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)

\[ \Psi_N(r_1, r_2, \ldots, r_N) = A\psi(r_1, r_2)\psi(r_3, r_4) \cdots \psi(r_{N-1}, r_N)(1 \uparrow)(2 \downarrow)(3 \uparrow)(4 \downarrow) \cdots (N - 1 \uparrow)(N \downarrow). \]

\[ \Delta(0) = 1.76 k_B T_c \]

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

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

Which is the material with the highest $T_c$?
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

The many phases of hydrogen

Temperature (kelvins) vs. Pressure (atmospheres)

Phase I

Liquid

Solid

Solid metal?

Liquid metal

1899: Dewar suggests that liquid hydrogen produces solid hydrogen

2016: 400 GPa
Claims of different phases

2017: Silvera

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

1968: Ashcroft's proposal
Superconducting phase
Hydrogen metallization: \( P > 450 \text{ GPa} \)

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

Hydrogen Dominant Metallic Alloys: High Temperature Superconductors?

N.W. Ashcroft

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501, USA
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.

Lesson 2: find the right crystal structure

Superconductivity in Hydrogen Dominant Materials: Silane

M. I. Erements, I. A. Trojan, S. A. Medvedev, J. S. Tse, Y. Yao

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.
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$_2$S) has not previously been considered a superconductor because, upon metallization under pressure, it was believed to dissociate into its constituent elements.

The metallization and superconductivity of dense hydrogen sulfide

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

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)
SQUEEZING SULFUR HYDRIDE in a diamond anvil cell.

The cell is first cooled to 200 K, then hydrogen sulfide (H$_2$S) gas is sent into the cell through a capillary.

Inside the cell, H$_2$S liquefies; only then pressure is applied.
200K (-73 °C) superconductivity?

Isotope effect (phonons are involved)

Meissner effect (Magnetic field)

Electronic energy gap
Lesson 3: New chemistry

Maxwell plot

Duan et al. (2014)
It is true

Crystal structure of the superconducting phase of sulfur hydride

Mari Einaga1, Masafumi Sakata1, Takahiro Ishikawa1, Katsuya Shimizu1†, Mikhail I. Eremets2†, Alexander P. Drozdov2, Ivan A. Troyan2, Naohisa Hirao3 and Yasuo Ohishi3
Is H₂S (H₃S) an isolated example?
Superconducting phosphines (PH₃)

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

**Superconductivity above 100 K in PH₃ 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, Ref1) we searched for superconductivity in other hydrides and found that a covalent hydride phosphine (PH₃) also exhibits a high T_c >100 K at pressure P > 200 GPa as determined from four-probe electrical measurements.
Which is the stable crystal structure?

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 PH₂)

PH₃ decomposes at high P

PH₂ seems to be the best candidate (?)
Lesson 4: Metastability, a new possibility

Diamond is more stable than graphite above 1 GPa.
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.
Phosphorus superconducting phase diagram

old problem new solution

Exp. 1

Exp. 2
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. Hamlin1, 6

1Department of Physics, University of Florida, Gainesville, FL 32611
2Department of Physics, University of Alabama at Birmingham, Birmingham, AL, 35294
3Physics Division, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

(Dated: July 20, 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 Ma3,7,*

1Institute of Physics, Chinese Academy of Sciences, Bejing 100190, China
2Department of Physics, University of Cambridge, Cambridge CB2 1SW, United Kingdom
3School of Physics & Technology, Southwest Jiaotong University, Chengdu 610031, China
4School of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom
5School of Physics, University of Bristol, Bristol BS8 1TL, United Kingdom
6Department of Physics, Peking University, Beijing 100871, China

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

Ivan A. Kruglov1,2, Alexander G. Kvashnin3,2, Alexander F. Goncharov4,5, Artem R. Oganov3,6,2,1
Sergey Lobanov4,7, Nicholas Holtgrewe4,8, & Alexey V. Yanilkin1,2

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

D.D. KOELLING
Materials Science and Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

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

The electronic structure of the high $T_c$ superconductor, YBa$_2$Cu$_3$O$_{y-}$, as determined from highly precise all-electron local density calculations, exhibits a relatively simple electronic band structure consisting of two 2D Cu-O bands (one almost empty and one almost full at $\varepsilon = 0$, becoming full at $\varepsilon = 0$) near $E_f$. Detailed features (multi-peaks) of the density of states (DOS) at $E_f$, especially for $350 \text{K}$ which is much longer than that in La$_2$CuO$_4$, in agreement with experiment, and (ii) a relatively large magnetic moment.

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$_2$Cu$_3$O$_{y-}$, and its structure determined by neutron scattering. 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 [3]. These results demonstrate the close relation of the band structure to the structural arrangements of the con-
Are we close to room temperature superconductivity?
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 $T_c$ 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....
\[ \hat{H} = \hat{T}^e + \hat{T}^n + \hat{U}^{en} + \hat{U}^{ee} + \hat{V}^e_{\text{ext}} + \hat{V}^n_{\text{ext}} + \hat{\Delta}_{\text{ext}} - \mu \hat{N} \]

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

\[ n(r) = \sum_{\sigma} \langle \Psi^\dagger_{\sigma}(r) \Psi_{\sigma}(r) \rangle \Rightarrow V^e_{\text{ext}}(r) \]

\[ \chi(r, r') = \langle \hat{\Psi}^\uparrow(r) \hat{\Psi}^\downarrow(r') \rangle \Rightarrow \Delta_{\text{ext}}(r, r') \]

\[ \Gamma(R) \Rightarrow V^n_{\text{ext}}(R) \]
It works, it is predictive
The holy grail of condensed matter

Observation of the Wigner-Huntington transition to metallic hydrogen

Ranga P. Dias and Isaac Y. Silvras*
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 $32.5 \pm 2.1$ 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.

“\textit{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
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)
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 SiH4(H2)2 (250 GPa)
Vostok base in Antarctic

In 1983 a temperature of -89 °C was measured