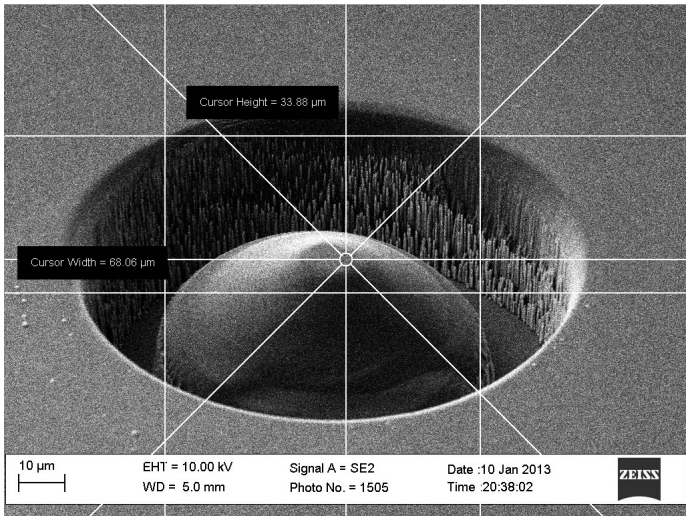
Reaching Terapascal Pressures

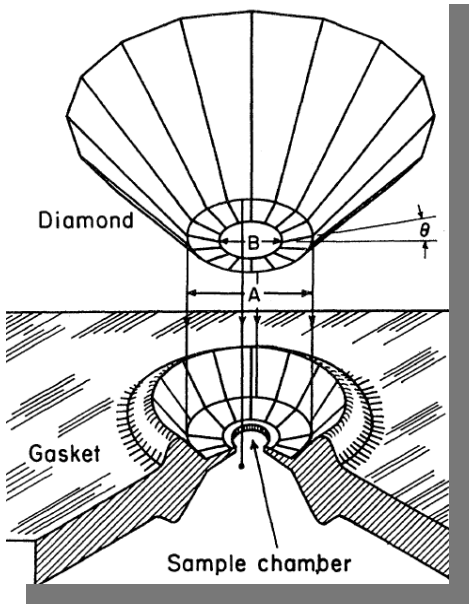
Opportunity

- High-pressure research opens fertile grounds for the observations of new phenomena and formations of new materials.
- The ultimate scope is defined by our capability to reach the highest pressures.

Challenge

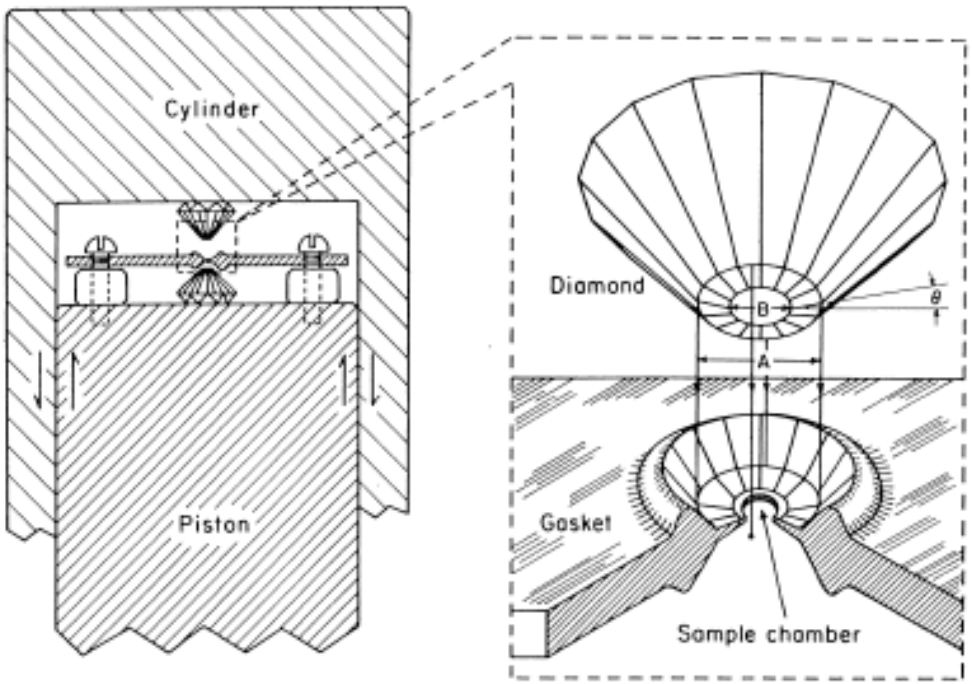
- To exceed the present ceiling of 400 GPa, we need ever smaller anvil tips.
- New FIB machining can produce submicron size diamond anvil tips necessary for terapascal pressures.
- Submicron x-ray diffraction is required for determination of the pressures based on the sample equations of state





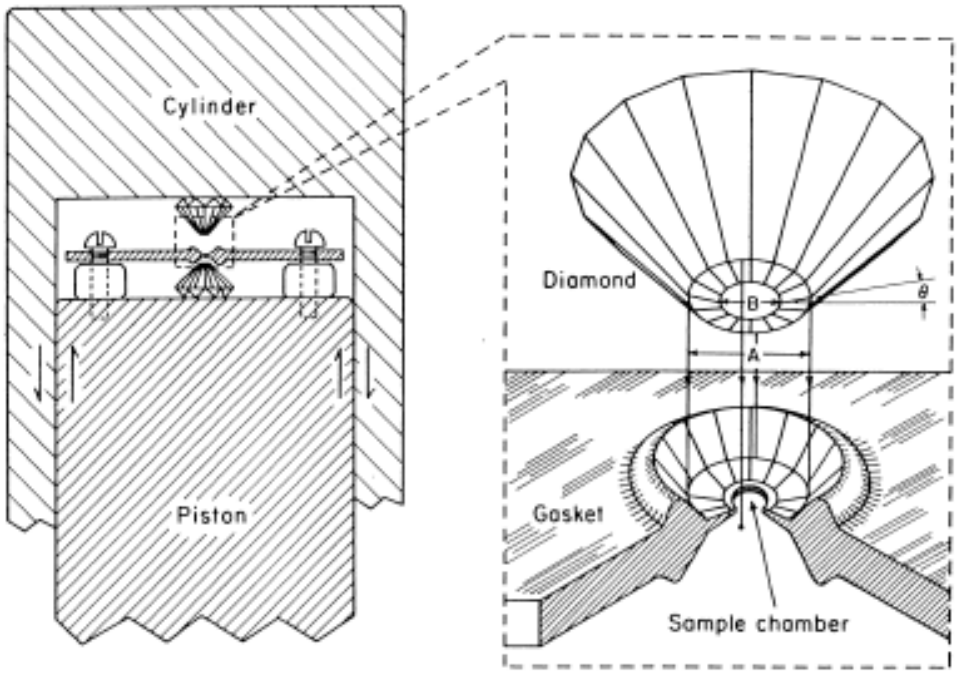
Extreme High Pressures Depends Upon Extreme Small Area

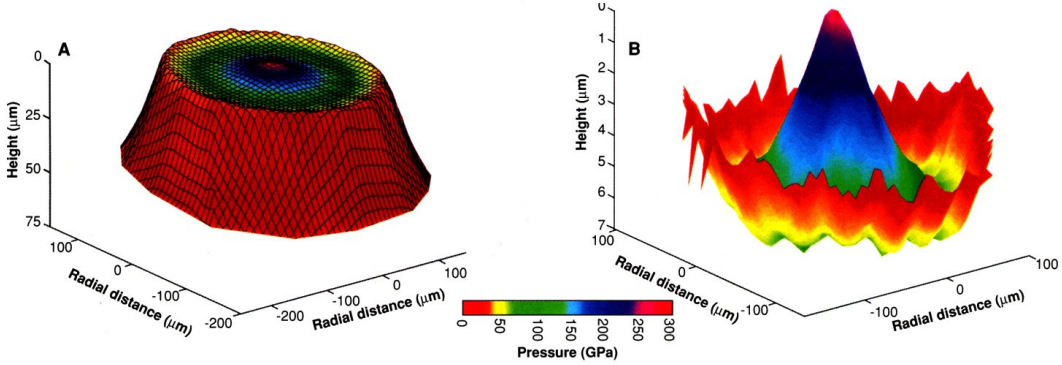
DAC: ***P*** = *F*/ ***A***

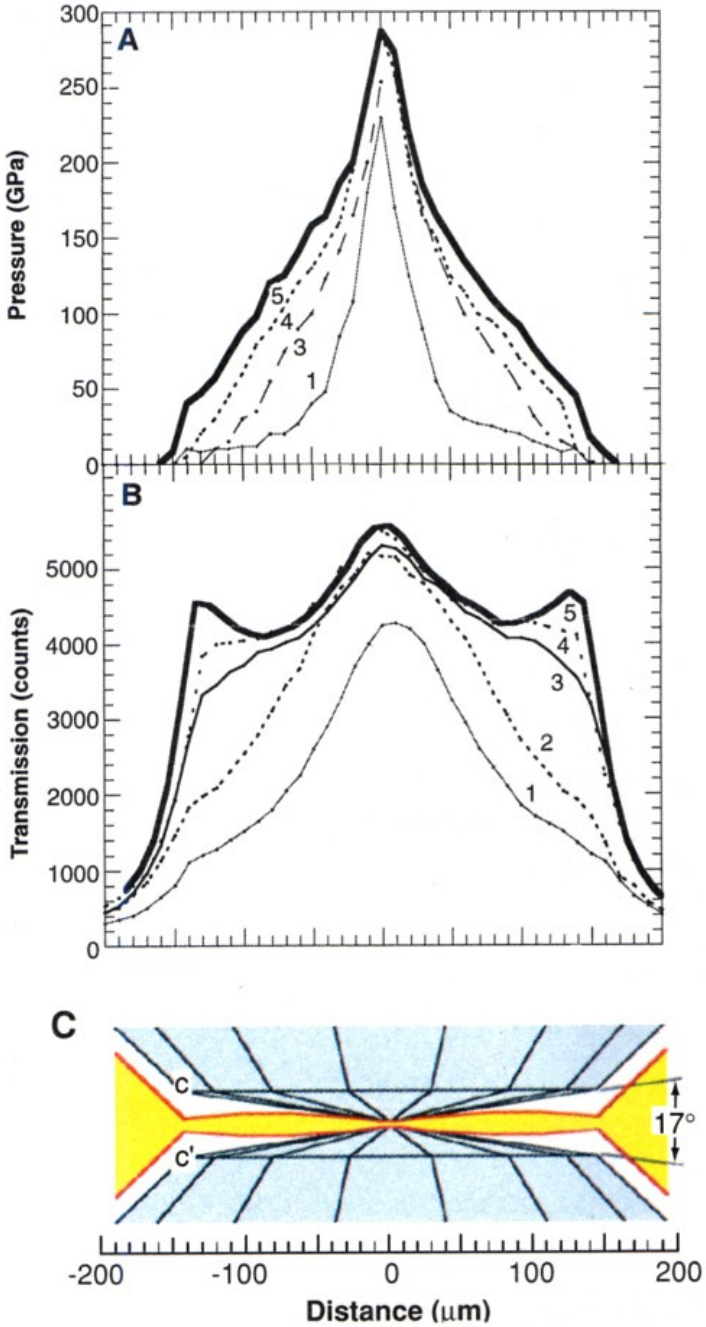


Example: A = 300 µm, B = 30µm, θ = 8.5° for 0.3 ct diamond to reach 300 GPa

Anvils on top of anvils to reach 400 GPa

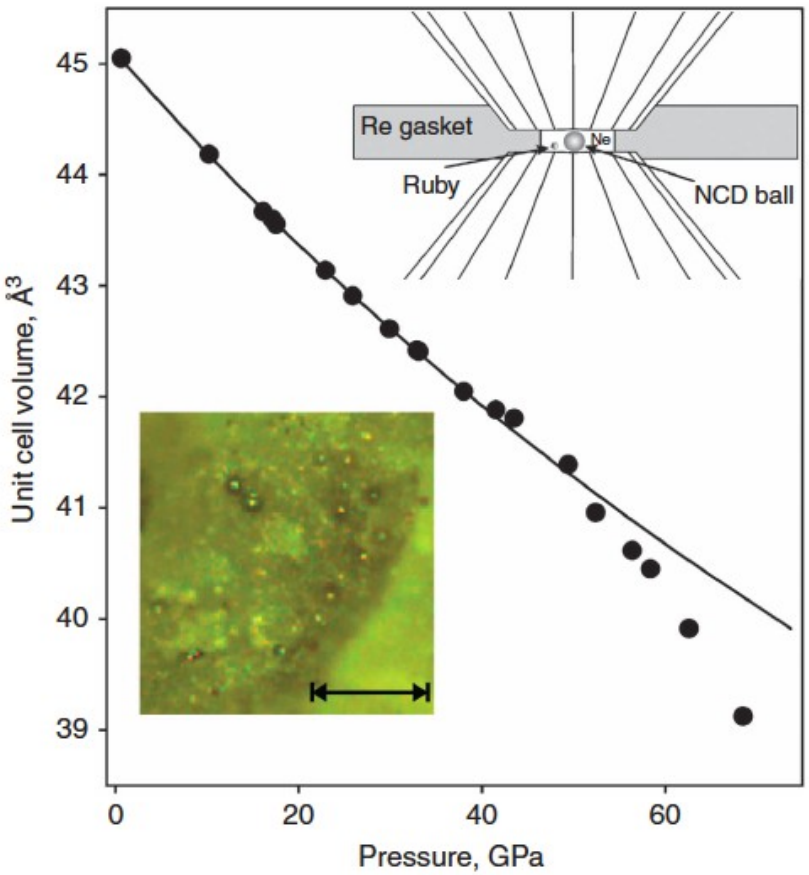


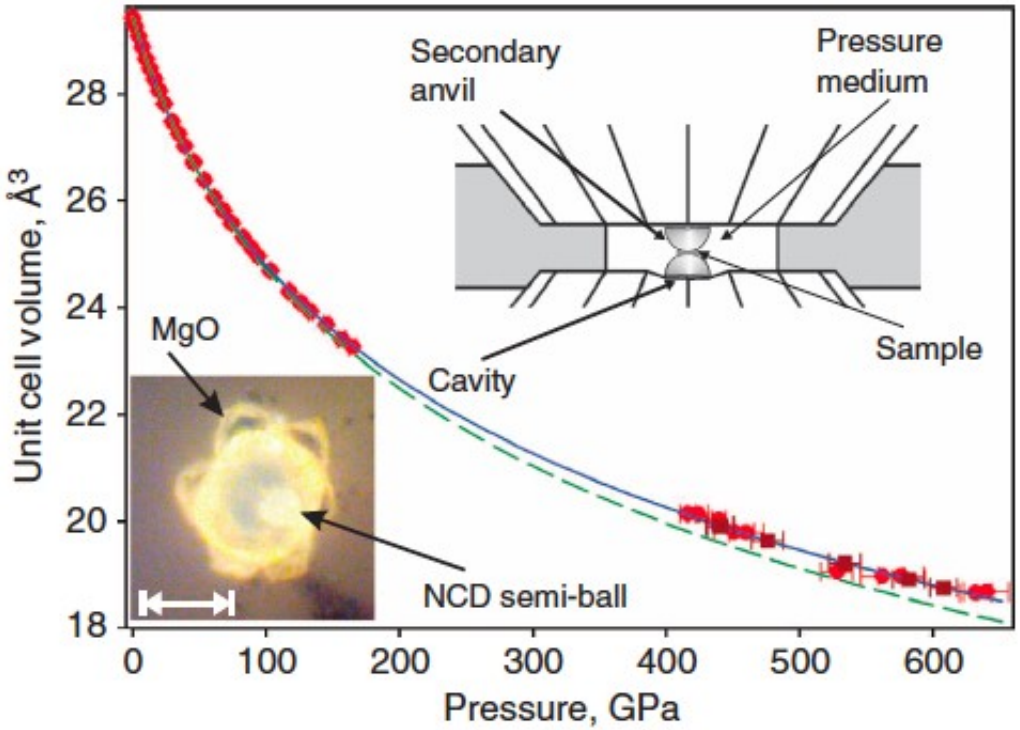




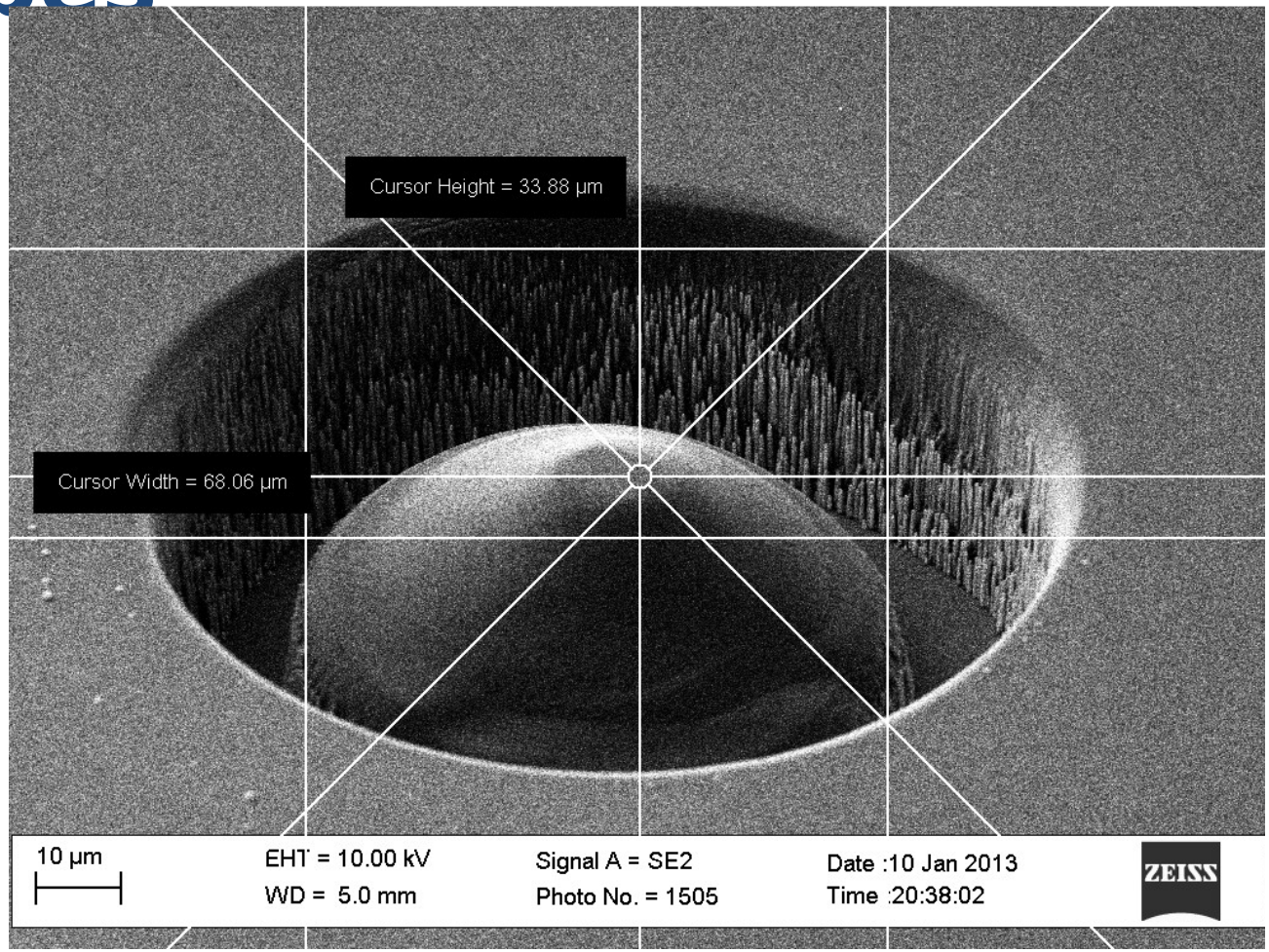
Static Pressures above 400 GPa

Dubrovinskaya et al., Nature Comm., 23 Oct. 2012

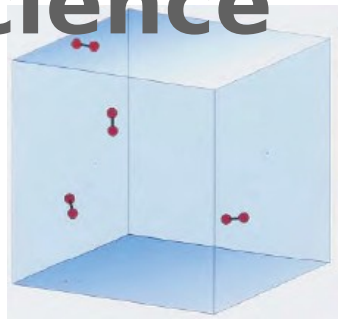




The Terapascal Race needs nm probes

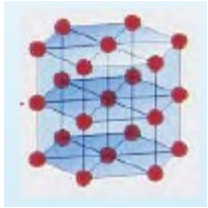


Metallic Hydrogen
the holy grail of high pressure Science



25GPa?

Not yet



Reports

77K, 250 GPa nearly opaque

Optical Studies of Hydrogen Above 200 Gigapascals: Evidence for Metallization by Band Overlap

H. K. Mao and R. J. Hemley

Direct optical observations of solid hydrogen to pressures in the 250-gigapascal (2.5-megabar) range at 77 K are reported. Hydrogen samples appear nearly opaque at the maximum pressures. Measurements of absorption and Raman spectra provide evidence that electronic excitations in the visible region begin at ~200 gigapascals. The optical data are consistent with a band-overlap mechanism of metallization.

Solid hydrogen at 342 GPa: no evidence for an alkali metal

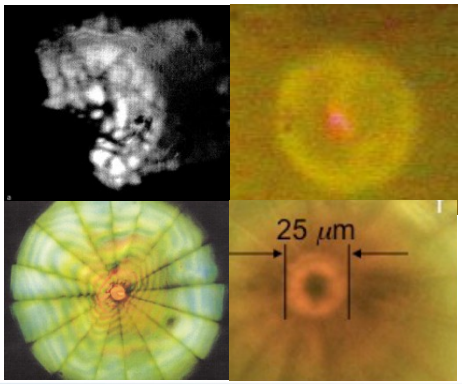
Chandrabhas Narayana*, Huan Luo*†, Jon Orloff‡ & Arthur L. Ruoff*

* Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, USA
‡ Institute for Plasma Research, University of Maryland, College Park, Maryland 20742-3511, USA

Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen

Paul Loubeyre*, Florent Occelli* & René LeToullec*†

* Département Physique Théorique et Applications, Commissariat à l'Energie Atomique, 91680, Bruyères-le-Châtel, France
† Université Paris 6, PMC, 4 place Jussieu, 75252 Paris, France



5402 (2012) PHYSICAL REVIEW LETTERS week ending 6 APRIL 2012

Synchrotron Infrared Measurements of Dense Hydrogen to 360 GPa

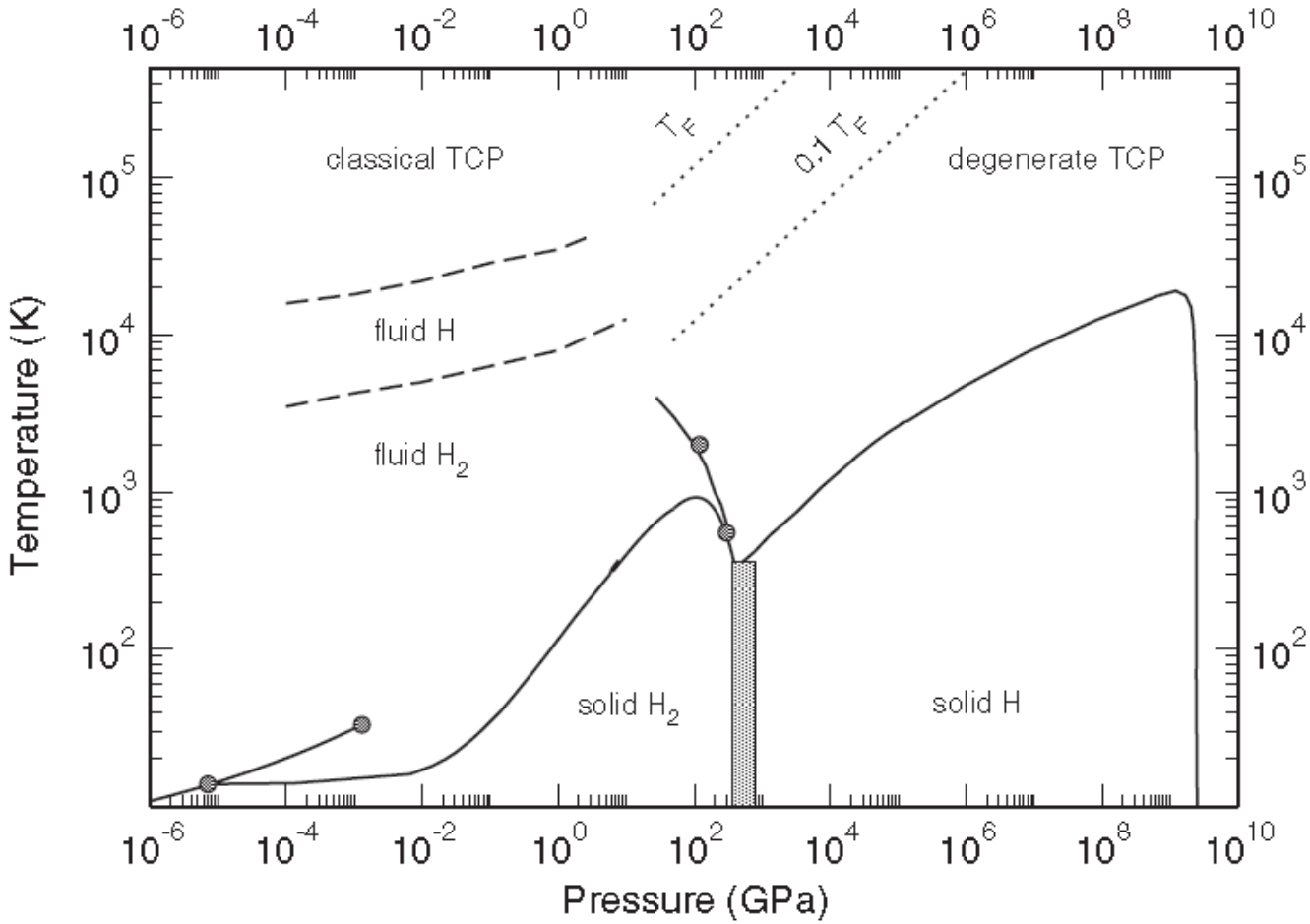
Chang-Sheng Zha, Zhenxian Liu, and Russell J. Hemley
al Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW, Washington D.C. 20015, USA
(Received 26 December 2011; published 3 April 2012)

Diamond-anvil-cell techniques have been developed to confine and measure hydrogen samples under static conditions to pressures above 300 GPa from 12 to 300 K using synchrotron infrared and optical absorption techniques. A decreasing absorption threshold in the visible spectrum is observed, but the material remains transparent at photon energies down to 0.1 eV at pressures to 360 GPa over a broad temperature range. The persistence of the strong infrared absorption of the vibron characteristic of phase III indicates the stability of the paired state of hydrogen. There is no evidence for the predicted metallic state over these conditions, in contrast to recent reports, but electronic properties consistent with semimetallic behavior are observed.

Metallization at 450 GPa?

Crystal structure?

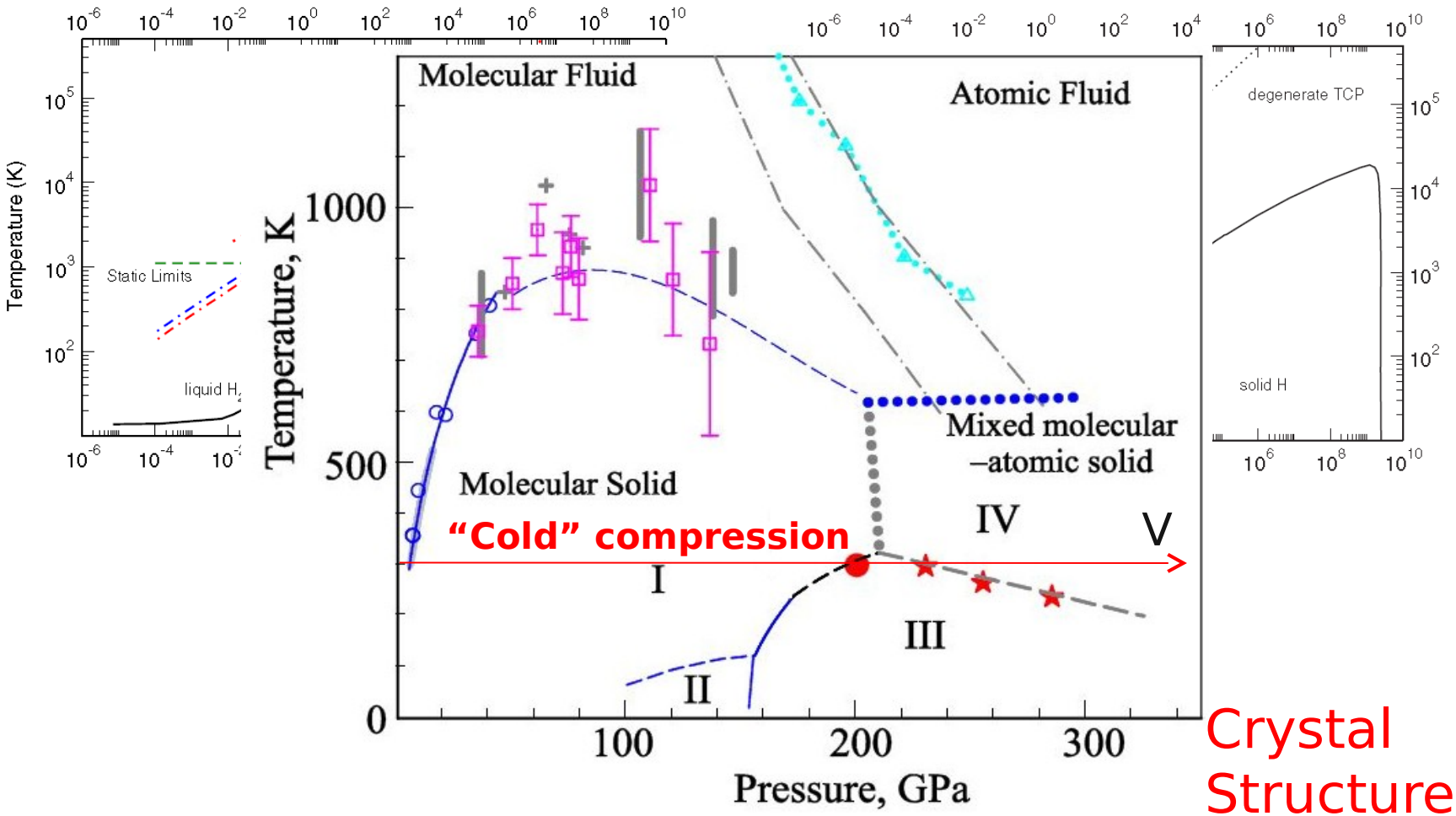
Phase diagram of hydrogen



From Theory

McMahon, et al. *Reviews of Modern Physics* ***84, 1607 (2012).***

Phase diagram of hydrogen



Crystal Structures Unknown!!

Goncharov, A. F., et al. *Low Temperature Physics* ***39, 402-408 (2013).***

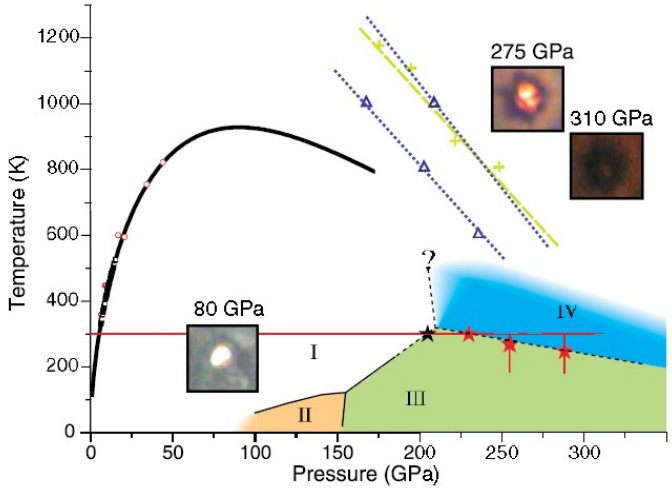
From IR and Raman spectroscopy

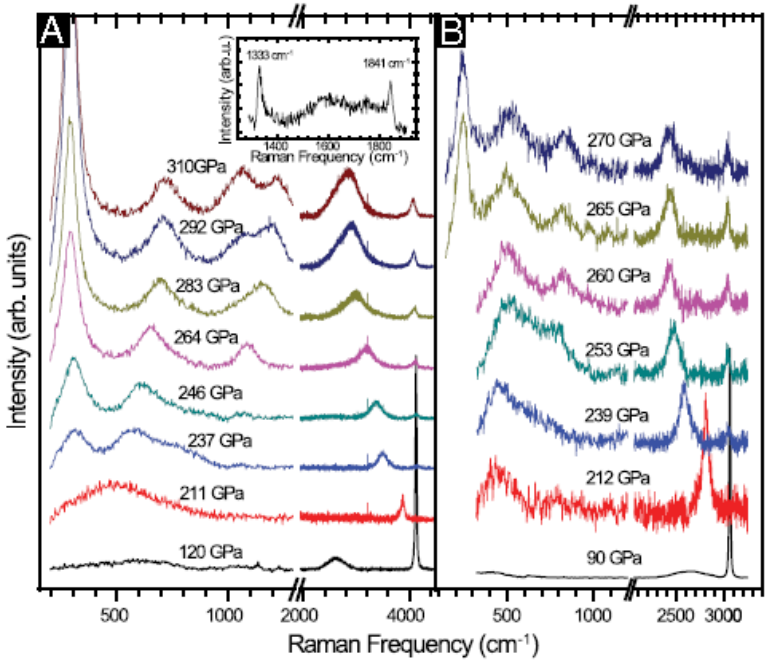
PRL 108, 125501 (2012) PHYSICAL REVIEW LETTERS week ending 23 MARCH 2012

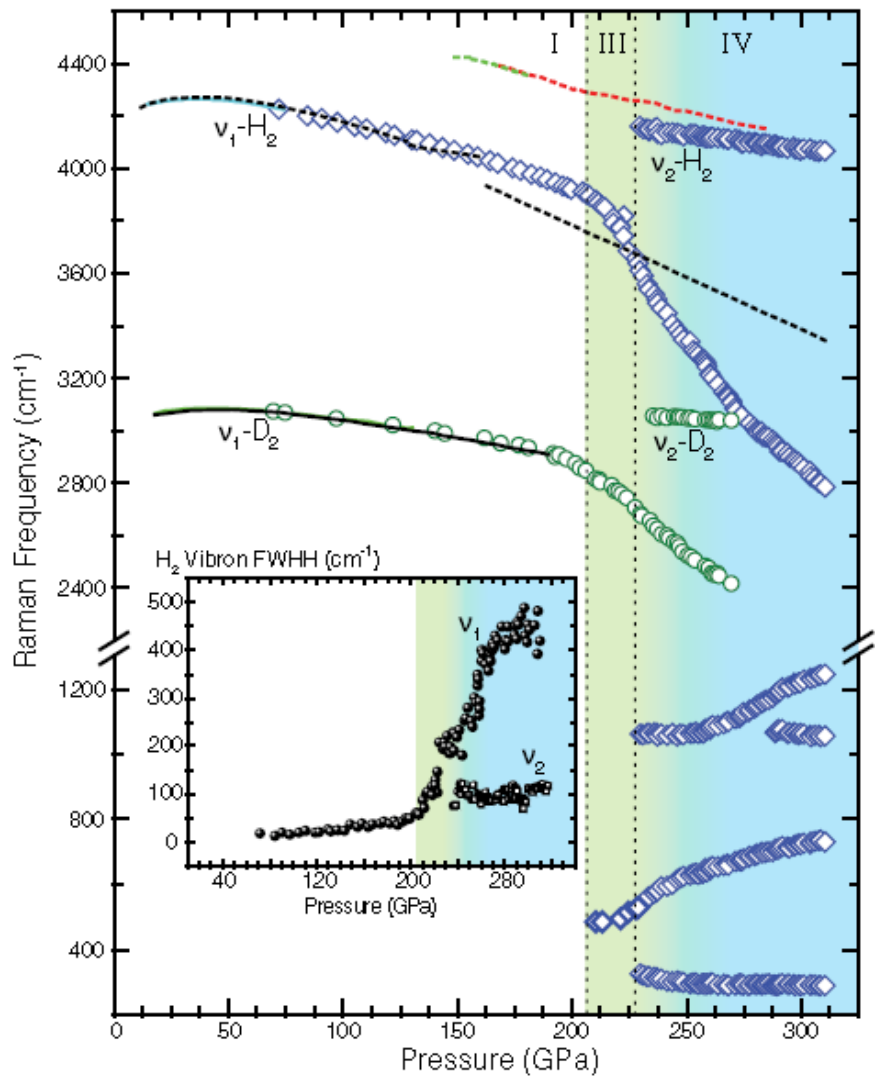
2012

Mixed Molecular and Atomic Phase of Dense Hydrogen

Ross T. Howie,[1] Christophe L. Guillaume,[1] Thomas Scheler,[1] Alexander F. Goncharov,[2] and Eugene Gregoryanz[1,*]



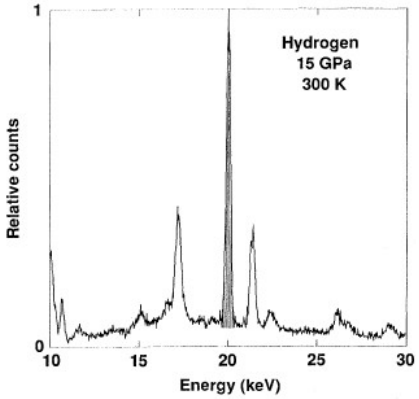


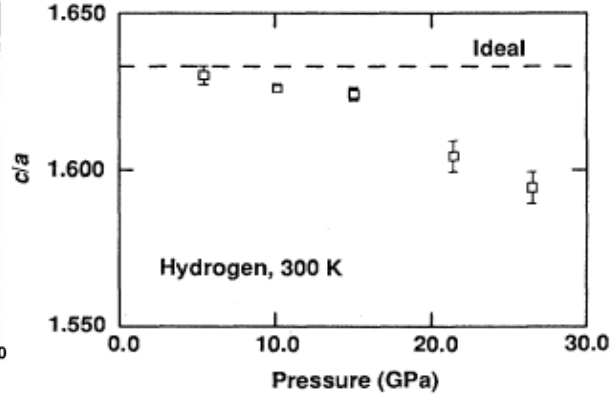


XRD of H2 Phase I

Synchrotron X-ray Diffraction Measurements of Single-Crystal Hydrogen to 26.5 Gigapascals 1989

H. K. Mao, A. P. Jephcoat, R. J. Hemley, L. W. Finger, C. S. Zha, R. M. Hazen, D. E. Cox

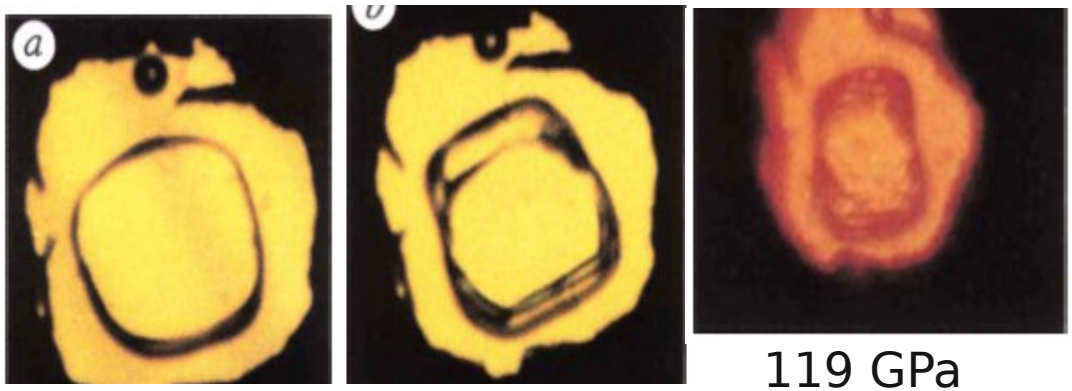




X-ray diffraction and equation of state of hydrogen at megabar pressures 1996

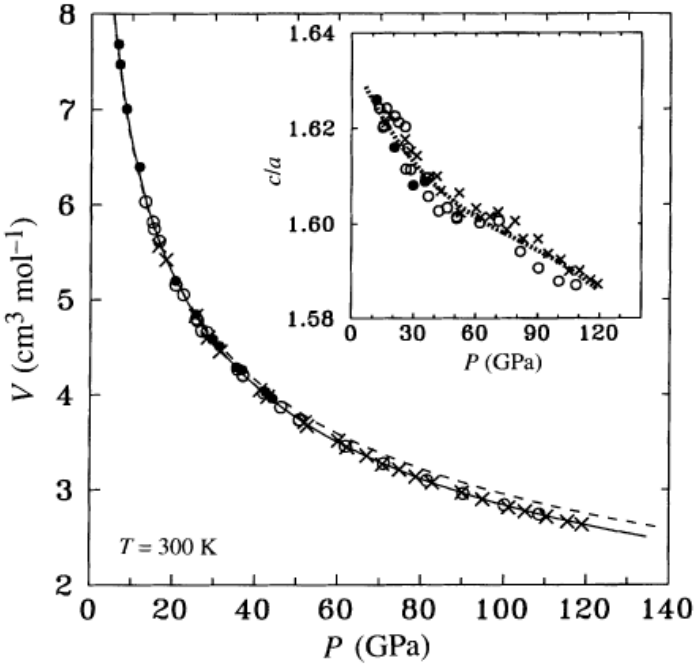
P. Loubeyre*, R. LeToullec*, D. Hausermann†, M. Hanfland†, R. J. Hemley‡, H. K. Mao‡ & L. W. Finger‡

* CNRS and Université Paris 6, PMC, boite 77, 4 place Jussieu, 75252 Paris, France
† ESRF, BP 220, 38043 Grenoble, France
‡ Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington DC 20015, USA



119 GPa

15µm hydrogen single crystal in a helium medium

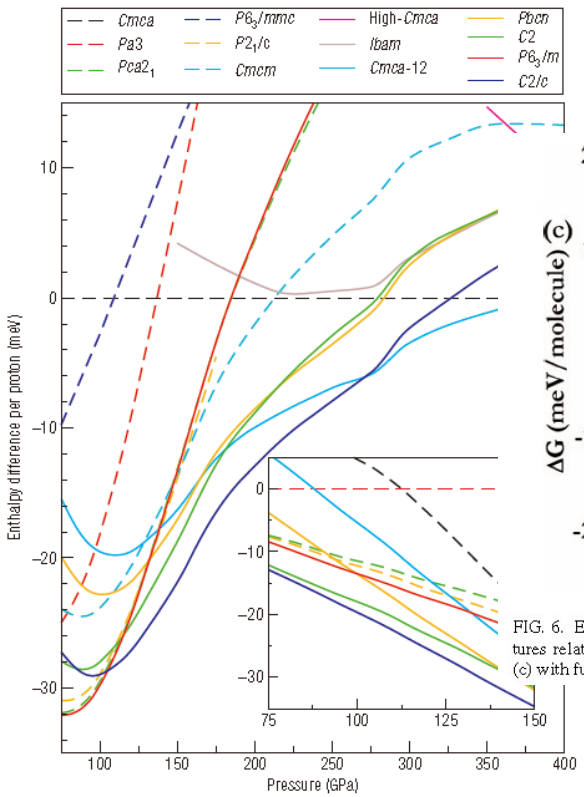


From Theory

LETTERS

Structure of phase III of solid hydrogen

CHRIS J. PICKARD[1]* AND RICHARD J. NEEDS[2]
[1] Scottish Universities Physics Alliance, School of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, UK
[2] Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge CB3 0HE, UK
*e-mail: cjp10@st-andrews.ac.uk



THE JOURNAL OF CHEMICAL PHYSICS 137, 074501 (2012)

Room-temperature structures of solid hydrogen at high pressures

Hanyu Liu, Li Zhu, Wenwen Cui, and Yanming Ma[a)]
State Key Lab of Superhard Materials, Jilin University, Changchun 130012, China

(Received 30 May 2012; accepted 27 July 2012; published online 15 August 2012)

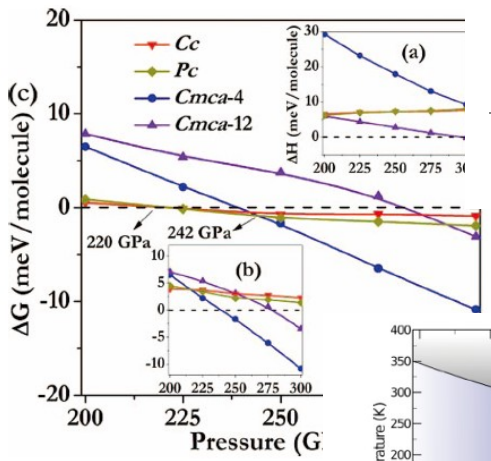


FIG. 6. Enthalpies/free energies of the *Cc*, *Pc*, tures relative to *C2/c* structure (a) for the static (c) with full vibrational motion at 300 K.

PHYSICAL REVIEW B 85, 214114 (2012)

Density functional theory study of phase IV of solid hydrogen

Chris J. Pickard* and Miguel Martinez-Canales
Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Richard J. Needs
Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge CB3 0HE, UK

(Received 15 April 2012; revised manuscript received 14 May 2012; published 15 June 2012)

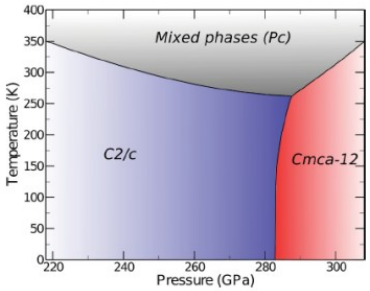
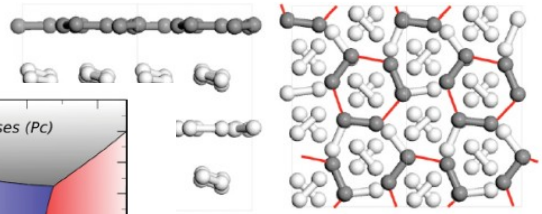
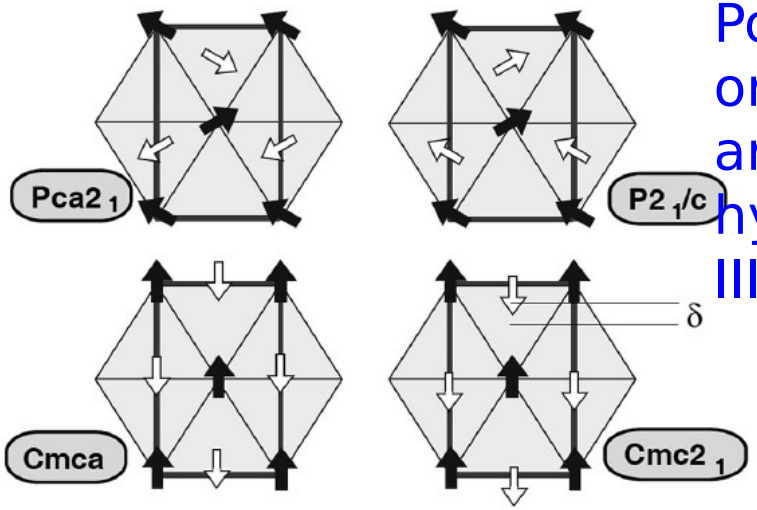


FIG. 5. (Color online) Computed phase diagram of hydrogen at high pressures.

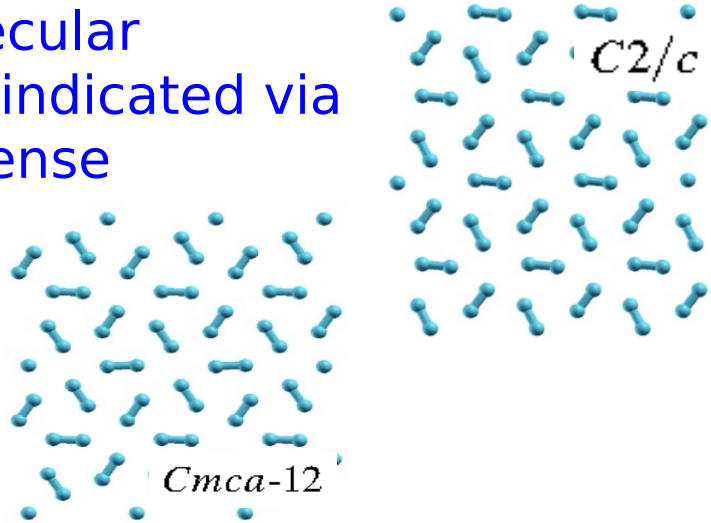


ıe) Side and top views of the *Pc* structure at
v shows the four-layer repeat with a weakly
yer on top (shaded atoms). The red lines show
s within the layer.

Theoretical Predictions



Possible molecular orientations (indicated via arrows) for dense hydrogen (ph III),

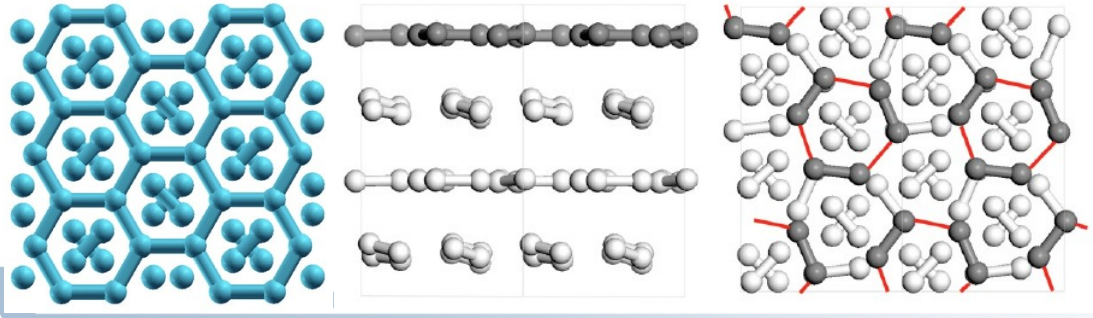


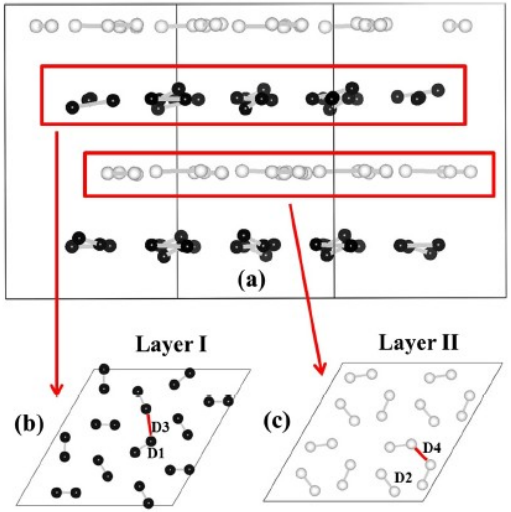
H2 Phase IV: Alternating graphene-like and molecular H2 layers?

PRL 110, 2[illegible] (2013) PHYSICAL REVIEW LETTERS week ending 11 JANUARY 2013

Proton or Deuteron Transfer in Phase IV of Solid Hydrogen and Deuterium

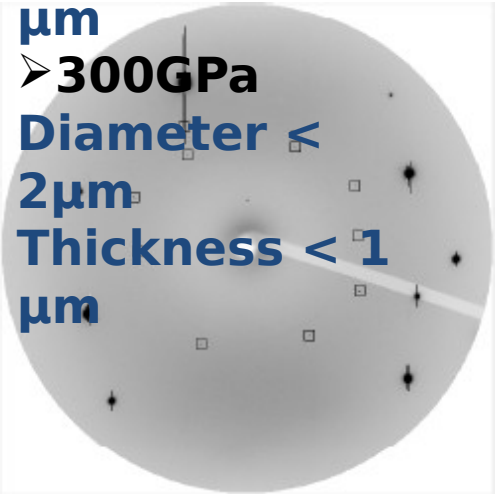
Hanyu Liu and Yanming Ma*
State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China
(Received 30 September 2012; revised manuscript received 9 November 2012; published 9 January 2013)



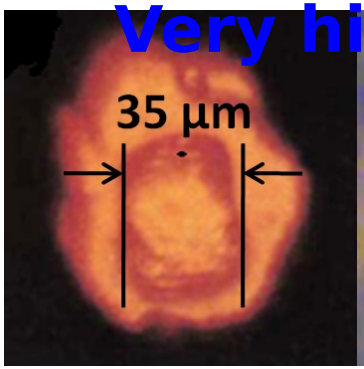


The Challenge of H2 XRD above 100 GPa

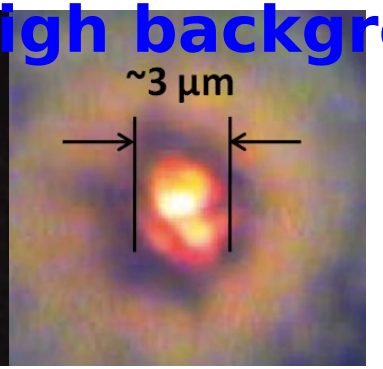
- **100GPa**
  Diameter < 10µm
  Thickness < 5 µm
- **200GPa**
  Diameter < 4µm
- **Thickness < 2 µm**
- **300GPa**
  Diameter < 2µm
  Thickness < 1 µm



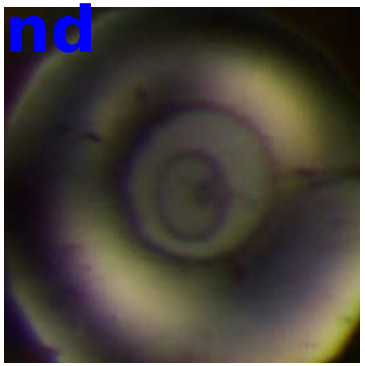
Very weak hydrogen diffraction,
Very small sample,
Very high background



~120 GPa



~300 GPa

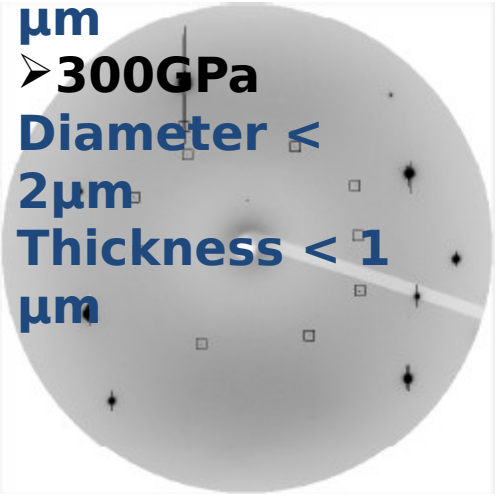


Growing a H2 single crystal in He

We can see a 10x10x5 µm3 H2 crystal at 16IDB □ but not 5x5x2 µm3 which is one order of magnitude less than the background □

The Challenge of H2 XRD above 100 GPa

- **100GPa**
  Diameter < 10µm
  Thickness < 5 µm
- **200GPa**
  Diameter < 4µm
- **Thickness < 2 µm**
- **300GPa**
  Diameter < 2µm
  Thickness < 1 µm



Very weak hydrogen diffraction,
Very small sample,
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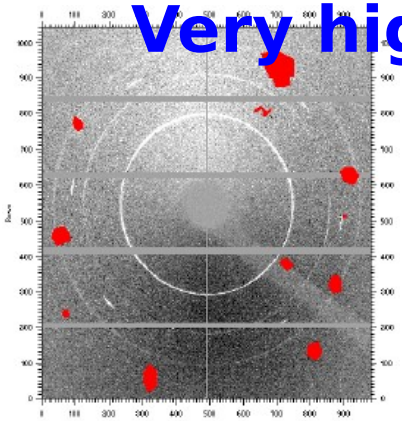
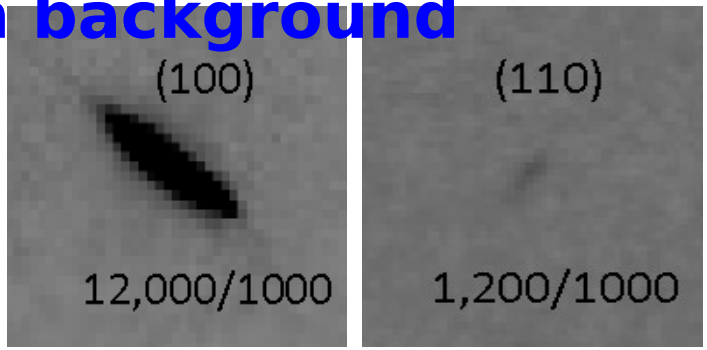




Signal/background ratio 1.2 for a 10µm H2 crystal

Pilatus detector

MBA provides the ideal answer

Crystal Structures of Ultradense Hydrogen

Opportunity

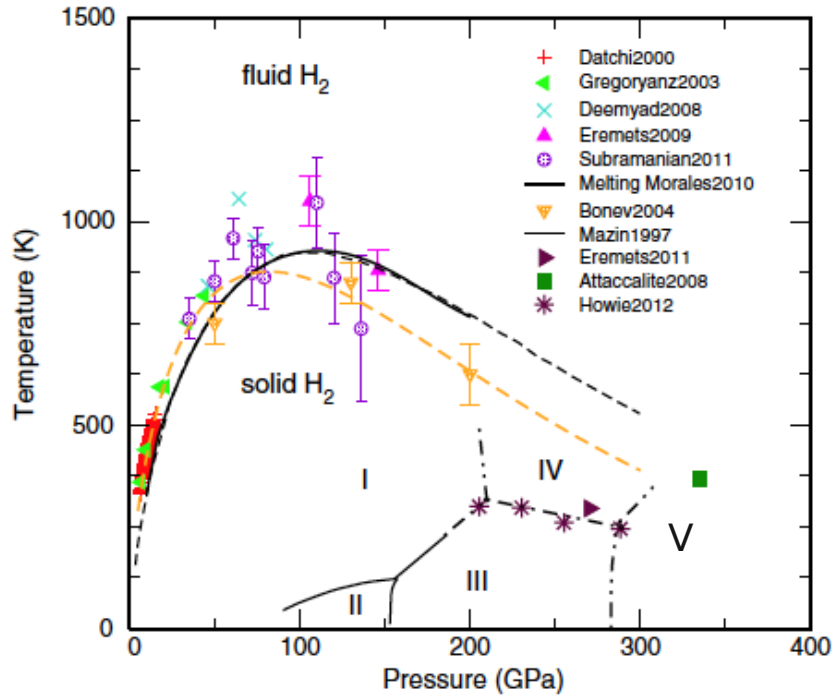
- As the most abundant element in the Universe, hydrogen under high pressures has been the focus of intense theoretical and experimental investigations.
- X-ray diffraction data are desperately needed to resolve the crystal structure of phase III, IV, and V.

Challenge

- Recently optical spectroscopy studies have revealed important new high-pressure phases of molecular hydrogen.
- As the lightest element, hydrogen yields very weak x-ray diffraction signal.

4GSR Strength:

- The submicron focusing capability and two of magnitude higher



Ultrahigh pressures are achieved at the expense of smaller sample size. Only the structures of hydrogen I and II have been determined by x-ray with 10 μm sample up to 120 GPa. The maximum size of 1-3 μm for phases III, IV, and V would required the new capabilities of MBA APS.