X-ray Diffraction at Extreme P,T Conditions

Mohamed Mezouar, ID27

Outline

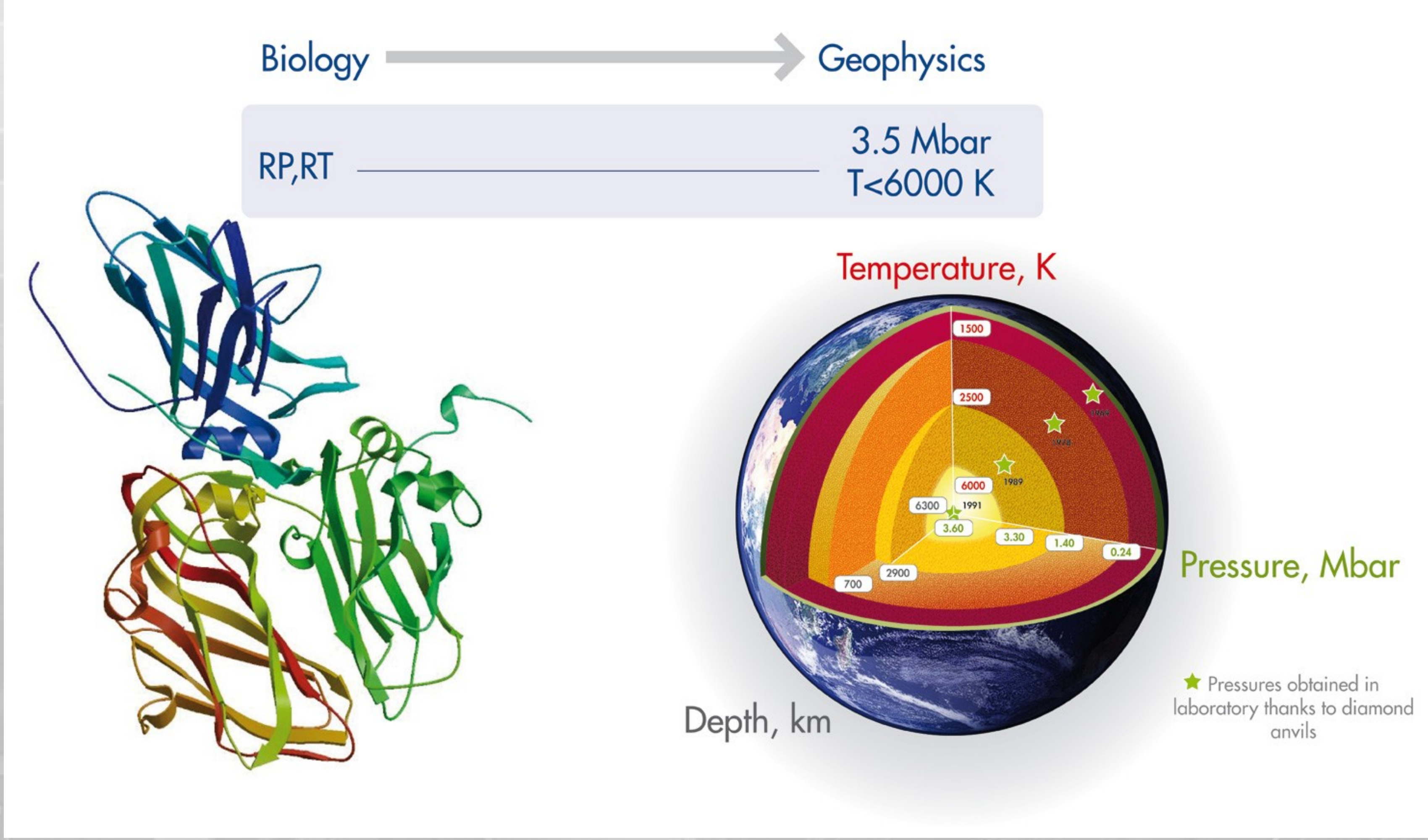
- Why?
- How?
- Research examples

-“In-situ” versus “ex-situ” experiments - sulfur

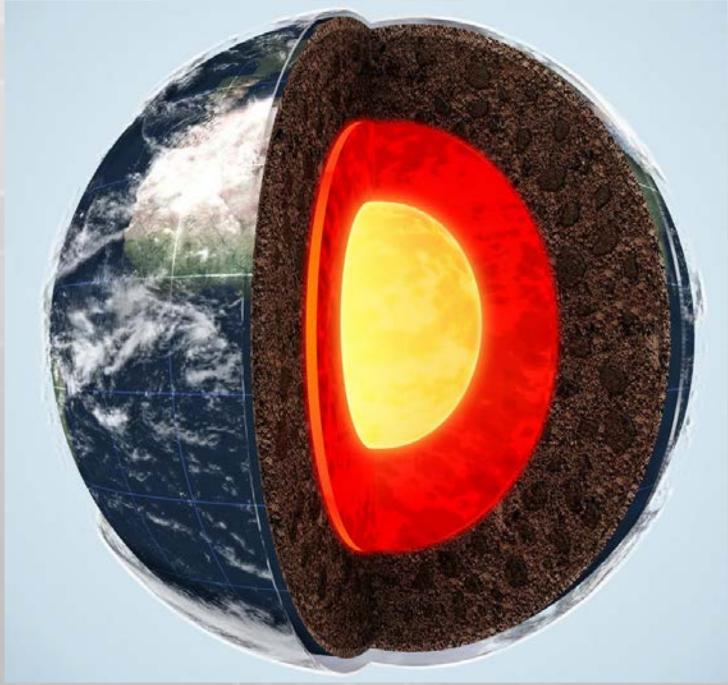
- Very HP-HT XRD in the laser heated DAC

- Perspectives - EBS

‘Science at Extreme Conditions’: multidisciplinary research



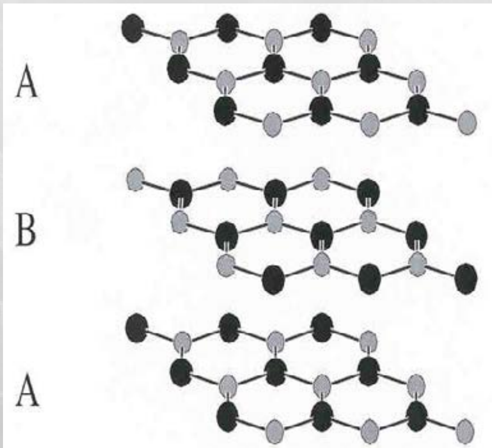
Exploring the interior of the Earth and other planets



Center of the Earth:
P~3.5 million atmospheres (350 GPa)
T~6000 K

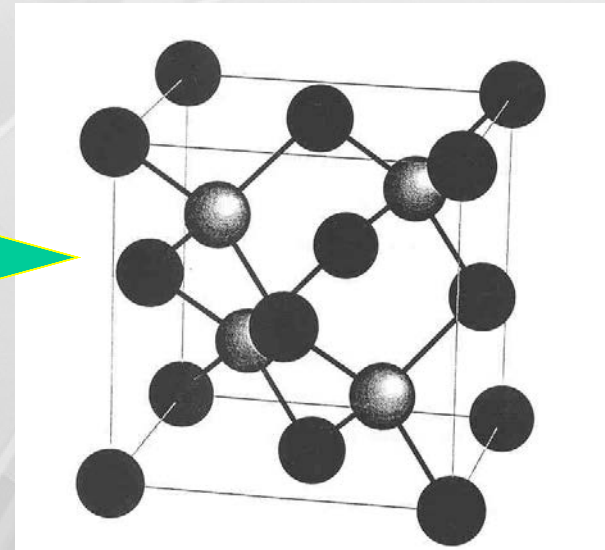
Questions:
-structure and chemistry of geo-materials?
-origin of volcanism?
-origin of earthquakes?
-role of water in subduction zones?
-…etc

Inducing chemical reactions that do not happen under ambient conditions

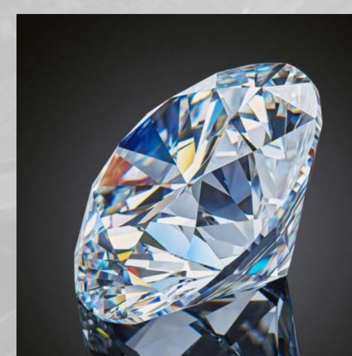


Graphite-like structure

HP, HT

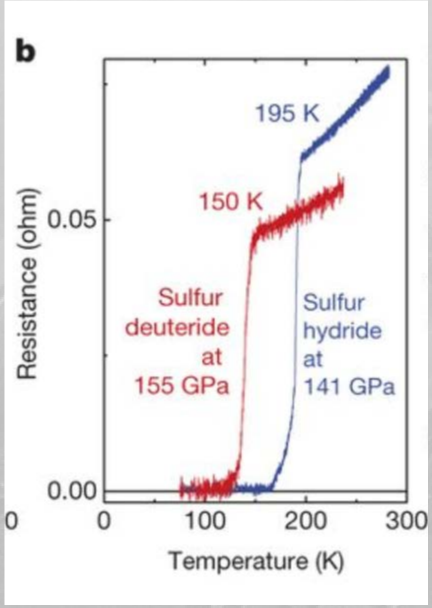


Diamond-like structure



Superconductivity record breaks under pressure

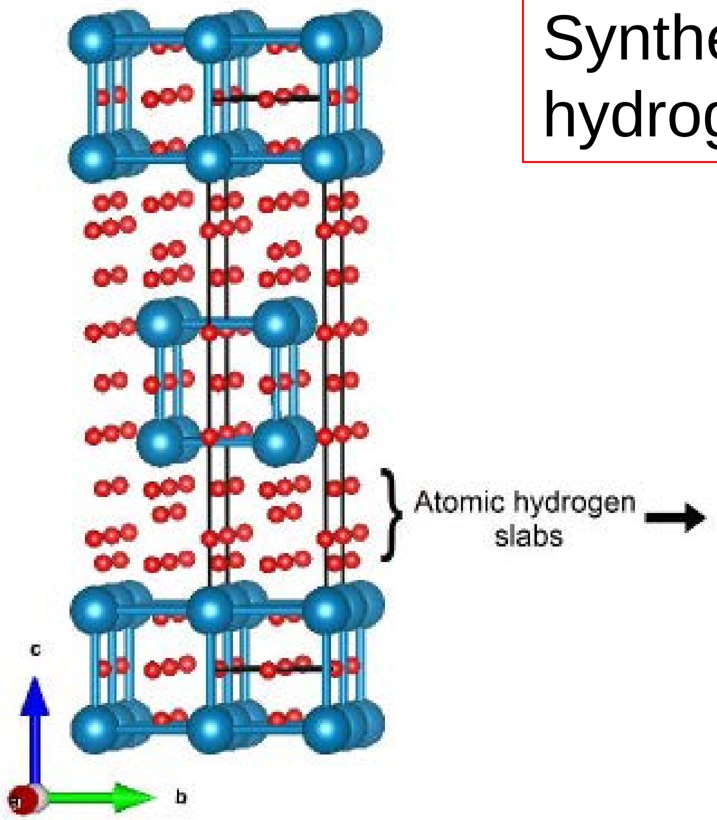
Tc>200K!



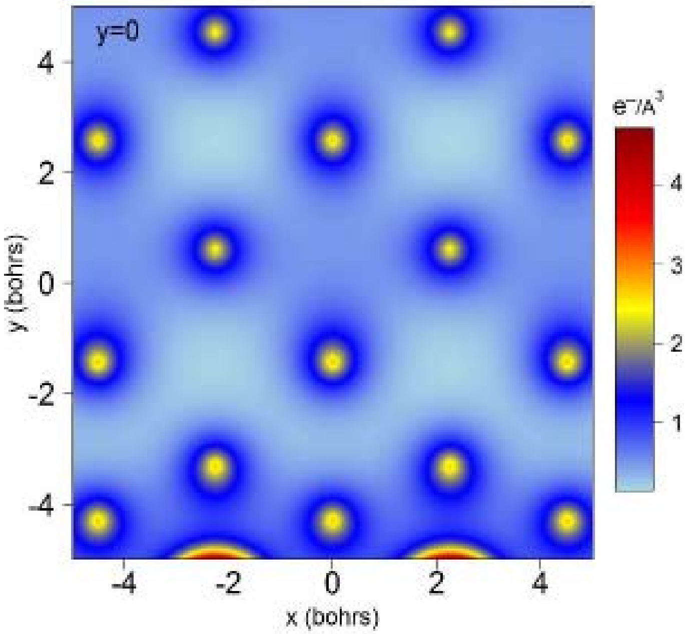
Conventional superconductivity at 203 Kelvin at high pressures in the sulfur hydride system

Ref.: A. P. Drozdov, M.I. Eremets, I.A. Troyan, V. Ksenofintov and S.I. Shylin, *Nature* **525** (2015)

Fundamental physics



Synthesis of FeH_5 with high hydrogen content



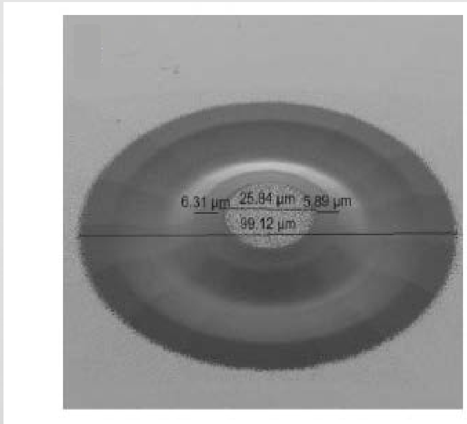
Planes of atomic H independent from the iron atoms

→ metallic-like hydrogen in the planes

Potential high T_c superconductor

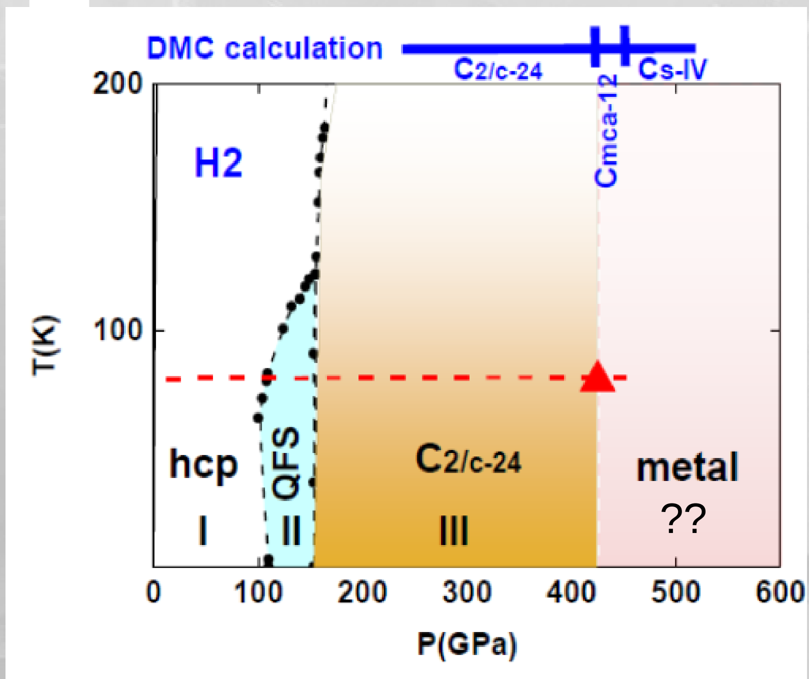
Pépin C.M., Geneste G., Dewaele A., Mezouar M., Loubeyre P., Science 357, 382-385 (2017)

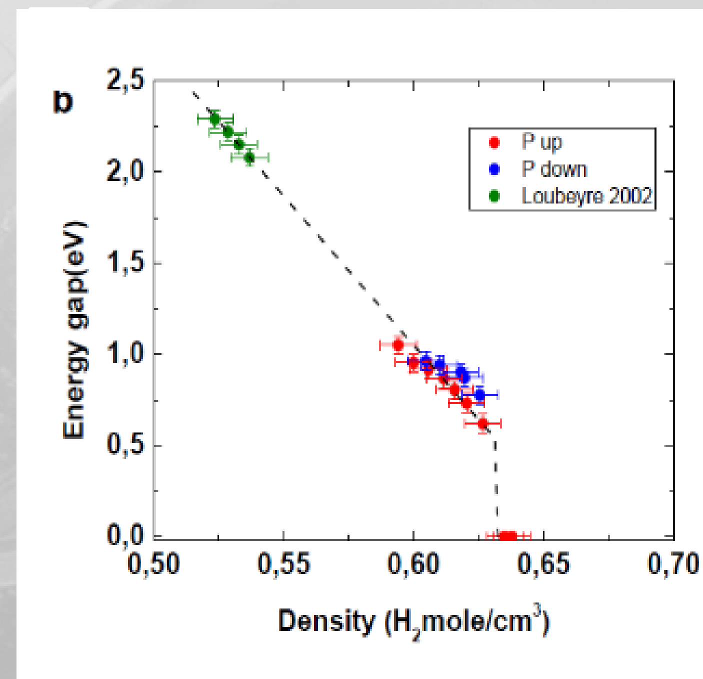
What about pure hydrogen?



New Toroidal diamond anvil cell:

Pmax: 380 → 650 GPa





Ref.: P. Loubeyre, F. Occelli, P. Dumas, Nature (2020)

‘Science at Extreme conditions’ is a major activity at the ESRF

- performed at many ESRF beamlines:

  ID02, ID06, ID09HP, ID12, ID18, ID20, ID22, ID24, ID26, ID27, ID28, BM01, BM23, BM30

- large variety of techniques:

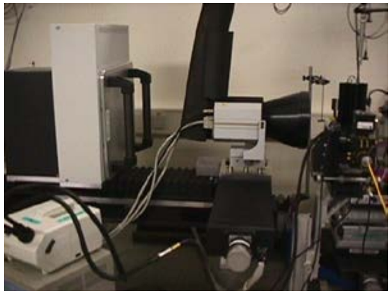
  XRD, XAS, IXS, NRS…

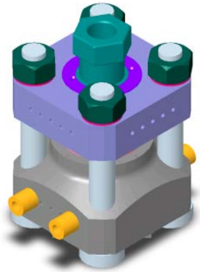
To study the electronic, magnetic and structural properties of materials under HP conditions

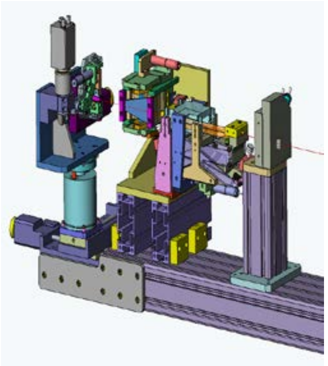
How?

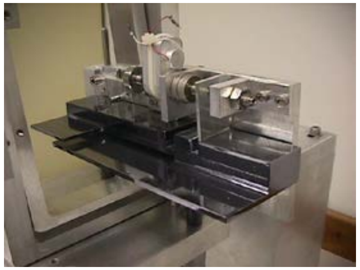
HP XRD beamline (e.g. ID27)

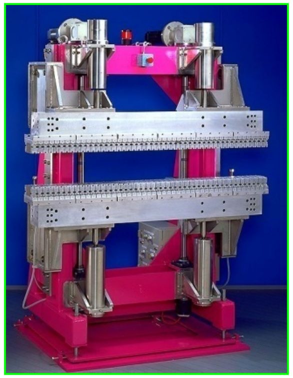
ESRF
6 GeV











Detectors

Sample environment

Mirrors

Monochromator

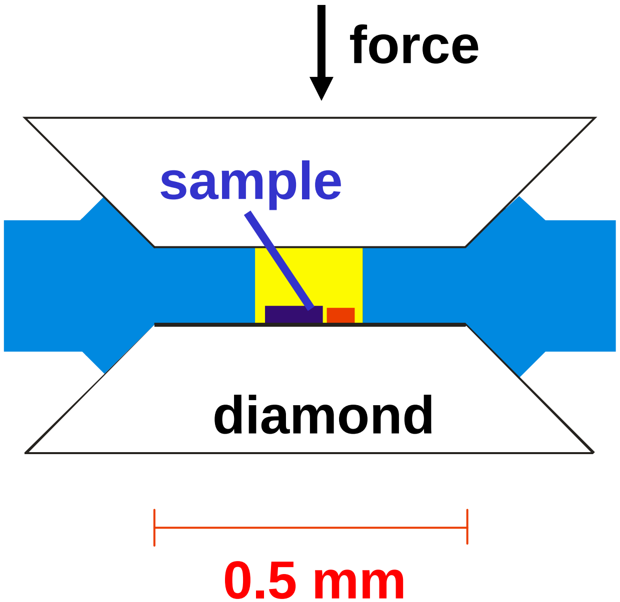
X-ray Source

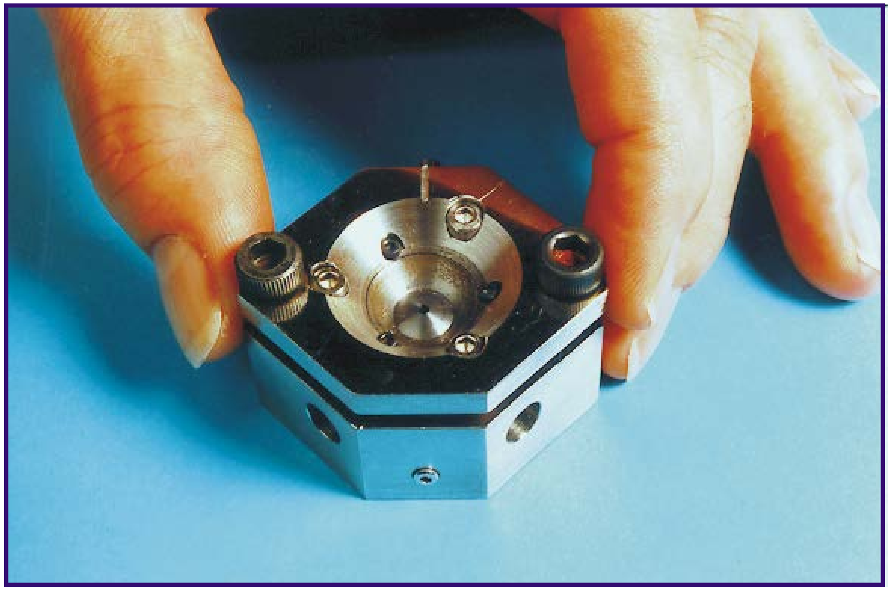
diamond anvils

- hard
- transparent

Pressure = Force / Surface

To reach high pressures →
Large force on a small area

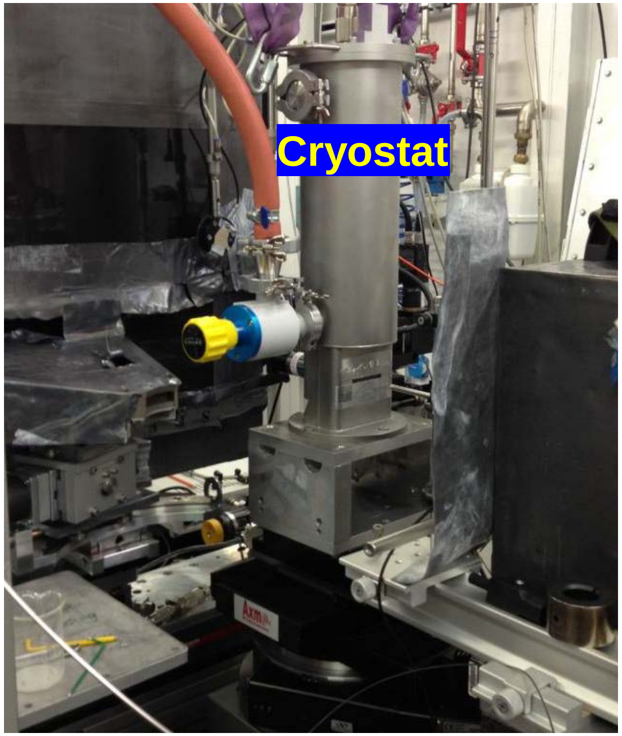




Max. Pressure: 300 GPa (3 Mbar)
Sample volume: 10^{-4} mm^3

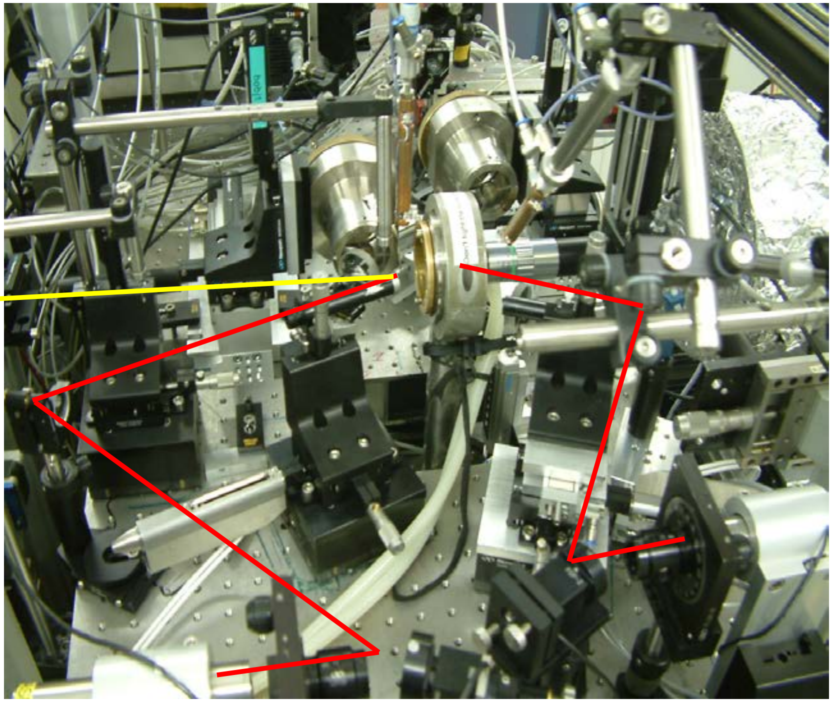
Pressures up to 3 Mbar

LT down to 4 K



Resistive heating up to 1300 K

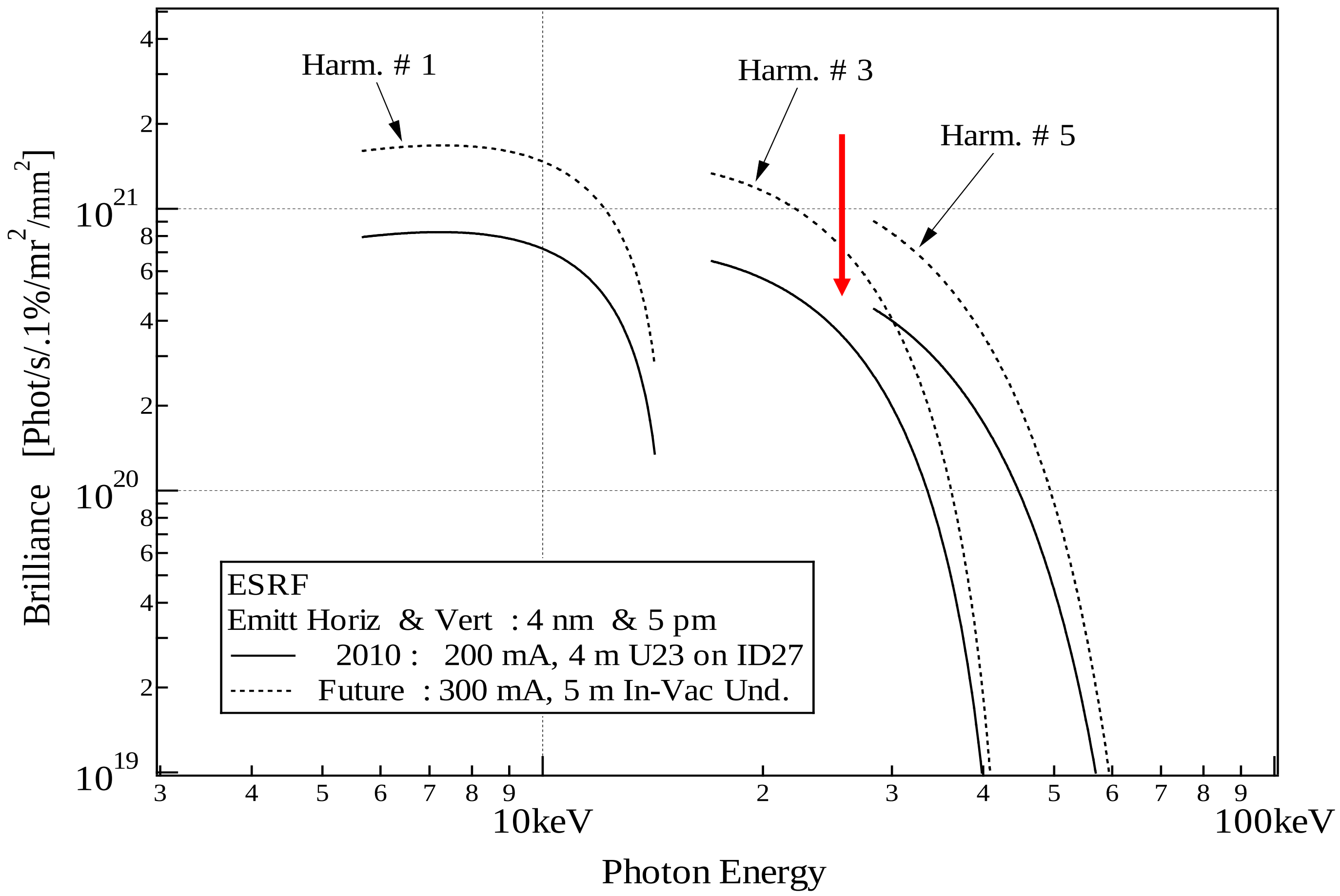
Laser heating T>5000 K



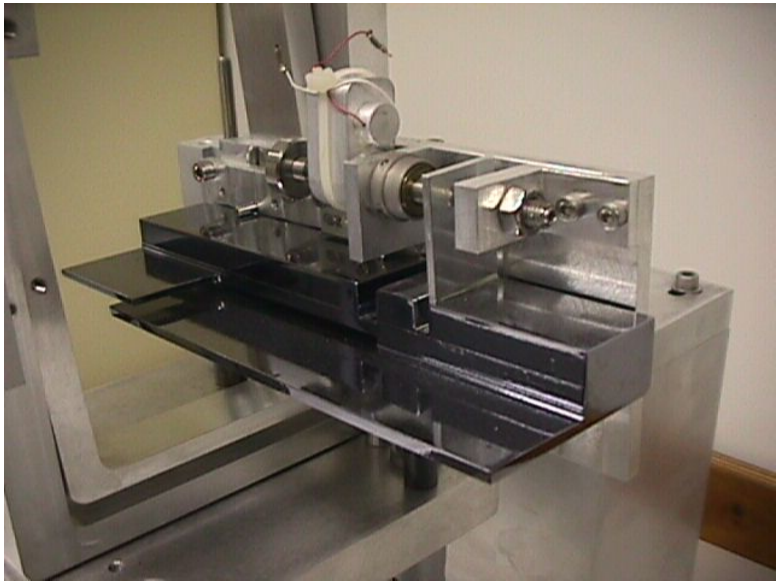
ID27 is equipped two U23 undulators providing very high flux at high energy

Two U23 in vacuum undulators of ID27

Optimized insertion devices: in-vacuum undulator with very high flux at high energy



X-ray optics for HP XRD beamlines

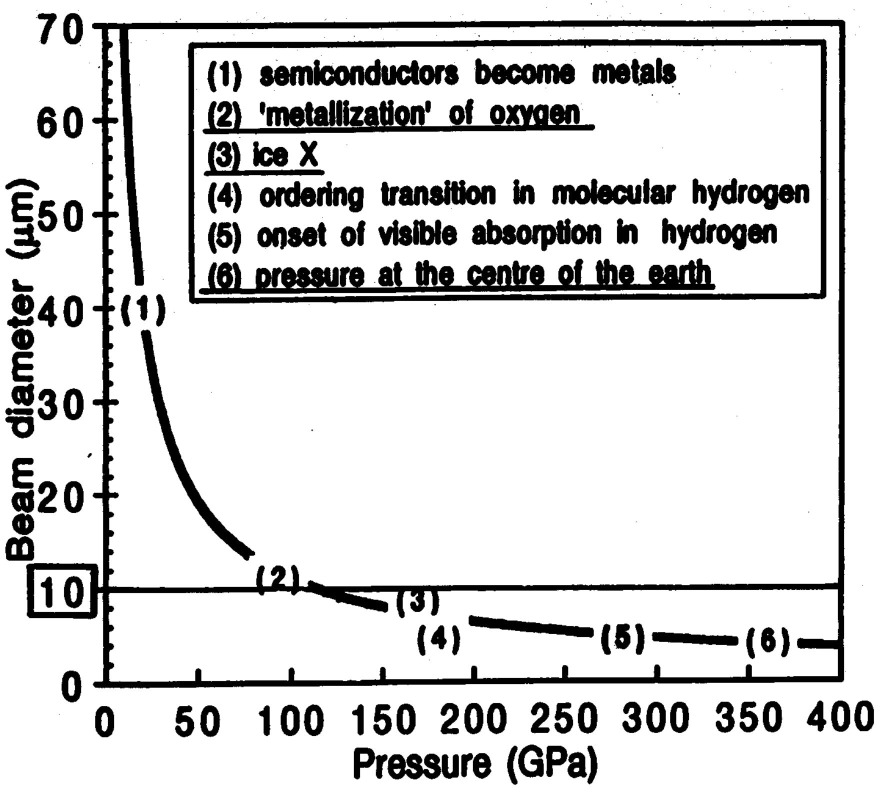


X-ray technique:
monochromatic XRD (fixed λ)

•Nitrogen cooled Si(111) double crystal monochromator

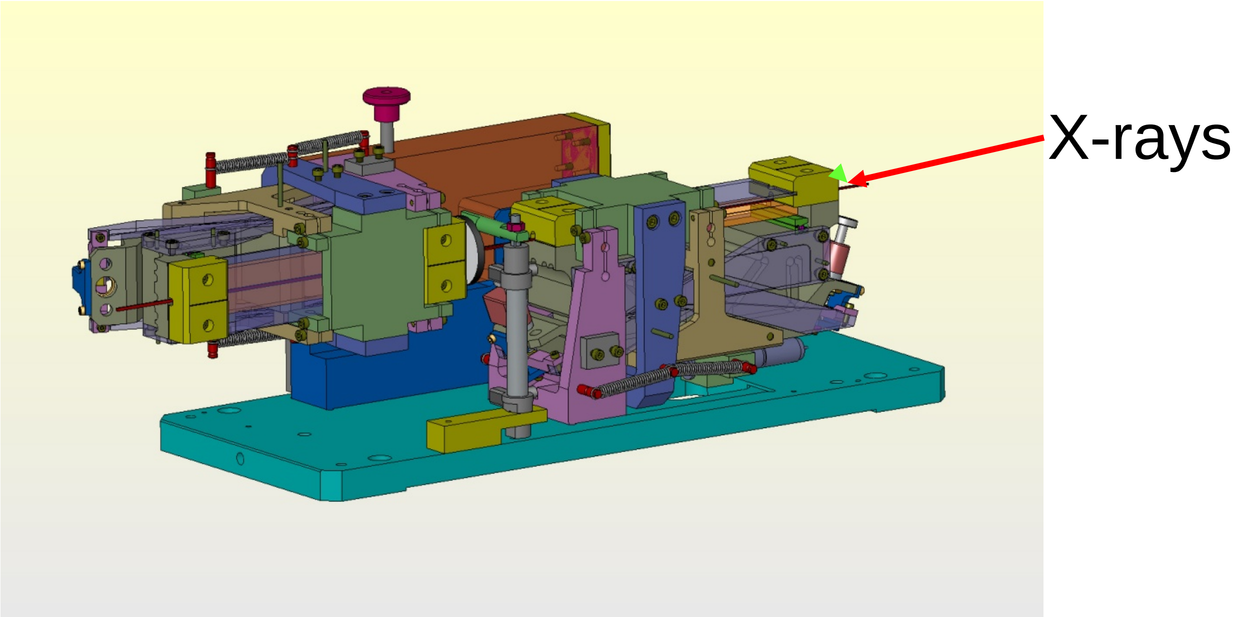
⇒ Good compromise between flux and energy resolution: $\Delta E/E \sim 10^{-4}$

X-ray optics for HP XRD beamlines



Focusing optics are mandatory for HP experiments because of the very small sample dimensions

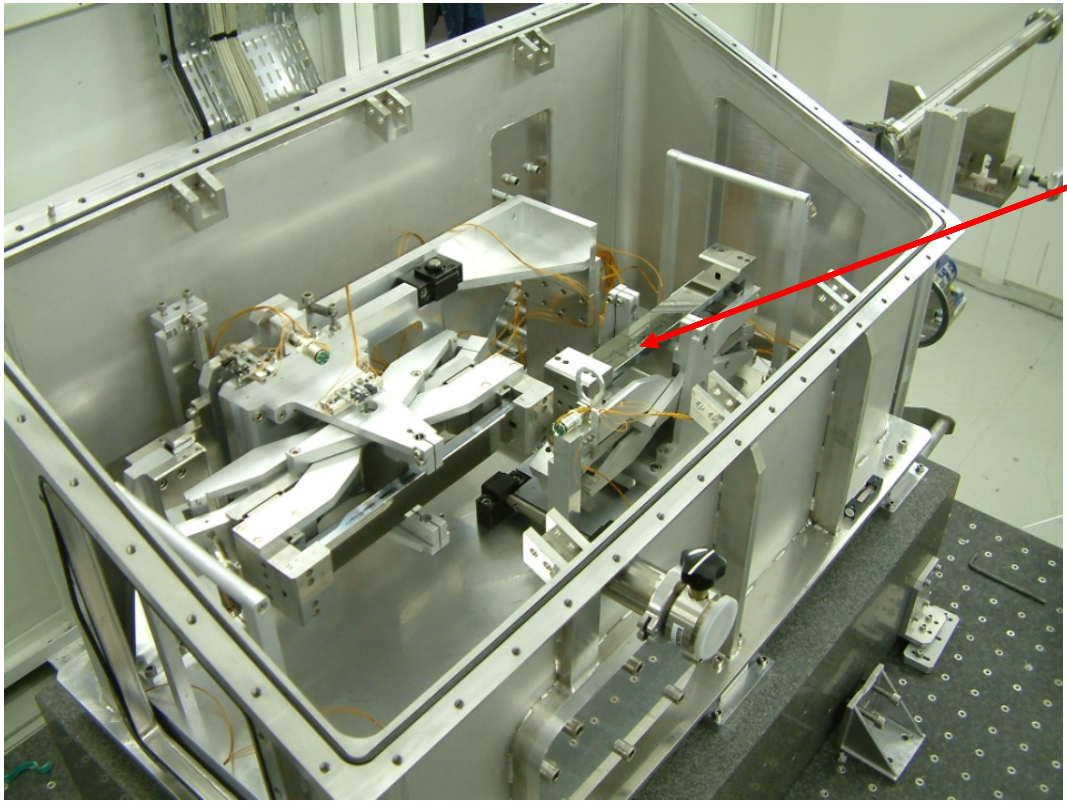
Kirkpatrick-Baez focusing mirrors



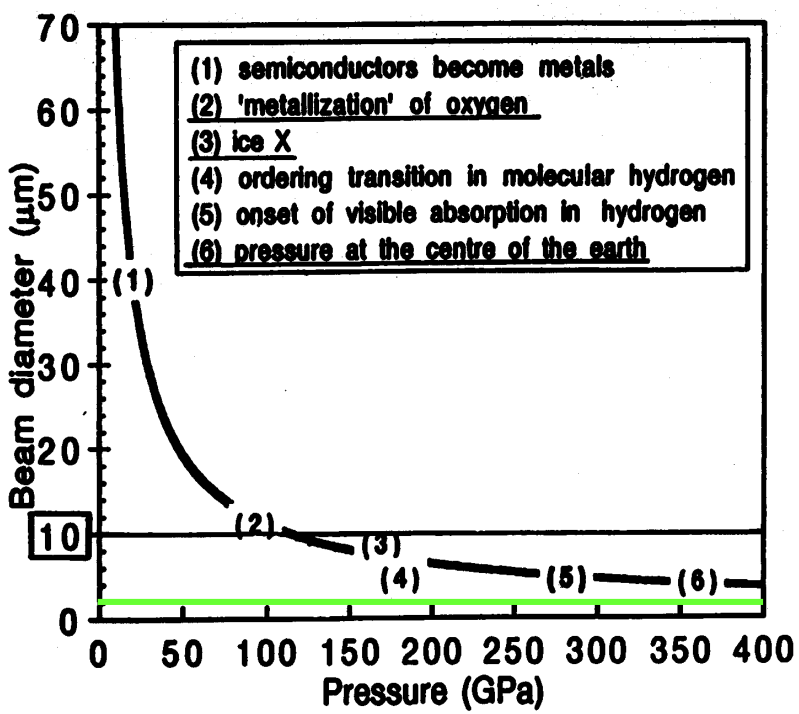
The size and quality of the focal spot at the sample position depend on:

- the source size
- the sample-mirrors distance/source-mirrors distance
- mirrors quality

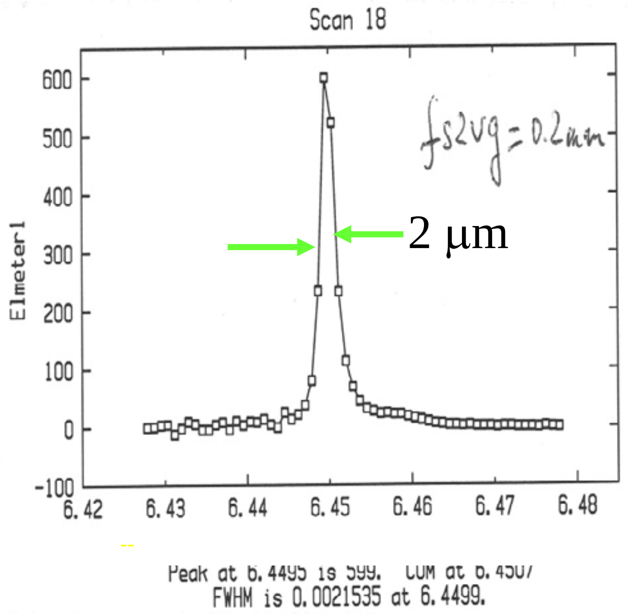
Kirkpatrick-Baez focusing mirrors



Vertical mirror

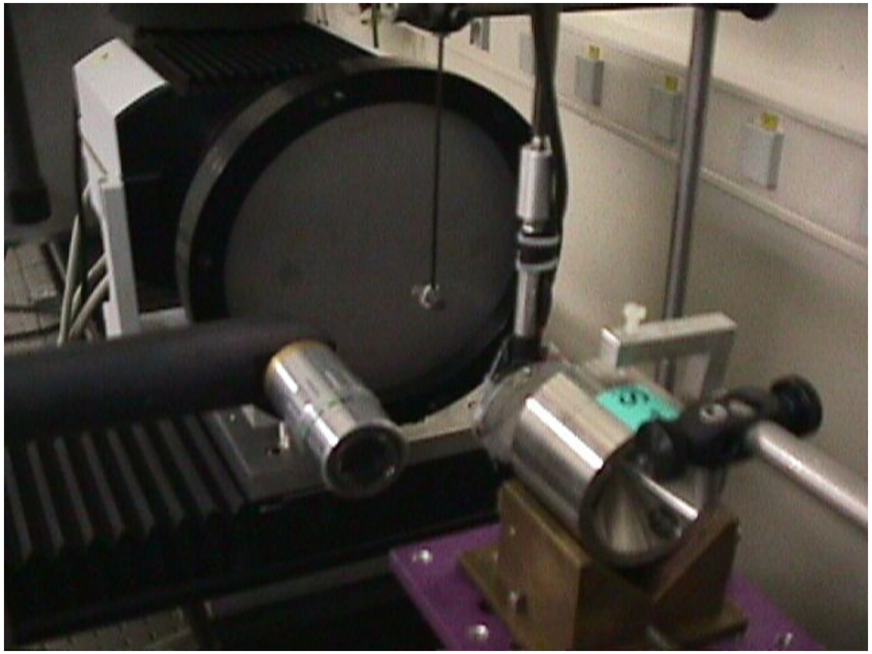


Measured beam size at ID27 before EBS

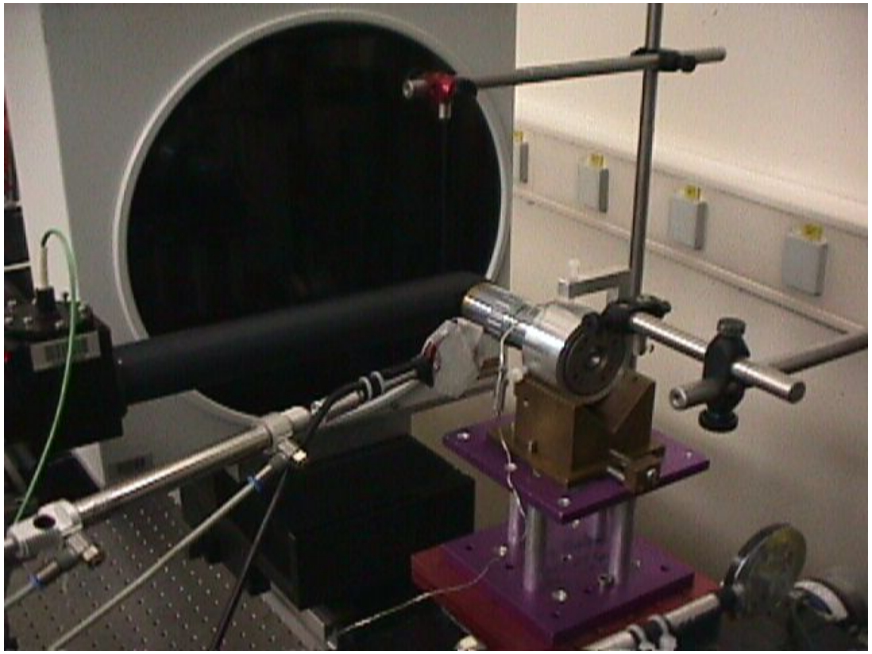


Detectors

A good detector for HP XRD must fulfill the following criteria:
- a large input surface (>150 mm diameter)
- high spatial resolution
- high dynamic range (14 bits or more)
- good sensitivity, even at high X-ray energies (60-80 keV)
- fast reading (a few seconds or less)



Bruker CCD: 165 mm diameter
14 bits dynamic range; readout time 4s
Low sensitivity at high X-ray energies

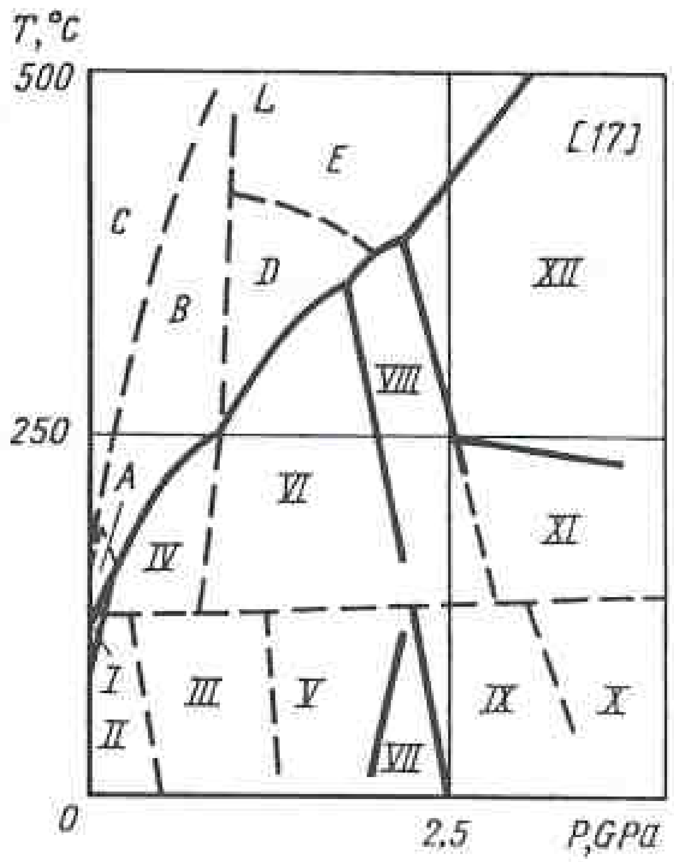


Mar345 on-line image plate: 345 mm diameter
14 bits dynamic range; readout time 60 s
High sensitivity at high X-ray energies

Large-area high energy pixel detector (e.g. CdTe from DECTRIS)

Offers high quantum efficiency (ε>80% at E>20 keV), high dynamic range and fast frame rate (250 Hz)

Accepted P-T phase diagram of sulfur
(Vezzoli et al., HT-HP (1977))



• Phase diagram based on ex-situ experiments (quench method)

•12 solid phases identified
(Only 3 with known structures, I, II, XII)

Question:

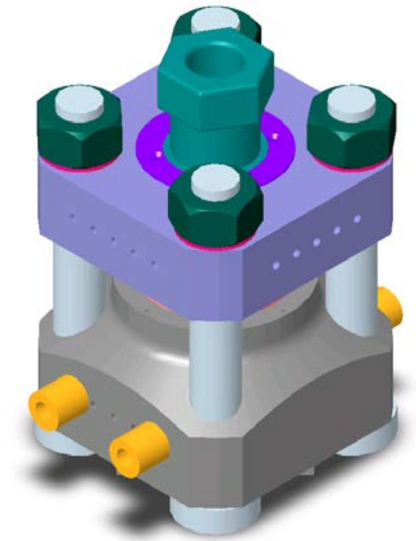
Local/global minima of the Gibbs free energy→ Metastable or stable phases?

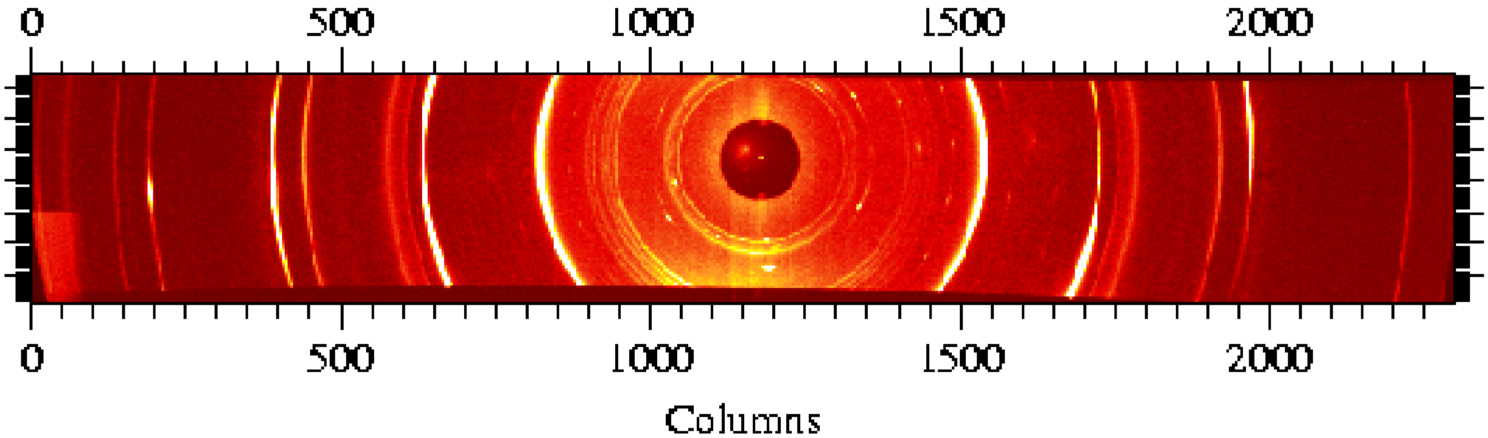
→In situ investigation at high P and T

Paris-Edinburgh press

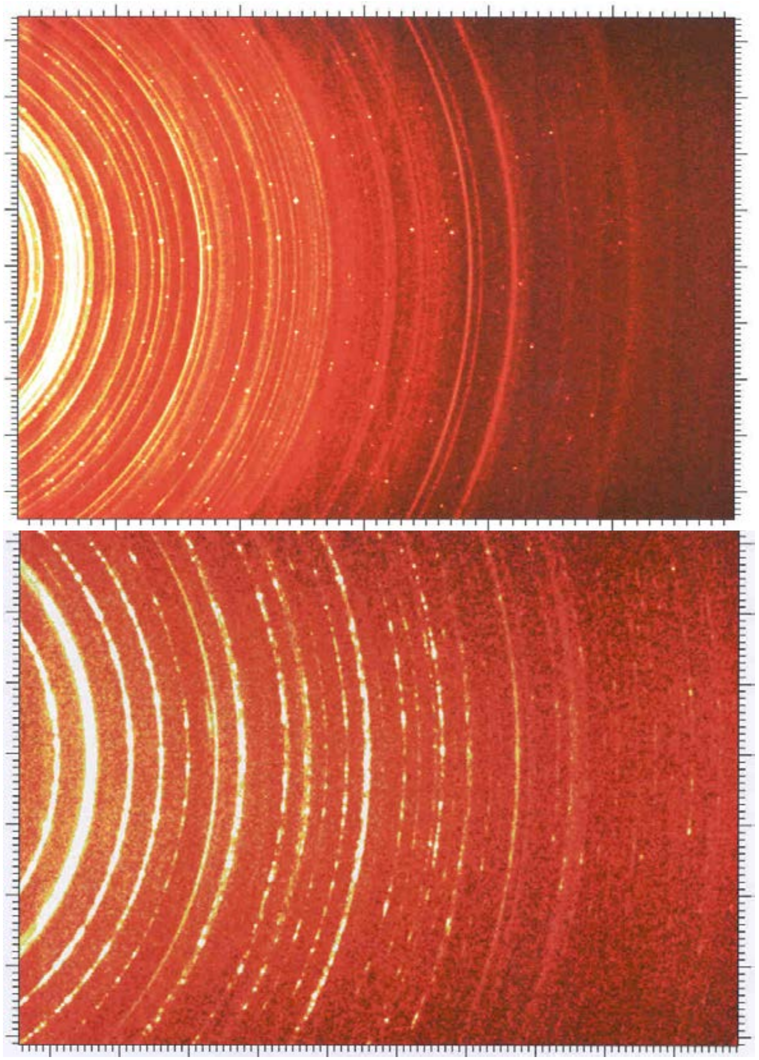
- Pressure up to 17 GPa on 2 mm^3 sample volume
- Resistive heating up to 2000 K

X-ray method: X-ray diffraction in monochromatic mode





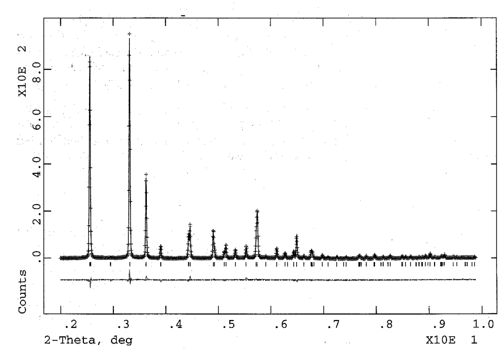
"In-situ" versus "ex-situ" - Sulfur -

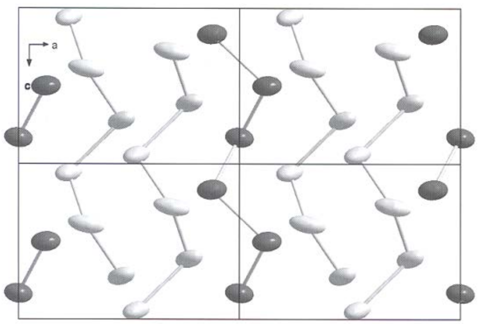


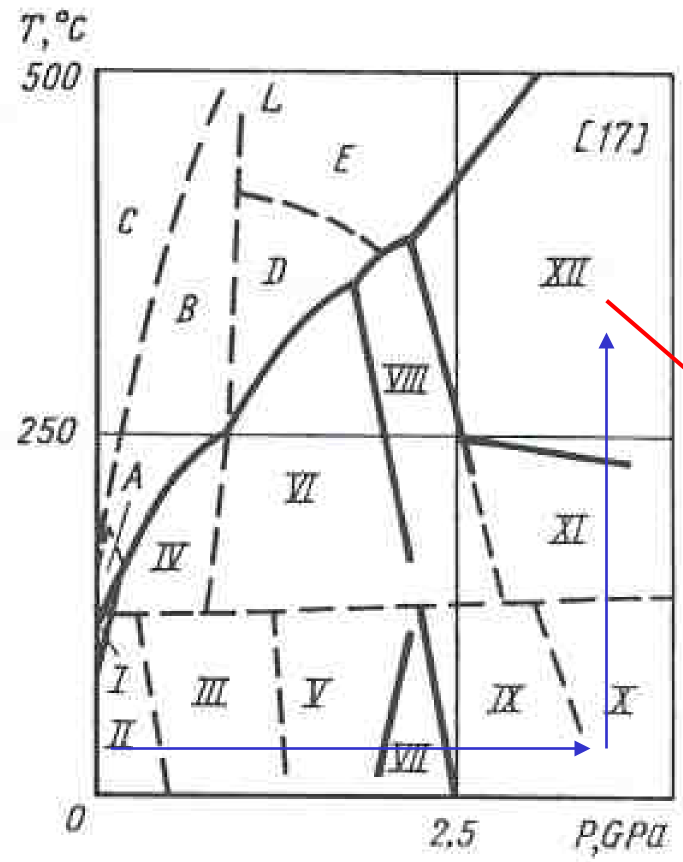
At RT-RP, Orthorhombic Fddd based on S_8 rings (molecular units)

P=3GPa T=600K

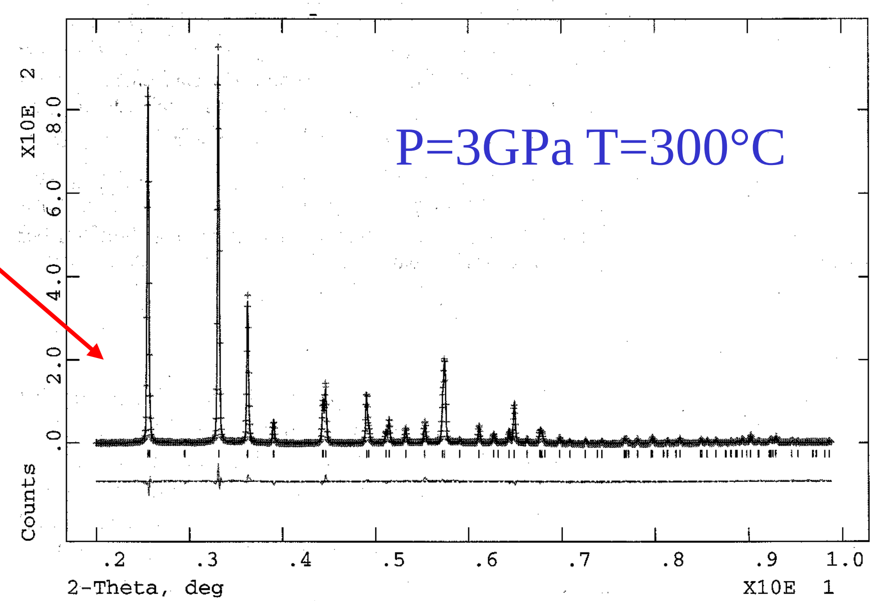
Hexagonal $P3_221$





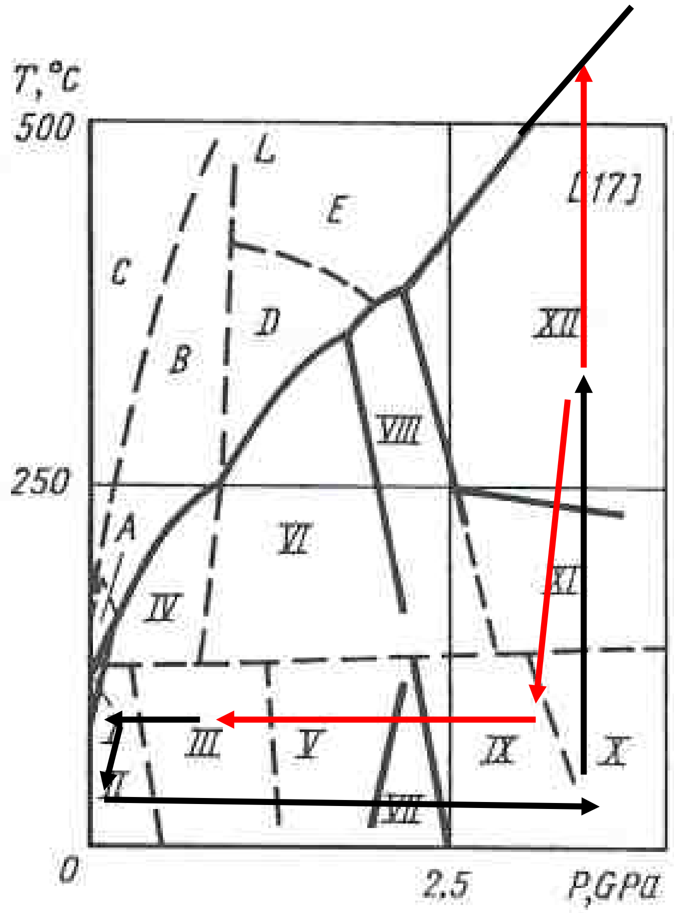


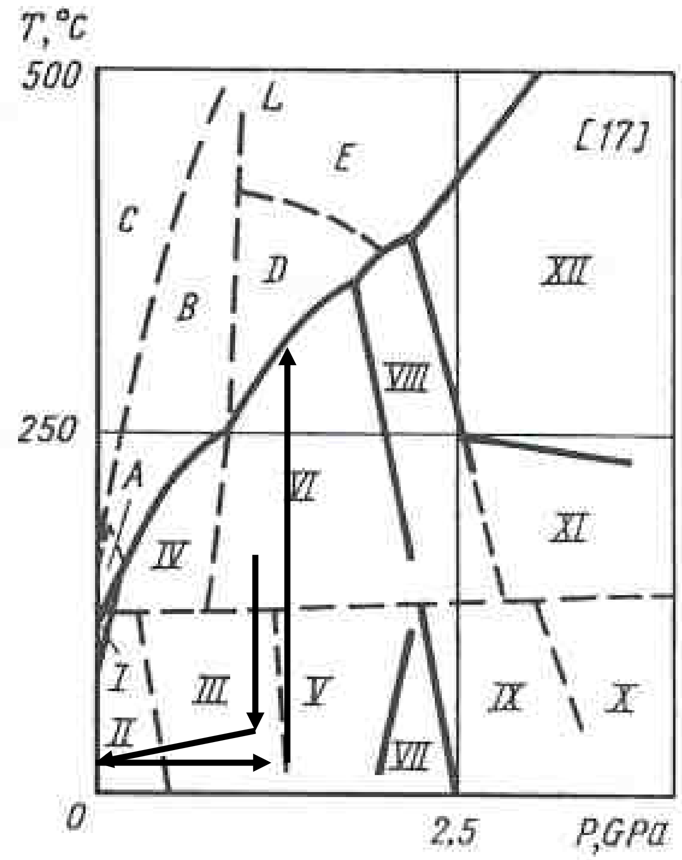
Ortho. Fddd → Direct Transformation → Hexagonal $P3_221$



Phase XII previously identified as monoclinic P2

"In situ" versus "ex-situ" - Sulfur -



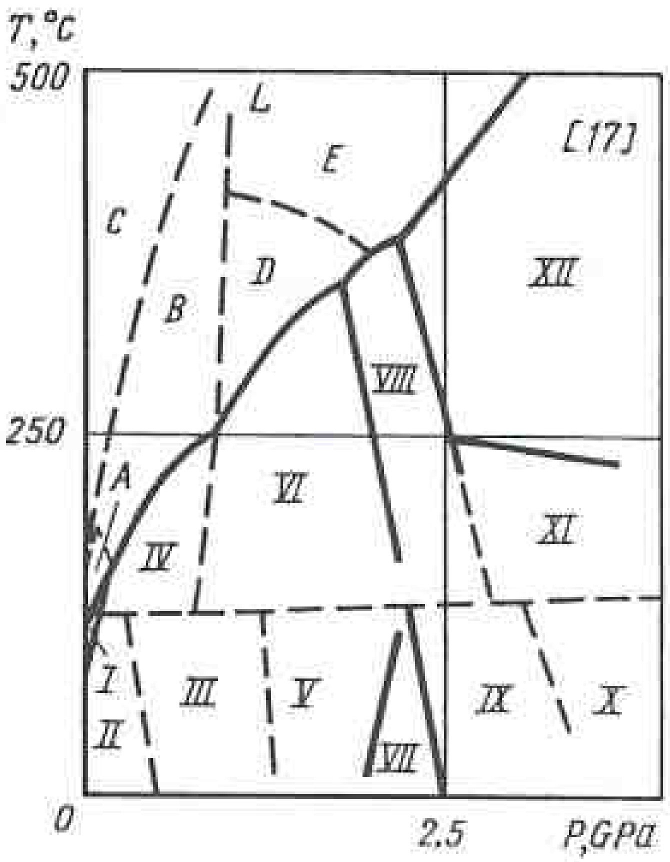


$P3_221$ (Hexagonal)

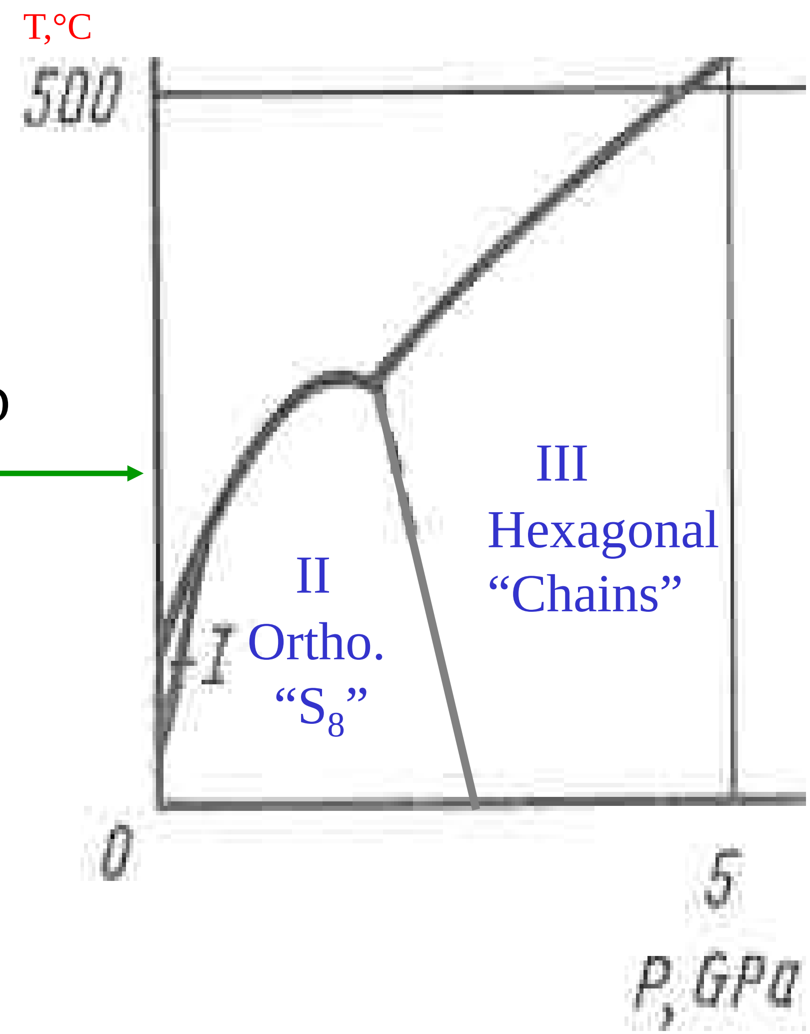
Fddd (Orthorhombic)

$P3_221$ kinetically inhibited at pressures below 1.5 GPa

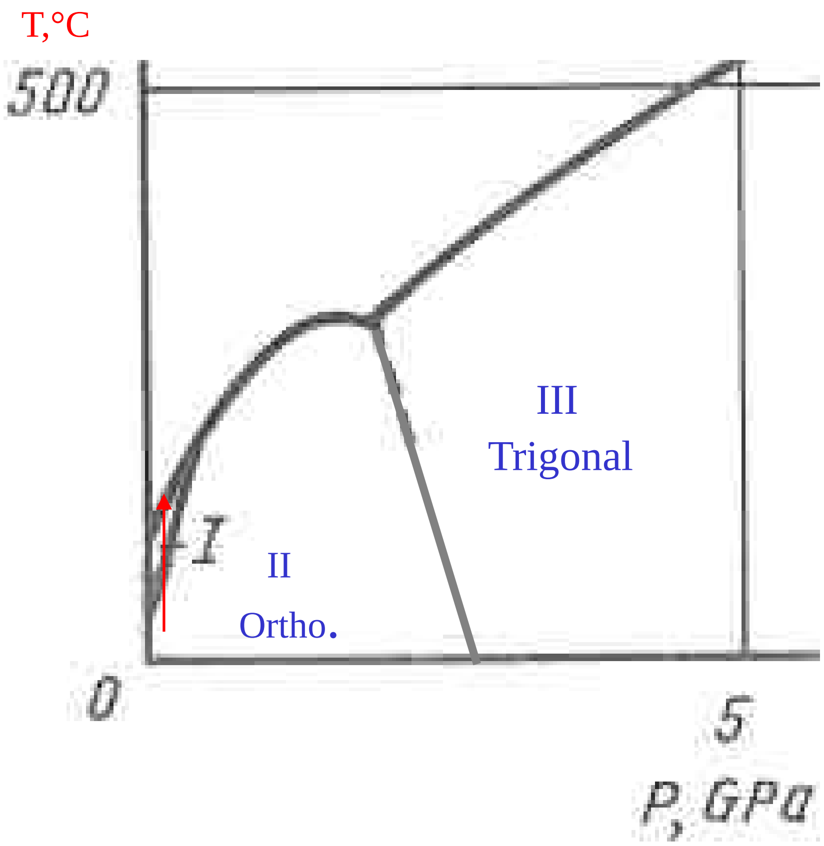
“In situ” versus “ex-situ” - Sulfur -



In situ XRD



Stability of phase I from *in situ* single crystal XRD



Phase I is monoclinic with space group P21/c. This phase exists in a very narrow P-T domain below the melting curve.

Question:
Is it a stable or metastable phase?

Technique:
Single crystal growth and in situ XRD in a resistively-heated DAC.

Resistive heating system

<u>Main Features:</u>

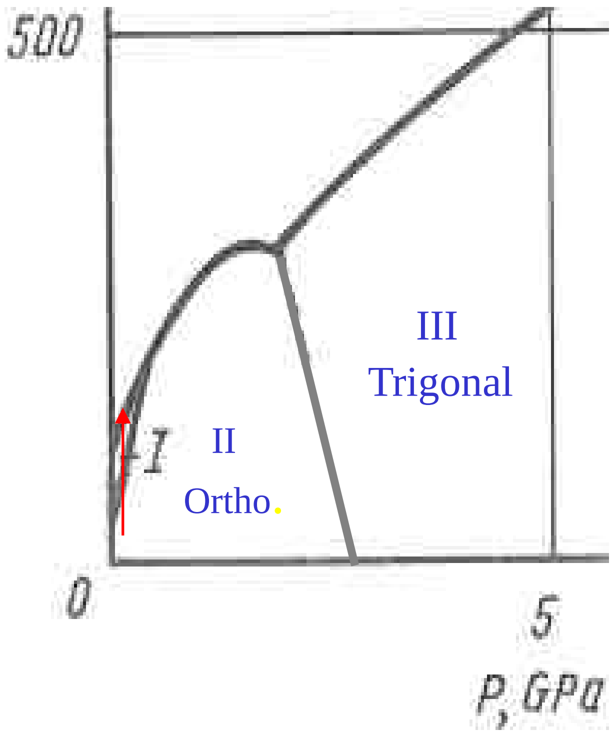
•Vacuum Vessel: 3.10^{-6} mbar
Two graphite heaters
Low T gradients

• Max T : 1300 K

• Very good P and T stability

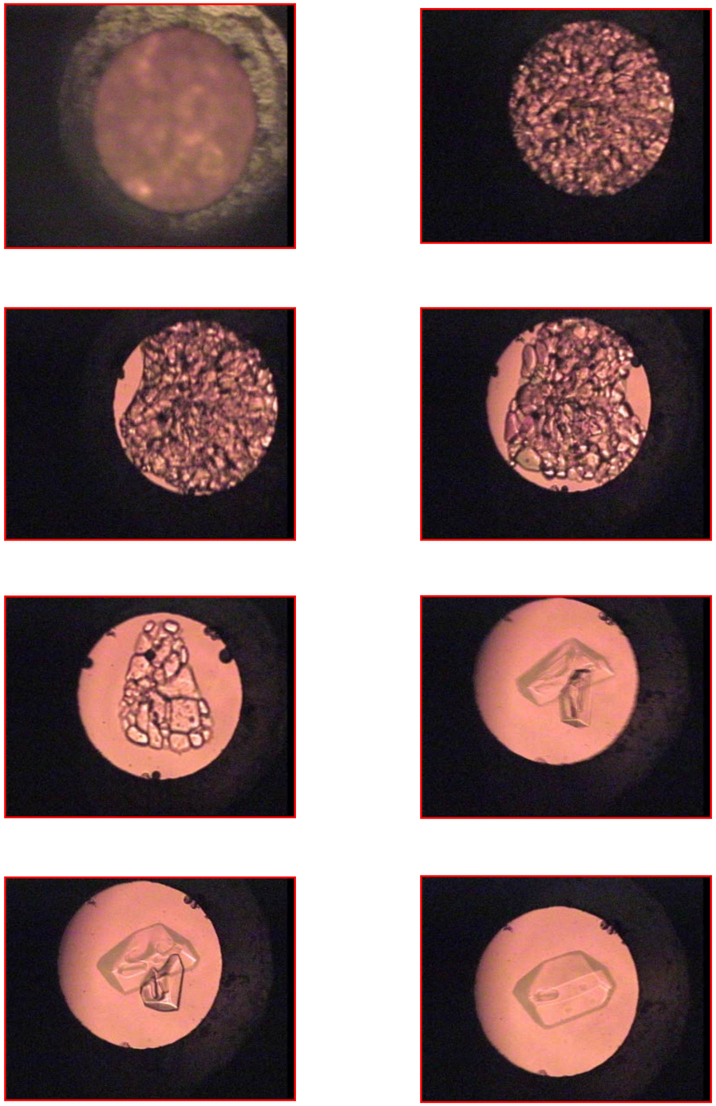
→ 1300 K (2K) for 72 hours

"In-situ" versus "ex situ" - Sulfur -



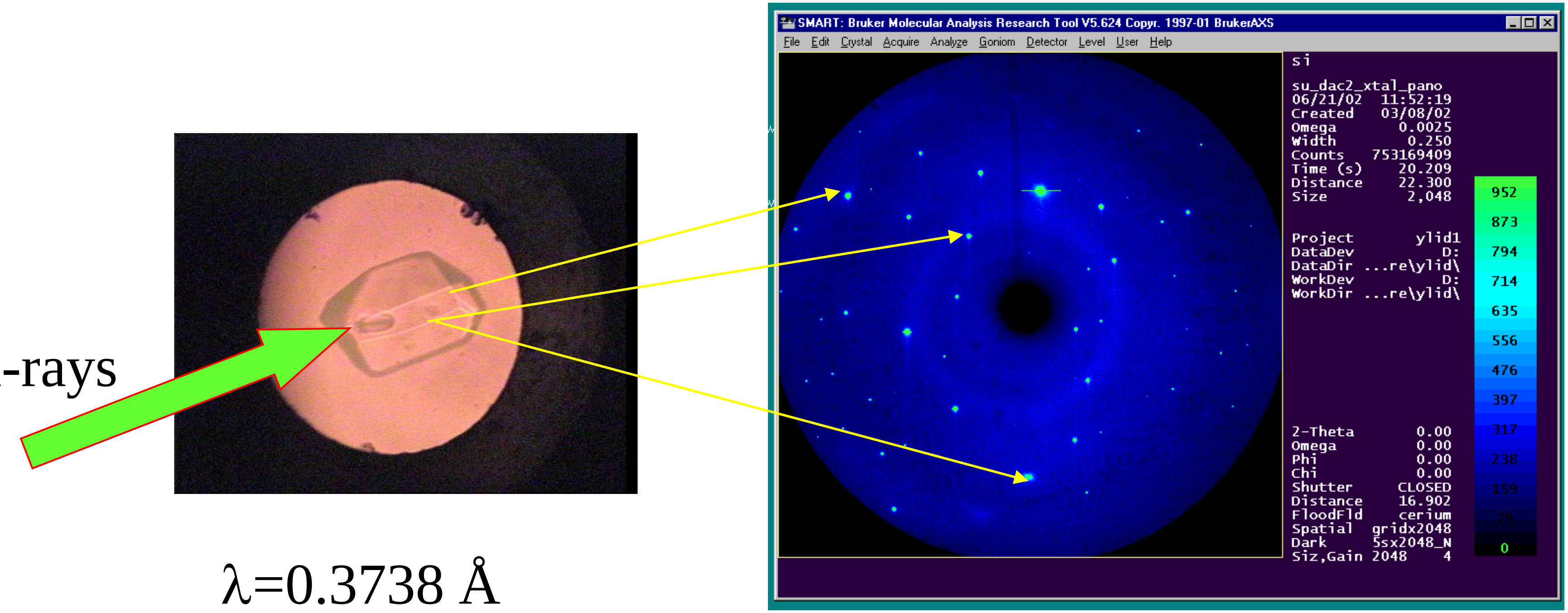
Isobaric growth of sulfur I at P=0.3 GPa

T=90°C
T=110°C
T=112°C



•Single crystal growth
in the stability field of phase I
• Coexistence solid-fluid
• No kinetic barriers
⇒Stable phase

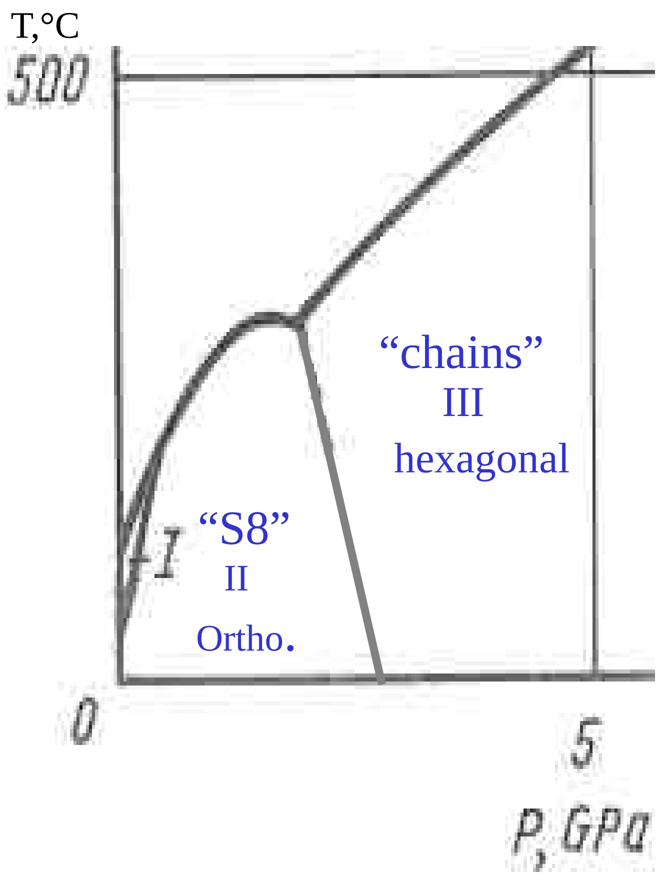
"In-situ" versus "ex-situ" - Sulfur -



λ=0.3738 Å

monoclinic P21/c symmetry
NOT orthorombic Fddd

"In situ" versus "ex-situ" - Sulfur -



Only 3 stable solid phases
-Phase I with symmetry P21/c is metastable
-phase II ortho. Fddd
-phase III hexagonal $P3_221$

Physics, chemistry and biology

•Effect of pressure on chemical bonds: neighbor distances, coordination number, angles...

•Structural relations between polymorphs in the solid and liquid states at high pressure are poorly understood.

Geophysics

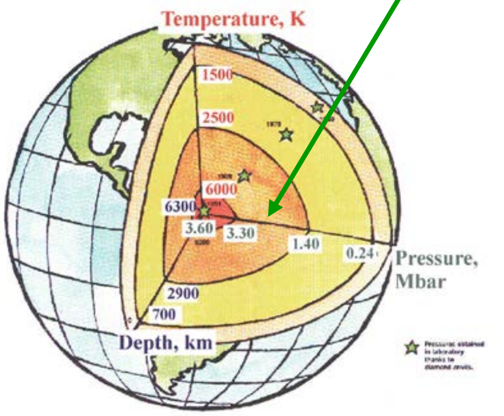
•Determination of planets cores structures

•Effect of light elements

•Water in the Earth's upper mantle

•Melting curves of geo-materials

Liquid Fe

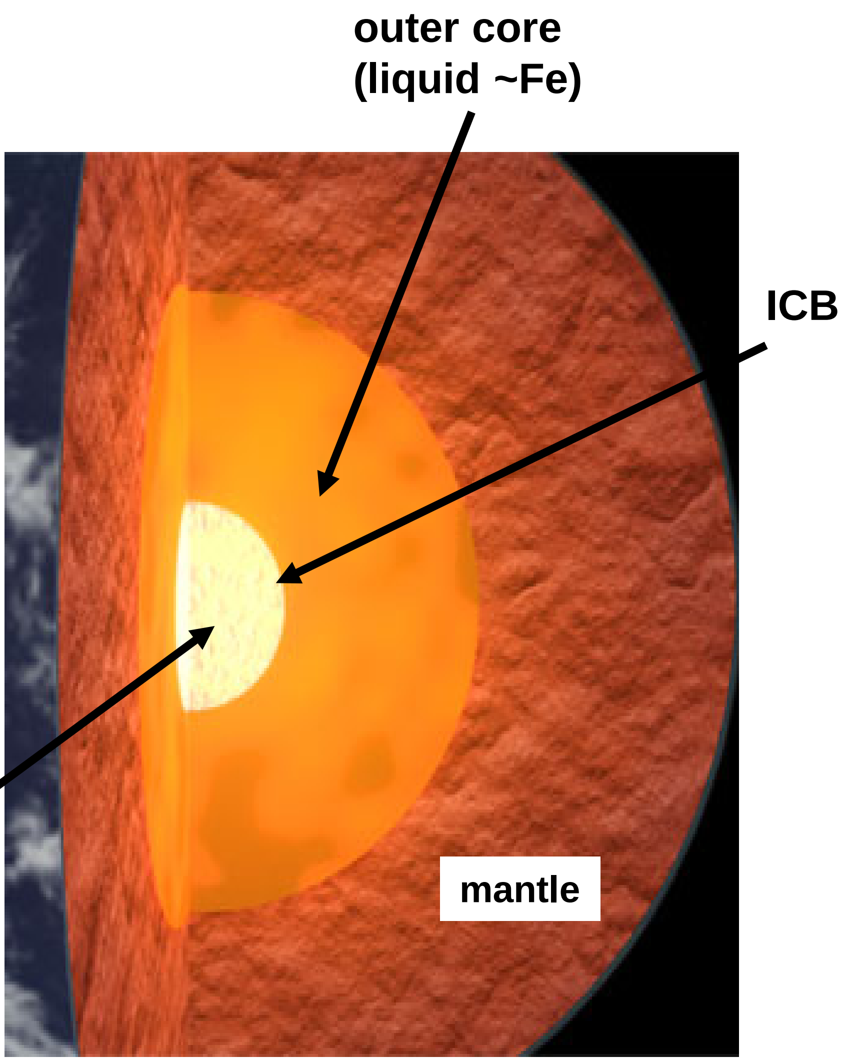


MELTING CURVE OF IRON TO 200 GPA

- The Earth's core is essentially composed of iron

- The melting point of iron at 330 GPa: constrain the inner core boundary temperature T_{ICB}

- Heat budget: energy available for the geodynamo, …



Melting curve debated

Melting at HP

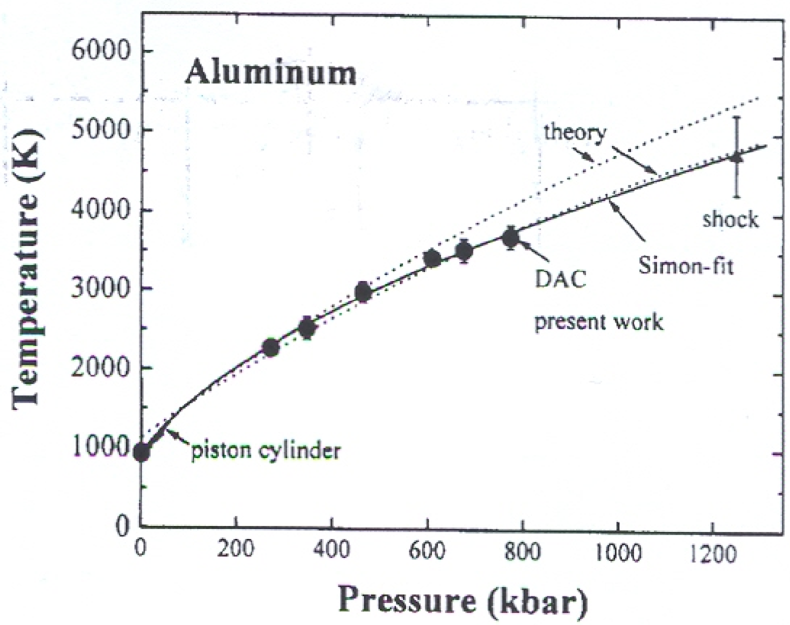
Two classical experimental methods

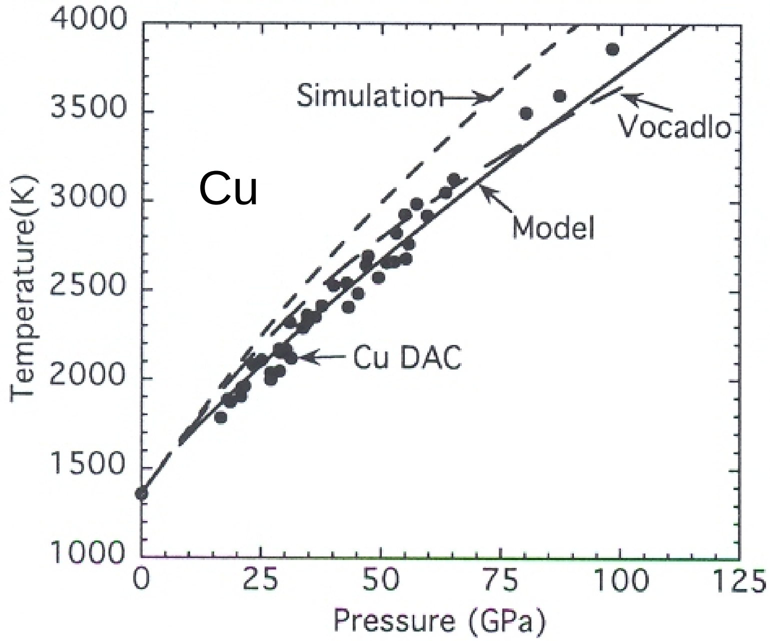
1. Optical measurements in the laser heated diamond anvil cell (speckle)

2. Melting induced by shock compression

Ab-initio calculations

Good agreement between DAC, shock compression and theory for several systems: i.e. Al, Cu



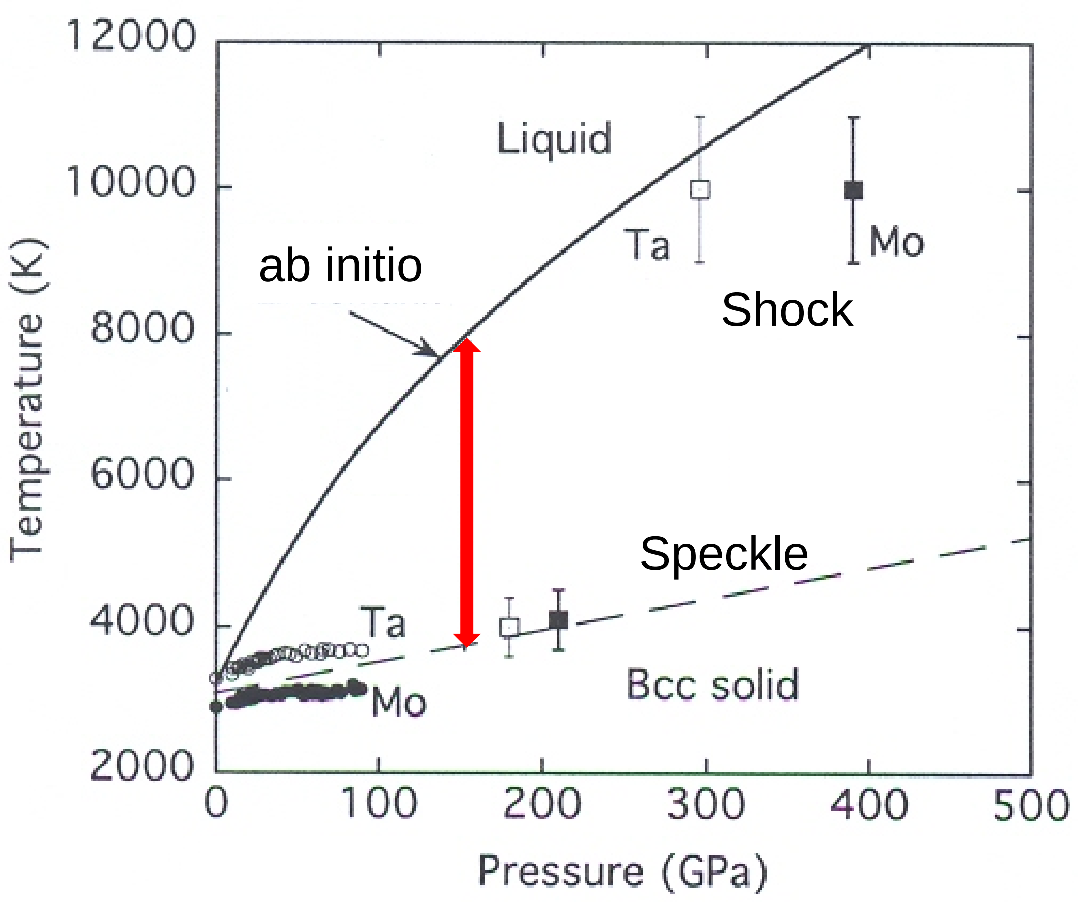


Ref. :

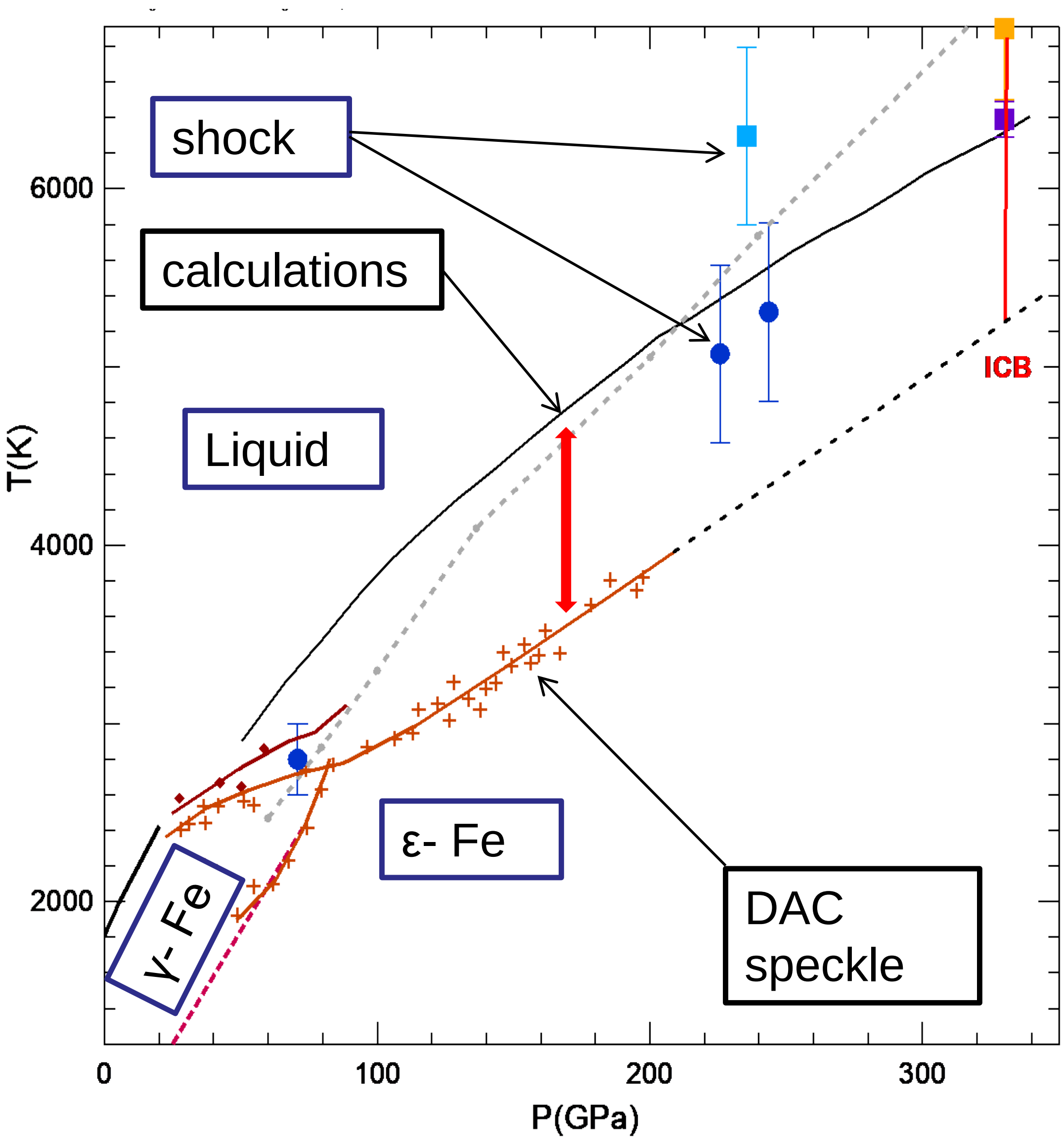
Al : R. Boehler, M. Ross, EPSL, 153, 223 (1997)

Cu: M. Ross, R. Boehler, D. Errandonea, PRB, 76, 184117 (2007)

But also large discrepancies for transition metals such as Ta, W, Mo… (ΔT>2000 K at 200 GPa!)



Ref.: M. Ross, D. Errandonea, R. Boehler, PRB, 77, 184118 (2007)



For iron:

Discrepancy in T:
ΔT>1000 K at 150 GPa

Why ??

⇒New approach developed at beamline ID27 :
Fast *in situ* X-ray diffraction in the double-sided laser heated diamond anvil cell.

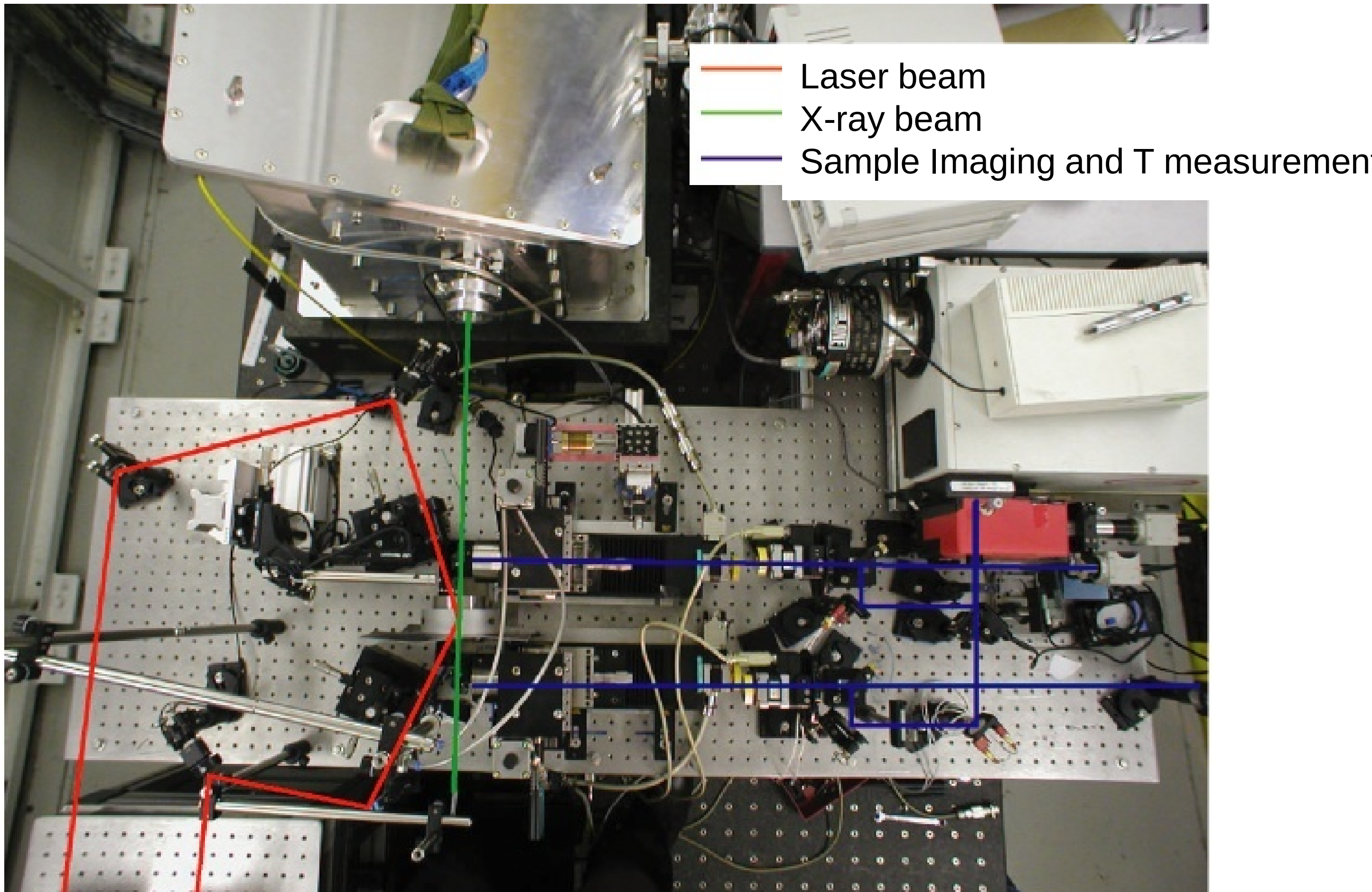
Advantages:
- It is sensitive to the bulk of the sample (#surface)
- The XRD measurements are performed at thermodynamic equilibrium
- It uses well established pyrometric methods

Also very important:

-X-ray diffraction in the laser heated DAC provides a clear signature of the melt: appearance of X-ray diffuse scattering

- and identifies chemical reactions if any

Accessible PT domain for in situ powder XRD: P>2 Mbar; T>5000 K

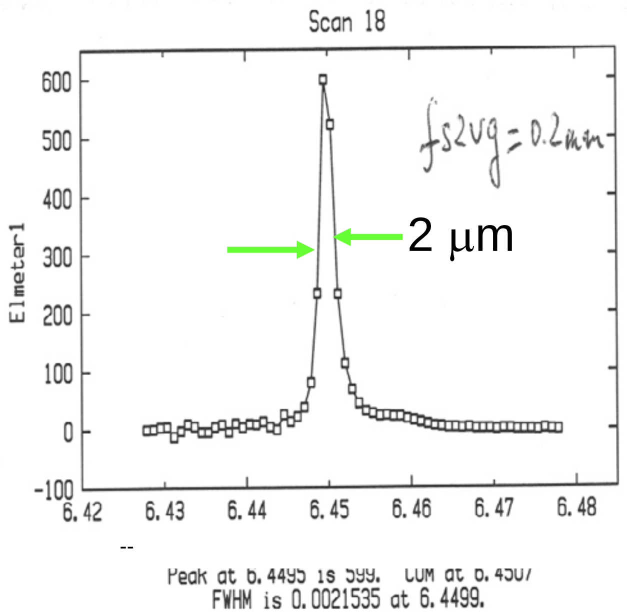


Double-sided laser heating system at ID27

- Main features:

  -Most important:
  Very intense micro-focused X-ray beam ~2 microns at short wavelengths: 0.15<λ<0.4 A

  →Low temperature gradients guaranteed
  (independently from the shape of the laser spot)



-The temperature is gradually increased by tuning the laser power

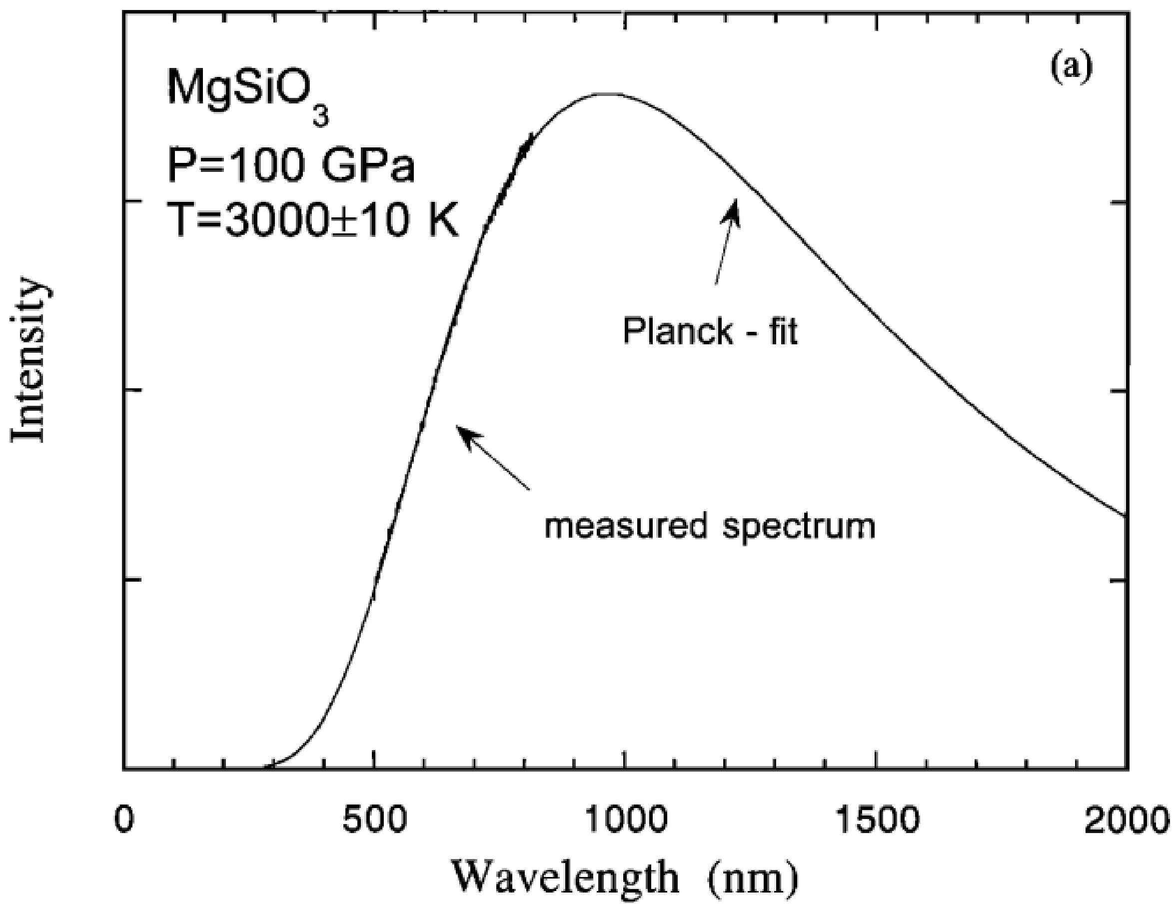
-For each increment of the laser power, the temperature is measured by pyrometry and a diffraction pattern is automatically collected

-The temperature increment is ~30 K

-The typical collection time is ~2 seconds

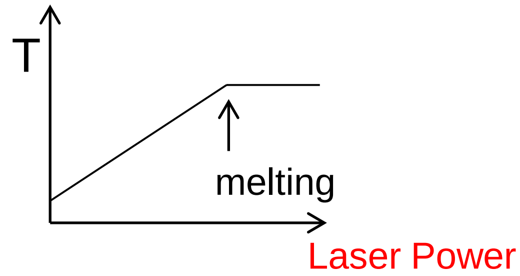
-The pressure is measured in situ using internal calibrants (KCl)

Pyrometry


MgSiO3
P=100 GPa
T=3000±10 K
(a)
Planck - fit
measured spectrum
Intensity
0
500
1000
1500
2000
Wavelength (nm)

In laser heated diamond anvil cell experiments 3 criteria are classically used to identify melting:

1.The existence of a "Plateau" in the laser power dependence of the temperature

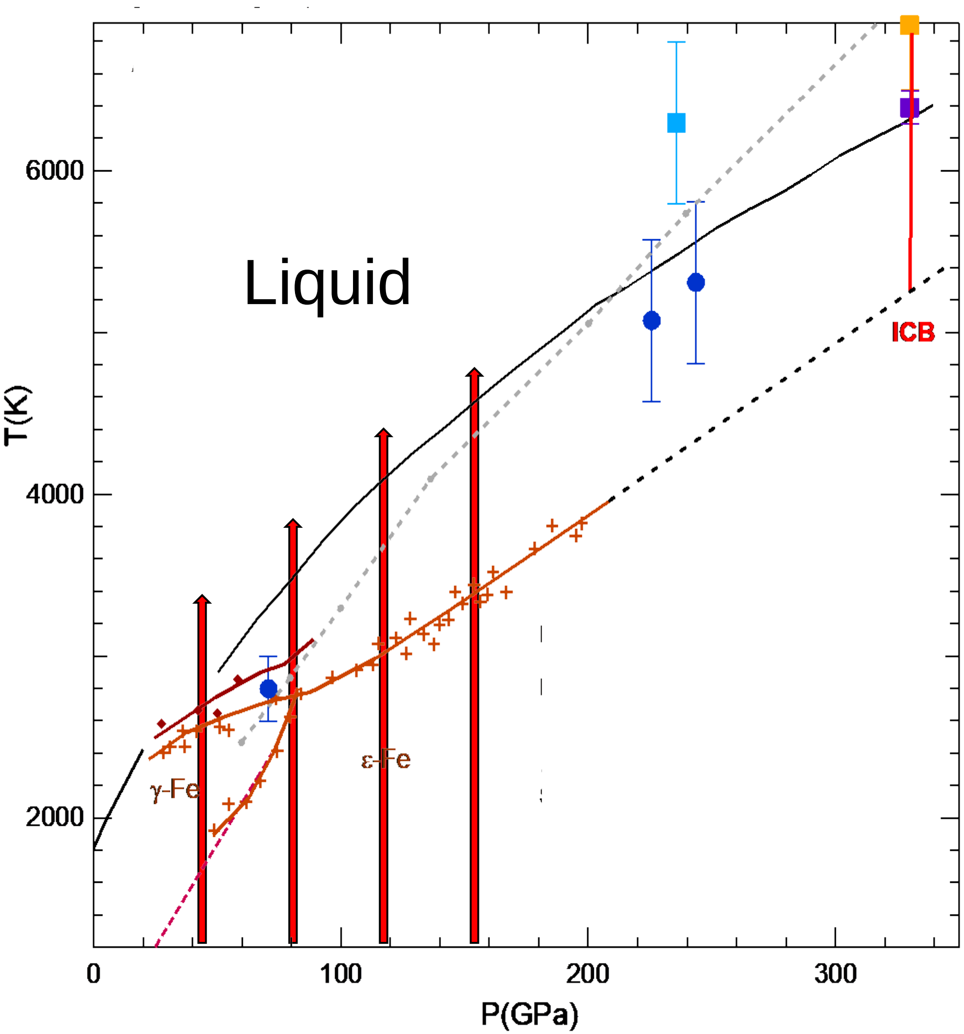


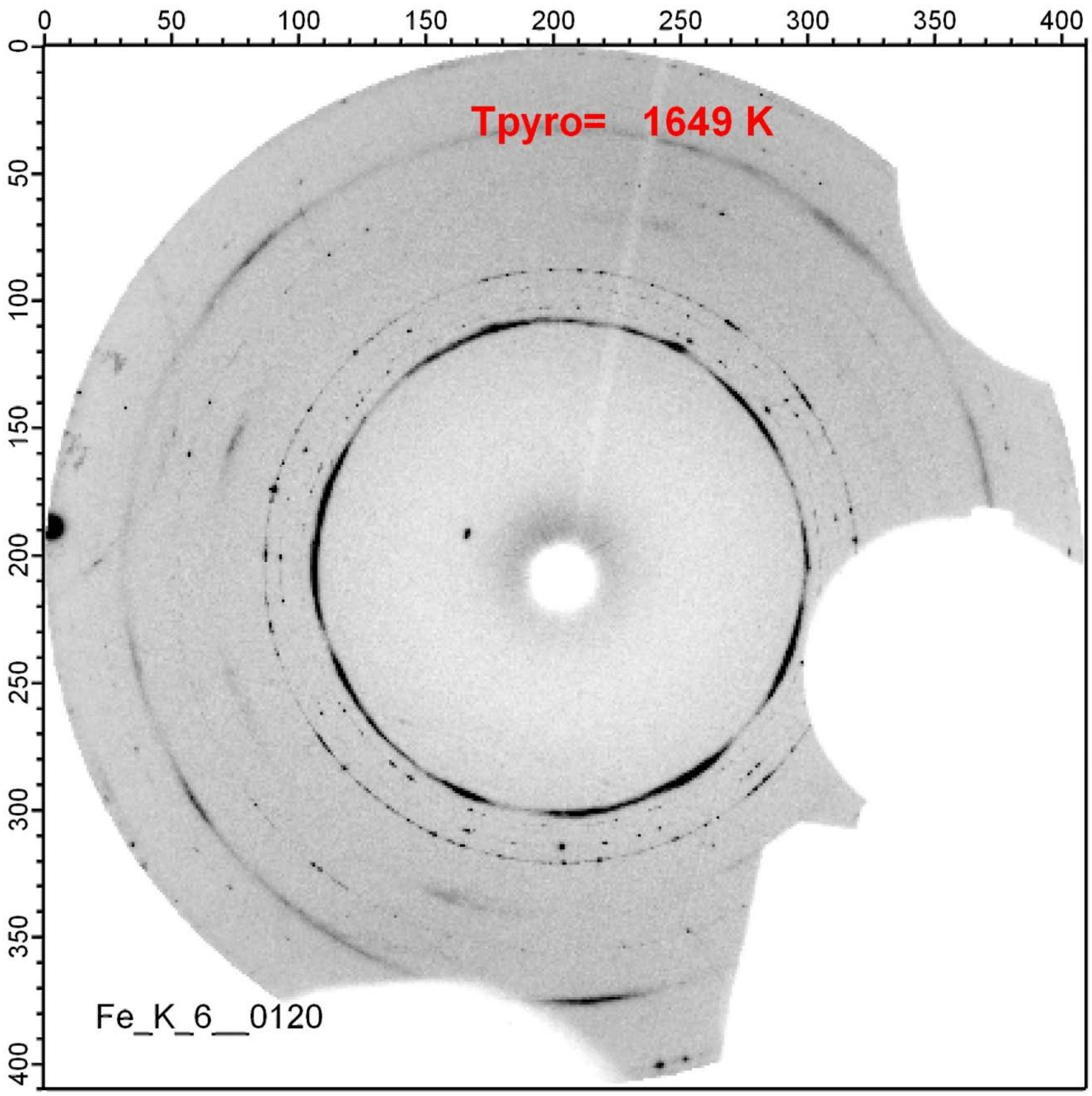
2. The "fast" sample recrystallisation observed using *in situ* XRD or the fast sample surface movement observed using the speckle method

3. The appearance of a X-ray diffuse signal

Question: Are those criteria always valid?

In-situ XRD investigation of the P-T phase diagram of iron





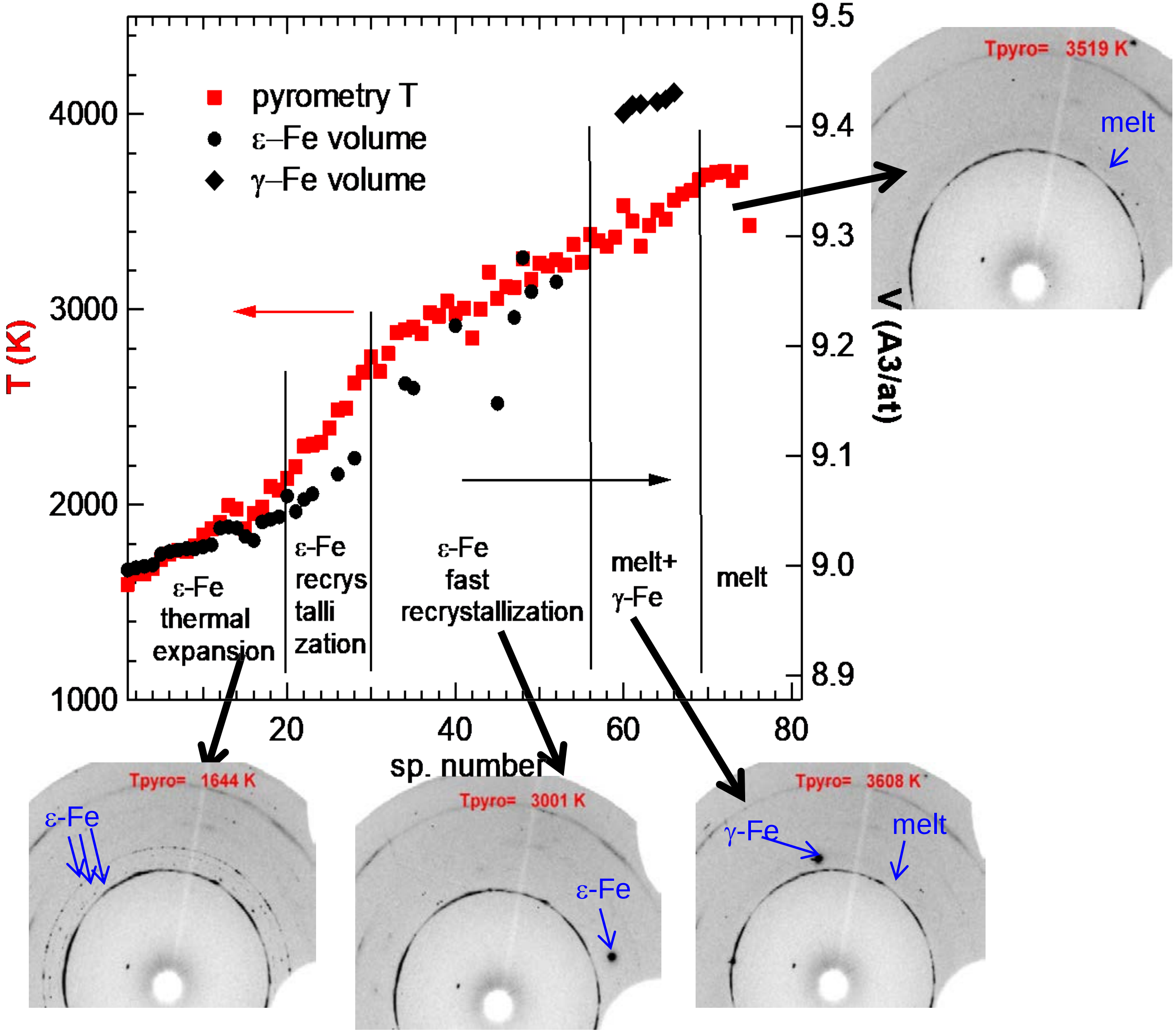
Gradual T increase
at P~80 GPa

t=2 sec.

4 regimes:

- Thermal expansion
- Recrystallization
- Fast recrystallization
- Melting

Melting of iron at ~80 GPa

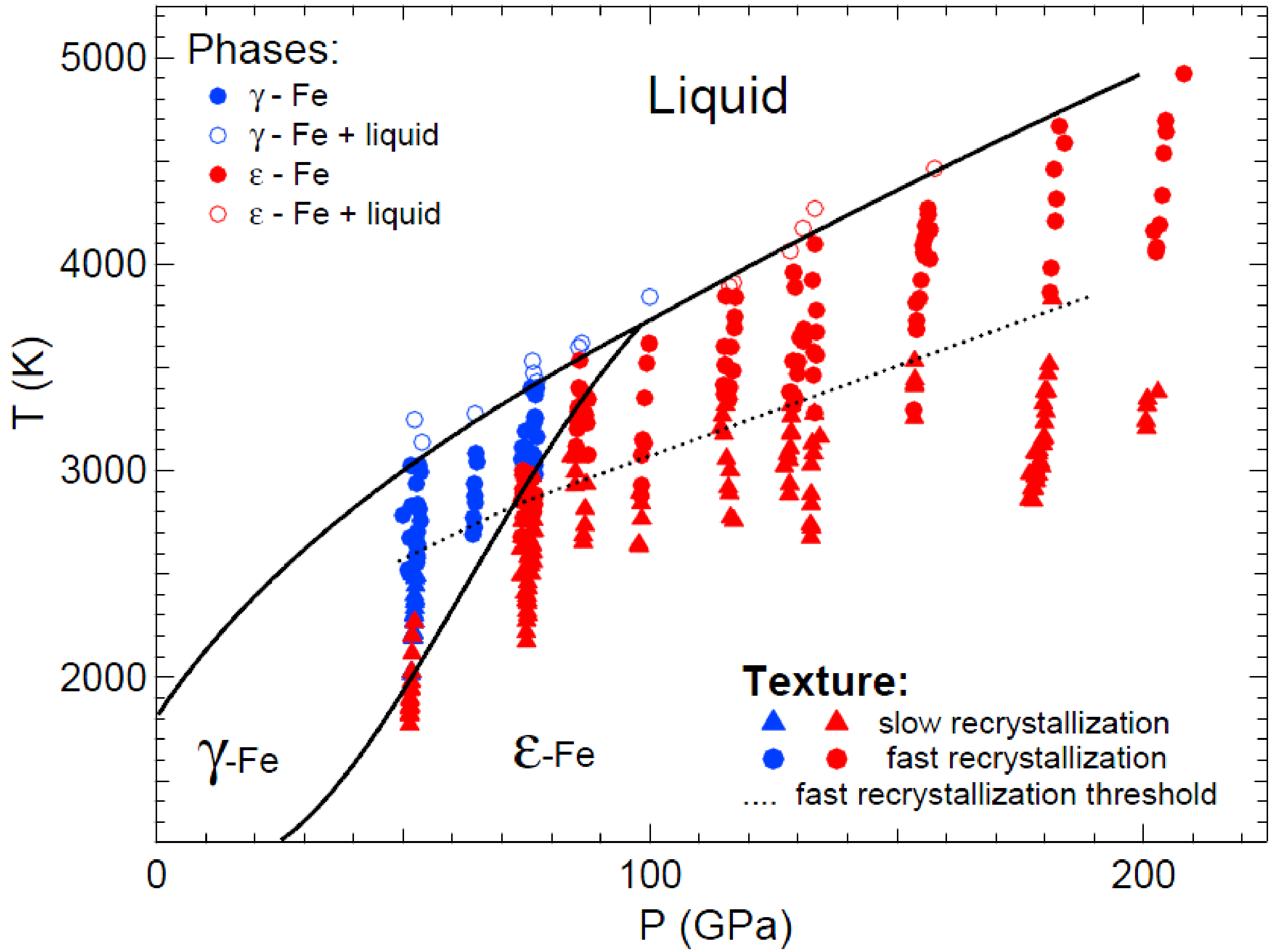


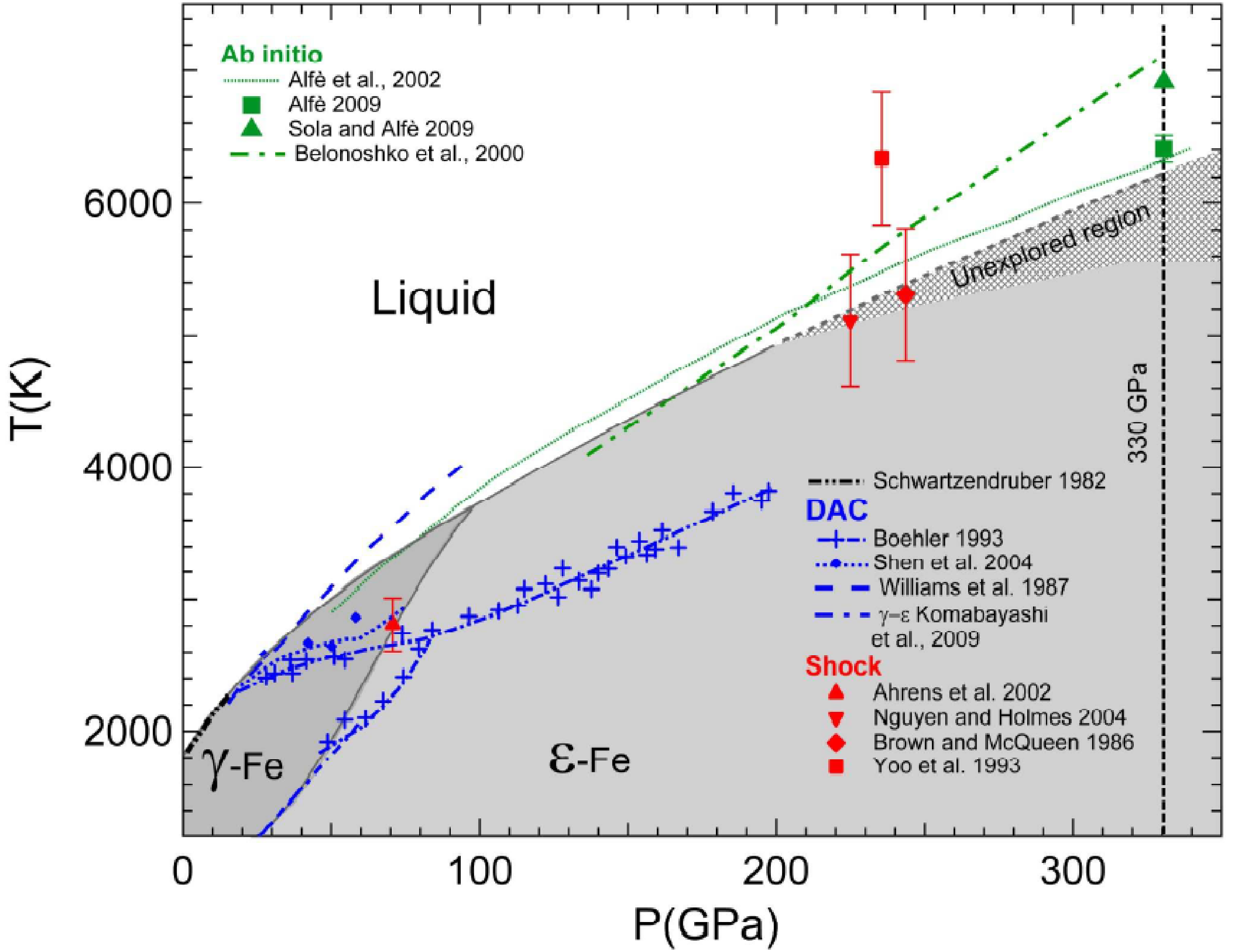
Assessment of melting criteria

1. Melting without “plateau” is observed

2. Fast recrystallization occur at much lower T than melting ($\Delta T > 1000$ K)

3. Onset of X-ray diffuse scattering : OK


Phases:
γ - Fe
γ - Fe + liquid
ε - Fe
ε - Fe + liquid
Liquid
γ-Fe
ε-Fe
Texture:
slow recrystallization
fast recrystallization
.... fast recrystallization threshold
5000
4000
3000
2000
T (K)
0
100
200
P (GPa)



S. Anzellini, A. Dewaele, M. Mezouar, N. Guignot, G. Morard, P. Loubeyre, *Science* (2013)