\mathrm{n}}_{\mathrm{ext}} + \hat{\Delta}_{\mathrm{ext}} - \mu \hat{N}$$

$$\hat{\Delta}_{\mathrm{ext}} = -\int d^3r \int d^3r' \left[\Delta^*_{ext}(r,r')\hat{\Psi}_{(}r)\hat{\Psi}_{(}r') + h.c.\right]$$

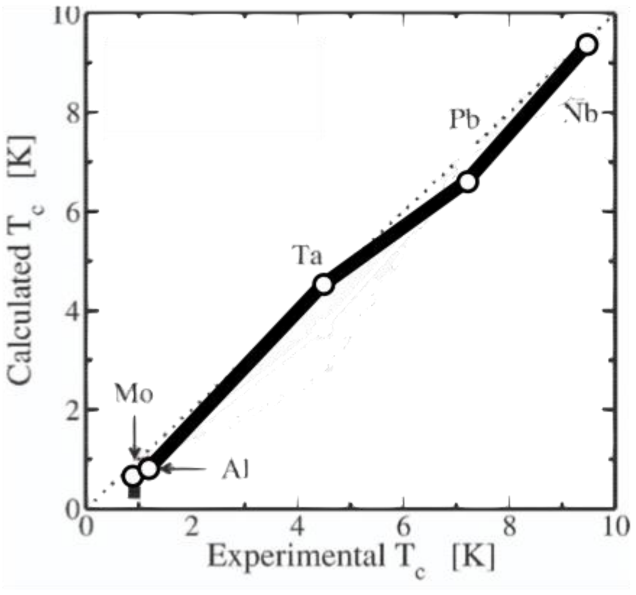


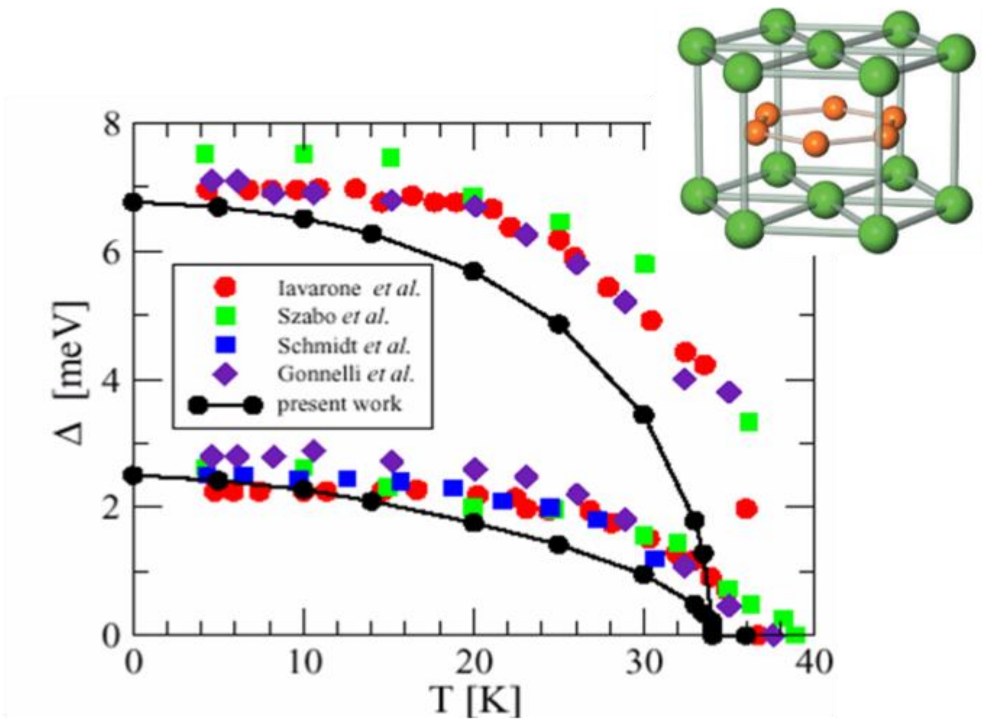
$$n(r) = \sum_\sigma \langle \Psi^\dagger_\sigma(r)\Psi_\sigma(r)\rangle \quad \Rightarrow \quad V^{\mathrm{e}}_{\mathrm{ext}}(r)$$

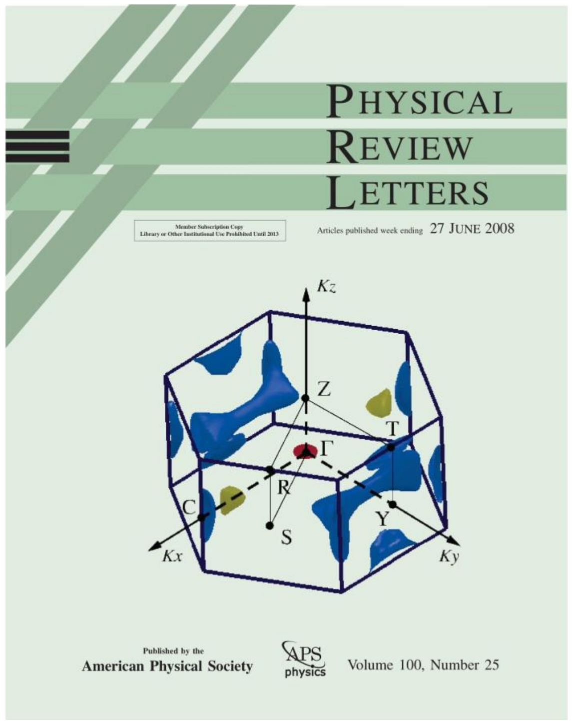
$$\chi(r,r') = \langle \hat{\Psi}_\uparrow(r)\hat{\Psi}_\downarrow(r')\rangle \quad \Rightarrow \quad \Delta_{\mathrm{ext}}(r,r')$$

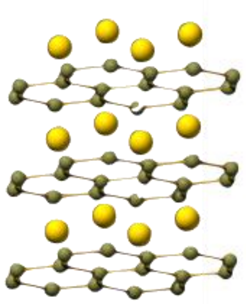
$$\Gamma(R) \quad \Rightarrow \quad V^{\mathrm{n}}_{\mathrm{ext}}(\underline{R})$$

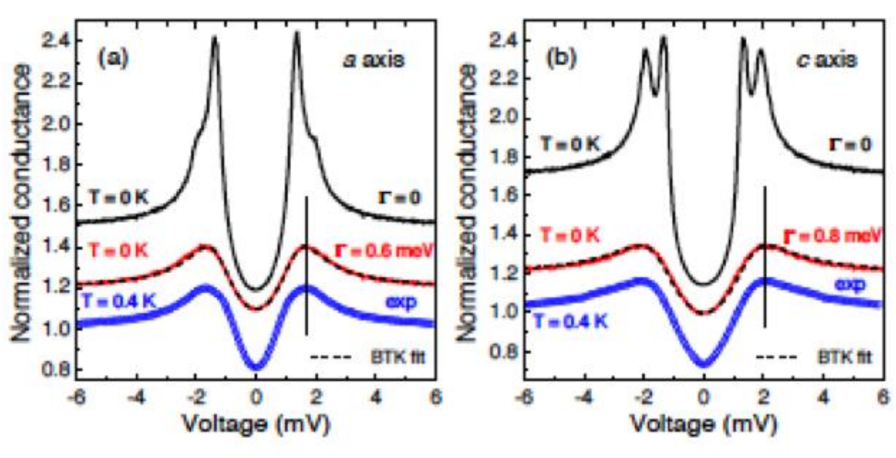
It works, it is predictive

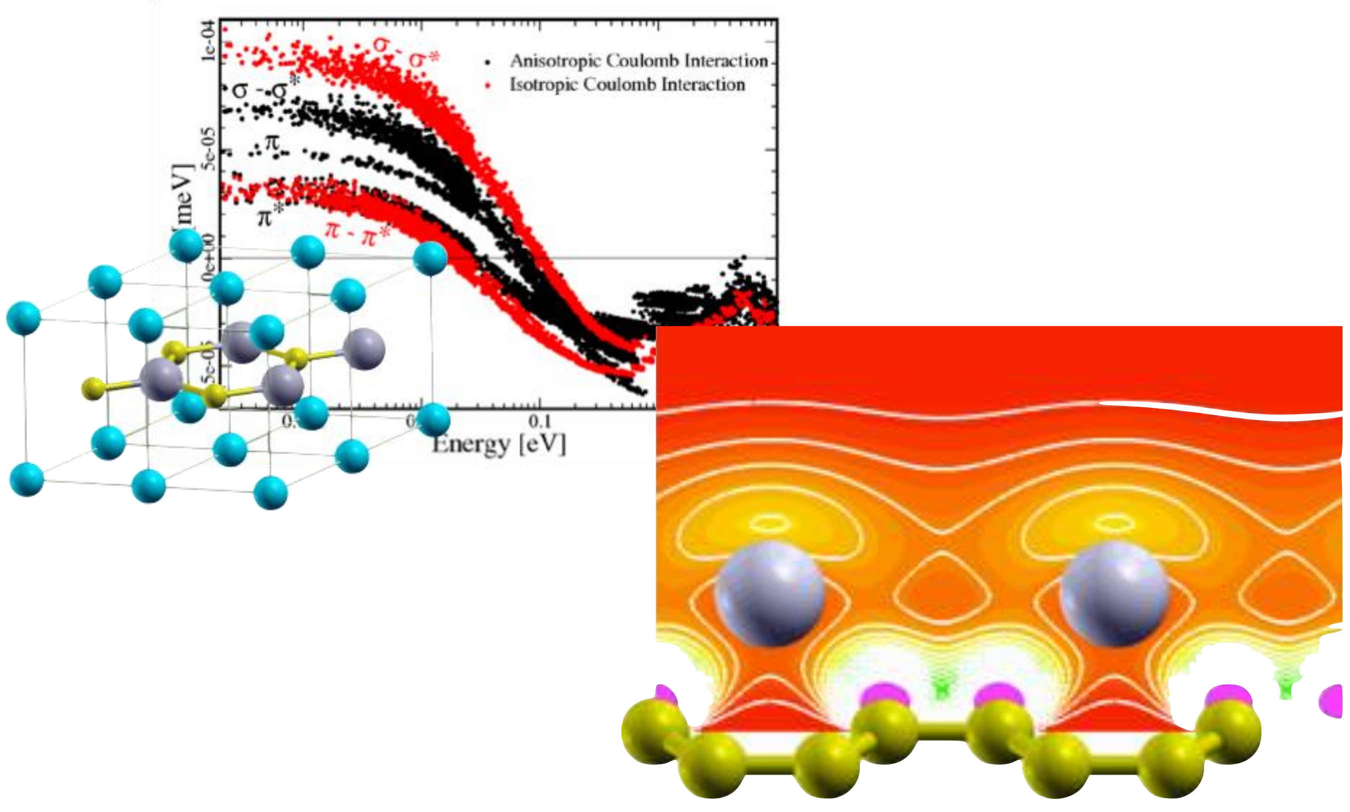












The holy grail of condensed matter

Science

REPORTS

Cite as: R. P. Dias *et al.*, *Science* 10.1126/science.aal1579 (2017).

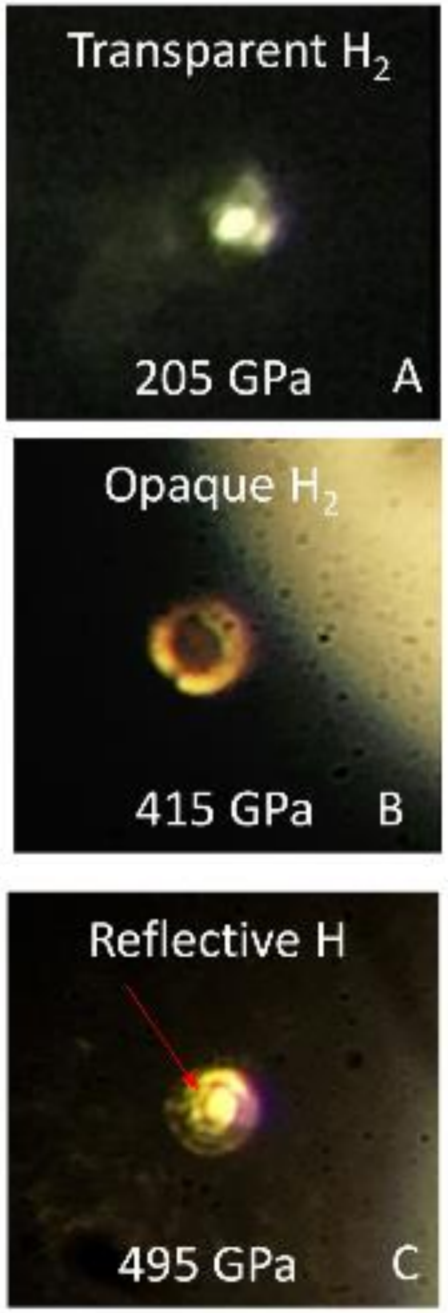
Observation of the Wigner-Huntington transition to metallic hydrogen

Ranga P. Dias and Isaac F. Silvera*

Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA.

*Corresponding author. Email: silvera@physics.harvard.edu

Producing metallic hydrogen has been a great challenge to condensed matter physics. Metallic hydrogen may be a room temperature superconductor and metastable when the pressure is released and could have an important impact on energy and rocketry. We have studied solid molecular hydrogen under pressure at low temperatures. At a pressure of 495 GPa hydrogen becomes metallic with reflectivity as high as 0.91. We fit the reflectance using a Drude free electron model to determine the plasma frequency of 32.5 ± 2.1 eV at $T = 5.5$ K, with a corresponding electron carrier density of $7.7 \pm 1.1 \times 10^{23}$ particles/cm^3, consistent with theoretical estimates of the atomic density. The properties are those of an atomic metal. We have produced the Wigner-Huntington dissociative transition to atomic metallic hydrogen in the laboratory.



INDEPENDENT

News InFact Politics Voices Indy/Life Business Sport Tech Culture

News › Science

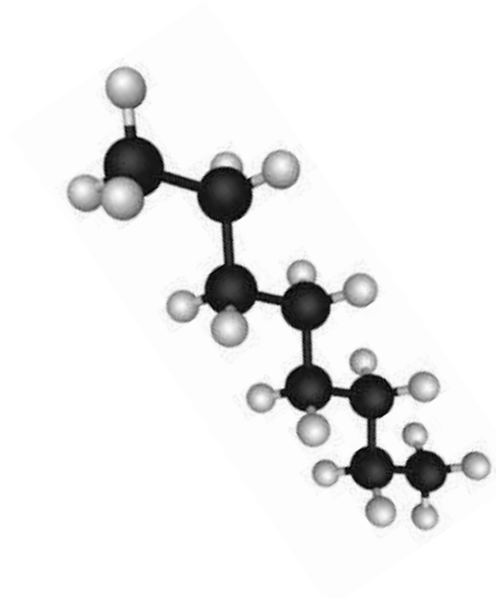
World's only piece of a metal that could revolutionise technology has disappeared, scientists reveal

Exclusive: Harvard University physicists say first-ever piece of metallic hydrogen on Earth has been lost after catastrophic failure of diamond holding it under enormous pressure

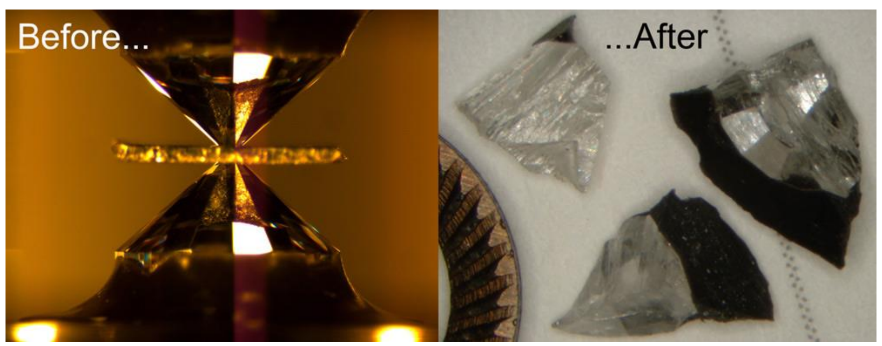
“It was said to have been the only piece on Earth of a metal that could have revolutionised life as we know it.
But a tiny sample of metallic hydrogen – purportedly created by scientists at Harvard University – has disappeared, The Independent can reveal.”

Hydrogen rich compounds under pressure
(so many)

Hydrates, hydrocarbons, etc…

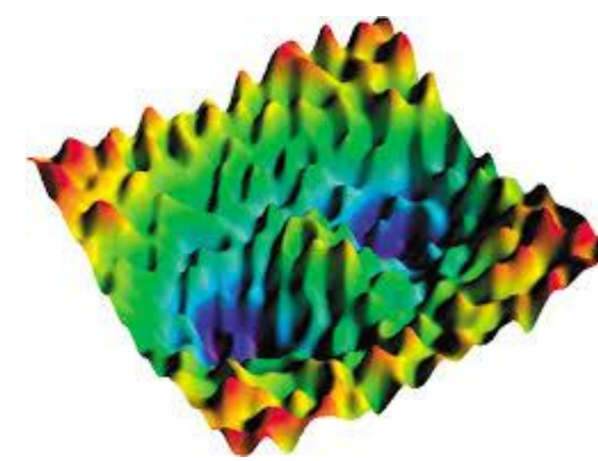


and high pressure experiments are too difficult (and long).

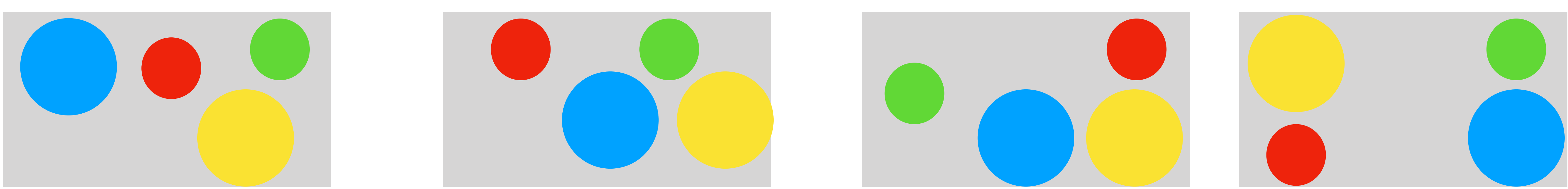


Discovery the superconducting phase in a computer?

Potential energy surfaces and the global searching problem



Determine the lowest enthalpy structure at a given pressure: a NP - hard problem



NATURE VOL. 335 15 SEPTEMBER 1988 NEWS AND VIEWS

Crystals from first principles

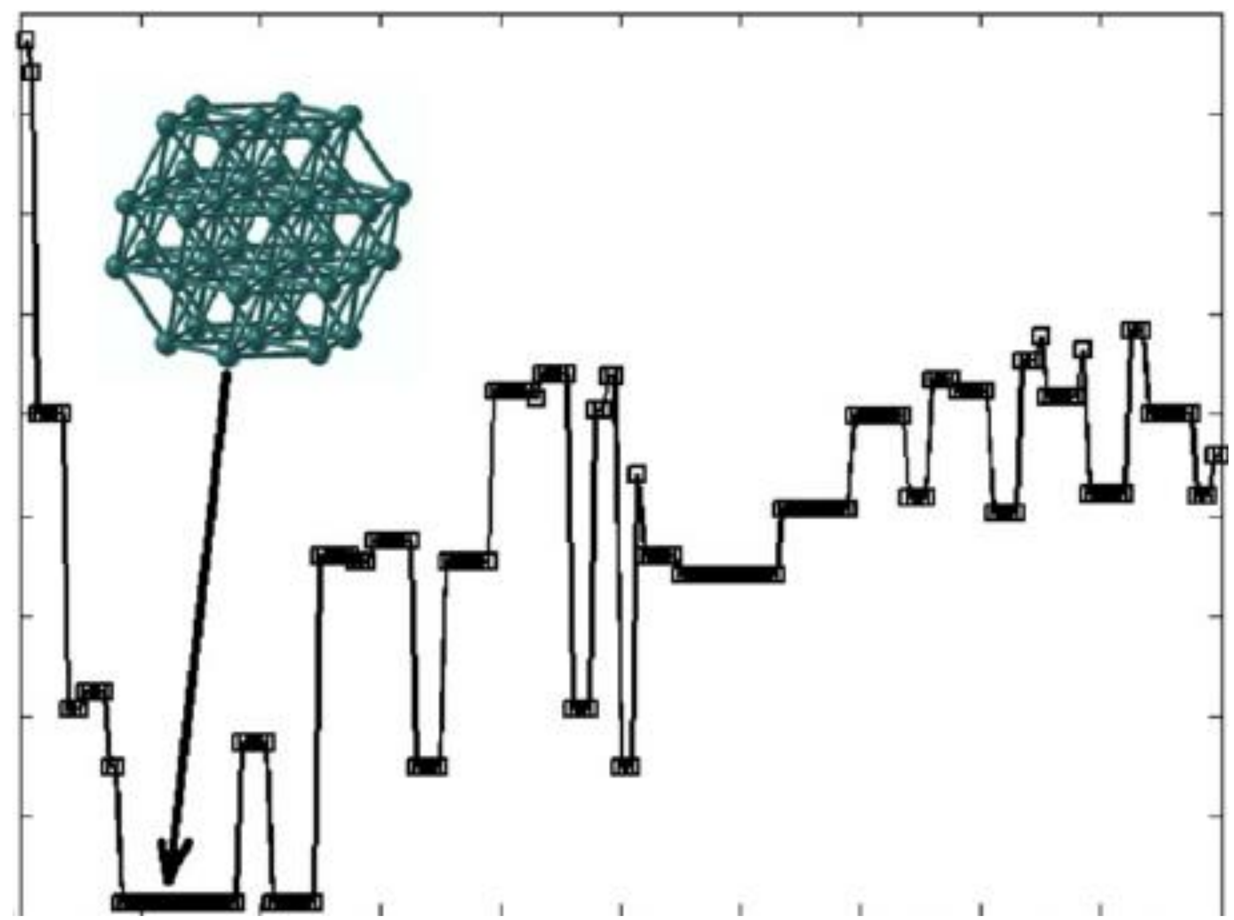
by J. Maddox

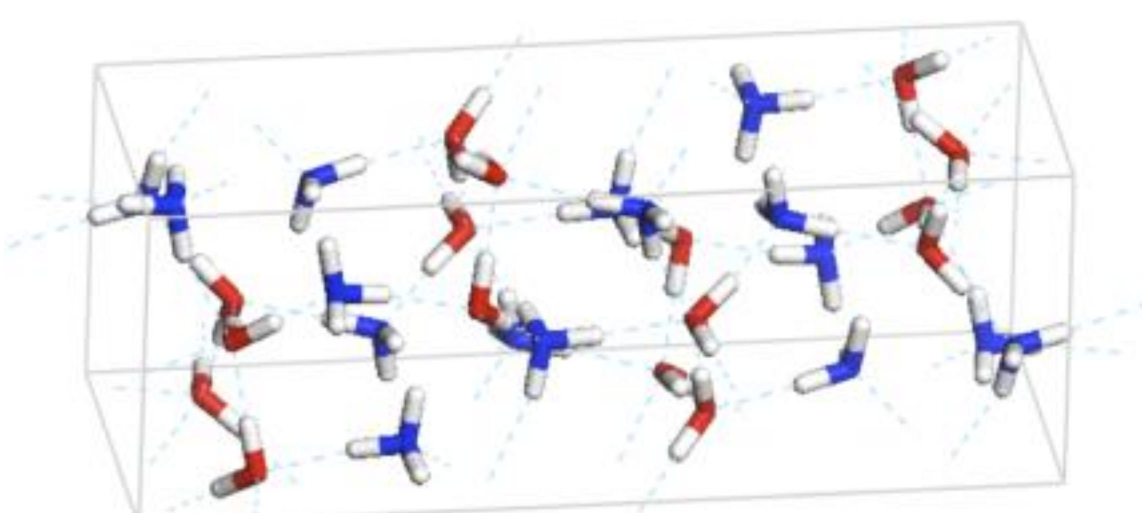
ONE of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even the simplest crystalline solids from a knowledge of their chemical composition. Who, for example, would guess that graphite, not diamond, is the thermodynamically stable allotrope of carbon at ordinary temperature and pressure? Solids such as crystalline water (ice) are still thought to lie beyond mortals' ken.

Yet one would have thought that, by now, it should be possible to equip a sufficiently large computer with a sufficiently large program, type in the formula of the chemical and obtain, as output, the atomic coordinates of the atoms in a unit cell.

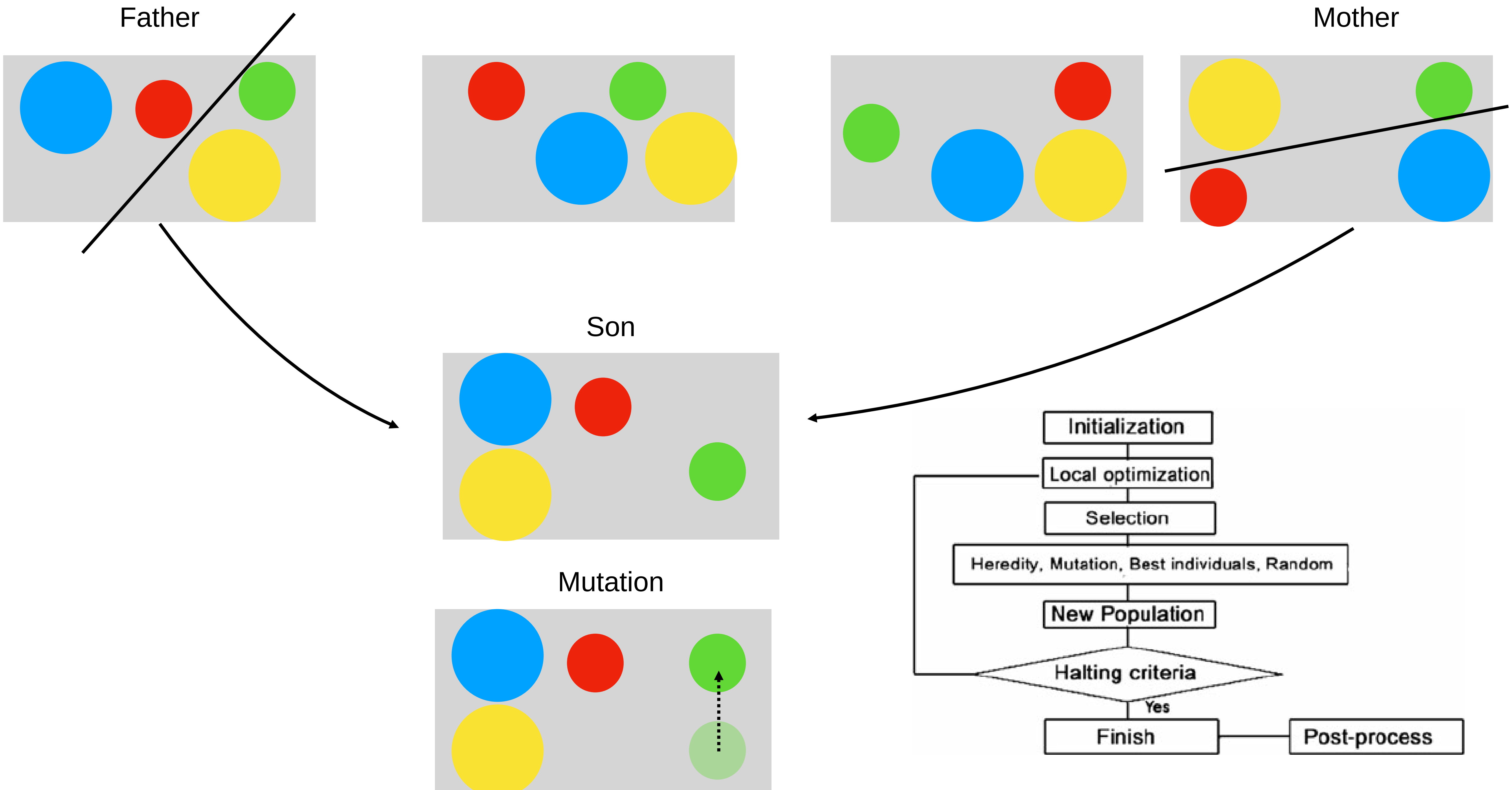
That time may not yet have arrived, but S. Tsuneyuki, M. Tsukada and H. Aoki from the University of Tokyo, with Y. Matsui from Okayama University, have brought it a good step nearer. Starting

Ab-initio random structure searching
(The Columbus egg)





Genetic Algorithms



Many hydrogen-containing compounds were predicted to possess very high Tc

64 K in GeH (220 GPa),

80 K in SnH (120 GPa),

100 K in $SiH_4(H_2)_2$ (250 GPa)

Room temperature superconductivity?

Vostok base in Antarctic

In 1983 a temperature of -89 ^{o}C was measured