High Temperature Superconductivity in Dense Hydrogen Systems

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Quantum Matter: Computation Meets Experiments
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OUTLINE

1. Background/Context
2. Superconductivity and Pressure
3. Dense Hydrogen
4. Superhydrides
5. New Materials

THEMES
• Hydrogen in Extremes
• Computation/Experiment Synergy
• ‘Materials by Design’
Materials at High Pressure

Exploring Energy Landscapes in the Search for New Materials and Phenomena

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

$>100's$ GPa (to $\sim$TPa)

$\sim eV$ energies

valence electrons
EXPERIMENTS

COMPRESSION TECHNIQUES

Static

Dynamic

>100’s GPa (to ~TPa)
~ eV energies

>100’s Mbars (1 Gbar)
~ keV energies

COMPUTATIONS

• Density Functional
• Path Integral, Quantum Monte Carlo
• Structure Search Methods

Advanced Photon Source

Spallation Neutron Source

NSLS II

National Ignition Facility

CVD
Pressure Effects on Superconductors

HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$

$T_c = 164$ K
(30 GPa)

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

Fe$_{1.01}$Se

$T_c = 36.7$ K
(8.9 GPa)

[Medevdev et al., Nature Mat. (2009)]

Sn and In


Low P-T Phase Diagram

Electrical Conductivity
Magnetic Susceptibility
X-ray Diffraction

High Pressure and Superconductivity

Superconductivity at Megabar Pressures

\[ T_c = 11 \text{ K at 250 GPa} \]

[Struzhkin et al., *Science* (2001)]

\[ T_c = 17 \text{ K at 160 GPa} \]

[Struzhkin et al., *Nature* (1997)]

\[ T_c = 9.8 \text{ K at 80 GPa} \]

[Struzhkin et al., *Phys. Rev. Lett.* (1997)]
“Let’s start at the very beginning, a very good place to start…”

*The Sound of Music*
Rogers and Hammerstein

**Element One**

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**Starting point for chemistry**

\[
\hat{H} = \sum_i \hat{T}_i + \sum_j \hat{T}_j + \sum_{k,l} \hat{V}_{k,l} + \sum_{m,n \geq m} \hat{V}_{m,n} + \sum_{o \neq p} \hat{V}_{o,p}
\]

**Most abundant element**

**Element of Uncertainty**

**Test of fundamental theory**
Metallic and Superconducting Hydrogen

On the Possibility of a Metallic Modification of Hydrogen

E. Wigner and H. B. Huntington, Princeton University
(Received October 14, 1935)

> 25 GPa

Bardeen-Cooper-Shrieffer (BCS)
Phonon-mediated; high $\Theta_D$

$T_c = 0.85\Theta_D \exp(-1/N_0 V)$,

$T_c >> 300 K?$
Dense Molecular Hydrogen

[Wigner & Huntington (1935)]

Predicted Topological Semimetal

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

Is Hydrogen Metallic at these $P$-$T$ Conditions?

- **Semiconducting/Semimetallic**
  - >200 GPa, 77 K
  - 360 GPa, 100 K
    - [Zha et al., *Phys. Rev. Lett.* (2012)]

- **Atomic Metallic?**
  - Reflective H
    - 495 GPa?
    - [Dias & Silvera, *Science* (2017)]
  - Infrared Absorption
    - 425 GPa
    - [Loubeyre et al., *Nature* (2020)]
should be considered with caution, and further in-depth theoretical analysis of superconducting properties may be required. We have tried to create polyhydrides of Li (without success, see also Ref. [85]) and Na (NaH3 and NaH7 synthesized, work in progress) [86]. We are optimistic and are looking forward to new polyhydrides coming to life very soon.

Notes added. When this paper was in review, the paper by Drozdov et al. was published reporting nearly 190 K conventional superconductivity in H2S hydride at 200 GPa [87]. The experimental procedure and theoretical results by Duan et al. [88] suggest that observed high $T_c$ values may correspond to a polyhydride H3S phase forming at high pressures when the sample is warmed up to room temperature [87]. The experiments have reported superconductivity from resistivity measurements. If these results will be confirmed by magnetic susceptibility measurements, there will remain no doubt that conventional phonon driven conductivity is possible close to room temperature. It is interesting to note that hydrogen in H3S and its homologues would represent a test case to study a long sought 'hole doped' metallic hydrogen, as discussed in this section.

4. Prospects for room temperature superconductor based on hydrogen-rich materials: concluding remarks

Current candidate materials for high-temperature or even room-temperature superconductivity were discussed at length in

**Fig. 8.** The modified Periodic Table shows hydrides of the elements belonging to main groups. A separate block on the left summarizes a variety of polyhydrides predicted recently and discussed in this section. NaH3 and NaH7 were synthesized recently in our group (submitted).

**Fig. 9.** The highest $T_c$ reached so far in a mercury based cuprate is 164 K at 30 GPa [95]. $T_c$’s close to room temperature were predicted for CaF6 at 150 GPa, and $T_c$’s well above room temperature are expected in metallic hydrogen (atomic form) [49]. Recent claim of superconducting hydrogen sulfide [87] may change the record of the $T_c$ to 190 K, if confirmed.
Breaking the Bond with Compression and Chemistry

DIATOMIC HYDROGEN

Charge Density

\[ E_b = 4.52 \text{ eV} \]

(a) Impurity stabilization (chemical doping)
(b) Electron-hole pair creation

electron doping to destabilize H\(_2\)

“Chemical Pre-Compression”

[Silvera, Rev. Mod. Phys. (1980)]

[Ashcroft, Phys. World (1995)]

Novel Dense Molecular Compounds

**CH$_4$(H$_2$)$_4$**

33.4 wt% H$_2$


**H$_2$O-H$_2$**

‘Stuffed ice VII’

11.3 wt% H$_{2D}$


**Xe(H$_2$)$_8$**

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

**Xe$_3$($N_4$)$_n$**

[Somayazulu et al., in preparation]

**(H$_2$O)$_2$H$_2$**

Quartz-type ice

[Strobel et al., J. Am. Chem. Soc. (2016)]

**(H$_2$S)$_2$H$_2$**

Al$_2$Cu type


➢ PRECURSOR TO H$_3$S
Success of Structure Search Methods

*Predicted Very High-$T_c$ Superconductors at 100-300 GPa*

- **SH$_3$**
  - $T_c = 203$ K

- **PH$_3$**
  - $T_c = 100$ K
  - [Liu et al., JPCC (2016); Shamp et al. JACS (2016); Drozdov et al. arXiv (2016)]

- **TeH$_4$**
  - $T_c = 107$ K
  - [Zhong et al., PRL (2010)]

- **CaH$_6$**
  - $T_c = 235$ K
  - [Wang et al., PNAS (2012)]

- **GeH$_4$(H$_2$)$_2$**
  - $T_c = 153$ K
  - [Jin et al., PNAS (2010)]

- **SiH$_4$(H$_2$)$_2$**
  - $T_c = 107$ K
  - [Li et al., PNAS (2010)]

- **YH$_6$**
  - $T_c = 251$ K

- **NaC$_6$**
  - $T_c = 116$ K
  - [Lu et al., Phys. Rev. B (2016)]

OBSERVED

[Ma, Oganov, Pickard, Zurek]
Higher Hydrides?

Rare Earth – Hydrogen System

DFT Structure-Search (CALYPSO)

[Liu et al., PNAS (2017)]

Superhydrides (AHₙ n > 6)
Predicted La and Y Superhydrides

‘Novel’ Clathrate Structure Type

LaH_{10} and YH_{10} predicted stable >200 GPa


H-H distances ~ 1.1 Å

Electron Localization Function

similar s-p hybridization

Predicted La and Y Superhydride Superconductors

$T_c$ versus pressure

LaH$_{10}$

YH$_{10}$

Pressure (GPa)

$T_c = \frac{\omega_{log}}{1.2} \exp \left[ -\frac{1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)} \right]$

[Liu et al., PNAS (2017)]

Energy (eV)

Frequency (cm$^{-1}$)

$\rightarrow \lambda$

$\rightarrow$ EPC

$\rightarrow T_c$
Synthesis of Lanthanum Superhydride

**X-RAY DIFFRACTION**
Laser heated \( \text{La} + \text{H}_2 \)

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**P-V EOS**

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[Image of X-ray diffraction patterns and P-V EOS graph]

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[Geballe et al., Angew. Chem. (2018)]
Lanthanum Superhydride Resistance Measurements

Nd-YLF Laser

La + NH₃BH₃
(B, hydrogen source)

~30 µm sample

SCHEMATIC

X-RAY RADIOGRAPHY

OPTICAL MICROSCOPY


[Hemley et al., Superconductivity and Pressure, Madrid (May 2018)]
Lanthanum Superhydride Resistance Measurements

Following laser heating synthesis to 1200 K

Pressure shift on warming
Conductivity onset varies with synthesis conditions
Reproducible onsets to >260 K


Hemley et al.,
Superconductivity and Pressure, Madrid (May 2018)]

Four-Probe Resistance

Normalized Resistance ($R/R_{300K}$)

188 GPa

Warming Cycle
Cooling Cycle

Temperature (K)

220 230 240 250 260 270

0.0 0.2 0.4 0.6 0.8 1.0 1.2

R (m$\Omega$)

10 mA 1.0 mA 0.1 mA

Current-Voltage

300 K

195 GPa

180 K

0 1 2 3 4 5 6 7 8 9 10

mA

**Subsequent Experimental Work**

**Synthesis at 150 GPa**

- 150 GPa

**Other Work**

- Confirm LaH$_{10}$ high $T_c$
- Different synthesis (e.g., 150 GPa)
- $T_c$ shift with field

**$T_c = 206$-225 K: R3m**

[Ahart et al., to be published]
**Phase Transition and Dynamics in LaH$_{10}$**

**Displacive Transition**

- Strongly anharmonic in $Fm3m$
- Lowers $Fm3m$-$R3m$ transition pressure

[Li et al., Phys. Rev. B (2018)]

**Quantum (PI) MD**

- Highly quantum H-lattice: rms $\delta H = 20\%$ of r(H-H)
- Sublattice melting at higher temperature
- ‘Giant’ H ZPM ($H_3S$): breakdown of Migdal

**Classical MD**

- $P_{\text{trans}} = 165 \text{ GPa}$
- $P_{\text{trans}} = 165 \text{ GPa}$

La

**POSITIONS**

- $Fm-3m$ to $R-3m$ to $C2/m$

[Geballe et al., Angew. Chem. (2018)]

**Extended Simulations**

- $P - P_{\text{trans}}$ (GPa)
- $V(R)$
- $E(R)$
- Classical description
- With quantum effects

[Errea et al., Nature (2020)]
Recent Developments: Other Superhydrides

ThH$_{10}$
[Semanok et al., arXiv (2019)]

PrH$_9$

YH$_6$
[Troyan et al., arXiv (2019)]

YH$_{9,10}$
[Snider et al., submitted]
Emerging Systematics

- **H-cage structures**
  - Higher $T_c$ in larger cages

- **Electron-doping of H lattice**
  - La$\delta^+$ charge transfer to H cages
  - Why La (Y, rare earths)?
    [Semenok et al., arXiv (2019)]


- Phase stability [Quan et al., arXiv (2019)]

- **Dominant role of H**
  - All high $T_c$ hydrides [Quan et al., arXiv (2019)]

- **Fully quantum system**
  - Phase stability
  - Pairing

La: [Xe]5d$^1$6s$^2$

La is ‘d-element’ – Additional electrons lowers predicted $T_c$
Towards Hot Superconductivity

- Mechanism?
  - full quantum treatment
- Still higher $T_c$?
  - More complex chemistries
- Recovery to ambient?
  - $H$ analog materials

[Mechnism, Ahart, Liu, & Somayazulu, Superconductivity and Pressure, Madrid, May 2018]

Ternary and More Complex Hydrides

**Li$_2$MgH$_{16}$**
Predicted $T_c$ to 470 K!
(250 GPa)

[Sun et al., *Phys. Rev. Lett.* (2019)]

**S-Se-H, Li-La-H…**

**C-’X’-H**
Sodalite-based

**NaC$_6$**
Predicted $T_c = 116$ K
1 bar stability

[Lu et al., *Phys. Rev. B* (2016)]
C-S-H Ternary: Structure Search

CH$_4$-H$_3$S (CSH$_7$)
Hydride Perovskites: A New Class of High $T_c$ Superconductors?

The relative enthalpies of the CSH$_2$ are stable at 130, 150, and 250 GPa at 300 K, respectively. Although the formation enthalpies of the CSH$_2$ are negative with respect to the elemental phases, these phases are metastable with respect to CH$_4$. The relative formation enthalpies are at least 30 meV/atom above the convex hull. Thus, the CSH$_2$ are metastable with respect to CH$_4$.

The three predicted 0 K structures of CSH$_2$ are based on the H$_3$S structure with a $Im3m$ structure. The CSH$_2$ structure is characterized by 5 S–H bonds (bond lengths of 1.38 to 1.55 Å) with a strong covalent character. The ELF values for the S–H and C–H bonds are close to 0.9, indicating their relatively perfect localization of the valence electrons indicative of a strong covalent bond. The ELF values in the range from 0 to 1, where 1 corresponds to free methane, the CH$_4$ molecule, and a perfect localization of the valence electrons. The rotation barrier of CH$_4$ is calculated by Nudged Elastic Band Method (NEB) as 0.75 eV. The barrier is tiny, only 0.01 eV.

The CSH$_2$ structure becomes enthalpically favored (Fig. S1b). In order to explore the bonding effects as the CSH$_2$ phase becomes enthalpically favored, the rotation energy was calculated as 0.75 eV. The barrier is tiny, only 0.01 eV. The central SH$_5$ structure of the CSH$_2$ is 33 meV/atom above the convex hull.

The CSH$_2$ phase (Fig. 1a) is not dynamically stable at 130 GPa, but stable relative to H$_3$S. The barrier is tiny, only 0.01 eV. The central SH$_5$ structure of the CSH$_2$ is 33 meV/atom above the convex hull.

The CSH$_2$ phase (Fig. 1b) is not dynamically stable at 130 GPa, but stable relative to H$_3$S. The barrier is tiny, only 0.01 eV. The central SH$_5$ structure of the CSH$_2$ is 33 meV/atom above the convex hull.

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Hydride Perovskites: A New Class of High $T_c$ Superconductors?

Enthalpy per formula as a function of pressure for CSH$_7$ structures relative to $R3m$
H₃S Hydride Perovskites

CH₄-H₃S (CSH₇) 150 GPa
Calculations reveal that a transition to 100 to 300 GPa are shown in Fig. S2. The convex hull of phosphorus, which are at least 30 meV/atom above metastable with respect to CH. Species do not lie on the 3D convex hull. In fact, they are negative with respect to the elemental phases, these if they are calculated to be dynamically stable.

These phases could potentially be realized experimentally, especially CSH phases between 7 and 300 GPa (Fig. S3). Molecular dynamics simulations found for LaH, stabilized by anharmonic or nuclear quantum effects as.

Although the formation enthalpies of the CSH phases could be realized experimentally, especially 7 phases between 7 and 300 GPa (Fig. S4), on the other hand, suggest that and 300 GPa (Fig. S3). Molecular dynamics simulations stabilize the ternary phase. It and 300 GPa (Fig. S3). Molecular dynamics simulations stabilize the ternary phase. It (instead of H3O+H2)

The relative enthalpies of the CSH phases are negative with respect to the elemental phases, these if they are calculated to be dynamically stable.

The three predicted 0 K structures of CSH are based on the H3 framework formed by two neighboring SH sublattices. In pure H3S, the S atoms form a bcc lattice with each S atom octahedrally coordinated by H atoms (Fig. 1a). In this structure, the H2O molecule, and a clathrate-like structure

On compression the phase transforms to 2 phase, which was calculated to be dynamically stable. The central SH sublattice is characterized by 5 S–H bonds (bond lengths of 1.38 to 1.55 Å) similar to the rigid C–H bonds are close to 0.9, indicating their relatively perfect localization of the valence electrons indicative of covalent bonds and lone pairs; it maps

The insert shows the experimental EOS for H2O + H2. The Shape of Water' Under Pressure

From H-S to H-O: ‘The Shape of Water’ Under Pressure

Structure Search / DFT Methods

Ab initio MD

<table>
<thead>
<tr>
<th>Solid H3O</th>
<th>Superionic H3O</th>
</tr>
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<tbody>
<tr>
<td>400 450 500 550 600</td>
<td></td>
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<tr>
<td>0.46 0.32 0.39</td>
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<tr>
<td>0.38 0.32 0.39</td>
<td></td>
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<tr>
<td>0.83</td>
<td></td>
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</tbody>
</table>

- Cmca clathrate-like structure
- "H3S-type" Im3m stable >2 TPa
- Predicted superionic solid and fluid metal

[Huang et al., PNAS (2020)]
Extreme Hydrogen-rich Quantum Materials: $\text{H}_3\text{O}$

- Explains anomalous magnetic fields: ‘thin-shell’ dynamos

[Huang et al., PNAS (2020)]
Towards Hot Superconductivity/Superfluidity in Dense Hydrogen

Observability of a Projected New State of Matter: A Metallic Superfluid

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CONCLUSIONS AND OUTLOOK

1. High pressure studies are revealing a variety of phenomena in quantum materials over a range of $P-T$ conditions as a result of the close synergy between experiments and computation.

2. Recent experiments on hydrogen provide evidence for a series of transitions to metallic phases at $>300$ GPa based on both static and dynamic compression, in good agreement with theory.

3. Studies of hydrogen-rich simple hydrides reveal high $T_c$ approaching room temperature, and new classes of novel phases continue to be found.
### Principal Collaborators

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