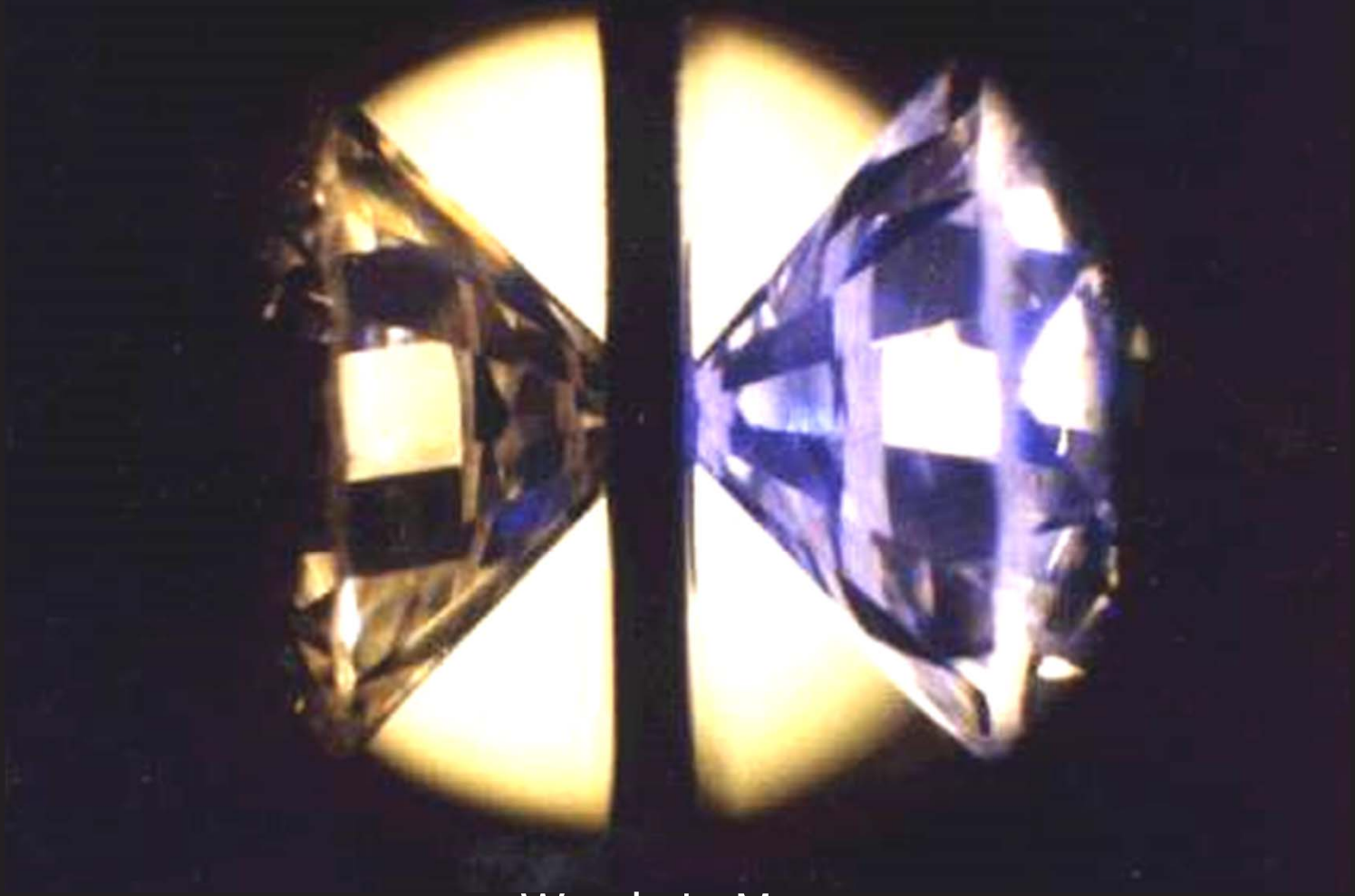
Opportunities for high pressure science with brighter, smaller x-ray beams



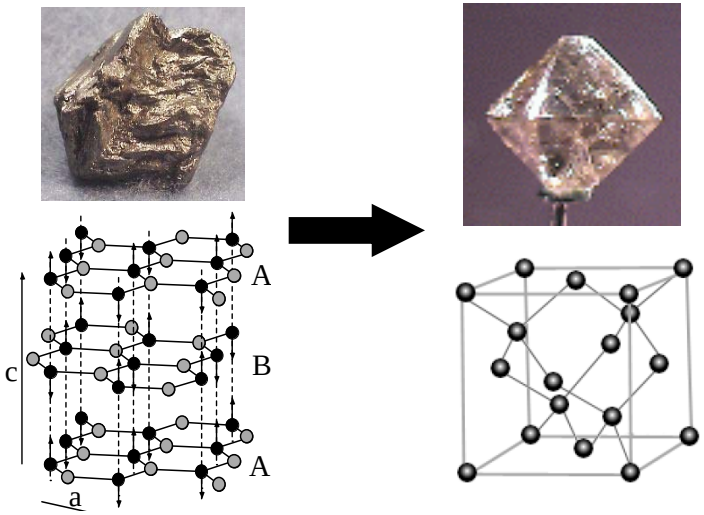
Wendy L. Mao

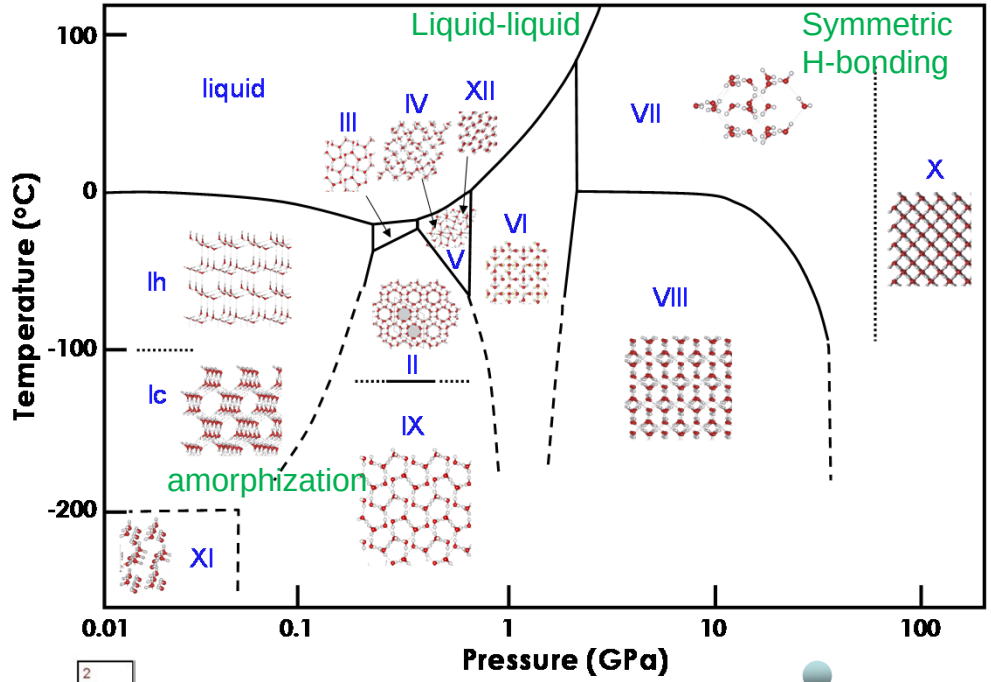
Geological Sciences, Stanford University

Photon Science, SLAC National Accelerator Laboratory

Pressure changes everything

superionic



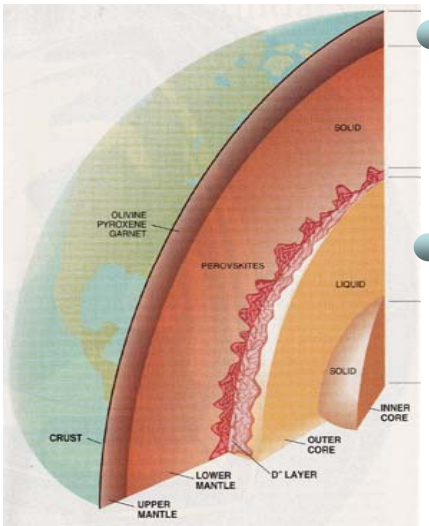


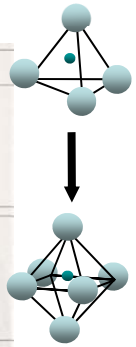
Periodic Table of Superconductors

P = 0
P > 0

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Ru	105 Ha	106 Unh	107 Uns	108 Uno	109 Une									

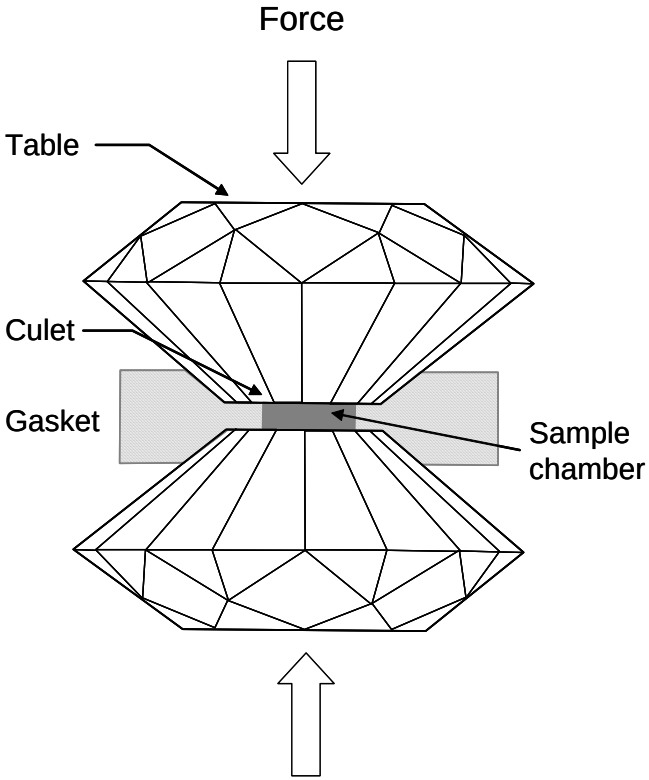
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

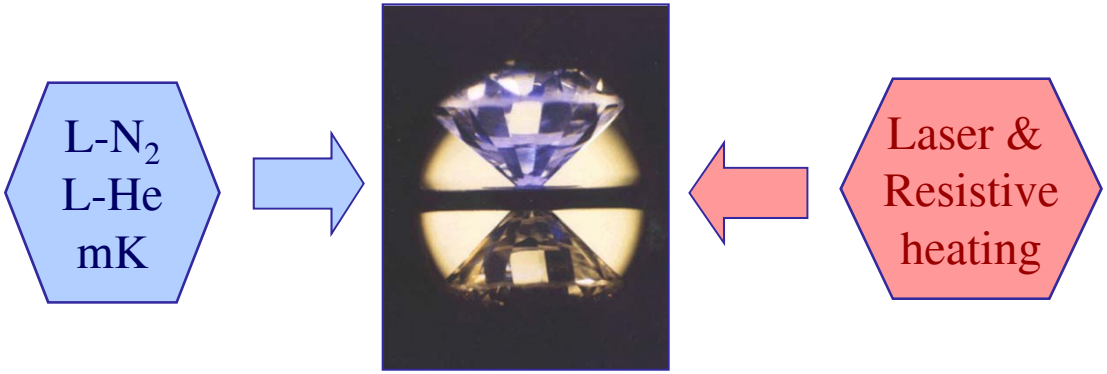




Diamond anvil cell

- Pressure: ambient to > 600 GPa (1 GPa= 10,000 bar)
- Temp: mK to 6000 K
- Sample size: < 0.001 mm^3
- Compatible with many *in-situ* probes





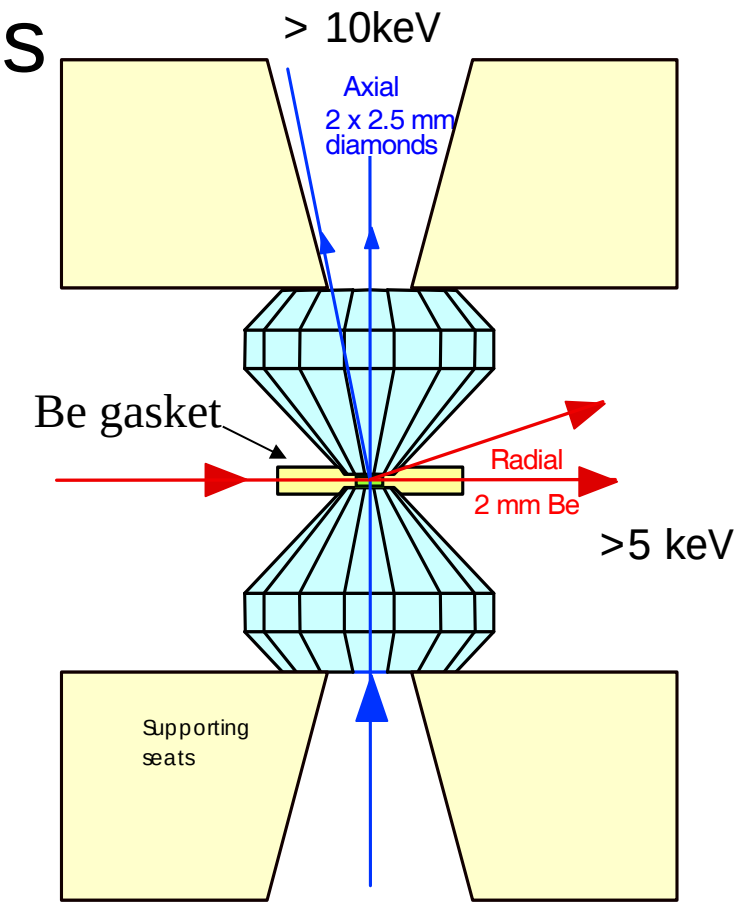
Diamond anvil cell

- Pressure: ambient to > 600 GPa (1 GPa= 10,000 bar)
- Temp: mK to 6000 K
- Sample size: < 0.001 mm^3
- Compatible with many *in-situ* probes

In-situ high pressure studies

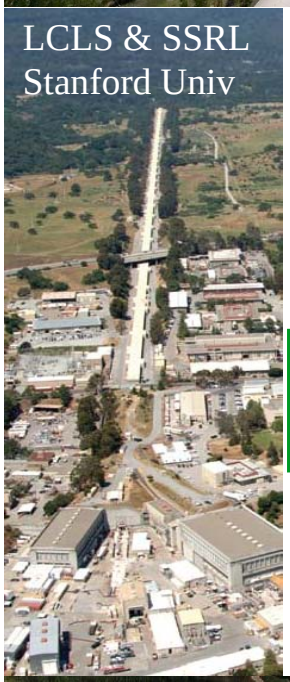
Penetrate the pressure vessel to reach the sample

- optical probes can be limited depending on quality of window and sample (diffraction limit)
- vacuum probes (vuv, soft x-ray, electrons & ions) are excluded.
- neutrons require larger volumes
- x-rays, axial direction need > 10 keV, radial need > 5 keV



Advantages of synchrotron X-ray techniques

- Small, penetrating, bright x-ray beams
- Tunable wavelength



Angle-dispersive X-ray Diffraction

X-ray Absorption Spectroscopy

Synchrotron Mössbauer Spectroscopy

Resonant Inelastic X-ray Scattering

Energy-dispersive X-ray Diffraction

X-ray Magnetic Circular Dichroism

Nuclear Res. Inelastic X-ray Scattering

Inelastic X-ray Scattering

Micro-nano diffraction

X-ray Raman

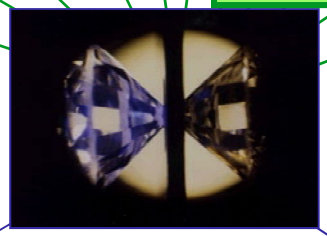
Radial X-ray Diffraction

Small Angle X-ray Diffraction

X-ray Emission Spectroscopy

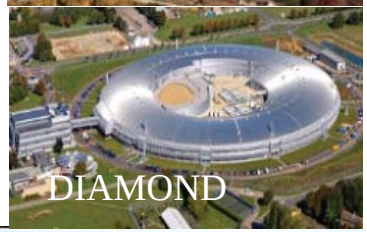
Coherent Diff. Imaging

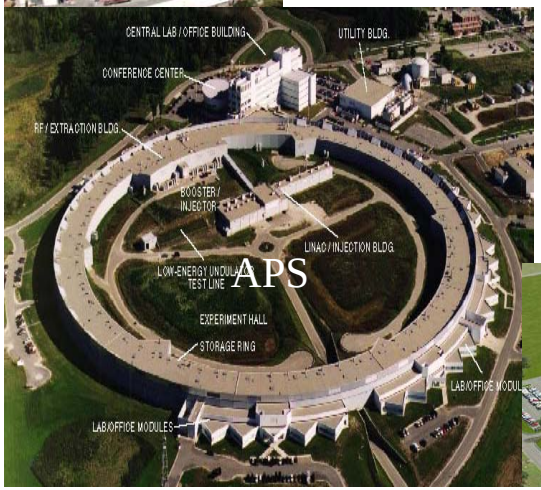
Transmission X-ray Microscopy

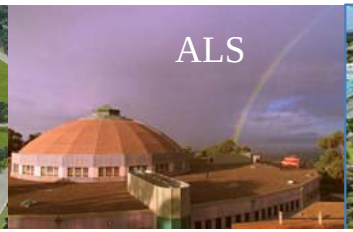


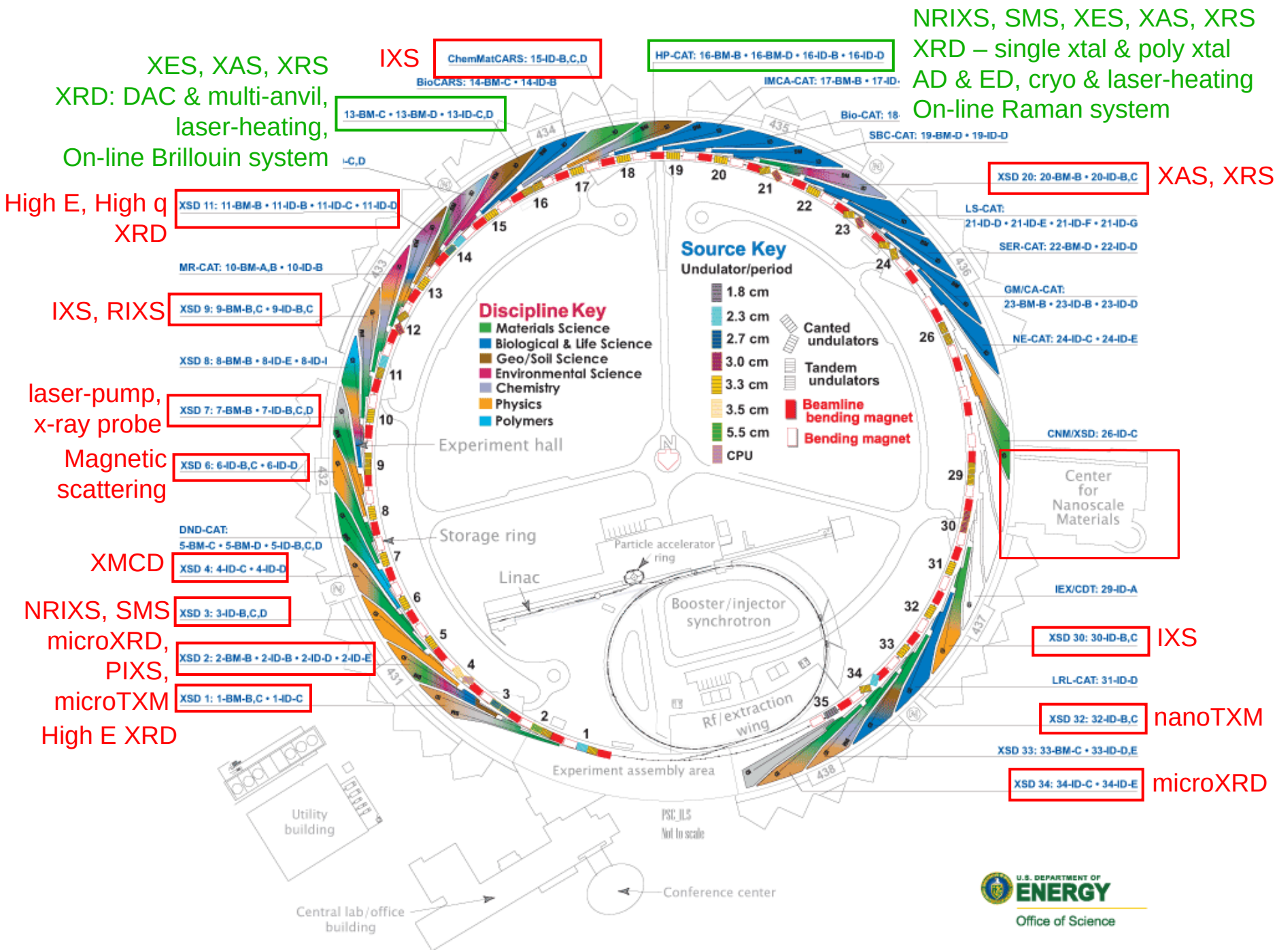
Mineral Physics

Energy Materials





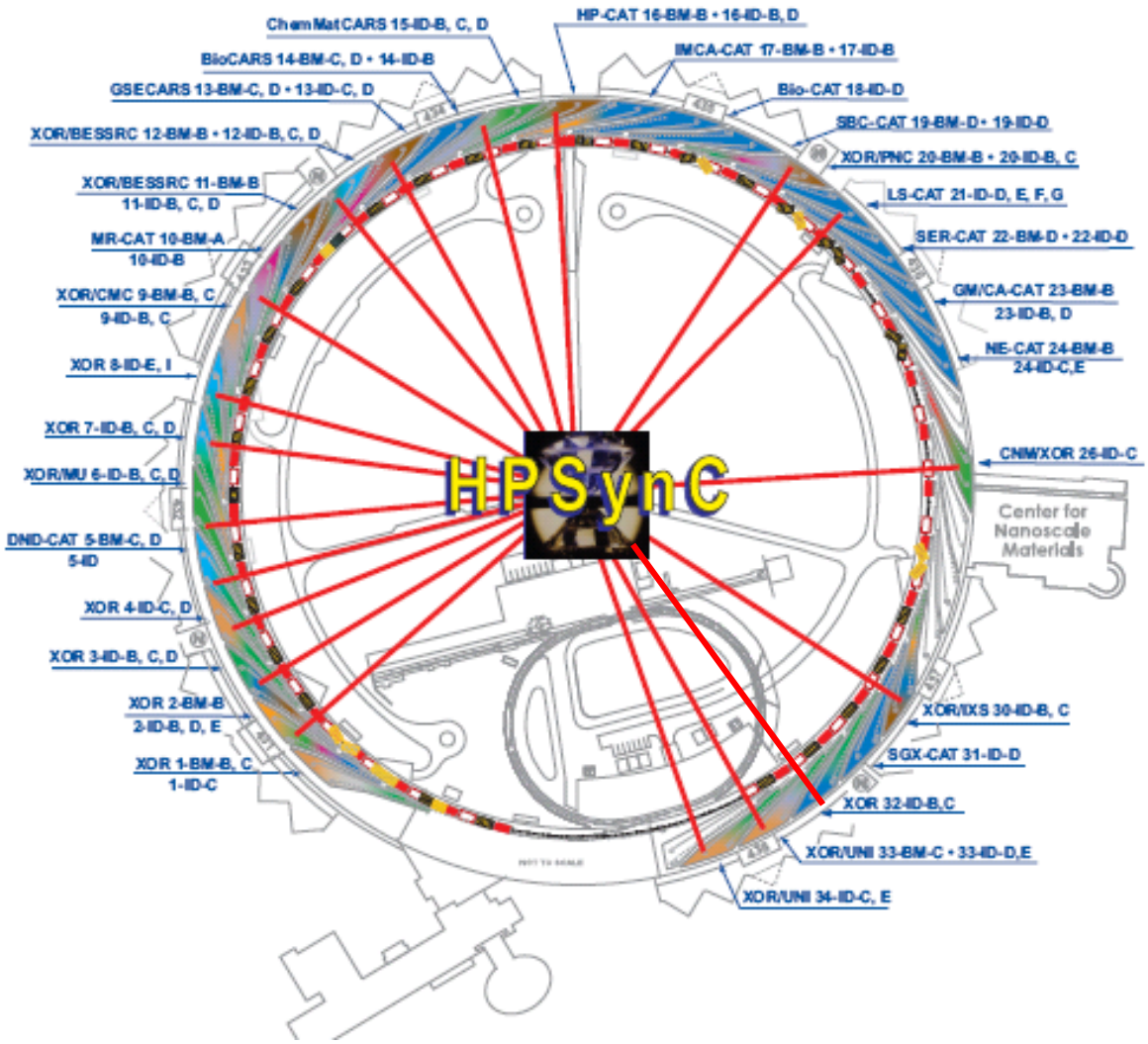



XES, XAS, XRS
XRD: DAC & multi-anvil, laser-heating,
On-line Brillouin system
IXS
ChemMatCARS: 15-ID-B,C,D
BioCARS: 14-BM-C • 14-ID-B
13-BM-C • 13-BM-D • 13-ID-C,D
HP-CAT: 16-BM-B • 16-BM-D • 16-ID-B • 16-ID-D
IMCA-CAT: 17-BM-B • 17-ID-
Bio-CAT: 18-
SBC-CAT: 19-BM-D • 19-ID-D
NRIXS, SMS, XES, XAS, XRS
XRD – single xtal & poly xtal
AD & ED, cryo & laser-heating
On-line Raman system
XSD 20: 20-BM-B • 20-ID-B,C
XAS, XRS
High E, High q XRD
XSD 11: 11-BM-B • 11-ID-B • 11-ID-C • 11-ID-D
LS-CAT: 21-ID-D • 21-ID-E • 21-ID-F • 21-ID-G
SER-CAT: 22-BM-D • 22-ID-D
MR-CAT: 10-BM-A,B • 10-ID-B
GM/CA-CAT: 23-BM-B • 23-ID-B • 23-ID-D
IXS, RIXS
XSD 9: 9-BM-B,C • 9-ID-B,C
NE-CAT: 24-ID-C • 24-ID-E
XSD 8: 8-BM-B • 8-ID-E • 8-ID-I
laser-pump, x-ray probe
XSD 7: 7-BM-B • 7-ID-B,C,D
Magnetic scattering
XSD 6: 6-ID-B,C • 6-ID-D
CNM/XSD: 26-ID-C
Center for Nanoscale Materials
DND-CAT: 5-BM-C • 5-BM-D • 5-ID-B,C,D
XMCD
XSD 4: 4-ID-C • 4-ID-D
IEX/CDT: 29-ID-A
NRIXS, SMS
XSD 3: 3-ID-B,C,D
microXRD, PIXS, microTXM
XSD 2: 2-BM-B • 2-ID-B • 2-ID-D • 2-ID-E
XSD 30: 30-ID-B,C
IXS
LRL-CAT: 31-ID-D
XSD 1: 1-BM-B,C • 1-ID-C
High E XRD
XSD 32: 32-ID-B,C
nanoTXM
XSD 33: 33-BM-C • 33-ID-D,E
XSD 34: 34-ID-C • 34-ID-E
microXRD
Source Key
Undulator/period
1.8 cm
2.3 cm
2.7 cm
3.0 cm
3.3 cm
3.5 cm
5.5 cm
CPU
Canted undulators
Tandem undulators
Beamline bending magnet
Bending magnet
Discipline Key
Materials Science
Biological & Life Science
Geo/Soil Science
Environmental Science
Chemistry
Physics
Polymers
Experiment hall
Storage ring
Linac
Particle accelerator ring
Booster/injector synchrotron
Rf/extraction wing
Experiment assembly area
Utility building
Central lab/office building
Conference center
PSC_ILS
Not to scale
U.S. DEPARTMENT OF ENERGY
Office of Science

HPSynC

High Pressure Synergetic Consortium at theAdvanced Photon Source

Established in 2007



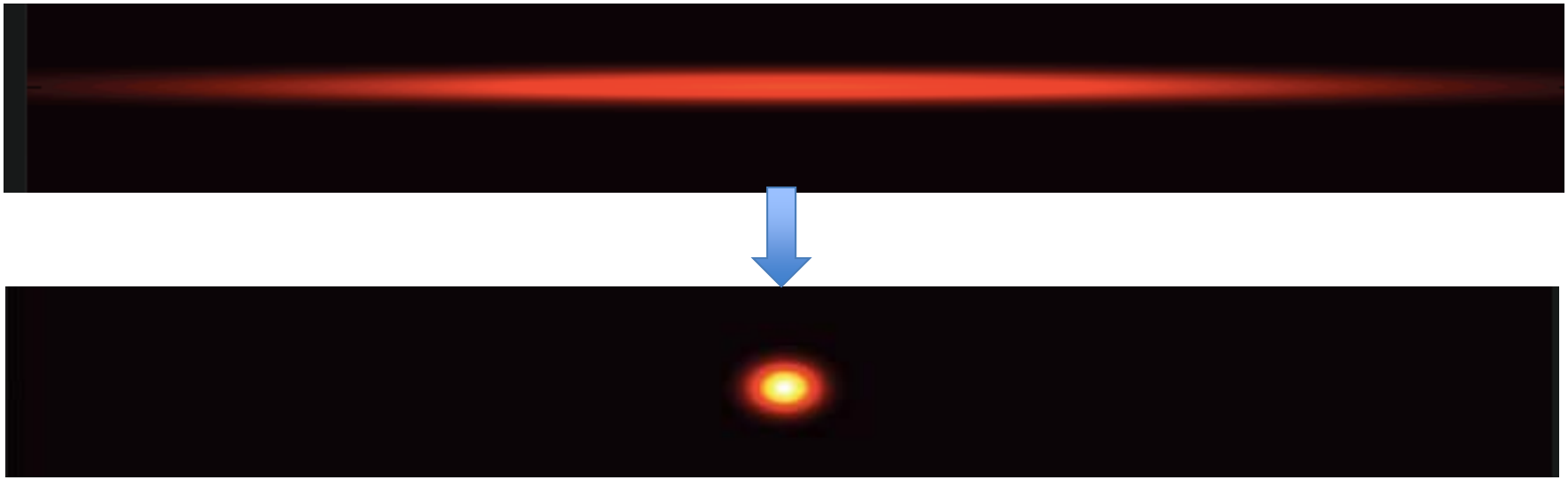
Mission:

Develop high risk, high return, high pressure synchrotron science and technologies

Current focus of activities is new science and novel HP-SR techniques

Nano imaging (TXM),
Coherent diffraction imagine (CDI)
High energy scattering (PDF)
High energy resolution (HERIX, MERIX)
Various novel spectroscopy
Time resolved (Shock wave, XPCS)
Magnetic study (XMCD)

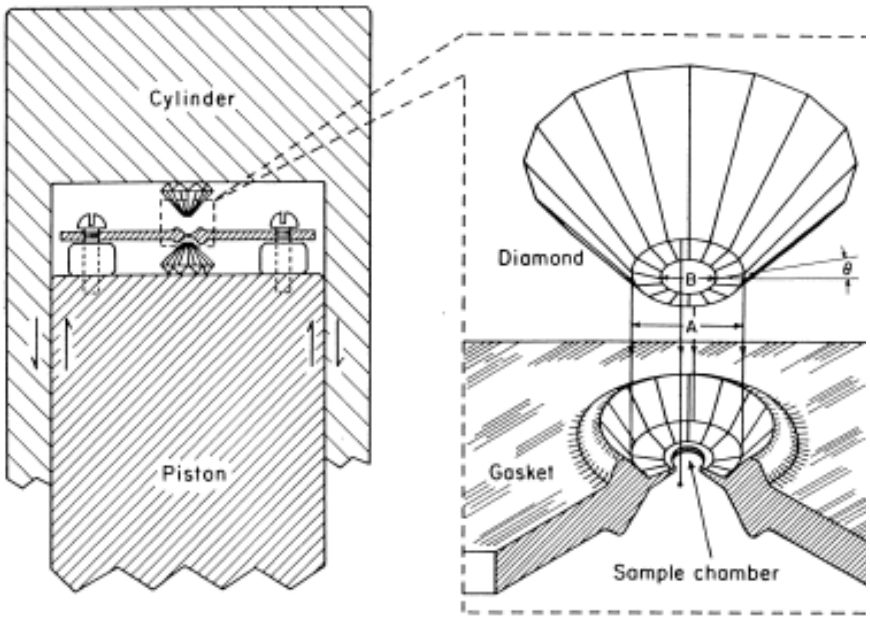
The APS-MBA upgrade and its impact on high pressure science



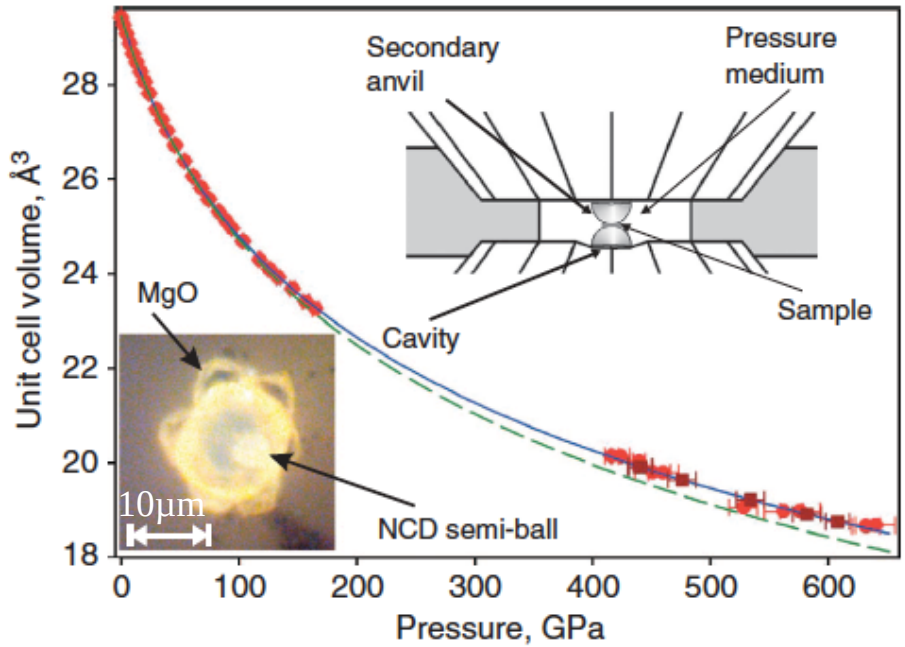
A hundred-fold increase in source brightness

Reaching ultrahigh pressures depends upon extremely small areas

$$P = F/A$$



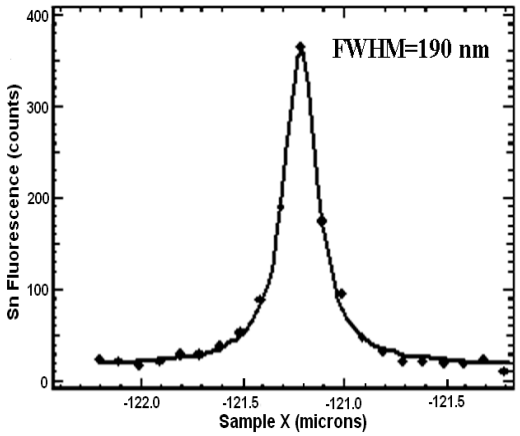
A = 300 µm, B = 30µm, θ = 8.5 to reach 300 GPa
Mao (1980)



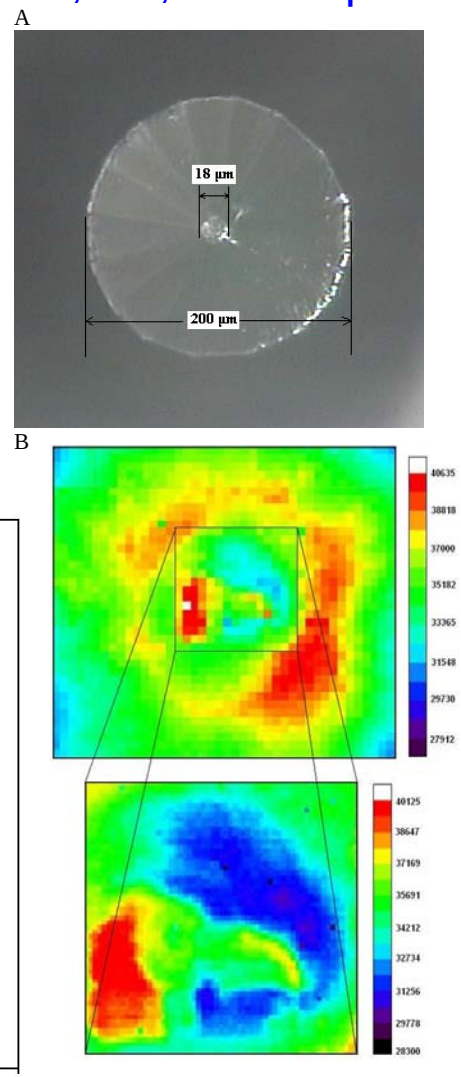
Dubrovinsky et al. Nature Comm. (2012)

Characterization depends on
sub-µm x-ray probes with sufficient flux.

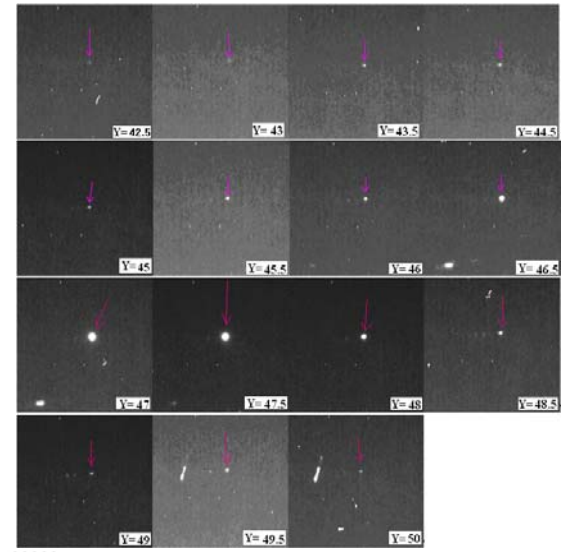
Using submicron focused x-ray beam we can…

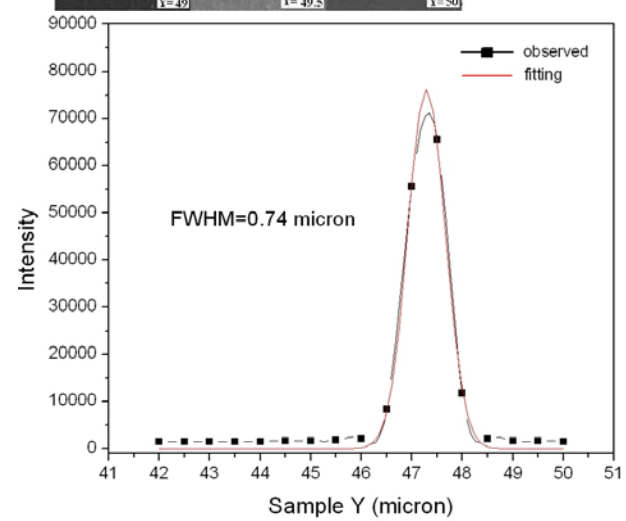


Separate submicron Pt, Re, Fe samples

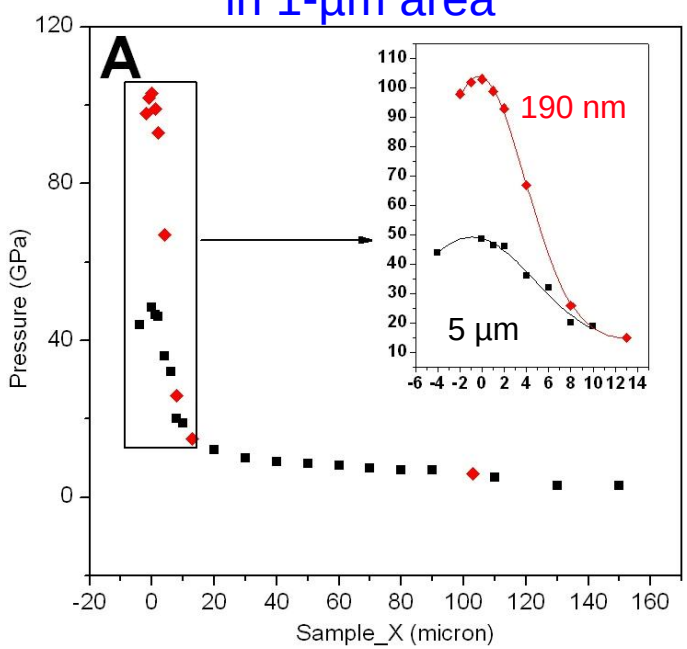


Conduct single-crystal XRD on submicron powder



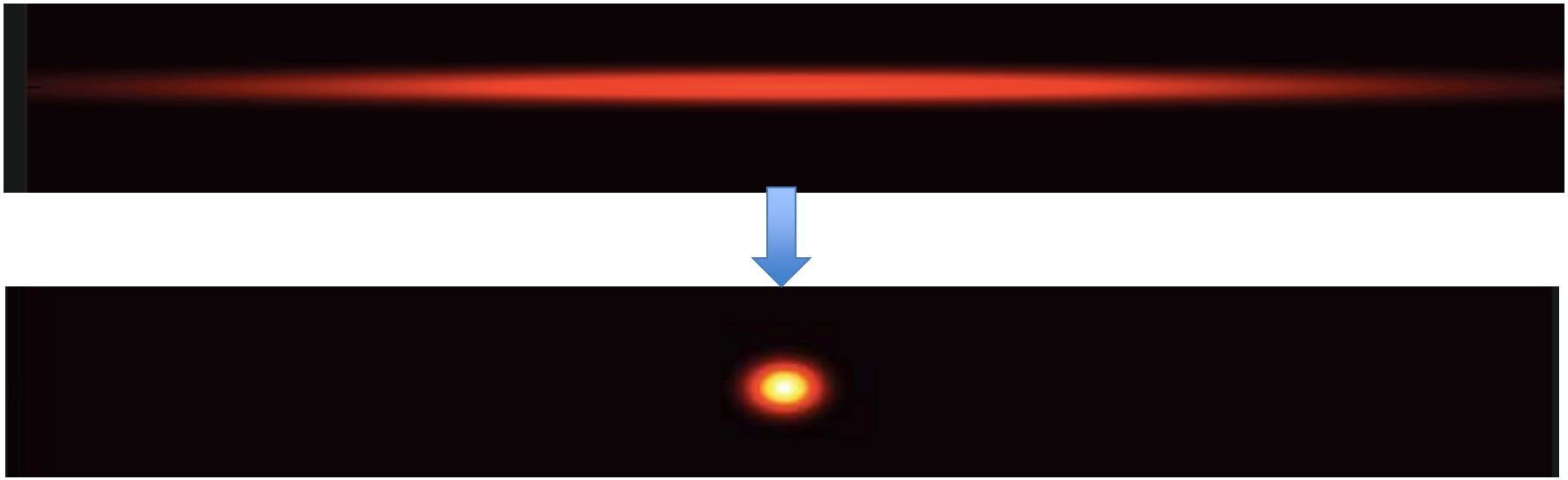


Observe 20 GPa/µm gradient & peak-pressure in 1-µm area



Wang *et al.*, *PNAS* 2010

Advantage of 100X higher brightness for ultrahigh *P-T* experiments



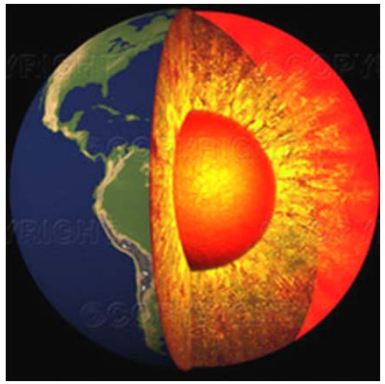
Would enable for example:

✧Rapid experiments on a transient high *P-T* sample

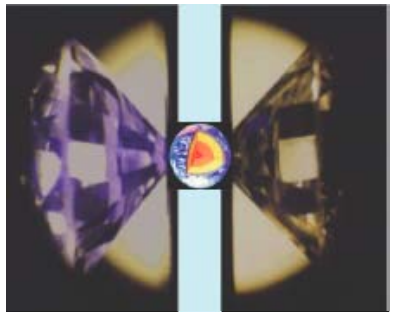
✧Probing a single crystal in a polycrystalline aggregate

✧Study of light elements under extreme pressure

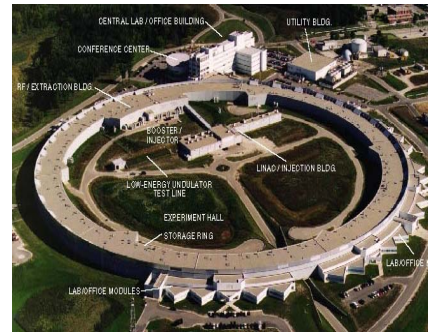
✧Characterization of μm sized sample at multimegabar pressures



•Geophysical observations



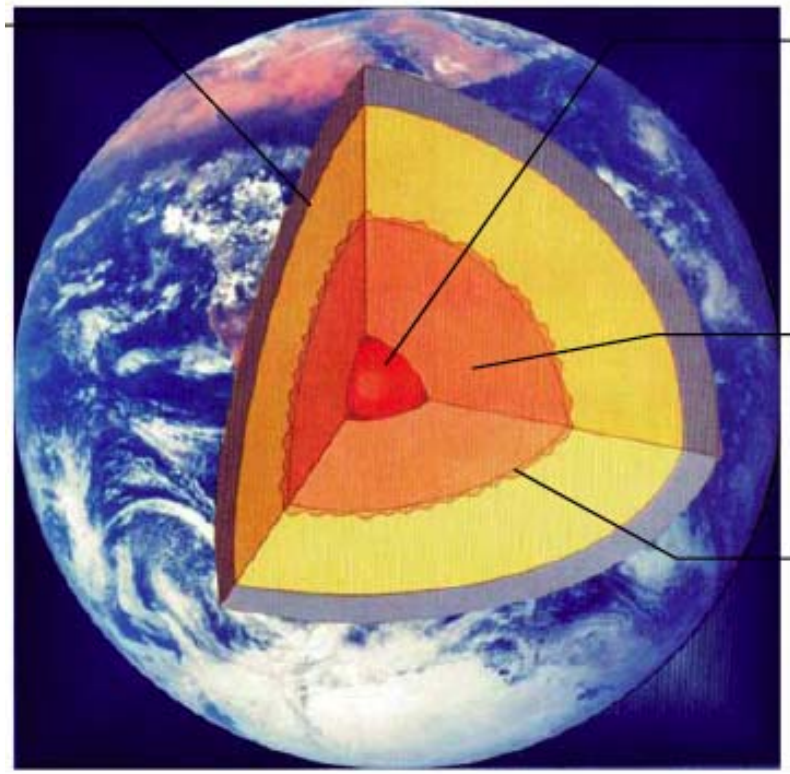
• High P-T experiments



• Materials properties

Theories, Models & Interpretations

Core Study



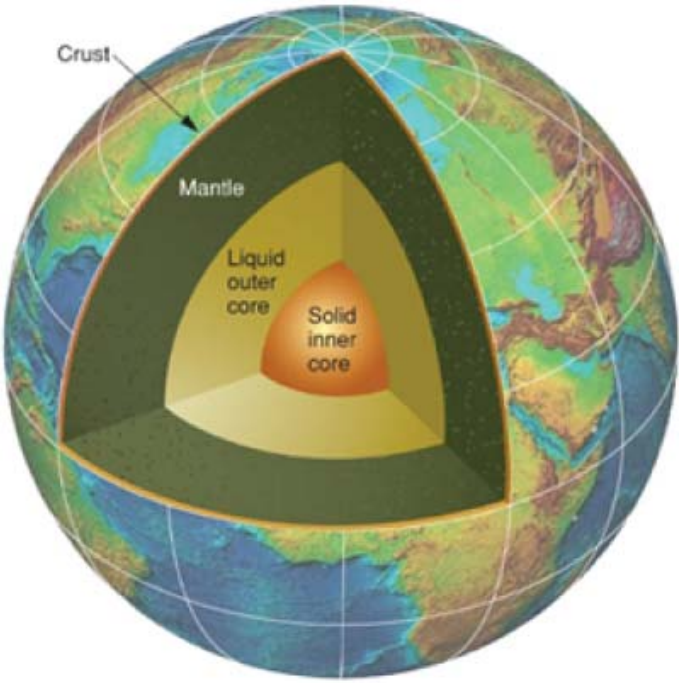
Inner core
anisotropy?
Super-rotation?
Magnetism?

Core dynamo?
Composition?
Temperature?

CMB reactions?
Partitioning?
Anisotropy?
Melting?

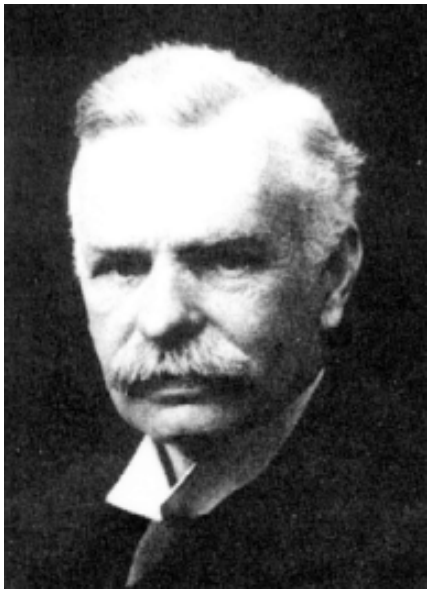
Understanding Iron at Earth's Core Conditions

Grand challenge of deep Earth research



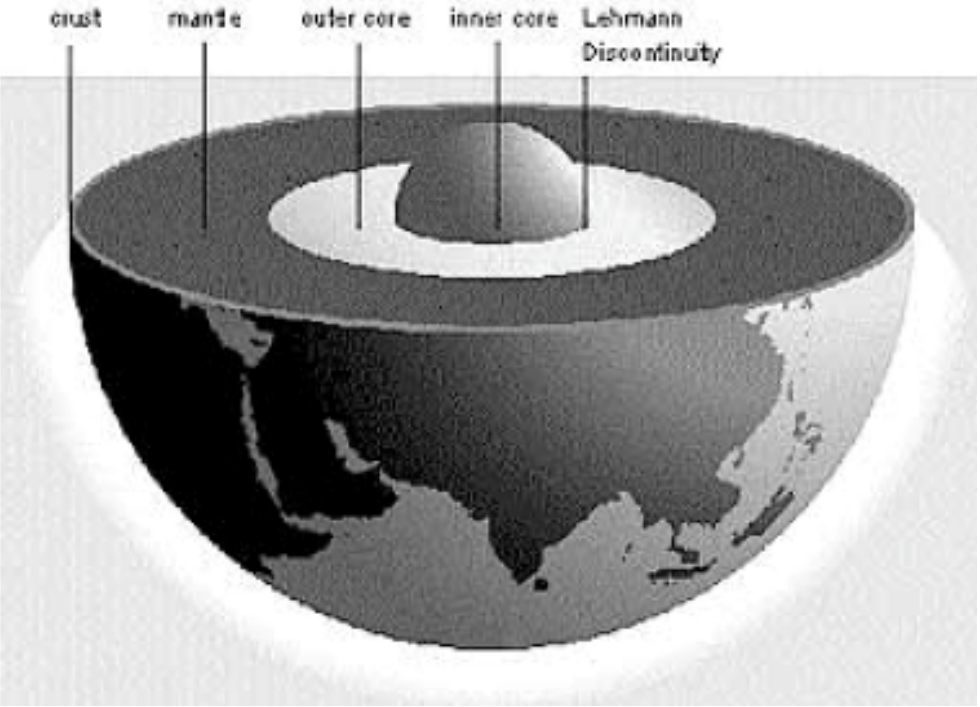
…limited by the existing tools

Francis Birch demonstrated the core is mainly Fe (1952, 1961)



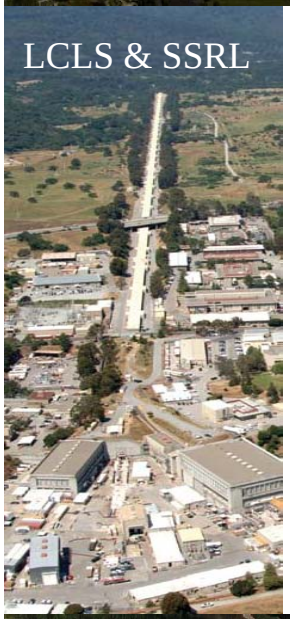
Richard Dixon Oldham discovered core (1906)

Inge Lehmann discovered the inner core (1936)



Crucial knowledge of Fe is still missing at core *P-T*

- ✧ Phase diagram and crystal structure
- ✧ Elasticity and elastic anisotropy
- ✧ Rheology and strength
- ✧ …



Despite of major efforts…

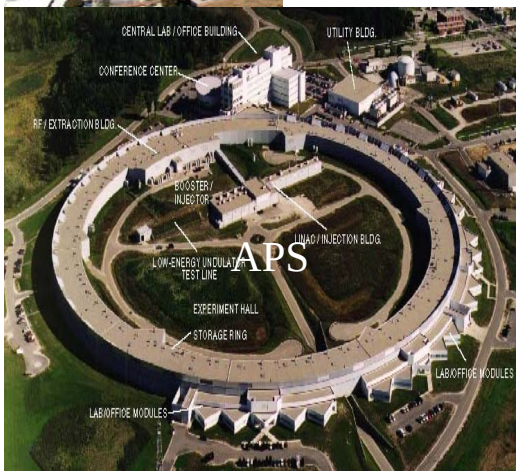
Micro X-ray diffraction

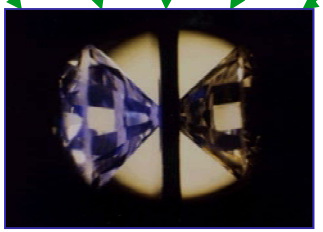
Non-resonant Inelastic X-ray Scattering

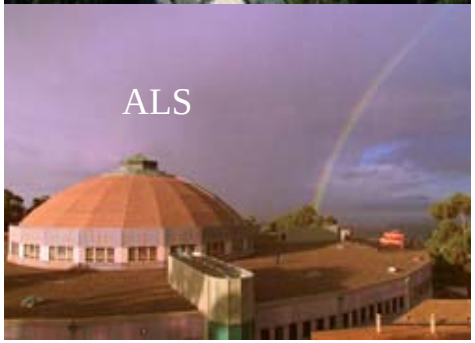
Nuclear Resonant Inelastic X-ray Scattering

Radial X-ray Diffraction

Synchrotron Mössbauer Spectroscopy

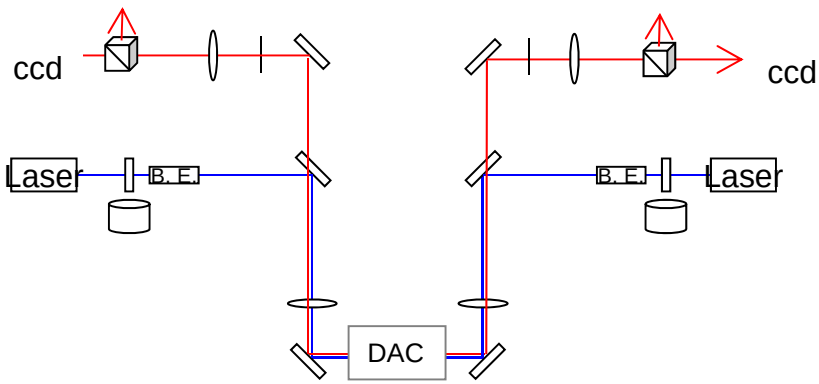




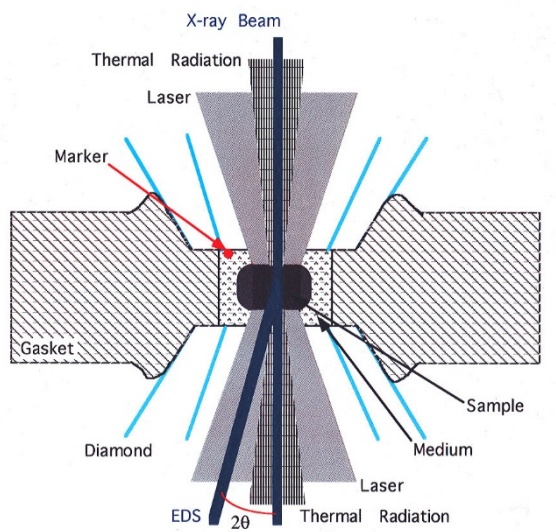


Double-sided laser-heating was invented to study Fe melting

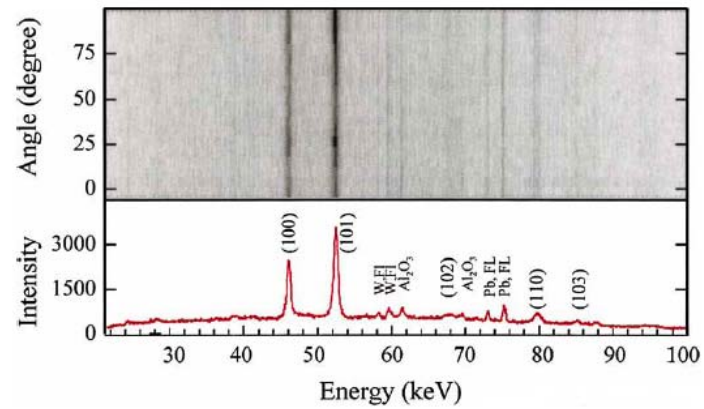
Double-sided laser heating: 1000 – 6,000K

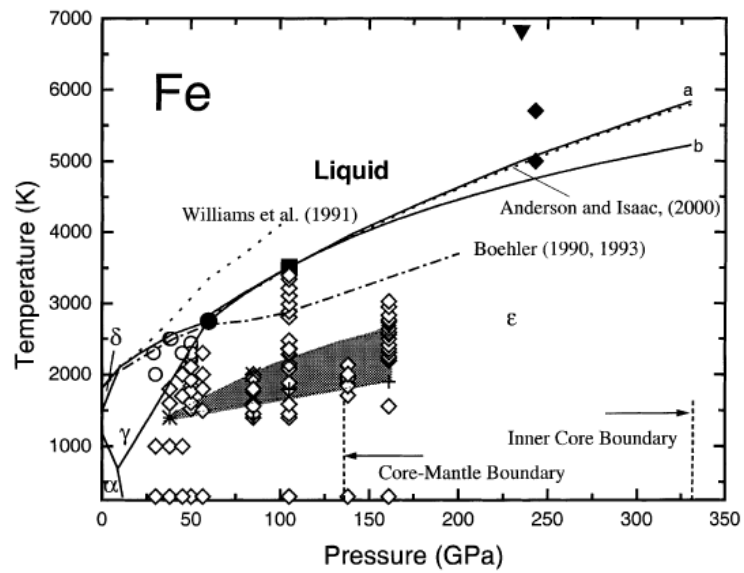


Shen et al (1996)



Melting of Fe





High P-T phase diagram of Fe
Ma *et al., PEPI.* **143**, 455 (2004)

Crucial knowledge of Fe is still missing at the core *P-T*

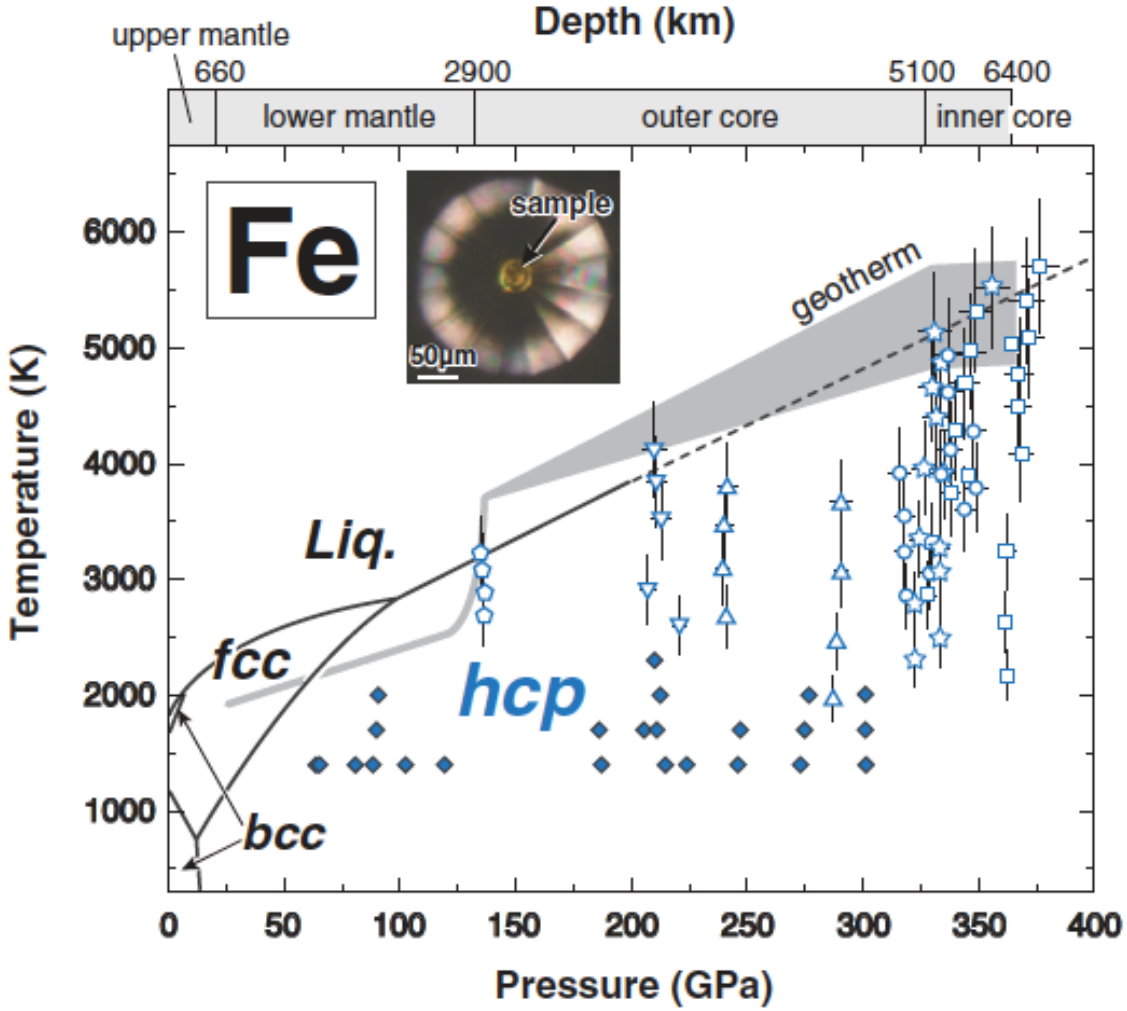
- ✧ Phase diagram and crystal structure
- ✧ Elasticity and elastic anisotropy
- ✧ Rheology and strength
- ✧ …

MBA upgrade may provide the long-awaited tools for measuring these properties

The Structure of Iron in Earth's Inner Core

SCIENCE VOL 330 15 OCTOBER 2010

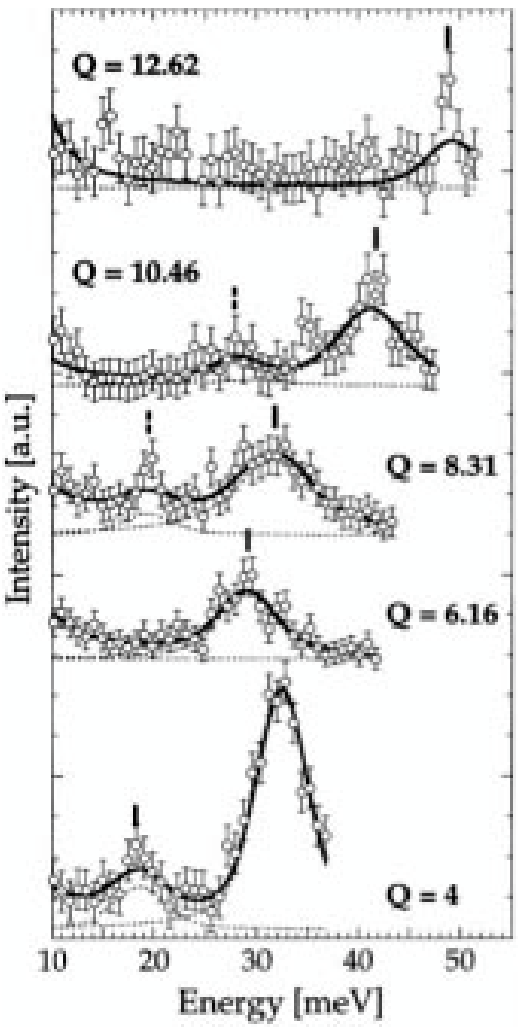
Shigehiko Tateno,[1,2]* Kei Hirose,[1,2]* Yasuo Ohishi,[3] Yoshiyuki Tatsumi[2]



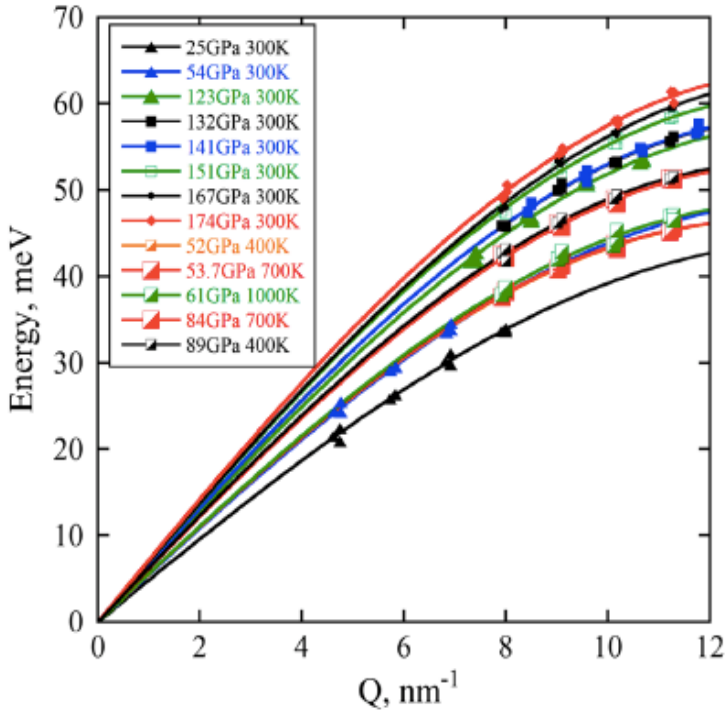
Fe has been studied at the *P-T* of Earth's inner core, but the data quality is limited.

100X higher brightness will provide sufficiently high-quality data to clinch the answer.

Sound velocity of Fe at core pressures from IXS measurements



Fiquet *et al., Science (*2001)

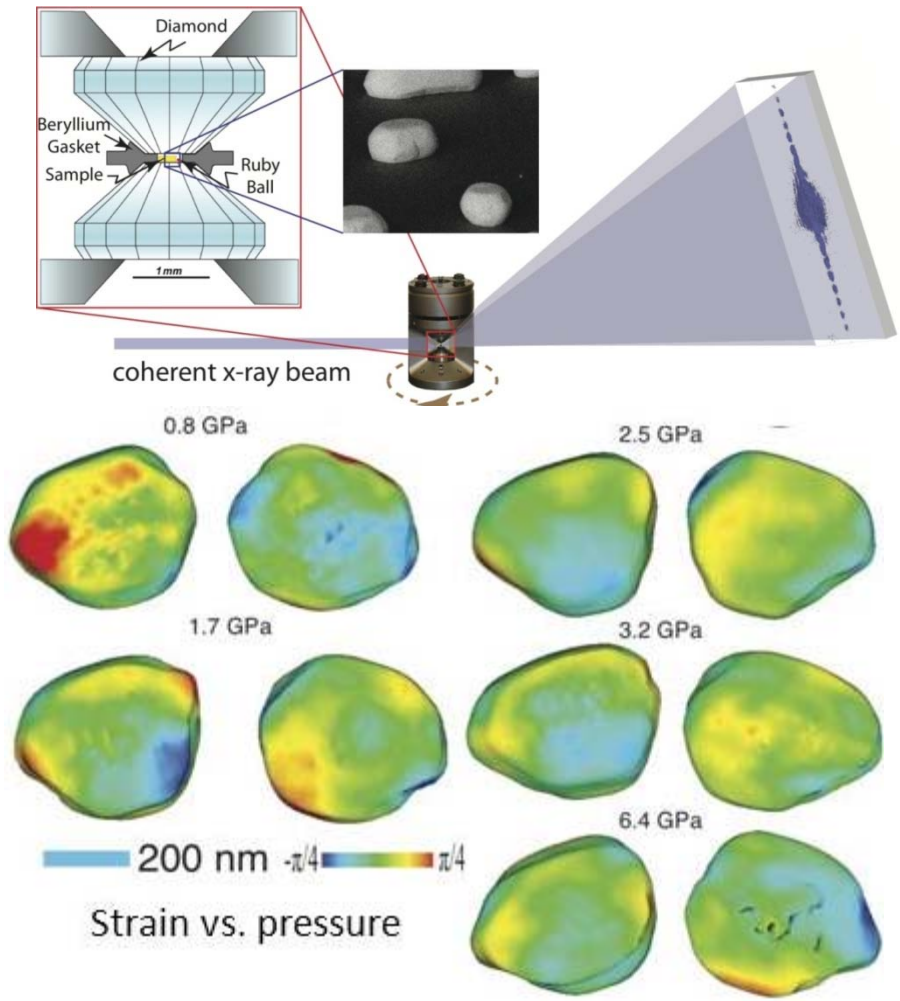


Ohtani *et al., GRL (*2013)

Powder sample only yields bulk sound velocity information with uncertain error in assumption of the sine function.

Sub-µm probe will allow selection of a µm-sized Fe single crystal for full phonon dispersion & elasticity determination.

Coherent Diffraction Imaging of Nanoscale Strain Evolution Under Pressures



Successful CDI has been demonstrated for 3D strain determination of a model nano-Au crystal up to 6 GPa.

100X brilliance & improved coherence will enable similar studies of nano-Fe to megabar pressures.

W. Yang et al *Nature Comm*. (2013)

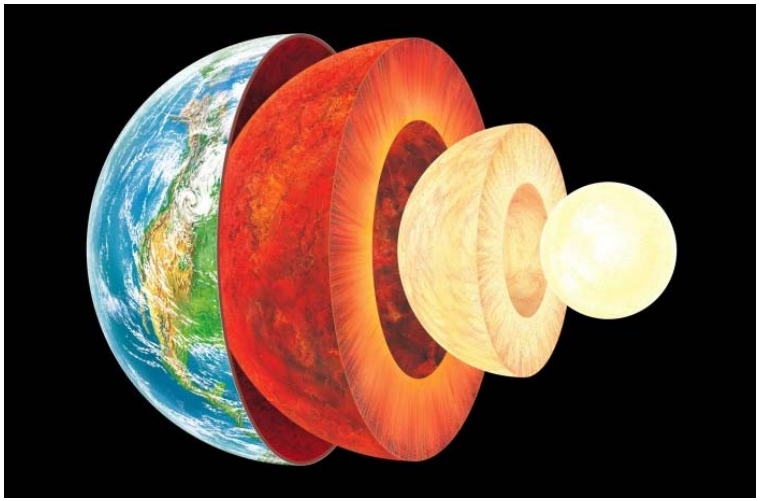
nature geoscience

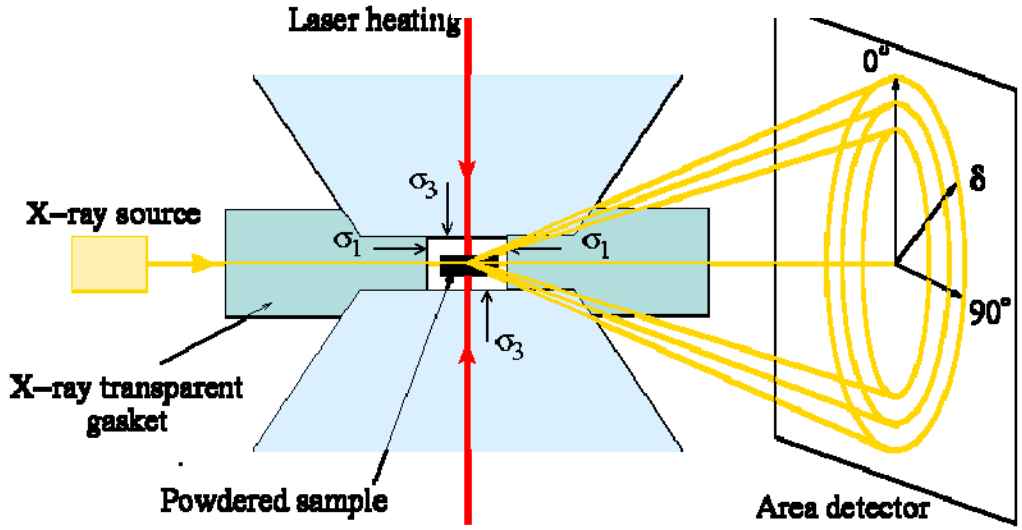
LETTERS

PUBLISHED ONLINE: 12 MAY 2013 | DOI: 10.1038/NGEO1808

Strength of iron at core pressures and evidence for a weak Earth's inner core

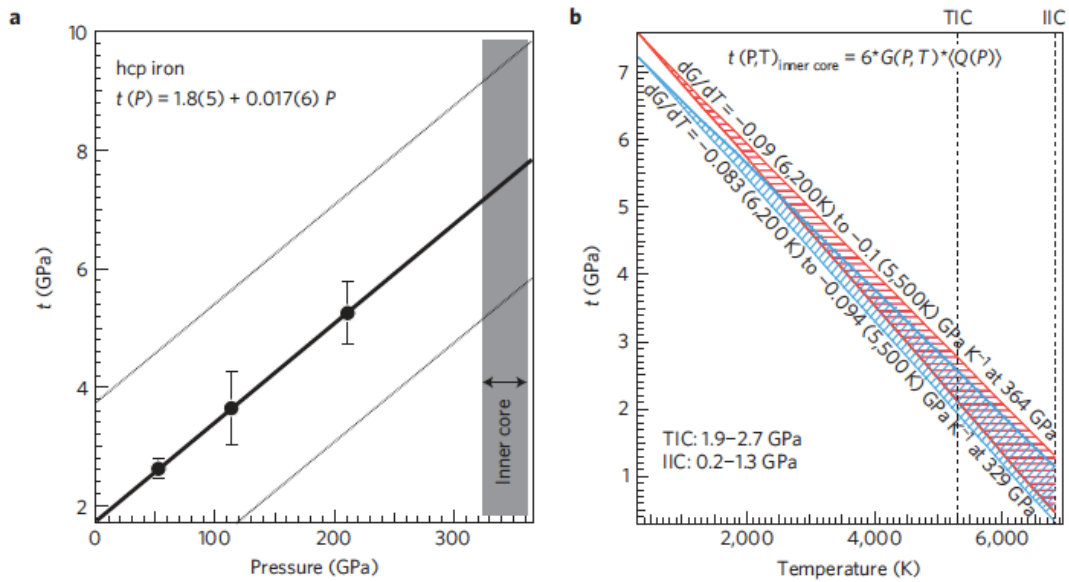
A. E. Gleason[1]* and W. L. Mao[1,2]





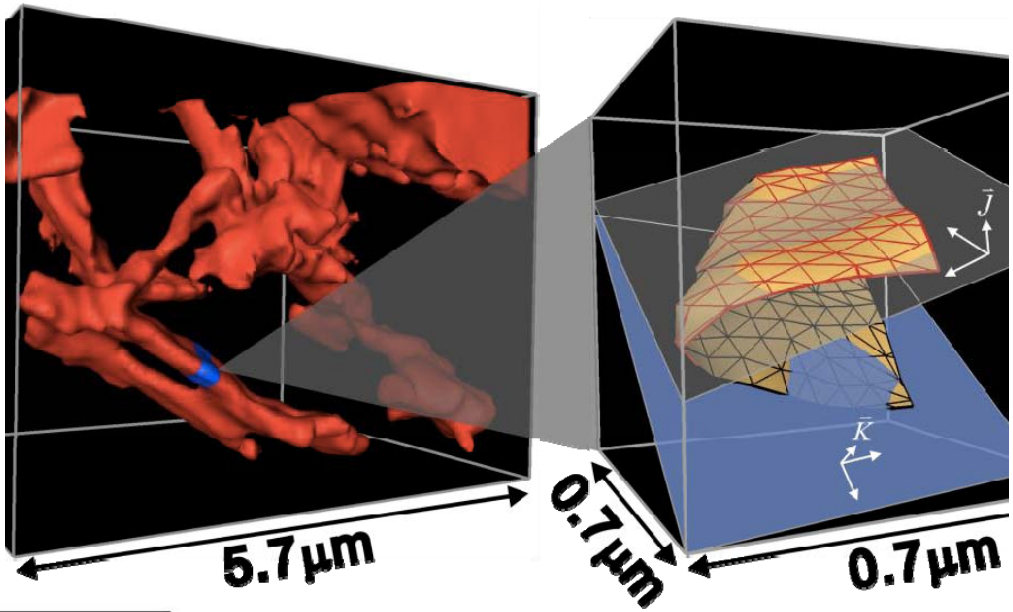
HP rheological studies with radial XRD and NRIXS were limited to room *T*.

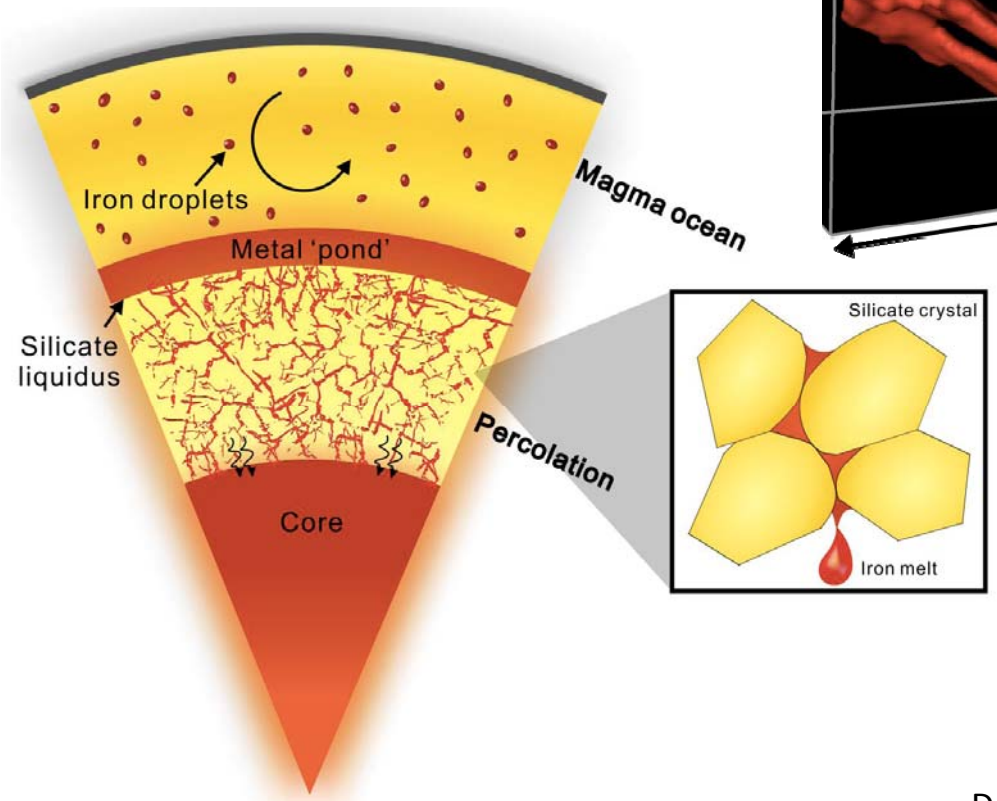
100X brilliance will enable similar studies at the relevant high *P-T* of the inner core.

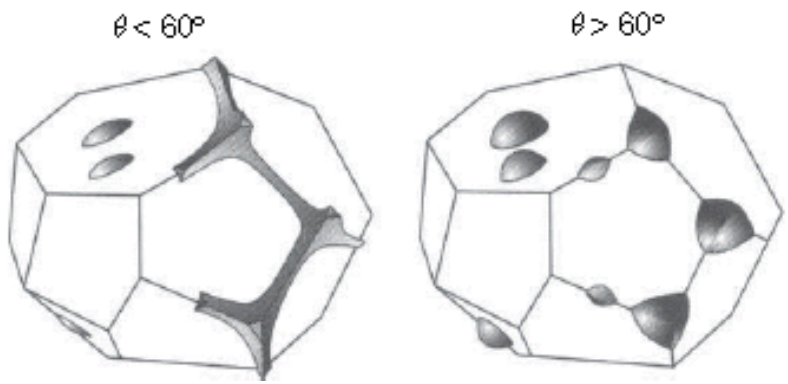


TXM study of core formation

Percolation of liquid iron alloy through solid silicate matrix is one possible mechanism



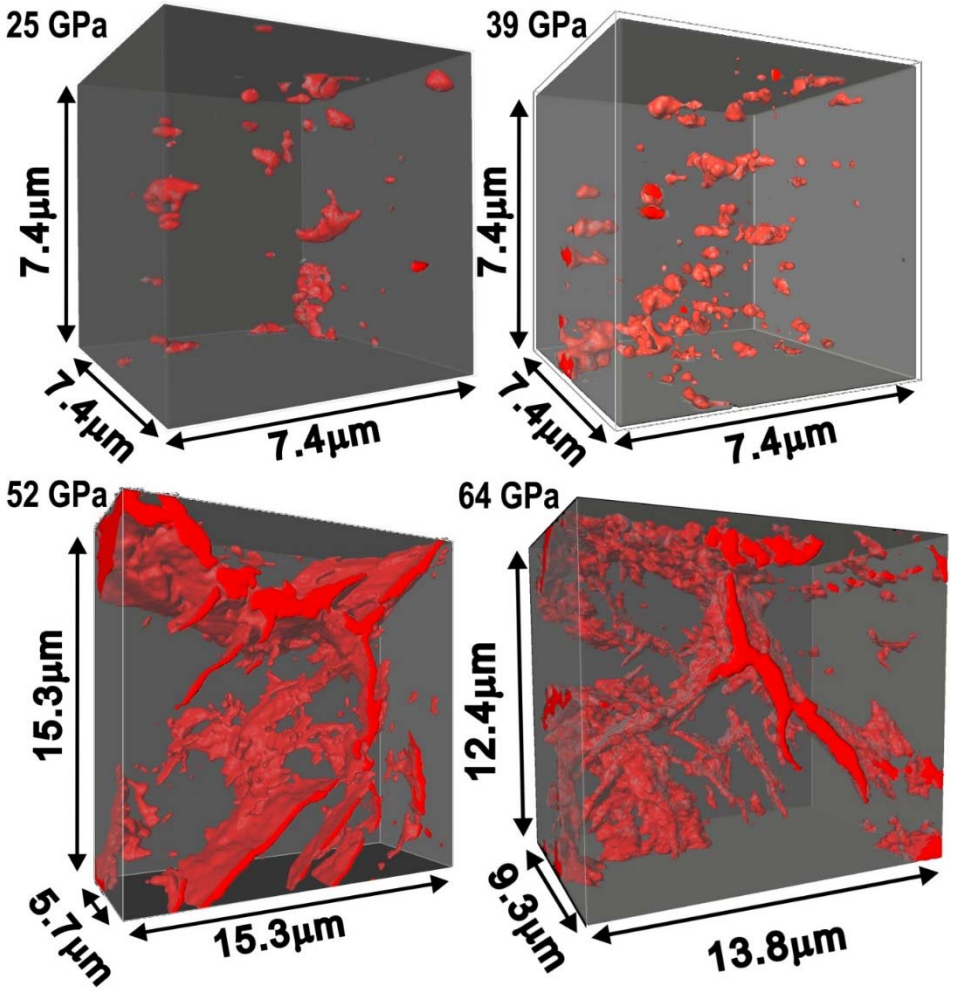




D. J. Stevenson, *In: Origin of the Earth*, 231-250 (1990)

C. Shi *et al*, *Nature Geoscience* (2013)

3D reconstructions of high P-T samples

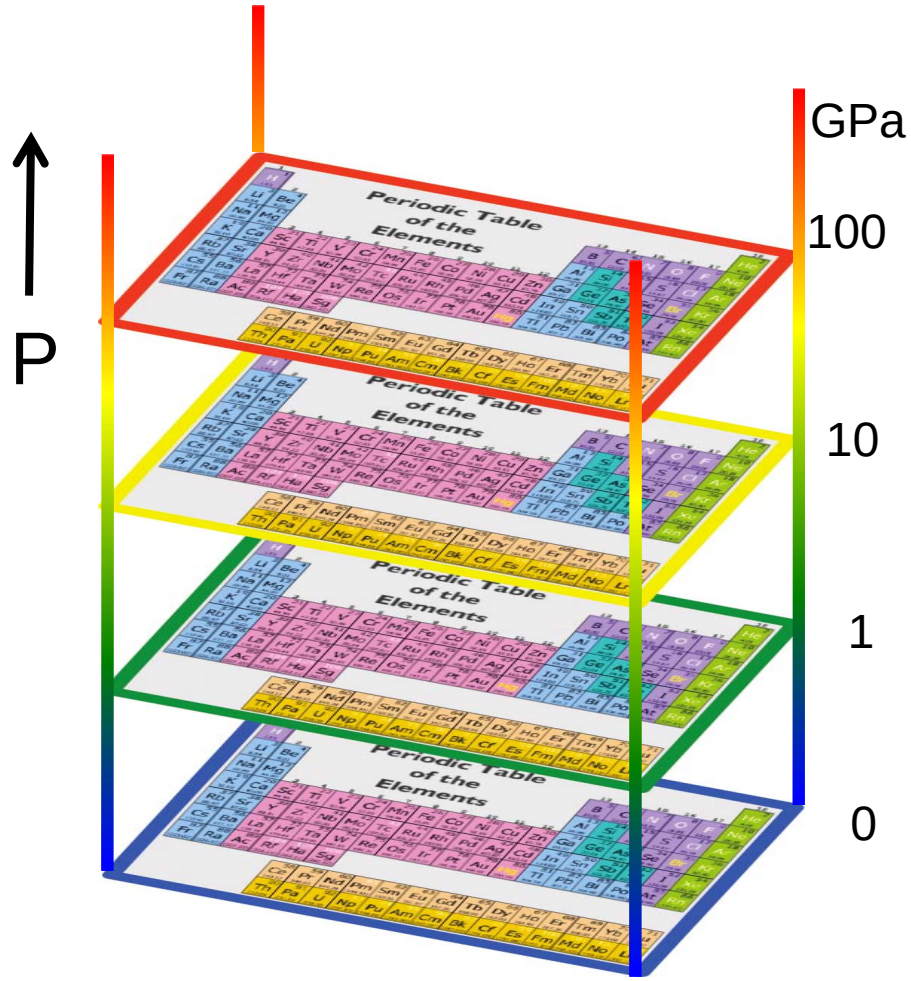


Percolation study is based on TXM imaging of samples quenched from high *P-T.*

100X brilliance will enable *in-situ* imaging studies using variety of contrast mechanisms (emission, XRS, etc.) of multiple phase assemblages *in-situ* at high *P-T* in real time.

C. Shi *et al*, *Nature Geoscience (*2013)

New materials at high pressure



- HP discoveries of novel materials and phenomena

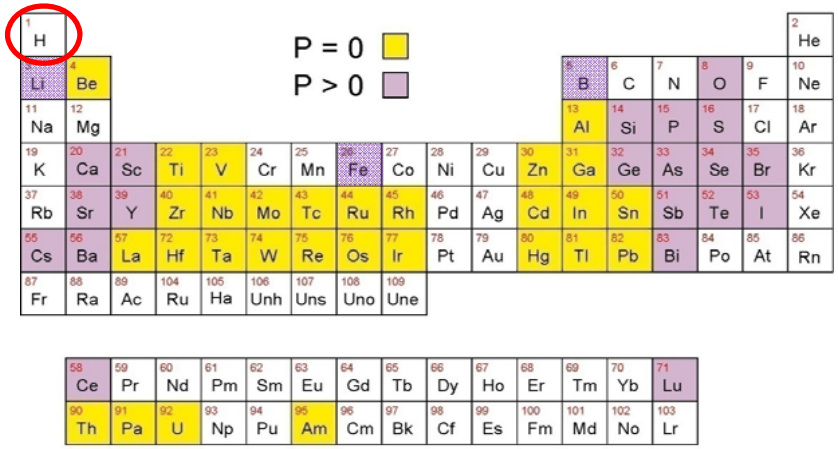
Grand challenges in high pressure energy materials

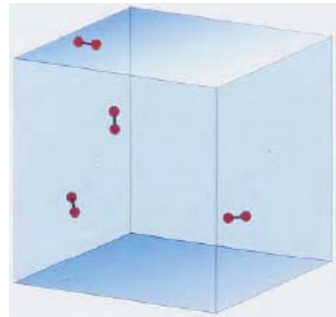
- ✧ Metallization of hydrogen
- ✧ Room temperature superconductivity
- ✧ Structures under extreme pressure
- ✧ Bonding under extreme pressure

MBA upgrade enables the critical tools for addressing these areas

Metallic Hydrogen

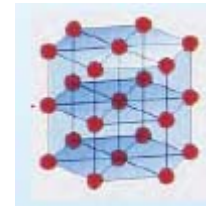
Periodic Table of Superconductors





25 GPa?

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

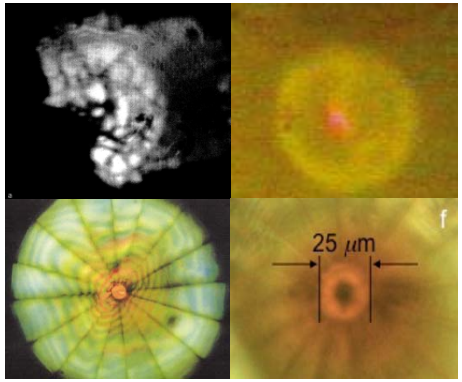
Chandrabhas Narayana*, Huan Luo*†, Jon Orloff‡ & Arthur L. Ruoff*

** 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)

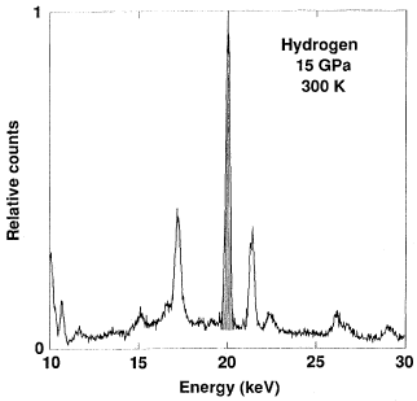
Diamond-anvil-cell techniques have been developed to confine and measure hydrogen samples under static conditions to pressures above 300 GPa from 12 to 300 K using synchrotron infrared and optical absorption techniques. A decreasing absorption threshold in the visible spectrum is observed, but the material 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.

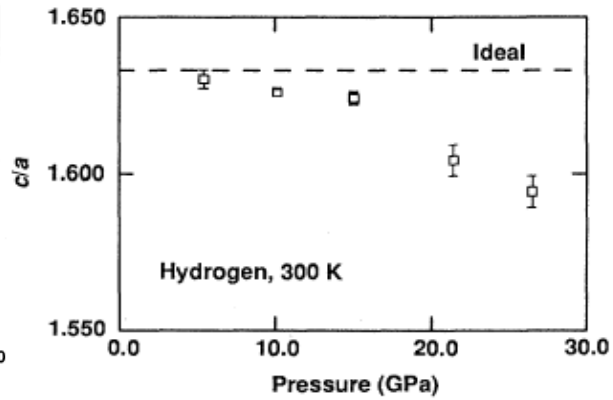
Metallization at >500 GPa?
Crystal structure?
Phase diagram?

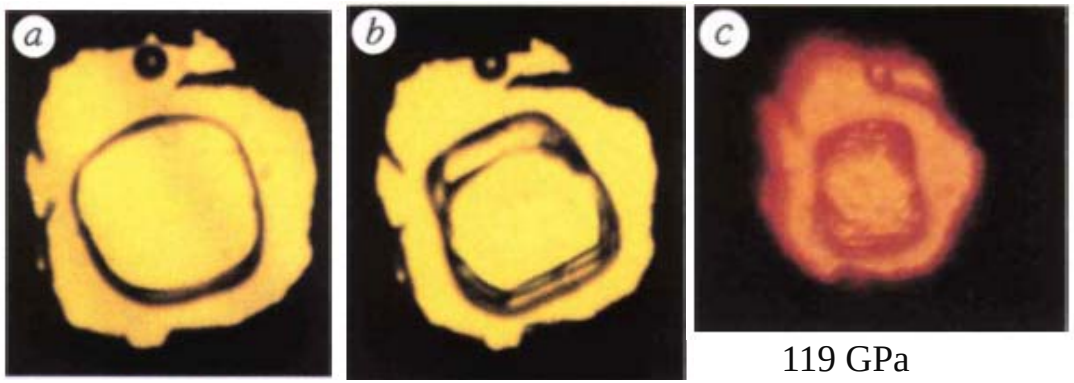
XRD of H_2 Phase I

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







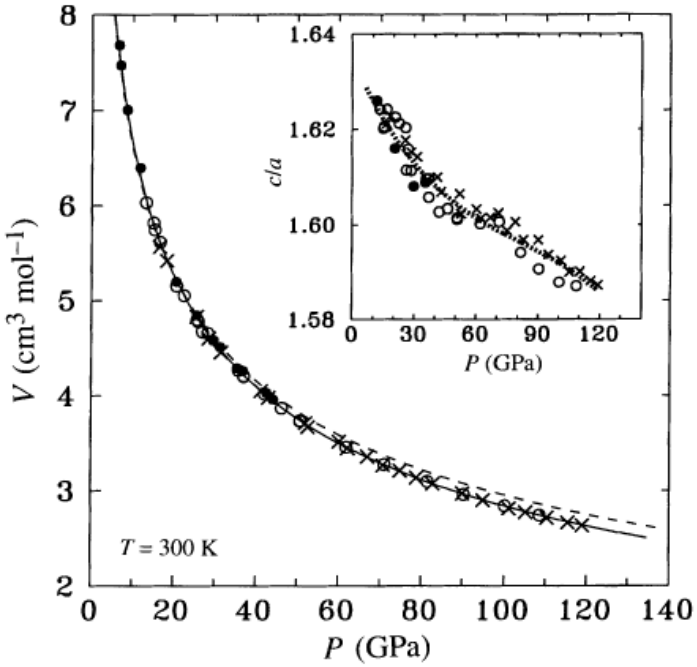
119 GPa

15μm hydrogen single crystal in helium medium

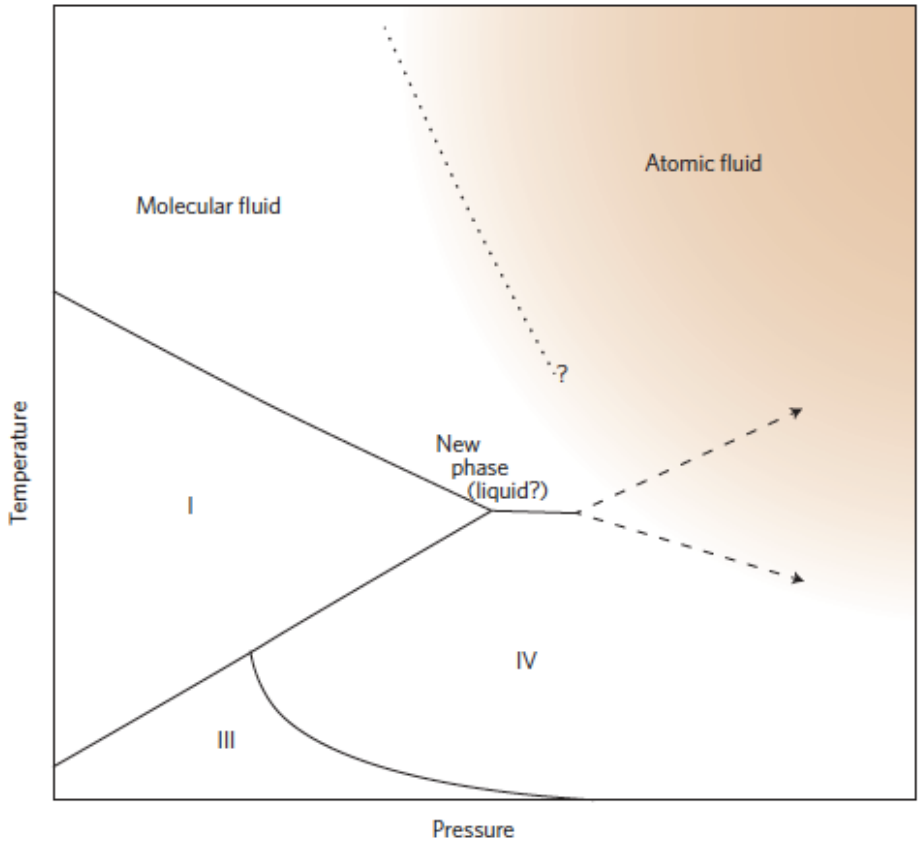
X-ray diffraction and equation of state of hydrogen at megabar pressures 1996

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



Phase diagram of hydrogen



W. Mao, *Nature Materials* (2015)

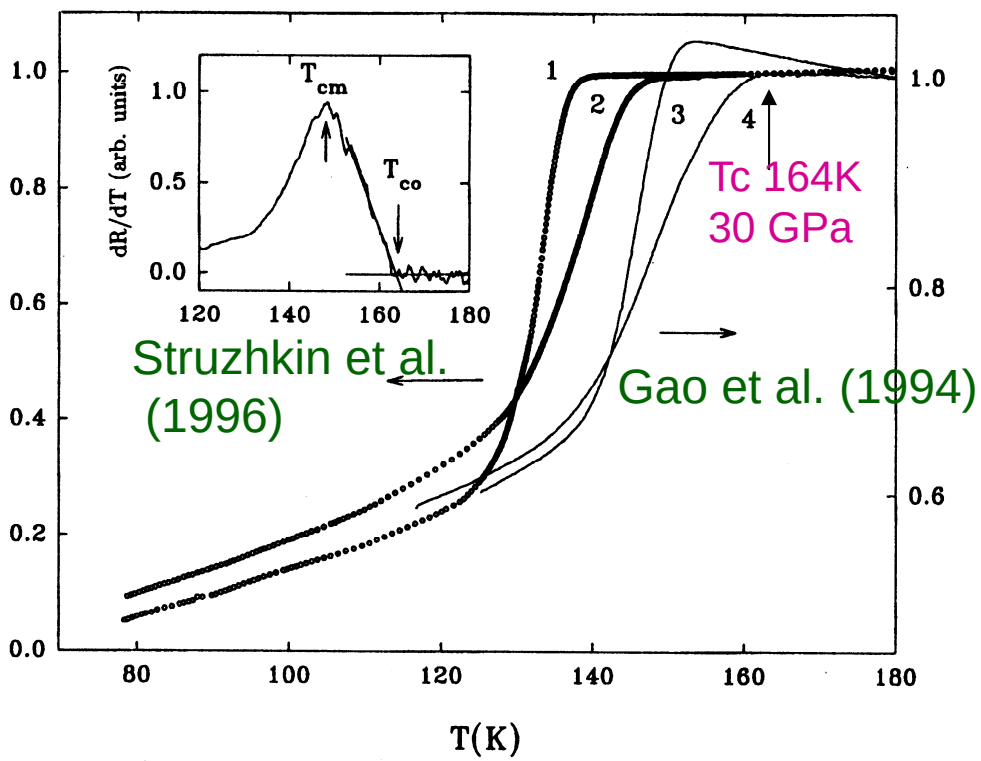
Multiple high *P-T* phase transitions have been observed by Raman spectroscopy and have been predicted by theory, but their crystal structures remain unknown.

With 100X brilliance we will be able to observed XRD from the very light hydrogen, and determine its structure.

Reaching higher Tc

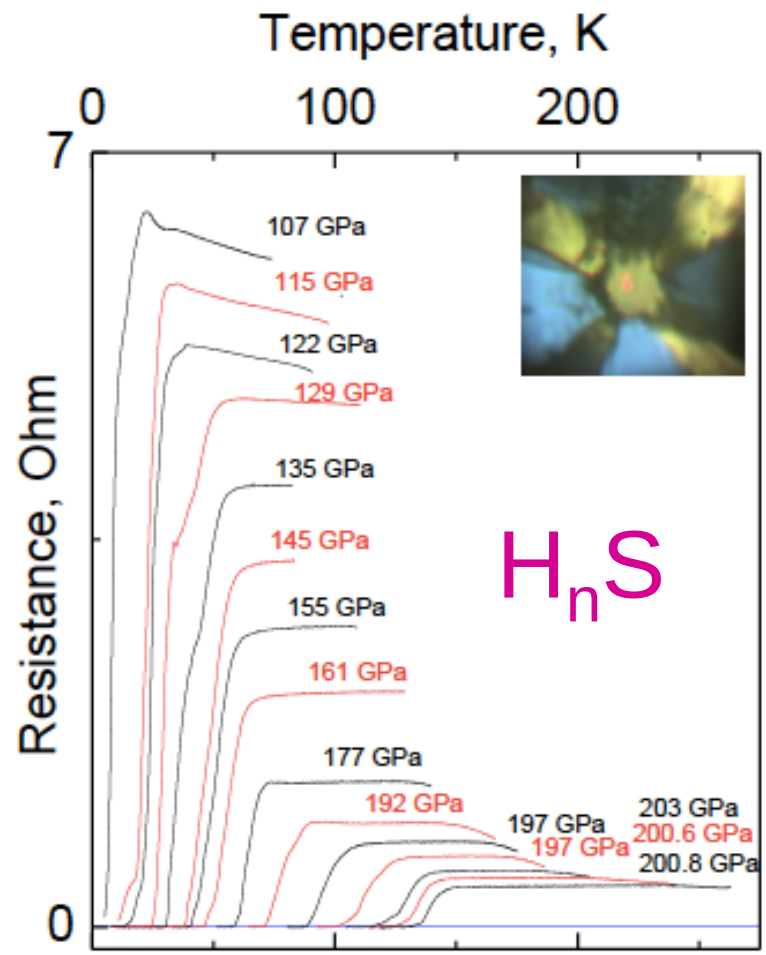
Previous Record
Tc = 164 K at 30 GPa

$HgBa_2Ca_2Cu_3O_{8+\delta}$



New Record
Tc = 203 K >150 GPa

Drozdov et al., *online (arxiv)*



Needs XRD to confirm the phase & composition

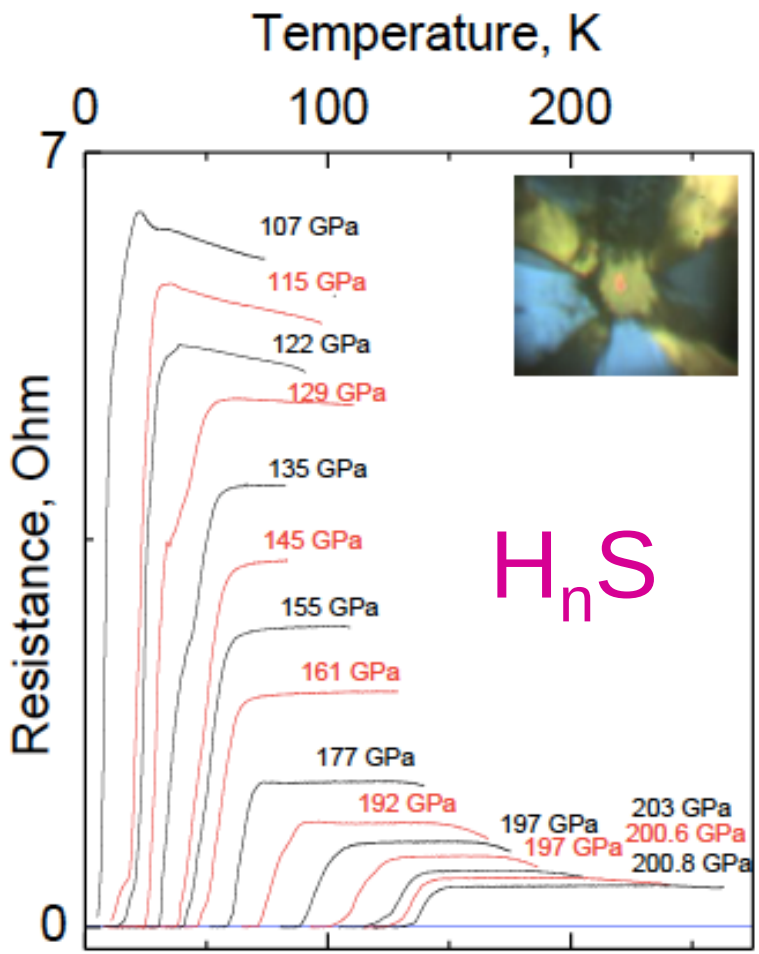
Reaching higher Tc

New Record
Tc = 203 K >150 GPa

Drozdov et al., *online (arxiv)*

Astonishingly high T_c was reported online Dec 2014, but not yet published - composition and structure information still needed

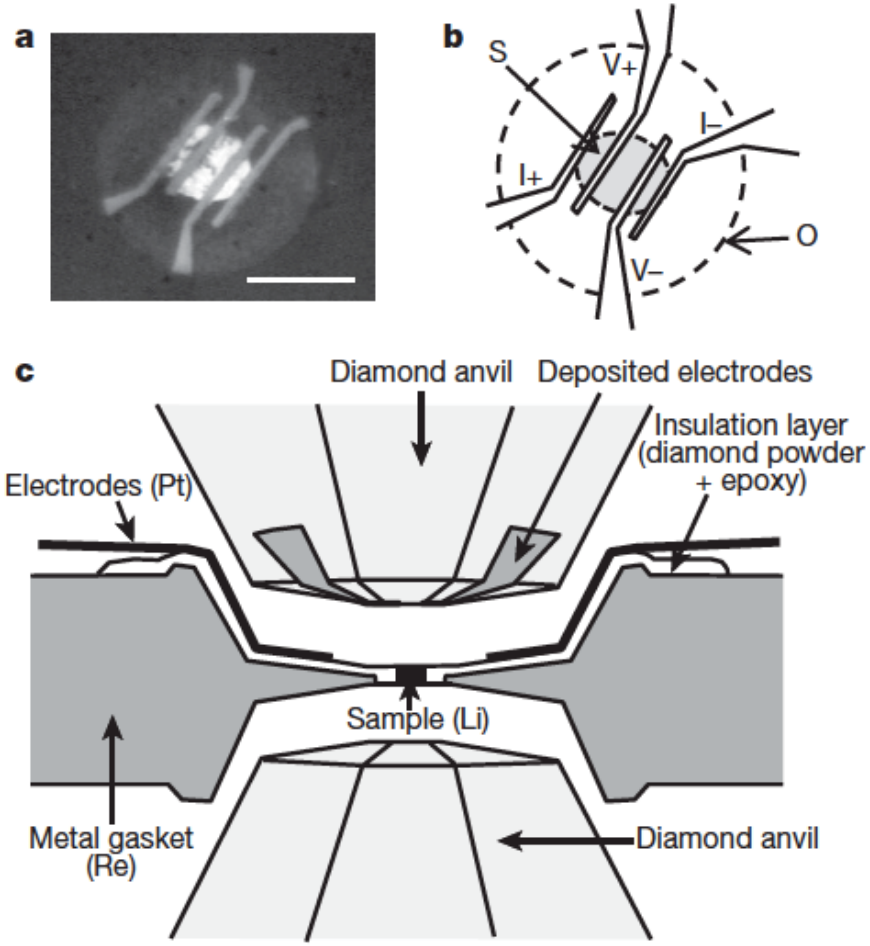
100X brilliance would enable determination of crystal structure and composition.



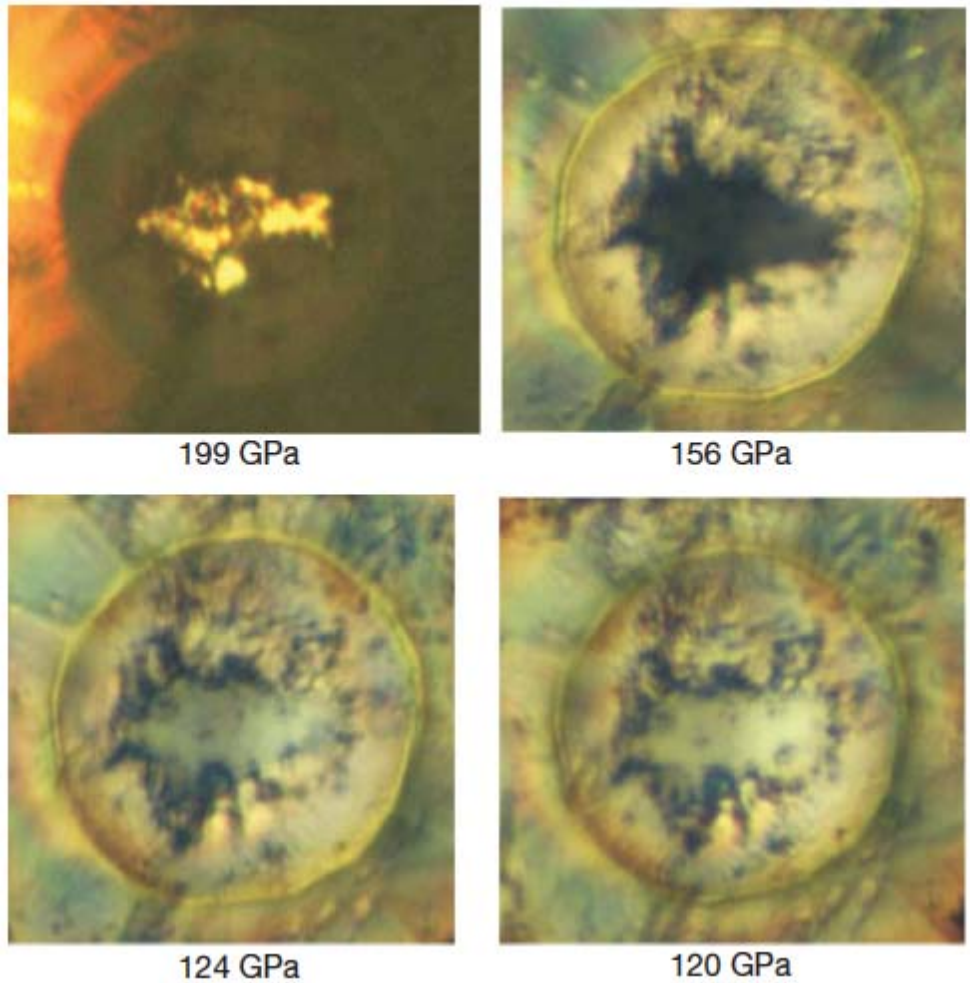
Needs XRD to confirm the phase & composition

Free Electron Metal to Insulator

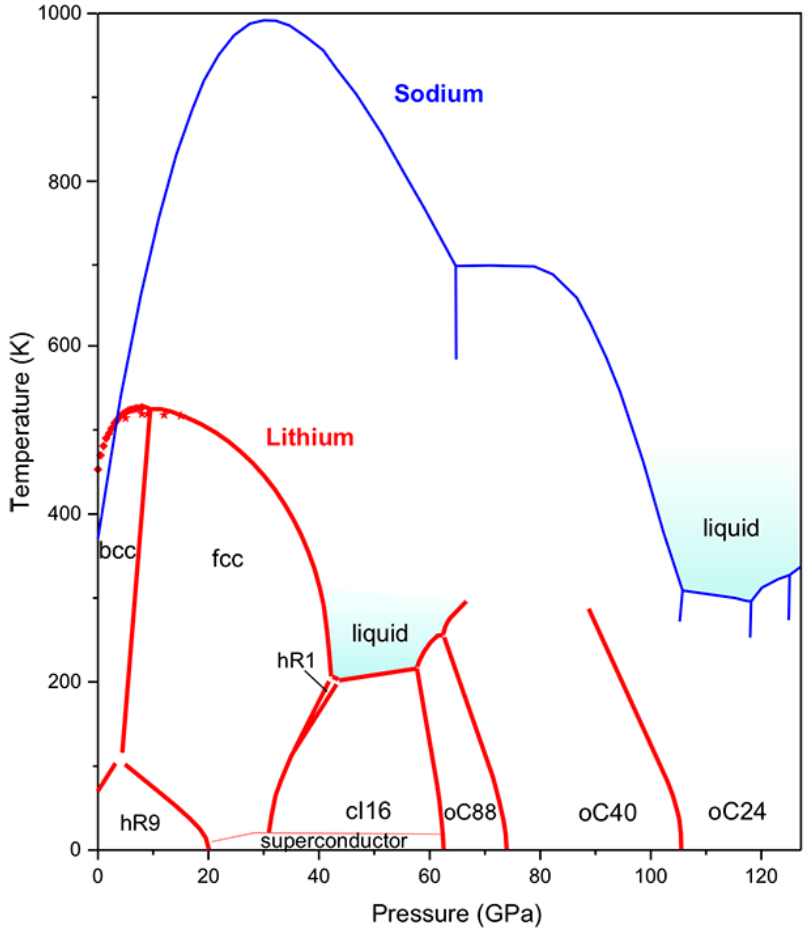
Semiconducting Li above 80 GPa
Matsuoka & Shimizu, *Nature* (2009)



Transparent Na ~200 GPa
Ma et al, *Nature* (2009)



Phase diagram of light alkali metals



Na phase diagram, Gregoryanz et al, *PRL* (2005); *Science* (2008)

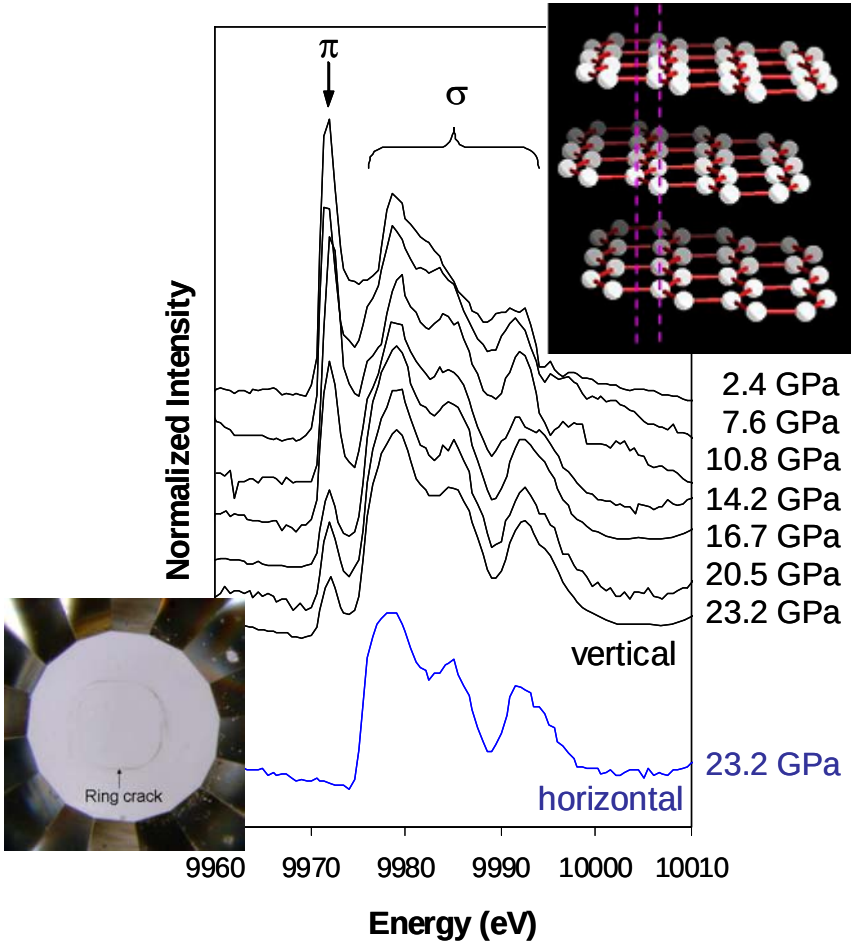
Li phase diagram, Guillaume et al, *Nature Physics* (2008)

Very complicated phase diagrams are observed in 'simple' alkali metals at high pressure.

100X brilliance will enable the extension phase diagram to the intriguing insulating and transparent phases.

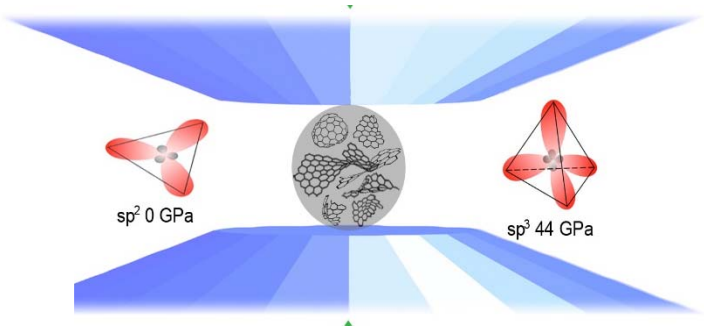
New Carbon Allotropes at High Pressure

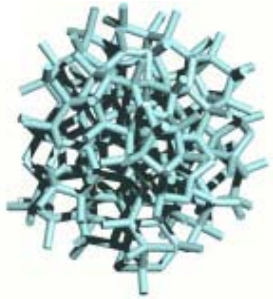
Bonding changes in light elements



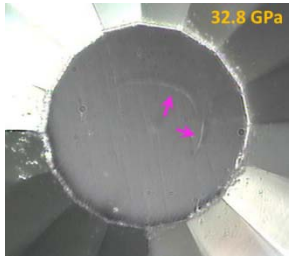
X-ray raman of graphite at high pressure shows the evolution of bonding and transformation to a new, superhard phase

W. Mao *et al*, *Science* (2003)

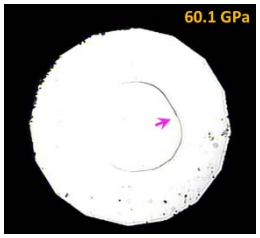


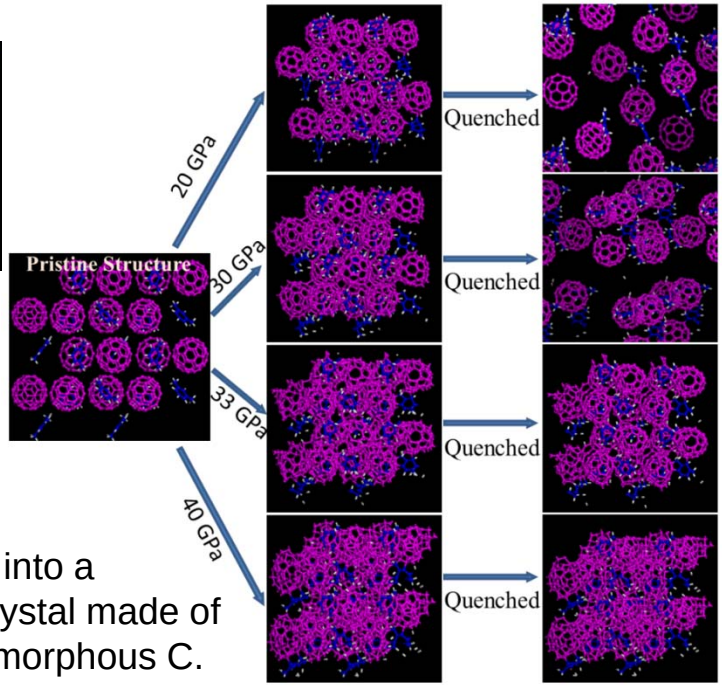


sp^2 bonds in glassy carbon compressed into sp^3, creating a new superhard amorphous diamond



Lin *et al.*, *PRL* **107**, 175504 (2011)
Niu *et al.*, *PRL* **108**, 135501 (2012)

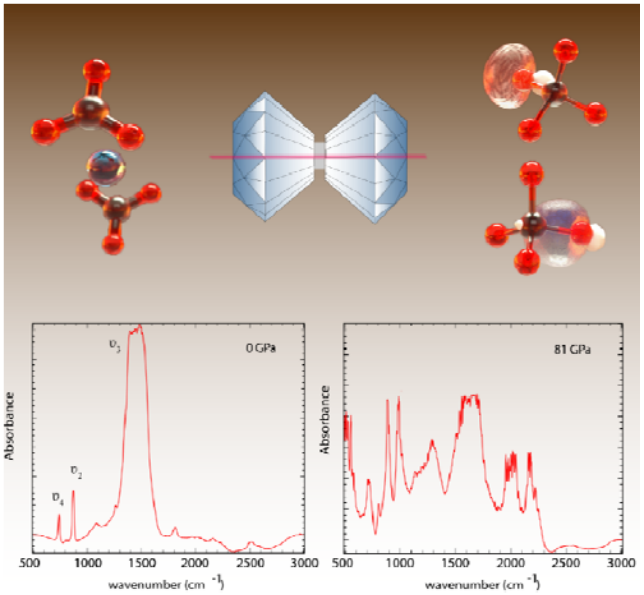


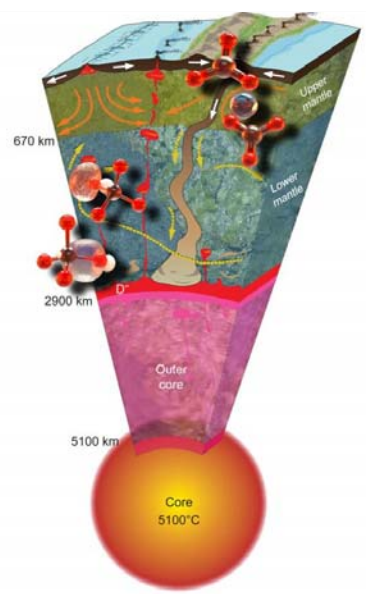


Solvated C_{60} compressed into a superhard crystal made of clusters of amorphous C.

Wang *et al*, *Science* (2012).

Bonding changes in planetary interiors





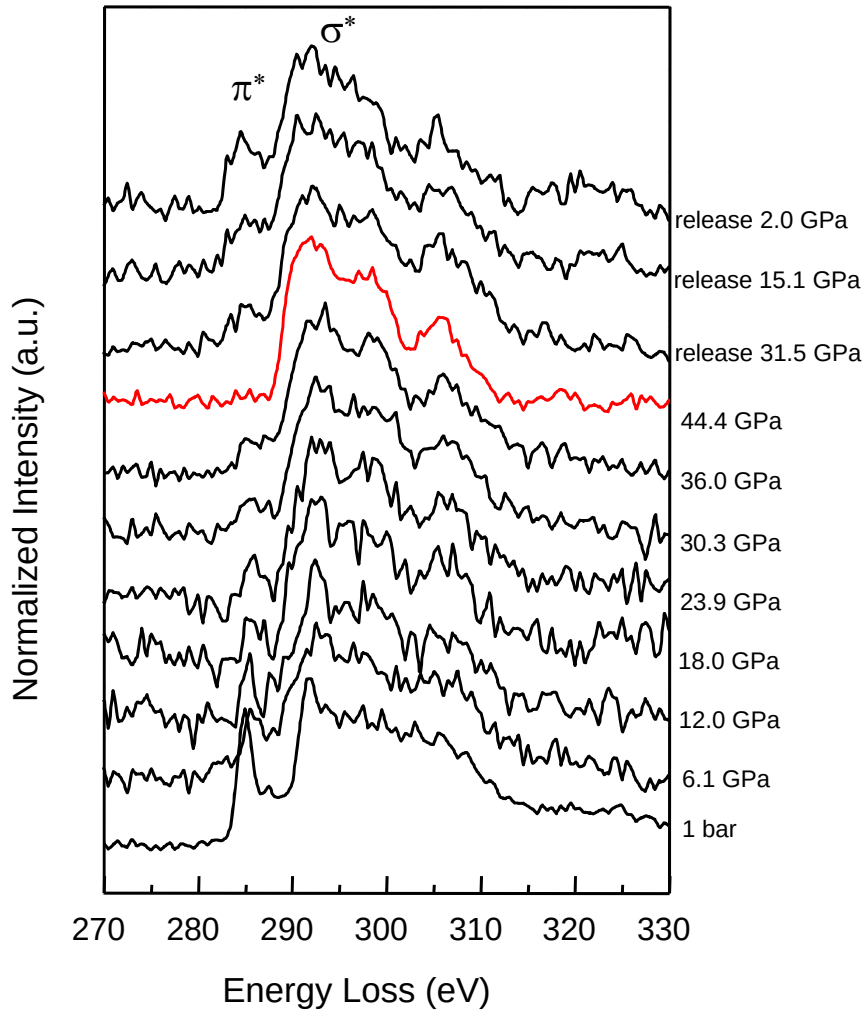
- Change from three to four coordination in carbonates above 80 GPa from IR and quenched samples
- Impact on carbonate behavior
  - Elasticity
  - P-T-x stability
  - Reactivity with other mantle phases
  - Properties of melt (e.g. viscosity)
- Can we measure bonding at very high pressures and temperatures?

Boulard *et al*, *Nature Comm.* (*2015*)

PRL 107, 175504 (2011) PHYSICAL REVIEW LETTERS week ending 21 OCTOBER 2011

Amorphous Diamond: A High-Pressure Superhard Carbon Allotrope

Yu Lin,[1,*] Li Zhang,[2] Ho-kwang Mao,[2] Paul Chow,[3] Yuming Xiao,[3] Maria Baldini,[4] Jinfu Shu,[2] and Wendy L. Mao[1,5]



X-ray Raman spectroscopy of the carbon K-edge shows pressure-induced bonding changes of sp^2 to sp^3.

100X brilliance will enable studies of light element bonding to multi-megabar pressure (coupled with high temperature) where we expect dramatic changes.

Outlook for high *P-T* experiments

100X brilliance can be used for transformative advances in energy, spatial, and temporal resolution of HP-SR techniques

- Nano-XRD
- Time-resolved XRD and XAS
- Near & extended edge x-ray absorption & emission spectroscopy
- Resonant & non-resonant inelastic x-ray scattering spectroscopy
- Nano tomography
- …

Outlook for high *P-T* experiments

The new generation of HP-SR techniques enable the full investigation of crucial properties and behavior

- Crystallography to inner core *P-T*, high *P*- variable *T* phase diagrams
- Site occupancy, bonding, charge, partitioning, electronic and magnetic structures
- Dynamics of phase transitions and melting
- Melt density, viscosity, and transport
- ...

Outlook for high *P-T* experiments

The resulting knowledge will allows us to address fundamental questions in a wide range of research areas

- Deep Earth
  - Crystal structure, texture, and rheology of the inner core
  - Core formation and separation from the mantle
  - Composition and temperature of the outer core
  - Origin of the D” layer – boundary between mantle and core
  - …
- Energy Materials
  - Developing materials for a wide range of energy applications – superconductors, hydrogen storage, batteries, superhard materials, photonics, etc.

Outlook for high *P-T* experiments

…also many opportunities in other high pressure research areas, also dynamic compression

Thank you!