High Pressure Techniques

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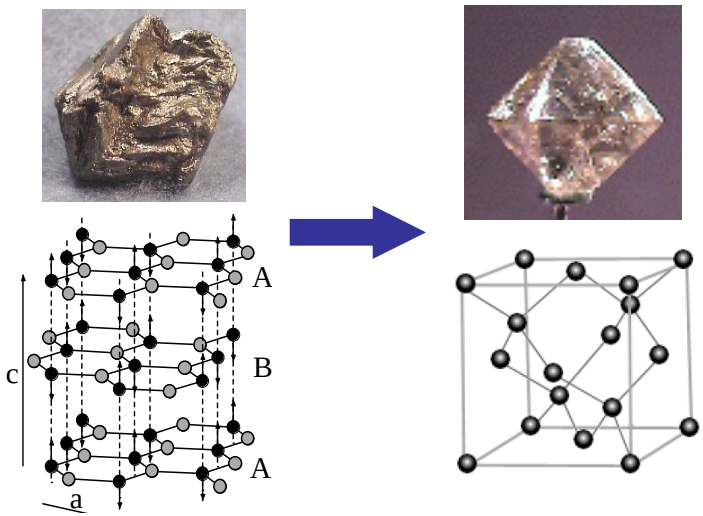
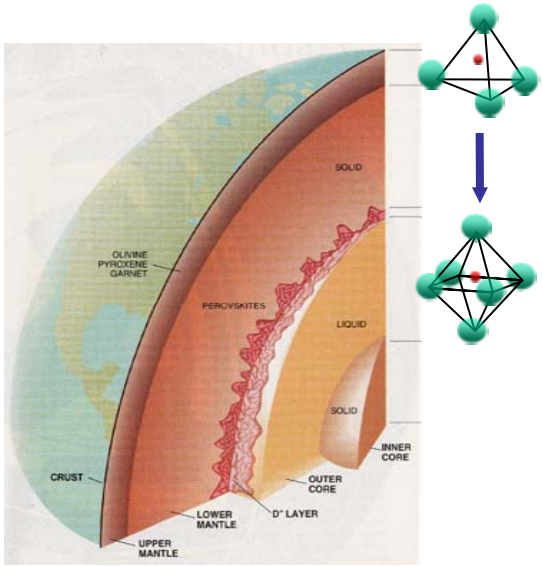
Pressure changes everything



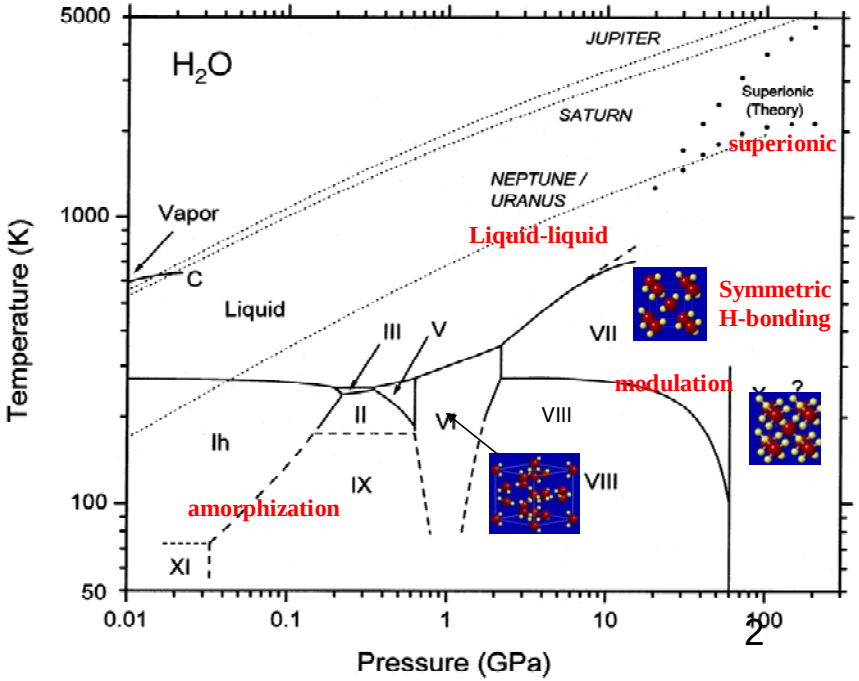


Periodic Table of Superconductors

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									

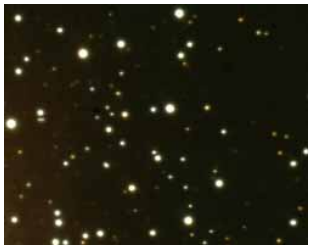
58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr



Range of Pressure in the Universe

Pressure (Atmospheres)

10^{-32} Hydrogen gas in intergalactic space



10^{-24}

Interplanetary space

10^{-16}

Atmosphere at 300 miles

10^{-8}

1

10^{8} Center of Jupiter

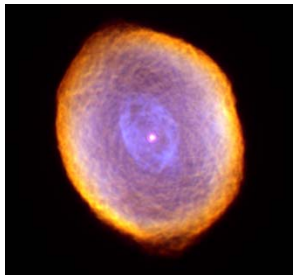
Center of Sun

10^{16}

Center of white dwarf

10^{24}

Center of neutron star



10^{32}

Pressure (Atmospheres)

1 GPa = 10^4 bar

10^{-8}

10^{-6} Best mechanical pump vacuum

10^{-4}

10^{-2} Water vapor at triple point

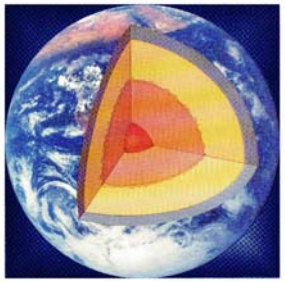
1 Atmospheric pressure (sea level)

10^{2}

Deepest ocean

10^{4}

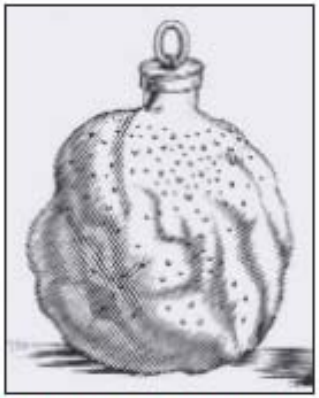
10^{6} Center of the Earth



10^{8}

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

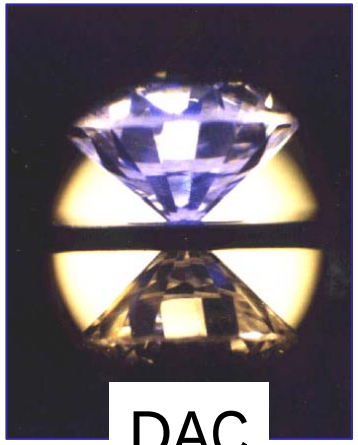
- Diamond anvil cell (DAC) reaches beyond 300 GPa

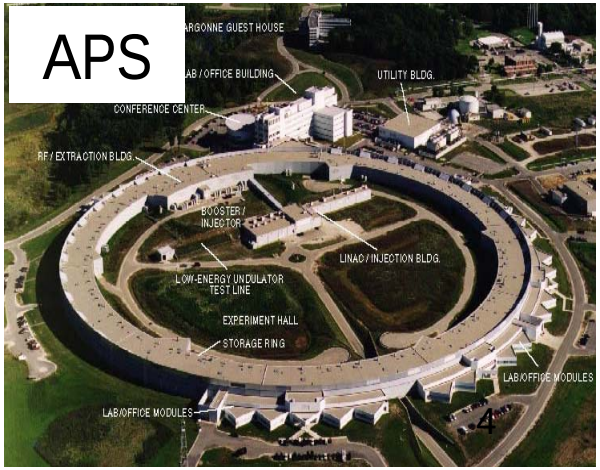
~2000

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

Now

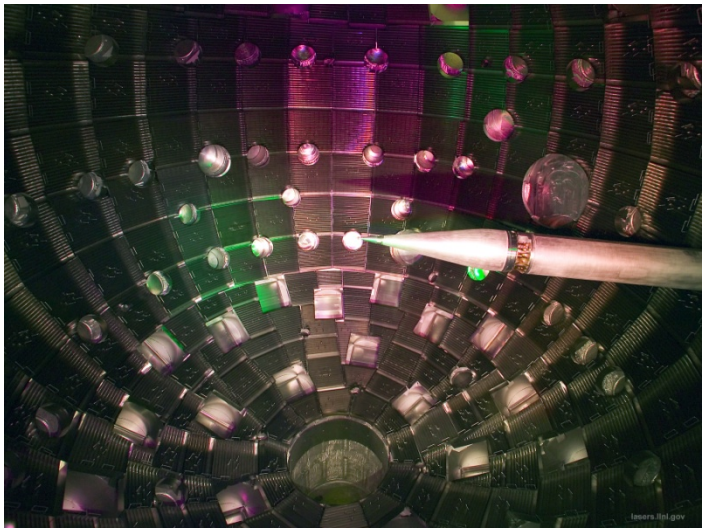
- exciting science to be reaped



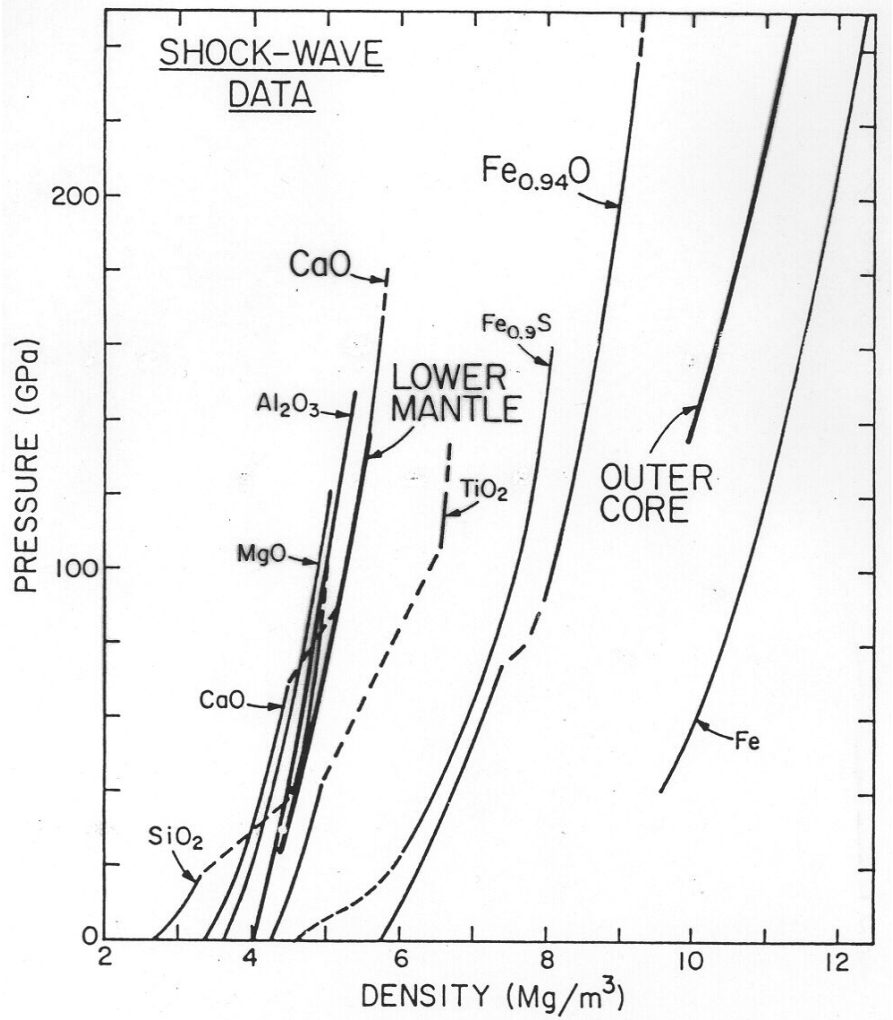


How do we reach high pressure?

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



NIF target chamber

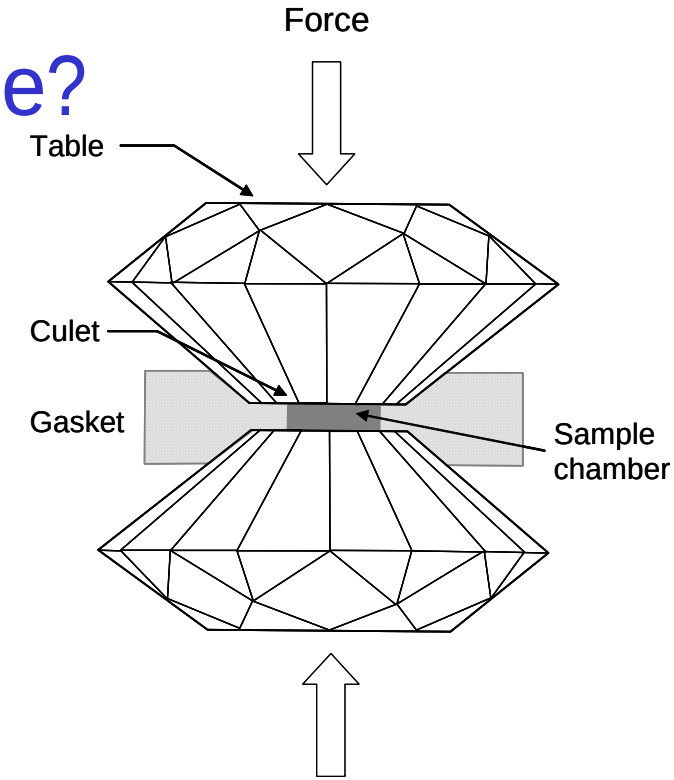


How do we reach high pressure?

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

- Multi-anvil apparatus
  - Pressure: 50 GPa
  - Temp: 2500°C
  - Sample size: mm^3

How do we reach high pressure?



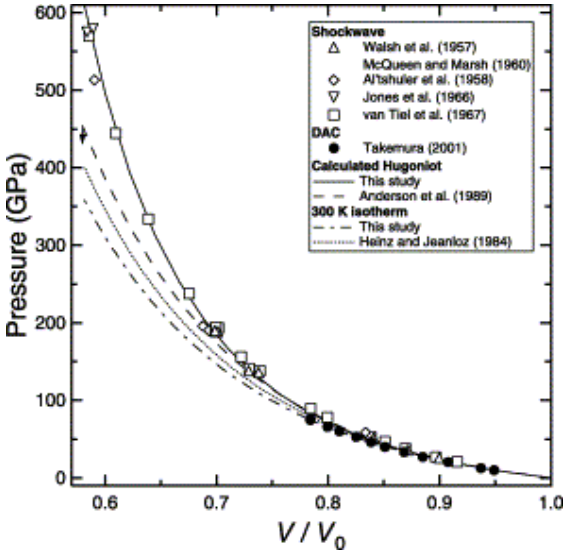
- Diamond Anvil Cell
  - Pressure: ambient to 500 GPa (1 GPa= 10,000 bar)
  - Temp: mK to 5000 K
  - Sample size: < 0.001 mm^3
  - Transparent to large range of E-M radiation

L-N_2
L-He
mK

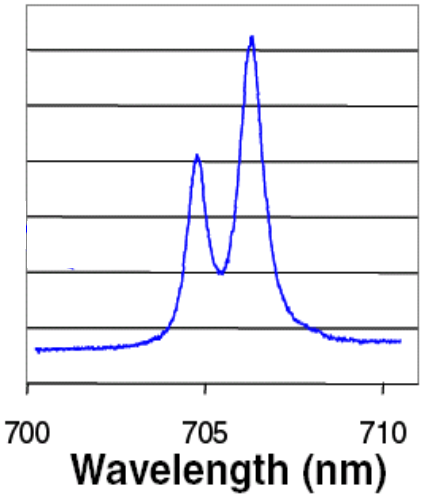
Laser &
Resistive
heating

How do we measure pressure?

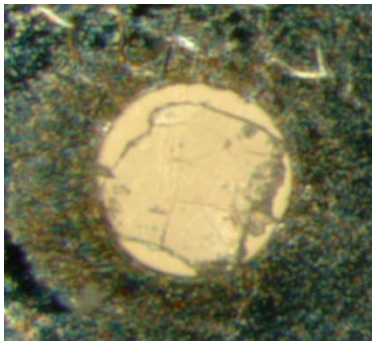
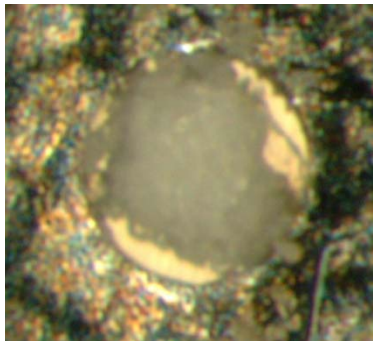
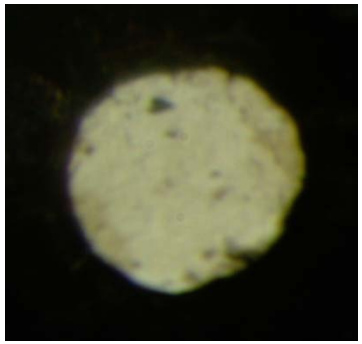
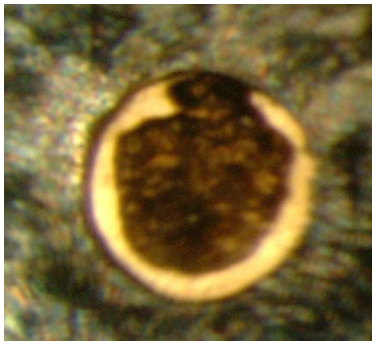
- Internal standards
  - Ruby fluorescence
  - Equation of state (Au, Ag, Pt, NaCl, etc.)
- Pressure calibration
  - Piston-cylinder
  - Shock wave
  - Brillouin spectroscopy
  - Ultrasonics

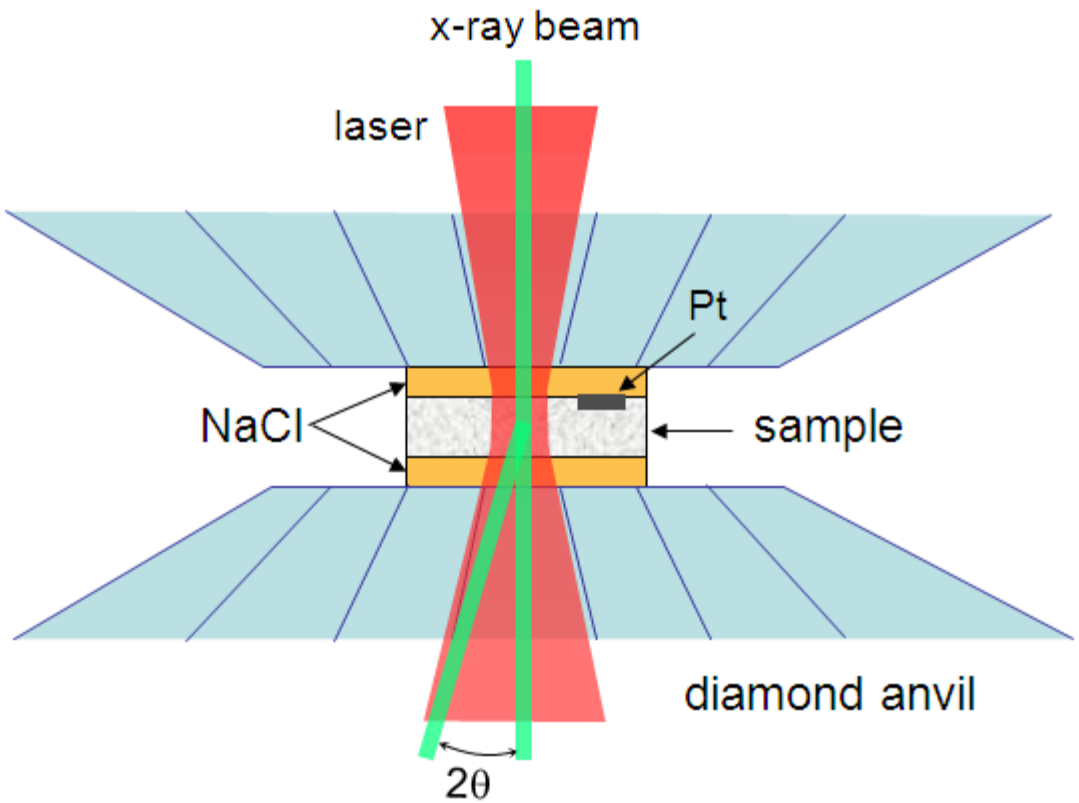


Shim *et al*, EPSL 2002



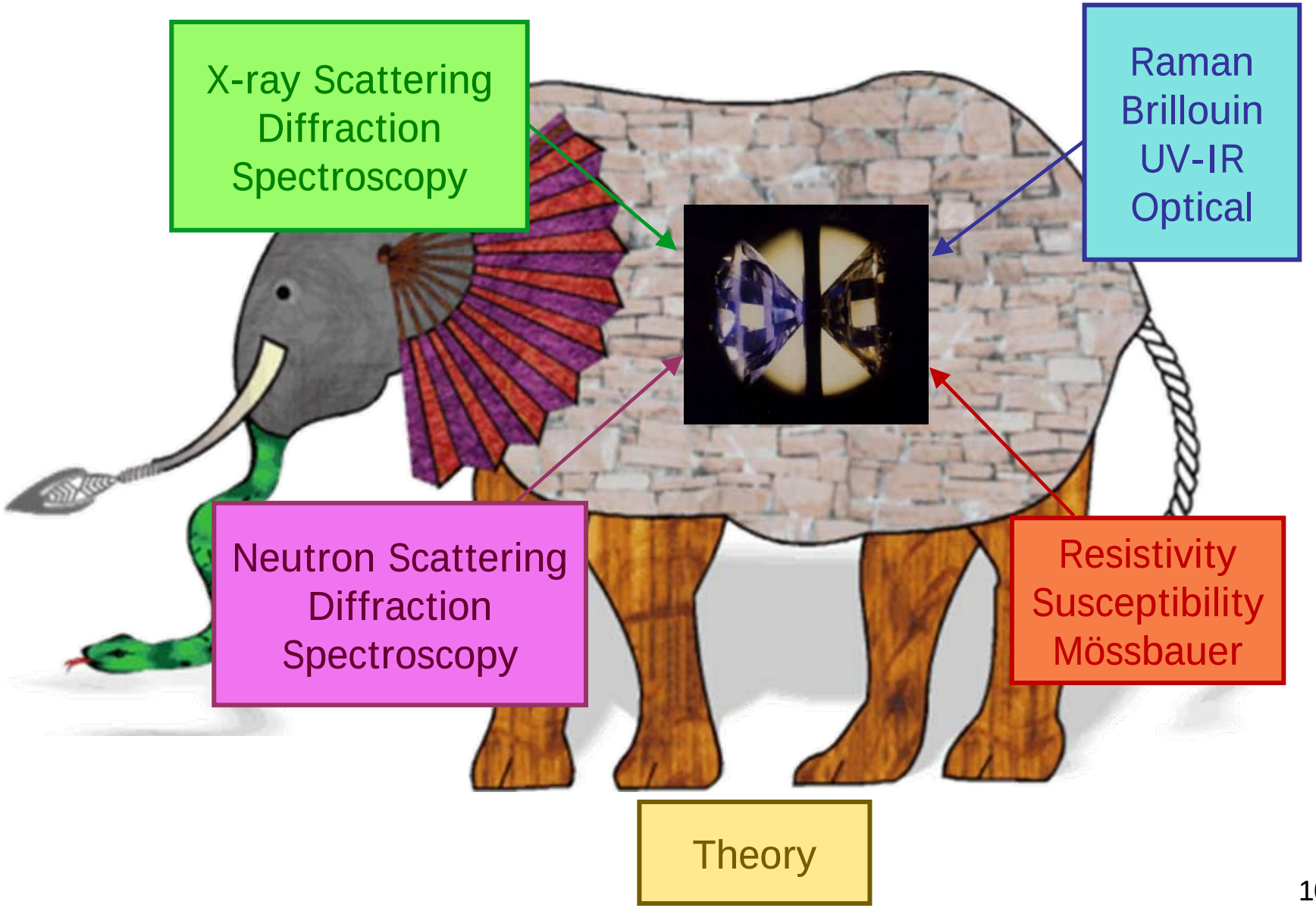
Sample preparation



- 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

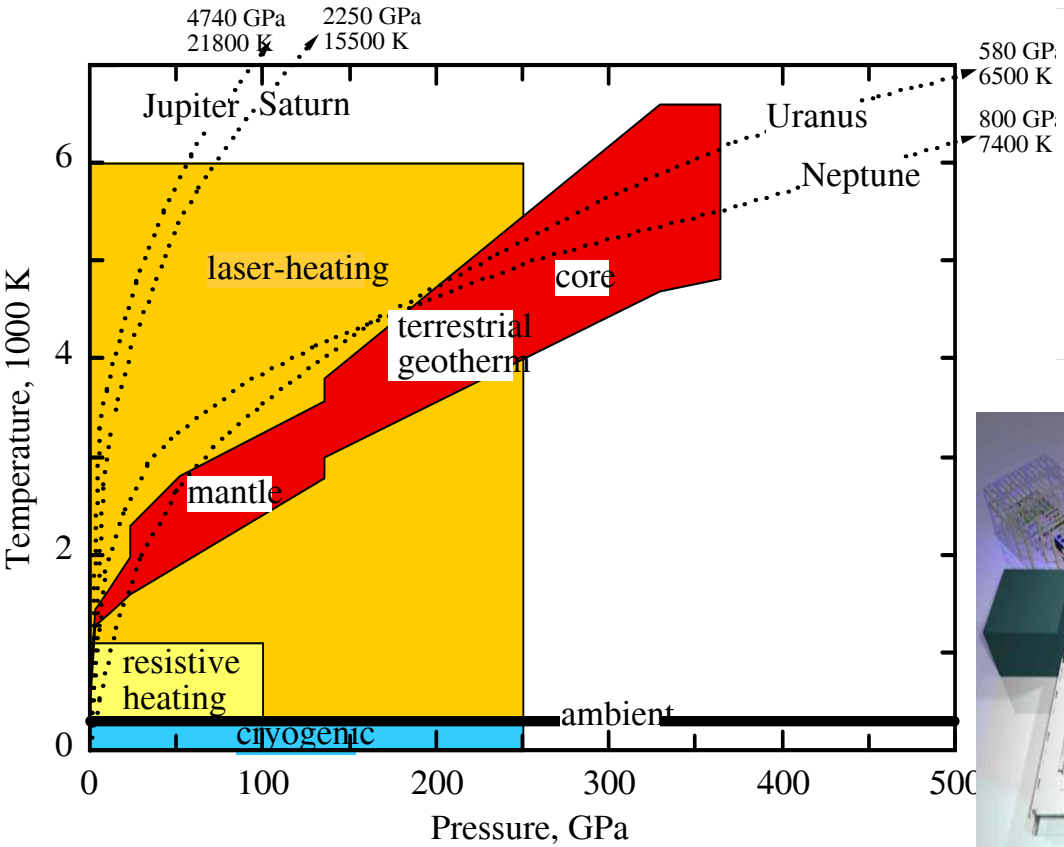


P-T conditions

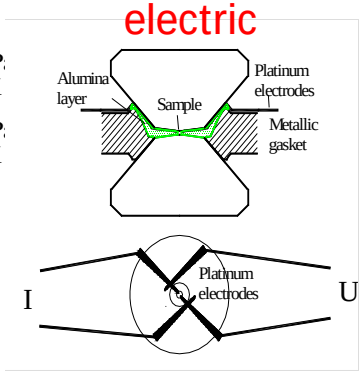
>300 GPa, 0.03 - 6000 K are reached in DAC

Diagnostic probes

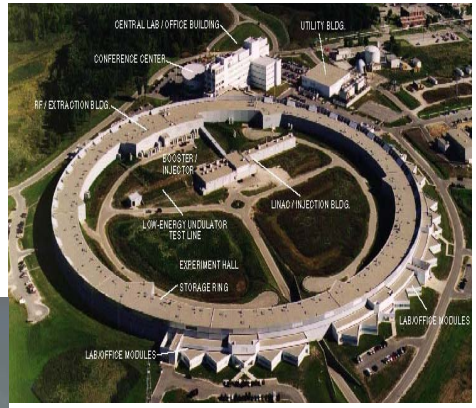
High *P-T in-situ,* x-ray, neutron, optical and electromagnetic probes



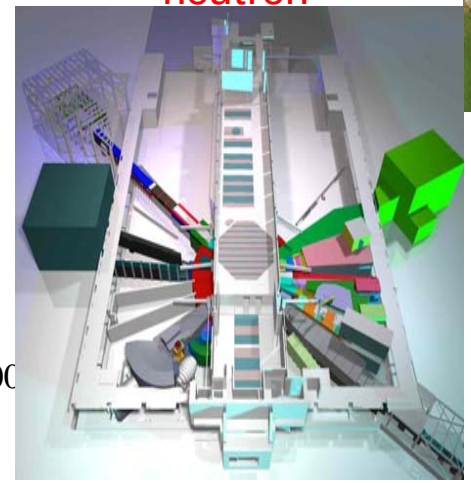
electric



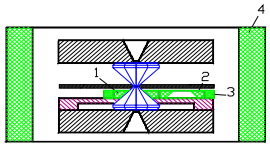
synchrotron



neutron

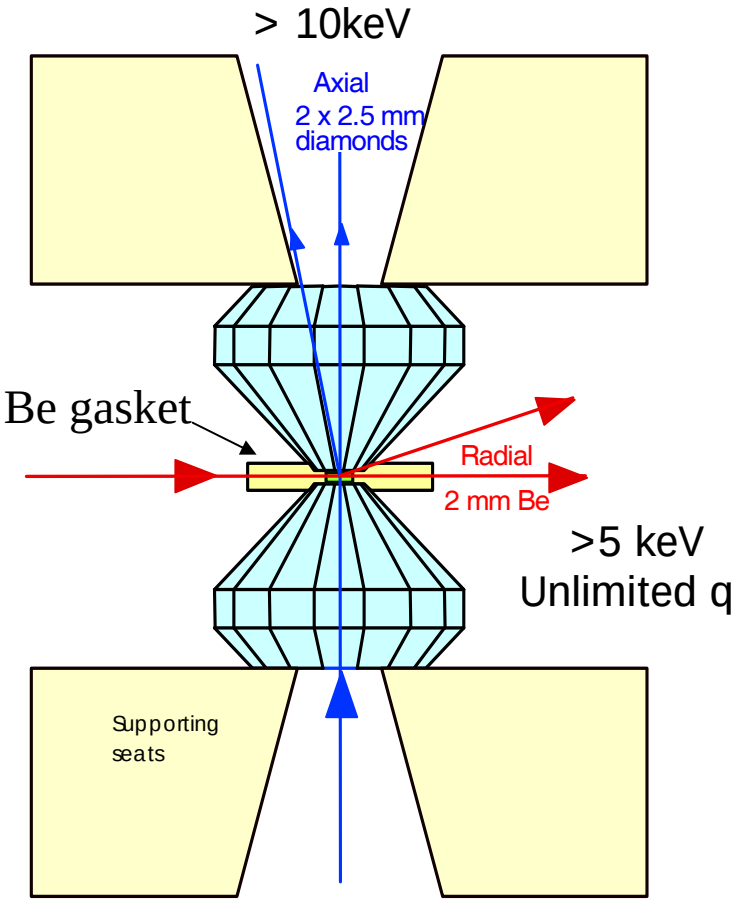


magnetism



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

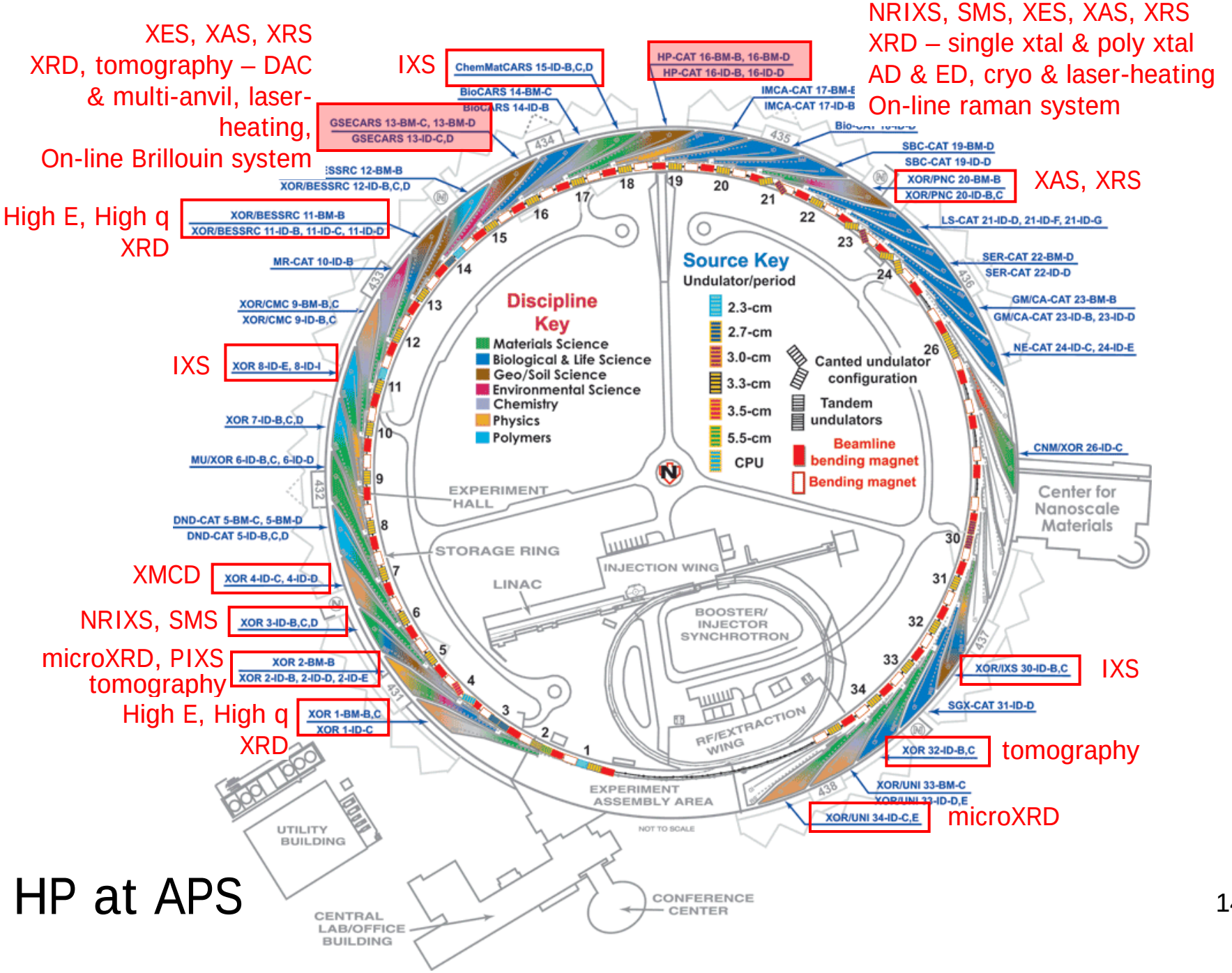
- Brilliance
- High energy
- Energy resolution
- Spatial resolution
- Temporal resolution
- Coherence

Rapid advances and impacts in high pressure

Enormous potential to be harnessed

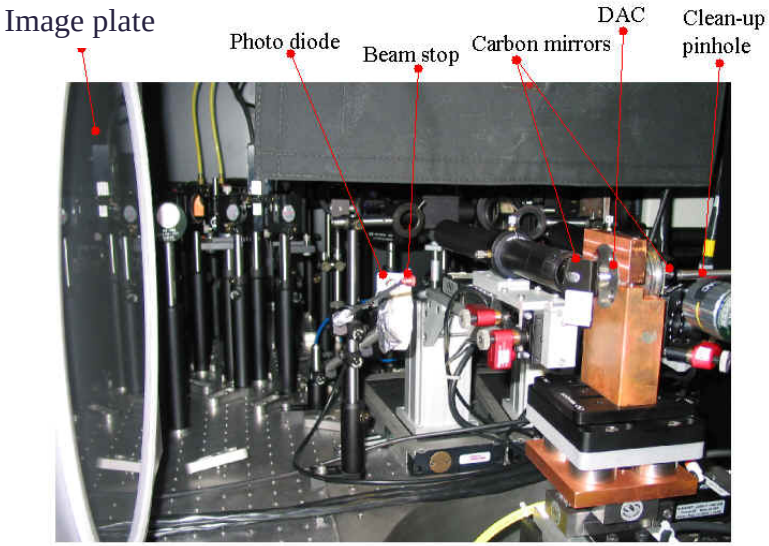
As yet unexplored

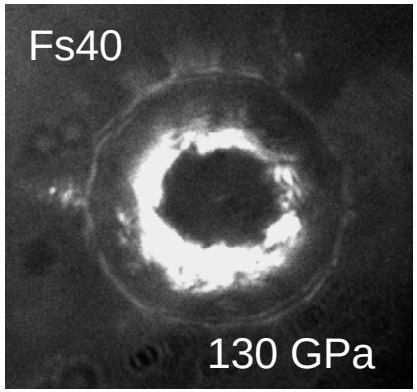
Already is an impressive suite of synchrotron techniques which are compatible with DAC, but still a lot of opportunities for further development

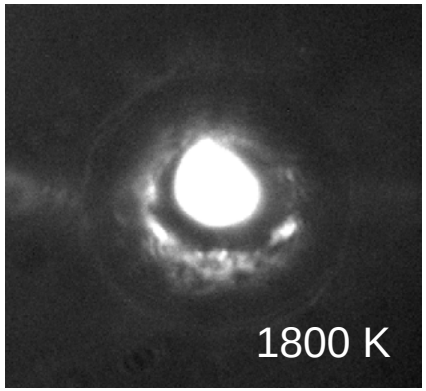

XES, XAS, XRS
XRD, tomography – DAC
& multi-anvil, laser-
heating,
On-line Brillouin system
IXS
ChemMatCARS 15-ID-B,C,D
HP-CAT 16-BM-B, 16-BM-D
HP-CAT 16-ID-B, 16-ID-D
NRIXS, SMS, XES, XAS, XRS
XRD – single xtal & poly xtal
AD & ED, cryo & laser-heating
On-line raman system
BioCARS 14-BM-C
BioCARS 14-ID-B
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/PNC 20-BM-B
XOR/PNC 20-ID-B,C
XAS, XRS
XOR/BESSRC 12-BM-B
XOR/BESSRC 12-ID-B,C,D
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
IXS
XOR 8-ID-E, 8-ID-I
NE-CAT 24-ID-C, 24-ID-E
XOR 7-ID-B,C,D
MU/XOR 6-ID-B,C, 6-ID-D
CNM/XOR 26-ID-C
DND-CAT 5-BM-C, 5-BM-D
DND-CAT 5-ID-B,C,D
XMCD
XOR 4-ID-C, 4-ID-D
NRIXS, SMS
XOR 3-ID-B,C,D
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
XOR 32-ID-B,C
tomography
XOR/UNI 33-BM-C
XOR/UNI 33-ID-D,E
XOR/UNI 34-ID-C,E
microXRD
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
EXPERIMENT HALL
STORAGE RING
LINAC
INJECTION WING
BOOSTER/ INJECTOR SYNCHROTRON
RF/EXTRACTION WING
EXPERIMENT ASSEMBLY AREA
NOT TO SCALE
Center for Nanoscale Materials
UTILITY BUILDING
CENTRAL LAB/OFFICE BUILDING
CONFERENCE CENTER

HP at APS

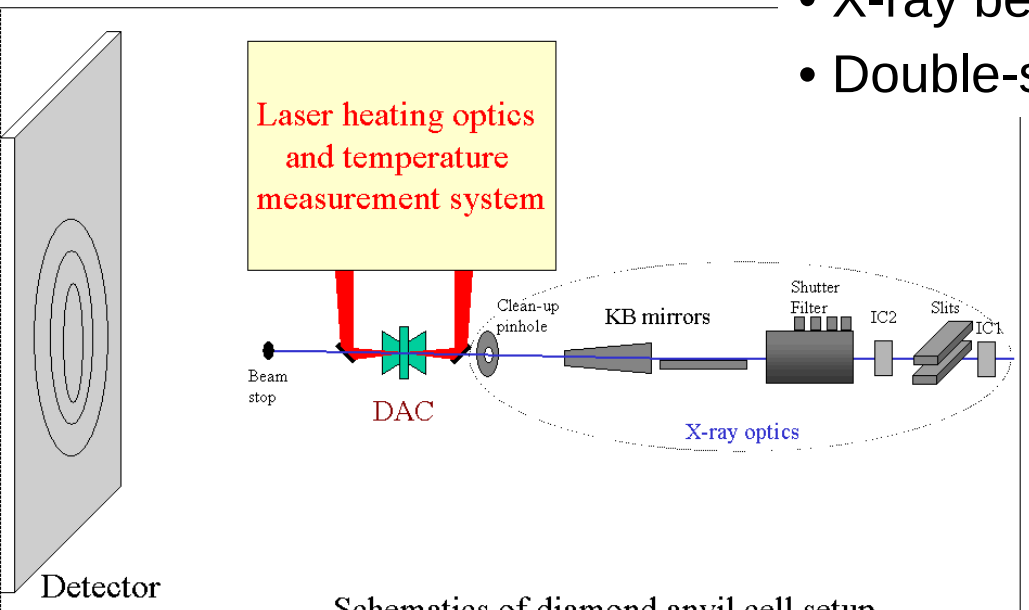
HP XRD + laser-heated DAC



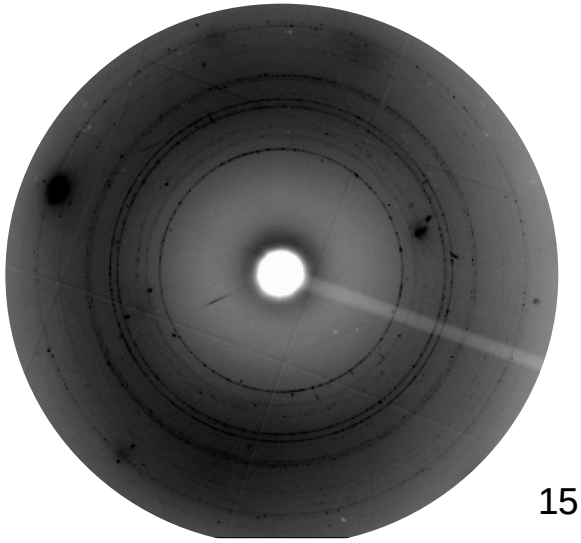




- Gasket hole ~ 60 μm (culet =150 μm, bevel diameter = 300 μm)
- X-ray beam ~ 6 x 7 μm
- Double-sided Nd:YLF laser heating

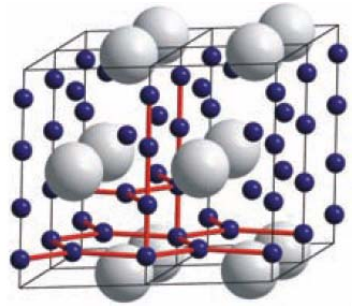


Schematics of diamond anvil cell setup at 13ID-D at the Advanced Photon Source

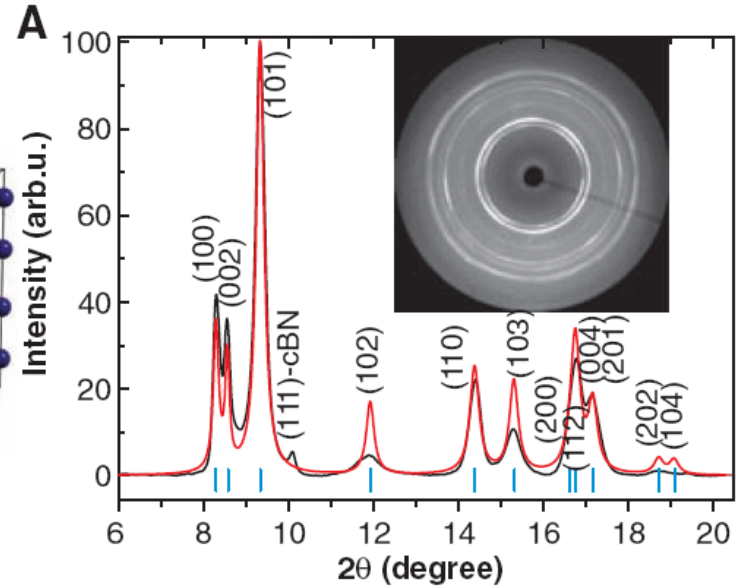


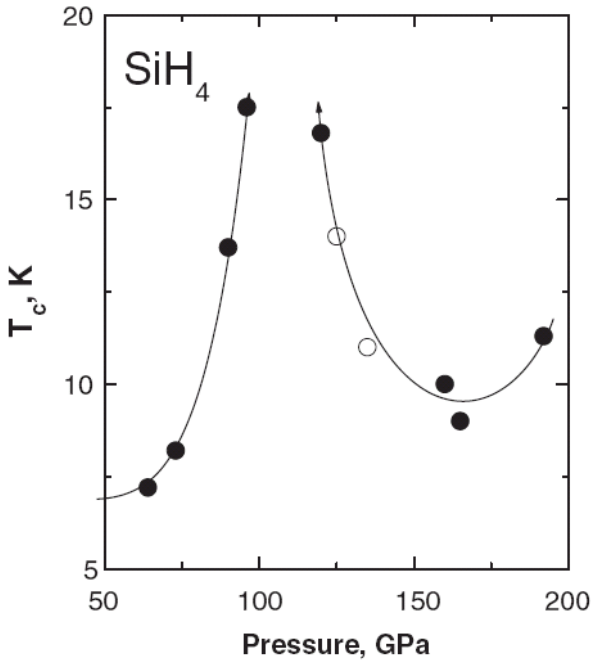
HP Powder XRD

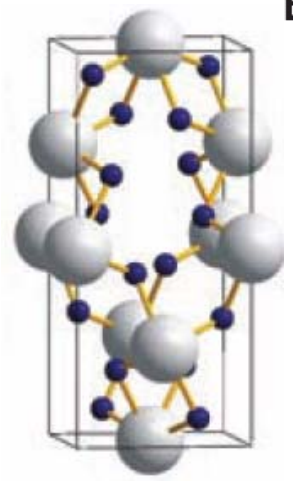
- Superconductivity in hydrogen-rich group IV hydride, SiH_4
- Implications for understanding superconductivity in hydrogen?



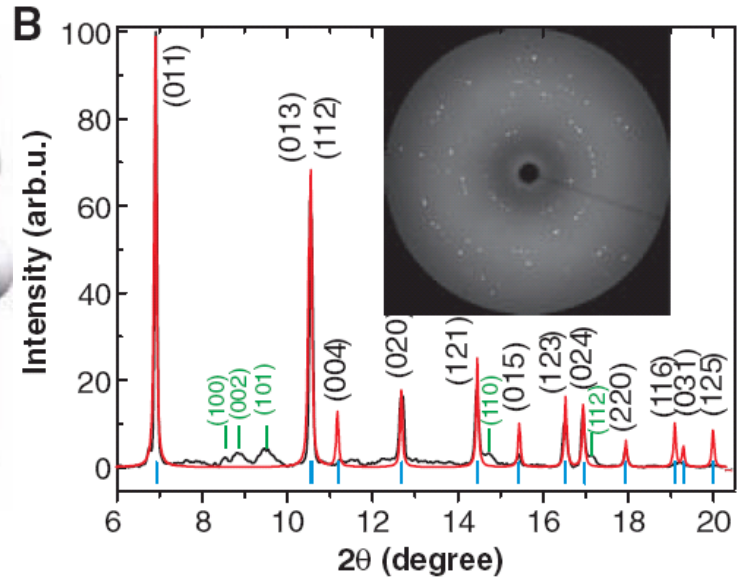
113 GPa







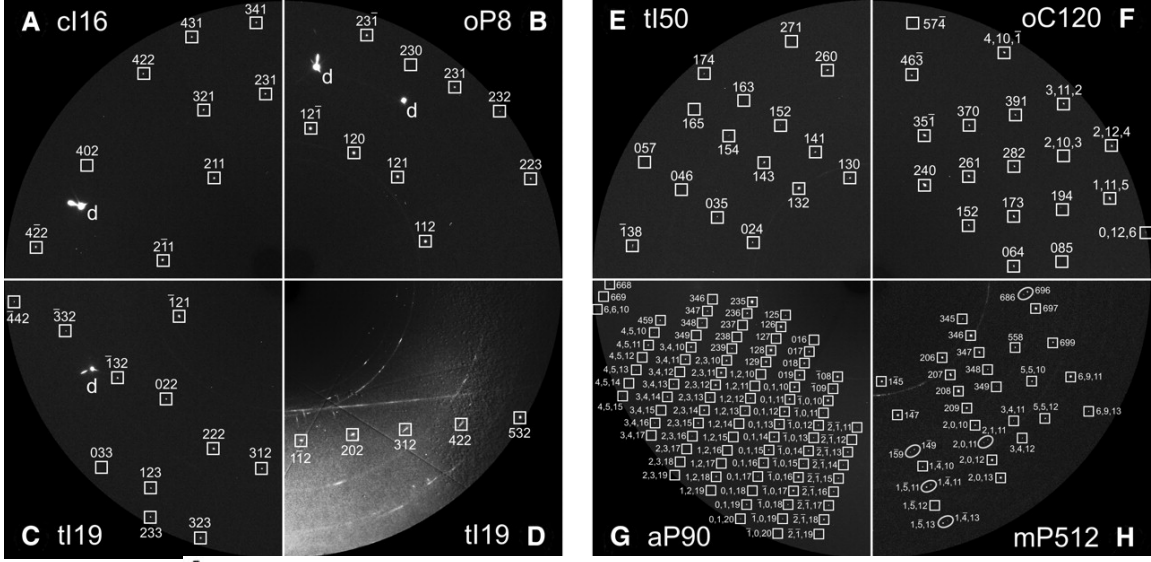
160 GPa

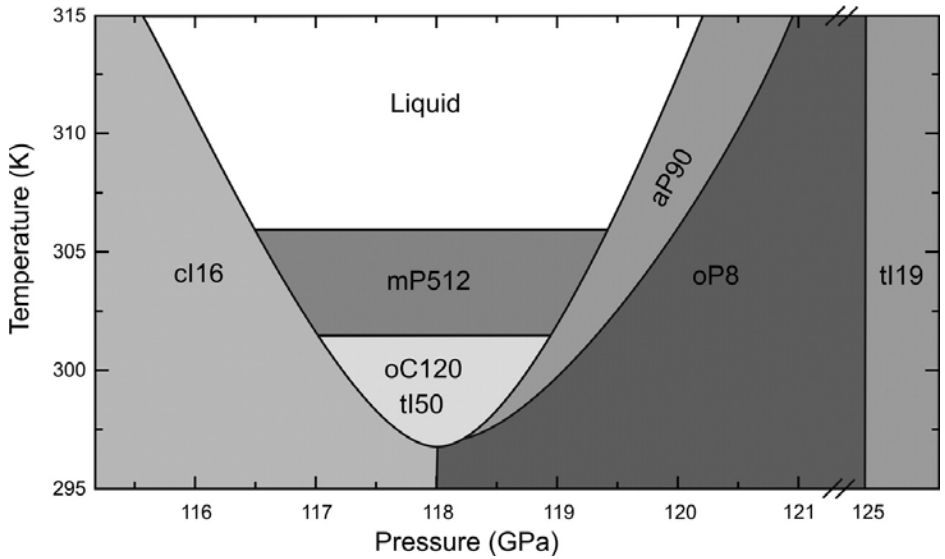


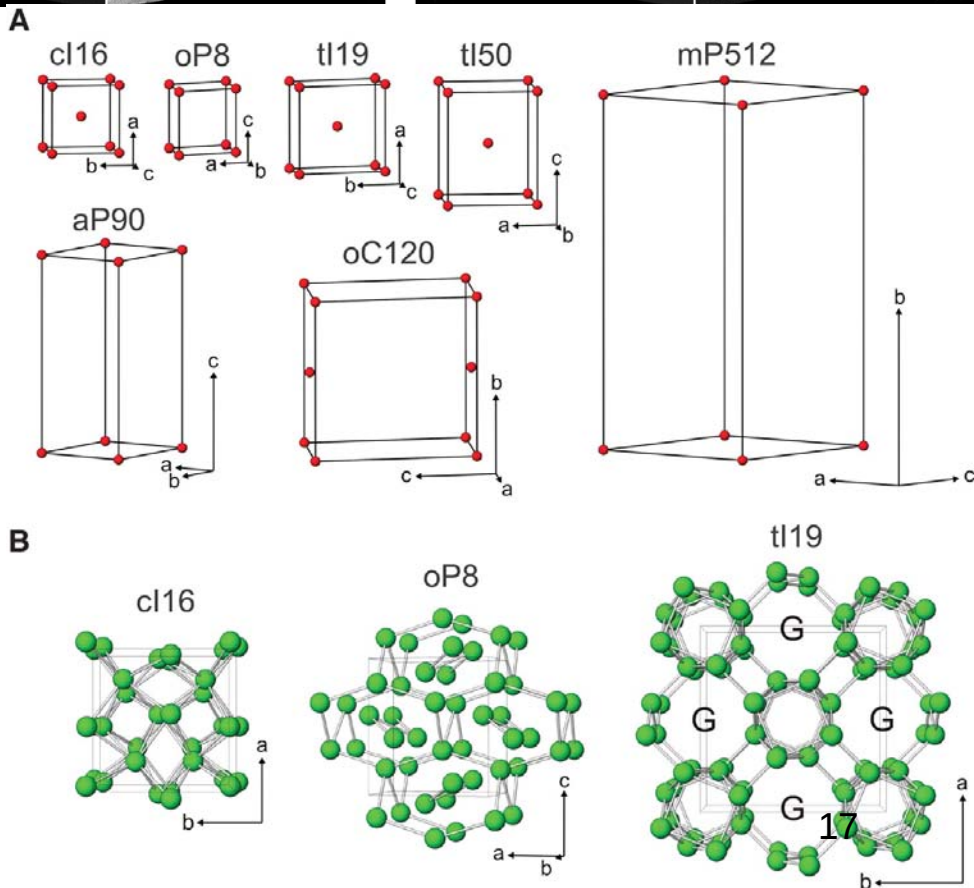
Eremets et al, *Science* 2008

HP Single crystal XRD

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

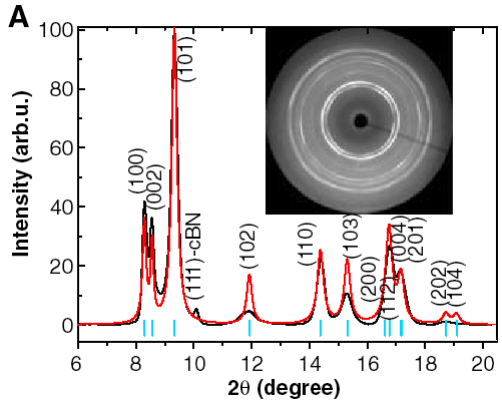






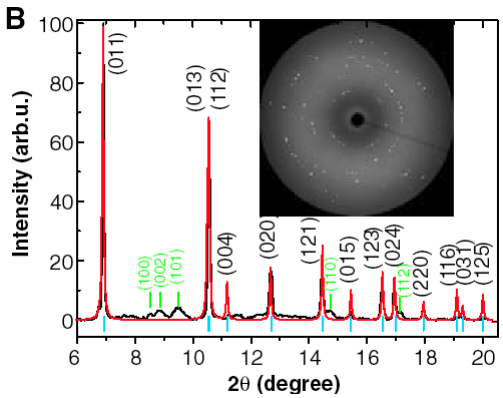
Gregoryanz et al, *Science* 2008

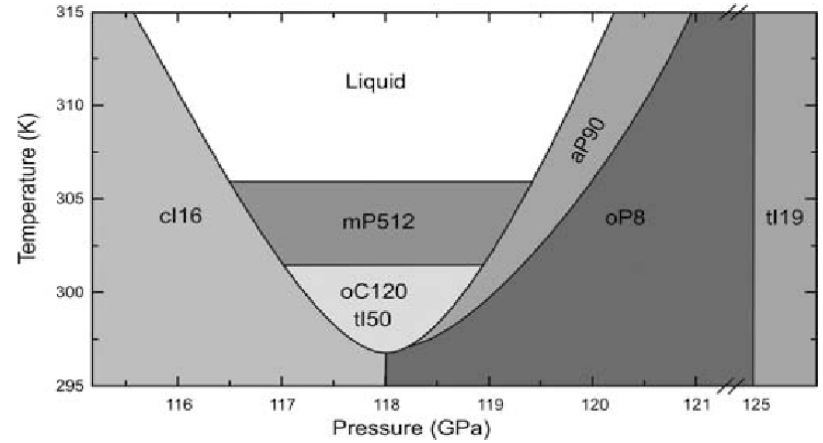
The need for XRD with submicron x-ray beam



SiH_4

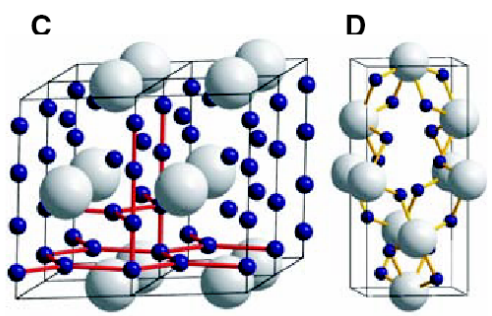
Many HP structures were determined with μm-size powder XRD; assignments can be questionable.

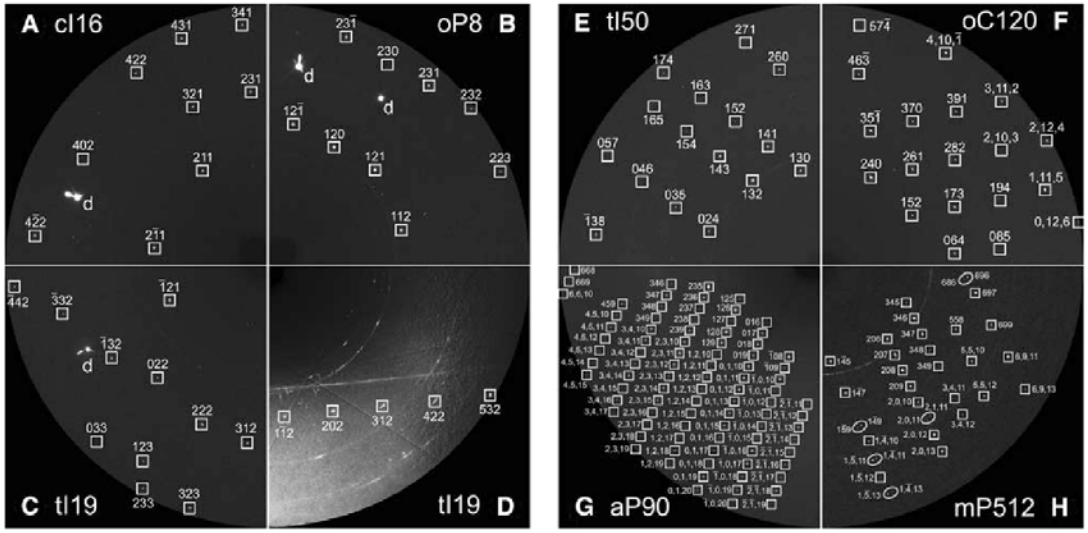




Na

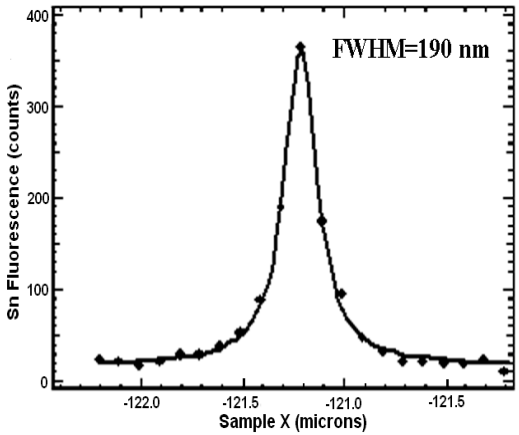
Single-crystal XRD gives definitive answer, but requires crystals larger than the x-ray probe.



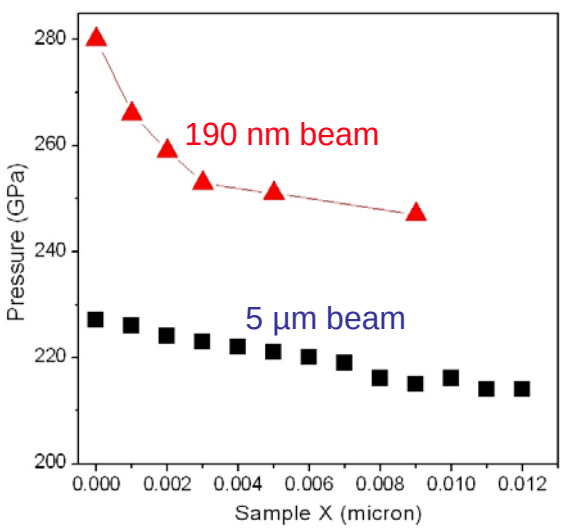


Using 200 nm focused x-ray beam we can...

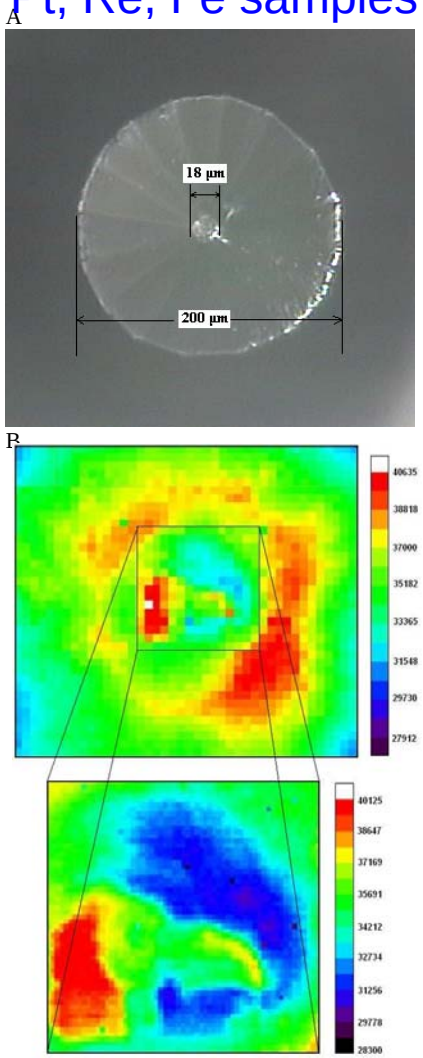
Wang et al., in prep.



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

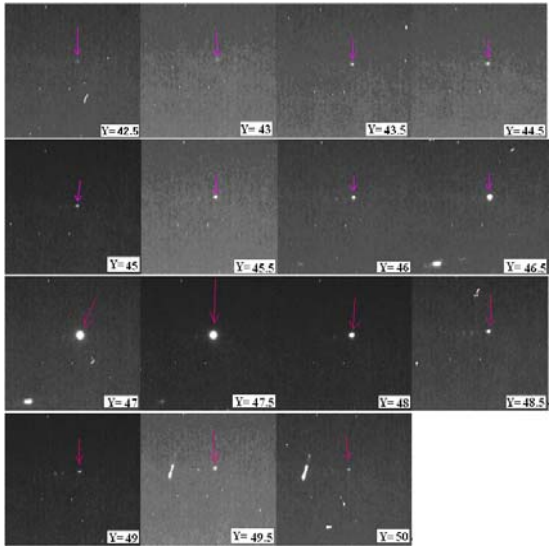


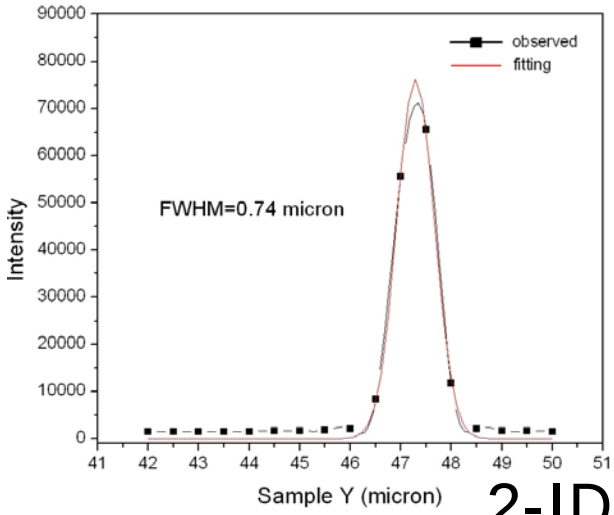
Separate submicron Pt, Re, Fe samples



34-ID

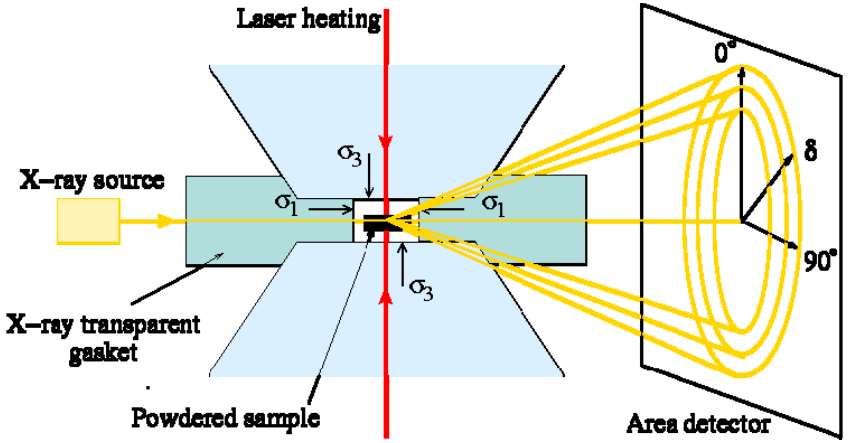
Conduct single-crystal XRD on submicron powder

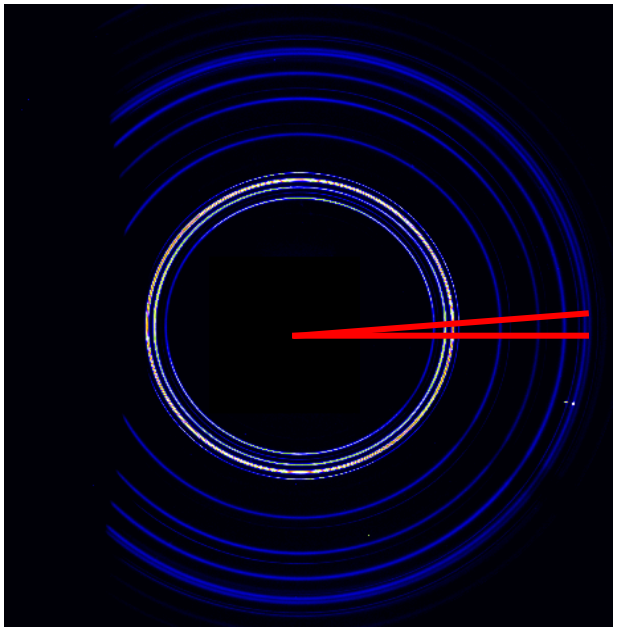




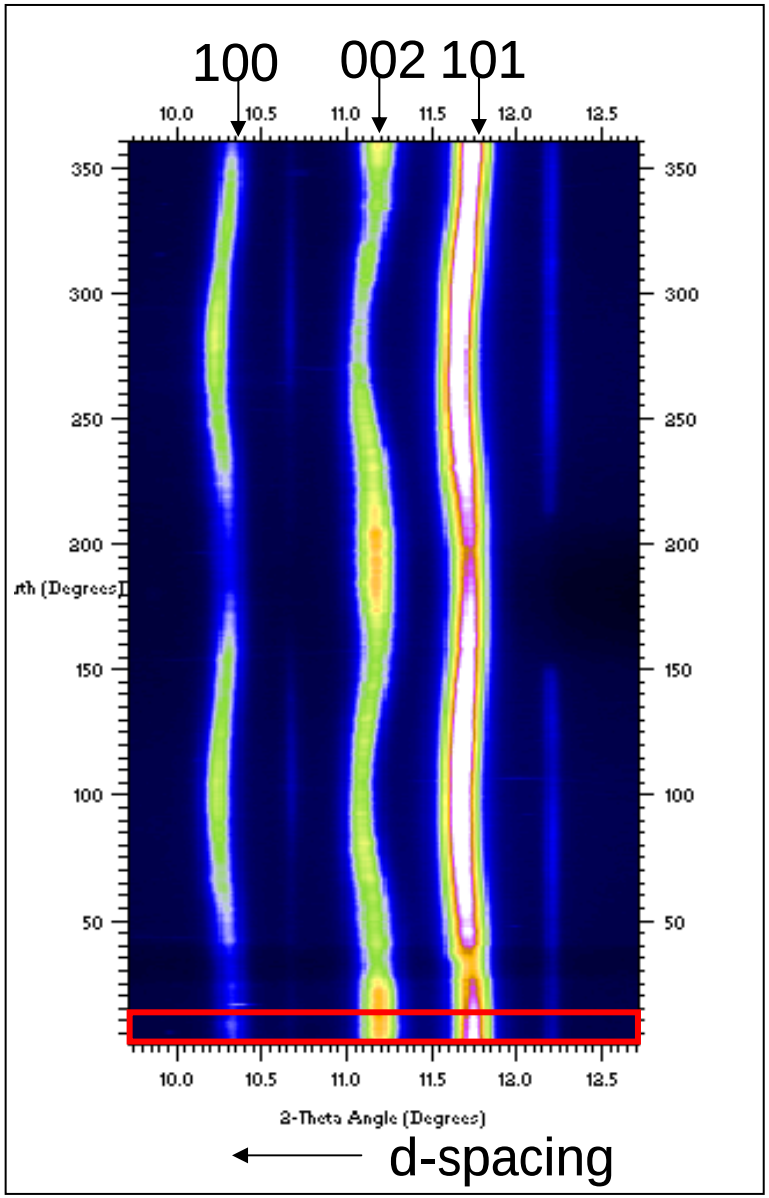
2-ID

Radial x-ray diffraction





hcp-Fe

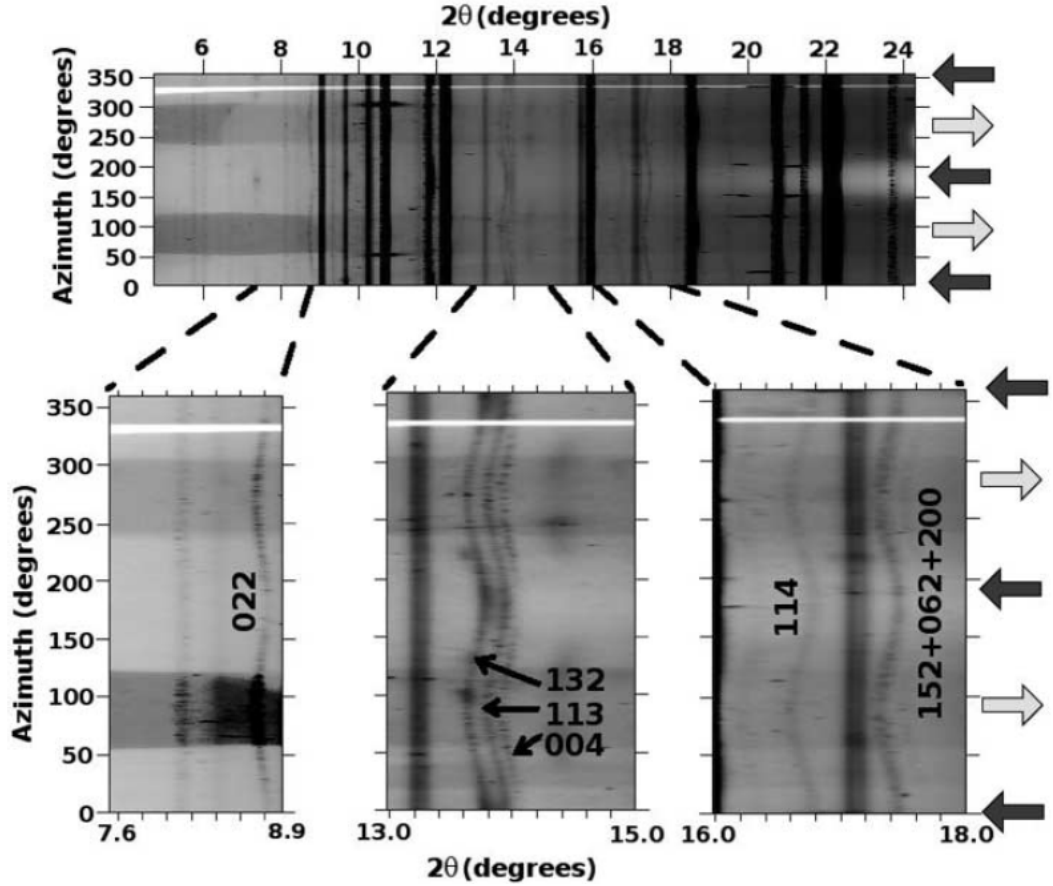


- Preferred orientation

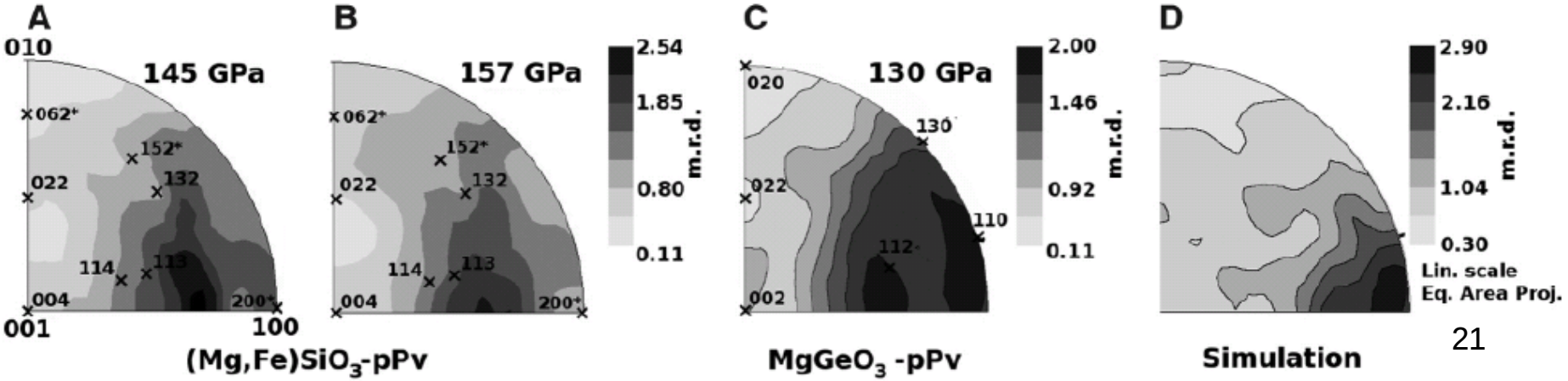
W. Mao et al, JGR 2008

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

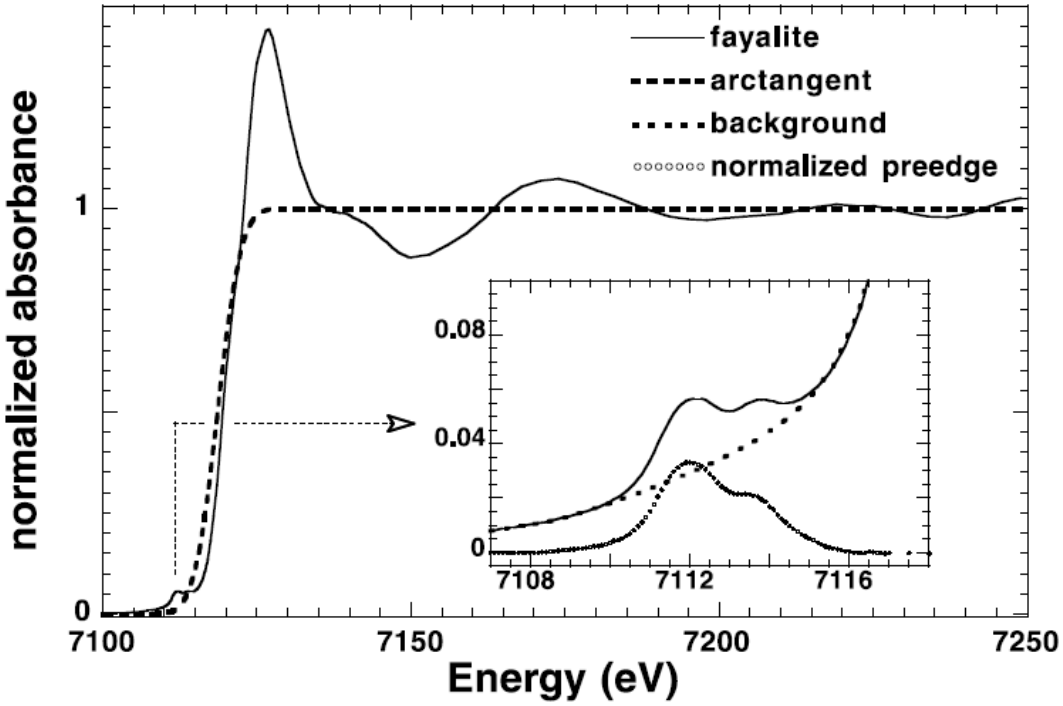


Merkel et al, Science 2007



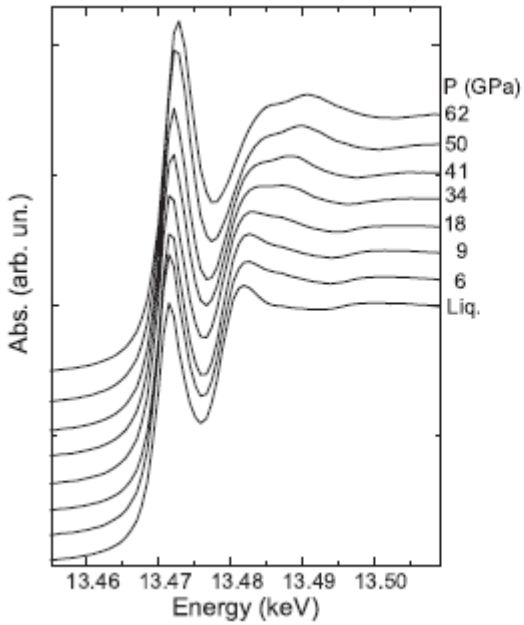
HP X-ray absorption spectroscopy (XAS)

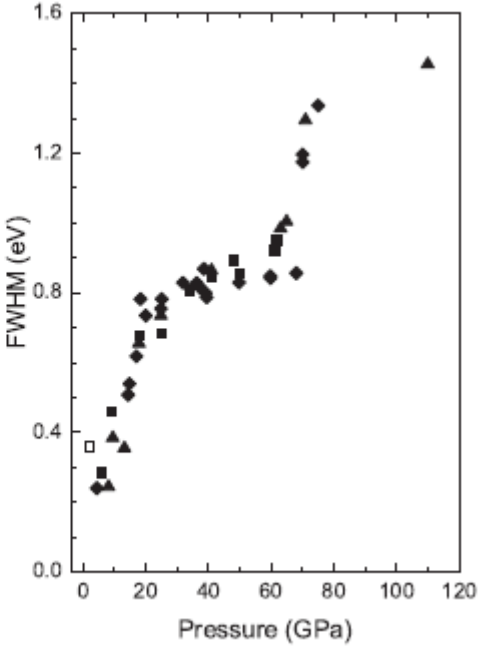
- Pre-edge position and intensity: oxidation state
- Edge height: concentration
- XAFS: coordination & structure

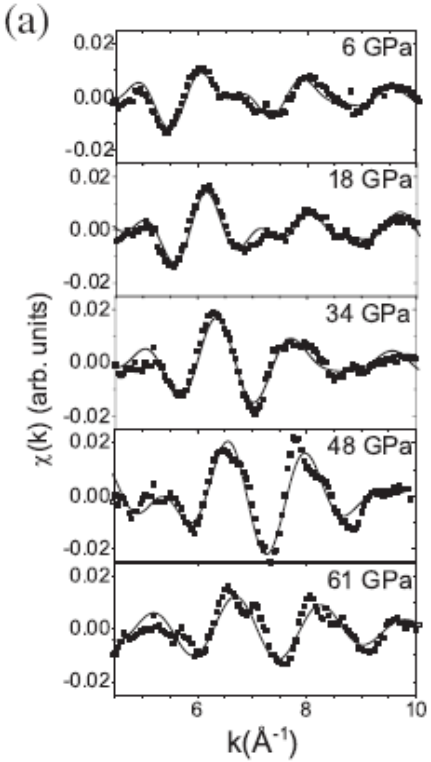


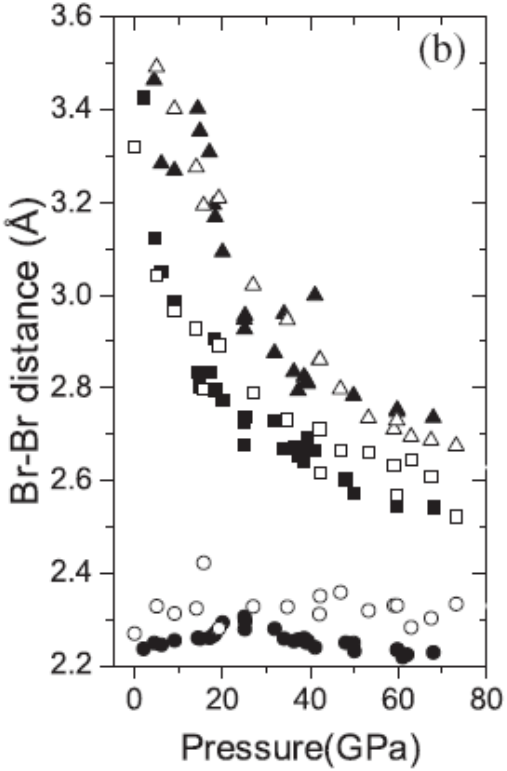
Wilke et al, Amer. Min. 2001

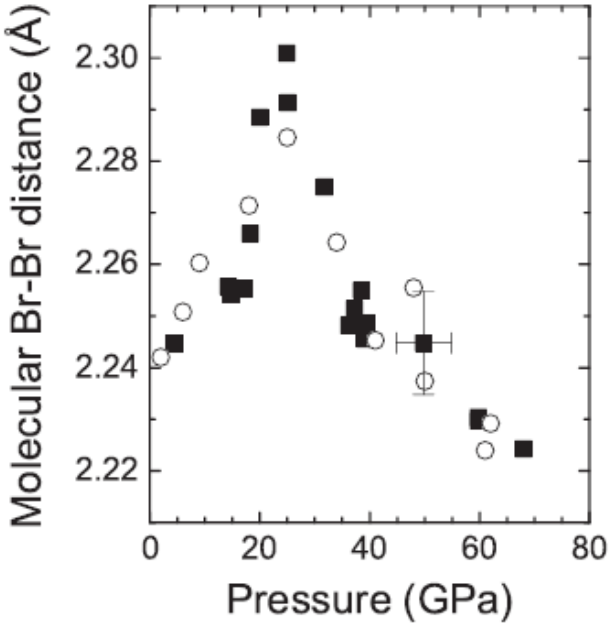
Phase transitions in solid Br at 25 GPa & 65 GPa





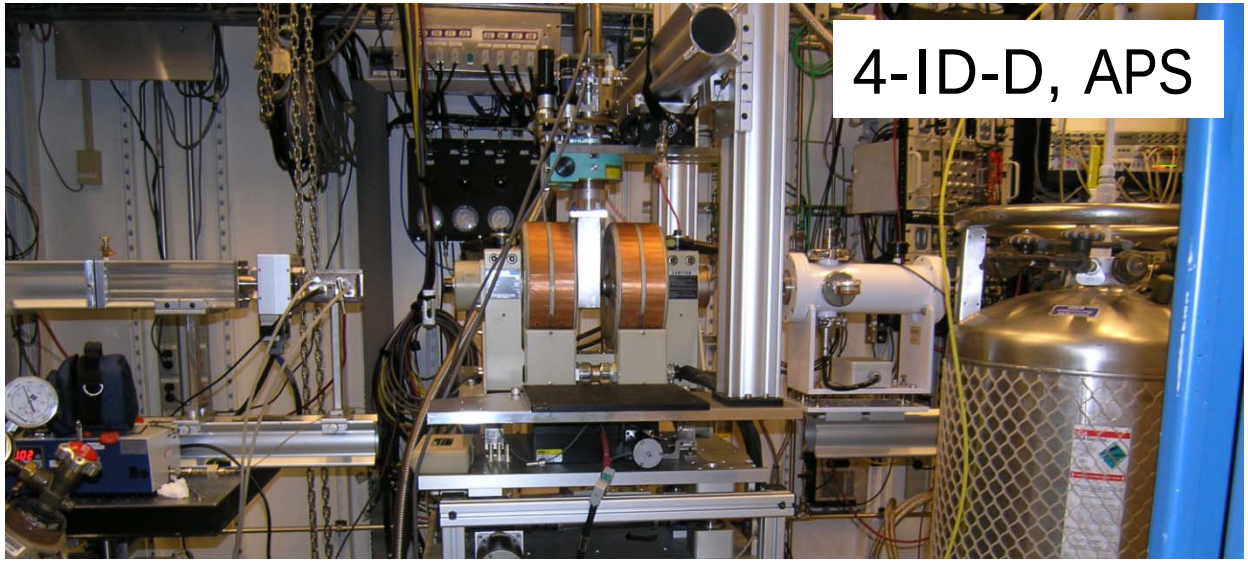


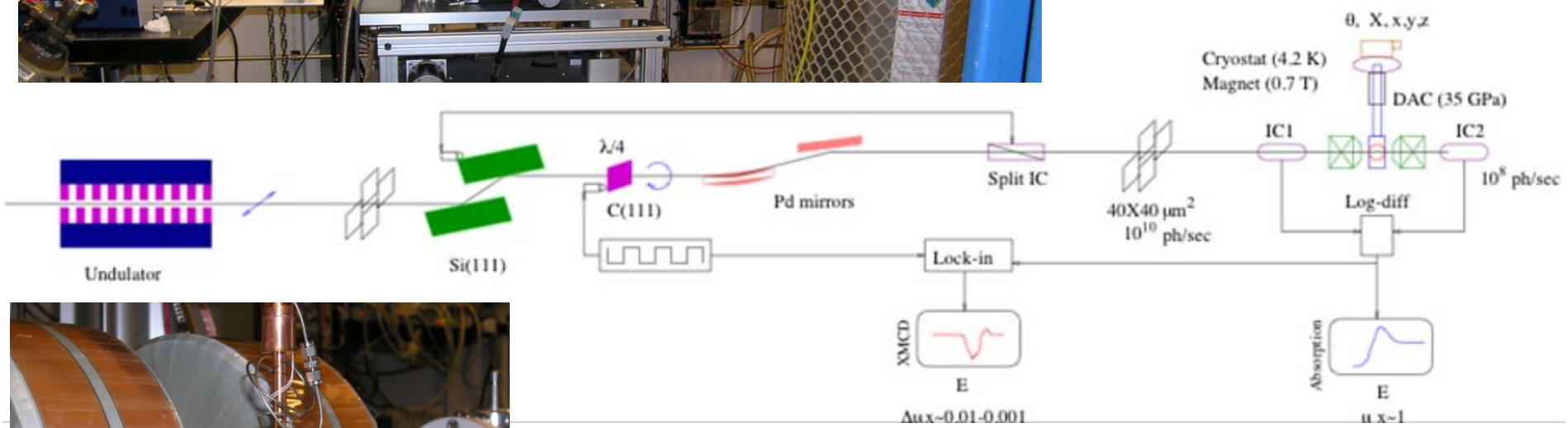


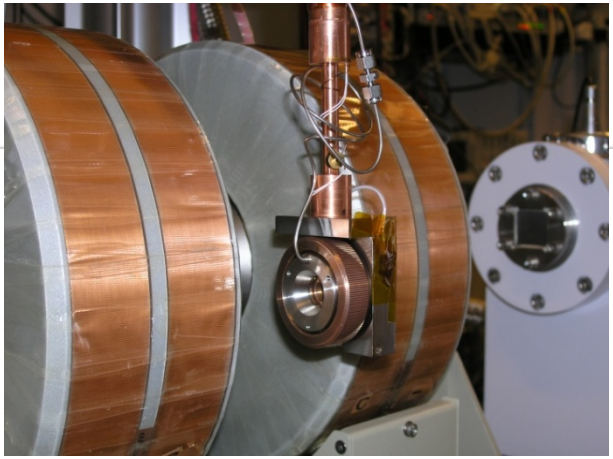


San-Miguel et al, *PRL* 2007

X-ray magnetic circular dichroism (XMCD) at HP



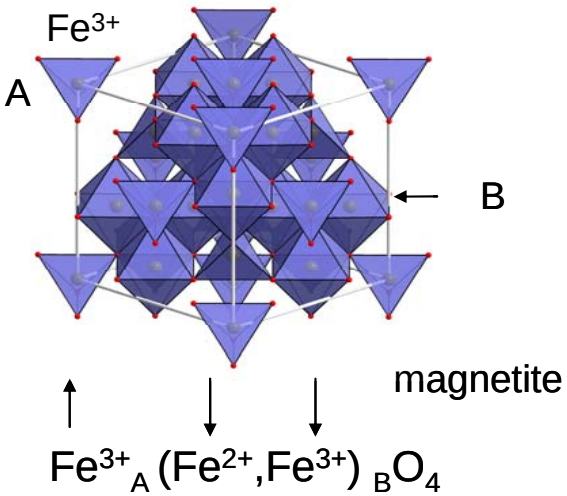


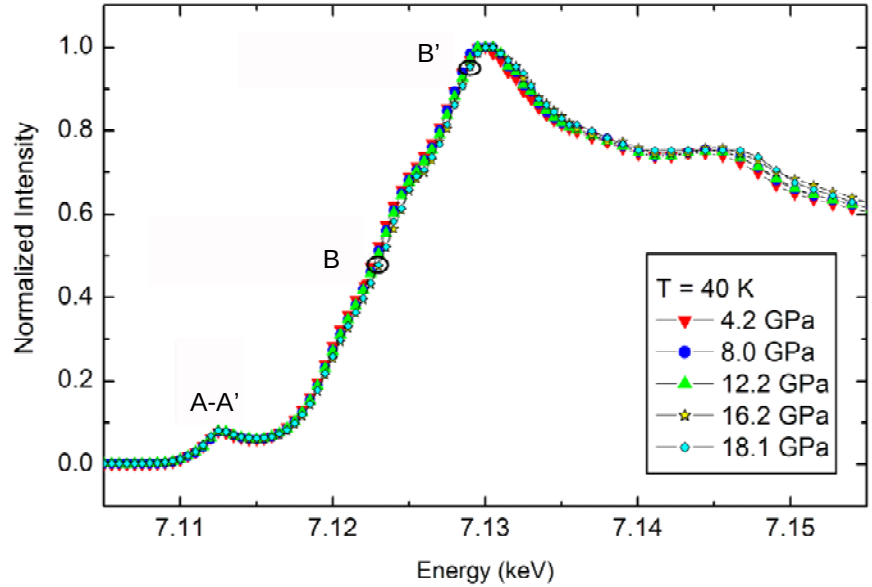


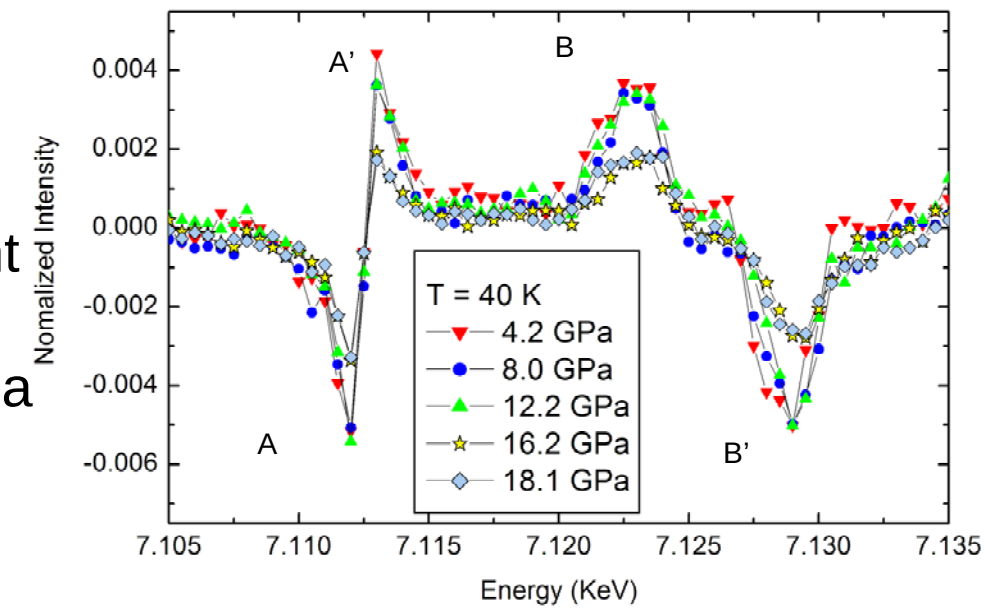
$$XMCD = \frac{\Delta\mu t}{\mu t_{jump}}; \Delta\mu = \mu(-,+) - \mu(+,+)$$

Haskel et al, *RSI* 2007

XMCD of Fe_3O_4 at HP



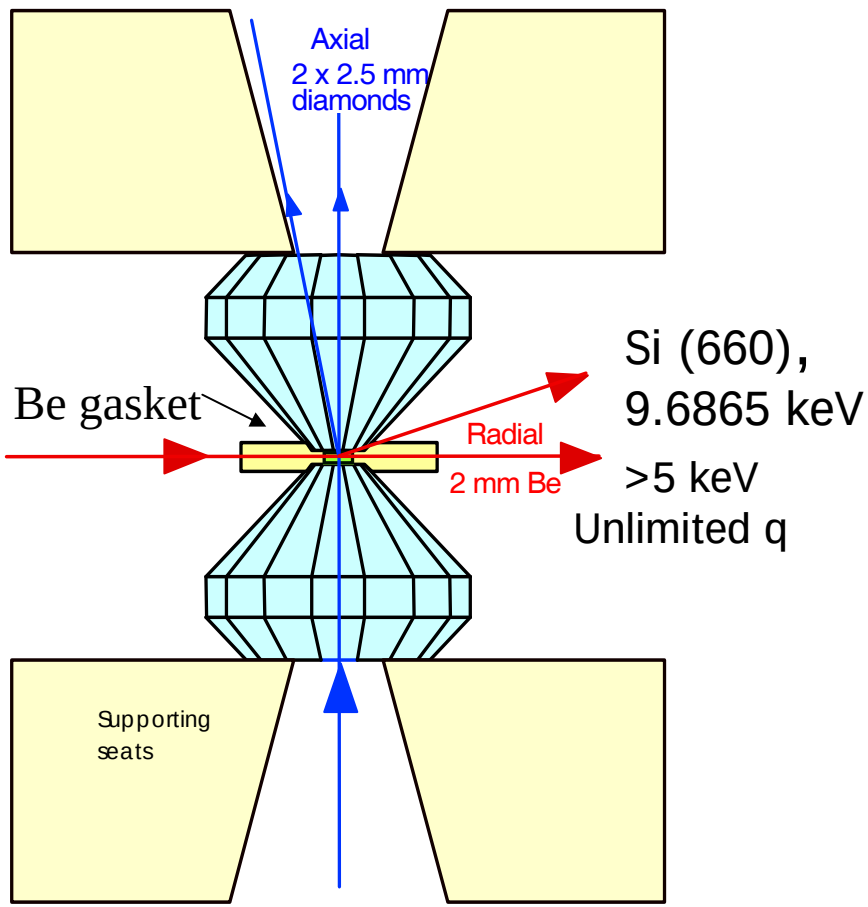




- 50% drop in net magnetic moment at 14 GPa.
- loss of magnetism is attributed to a high-spin to intermediate-spin transition of Fe^{2+} in the octahedral site (confirmation from XES).

Y. Ding et al, *PRL* 2008

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



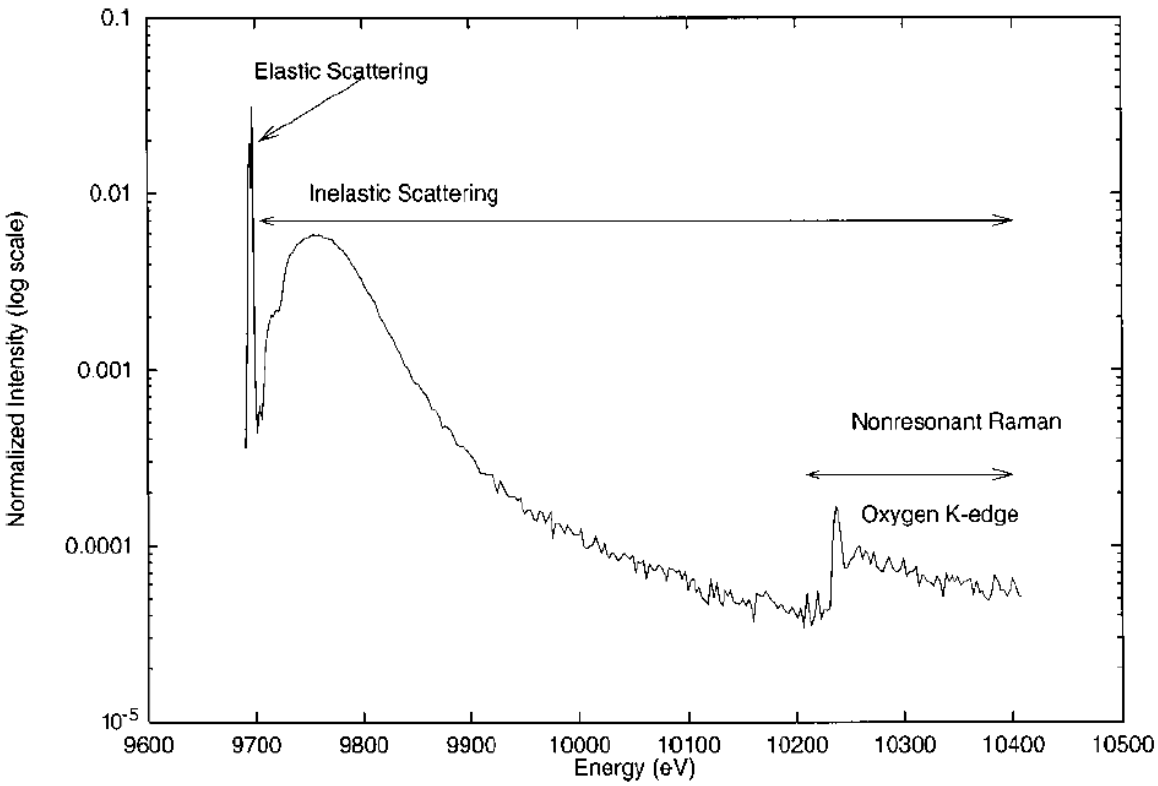
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$
1 H	13.6		
2 He	24.6*		
3 Li	54.7*		
4 Be	111.5*		
5 B	188*		
6 C	284.2*		
7 N	409.9*	37.3*	
8 O	543.1*	41.6*	
9 F	696.7*		
10 Ne	870.2*	48.5*	21.7*
11 Na	1070.8†	63.5†	30.65
12 Mg	1303.0†	88.7	49.78
13 Al	1559.6	117.8	72.95
14 Si	1839	149.7*b	99.82
15 P	2145.5	189*	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)

$$\Delta E = E - E_0$$

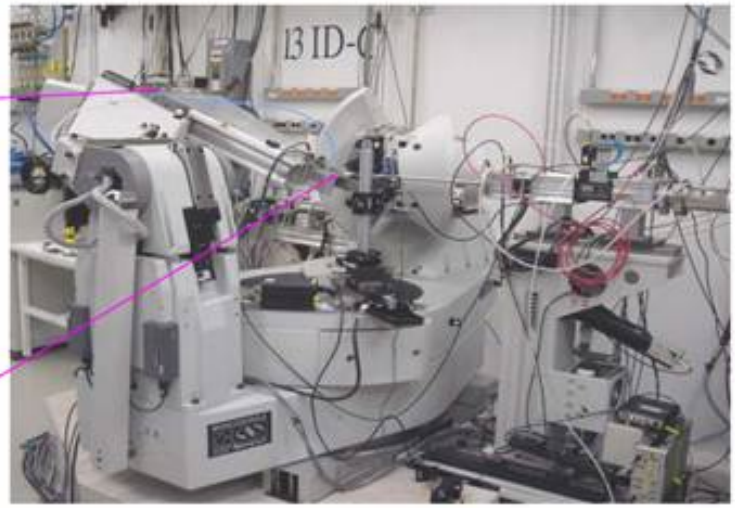


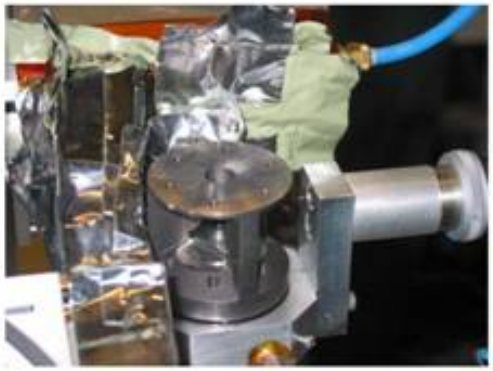
Bowron *et al, PRB* 2000

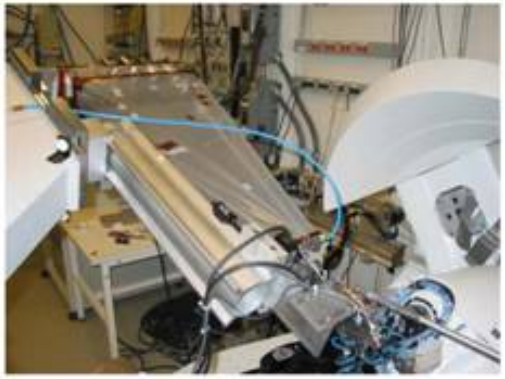
XRS Set-up

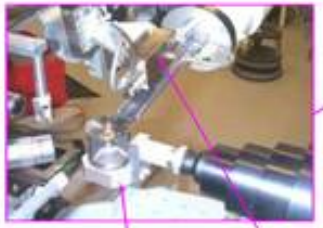
Si Analyzer Crystals

13-IDC, GSECARS, APS, ANL









Detector

DAC

Analyzed Beam Focused onto the Detector

Double Focused Undulator Beam

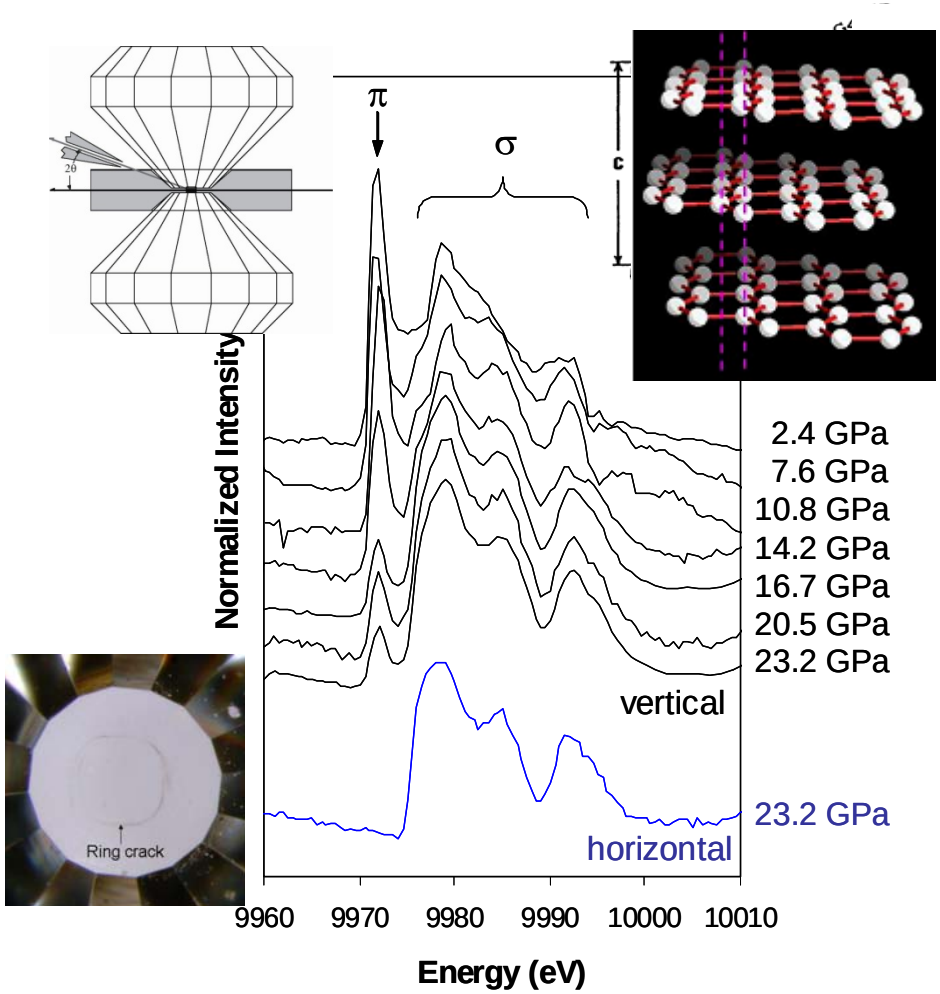
Scatter Beam Intercepted by the Analyzer

178° Scattering Angle

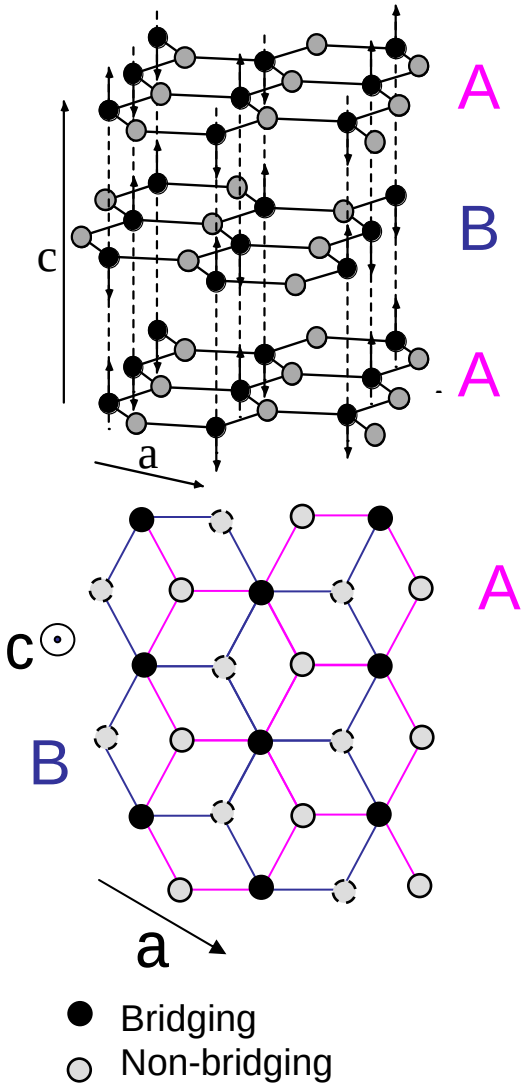
Si **660** Spherical Analyzer Crystal (R = 1m)

9.6865 keV

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



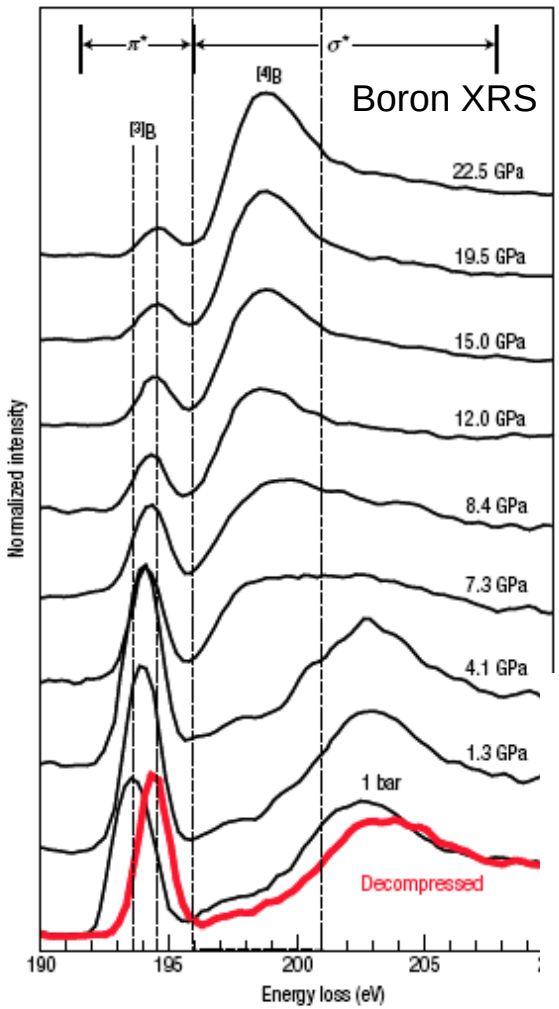
X-ray raman of graphite at high pressure showing the evolution of bonding and transformation to a new, superhard phase



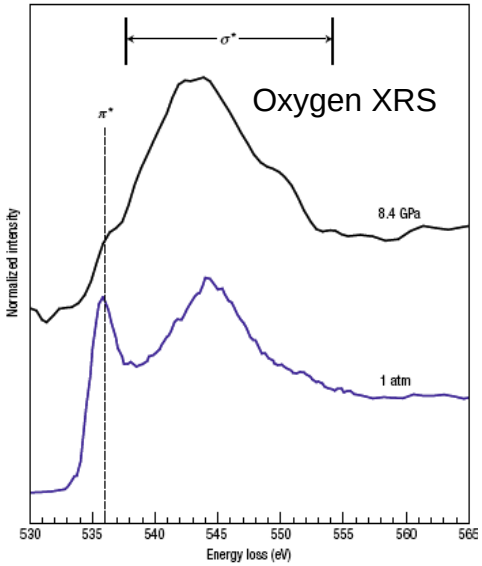
W. Mao *et al*, *Science* 2003

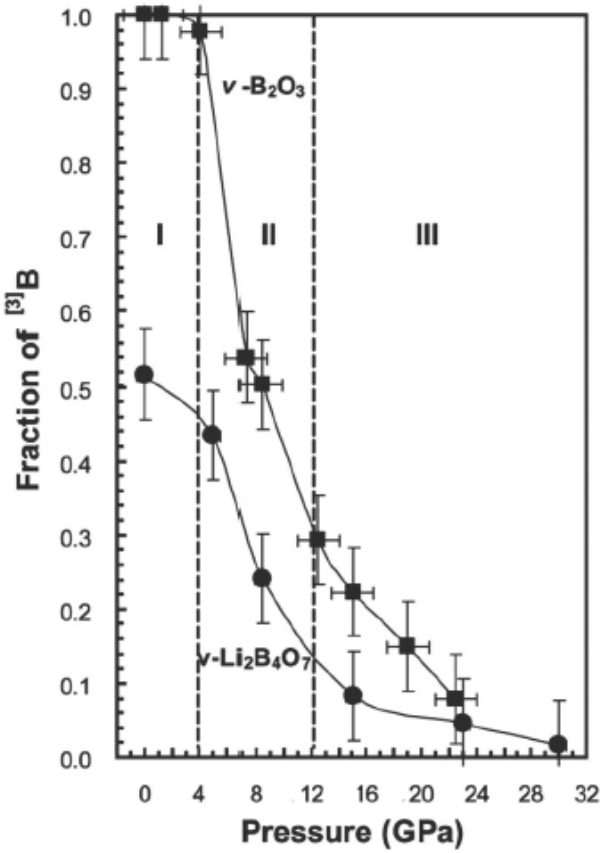
Pressure-induced bonding changes in B_2O_3 and $Li_2B_4O_7$

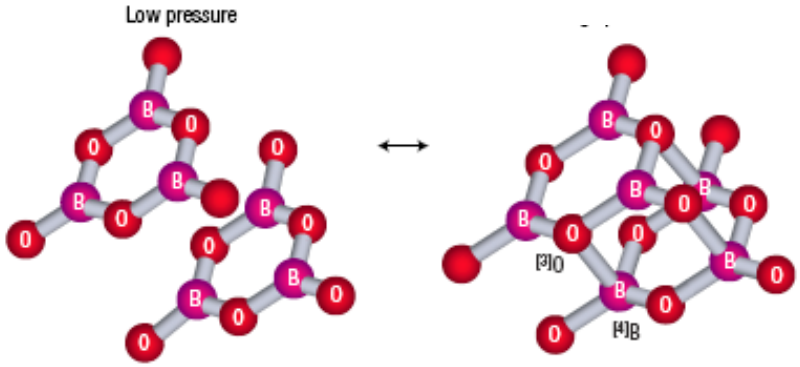
S K Lee, *et al*, *PRL* 2007



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



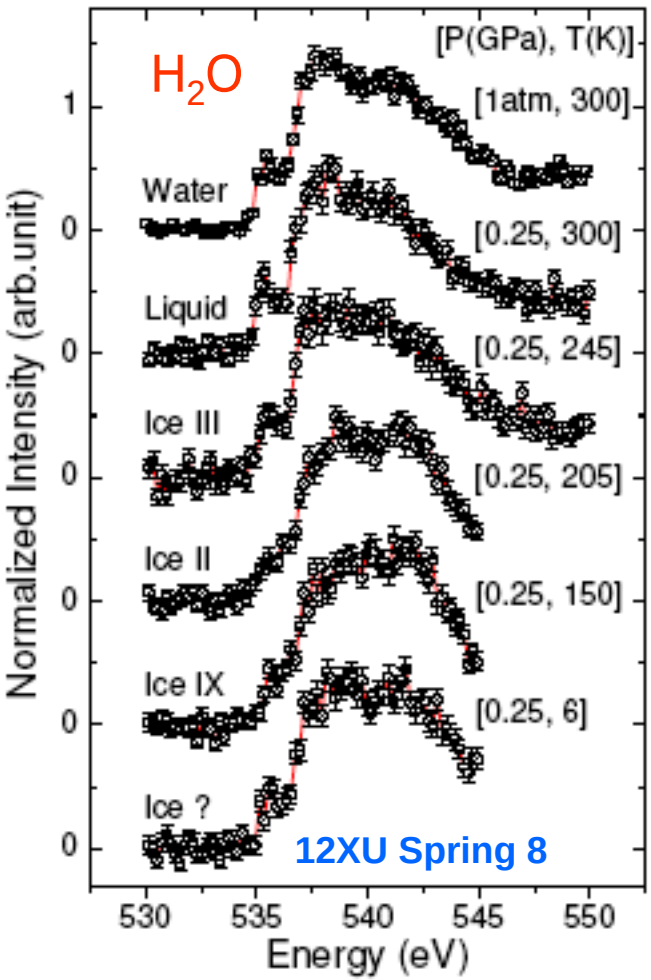




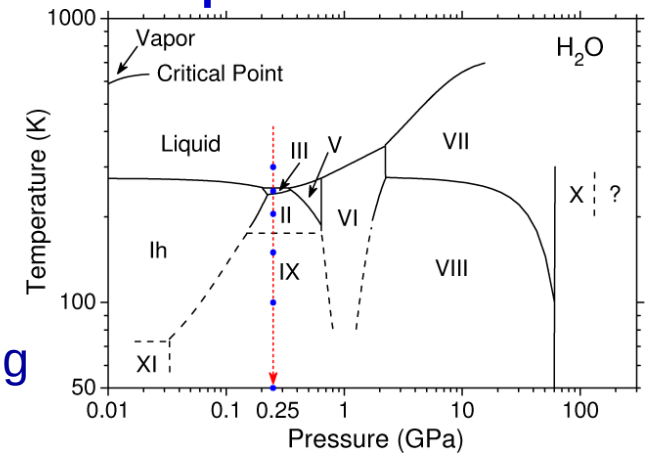
X-ray Raman measurements reveal pressure-induced bonding changes in low *P-T* phases

Oxygen IXS near K-edge spectra of H_2O

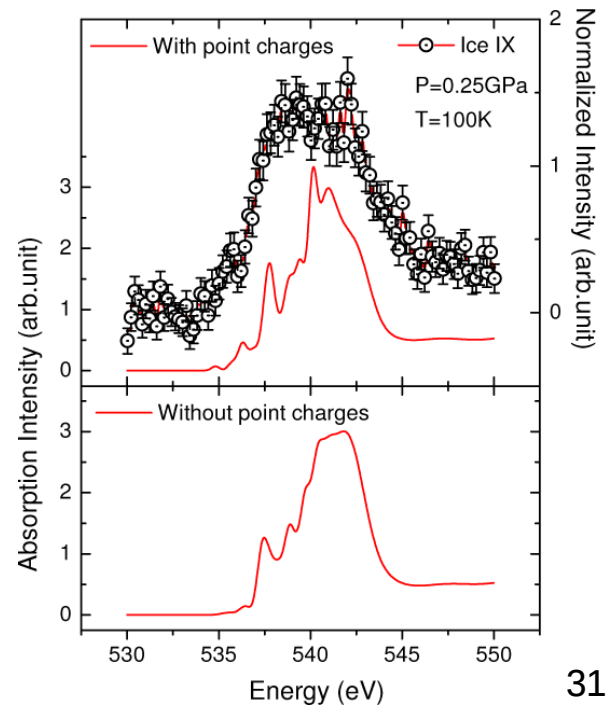
***E_0* = 9686.5 eV**



Effect of hydrogen bond ordering on K edge spectra

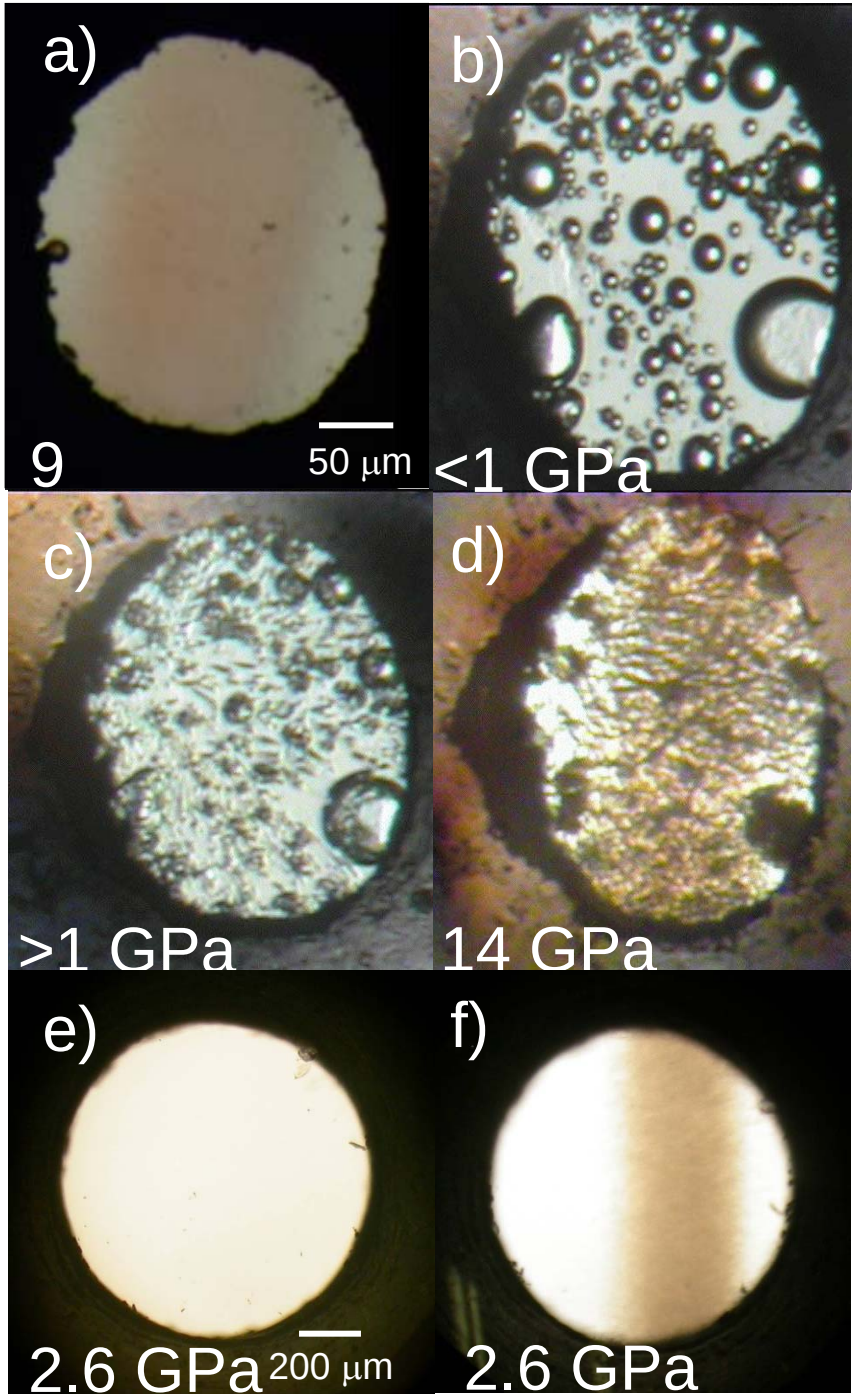


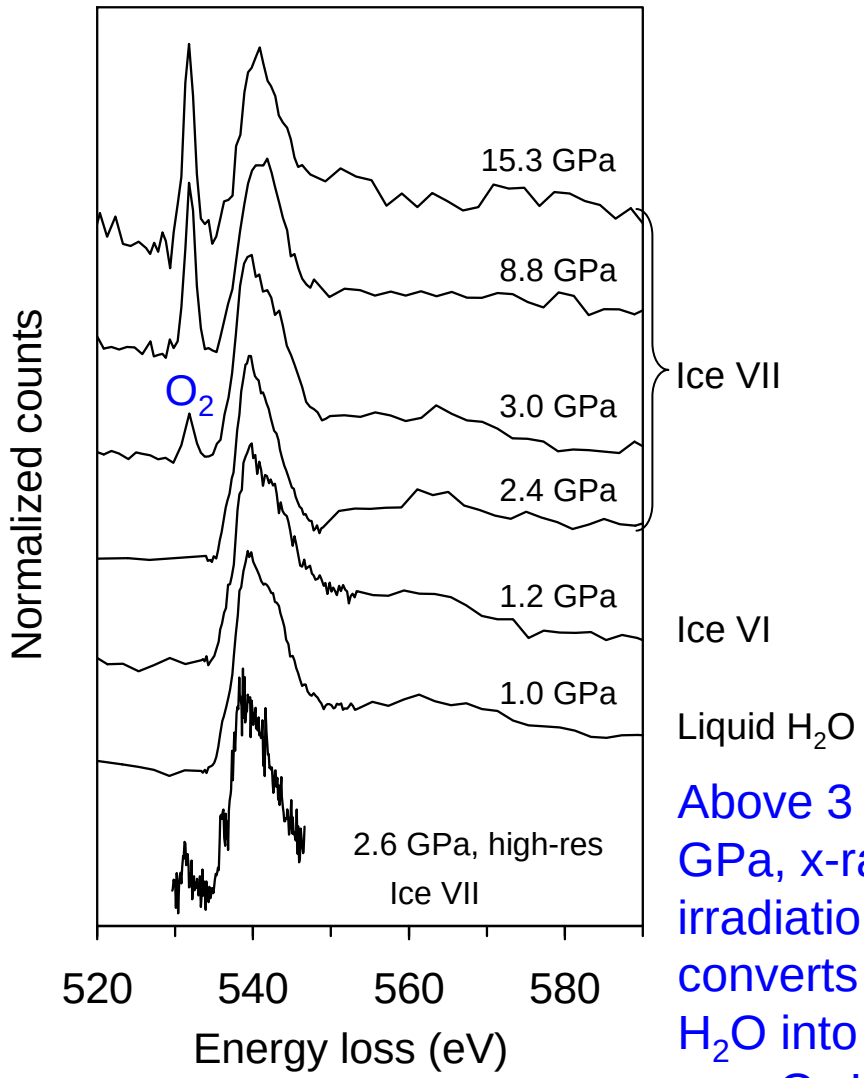
Evidence for a new low-*T* phase



Cai *et al.*, *PRL* 2005

Novel radiation chemistry at HP



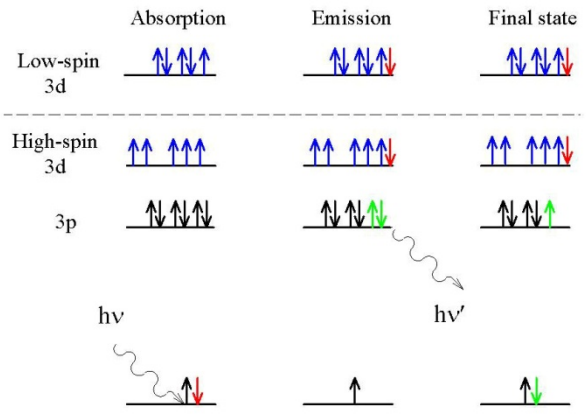


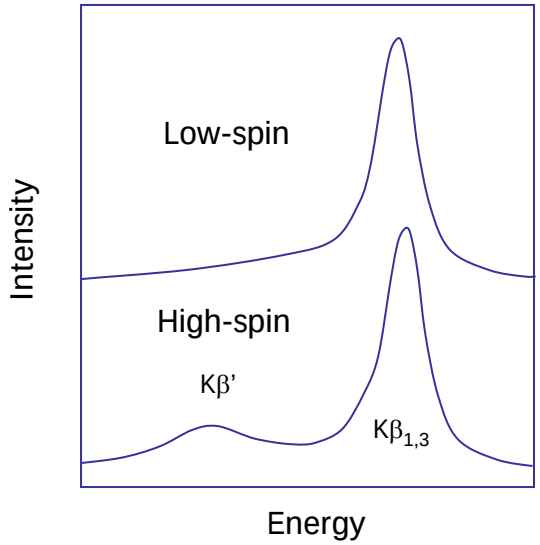
W. Mao *et al*, *Science* 2006

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

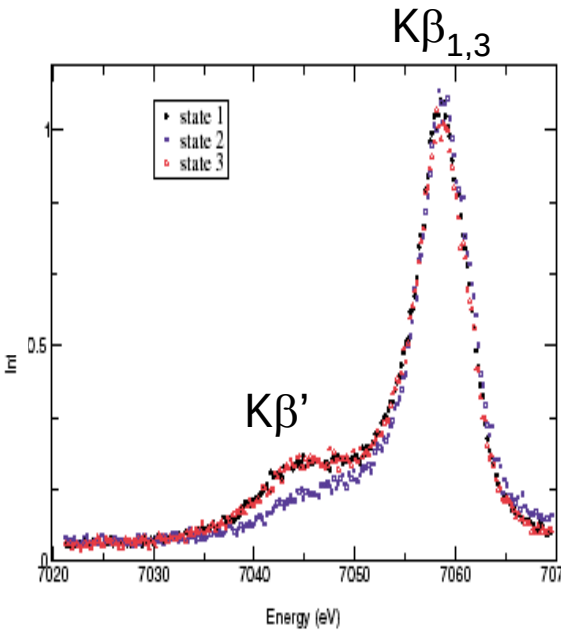
High-pressure x-ray emission spectroscopy (XES)

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



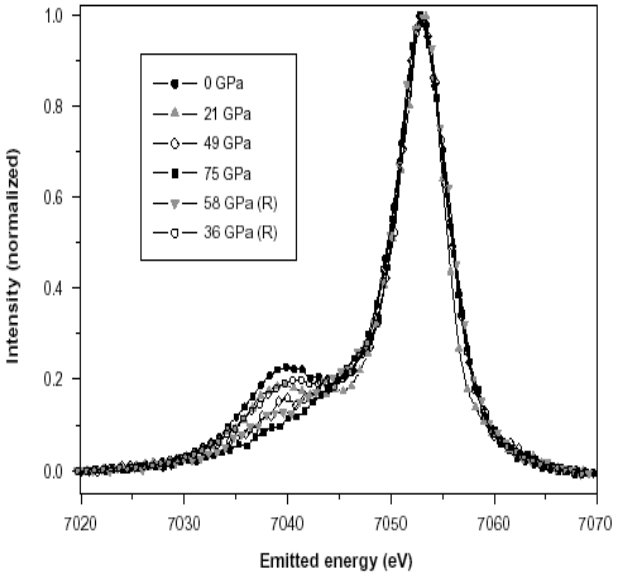


FeO & Fe_2O_3



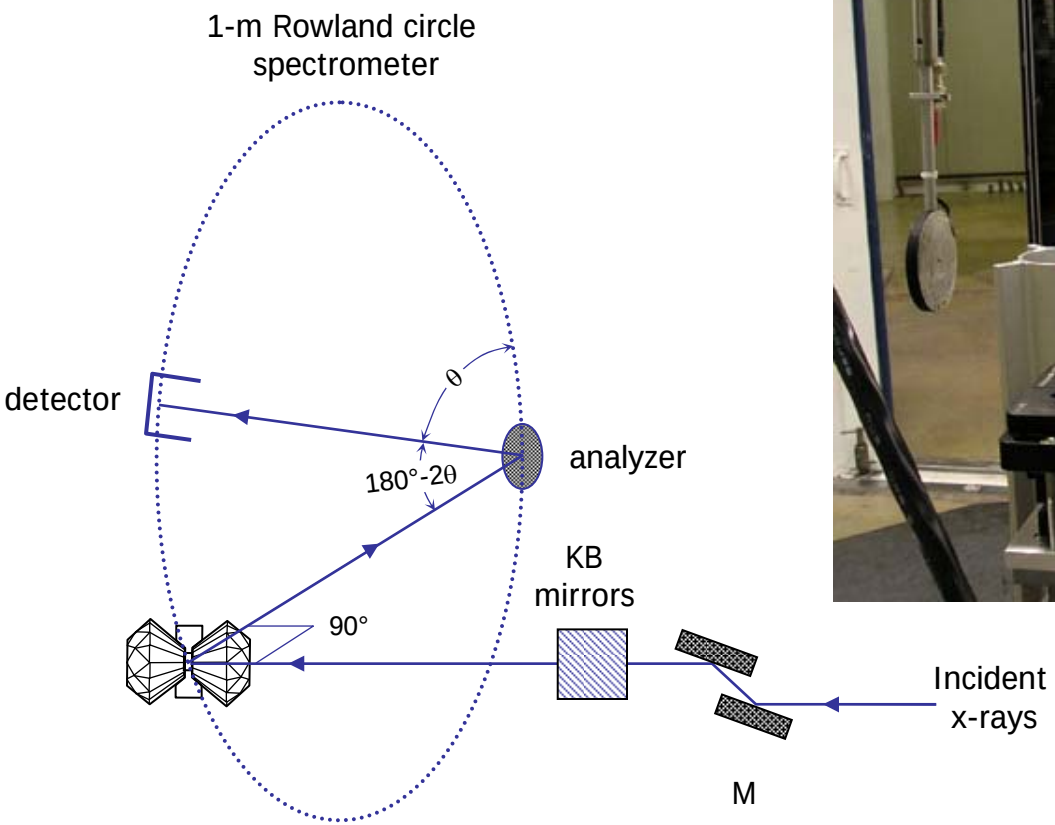
Badro *et al*, *PRL* 1999
Badro *et al*, *PRL* 2002

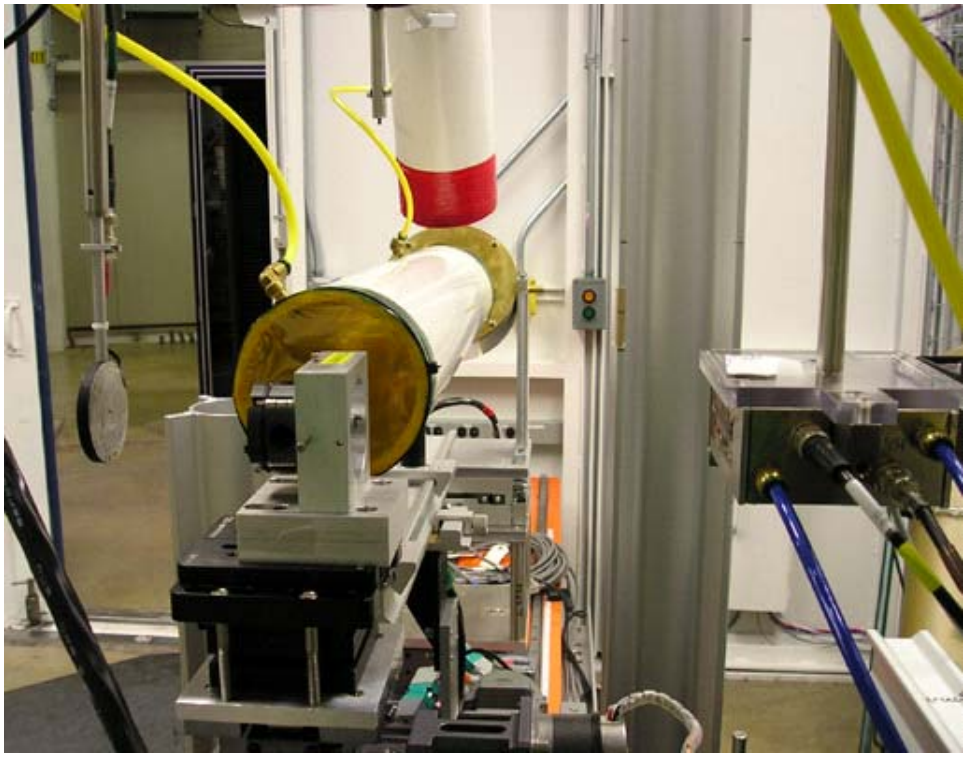
(Fe,Mg)O & $(Fe,Mg)SiO_3$



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

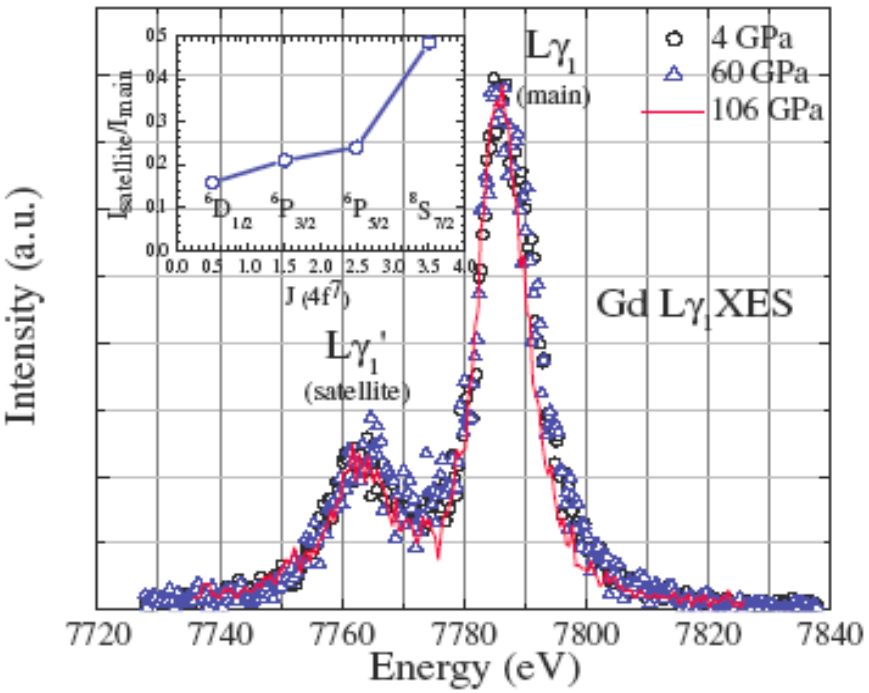




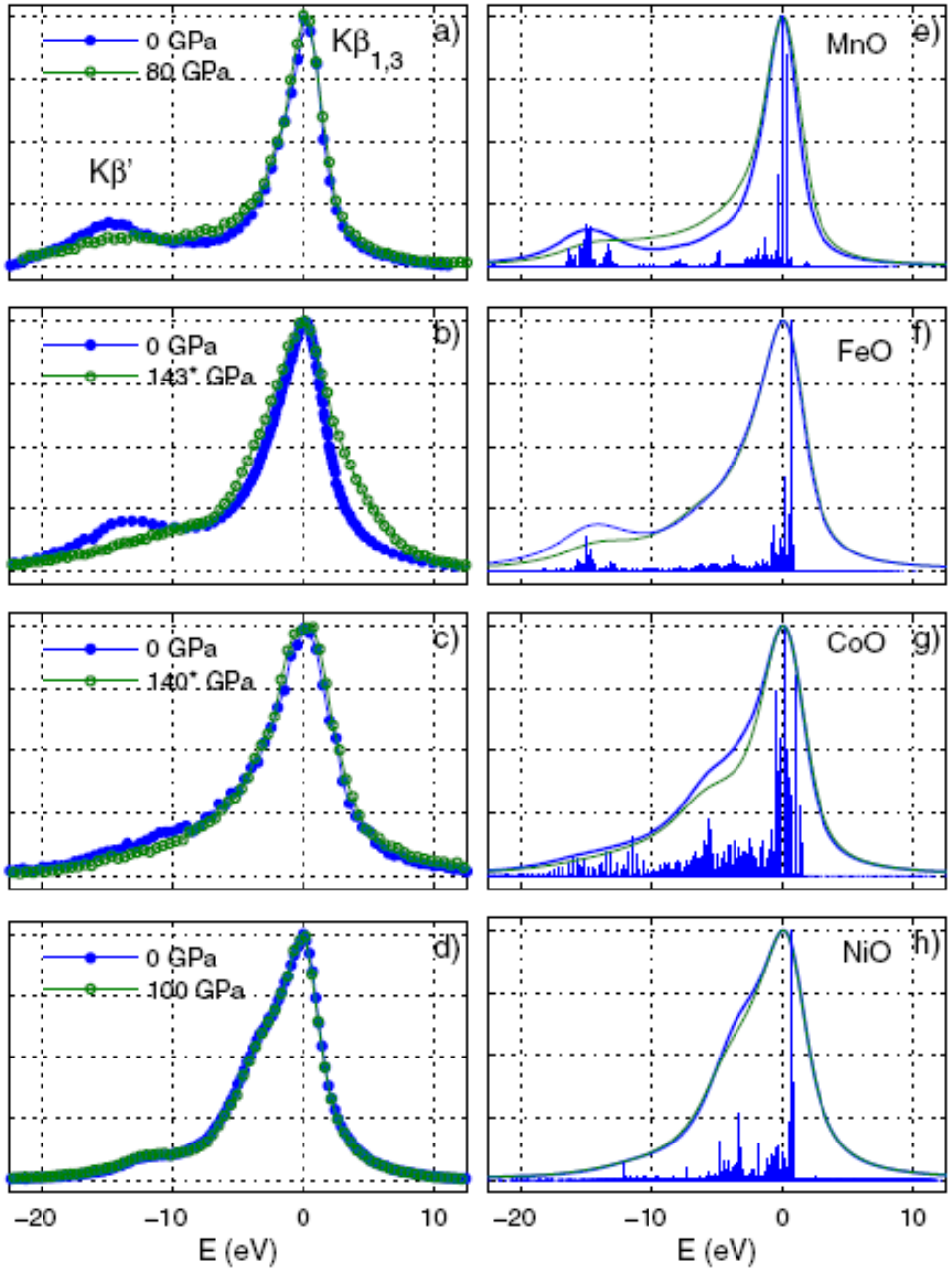
16-IDD, APS

XES

Gd

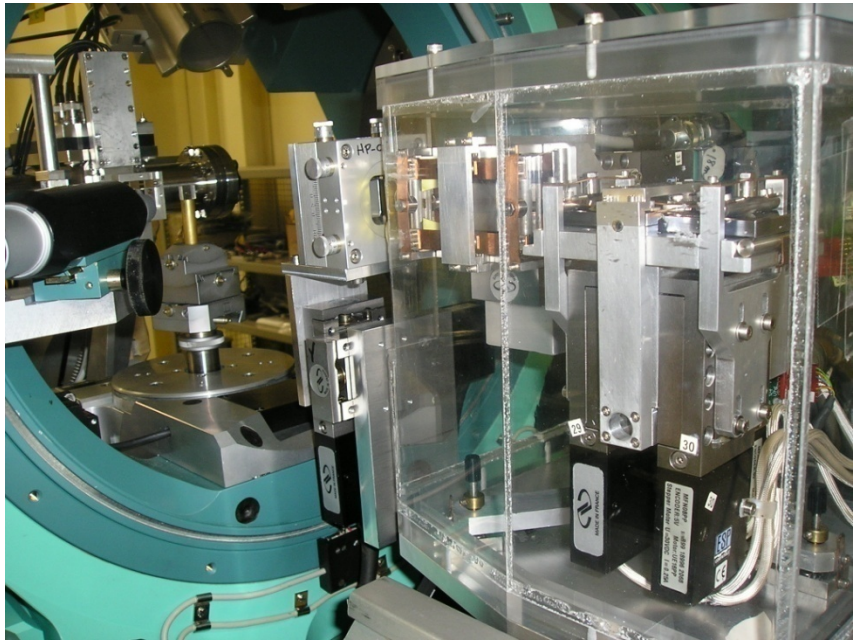


Maddox *et al.*, *PRL* 2006



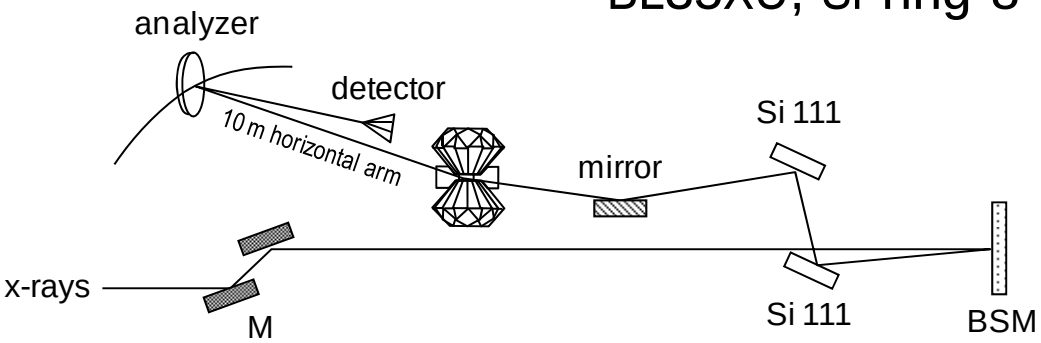
Mattila *et al.*, *PRL* 2007

Phonon IXS

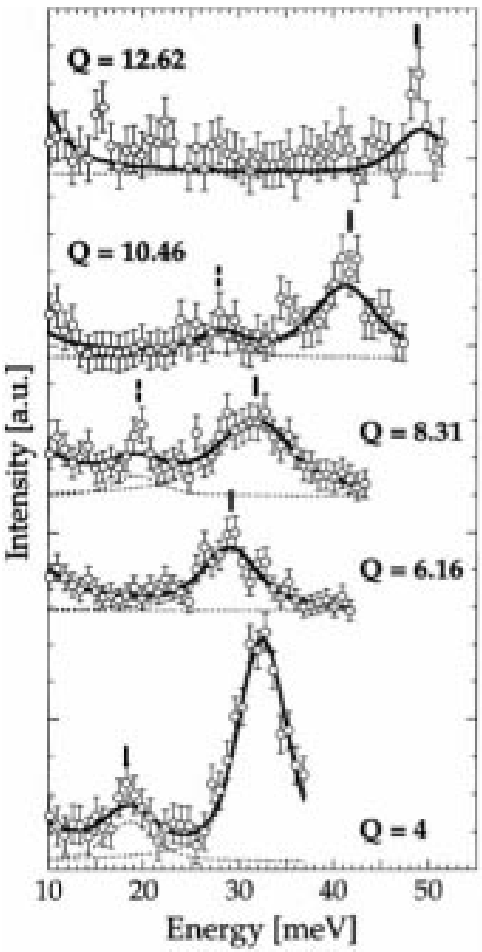


PANORAMIC DIAMOND ANVIL CELL

BL35XU, SPring-8

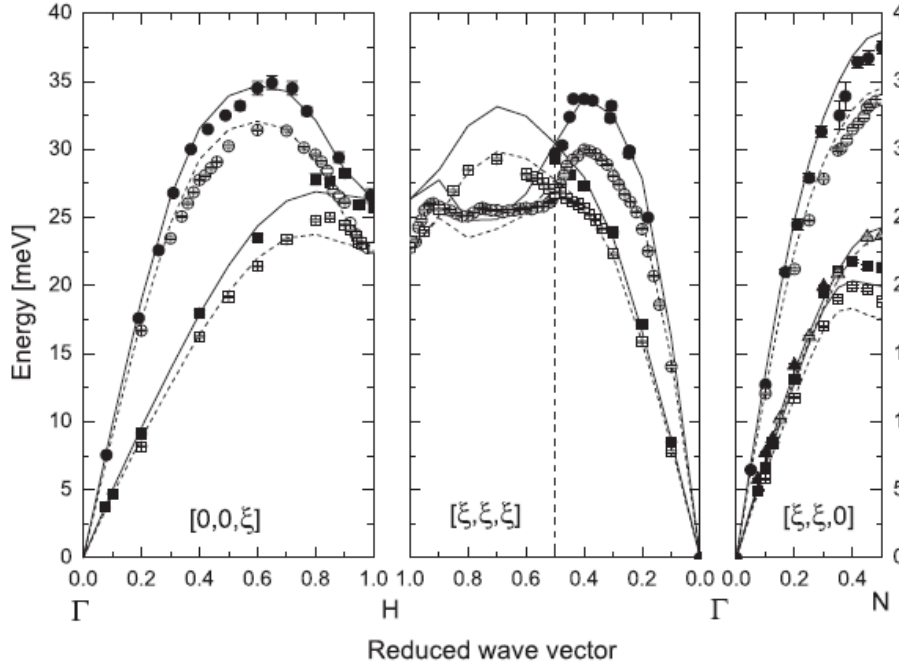


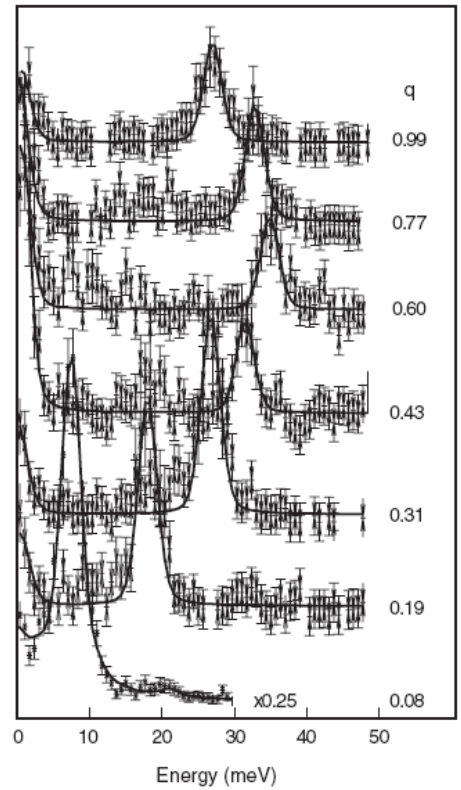
PIXS of hcp-Fe to over 100 GPa



Fiquet *et al.*, *Science* 2001

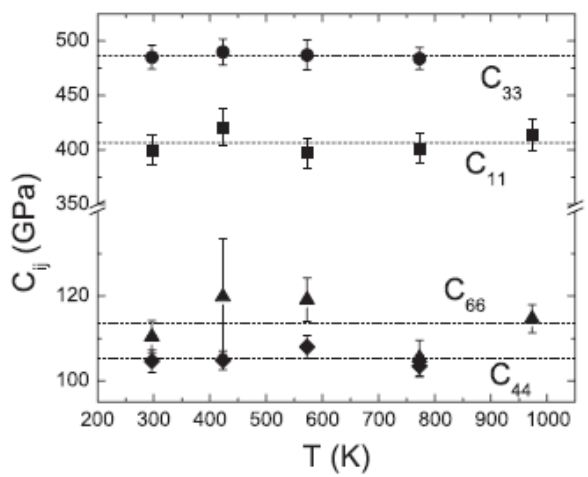
Lattice dynamics of Mo to 37 GPa



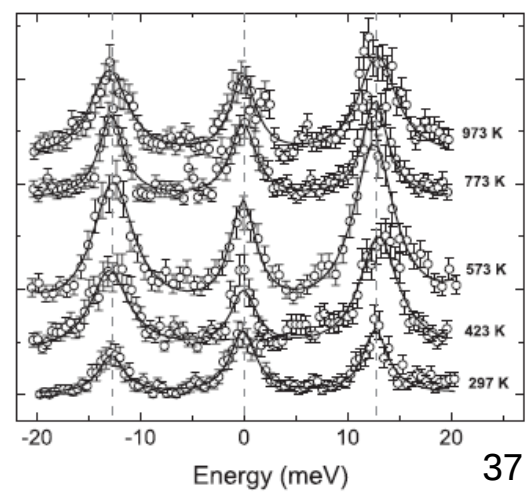


Farber *et al.*, PRL 2006

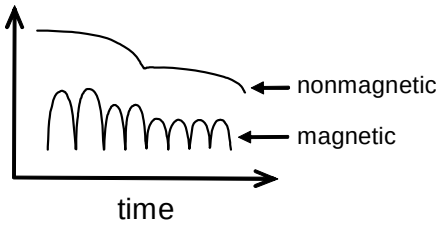
Single xtal Co at high *P-T*



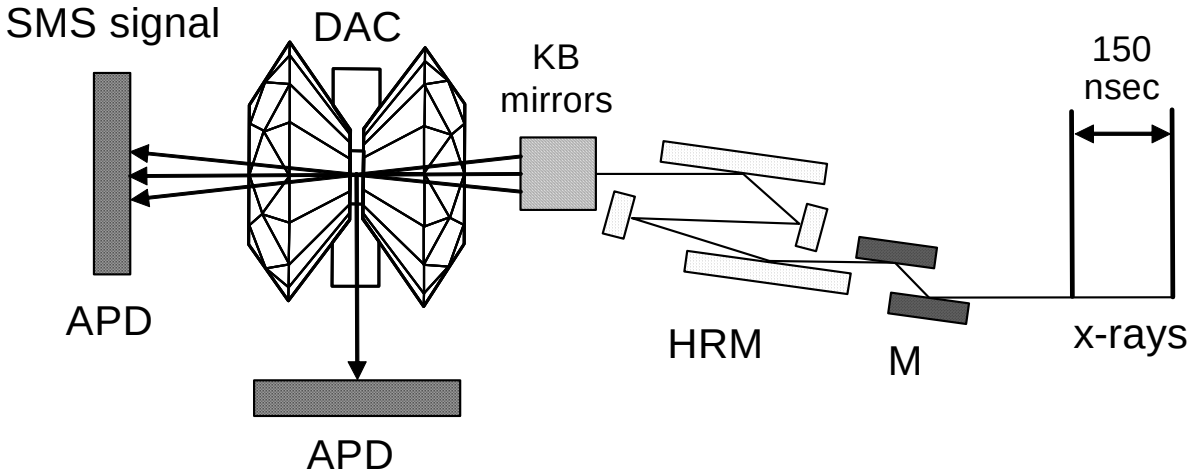
Antonangeli *et al.*, PRL 2008



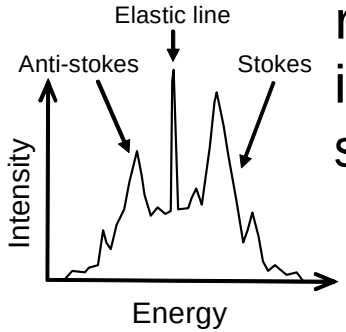
Nuclear resonant inelastic x-ray scattering



Synchrotron ^{57}Fe Mössbauer spectroscopy



NRIXS signal

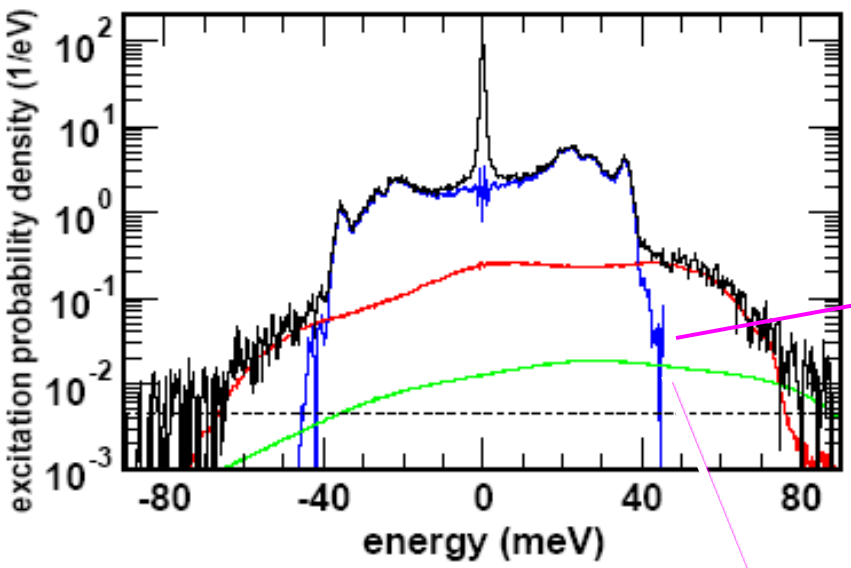


Nuclear resonant inelastic x-ray spectroscopy

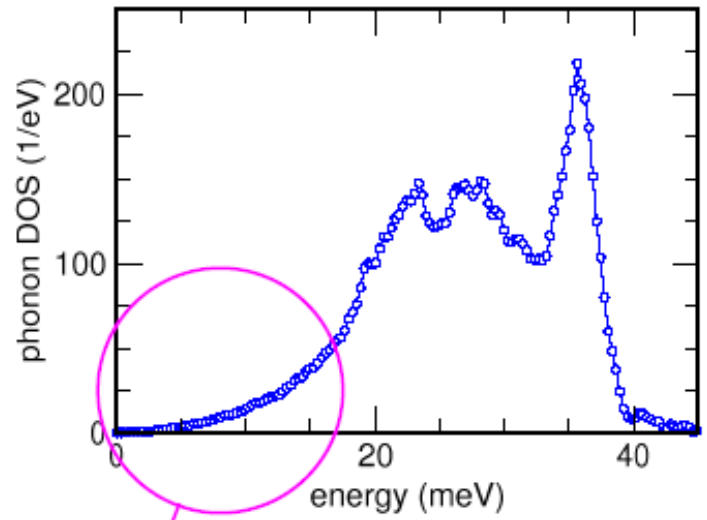
Energy = 14.4125 keV

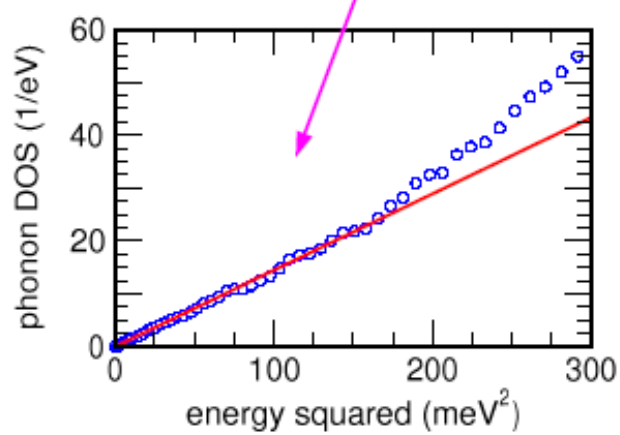
Extracting phonon density of states

Phonon excitation spectrum



Phonon density of states





From W. Sturhahn

Sturhahn *et al*, *PRL* 1995

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

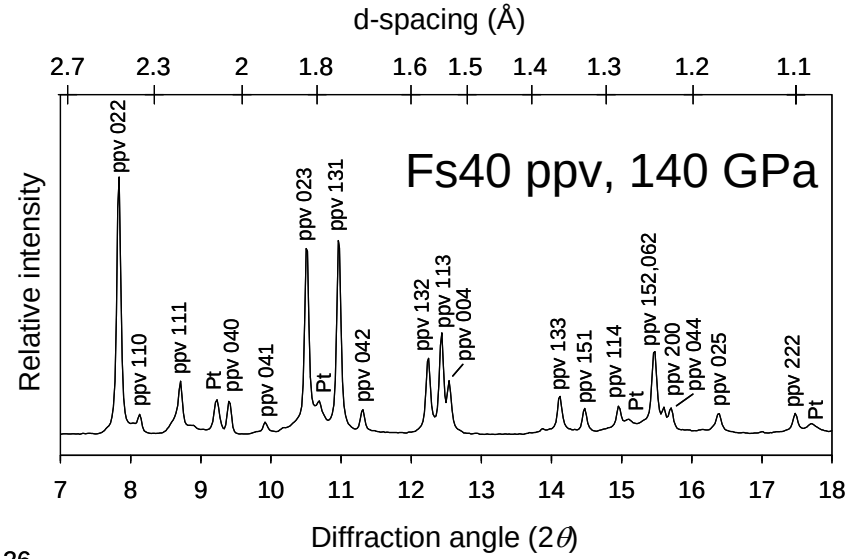
Sturhahn, *Hyp. Int.* 2000

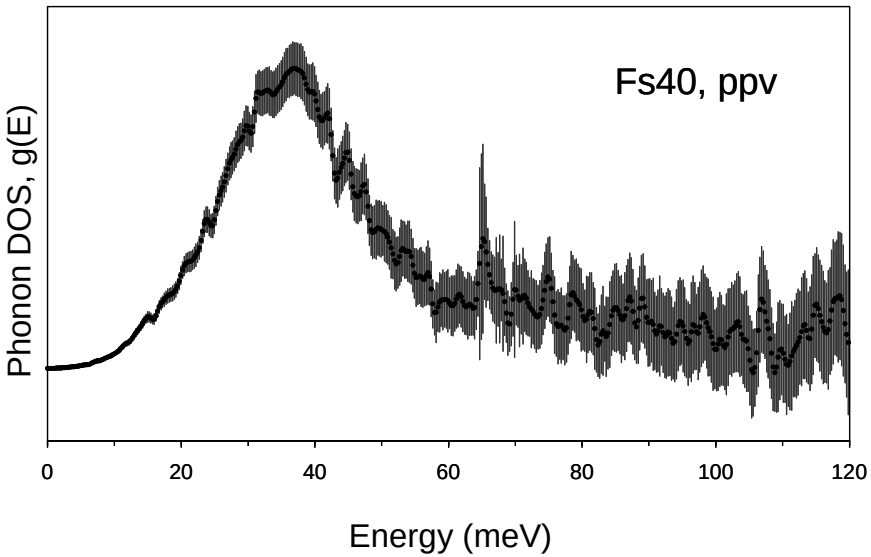
$$g(\omega) = \frac{V}{2\pi^2 \upsilon_D^3}\omega^2$$

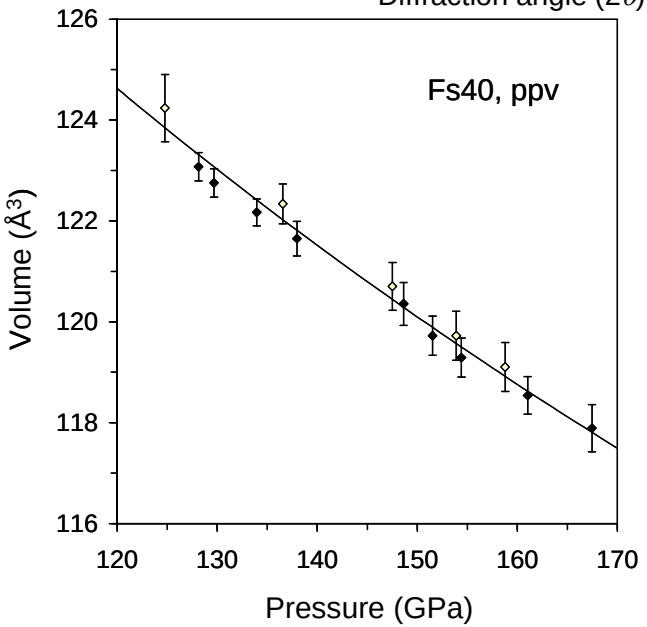
$$\frac{3}{\upsilon_D{}^3} = \frac{1}{\upsilon_p{}^3} + \frac{2}{\upsilon_S{}^3}$$

Debye velocity

How do we determine V_P and V_S?







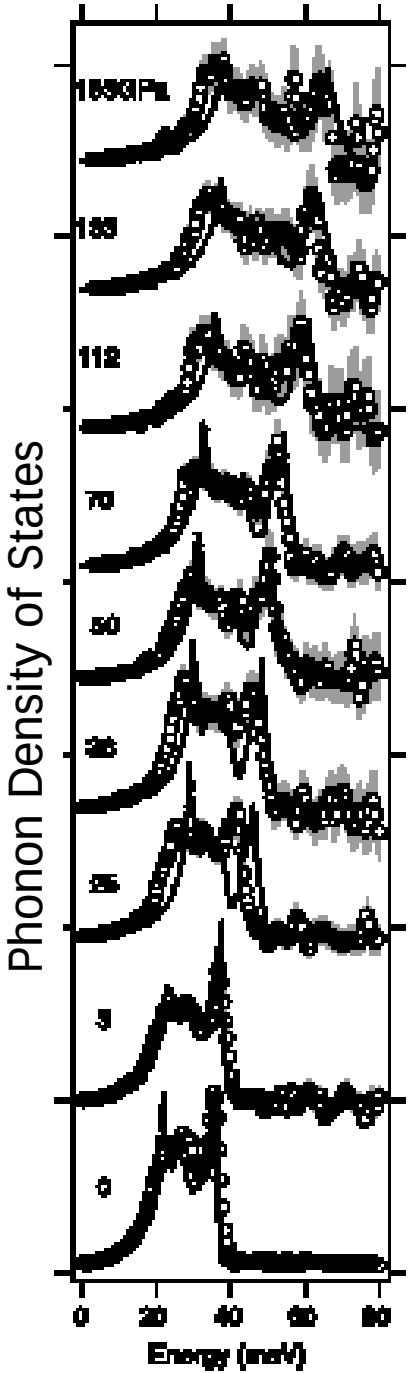
$$K = -V\left(\frac{\partial P}{\partial V}\right)$$

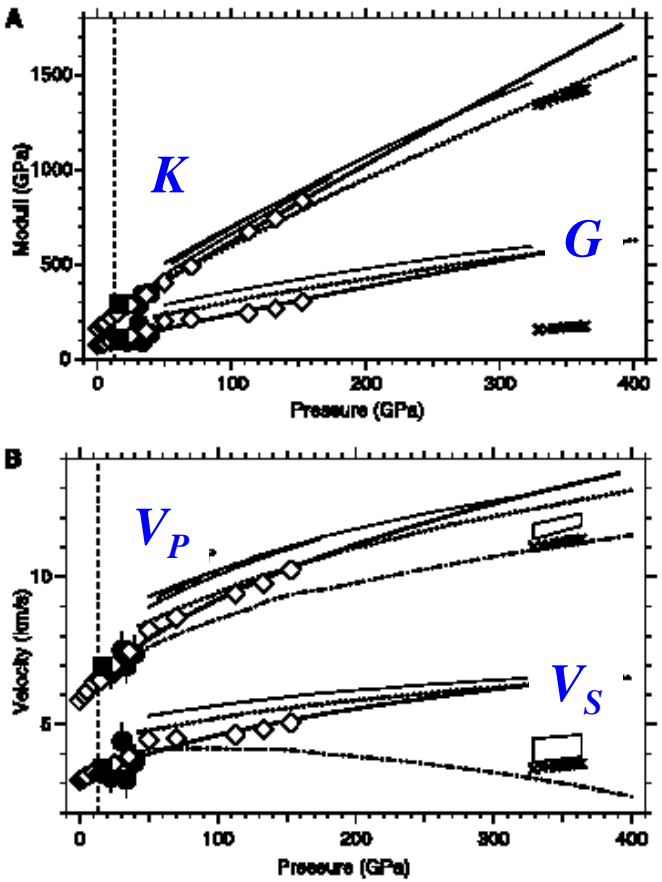
$$\frac{K}{\rho} = \upsilon_P^{\ 2} - \frac{4}{3}\upsilon_S^{\ 2} = \upsilon_\Phi^{\ 2}$$

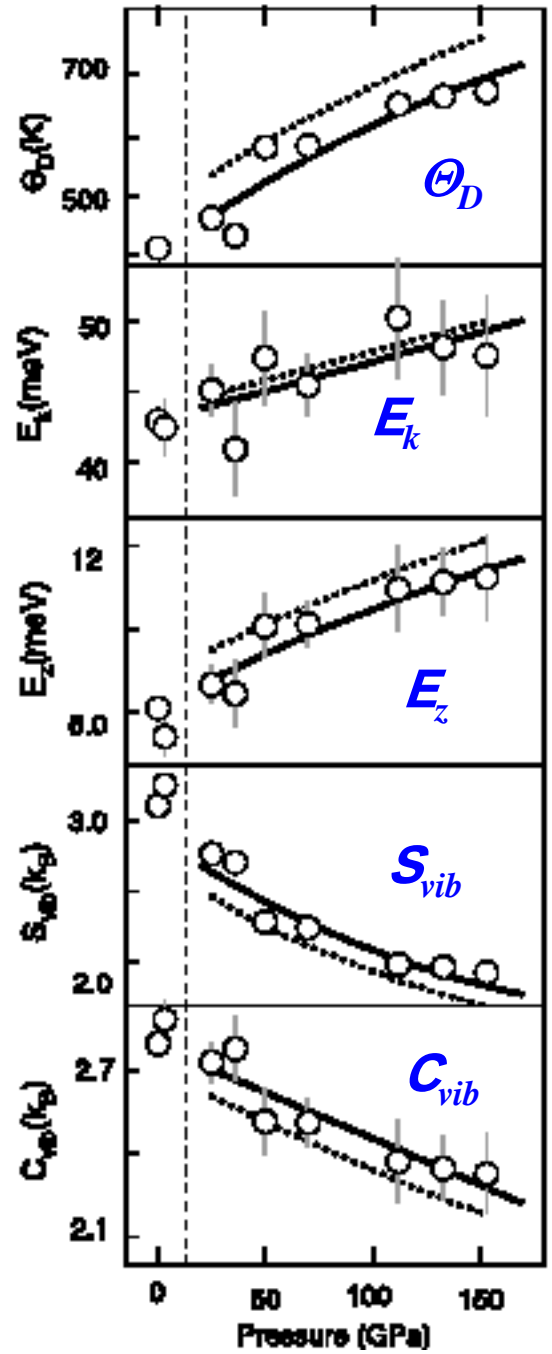
	V_P, km/sec	V_S, km/sec
PREM, mantle side of CMB	13.72	7.26
ULVZ (Thorne, JGR 2004)	12.35	5.08
Fs40 ppv at 130 GPa-300 K	12.72	4.86
Fs40 ppv at 130 GPa-3000 K	11.91	4.05

W. Mao *et al*, Science 2006

Elasticity and thermodynamic parameters of Fe to 153 GPa by NRIXS

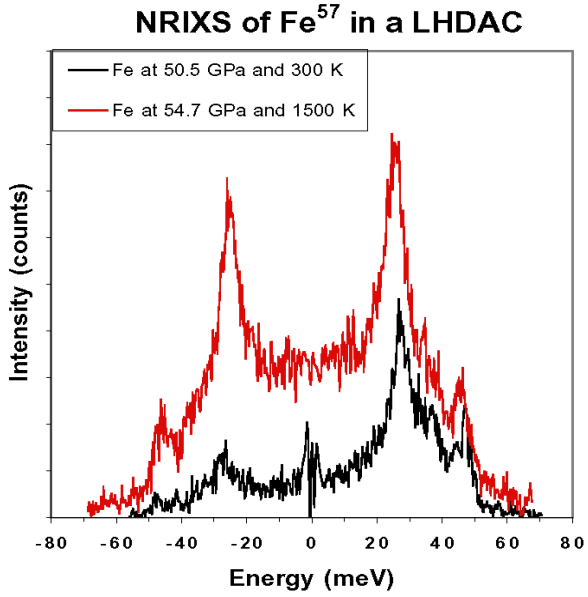




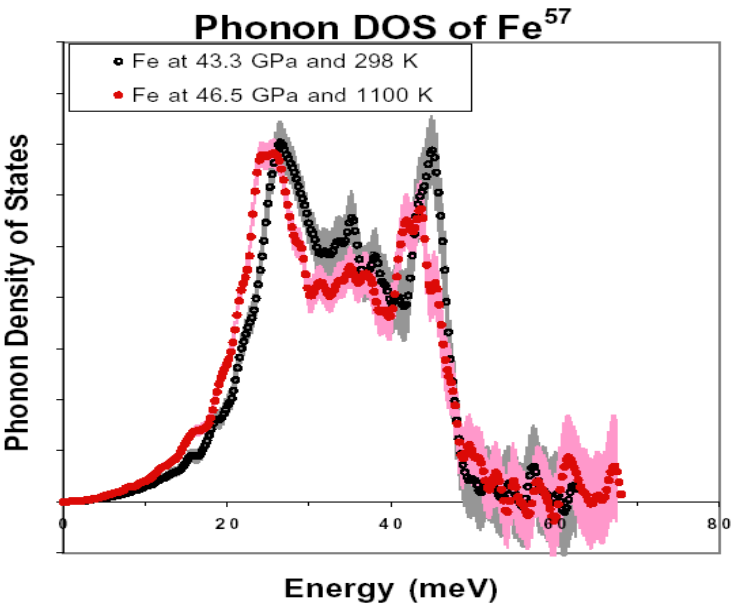


Mao *et al, Science* 2001

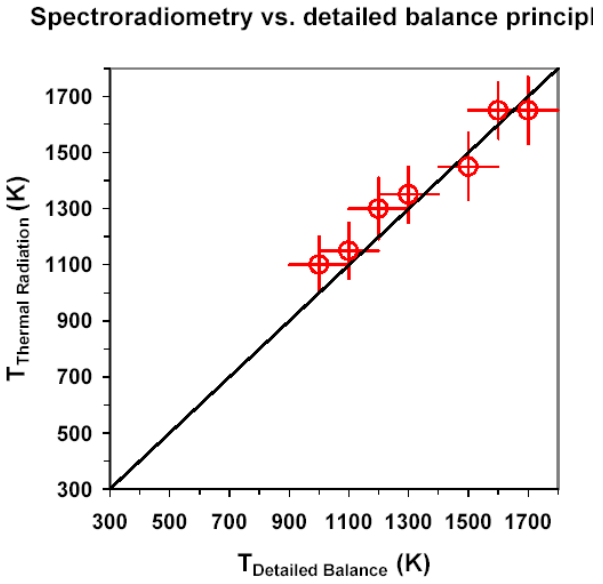
NRIXS at high *P* and high *T*



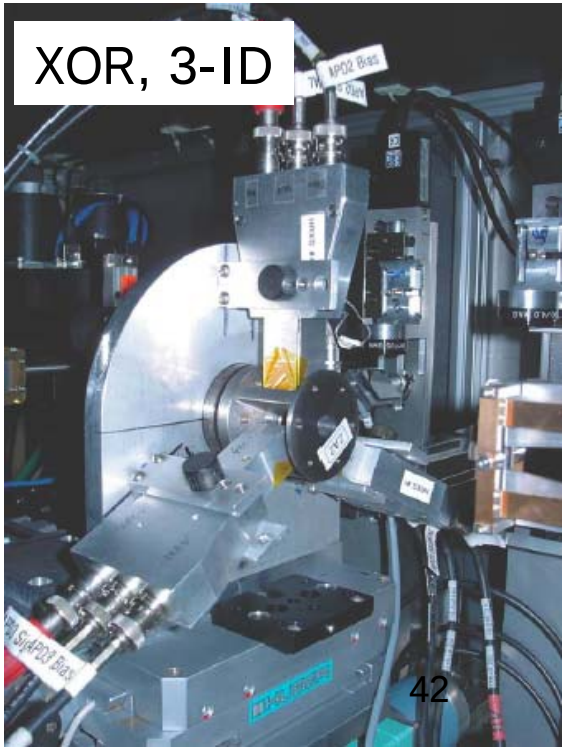
- Need x-ray and laser beam stability over many hours



Lin *et al.*, *Science* 2005

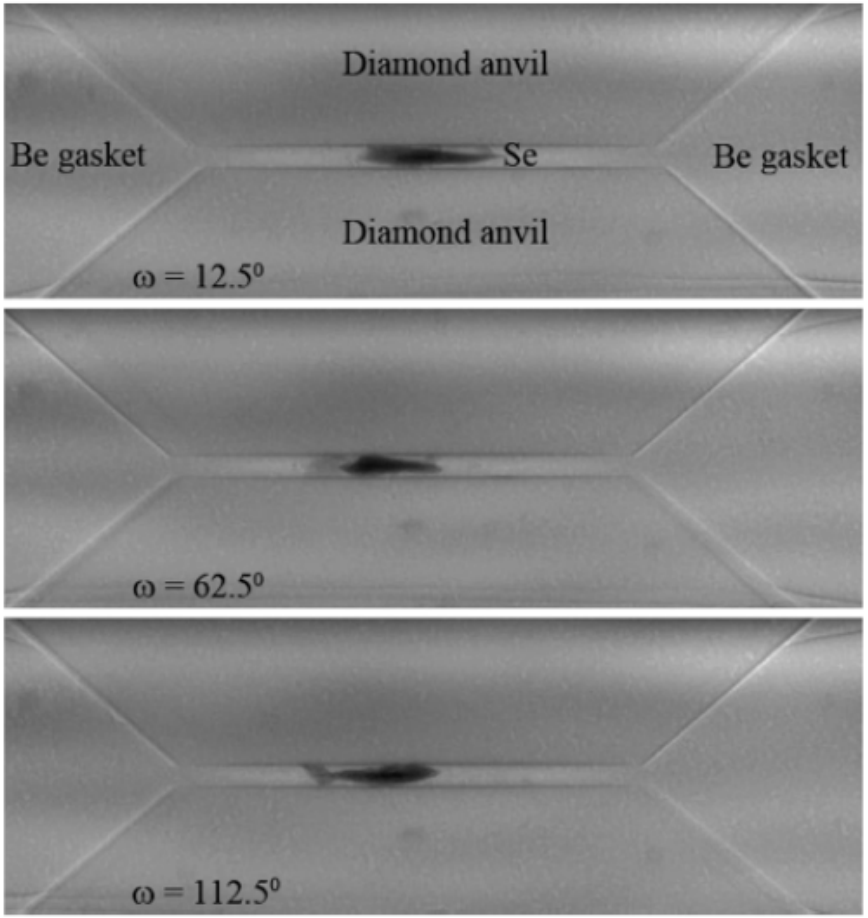


Calibration of temperature

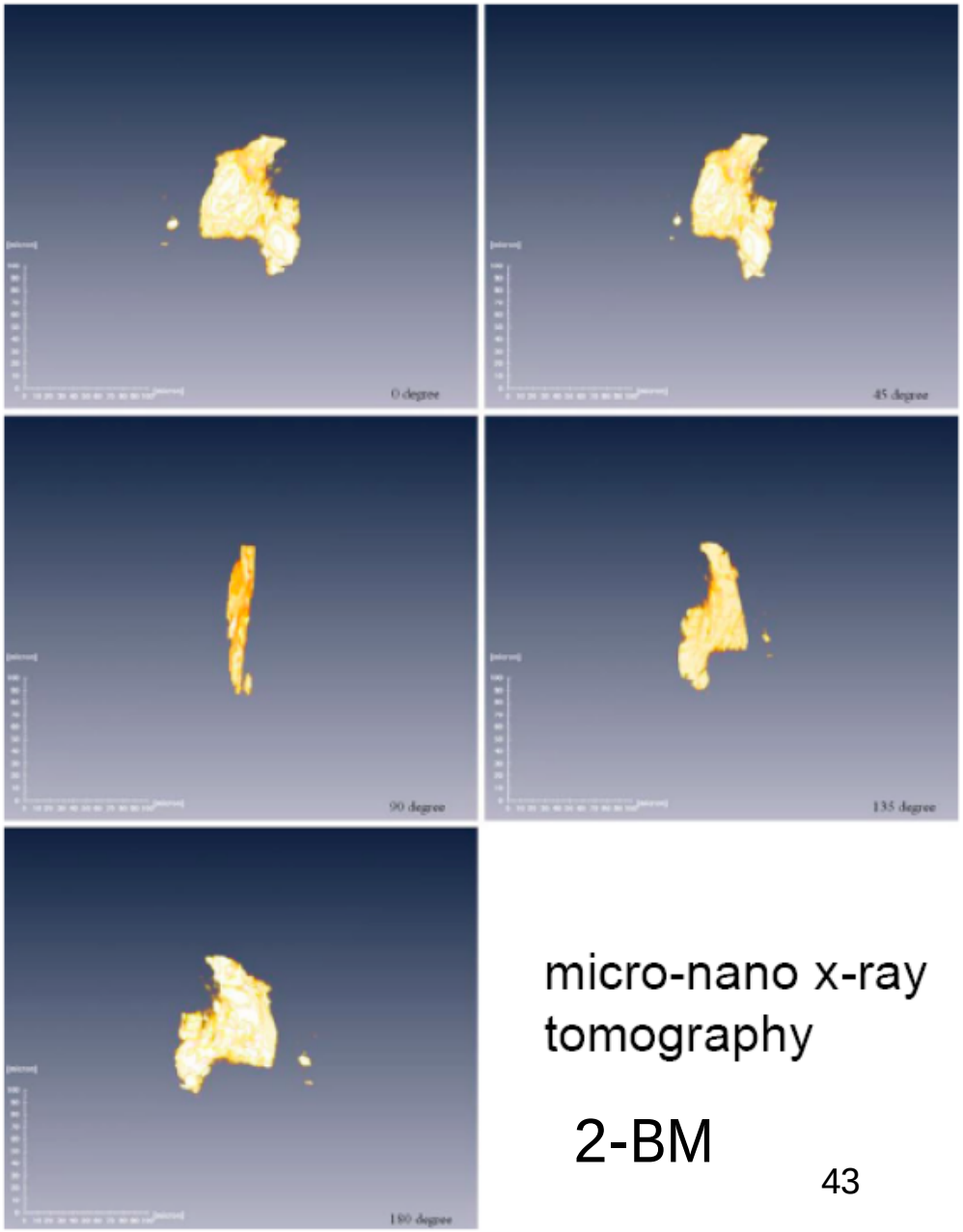


Micro-tomography

Accurate volume measurement of amorphous Se at high pressures



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

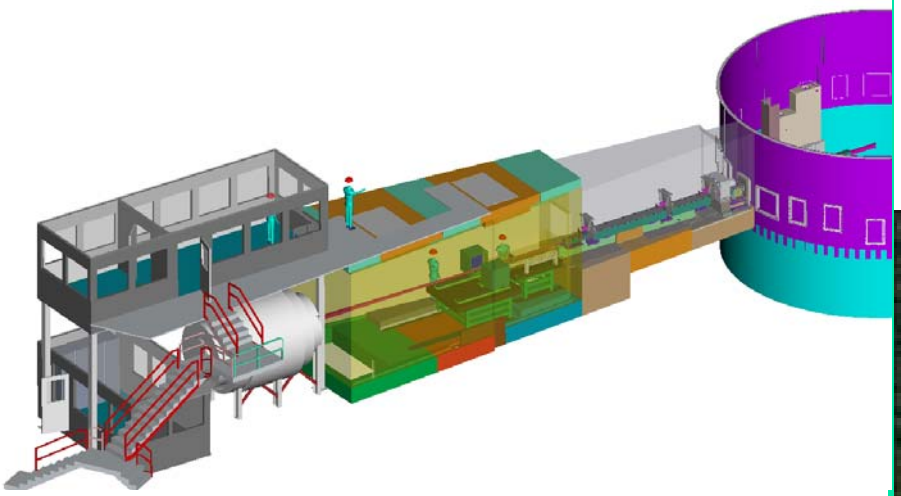


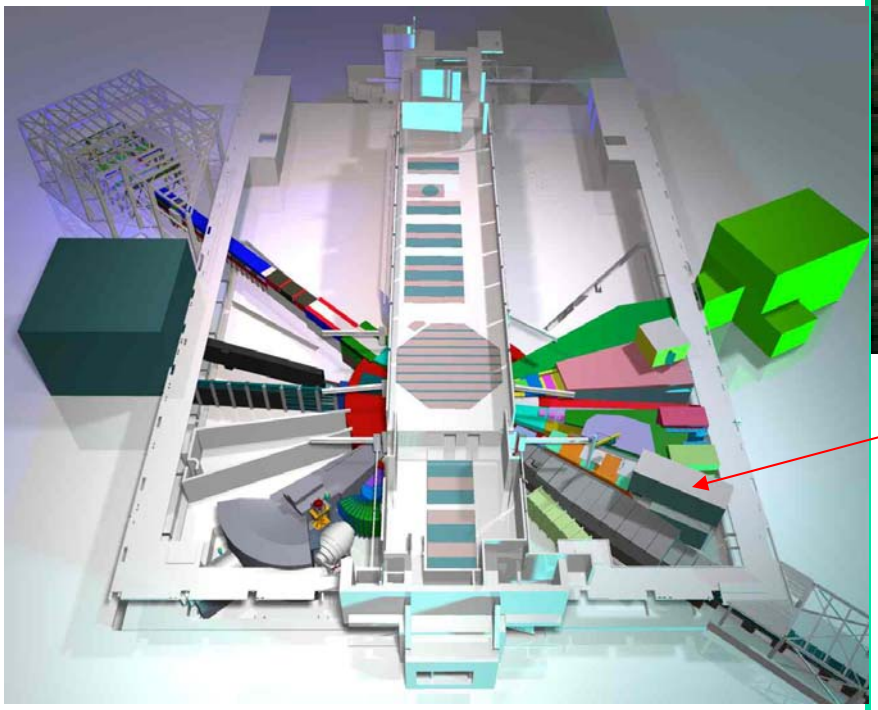
micro-nano x-ray tomography

2-BM

High *P-T* Neutron Probes

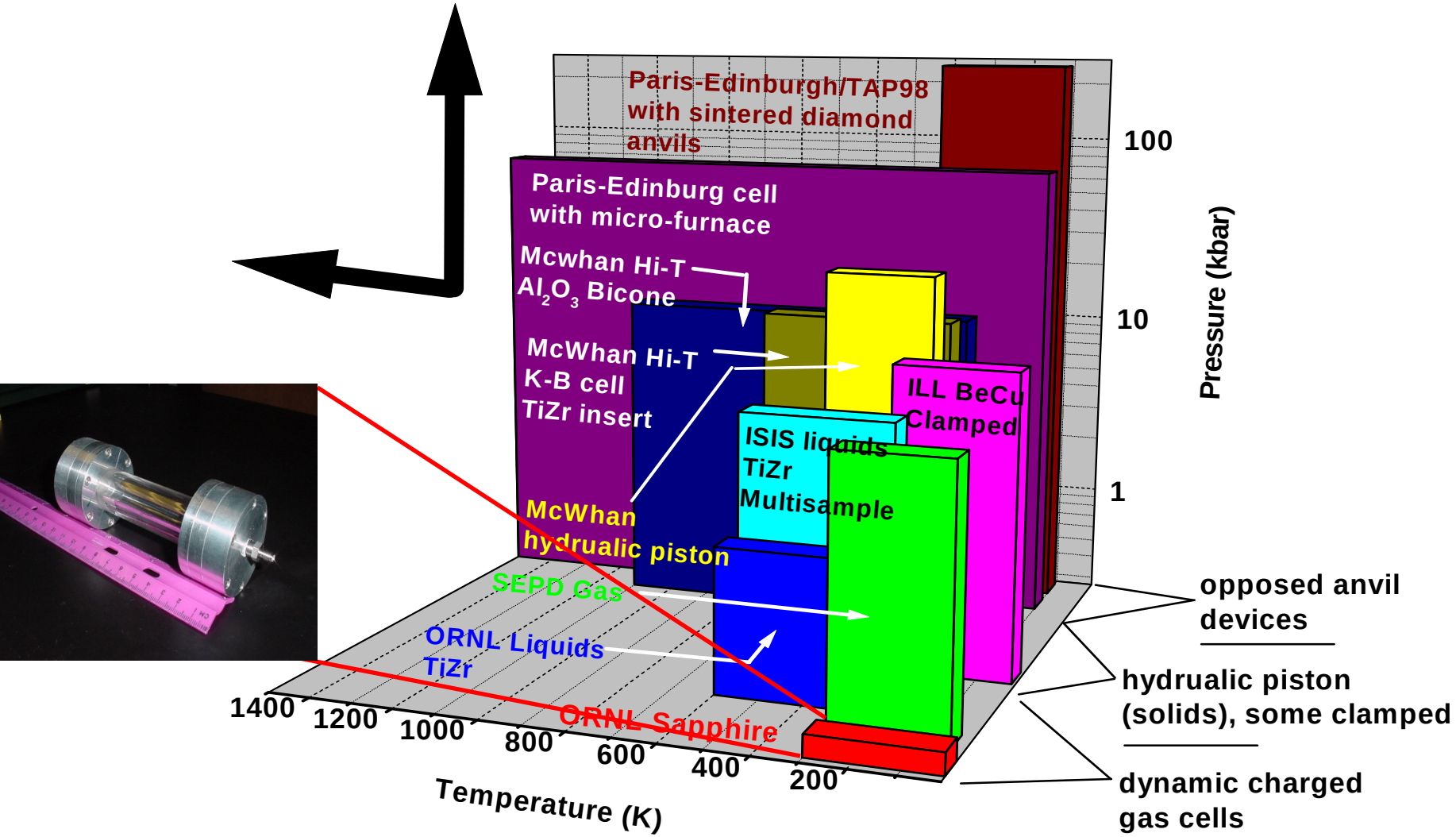
- hydrogen (deuterium)
- magnetic ordering
- large *q*
- phonon dynamics





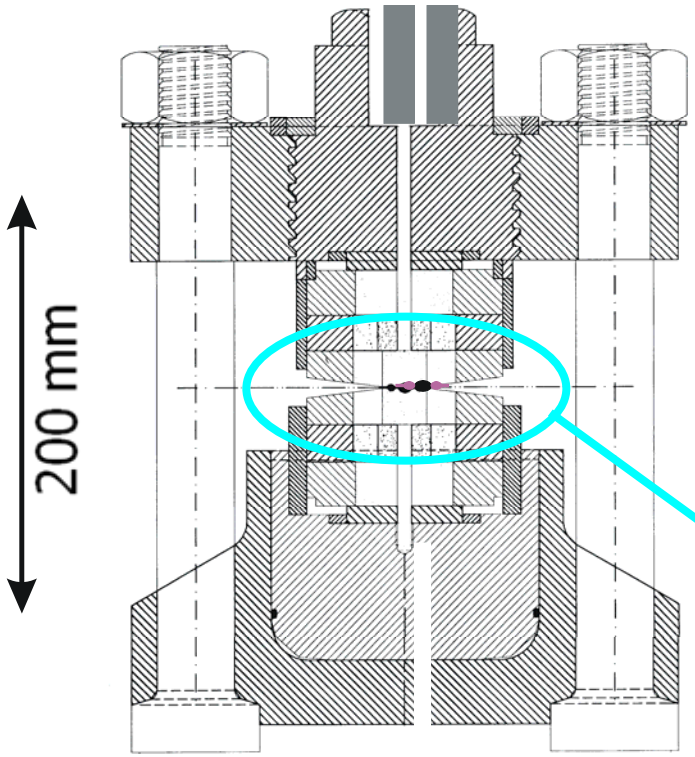
SNAP -- HP neutron diffraction beamline to be completed in commissioning phase at the new Spallation Neutron Source (SNS) at ORNL

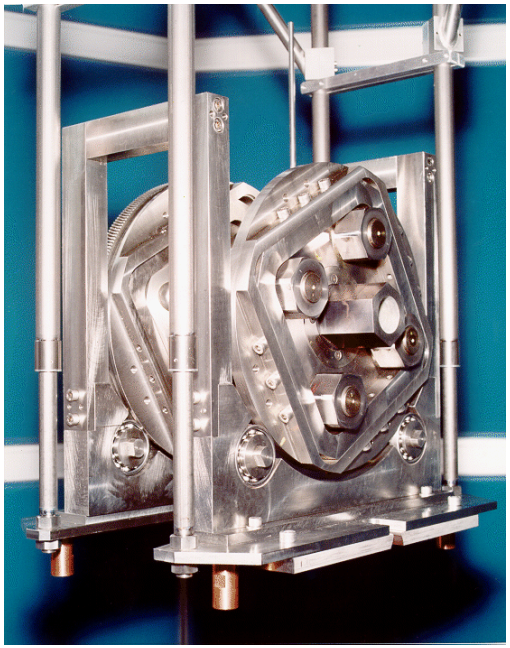
Survey of Neutron HP cells

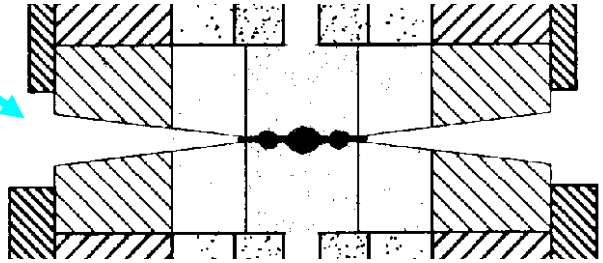


Adapted from C. Tulk

Paris-Edinburgh HP Cell





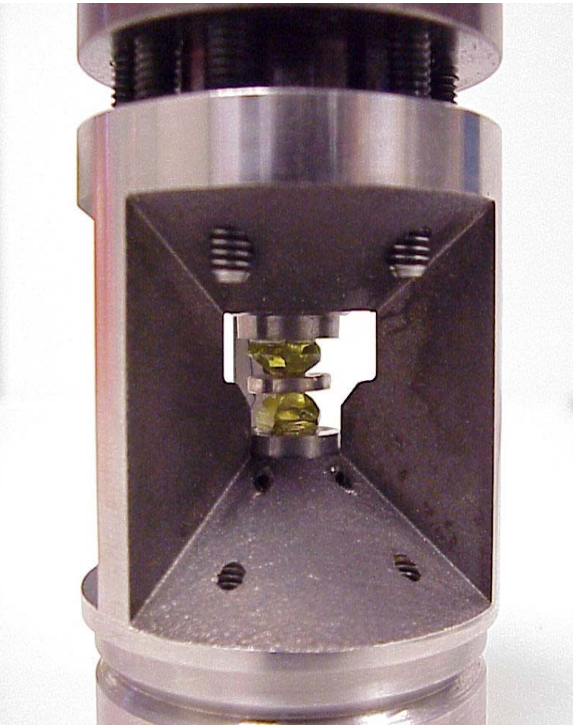


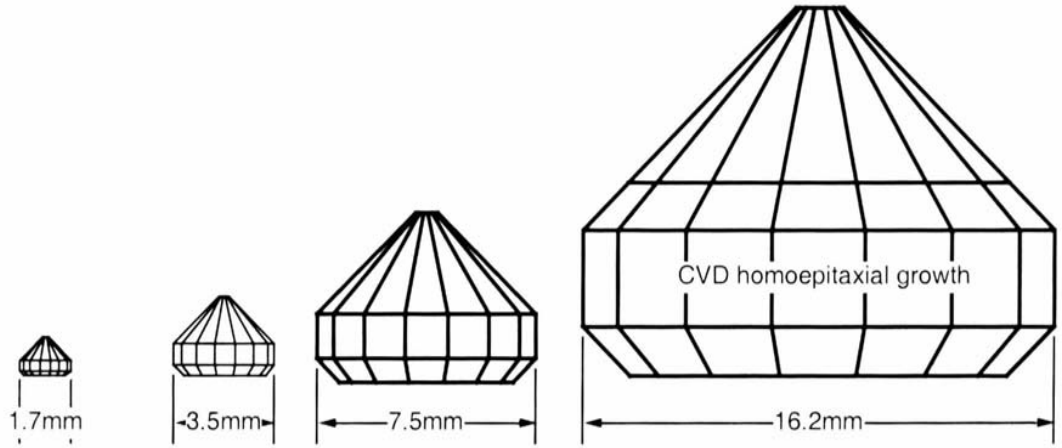
- First opposed anvil (WC or sintered diamond) device designed specifically for use at pulsed neutron source, ISIS. Relies on compression of gasket to reduce sample cell volume (200-400 ton press)
- Temperature ranges from < 100 - 1200 K with pressures up to ~ 25 GPa
- Primarily used for solid powdered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

Adapted from C. Tulk

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	----

Adapted from C. Tulk

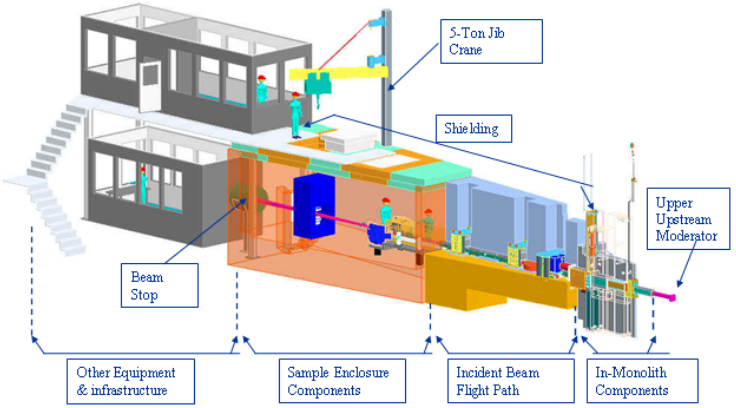
Future opportunities in high pressure

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

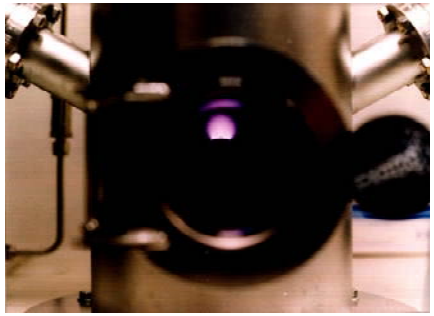
Single-crystal -- epitaxial growth

Strength -- hardness/toughness

Spectroscopic quality -- from UV to IR

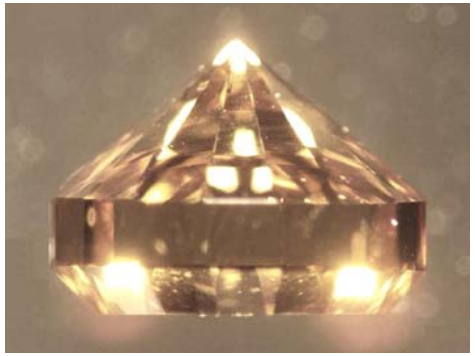
Giant, perfect, single-crystal diamonds can be grown by chemical vapor deposition (CVD) process

Diamond Growing in a Plasma Reactor



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

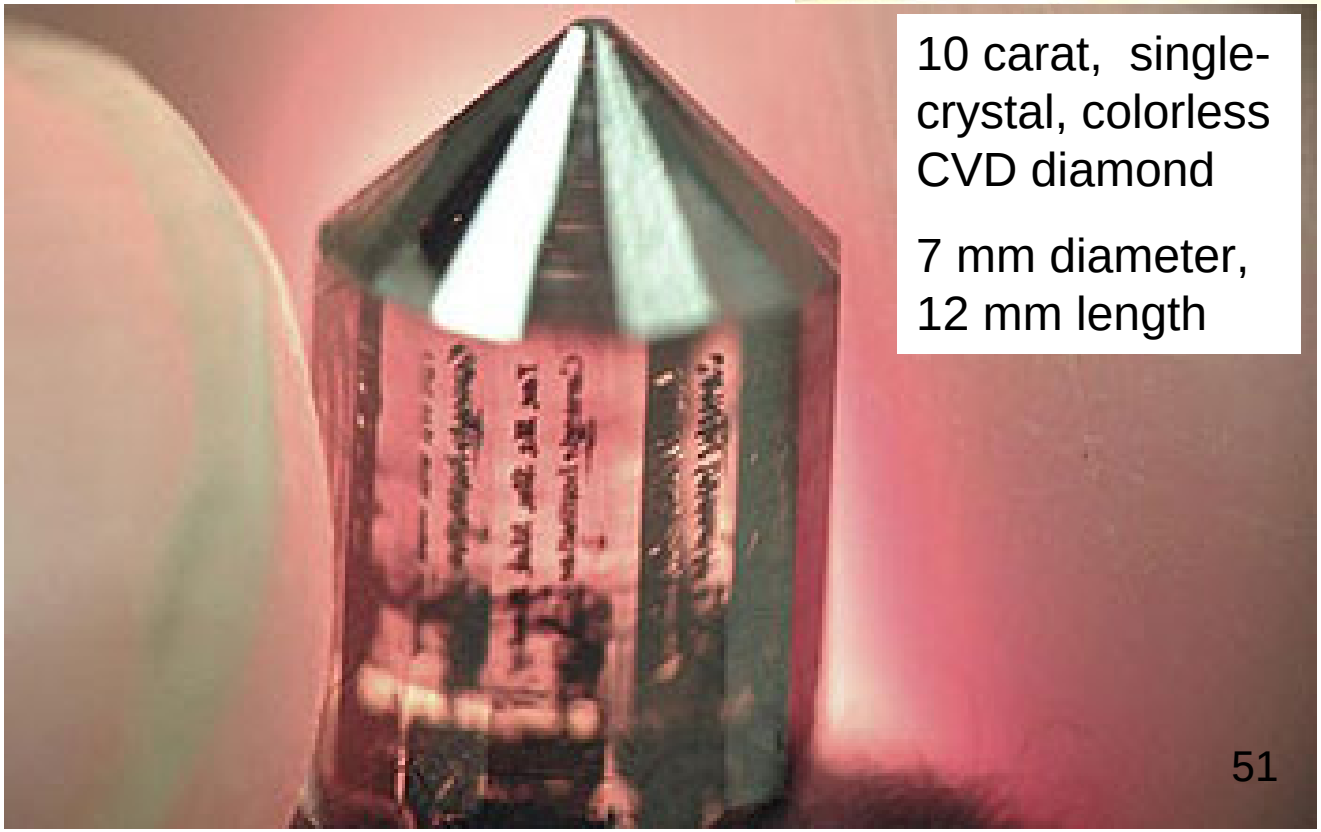
Yan *et al*. *PNAS* 2002



Production of regular diamond anvil

- 2.45 mm high
- 0.28 carats
- Grown in 1 day
- reached 200 GPa

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

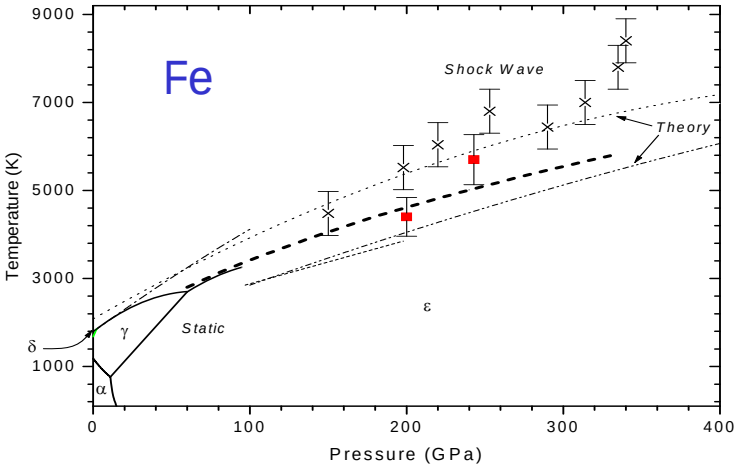


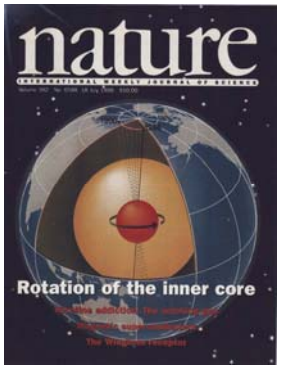
10 carat, single-crystal, colorless CVD diamond

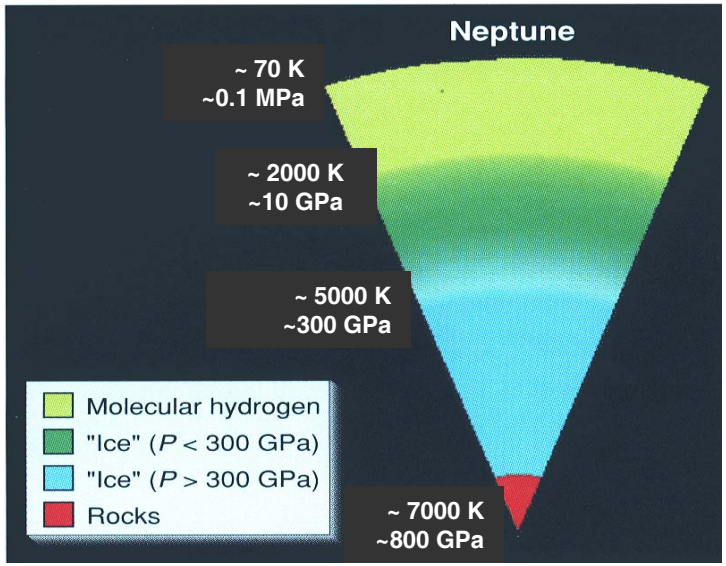
7 mm diameter, 12 mm length

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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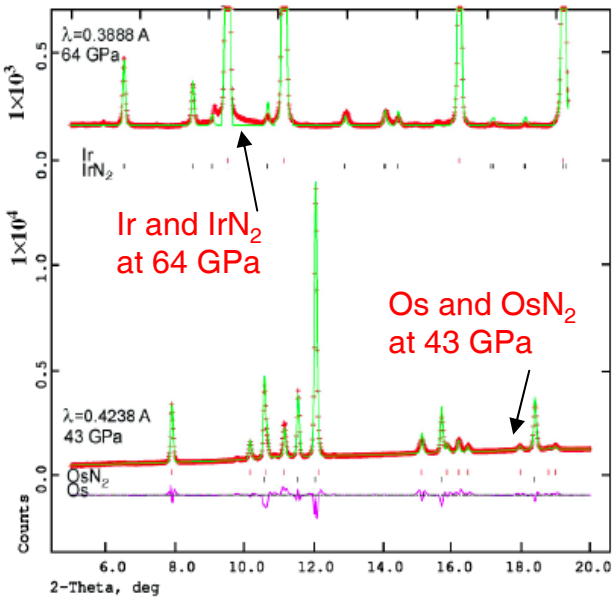
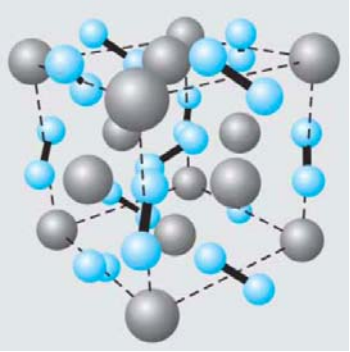
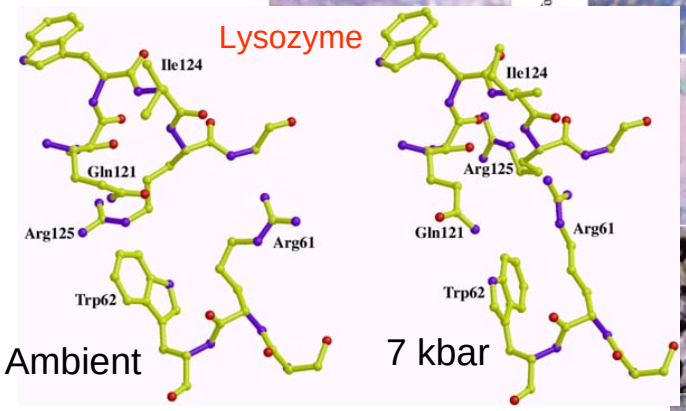


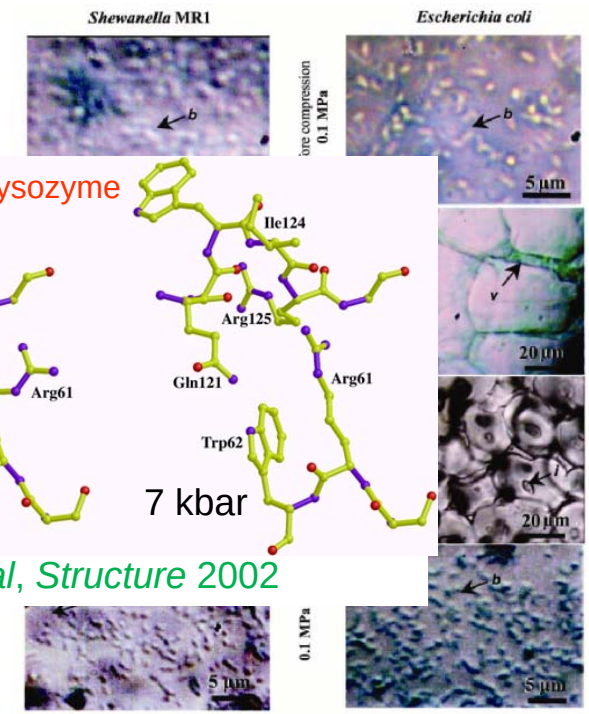


PtN_2 in pyrite structure

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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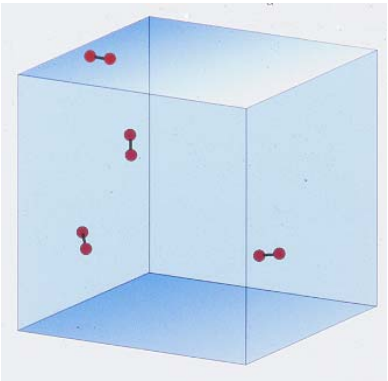
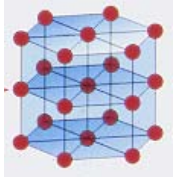
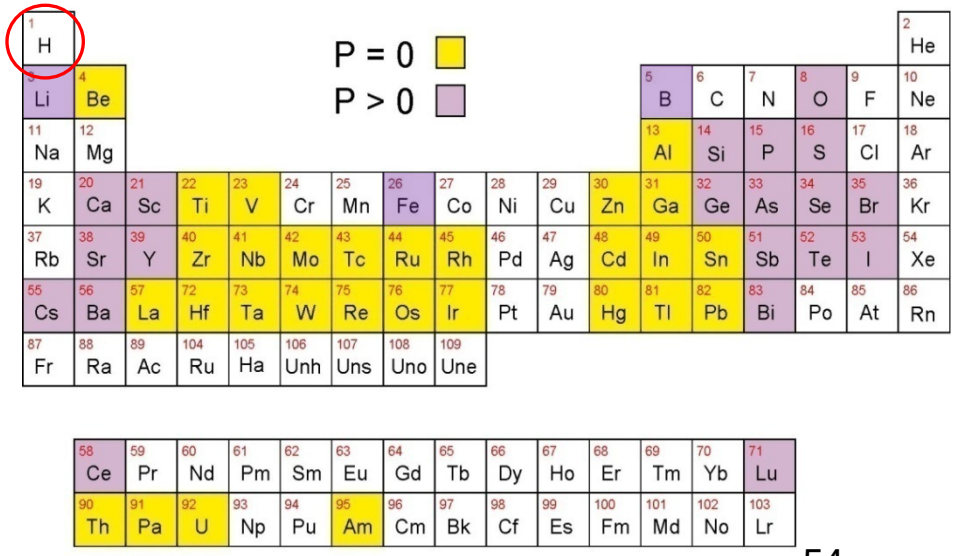




Periodic Table of Superconductors



- Pressure-induced metallization?
  Wigner & Huntington, *J. Chem. Phys.* **3**, 1935
- Exotic properties: Room-*T* super-conductor
  Ashcroft, *Phys. Rev. Lett.* **21**, 1968