# High Pressure Techniques

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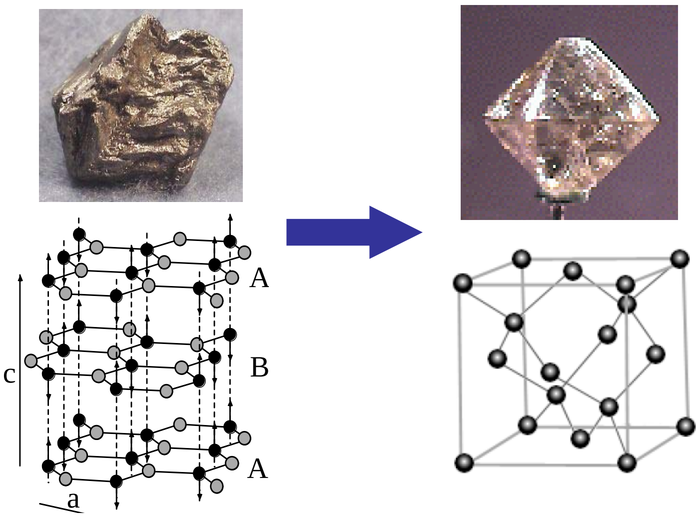
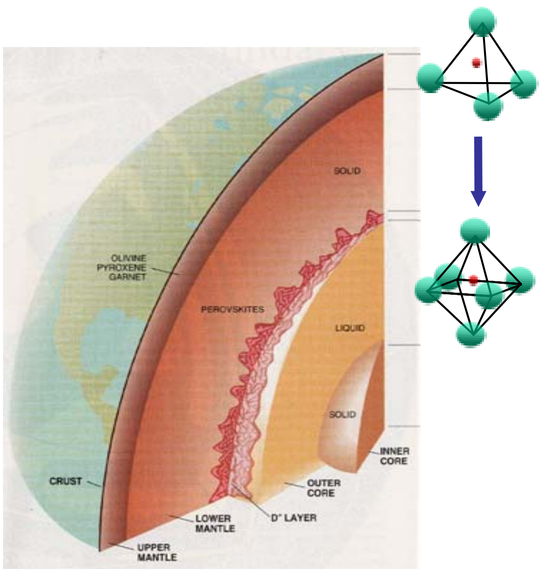
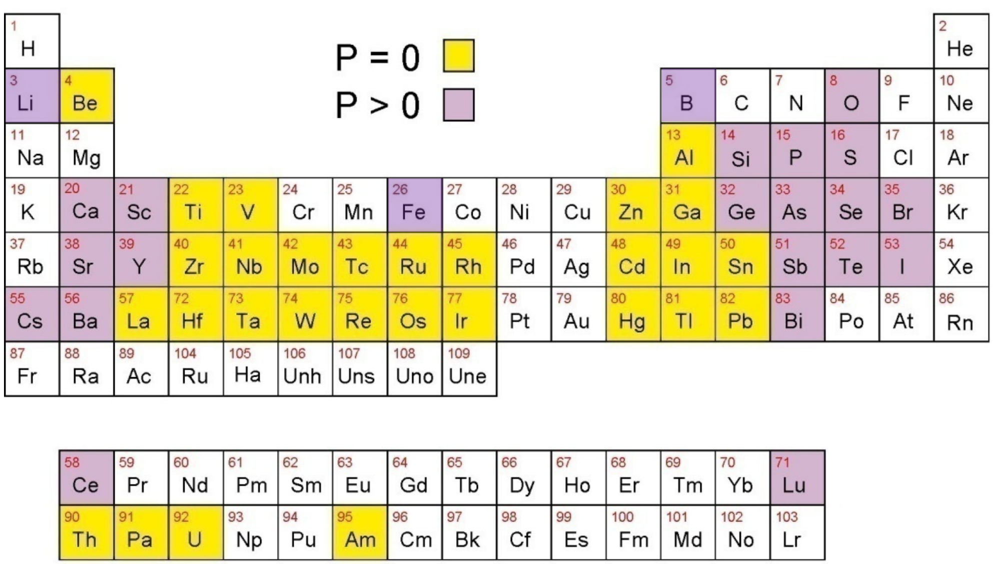
*& Photon Science, SLAC National Accelerator Laboratory*

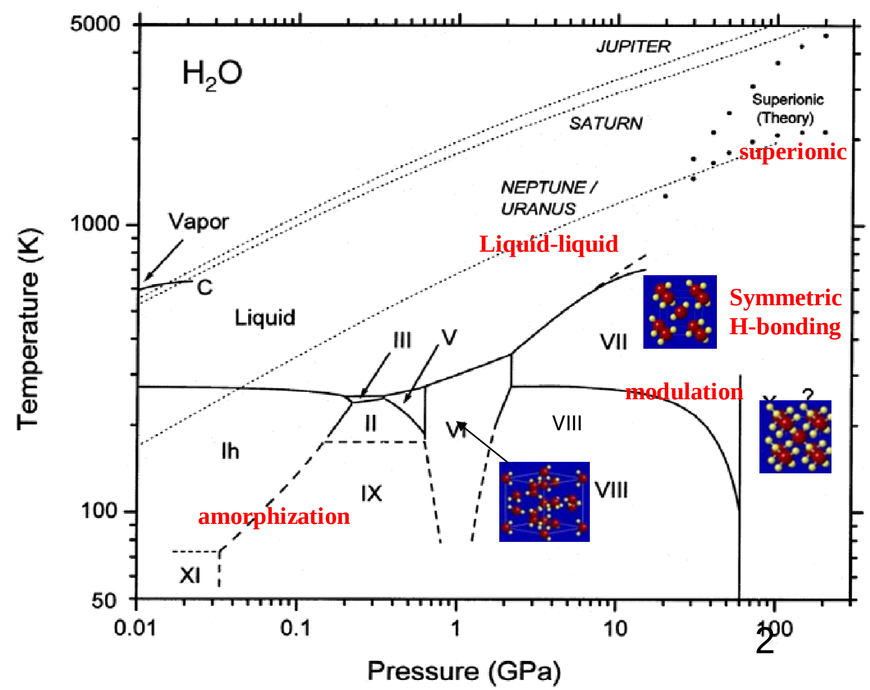
# Pressure changes everything



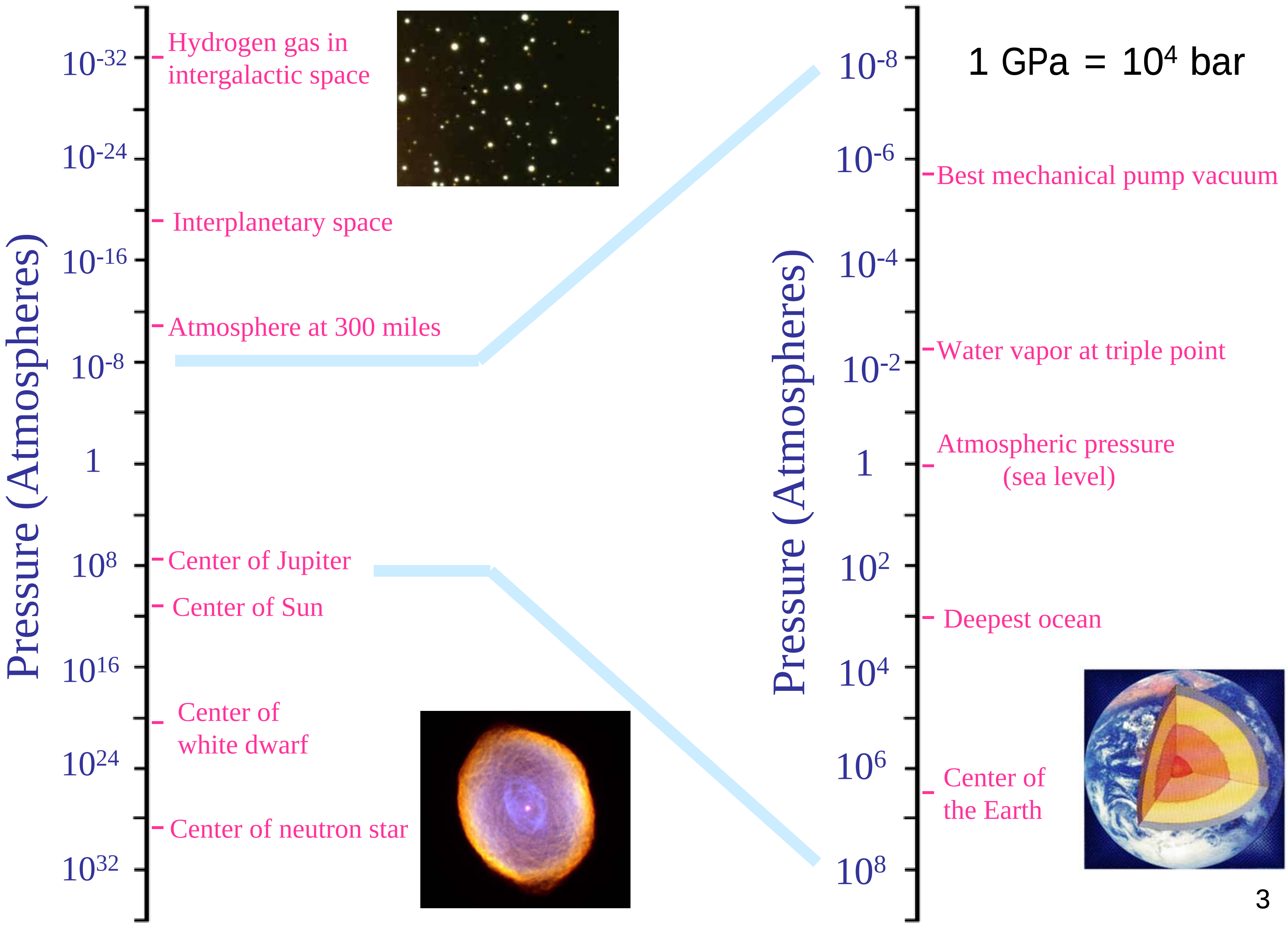




Periodic Table of Superconductors



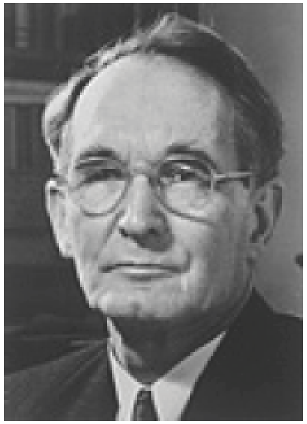



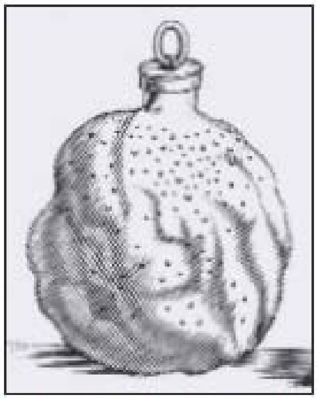
# Range of Pressure in the Universe



# High-pressure science has been enabled by experimental progress

Percy W. Bridgman
1882-1961





**Early experiments**
Scientists from the Accademia del Cimento in 17th-century Florence attempted to compress water by repeatedly striking a water-filled metal sphere.

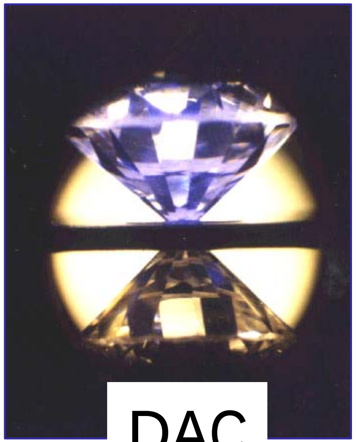
Before 20th Century
- Solids and liquids are nominally regarded as incompressible

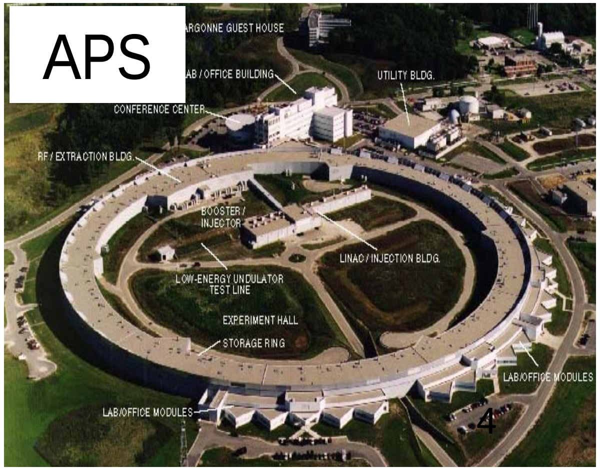
1946
- P. W. Bridgman receives Nobel prize in Physics "for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics"

1986
- Diamond anvil cell (DAC) reaches beyond 300 GPa

~2000
- Development of array of probes for high *P* & variable *T* characterization

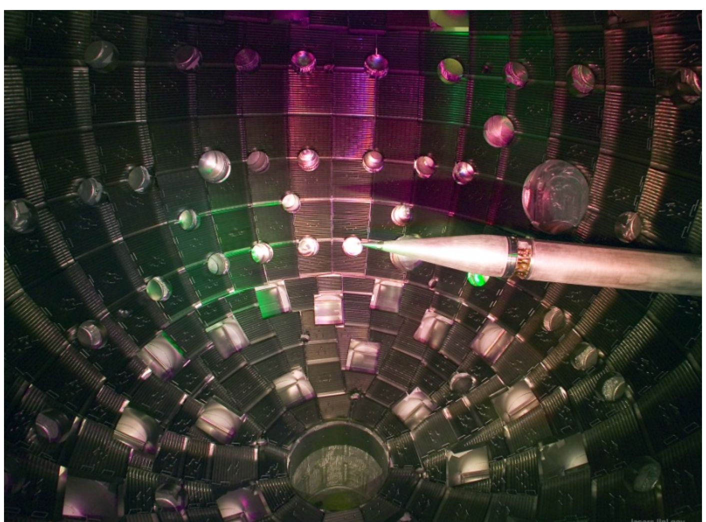
Now
- exciting science to be reaped



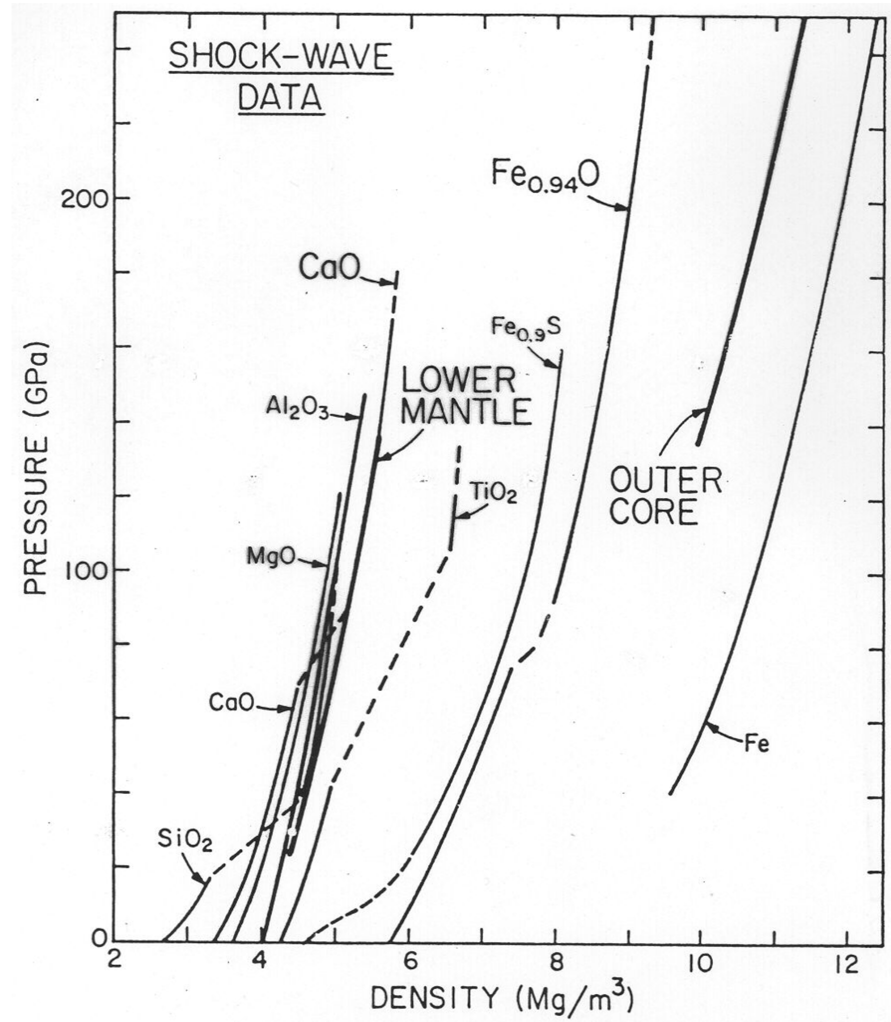



# How do we reach high pressure?

- Dynamic compression
  - Shockwave
    - Nuclear explosion
    - Gas guns
    - Magnetic field
    - Lasers
    - Duration: μsecs
    - P vs. ρ curve (Hugoniot)



NIF target chamber

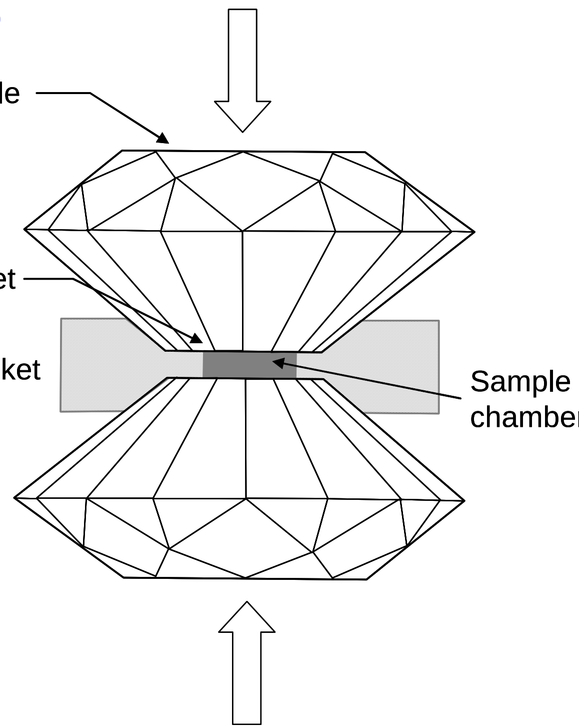


# How do we reach high pressure?

- Static compression
  - Piston cylinder & anvil devices
    - Duration: indefinite
    - Pressure=Force/Area

- Multi-anvil apparatus
  - Pressure: 50 GPa
  - Temp: 2500$^{o}$C
  - Sample size: mm$^3$

# How do we reach high pressure?



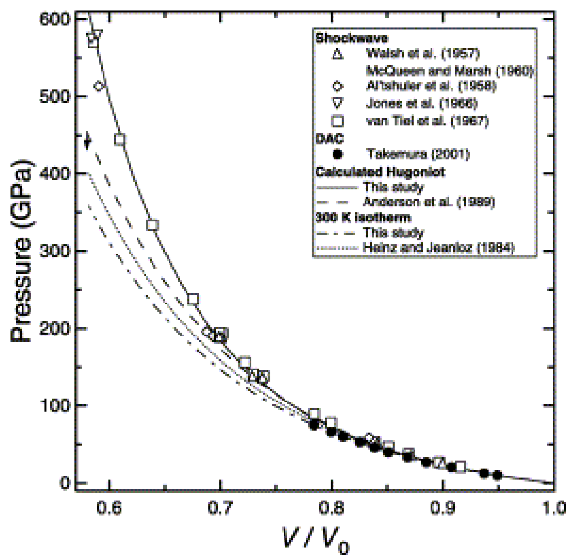

- Diamond Anvil Cell
  - Pressure: ambient to 500 GPa (1 GPa= 10,000 bar)
  - Temp: mK to 5000 K
  - Sample size: < 0.001 $mm^3$
  - Transparent to large range of E-M radiation

L-$N_2$
L-He
mK

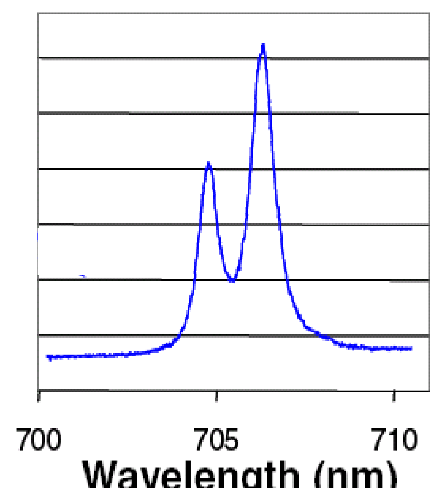
Laser & Resistive heating

# How do we measure pressure?

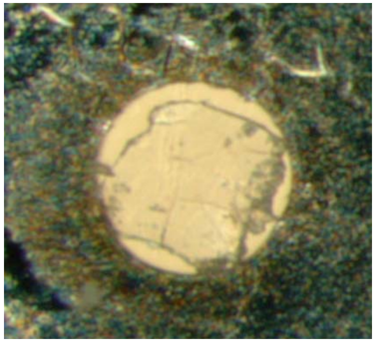
- Internal standards
  - Ruby fluorescence
  - Equation of state (Au, Ag, Pt, NaCl, etc.)
- Pressure calibration
  - Piston-cylinder
  - Shock wave
  - Brillouin spectroscopy
  - Ultrasonics

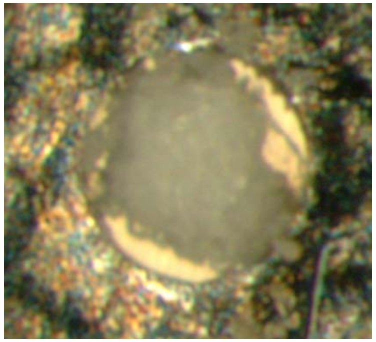


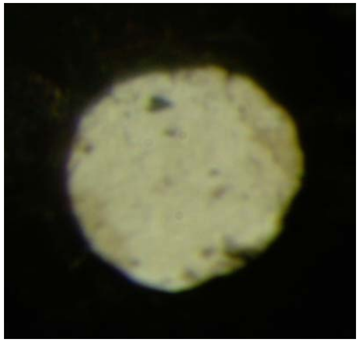

Shim *et al*, EPSL 2002

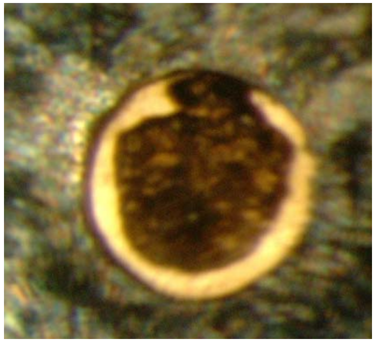


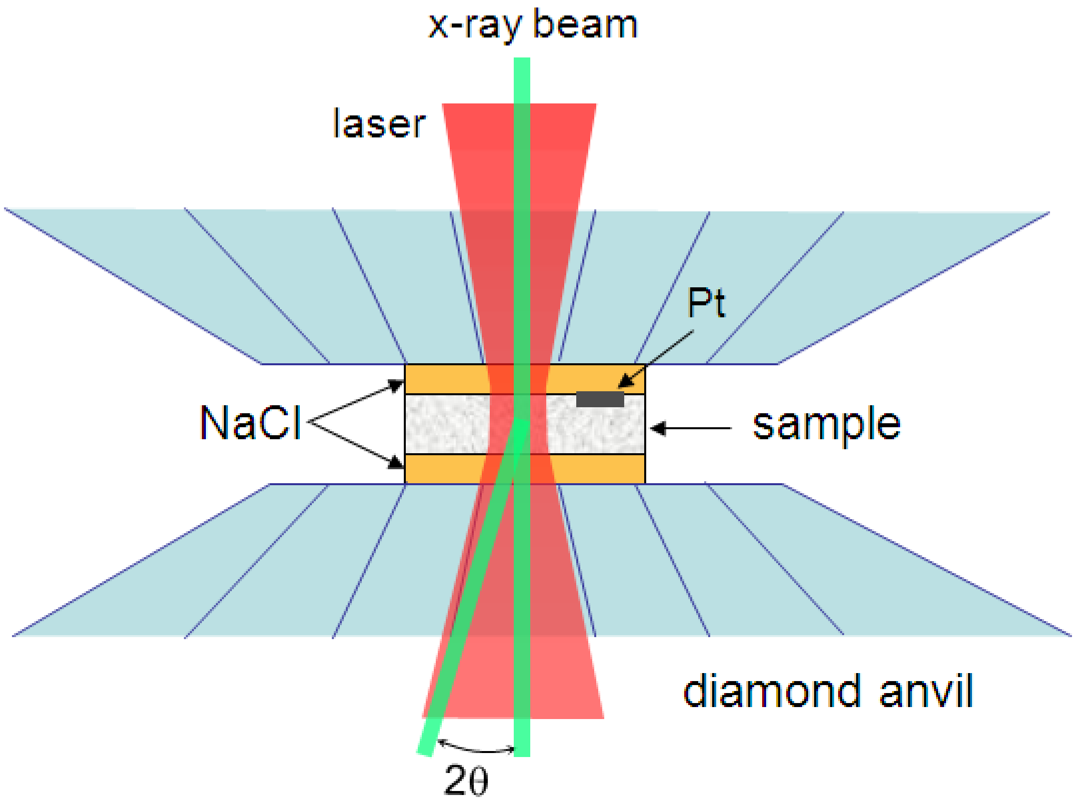
# Sample preparation





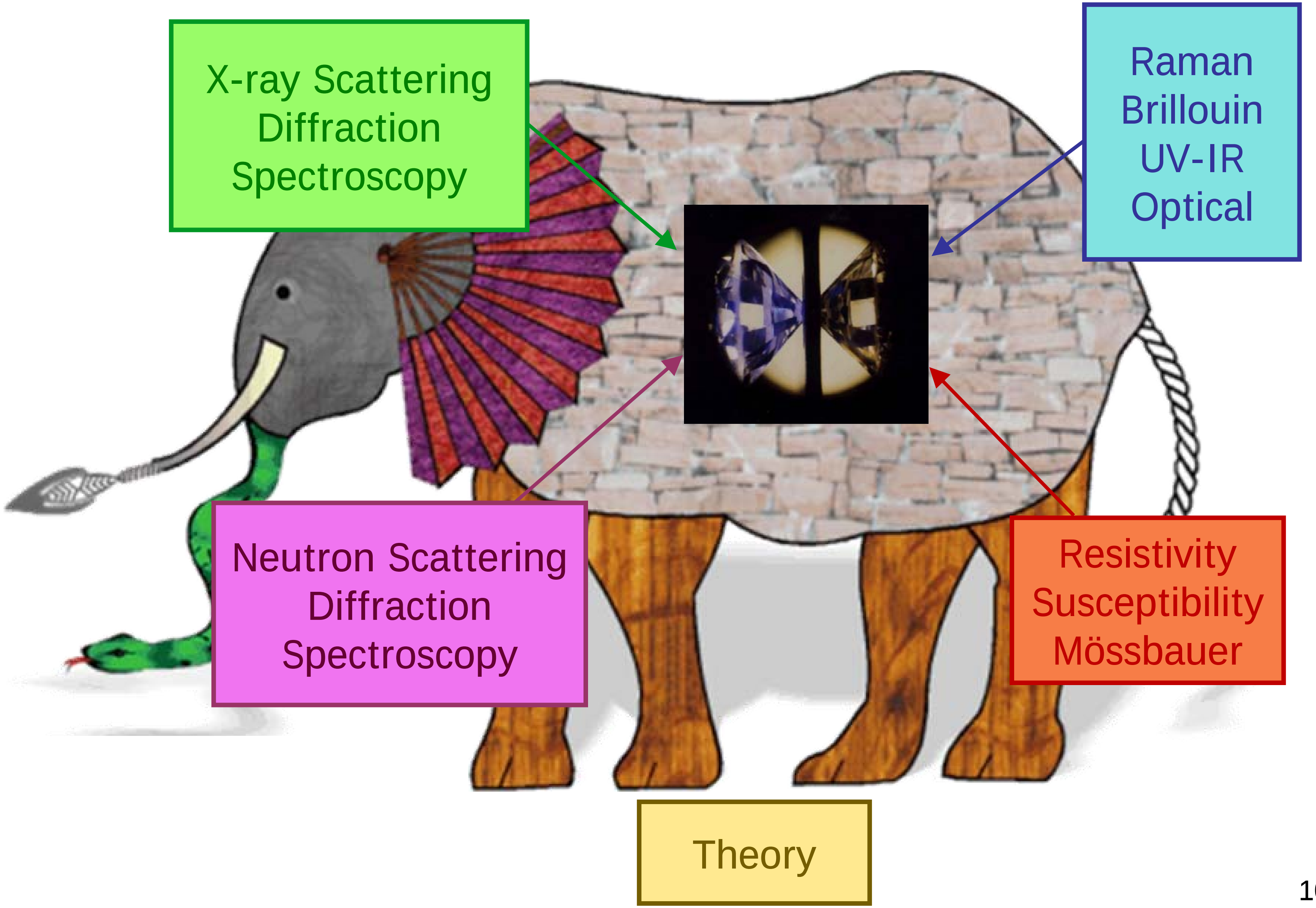




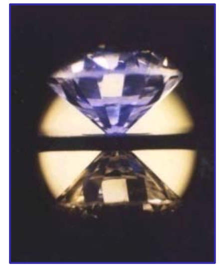



- Sample
- Internal pressure standard
- Thermal insulation and/or pressure transmitting media
  - NaCl, $SiO_2$
  - He
- Gasket
  - Re, stainless steel, Be

# Integration of Multiple *in situ* Probes



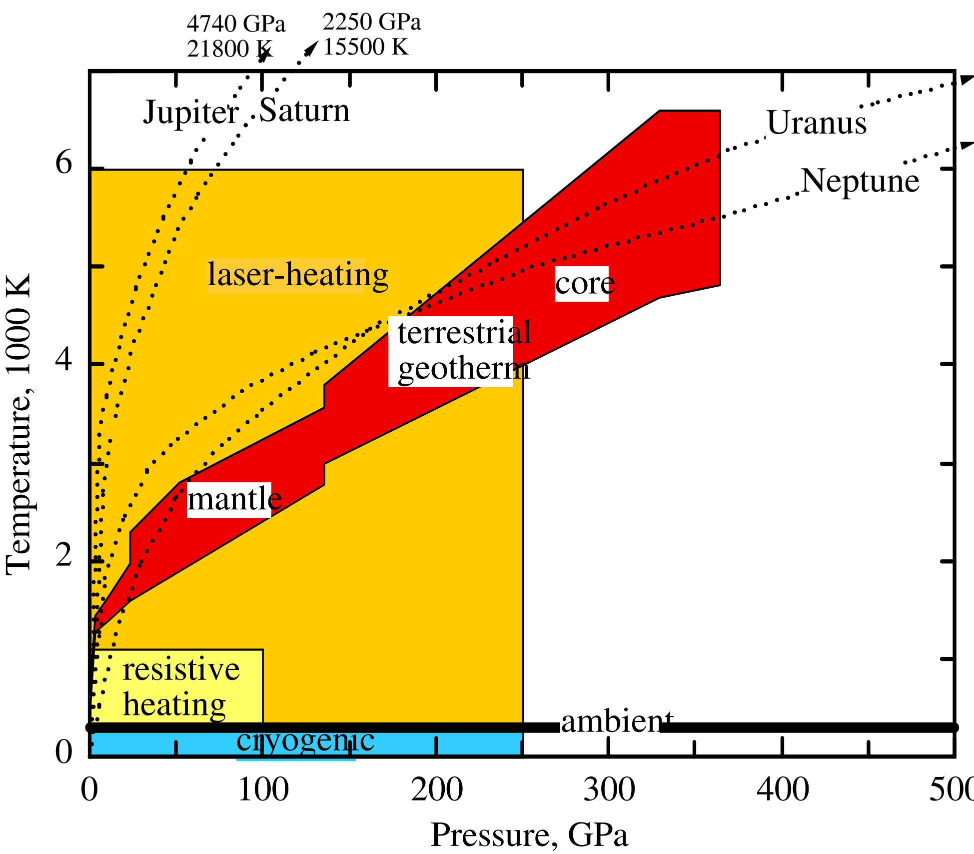
# *P-T* conditions



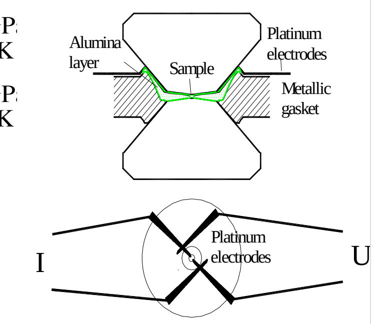
# Diagnostic probes

>300 GPa, 0.03 - 6000 K are reached in DAC

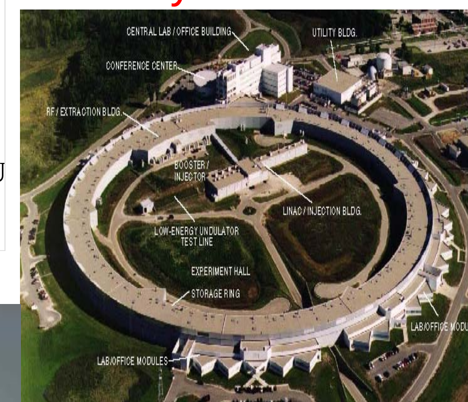
High *P-T in-situ*, x-ray, neutron, optical and electromagnetic probes



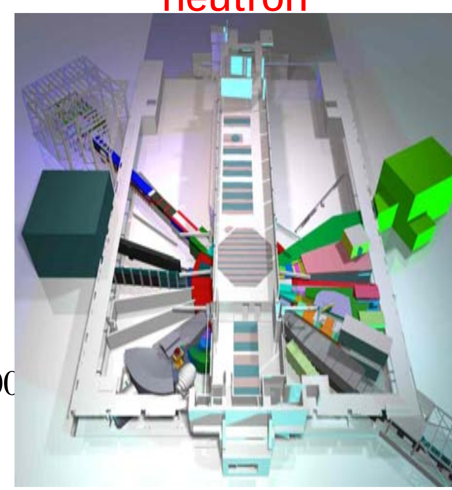

electric



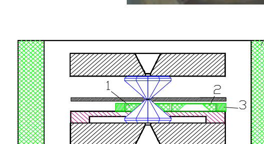

synchrotron




neutron

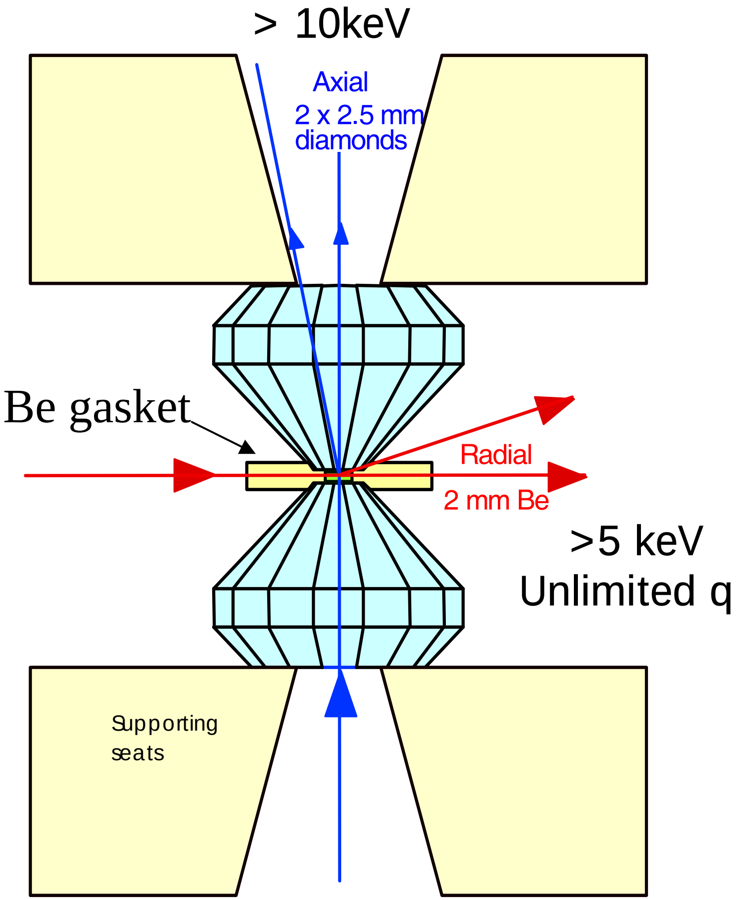


magnetism



# High Pressure Probes Must

1. Penetrate the pressure vessel to reach the sample
   - optical probes can be limited depending on optical quality of window and sample.
   - vacuum probes (vuv, soft x-ray, and electron spectroscopy) are excluded.
   - x-rays, axial direction need > 10 keV, radial need > 5 keV
2. Small sample volume
   - neutron scattering is limited.



# Synchrotron x-ray probes couple well with high-pressure science

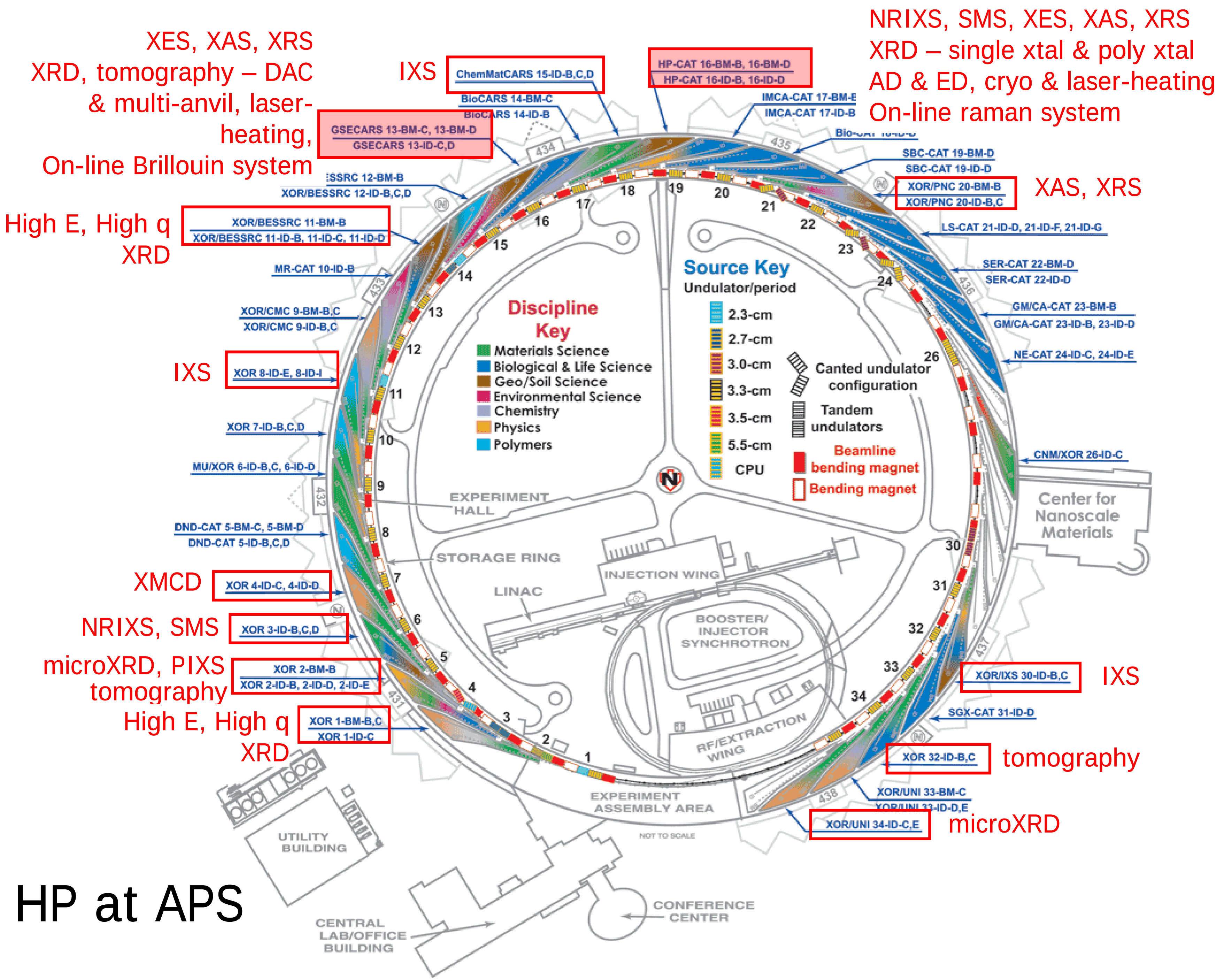
- Brilliance
- High energy
- Energy resolution
- Spatial resolution
- Temporal resolution
- Coherence

*Rapid advances and impacts in high pressure*

*Enormous potential to be harnessed*

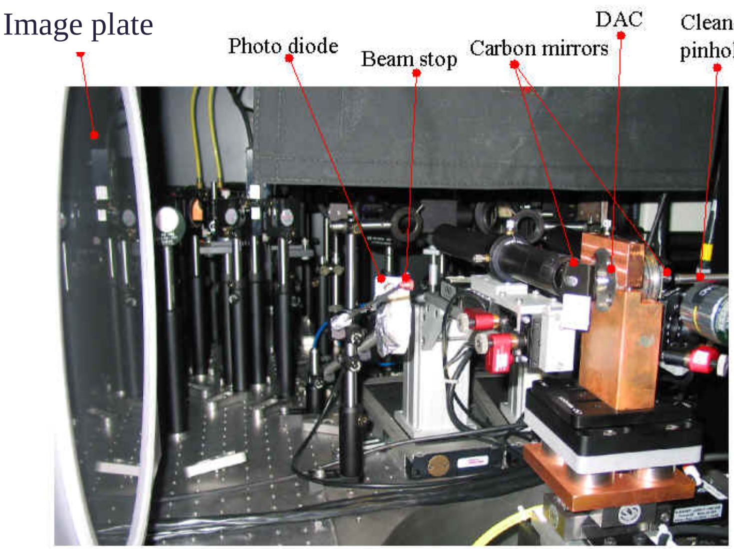
*As yet unexplored*

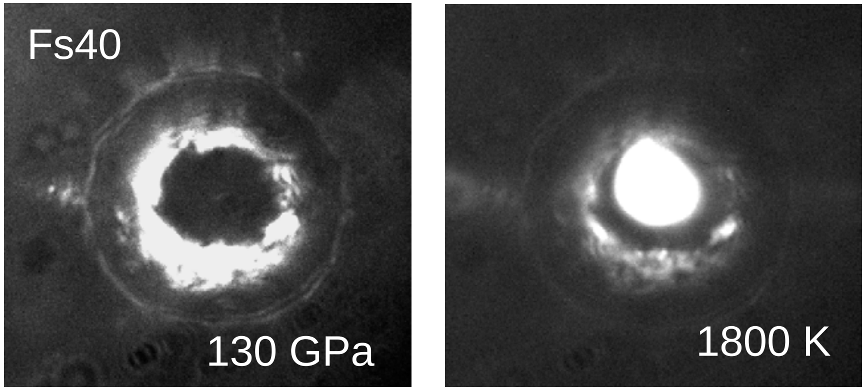
Already is an impressive suite of synchrotron techniques which are compatible with DAC, but still a lot of opportunities for further development


XES, XAS, XRS
XRD, tomography – DAC
& multi-anvil, laser-heating,
On-line Brillouin system
IXS
ChemMatCARS 15-ID-B,C,D
HP-CAT 16-BM-B, 16-BM-D
HP-CAT 16-ID-B, 16-ID-D
NRIXS, SMS, XES, XAS, XRS
XRD – single xtal & poly xtal
AD & ED, cryo & laser-heating
On-line raman system
BioCARS 14-BM-C
BioCARS 14-ID-B
GSECARS 13-BM-C, 13-BM-D
GSECARS 13-ID-C,D
IMCA-CAT 17-BM-B
IMCA-CAT 17-ID-B
SBC-CAT 19-BM-D
SBC-CAT 19-ID-D
XOR/BESSRC 12-ID-B,C,D
XOR/PNC 20-BM-B
XOR/PNC 20-ID-B,C
XAS, XRS
High E, High q XRD
XOR/BESSRC 11-BM-B
XOR/BESSRC 11-ID-B, 11-ID-C, 11-ID-D
LS-CAT 21-ID-D, 21-ID-F, 21-ID-G
MR-CAT 10-ID-B
SER-CAT 22-BM-D
SER-CAT 22-ID-D
XOR/CMC 9-BM-B,C
XOR/CMC 9-ID-B,C
GM/CA-CAT 23-BM-B
GM/CA-CAT 23-ID-B, 23-ID-D
NE-CAT 24-ID-C, 24-ID-E
IXS
XOR 8-ID-E, 8-ID-I
Discipline Key
Materials Science
Biological & Life Science
Geo/Soil Science
Environmental Science
Chemistry
Physics
Polymers
Source Key
Undulator/period
2.3-cm
2.7-cm
3.0-cm
3.3-cm
3.5-cm
5.5-cm
CPU
Canted undulator configuration
Tandem undulators
Beamline bending magnet
Bending magnet
XOR 7-ID-B,C,D
MU/XOR 6-ID-B,C, 6-ID-D
CNM/XOR 26-ID-C
Center for Nanoscale Materials
EXPERIMENT HALL
DND-CAT 5-BM-C, 5-BM-D
DND-CAT 5-ID-B,C,D
STORAGE RING
INJECTION WING
LINAC
XMCD
XOR 4-ID-C, 4-ID-D
NRIXS, SMS
XOR 3-ID-B,C,D
BOOSTER/ INJECTOR SYNCHROTRON
microXRD, PIXS tomography
XOR 2-BM-B
XOR 2-ID-B, 2-ID-D, 2-ID-E
XOR/IXS 30-ID-B,C
IXS
High E, High q XRD
XOR 1-BM-B,C
XOR 1-ID-C
SGX-CAT 31-ID-D
RF/EXTRACTION WING
XOR 32-ID-B,C
tomography
XOR/UNI 33-BM-C
XOR/UNI 33-ID-D,E
XOR/UNI 34-ID-C,E
microXRD
EXPERIMENT ASSEMBLY AREA
NOT TO SCALE
UTILITY BUILDING
CONFERENCE CENTER
CENTRAL LAB/OFFICE BUILDING

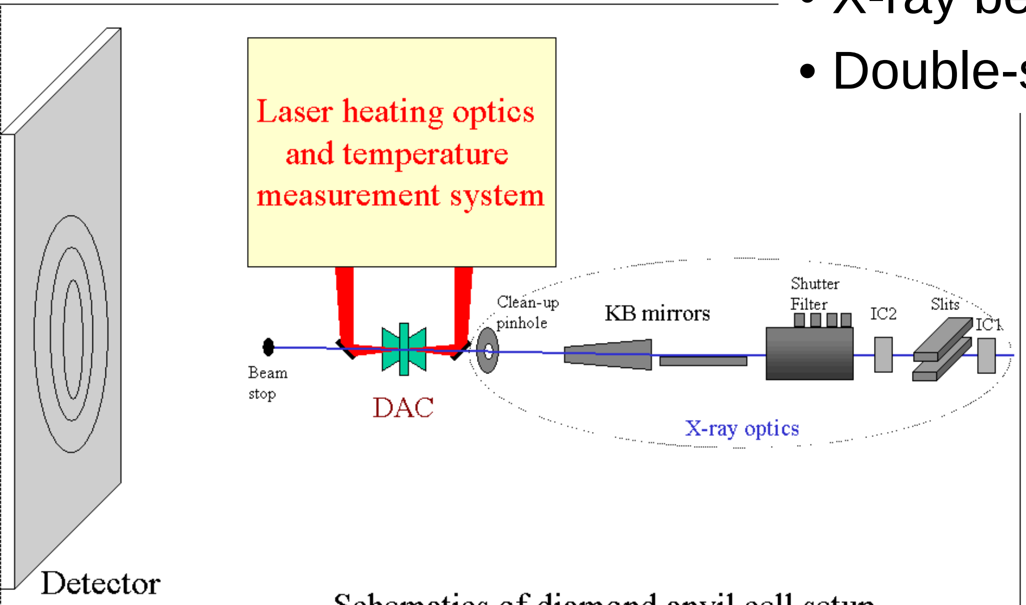
# HP at APS

# HP XRD + laser-heated DAC

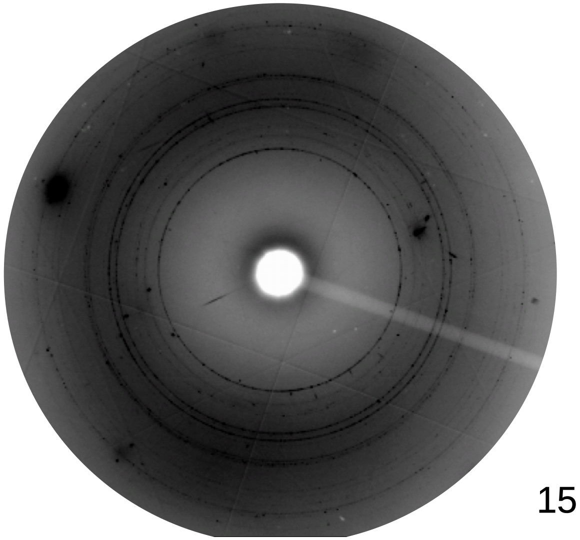



- Gasket hole ~ 60 μm (culet =150 μm, bevel diameter = 300 μm)
- X-ray beam ~ 6 x 7 μm
- Double-sided Nd:YLF laser heating

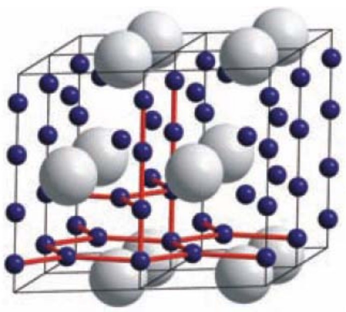



Schematics of diamond anvil cell setup at 13ID-D at the Advanced Photon Source

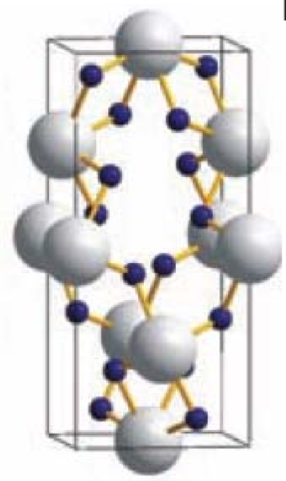


# HP Powder XRD

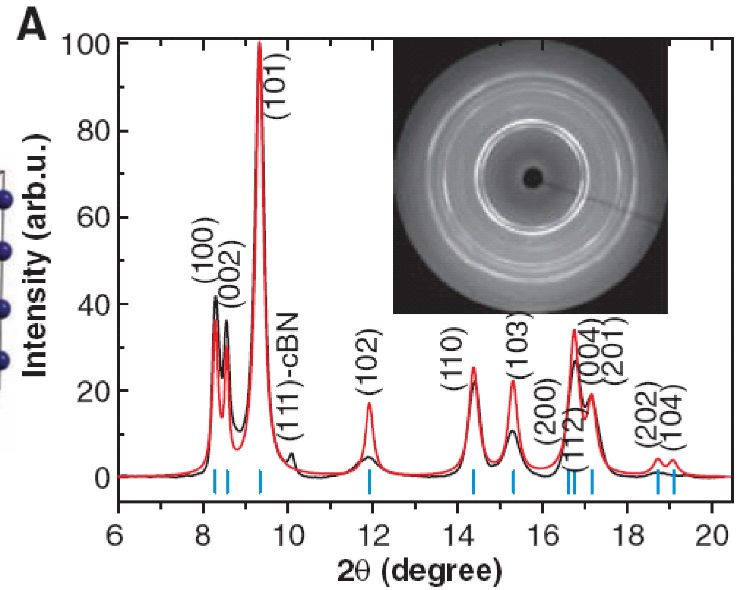
- Superconductivity in hydrogen-rich group IV hydride, $SiH_4$
- Implications for understanding superconductivity in hydrogen?

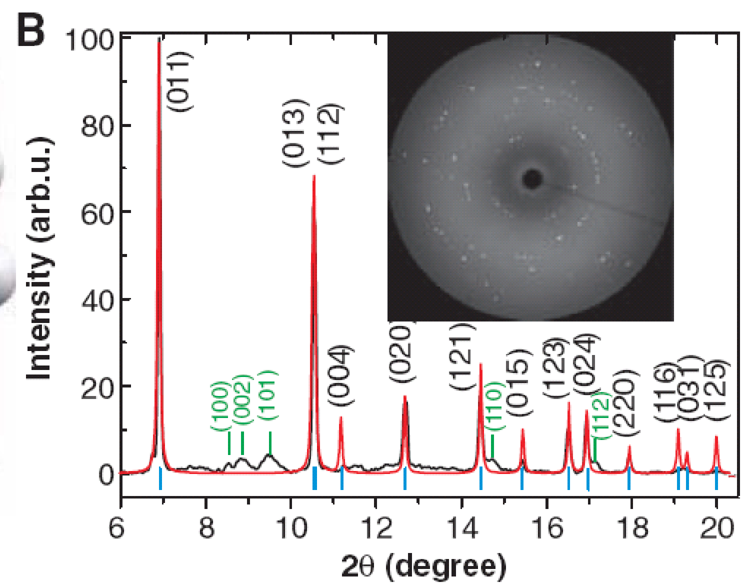


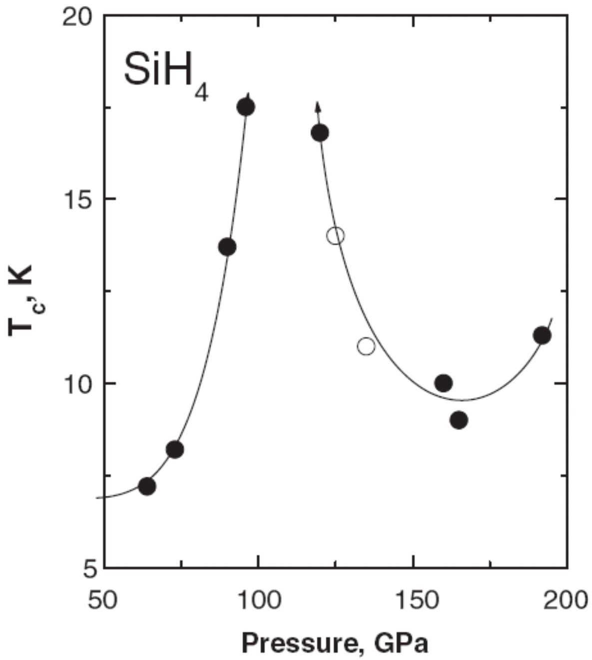
113 GPa



160 GPa



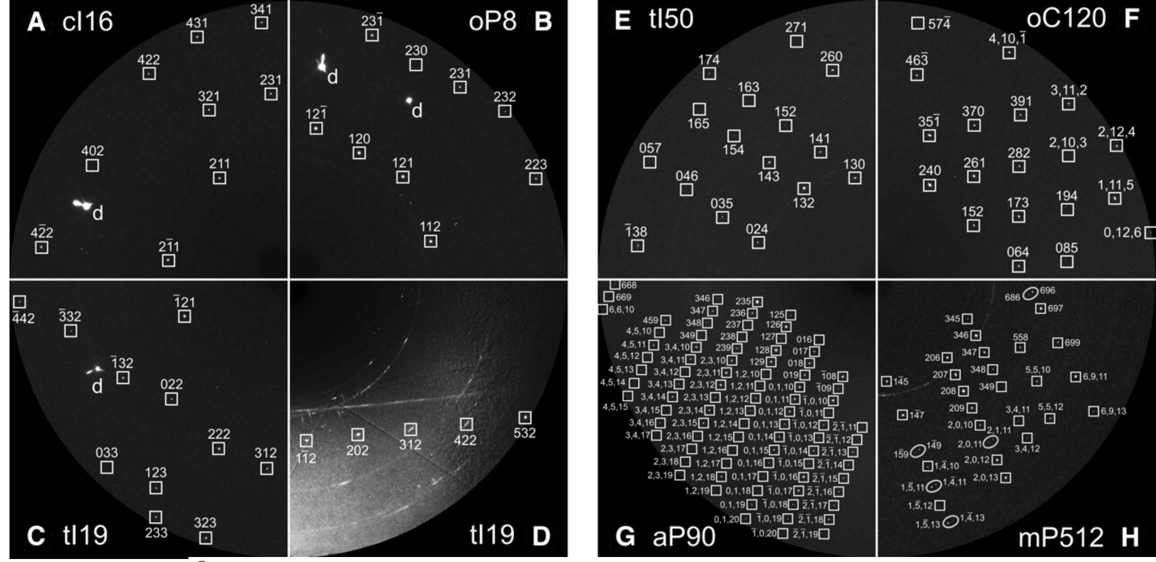



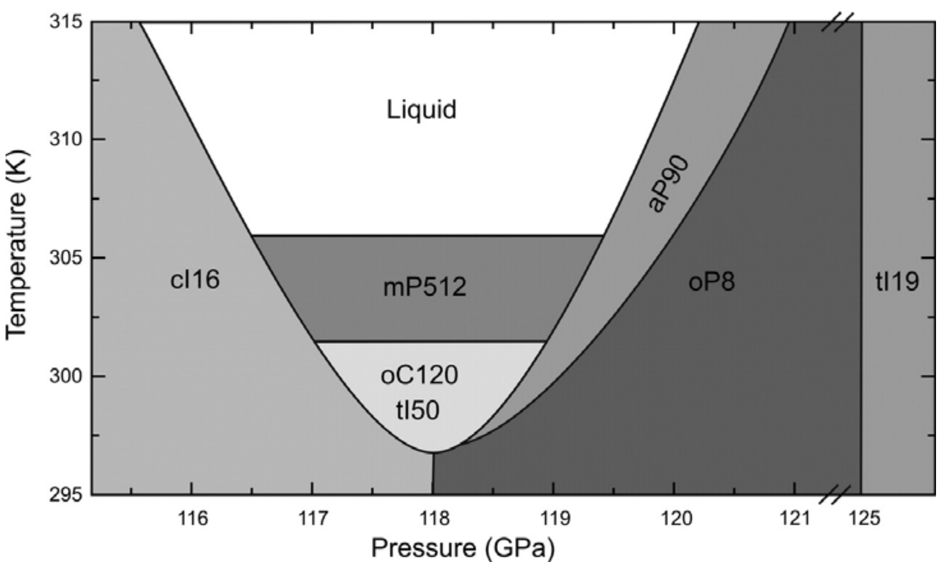



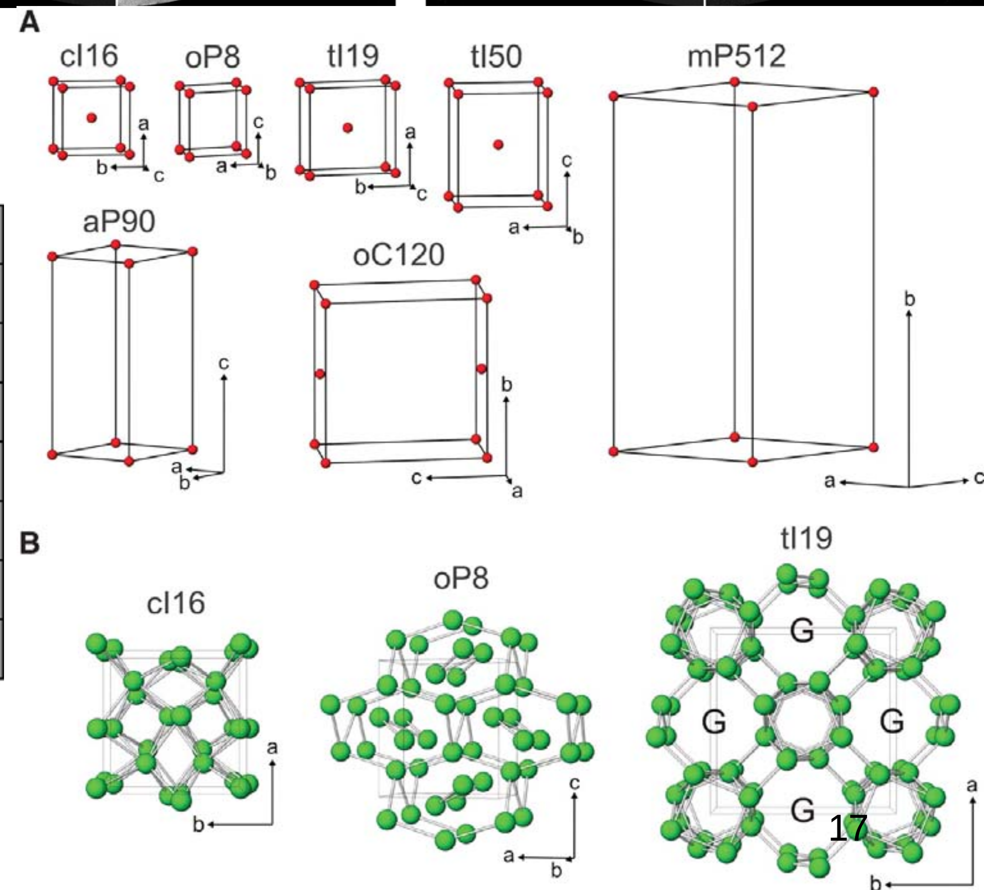

Eremets et al, *Science* 2008

# HP Single crystal XRD

- At minimum in melting curve of Na at ~118 GPa, 7 crystalline phases (many quite complex).

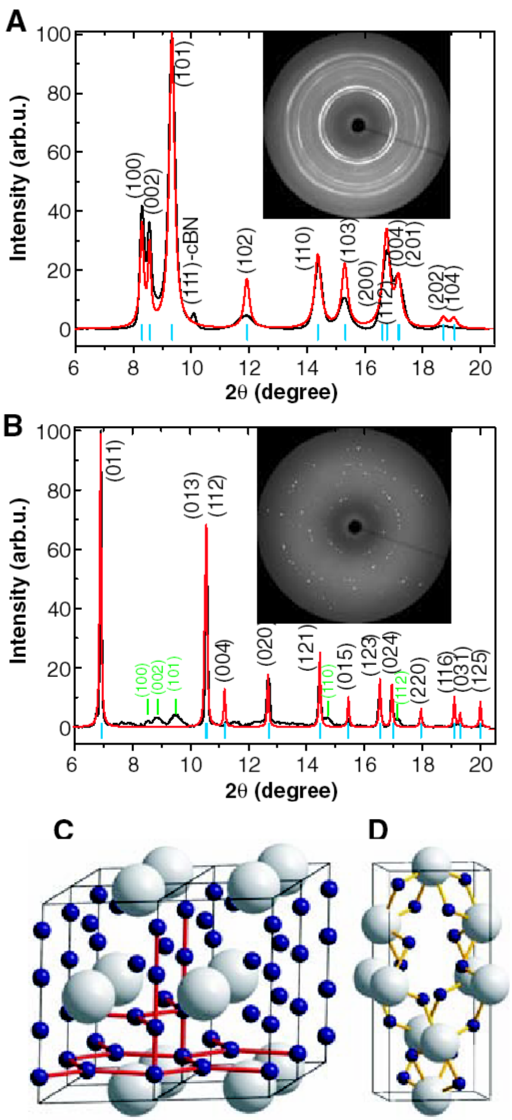


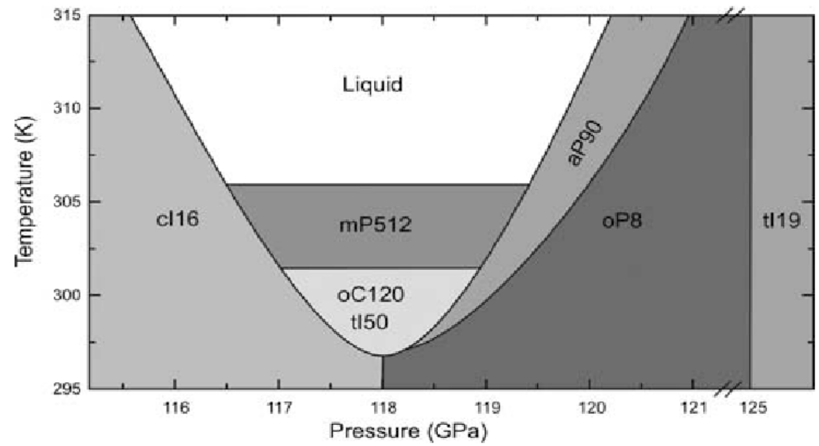

Gregoryanz et al, *Science* 2008

# The need for XRD with submicron x-ray beam



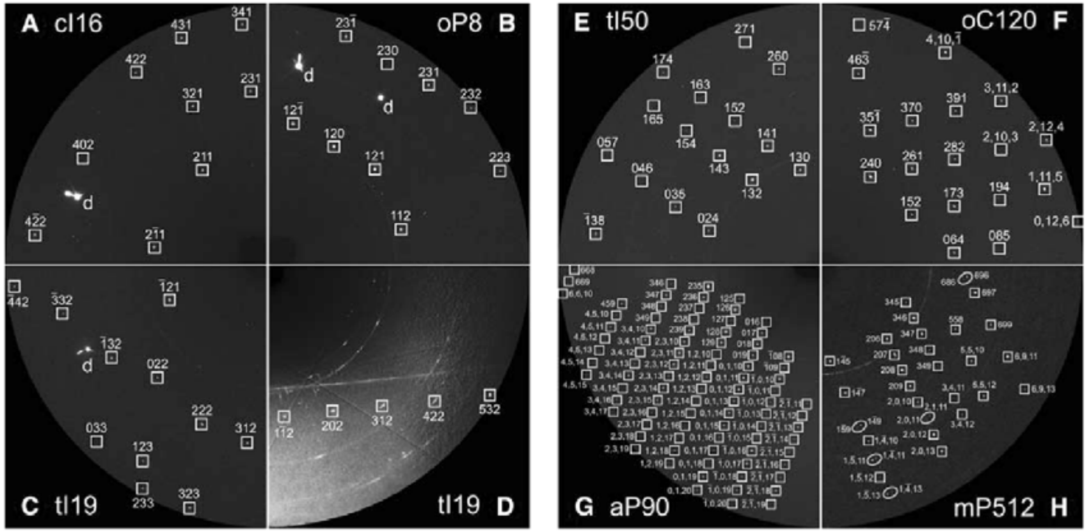

SiH$_4$

Many HP structures were determined with $\mu$m-size powder XRD; assignments can be questionable.



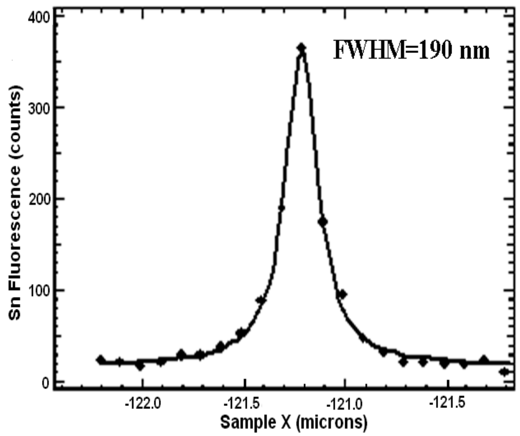

Na

Single-crystal XRD gives definitive answer, but requires crystals larger than the x-ray probe.

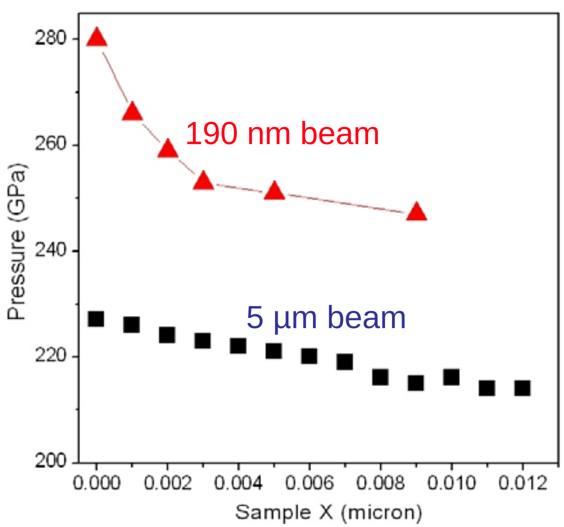


# Using 200 nm focused x-ray beam we can...

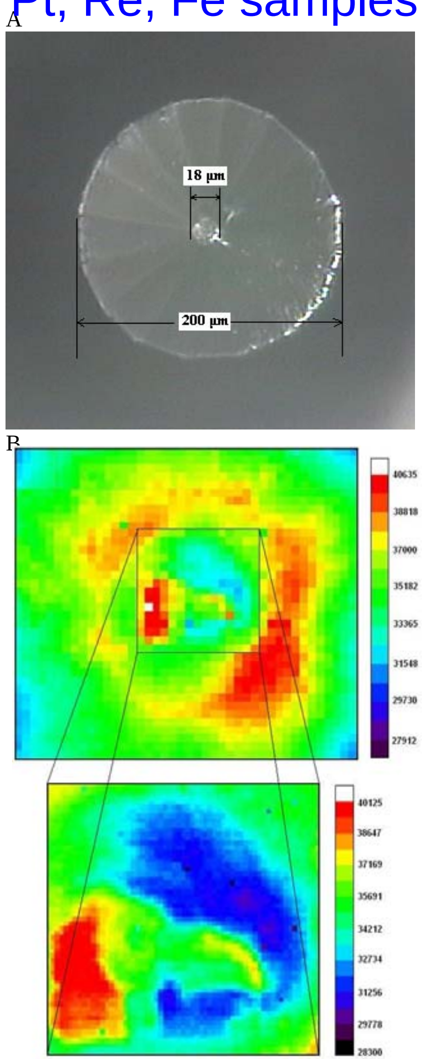
Wang et al., in prep.




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

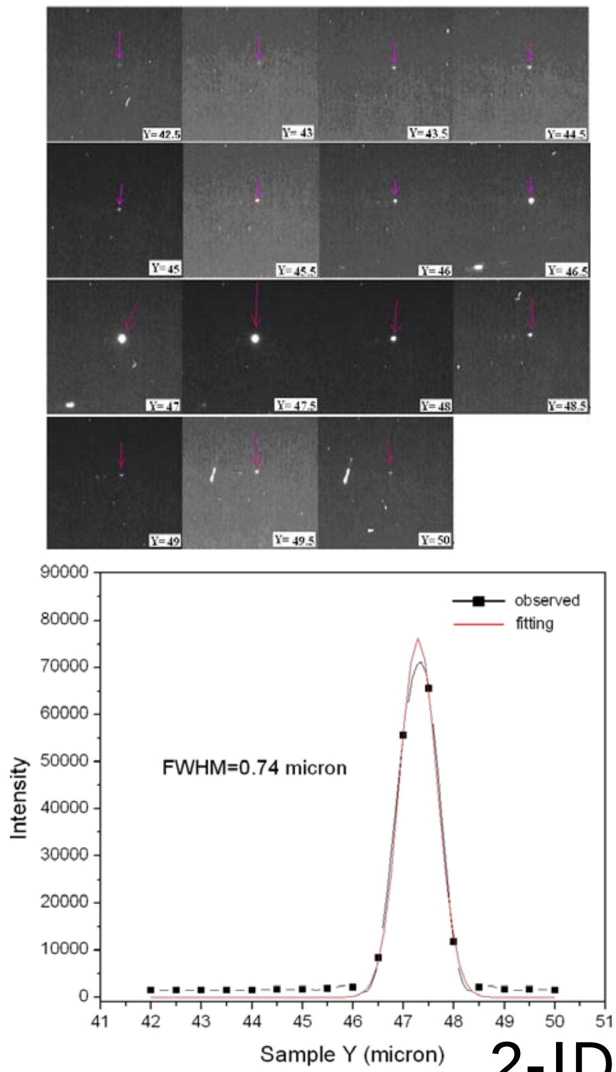



Separate submicron Pt, Re, Fe samples



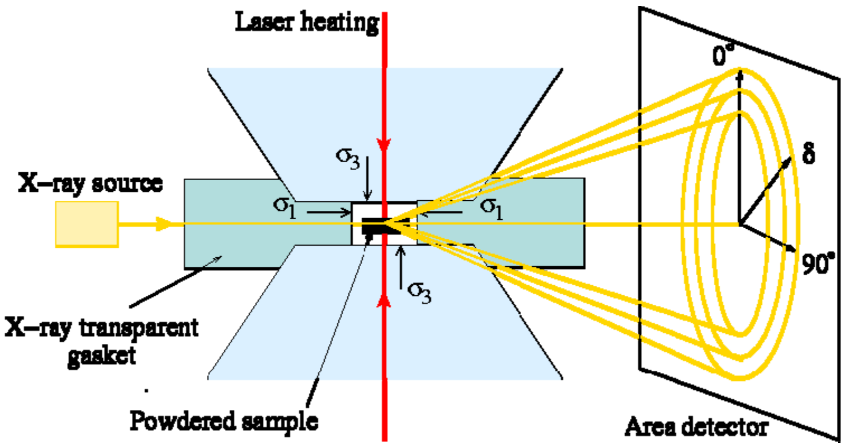

34-ID

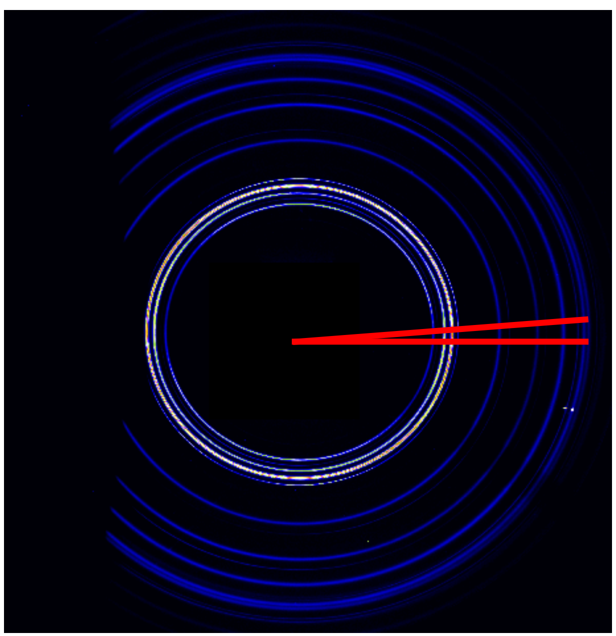
Conduct single-crystal XRD on submicron powder



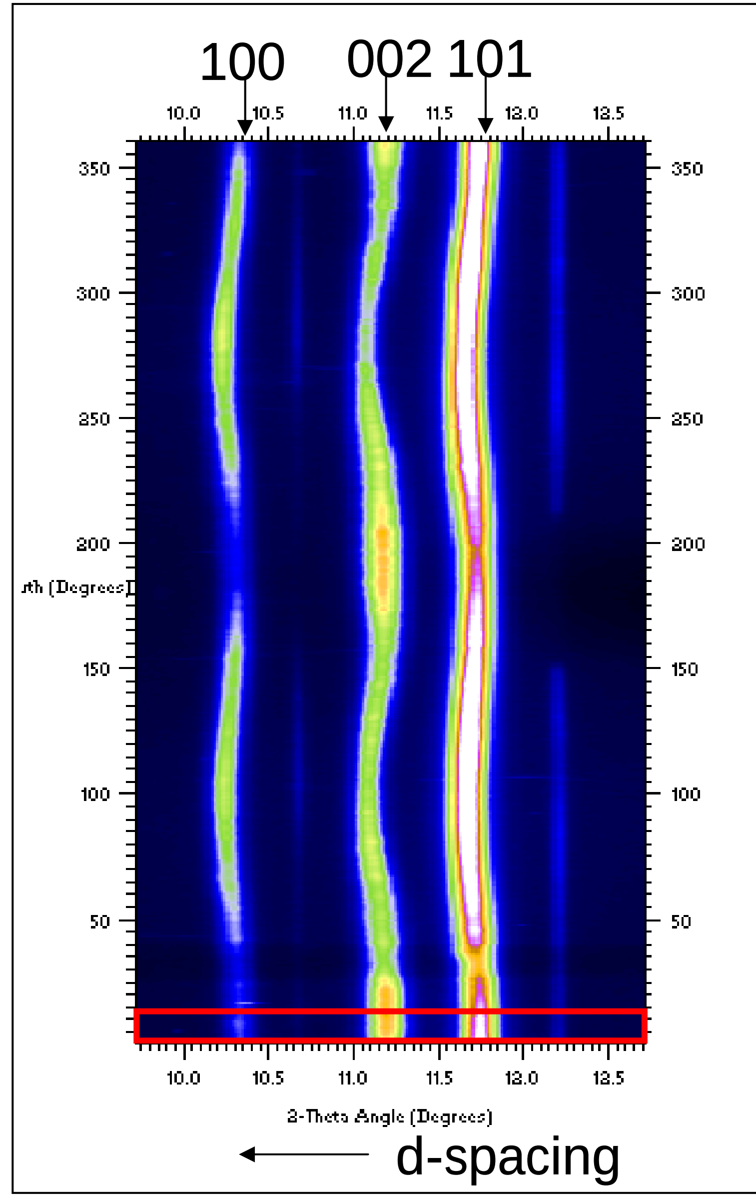

2-ID

# Radial x-ray diffraction



hcp-Fe

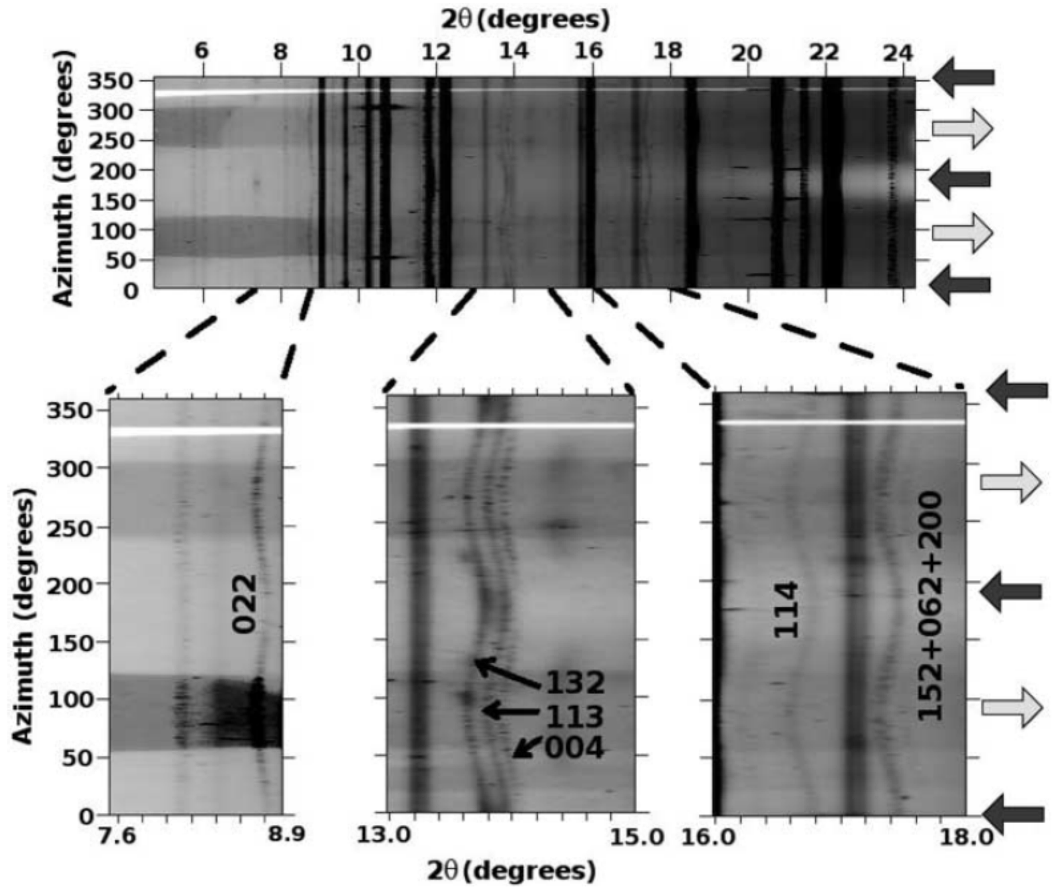



- Preferred orientation

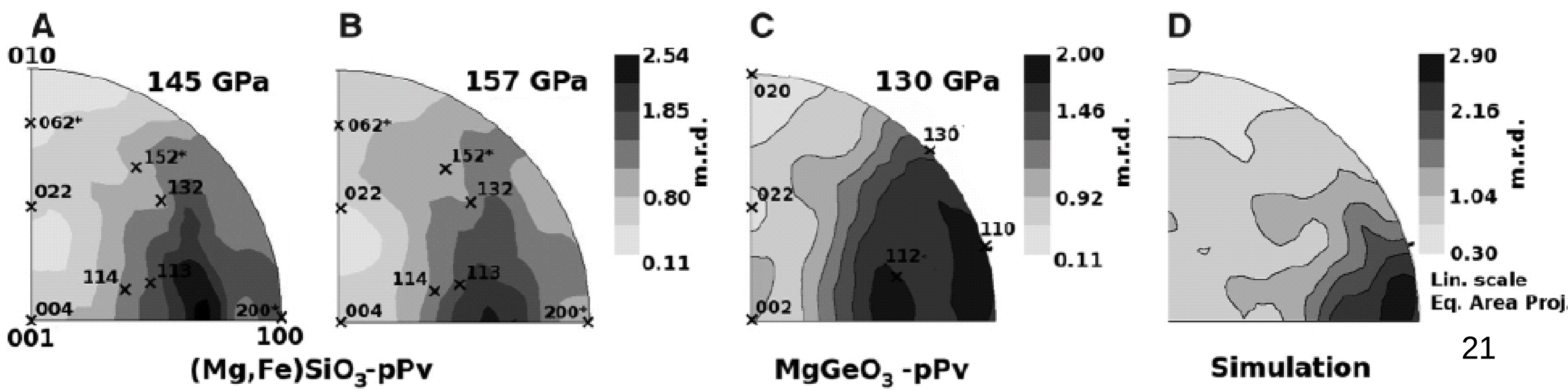
W. Mao et al, JGR 2008

# Texture in post-perovskite phase

- Measure preferred orientation in $(Mg,Fe)SiO_3$ at high P-T, texture and deformation at Earth's core-mantle boundary
- Need to know sound velocities (phonon dispersion, elastic tensor) to explain seismic anisotropy

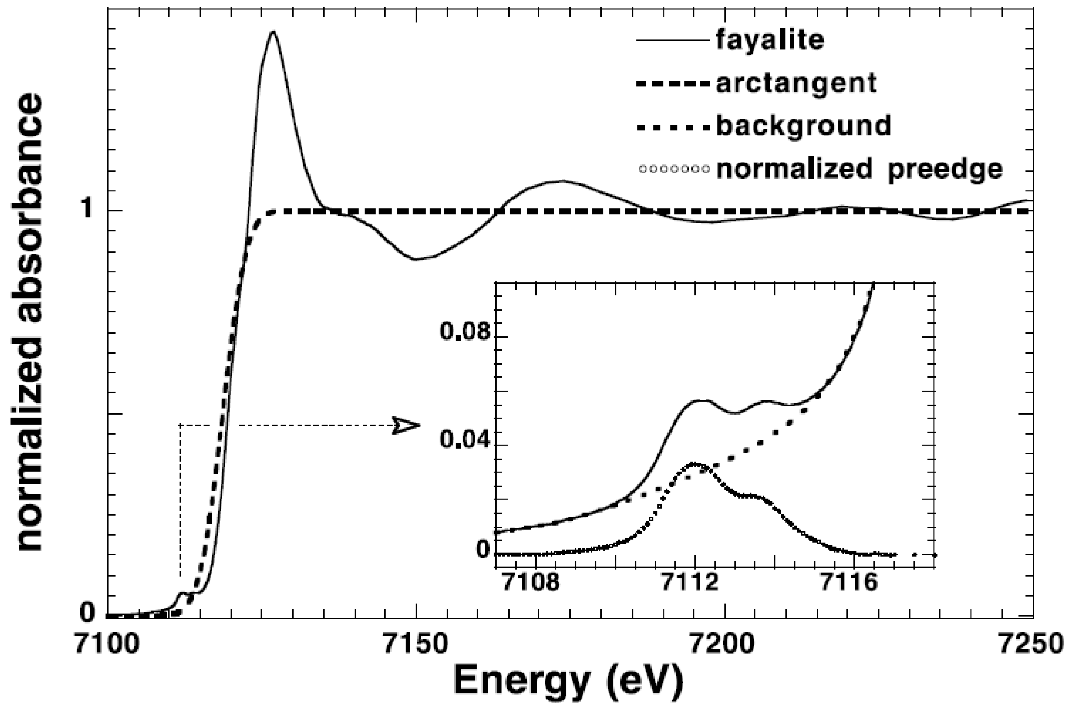



Merkel et al, Science 2007



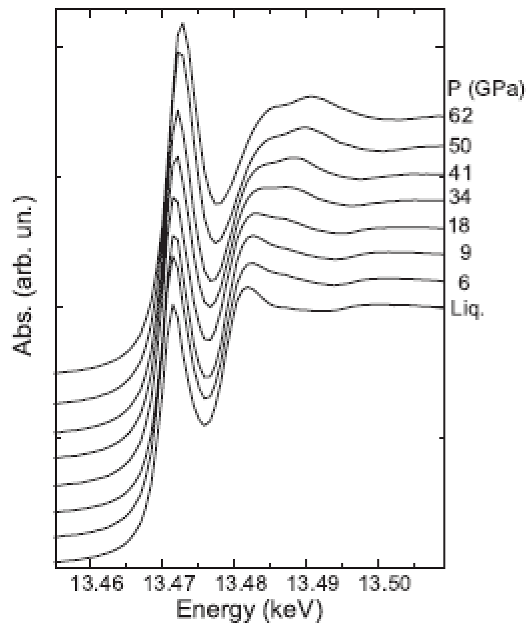
# HP X-ray absorption spectroscopy (XAS)

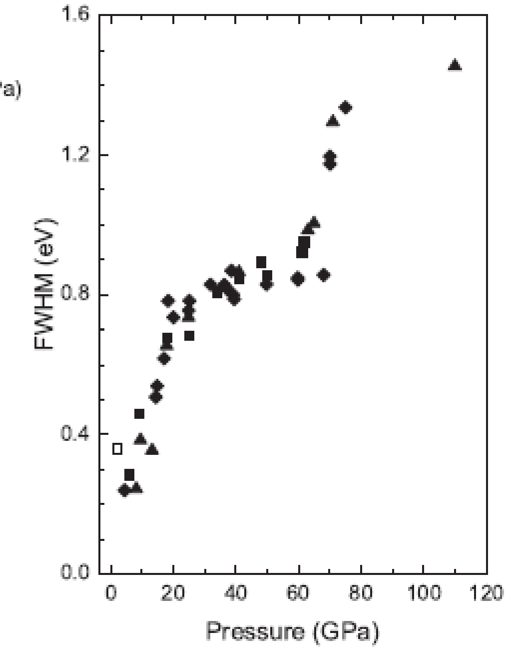
- Pre-edge position and intensity: oxidation state
- Edge height: concentration
- XAFS: coordination & structure

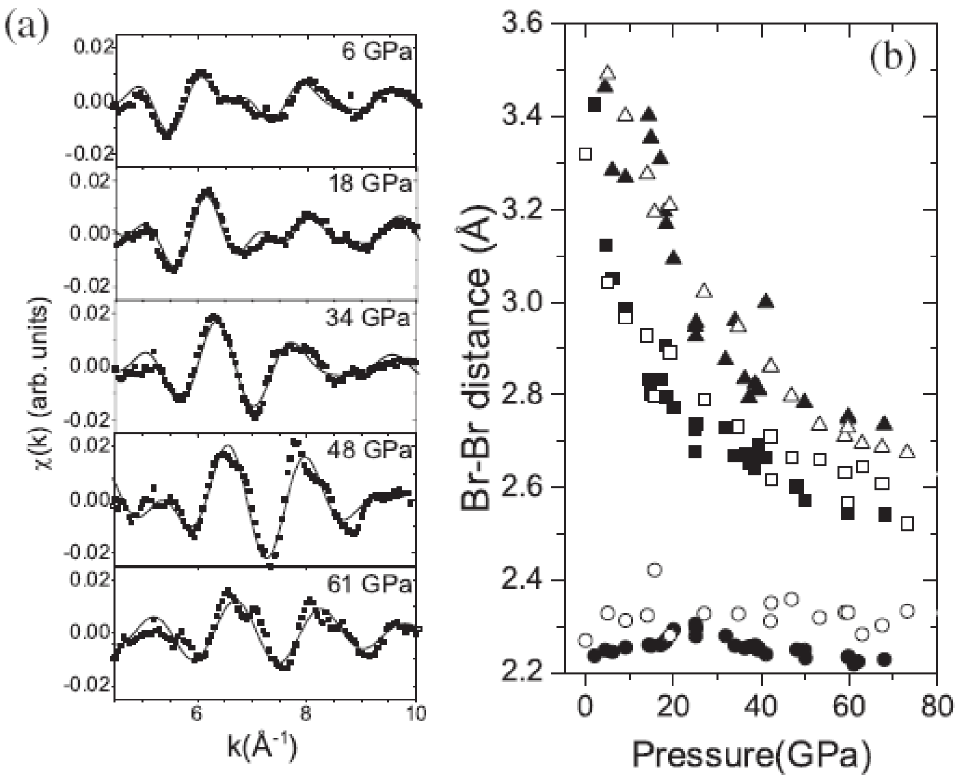


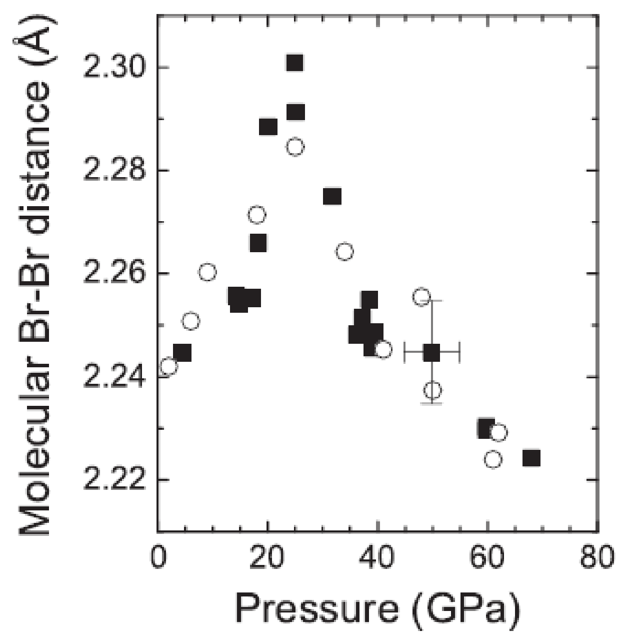

Wilke et al, Amer. Min. 2001

# Phase transitions in solid Br at 25 GPa & 65 GPa



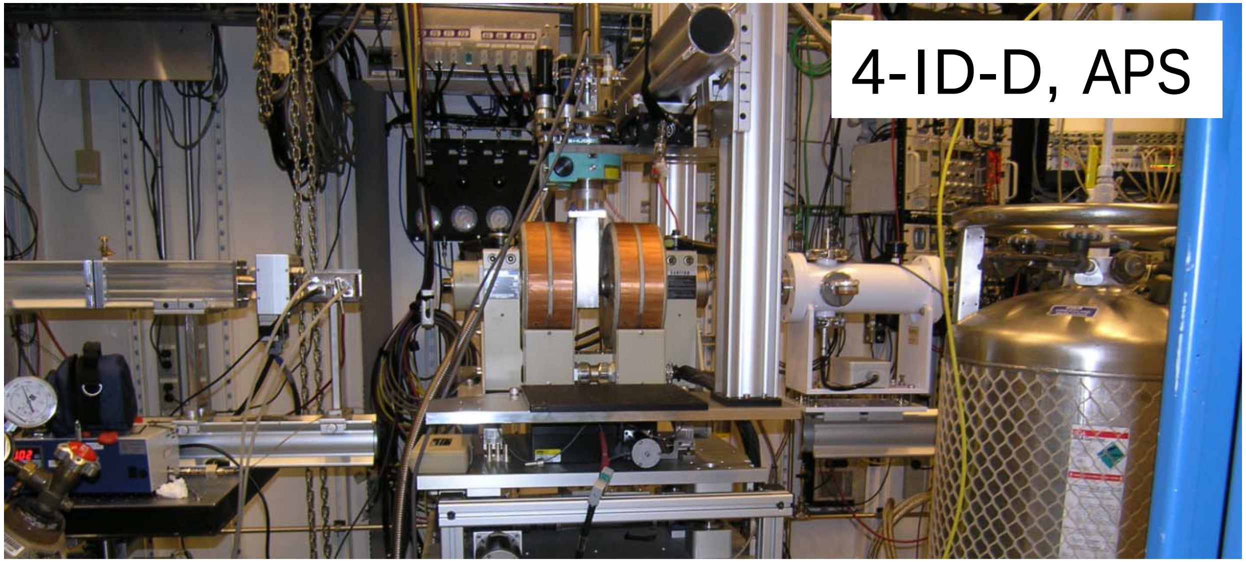



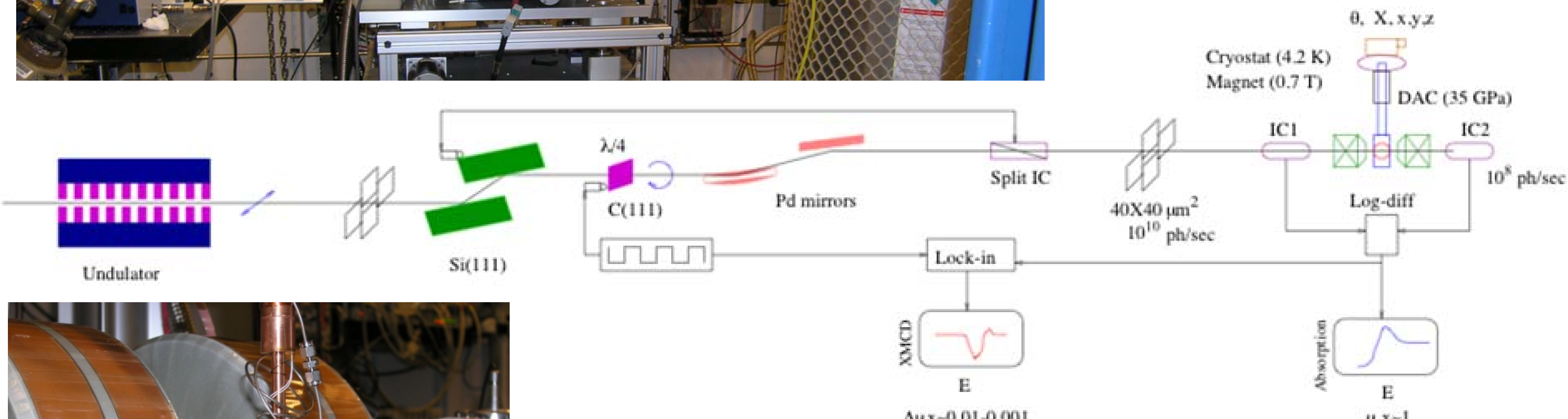



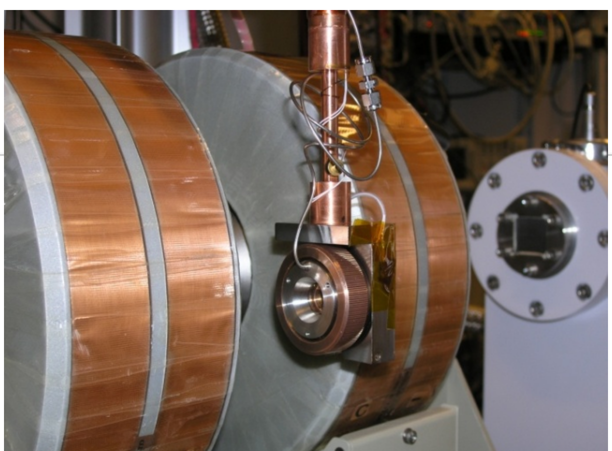




San-Miguel et al, *PRL* 2007

# X-ray magnetic circular dichroism (XMCD) at HP



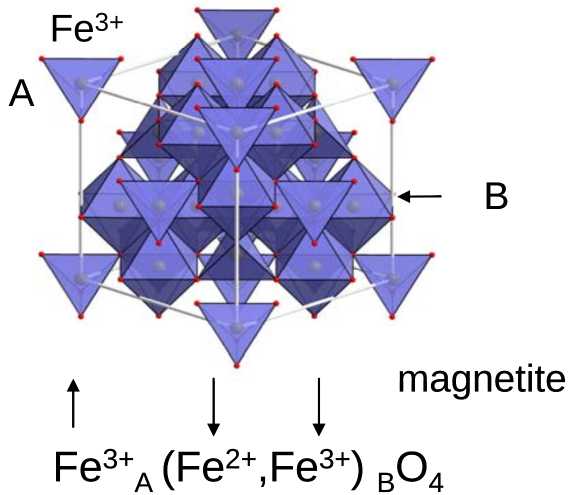



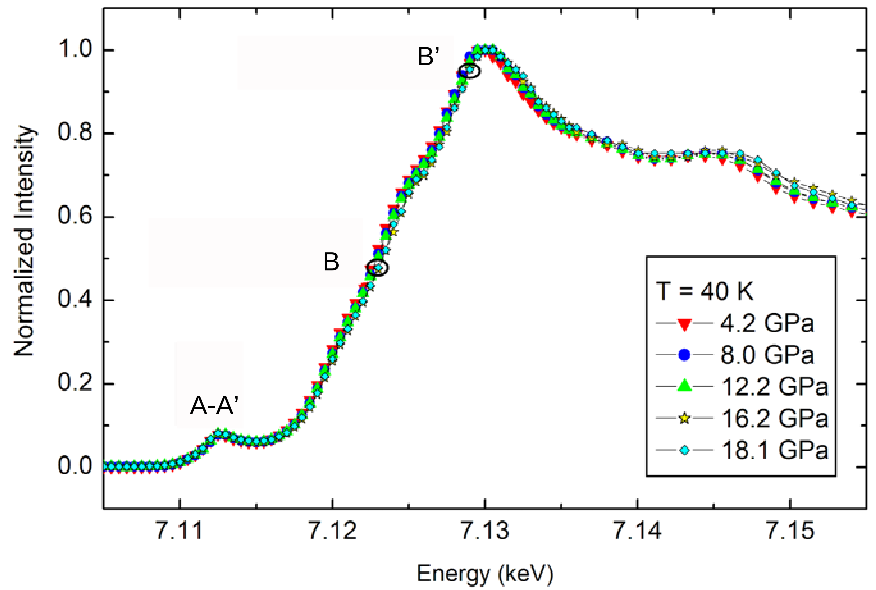



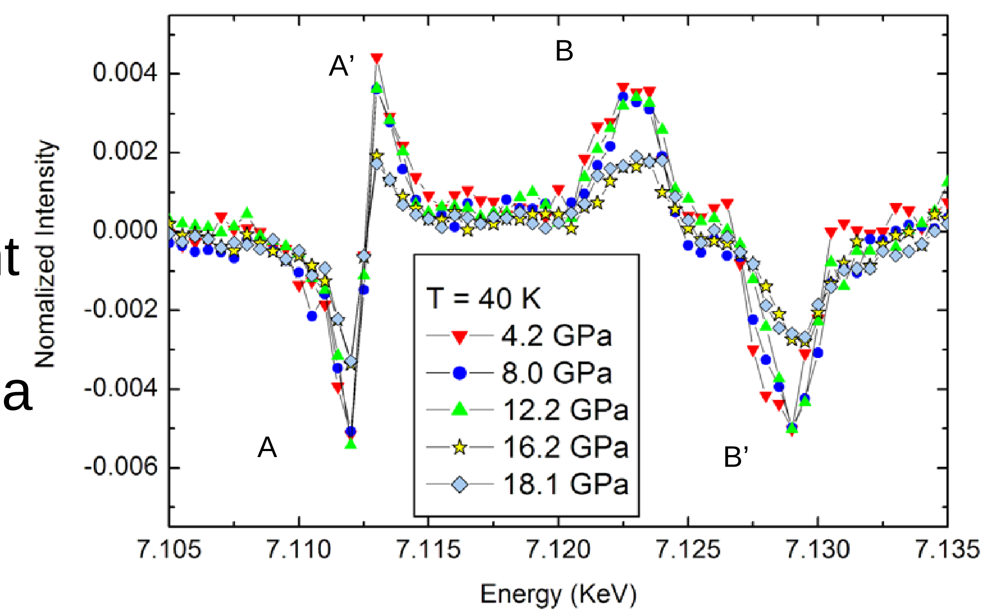
$$XMCD = \frac{\Delta \mu t}{\mu t_{jump}}; \Delta \mu = \mu(-,+) - \mu(+,+)$$

Haskel et al, *RSI* 2007

# XMCD of $Fe_3O_4$ at HP



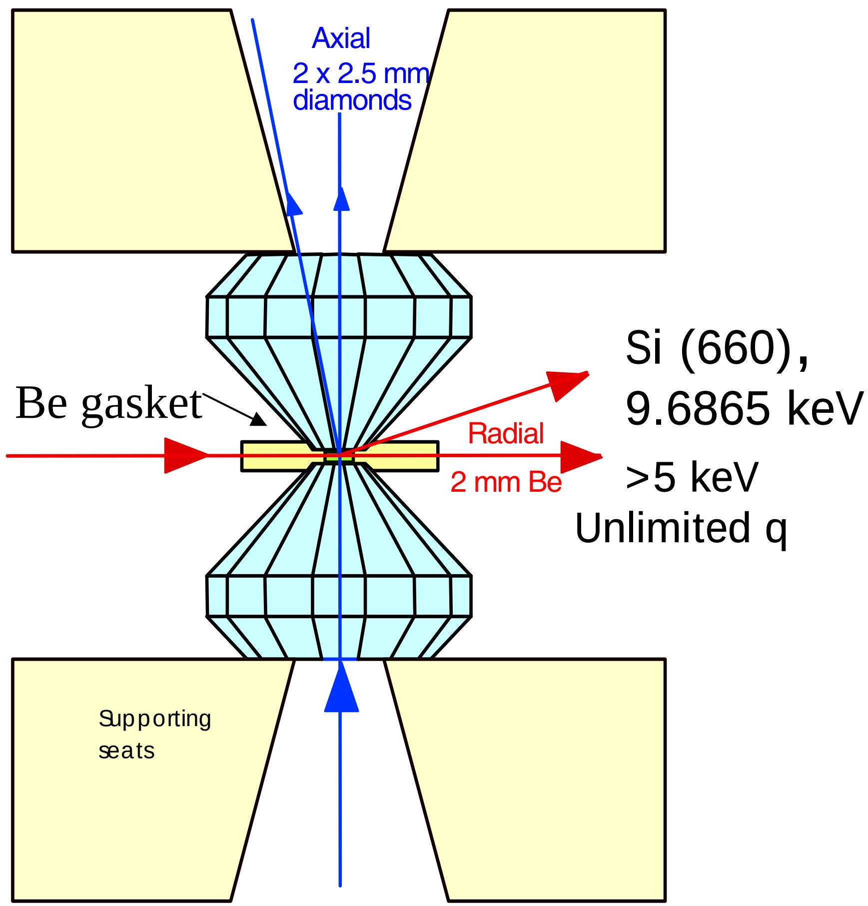




- 50% drop in net magnetic moment at 14 GPa.
- loss of magnetism is attributed to a high-spin to intermediate-spin transition of $Fe^{2+}$ in the octahedral site (confirmation from XES).

Y. Ding et al, *PRL* 2008

# How can we study the edges of low Z elements at high pressure?



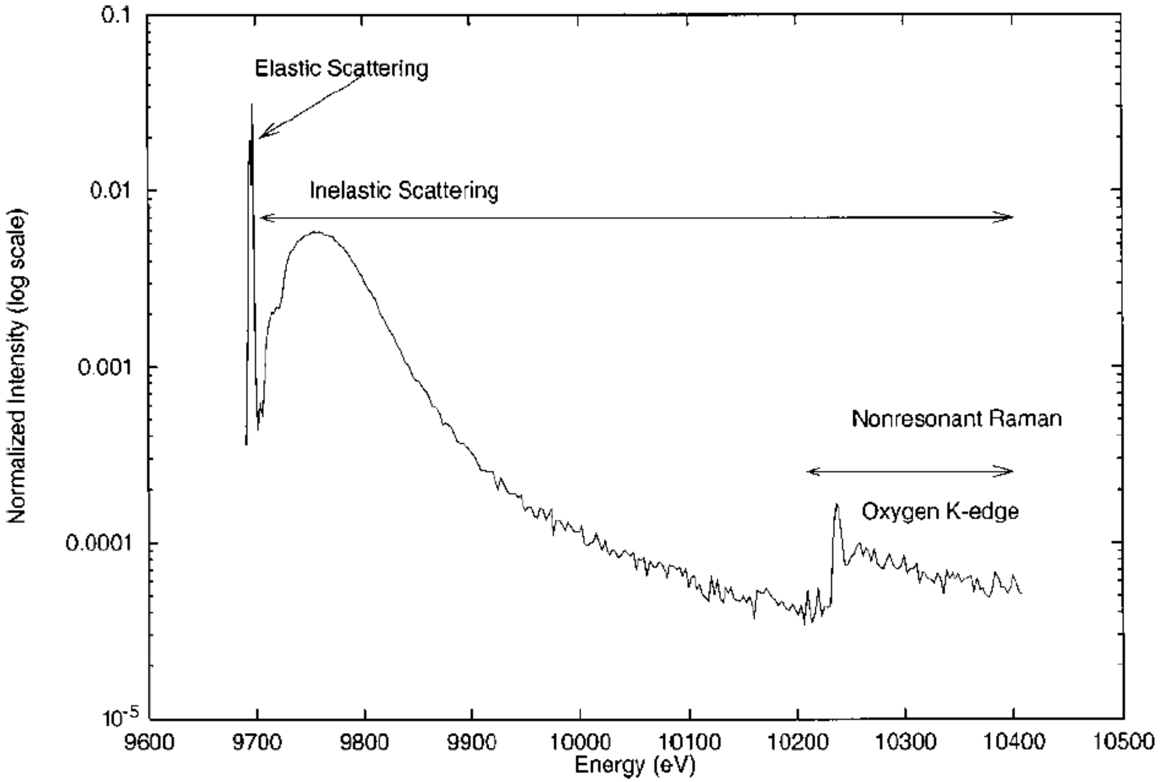

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ |
|---|---|---|---|
| 1 H | 13.6 | | |
| 2 He | 24.6* | | |
| 3 Li | 54.7* | | |
| 4 Be | 111.5* | | |
| 5 B | 188* | | |
| 6 C | 284.2* | | |
| 7 N | 409.9* | 37.3* | |
| 8 O | 543.1* | 41.6* | |
| 9 F | 696.7* | | |
| 10 Ne | 870.2* | 48.5* | 21.7* |
| 11 Na | 1070.8† | 63.5† | 30.65 |
| 12 Mg | 1303.0† | 88.7 | 49.78 |
| 13 Al | 1559.6 | 117.8 | 72.95 |
| 14 Si | 1839 | 149.7*b | 99.82 |
| 15 P | 2145.5 | 189* | 136* |
| 16 S | 2472 | 230.9 | 163.6* |
| 17 Cl | 2822.4 | 270* | 202* |
| 18 Ar | 3205.9* | 326.3* | 250.6† |

# X-ray Raman Spectroscopy (XRS)

Incident x-rays (monochromator)

Energy loss (k-edge) | Scattered x-rays (analyzer)

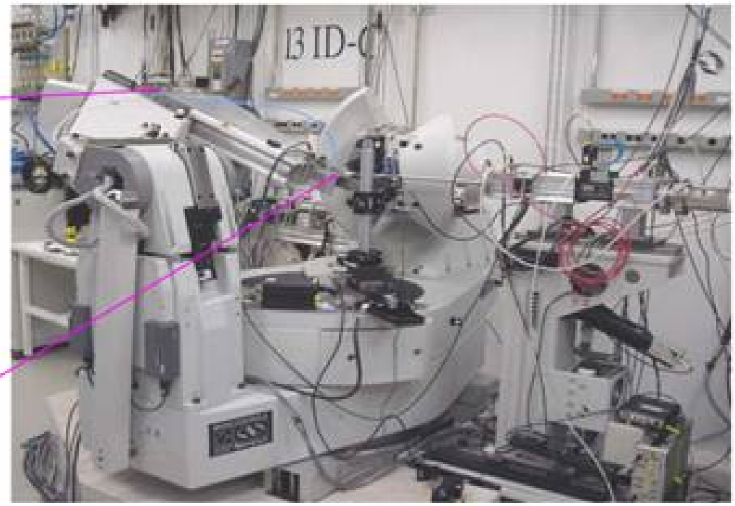
$$\Delta E = E - E_0$$

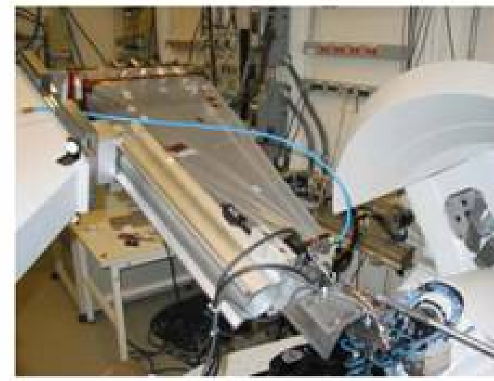


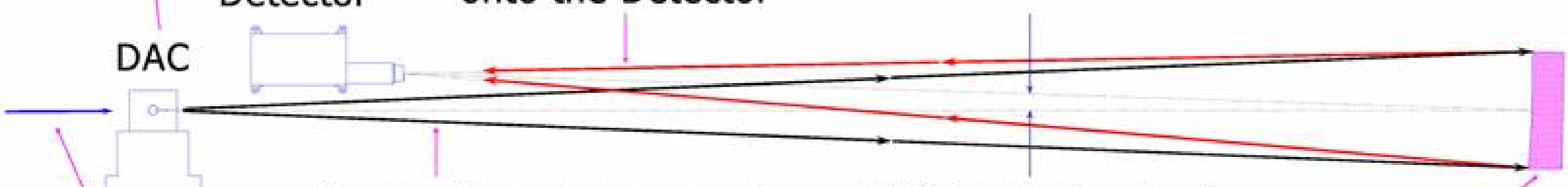

Bowron *et al, PRB* 2000

# XRS Set-up

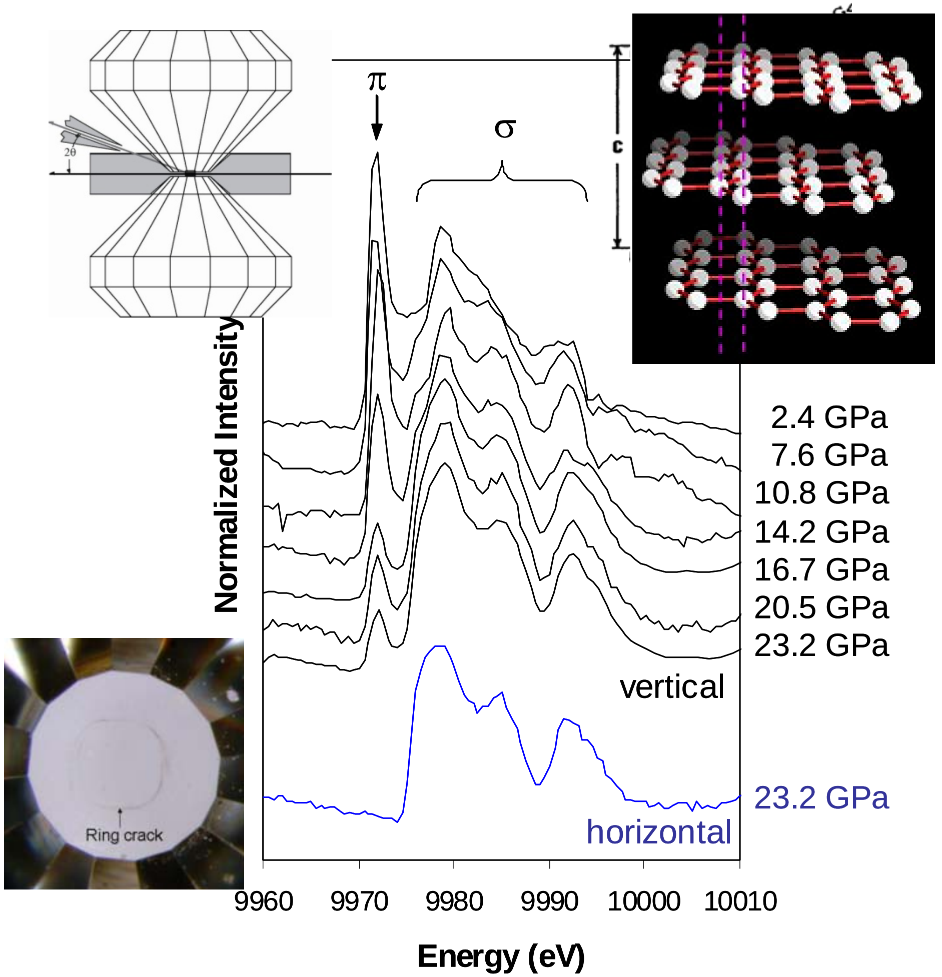
13-IDC, GSECARS, APS, ANL



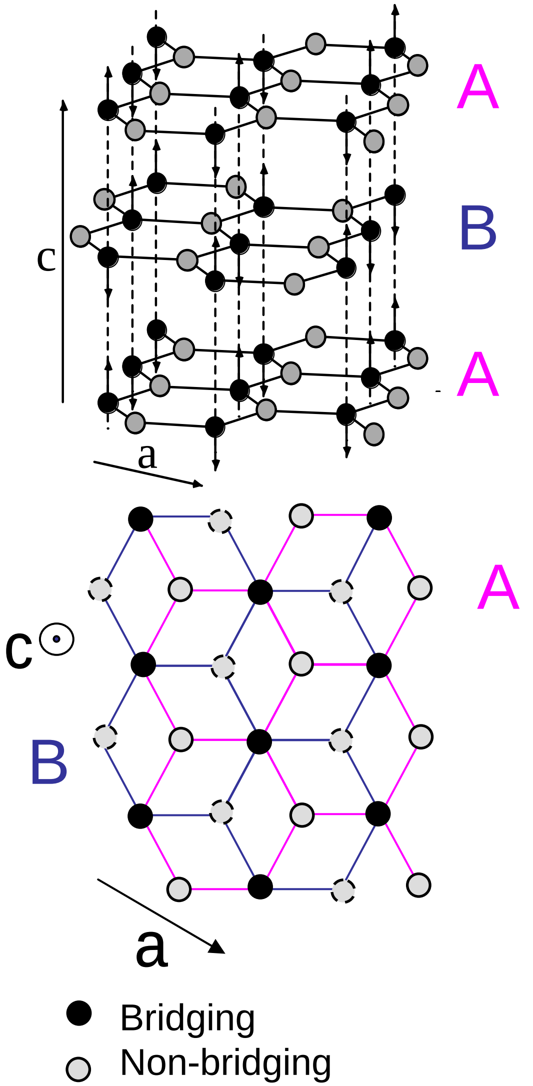




# Pressure changes bonding in graphite conversion of half $sp^2$ bonds to $sp^3$



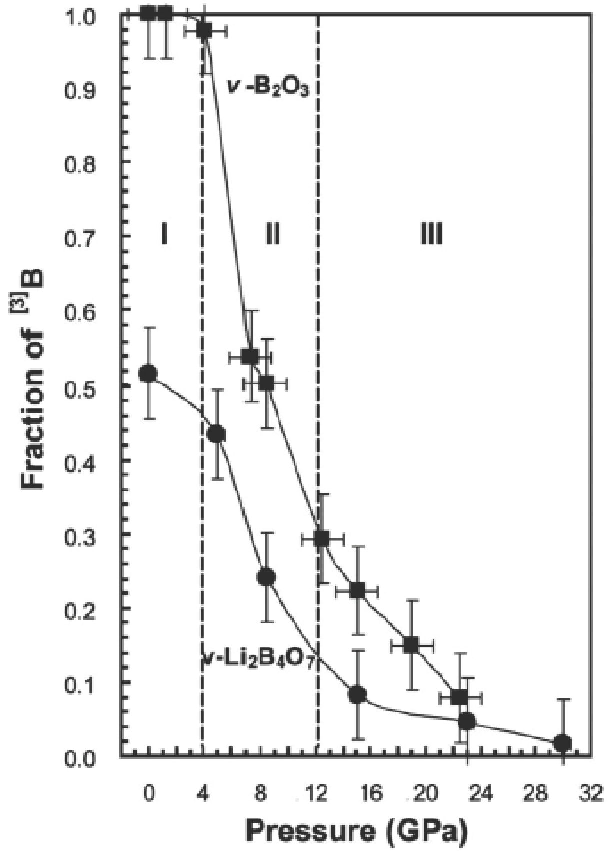

X-ray raman of graphite at high pressure showing the evolution of bonding and transformation to a new, superhard phase

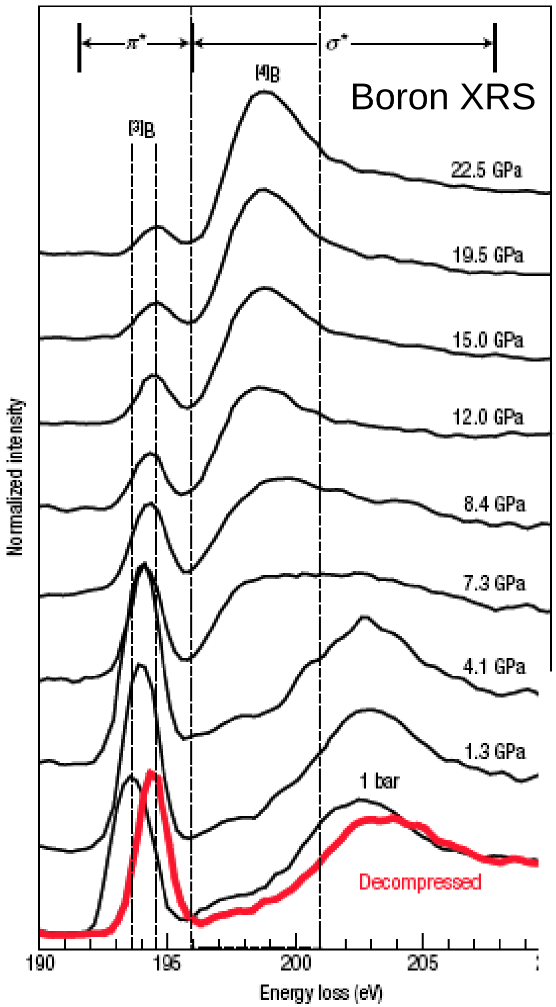



W. Mao *et al, Science* 2003

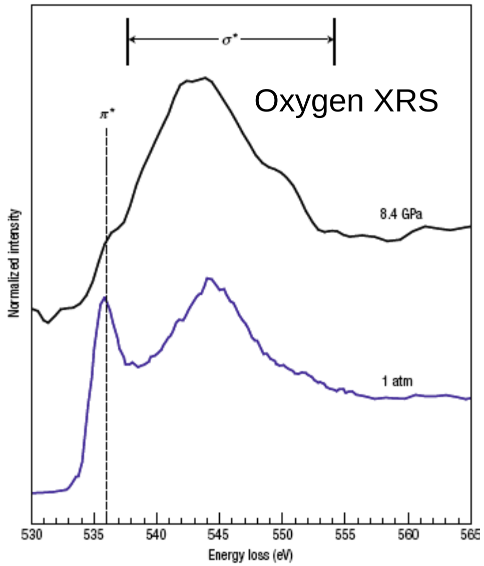
# Pressure-induced bonding changes in $B_2O_3$ and $Li_2B_4O_7$

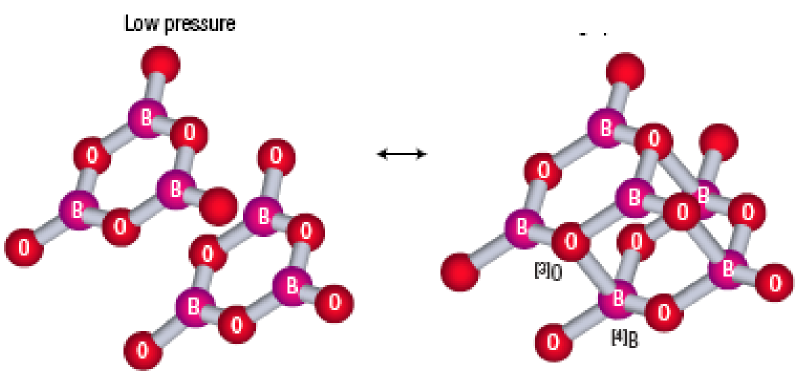
S K Lee, *et al*, *PRL* 2007



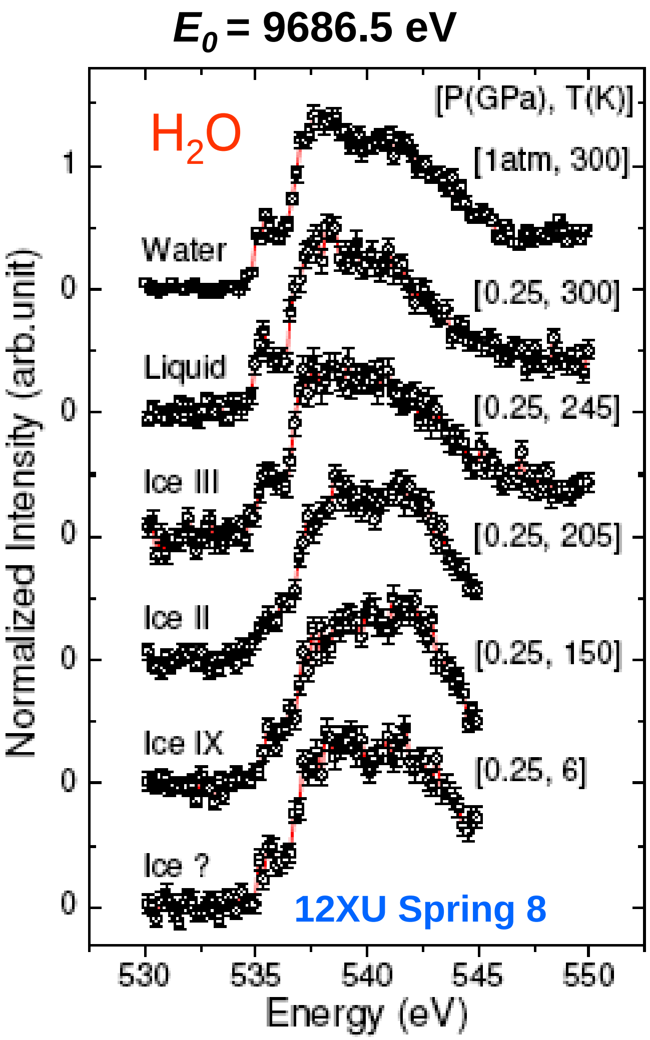

S K Lee, *et al*, *Nature Mat.* 2005



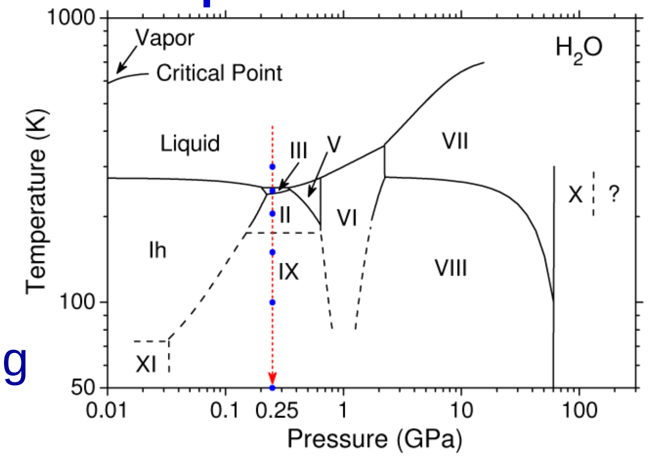



# X-ray Raman measurements reveal pressure-induced bonding changes in low *P-T* phases

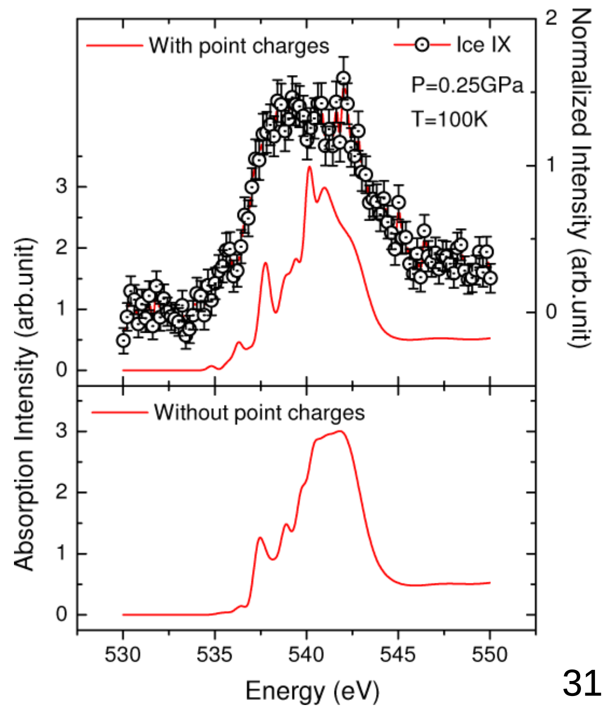
Oxygen IXS near K-edge spectra of $H_2O$




Effect of hydrogen bond ordering on K edge spectra

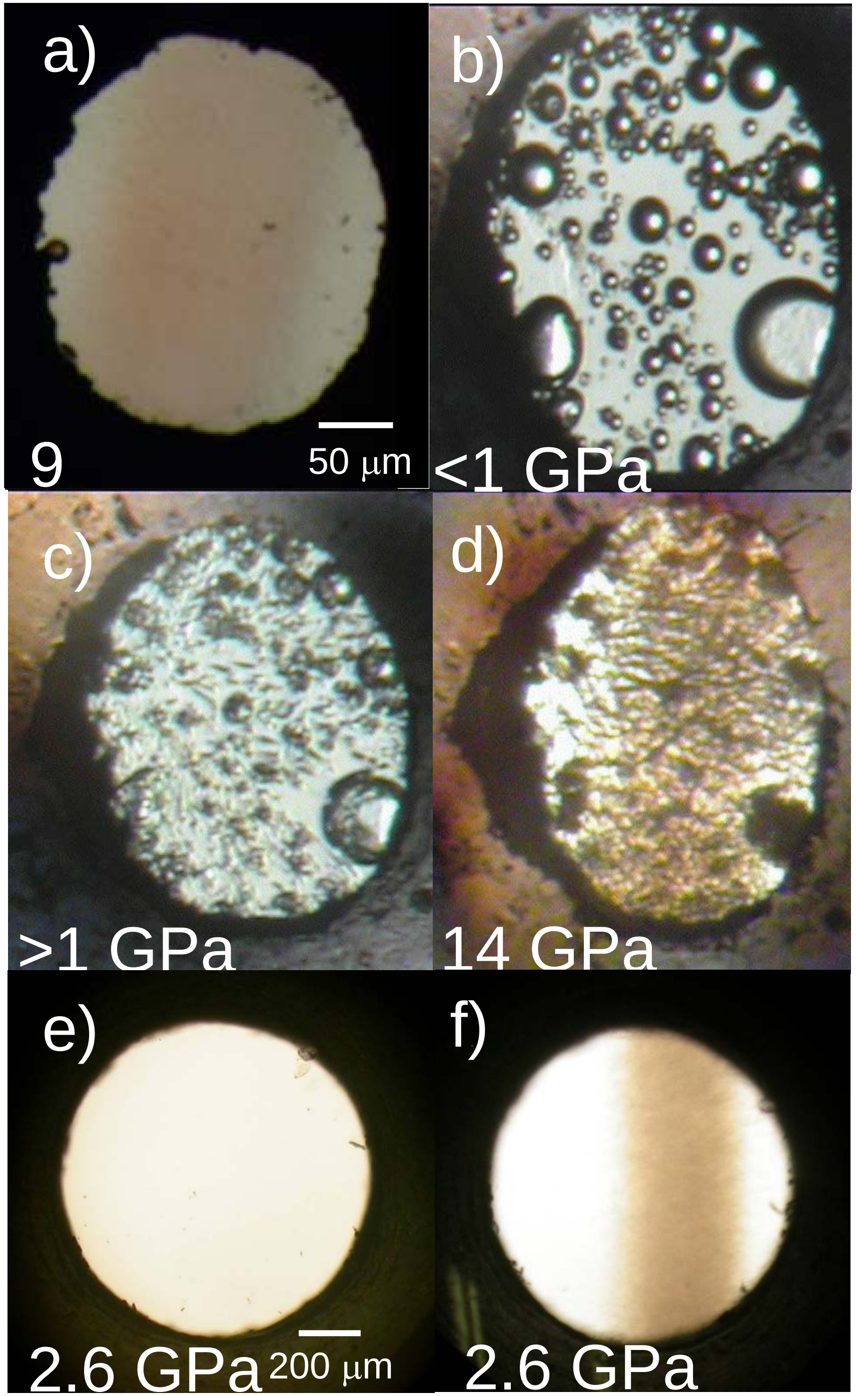


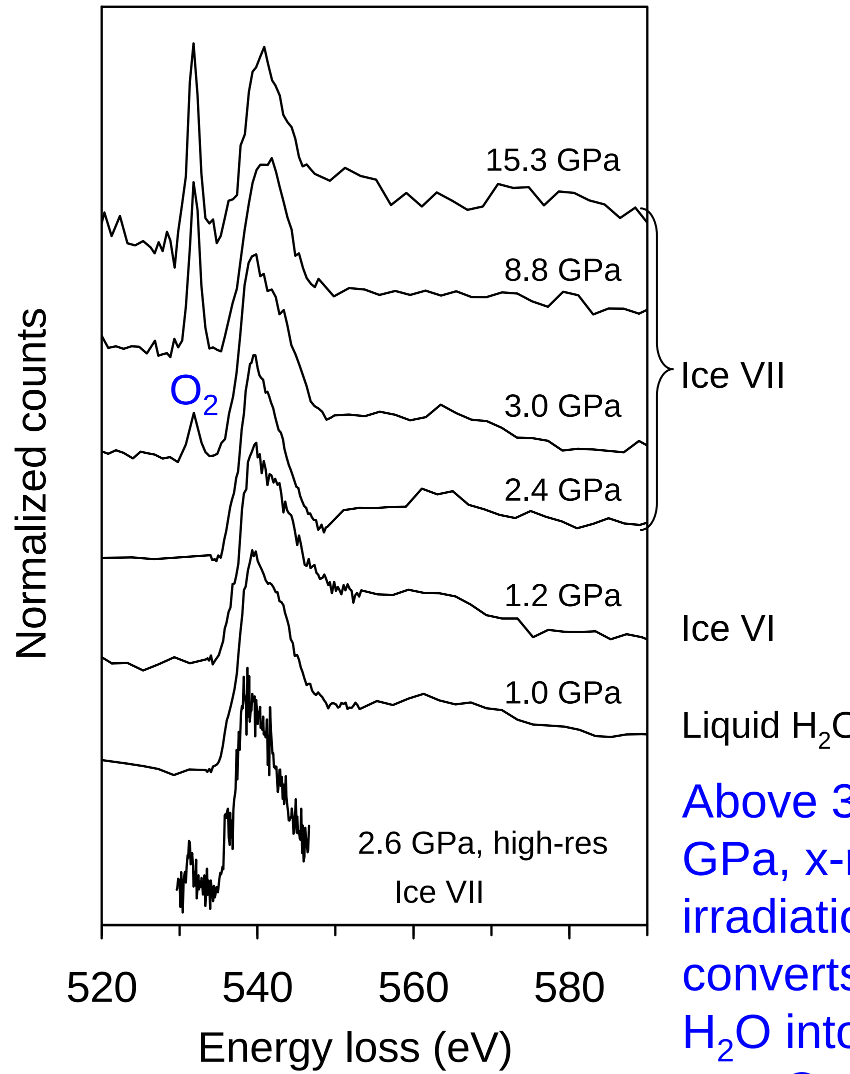

Evidence for a new low-*T* phase




Cai *et al.*, *PRL* 2005

# Novel radiation chemistry at HP



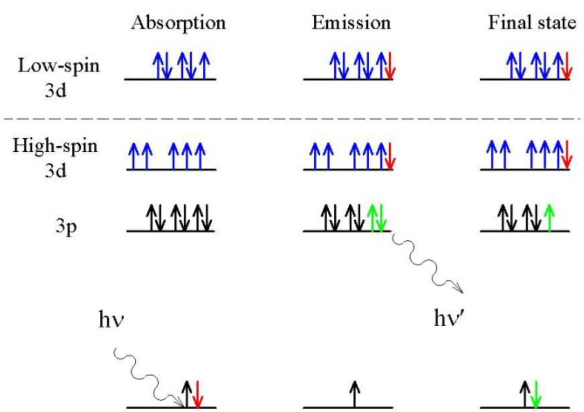



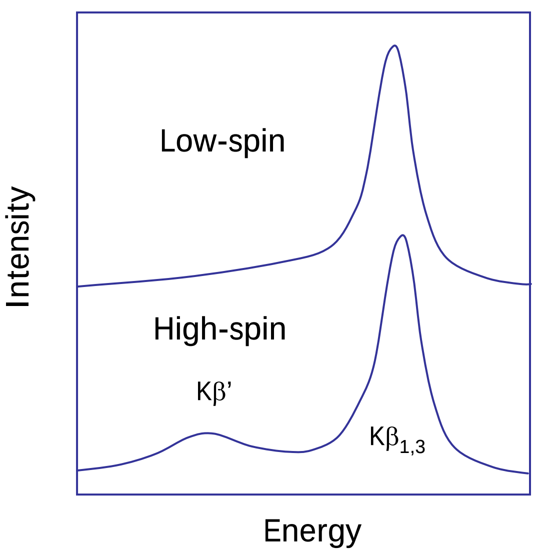

W. Mao *et al*, *Science* 2006

Above 3 GPa, x-ray irradiation converts $H_2O$ into a new $O_2$-$H_2$ alloy

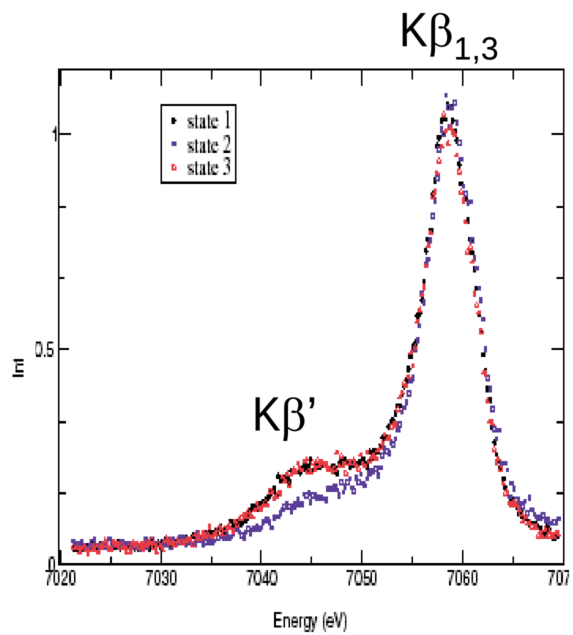
# High-pressure x-ray emission spectroscopy (XES)

Observations of high spin-low spin transitions in 3*d* elements



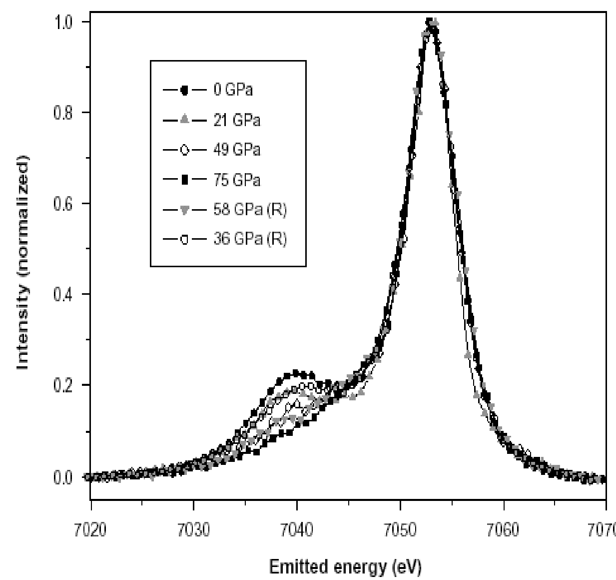




FeO & $Fe_2O_3$



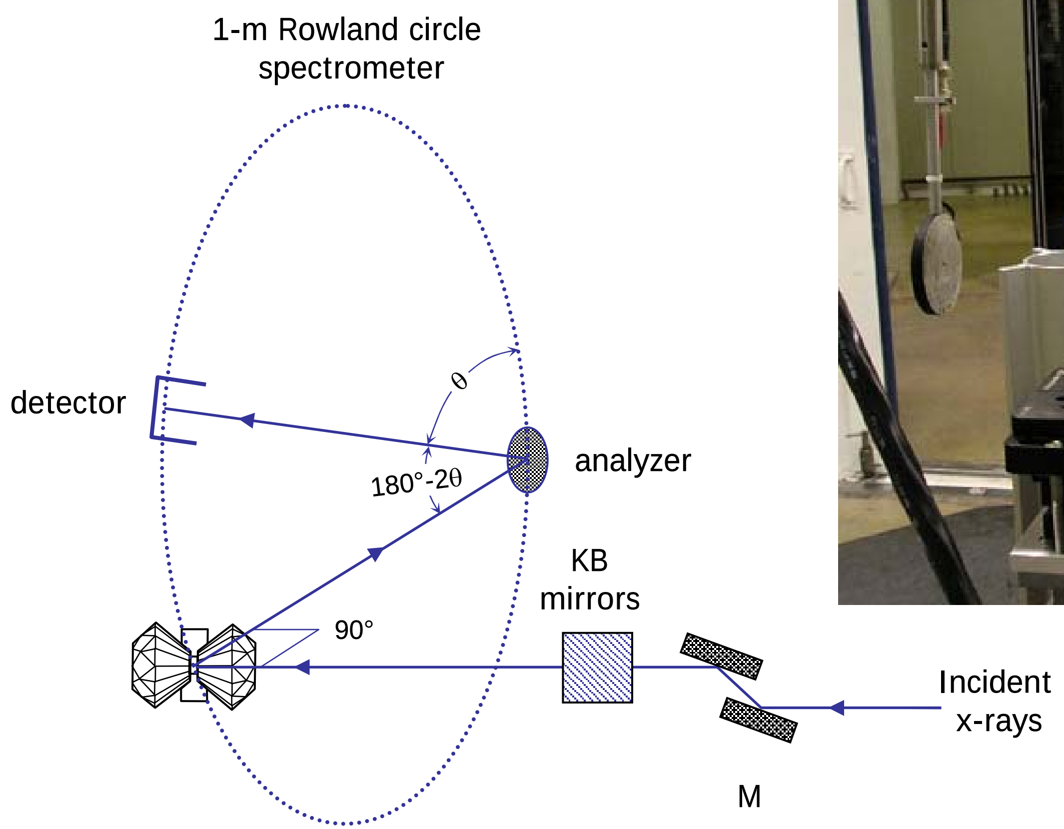

Badro *et al*, *PRL* 1999
Badro *et al*, *PRL* 2002

(Fe,Mg)O & (Fe,Mg)$SiO_3$




Badro *et al, Science* 2003
Badro *et al, Science* 2004
Li *et al*, *PNAS* 2004
Lin *et al*, Science 2007
Lin et al, Nature Geo. 2008

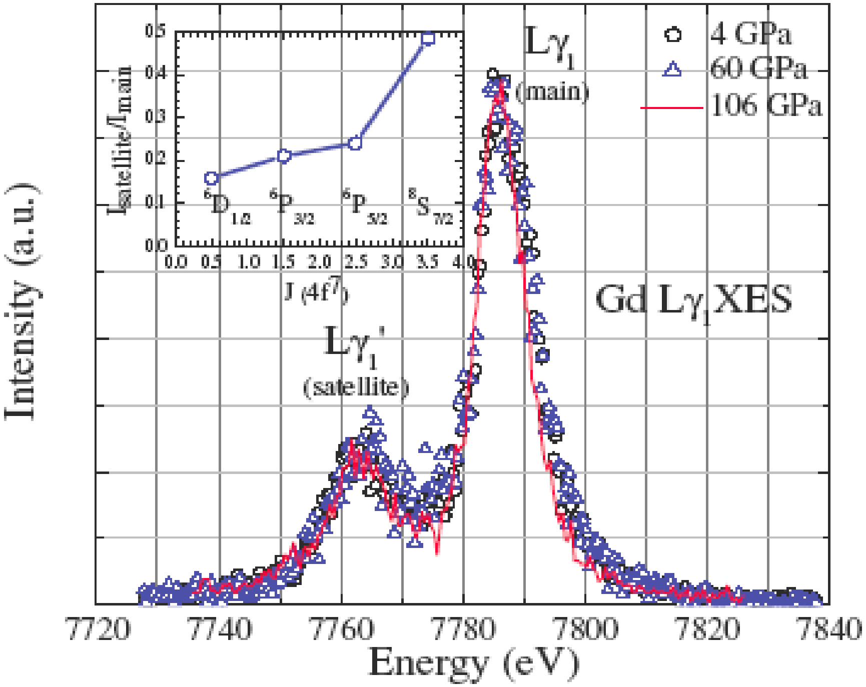
# XES Set-Up



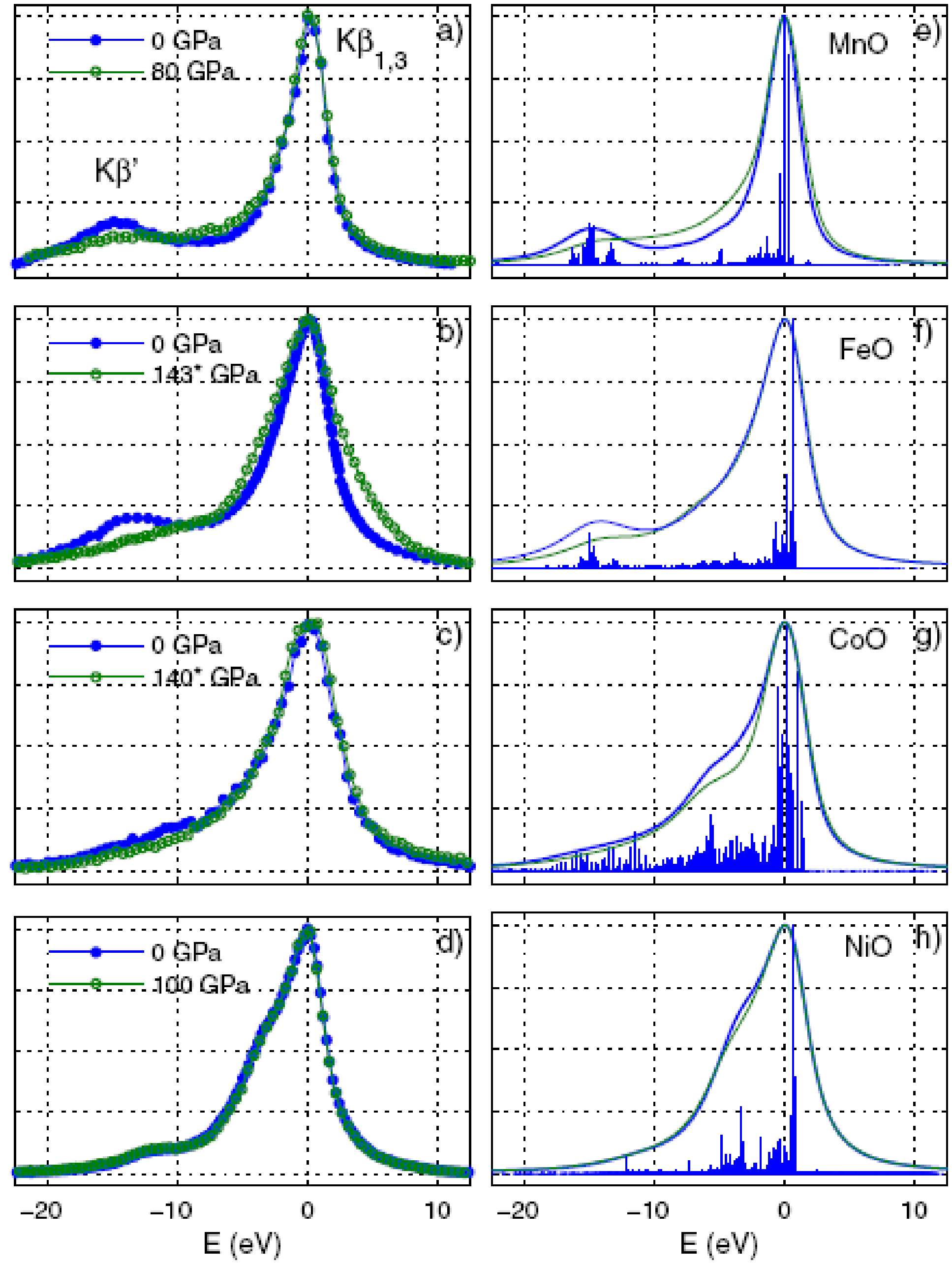

16-IDD, APS

# XES

Gd

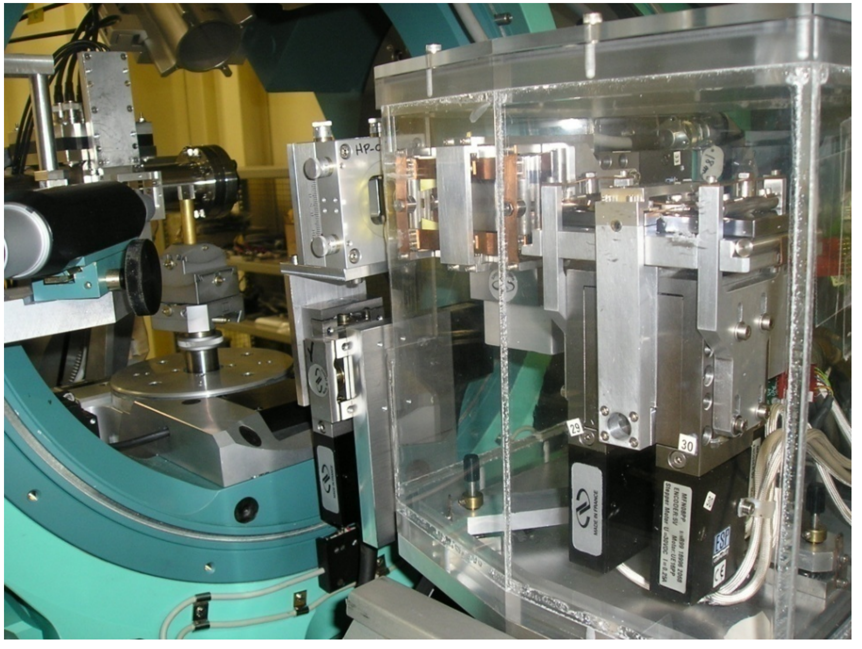



Maddox *et al.*, *PRL* 2006



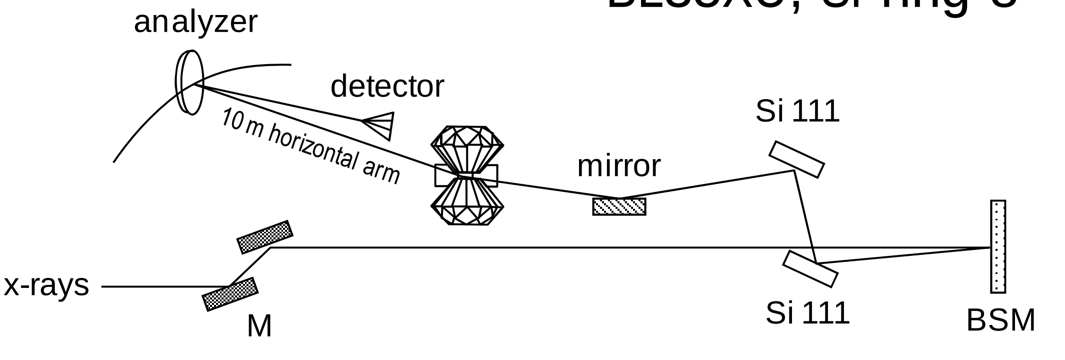

Mattila *et al.*, *PRL* 2007

# Phonon IXS

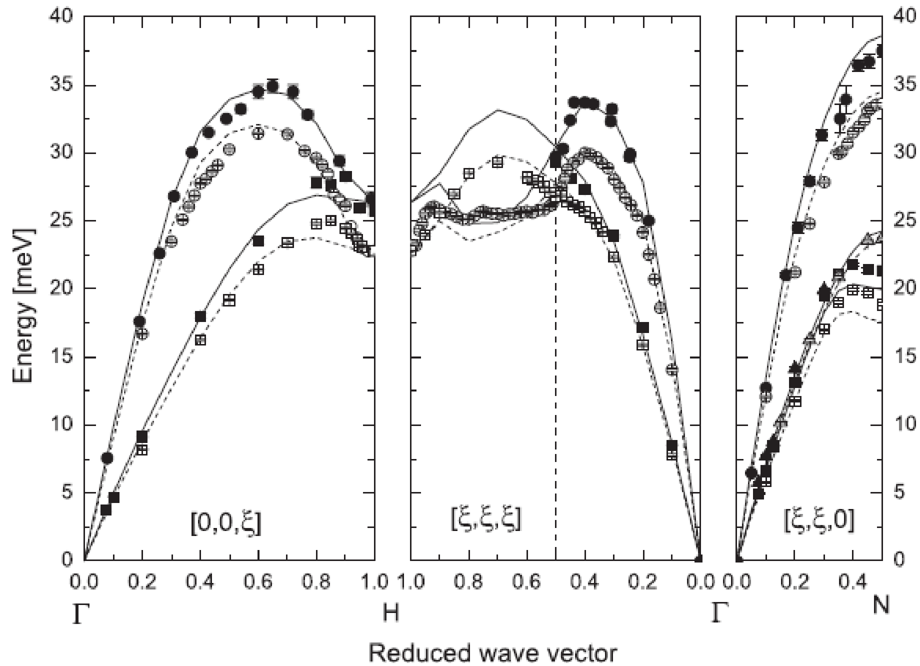


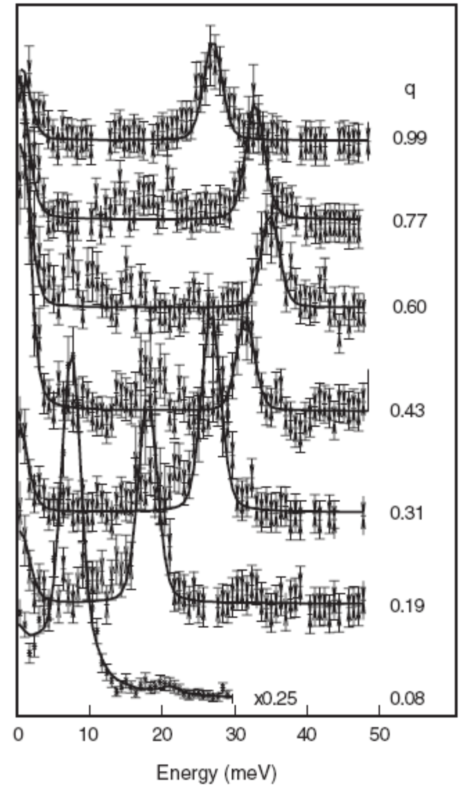
BL35XU, SPring-8

PANORAMIC DIAMOND
ANVIL CELL



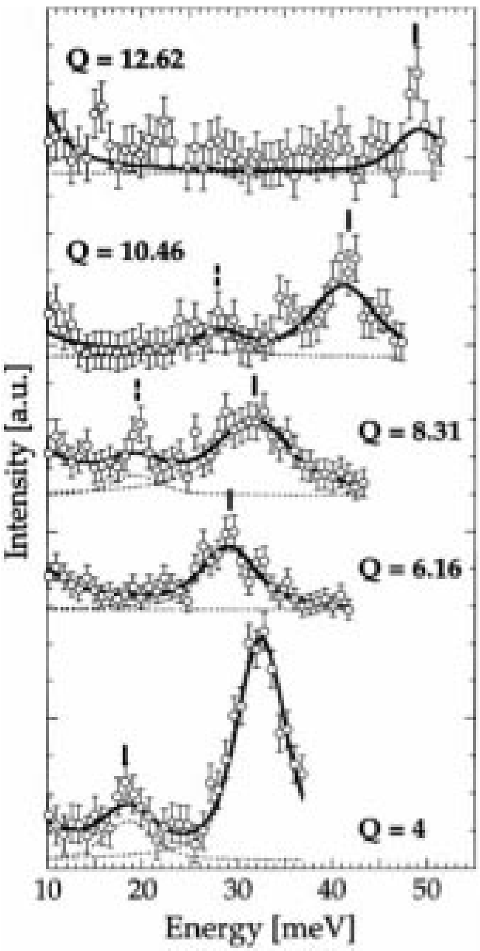
# Lattice dynamics of Mo to 37 GPa



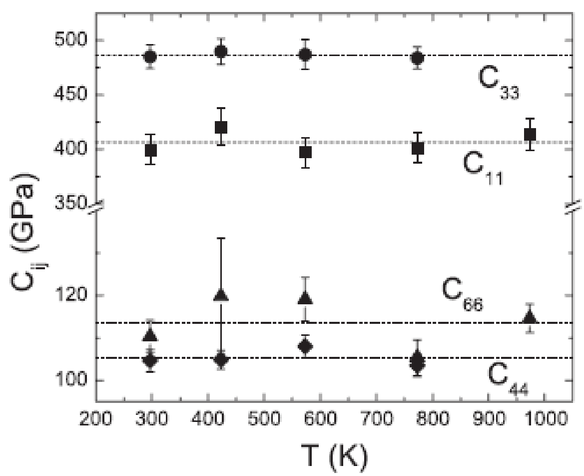

Farber *et al.*, PRL 2006

# PIXS of hcp-Fe to over 100 GPa

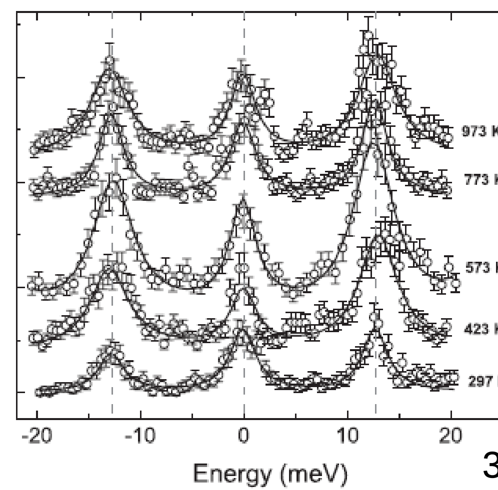



Fiquet *et al., Science* 2001

# Single xtal Co at high *P-T*

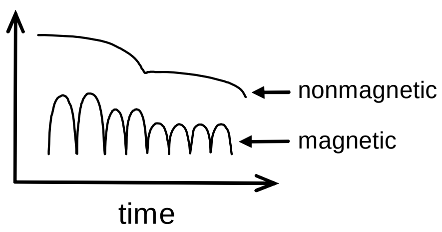


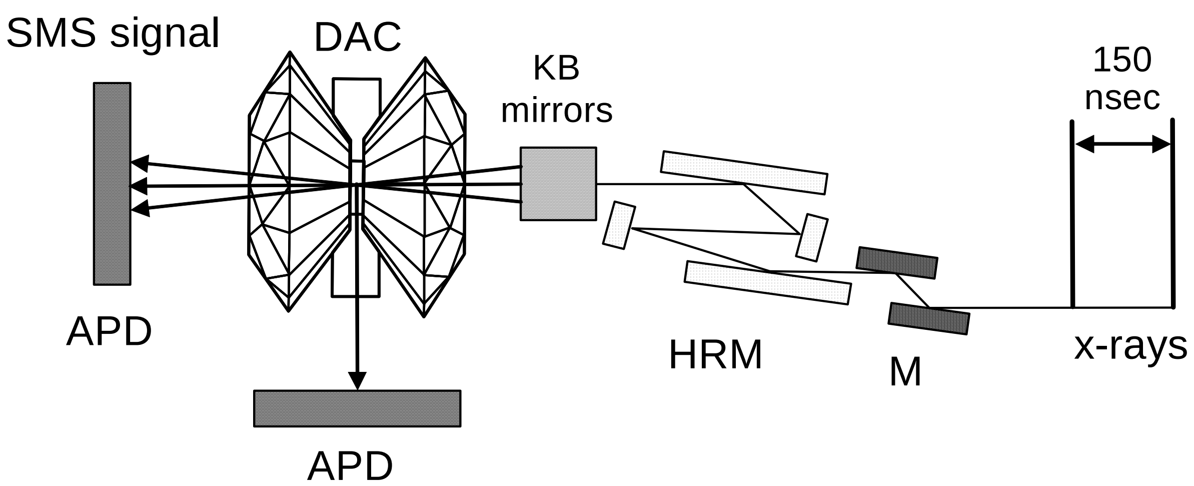

Antonangeli *et al.*, PRL 2008



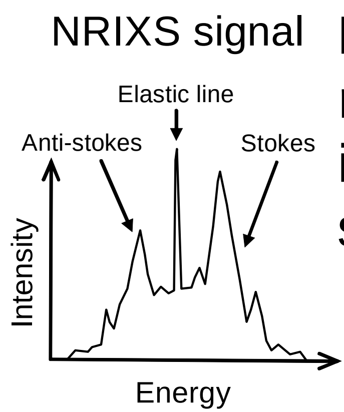
# Nuclear resonant inelastic x-ray scattering

Synchrotron $^{57}Fe$ Mössbauer spectroscopy



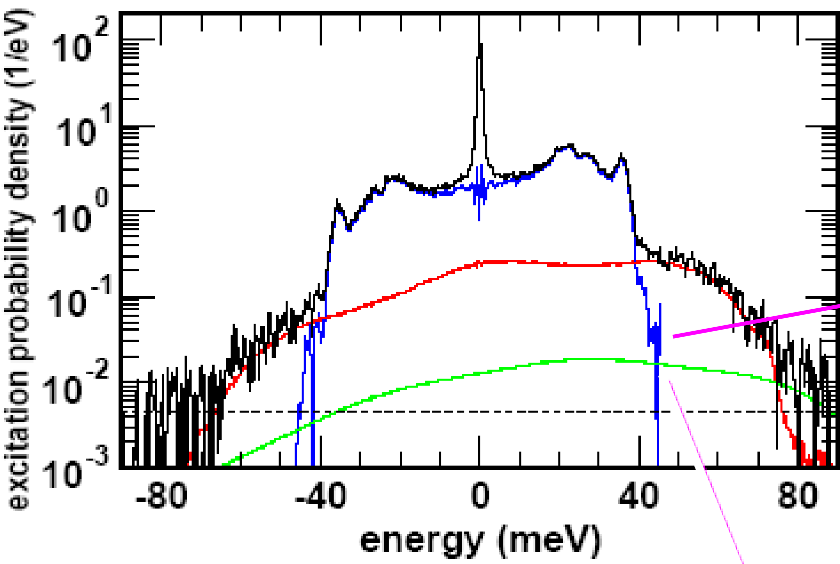

Nuclear resonant inelastic x-ray spectroscopy



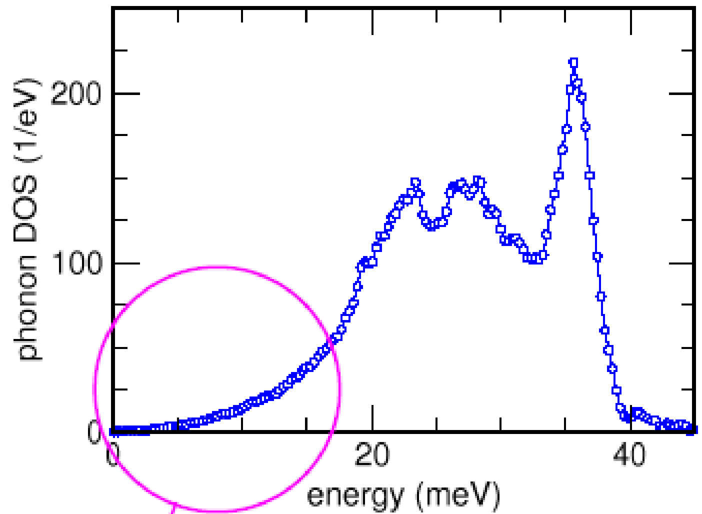

Energy = 14.4125 keV

# Extracting phonon density of states

## Phonon excitation spectrum




## Phonon density of states

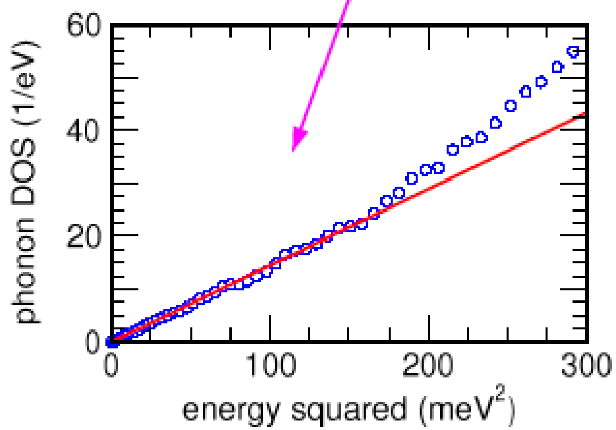



From W. Sturhahn

Sturhahn *et al*, *PRL* 1995

Hu *et al*, *Nucl. Instrum. Meth.* 1999

Sturhahn, *Hyp. Int.* 2000

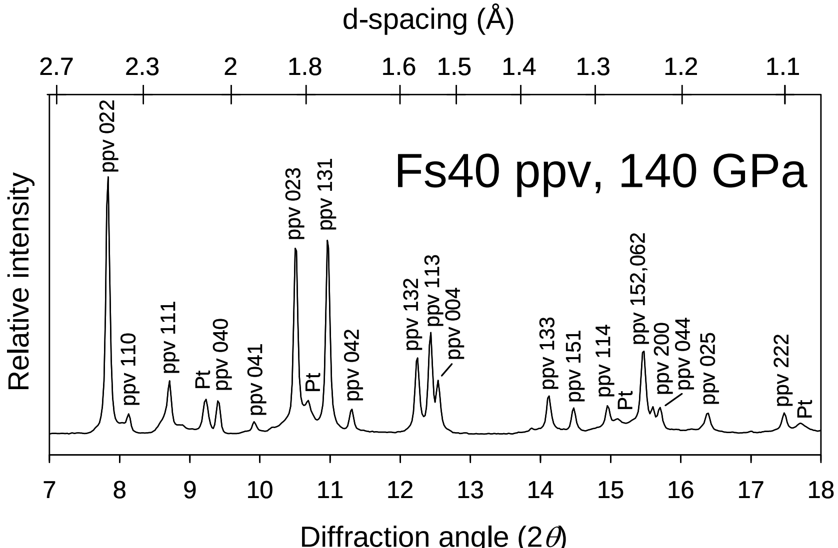


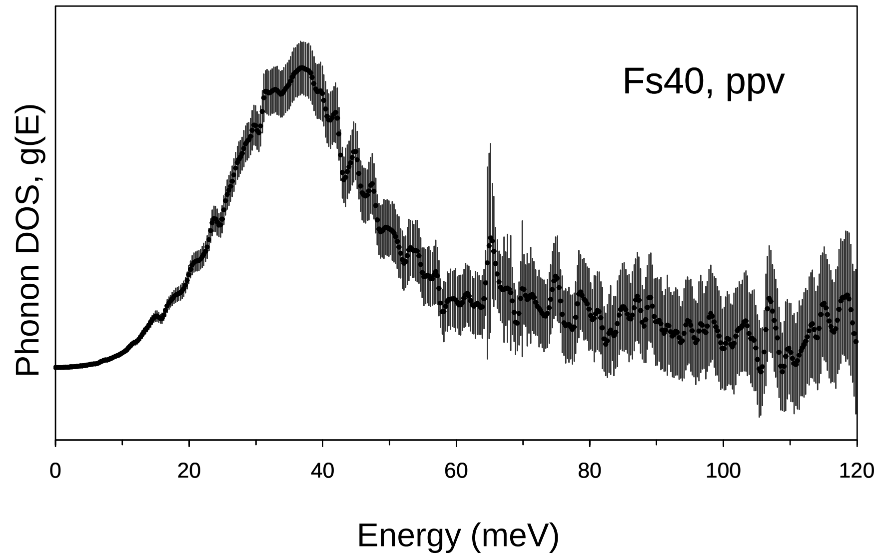

$$g(\omega) = \frac{V}{2\pi^2 \upsilon_D^3}\omega^2$$

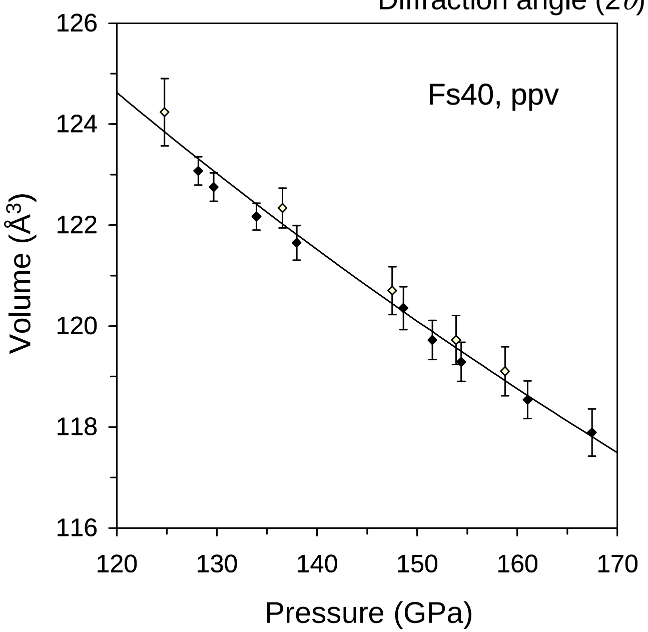
$$\frac{3}{\upsilon_D^{\;3}} = \frac{1}{\upsilon_p^{\;3}} + \frac{2}{\upsilon_S^{\;3}}$$

## Debye velocity

# How do we determine $V_P$ and $V_S$?



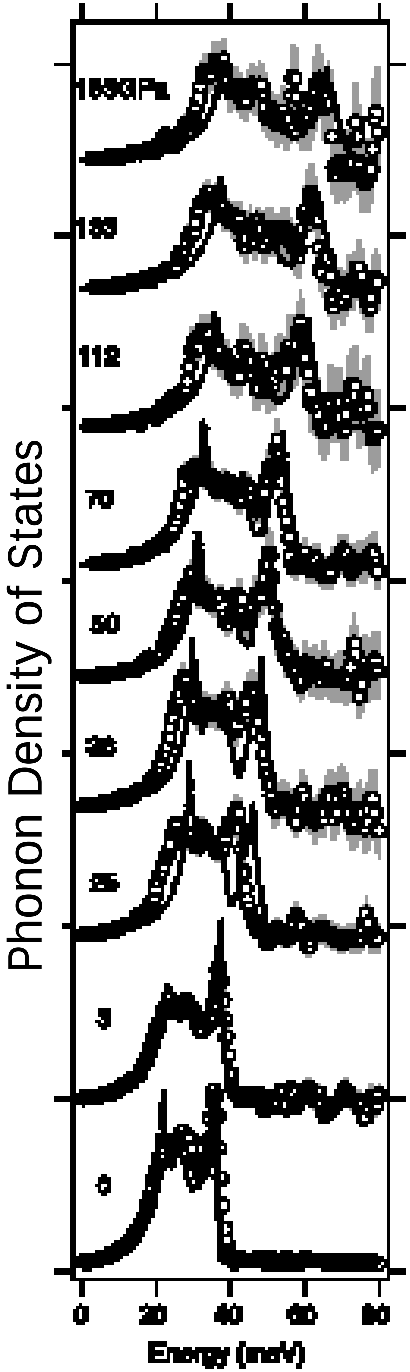

$$K = -V\left(\frac{\partial P}{\partial V}\right)$$

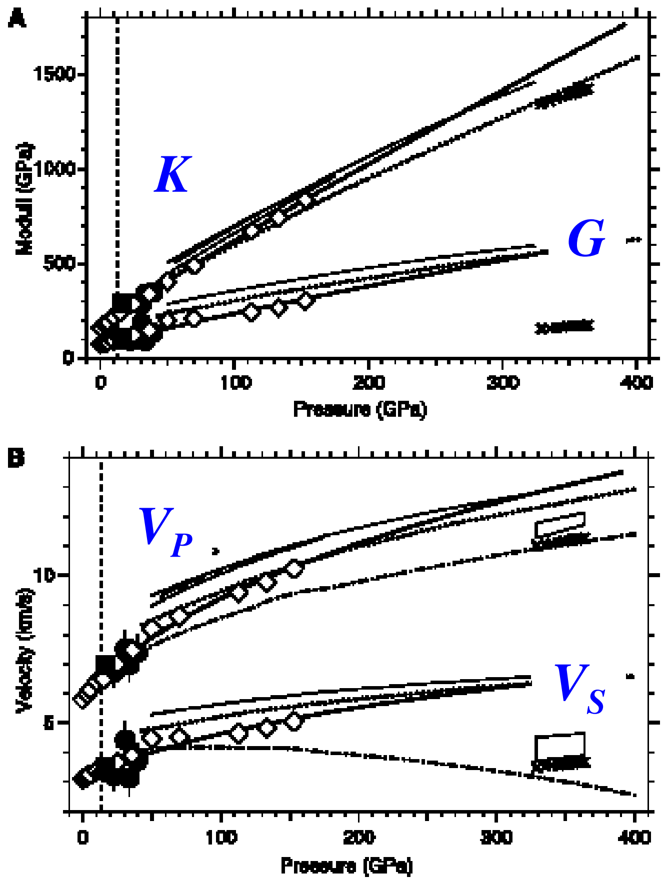
$$\frac{K}{\rho} = \upsilon_P^{\ 2} - \frac{4}{3}\upsilon_S^{\ 2} = \upsilon_\Phi^{\ 2}$$

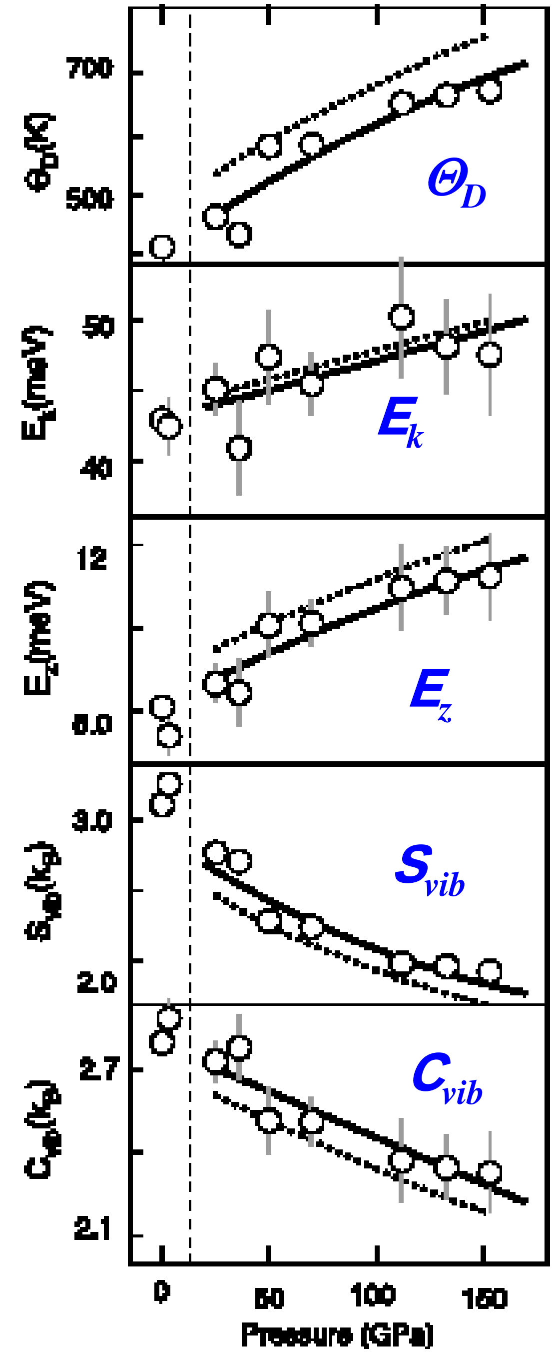
| | $V_P$, km/sec | $V_S$, km/sec |
|---|---|---|
| PREM, mantle side of CMB | 13.72 | 7.26 |
| ULVZ (Thorne, JGR 2004) | 12.35 | 5.08 |
| Fs40 ppv at 130 GPa-300 K | 12.72 | 4.86 |
| Fs40 ppv at 130 GPa-3000 K | 11.91 | 4.05 |

W. Mao *et al*, Science 2006

# Elasticity and thermodynamic parameters of Fe to 153 GPa by NRIXS

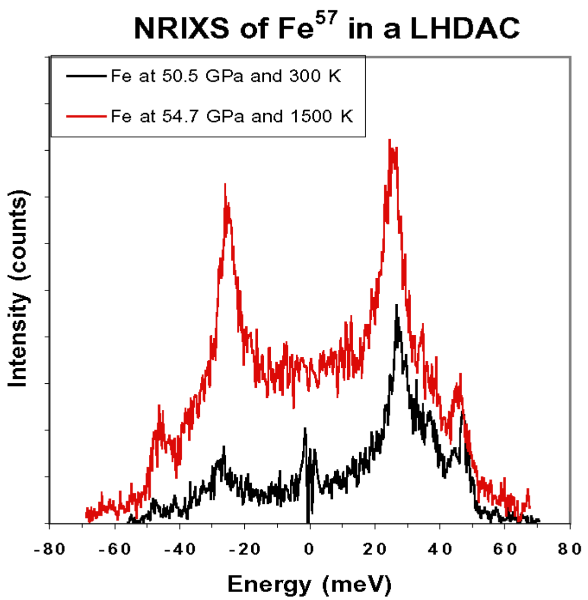


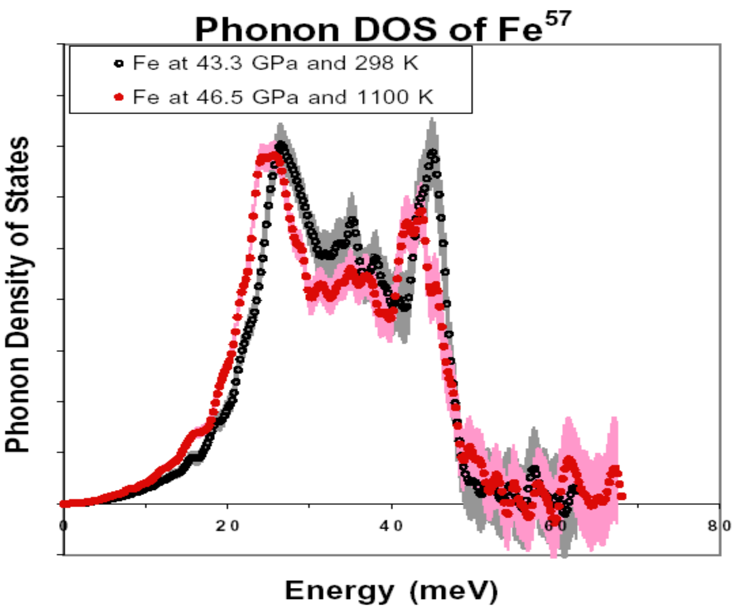



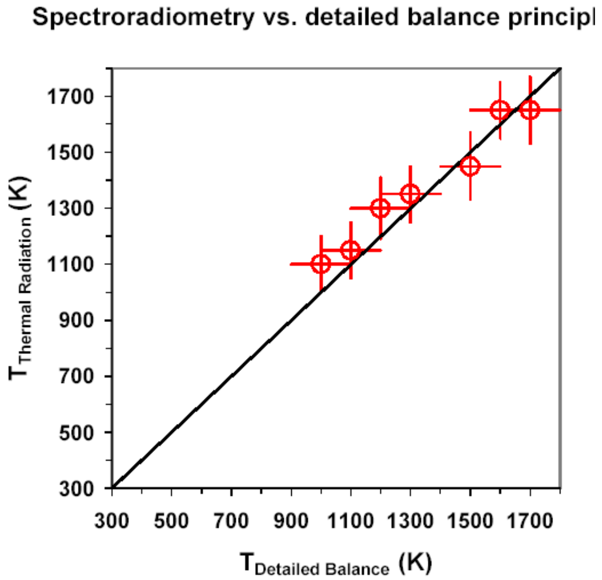

Mao *et al, Science* 2001

# NRIXS at high *P* and high *T*

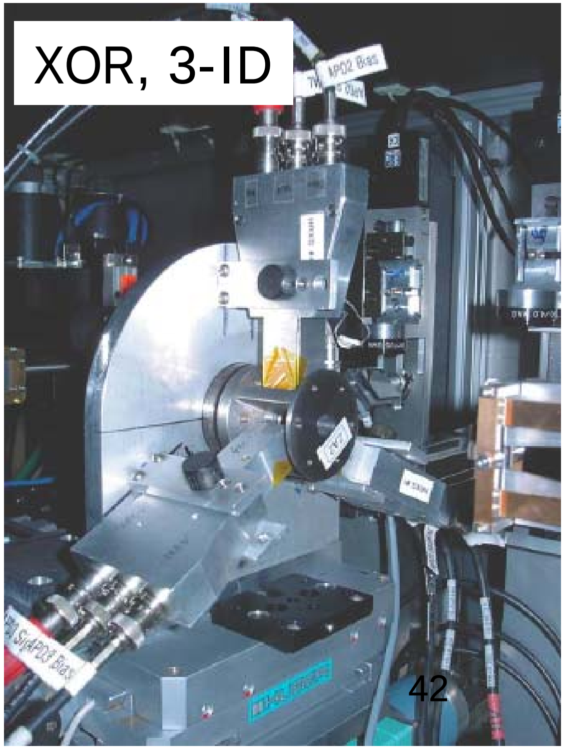



- Need x-ray and laser beam stability over many hours

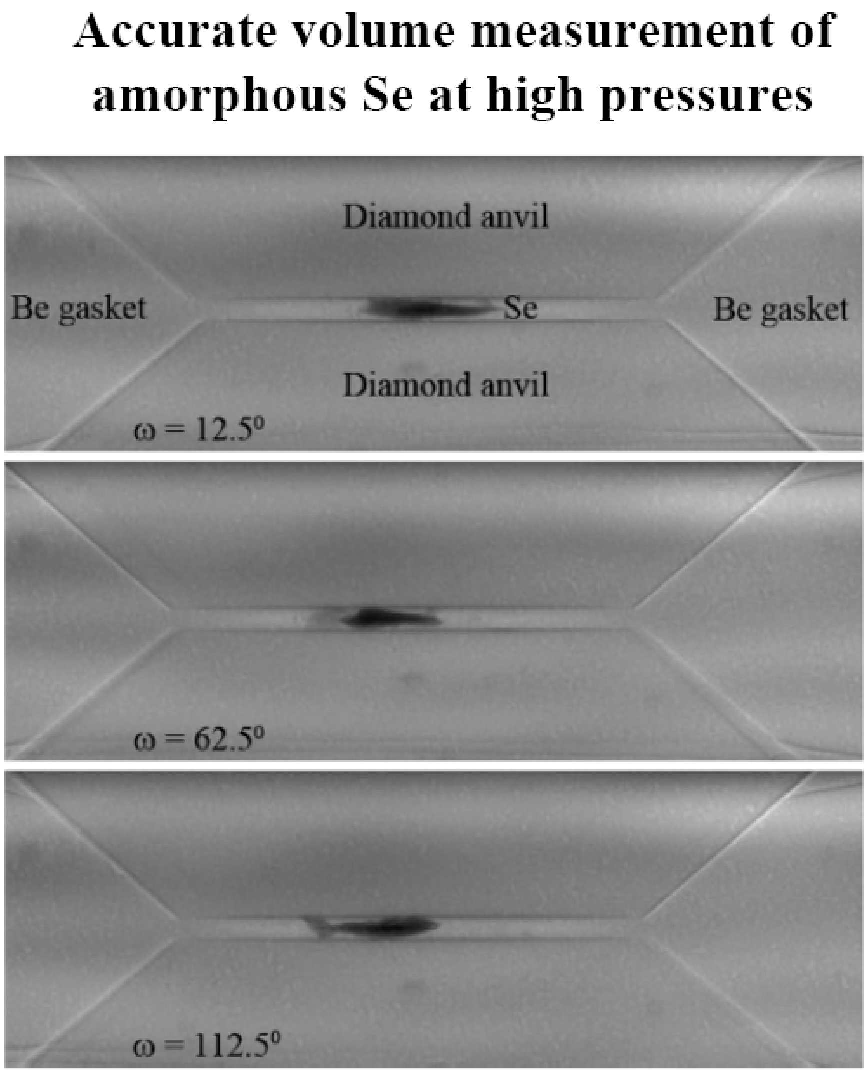


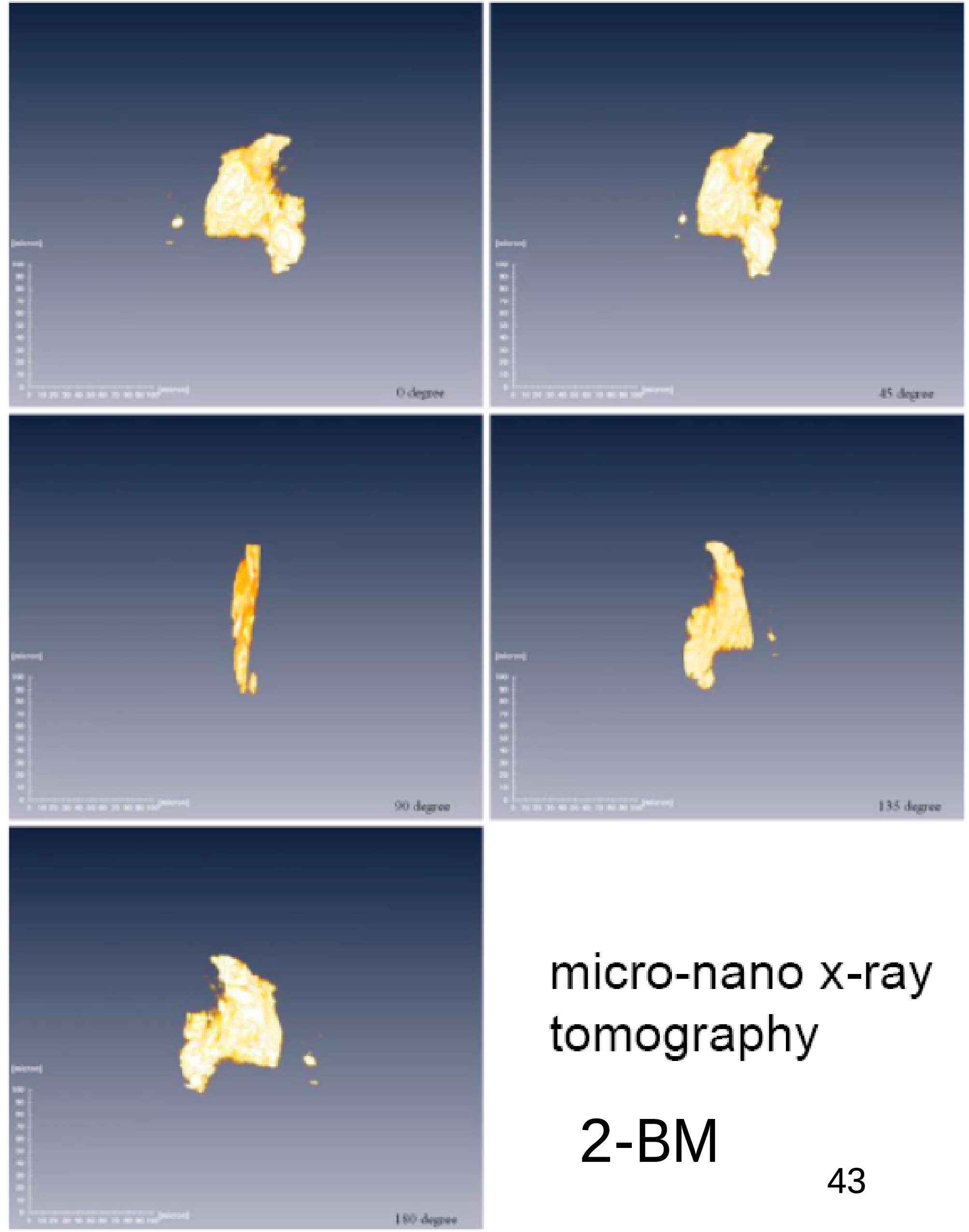

Calibration of temperature




Lin *et al.*, *Science* 2005

# Micro-tomography



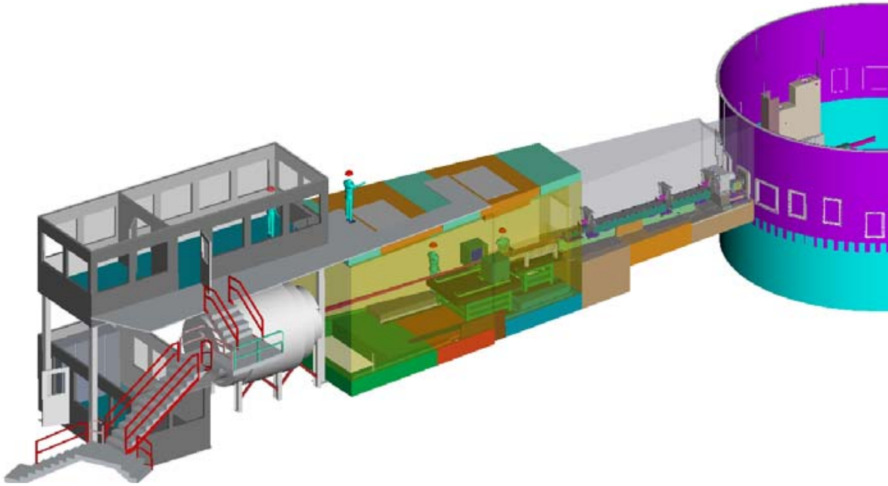



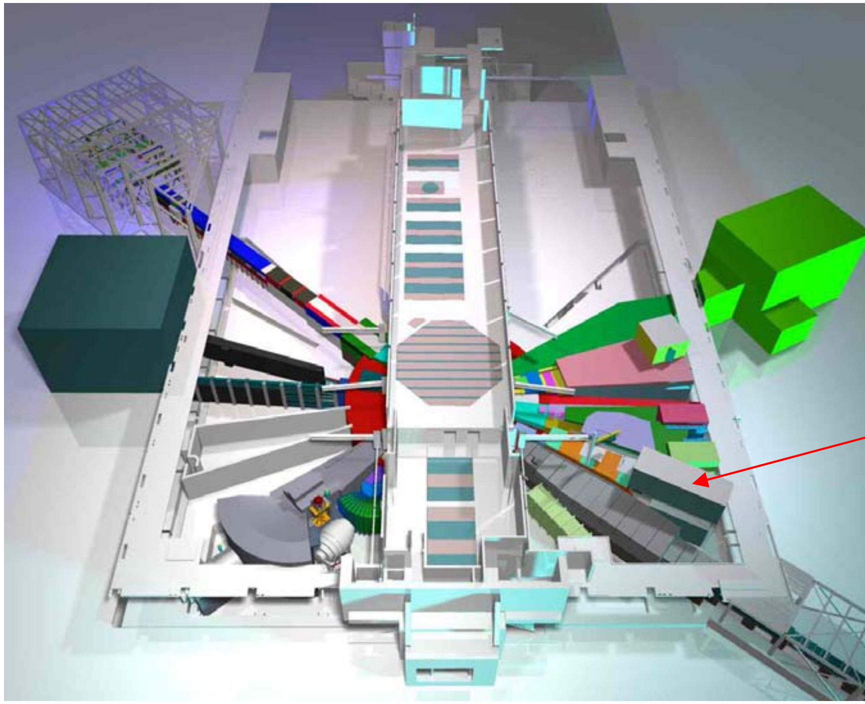
micro-nano x-ray tomography

2-BM

Liu *et al*, *Proc. Nat. Acad. Sci.* ***105***, 13229 (2008)

# High *P-T* Neutron Probes

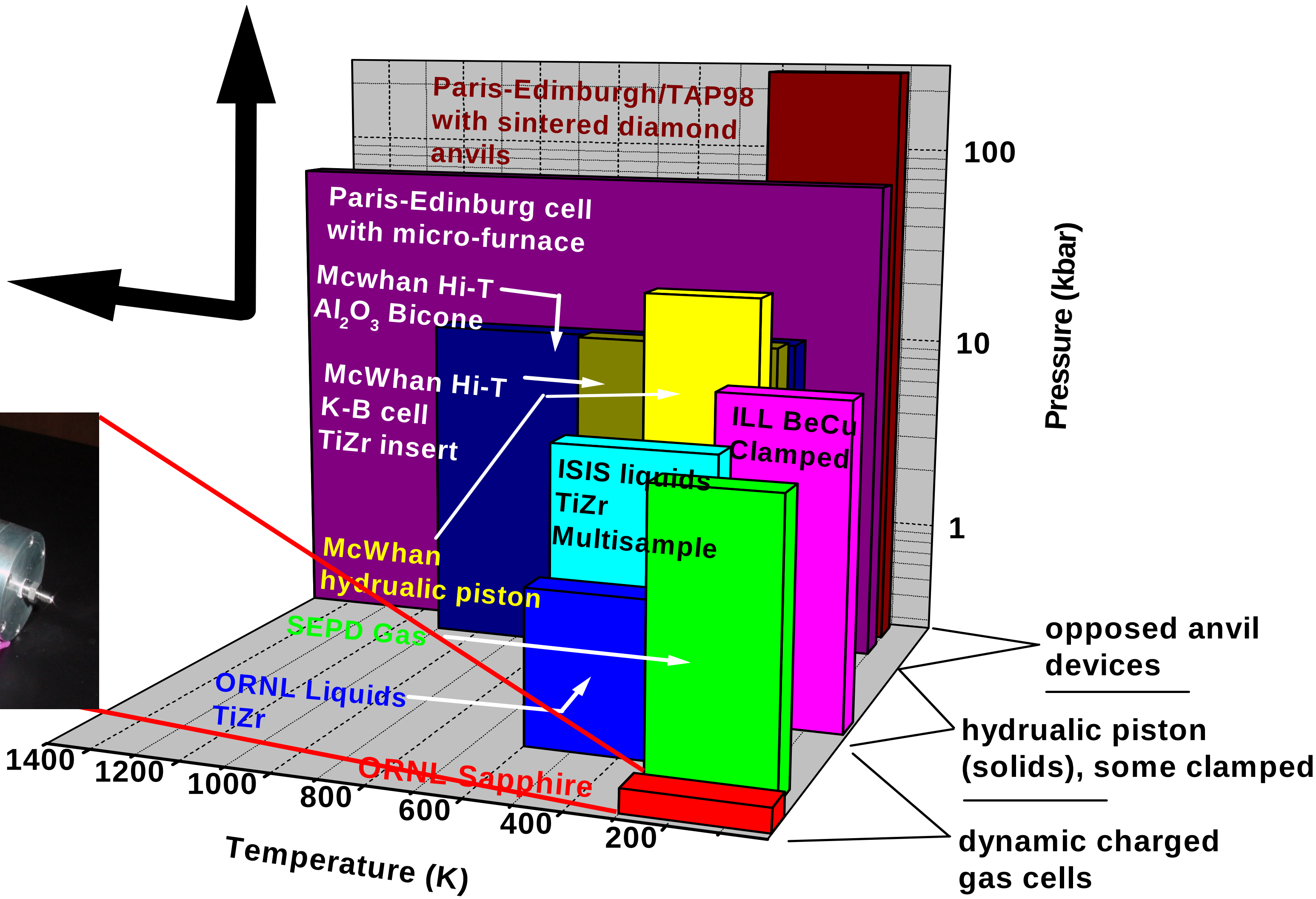


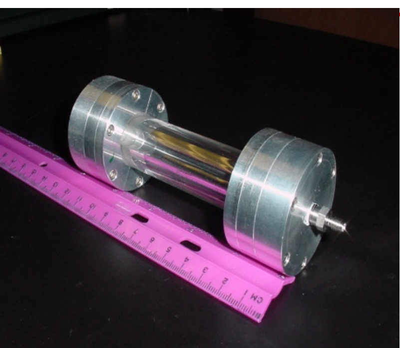


- hydrogen (deuterium)
- magnetic ordering
- large *q*
- phonon dynamics


SNAP -- HP neutron diffraction beamline to be completed in commissioning phase at the new Spallation Neutron Source (SNS) at ORNL

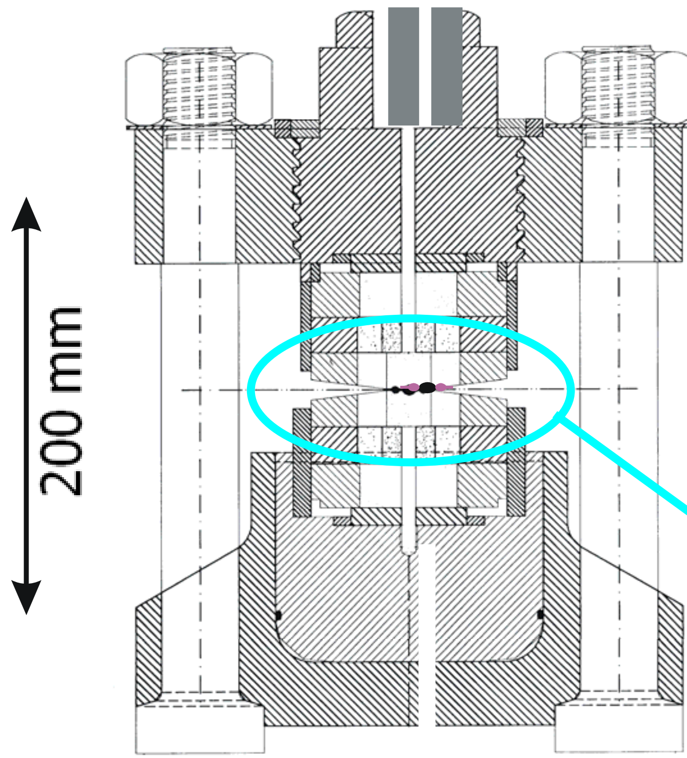
# Survey of Neutron HP cells

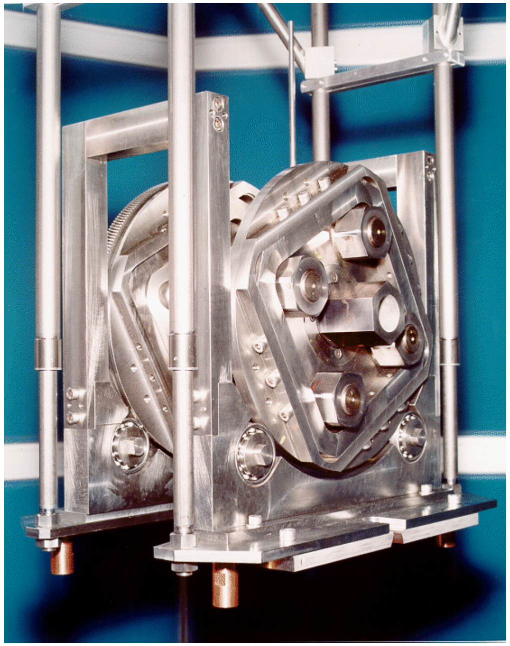


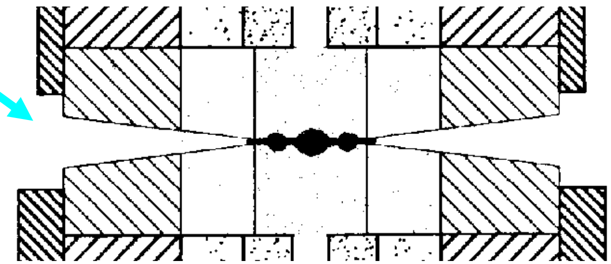



Adapted from C. Tulk

# Paris-Edinburgh HP Cell





- First opposed anvil (WC or sintered diamond) device designed specifically for use at pulsed neutron source, ISIS. Relies on compression of gasket to reduce sample cell volume (200-400 ton press)
- Temperature ranges from < 100 - 1200 K with pressures up to ~ 25 GPa
- Primarily used for solid powdered crystals, but has been used for single crystals and amorphous solids

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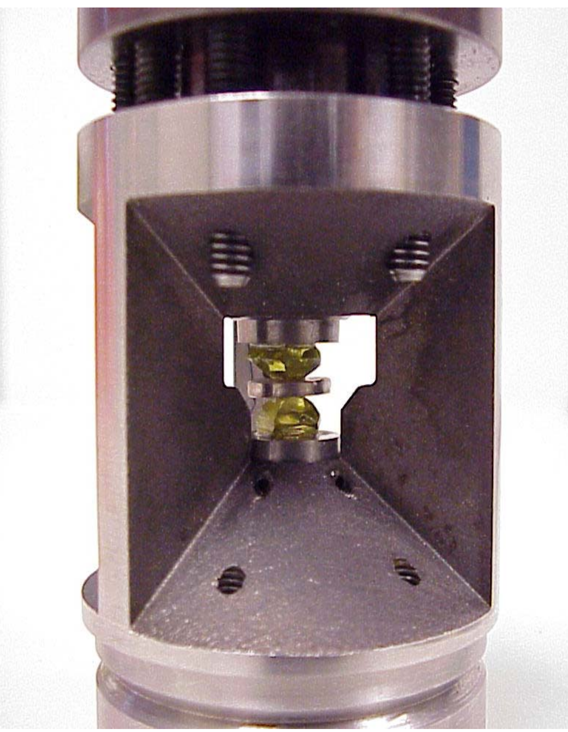
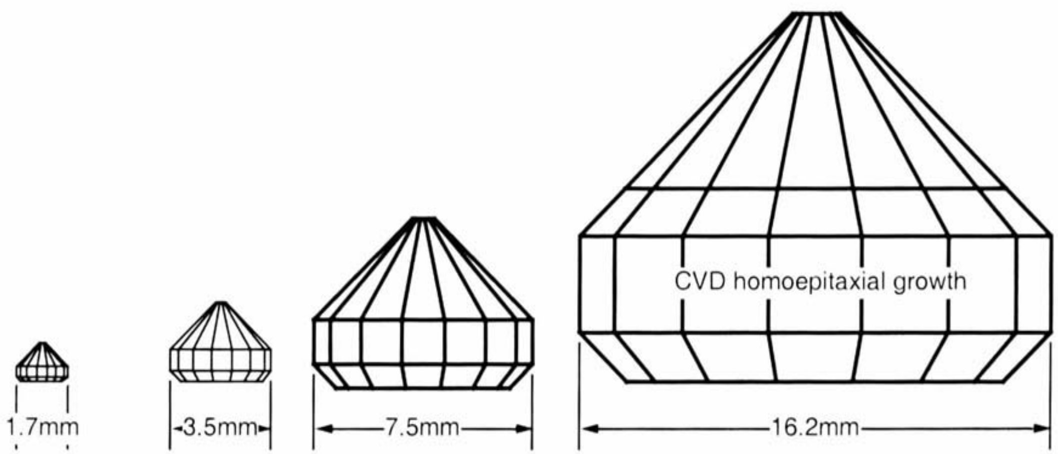
# Large volume anvil cells

- Large anvil required for the goal of 1 $mm^3$ samples (25 ct). Currently, synthetic sapphire, moissanite (hexagonal SiC), or diamonds are candidates.
- Natural diamonds far too expensive and likely not defect free.






| | | | | |
|---|---|---|---|---|
| weight, carat | 0.025 ct | 0.25 ct | 2.5 ct | 25 ct |
| Natural diamond | $200 | $1,200 | $25,000 | $2,000,000 |
| Synthetic diamond | $400 | $1,500 | $5,000 | ---- |

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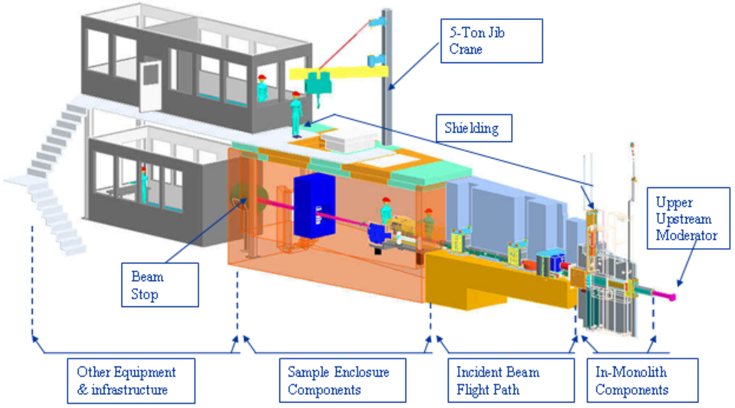
# Future opportunities in high pressure

## SYNCHROTRON RADIATION


- Inelastic scattering extreme *P-T*
- Sub-ps, nanoscale measurements
- New sources: ERL, LCLS, NSLSII

## NEUTRON SCATTERING

-large volume diamond cell



## New-generation high-pressure devices: need better diamonds than provided by Mother Nature

- Size
- Single-crystal
- Strength
- Spectroscopic quality

## New-generation high-pressure devices: need better diamonds than provided by Mother Nature

Size -- 1,000 ct anvil? Rapid, unlimited growth

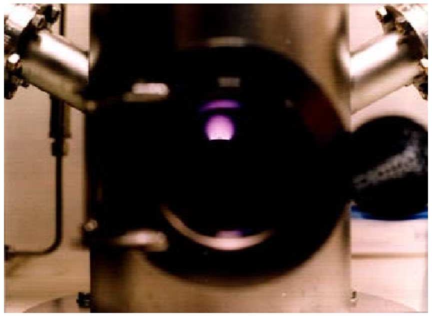
Single-crystal -- epitaxial growth

Strength -- hardness/toughness

Spectroscopic quality -- from UV to IR

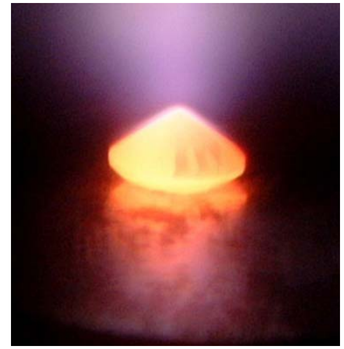
# Giant, perfect, single-crystal diamonds can be grown by chemical vapor deposition (CVD) process

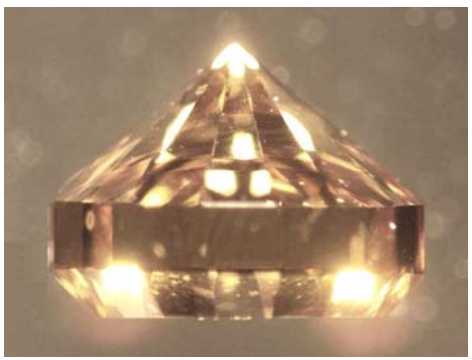
Diamond Growing in a Plasma Reactor



Growth rate improved from 1 µm/hr to 300-500 µm/hr

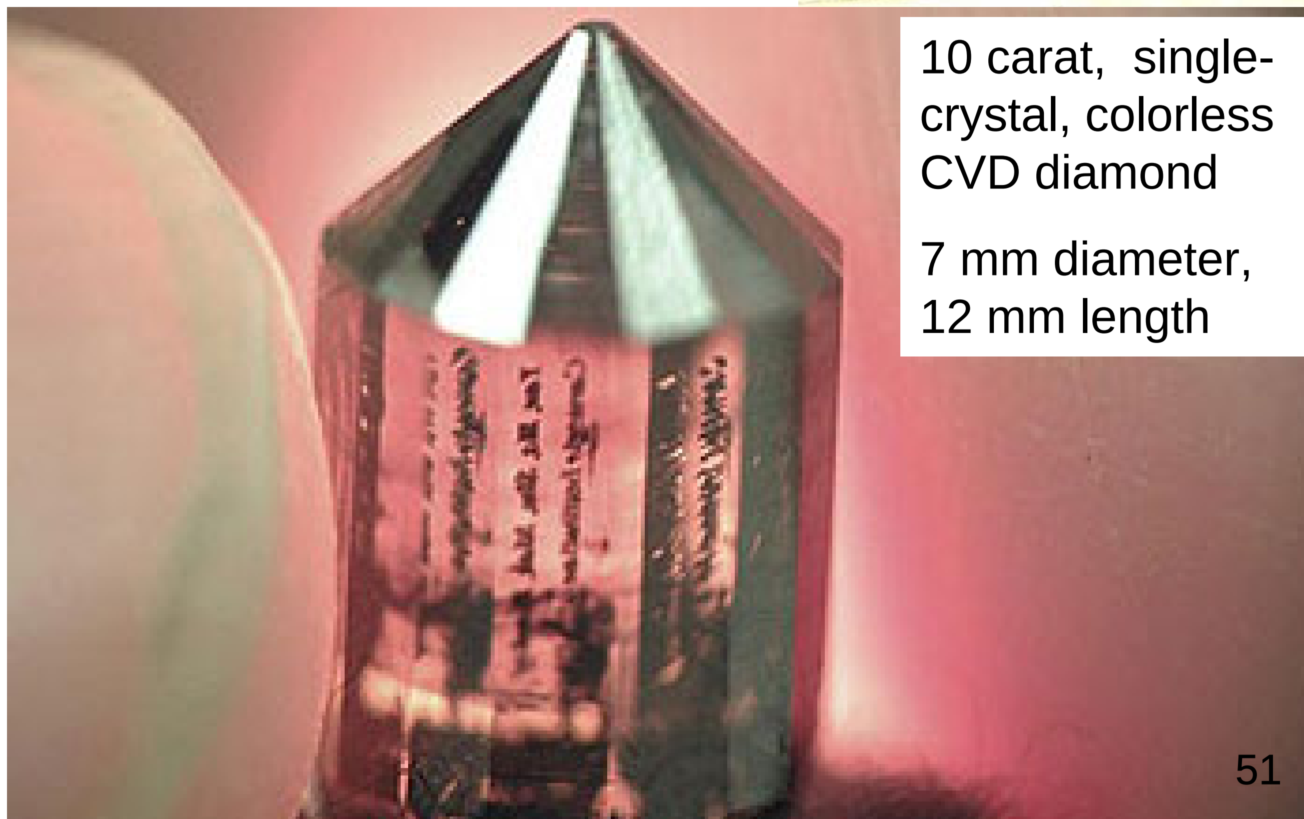
Yan *et al*. *PNAS* 2002





Production of regular diamond anvil
- 2.45 mm high
- 0.28 carats
- <u>Grown in 1 day</u>
- <u>reached 200 GPa</u>

Yan *et al*. *Phys. Stat. Sol.* 2004

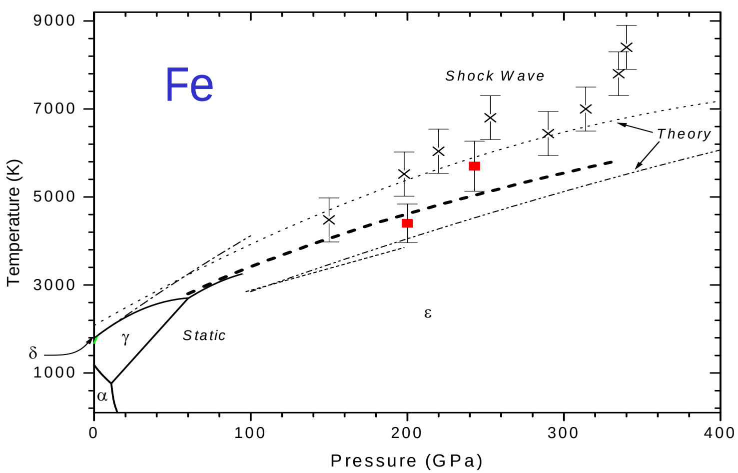


10 carat, single-crystal, colorless CVD diamond

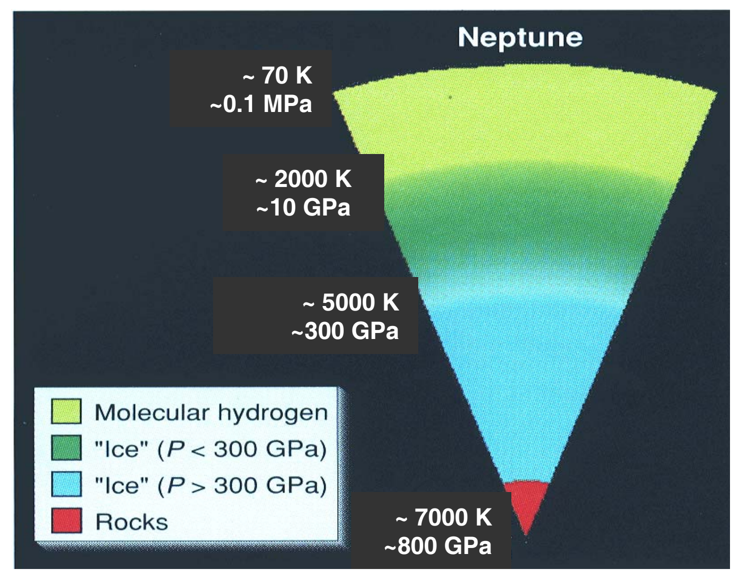
7 mm diameter, 12 mm length

# Pressure opens a new dimension for all sciences

- Earth and Planetary Sciences
  - *In situ* measurements from crust to core conditions
  - Icy satellites and extrasolar bodies
- Other Applied Fields
  - Biology: Life at extreme conditions, protein xtallography
  - Materials Science: Electronic, magnetic, superhard, nano-, energy-related materials
- Fundamental Chemistry & Physics
  - Novel behavior and new phases







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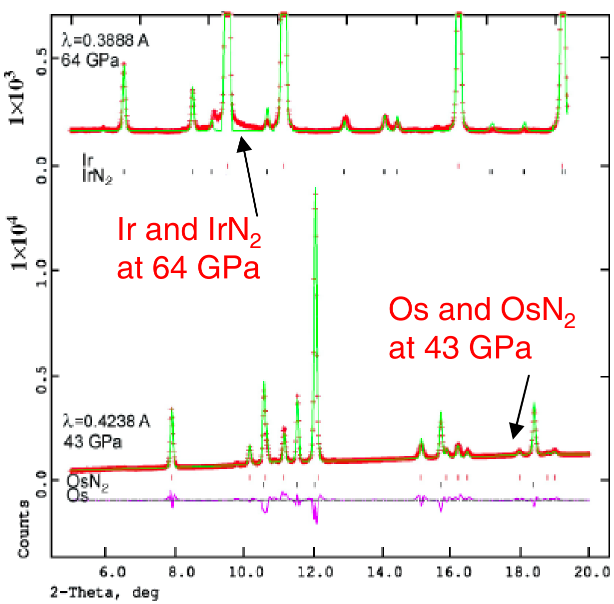
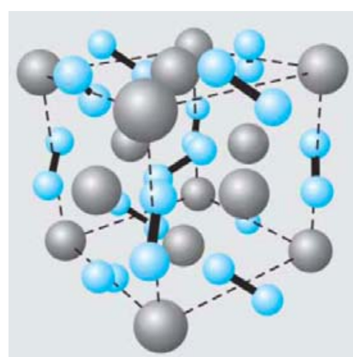
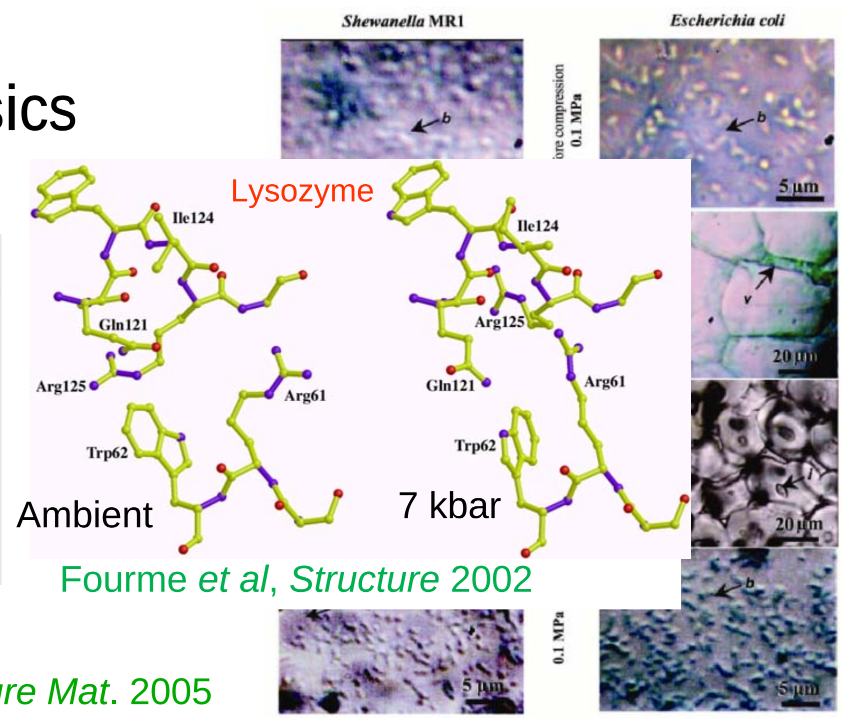


$PtN_2$ in pyrite structure

Degtyareva et al, *Nature Mat*. 2005
Crowhurst *et al, Science* 2006
Young *et al, PRL* 2006




Fourme *et al*, *Structure* 2002

Sharma *et al*, *Science* 2002

Evidence for microbial activity up to 1.6 GPa

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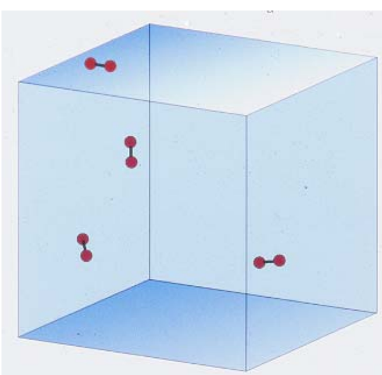
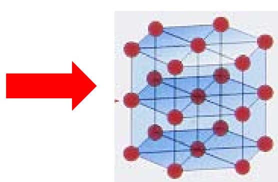
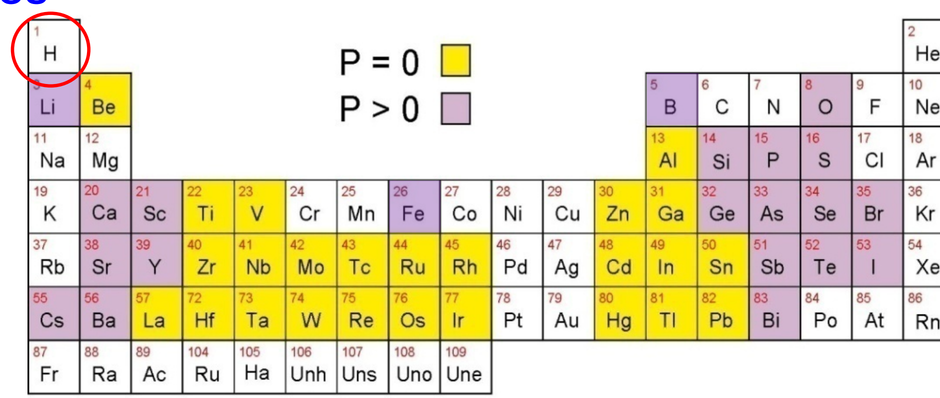
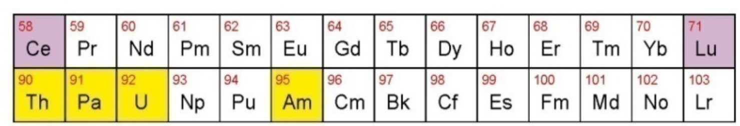




Periodic Table of Superconductors




- Pressure-induced metallization?

  Wigner & Huntington, *J. Chem. Phys*. **3**, 1935

- Exotic properties: Room-*T* super-conductor

  Ashcroft, *Phys. Rev. Lett*. **21**, 1968