Extreme Conditions at Synchrotron Sources

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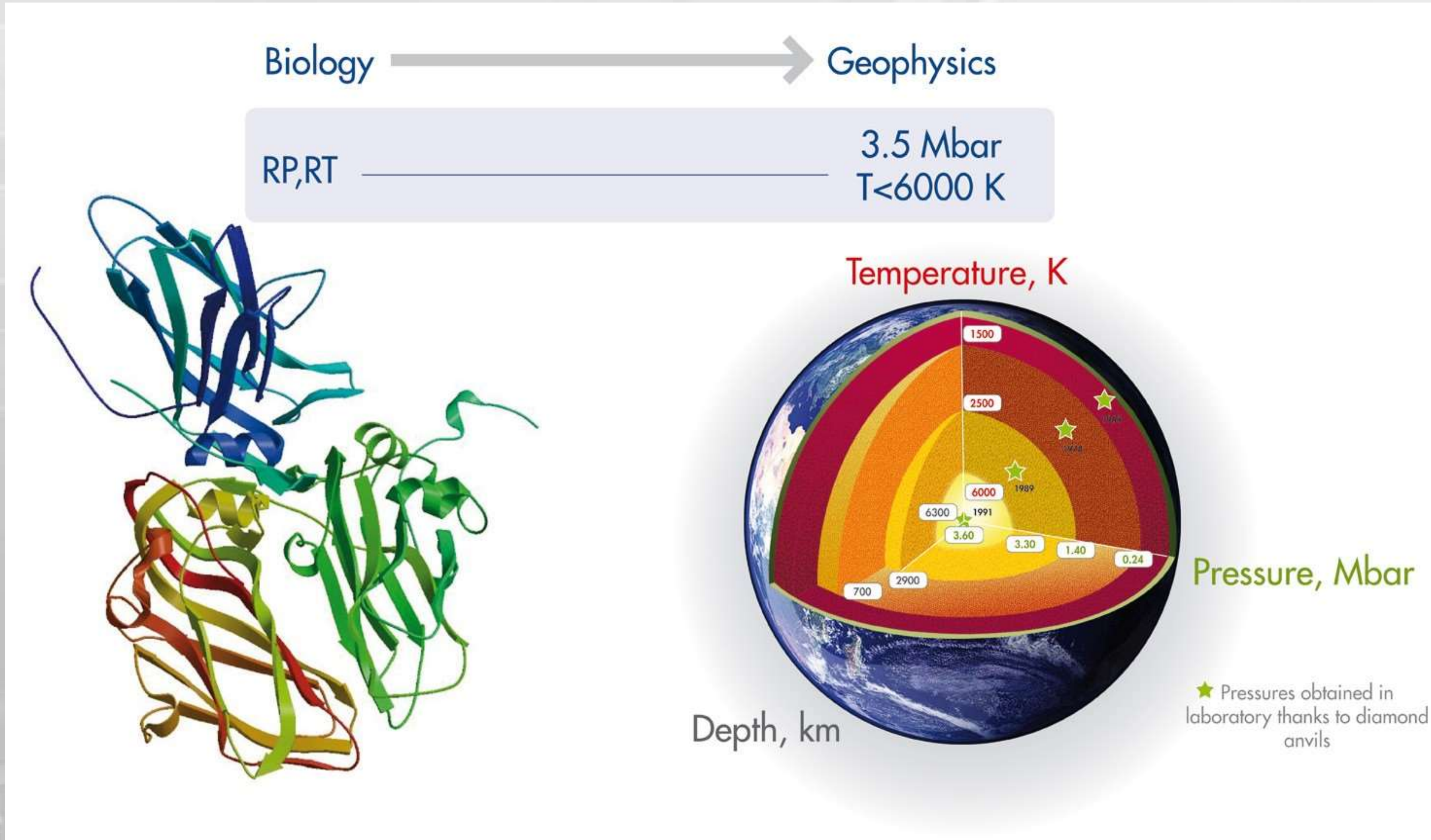
ESRF

Outline

- Introduction
- Description of a HP XRD beamline - ID27 -
- Data quality - Degrading factors -
- “In situ” versus “quenching” experiments - sulfur – CO_2
- Very HP-HT XRD in the laser heated DAC
- Summary

34 public beamlines
600 employees

‘Science at Extreme Conditions’: multidisciplinary research



Introduction

‘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 electronic, magnetic, structural properties of materials

The first High Pressure XRD experiment was performed at the end of the 60's using a conventional X-ray source.

Why so late?

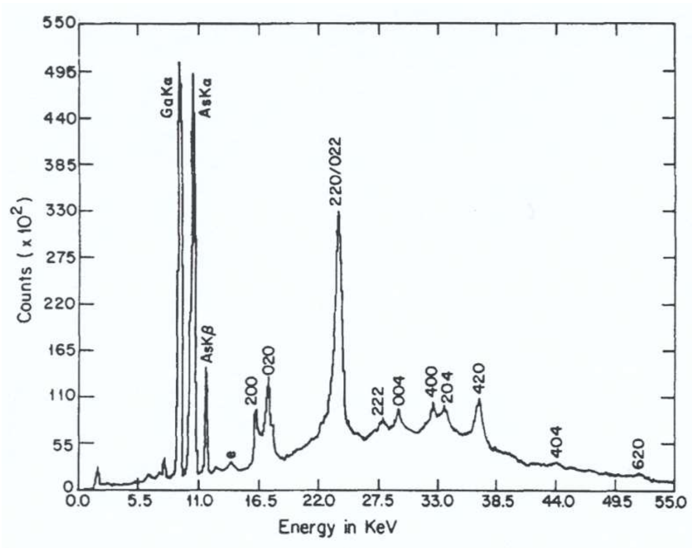
Major technical problems:

• Invention of diamond anvil cells and large volume presses compatible with XRD techniques.

•Technical challenges:
-Highly X-ray absorbing sample containers
-Diffraction signal contaminated by elastic/inelastic scattering from the sample environment.
- Limited accessible diffraction angle.
-…

Laboratory X-ray sources are not the optimum in terms of flux , energy and beam size (as well as divergence)

⇒Synchrotron radiation
High Flux at high X-ray energies

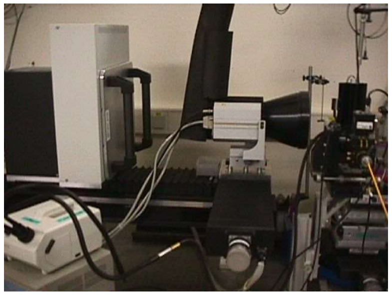


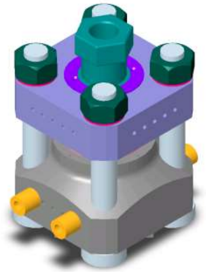
EDX spectrum of GaAs at P=27 GPa in a DAC, collected at CHESS (USA)

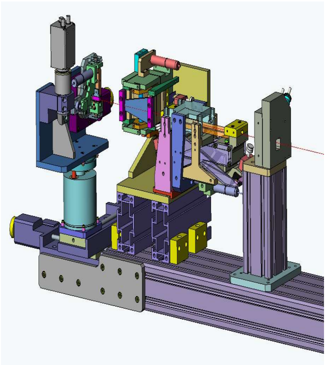
Ref: Baublitz and co., Rev. Sci. Instr., 52 (1981)

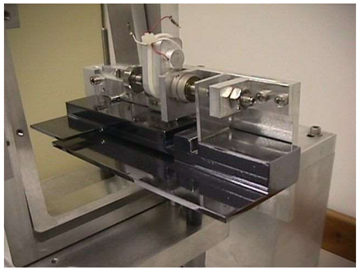
Modern HP XRD beamline (ID15B; ID27)

ESRF
6 GeV









Detectors

Sample environment

Mirrors

Monochromator

X-ray Source

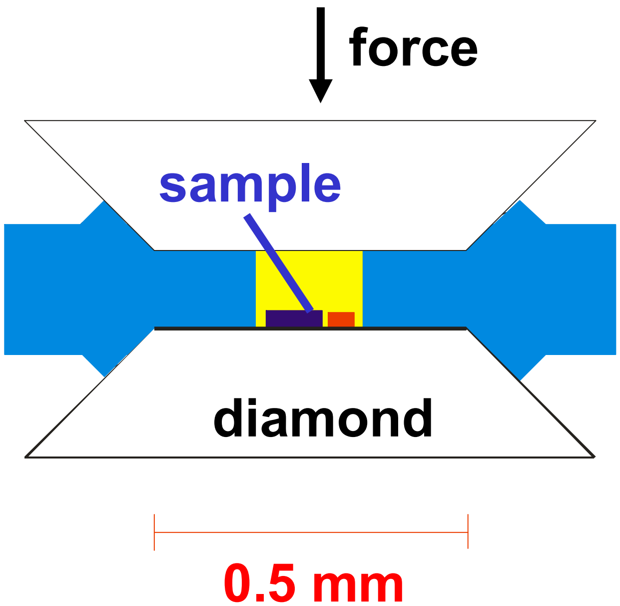
THE DIAMOND ANVIL CELL

diamond anvils

- hard
- transparent

Pressure = Force / Surface

To reach high pressures →
Large force on a small area

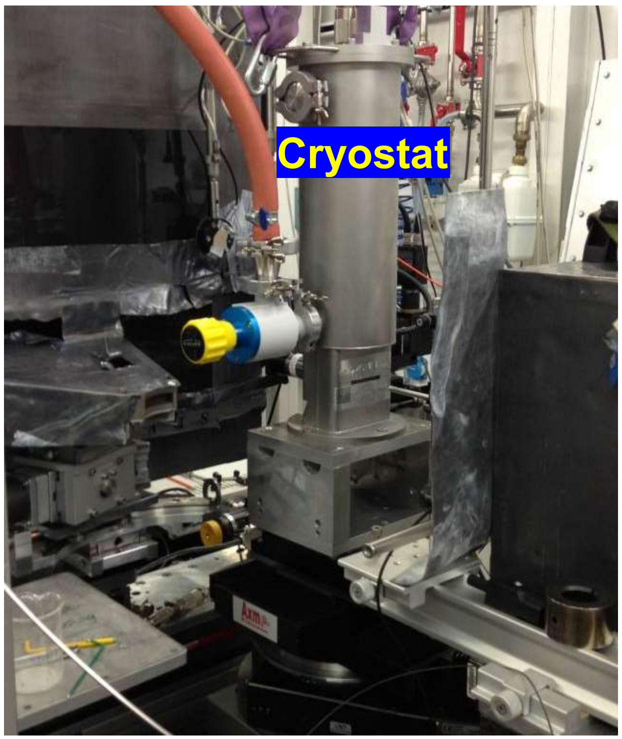


Max. Pressure: 300 GPa (3 Mbar)
Sample volume: 10^{-4} mm^3

Sample environments at HP beamlines

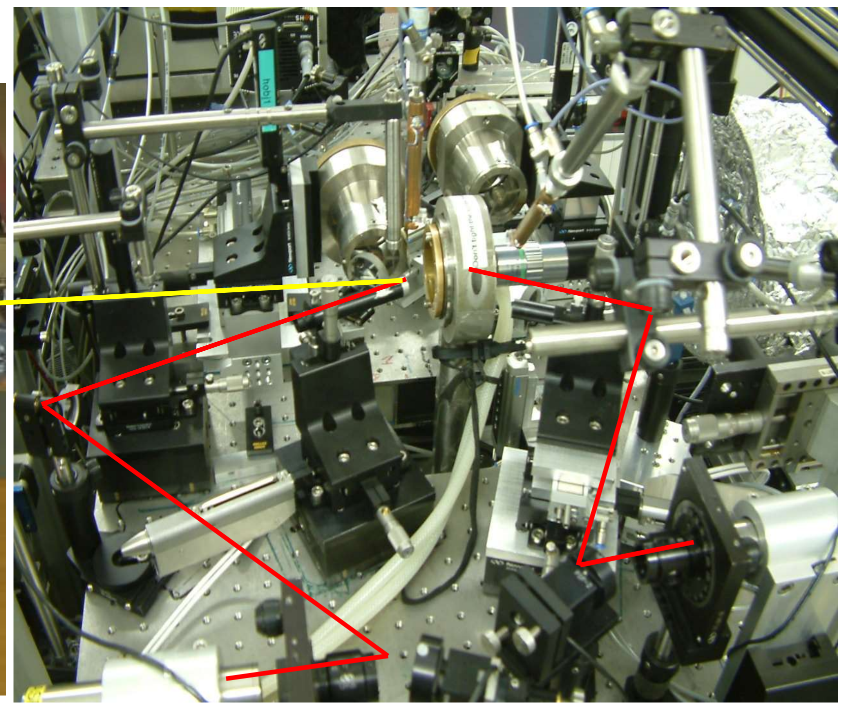
Pressures up to 3 Mbar

LT down to 4 K



Resistive heating up to 1300 K

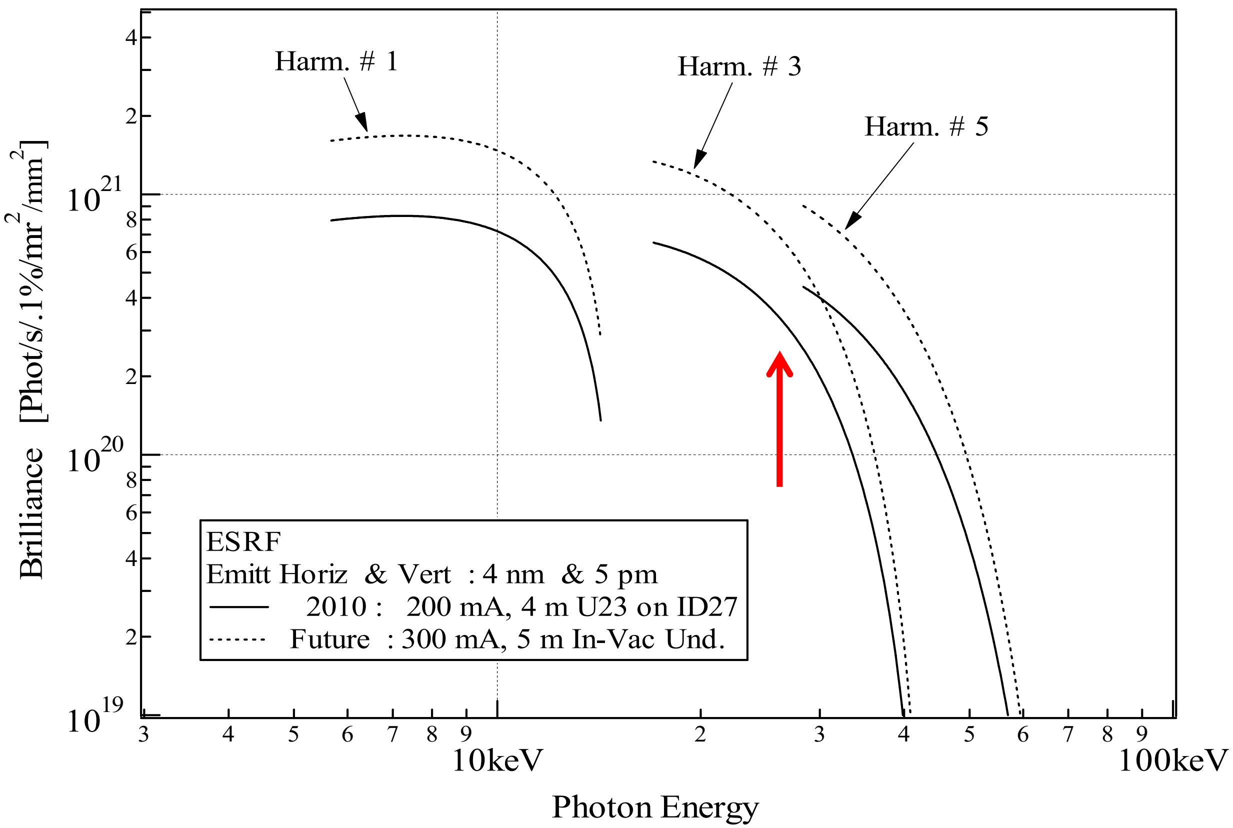
Laser heating T>5000 K

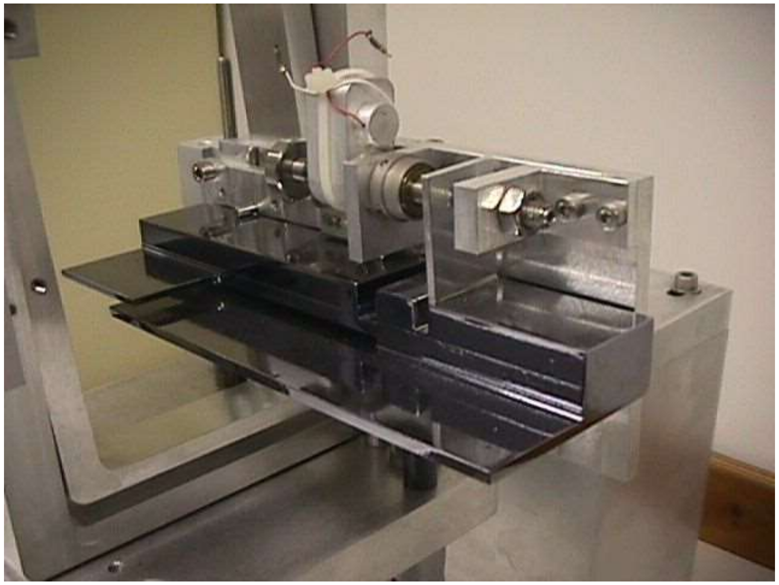


ID27 is equipped two U23 undulators providing very high flux at high energy

Two U23 in vacuum undulators of ID27

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





X-ray technique:
monochromatic XRD (fixed λ)

•Nitrogen cooled Si(111) double crystal monochromator

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

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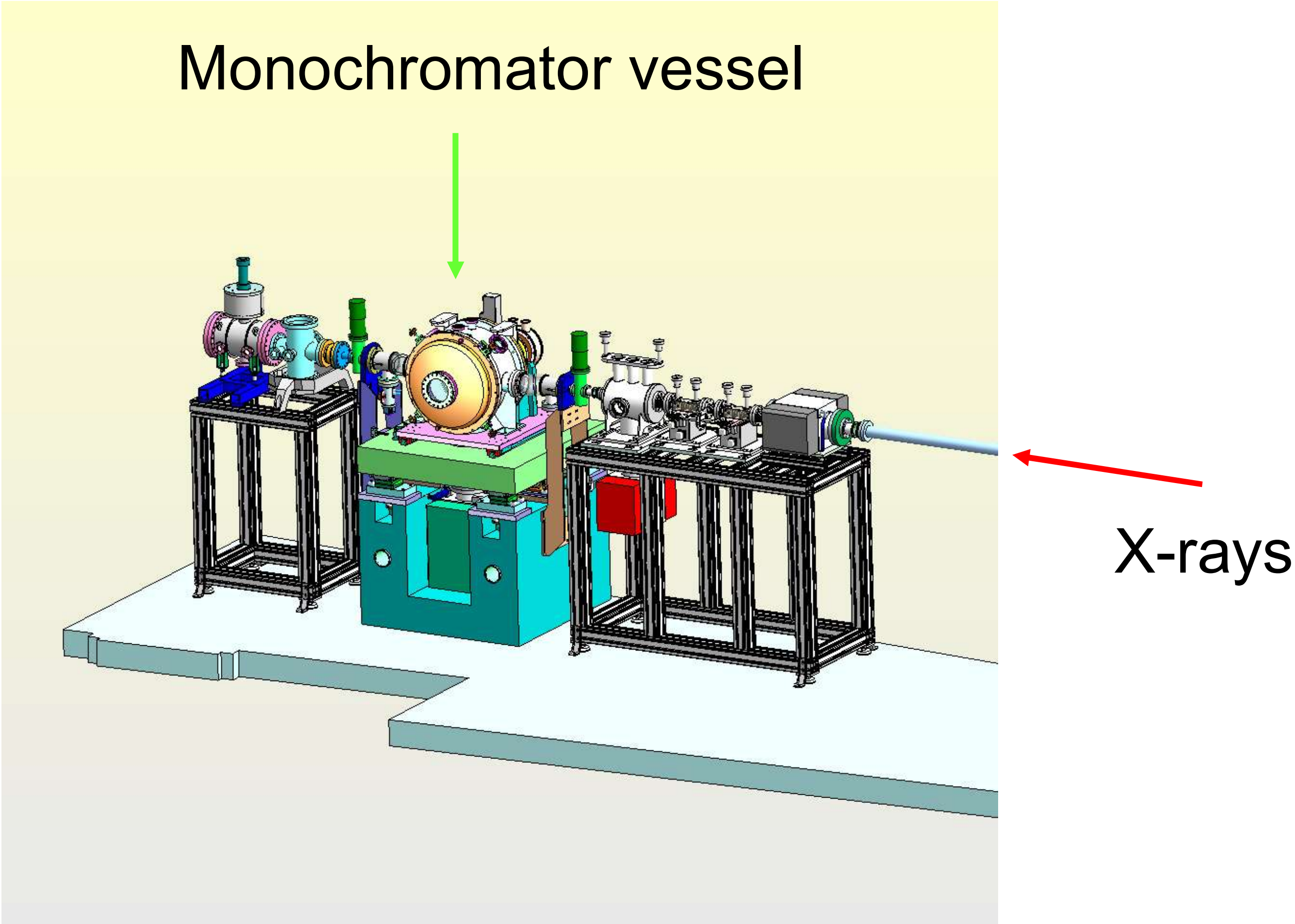
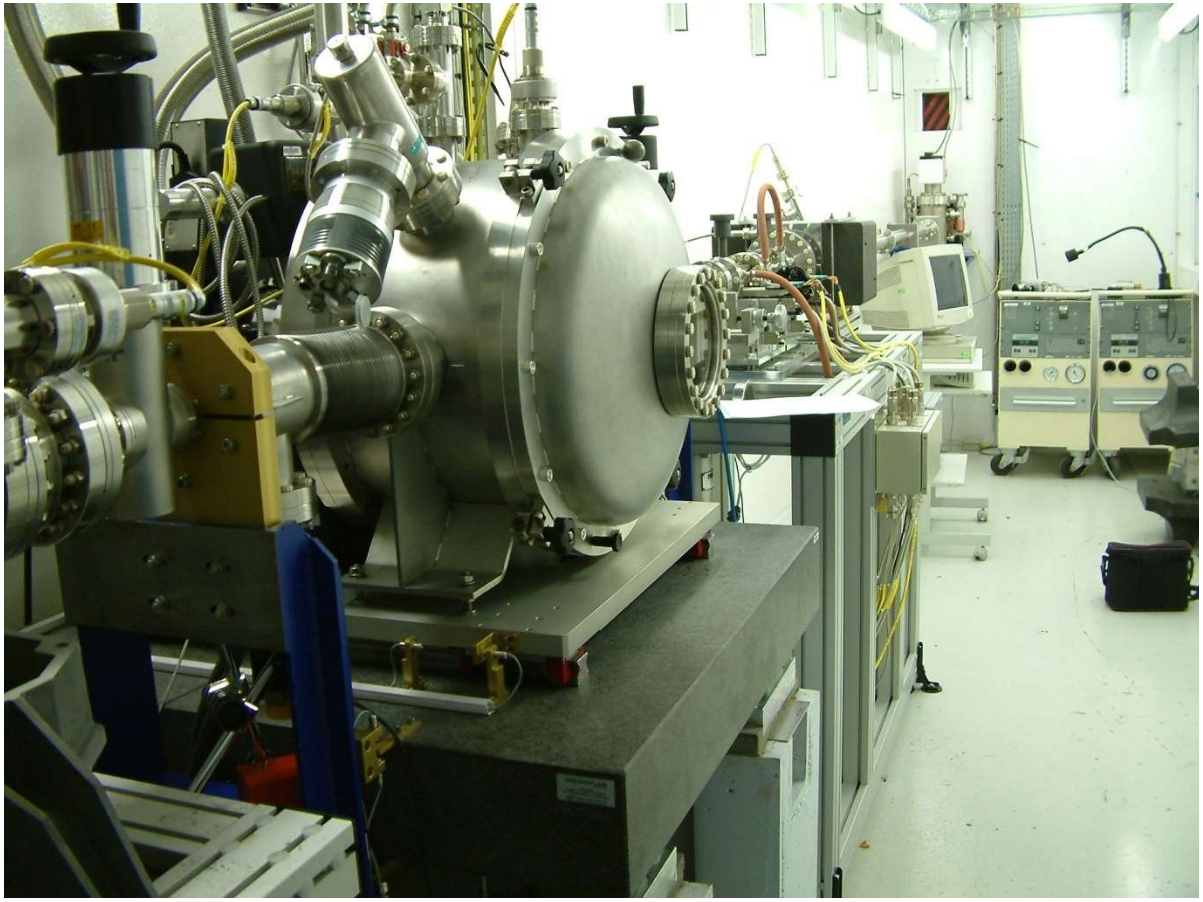
MM3 Mohamed Mezouar, 26/09/2010

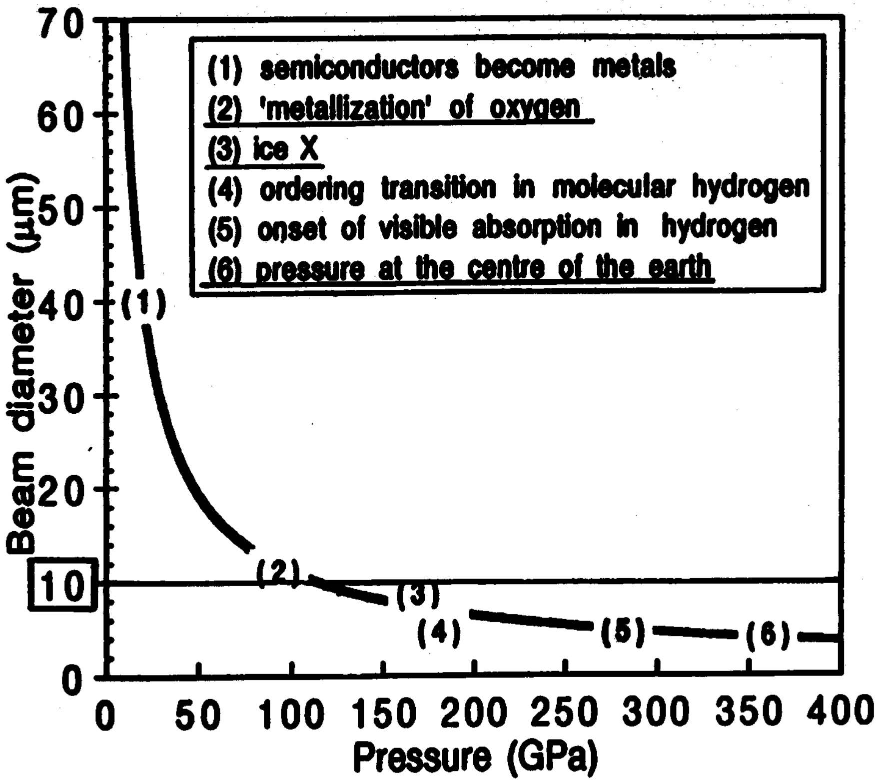
ID27 optics hutch



ID27 optics hutch

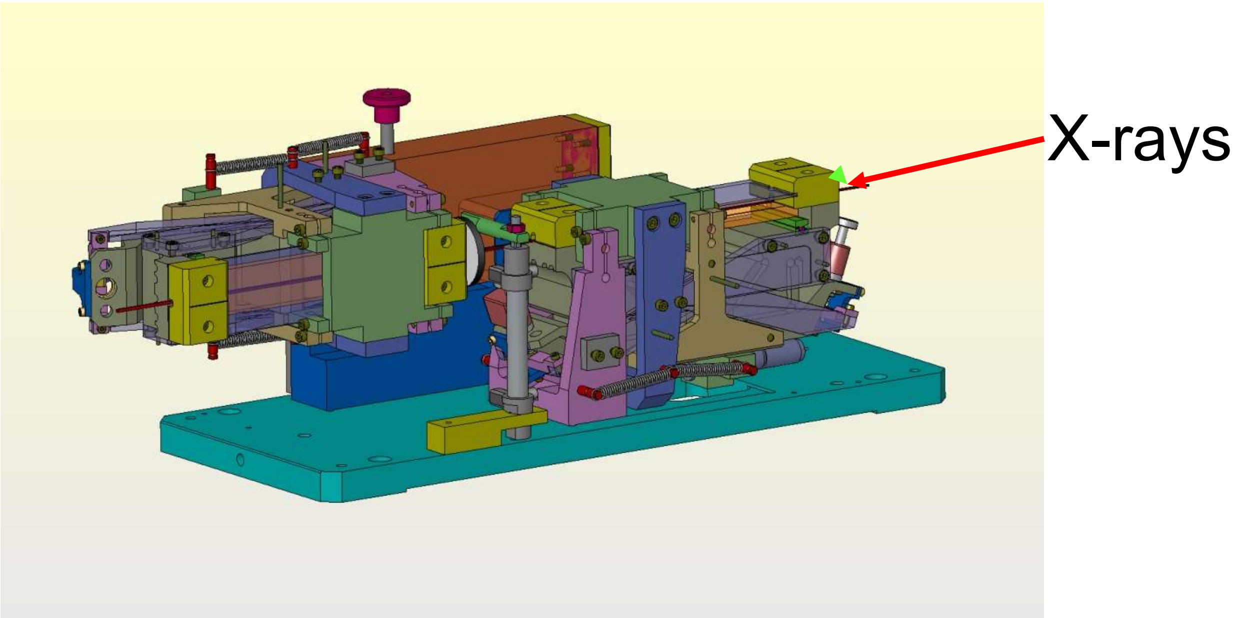


X-ray optics for HP XRD beamlines



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

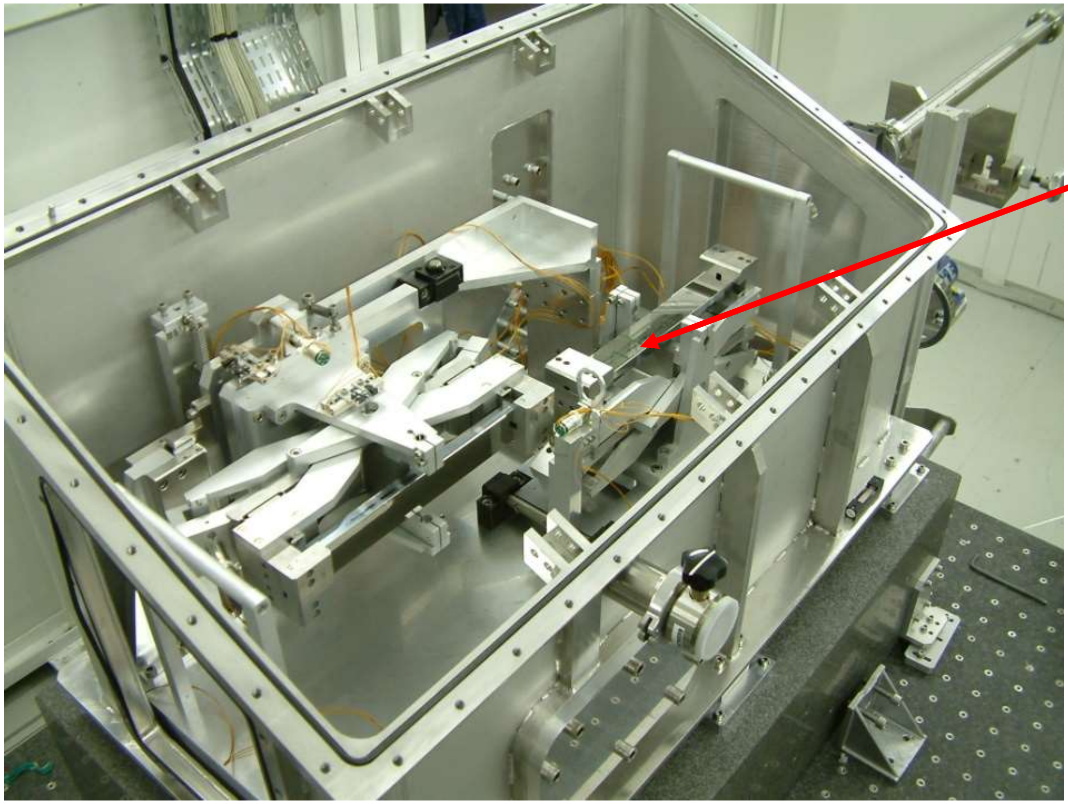
Kirkpatrick-Baez focusing mirrors



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

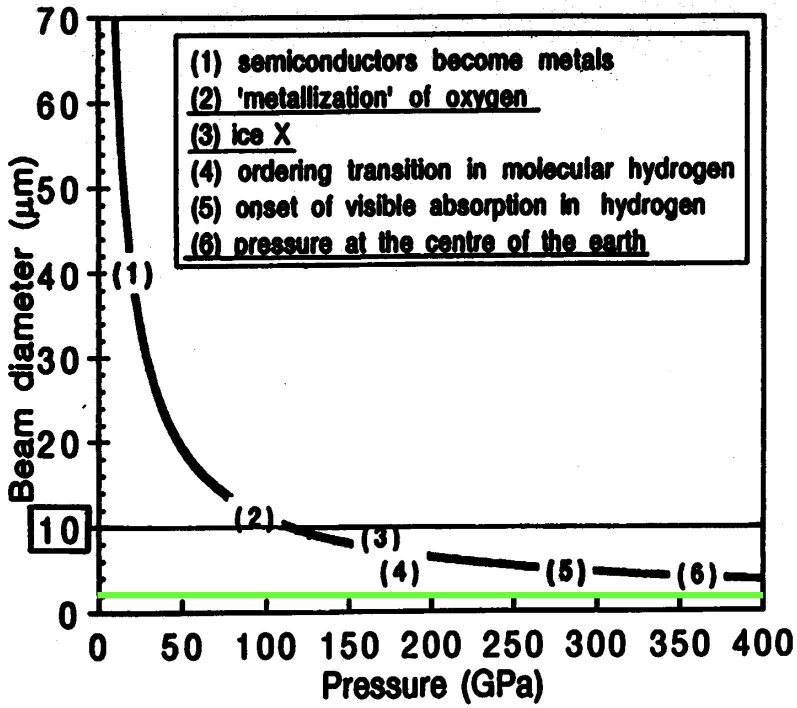
- the source size
- the sample-mirrors distance/source-mirrors distance
- mirrors quality

Kirkpatrick-Baez focusing mirrors

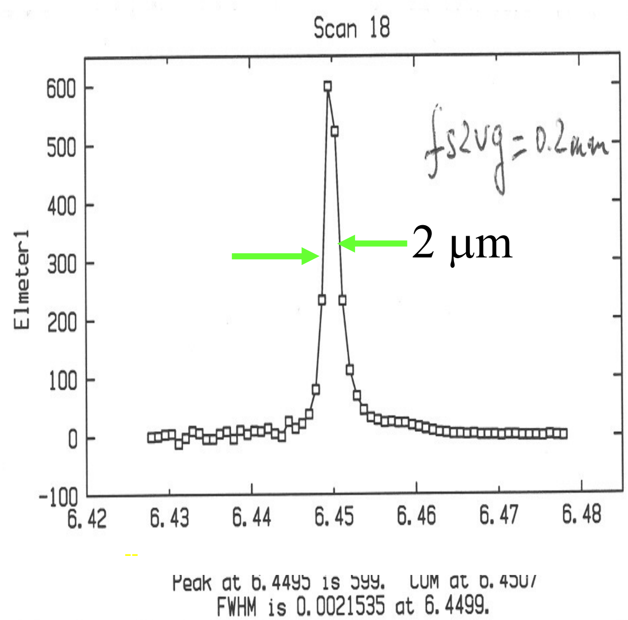


Vertical mirror

X-ray optics for HP XRD beamlines

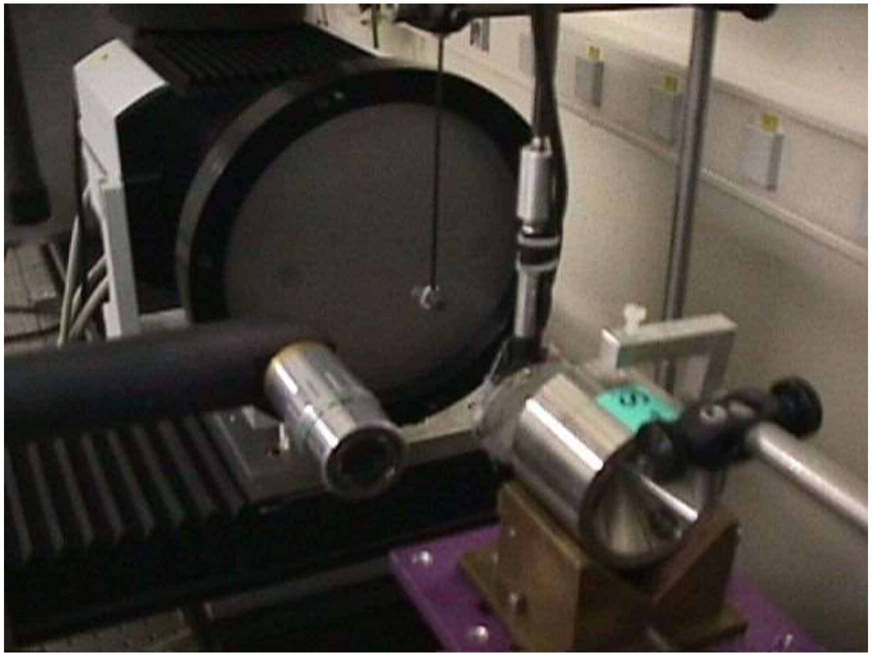


Measured beam size at ID27

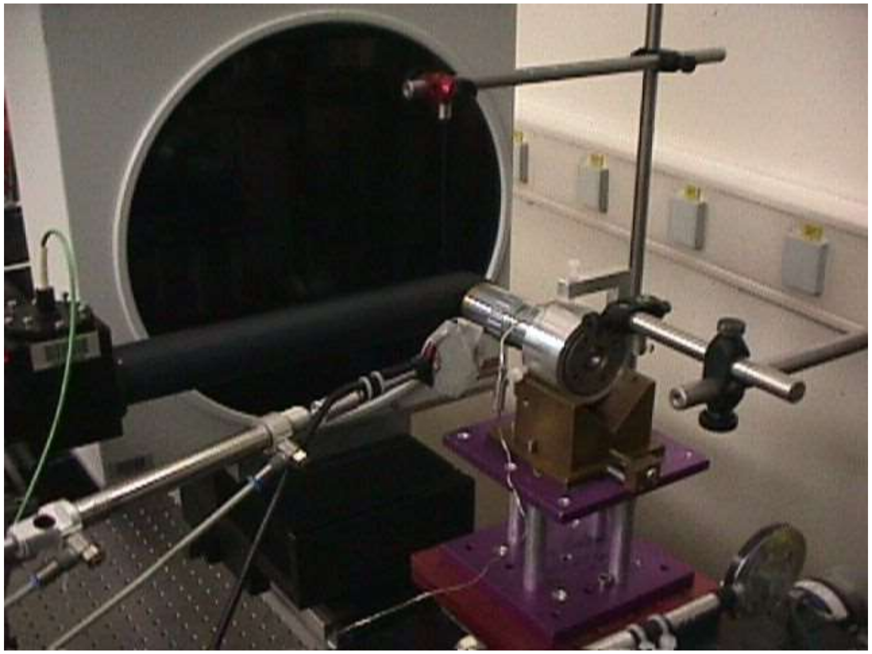


Detectors

A good detector for HP 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

Data quality - Degrading factors -

Question: what are the "degrading" factors?

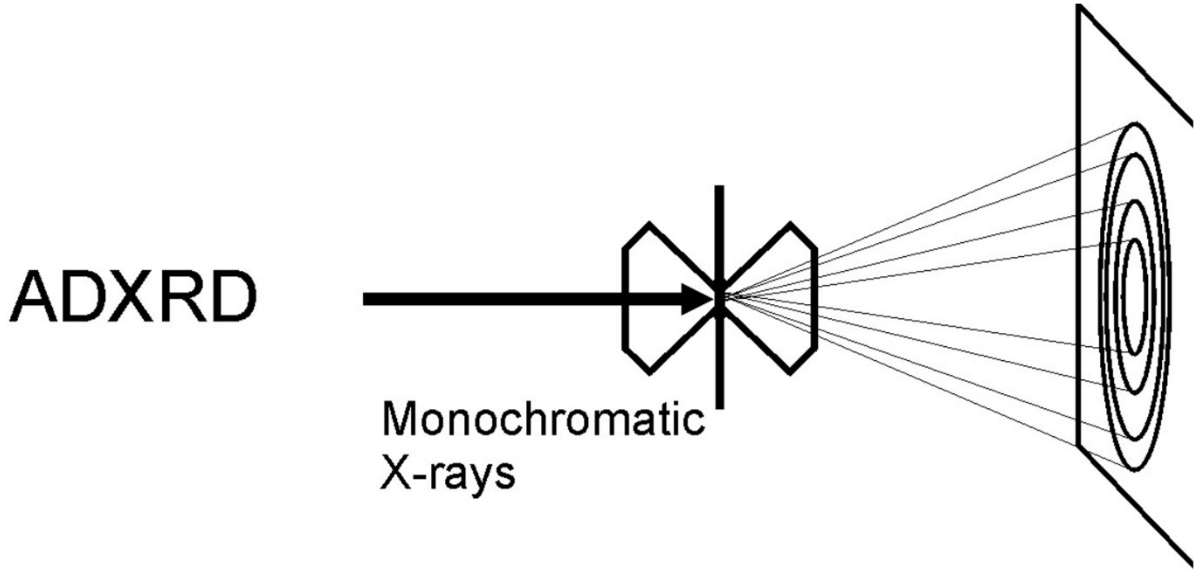
Sample environment

- Non-hydrostaticity of pressure medium
- Temperature gradients
- chemical reactions…

X-rays

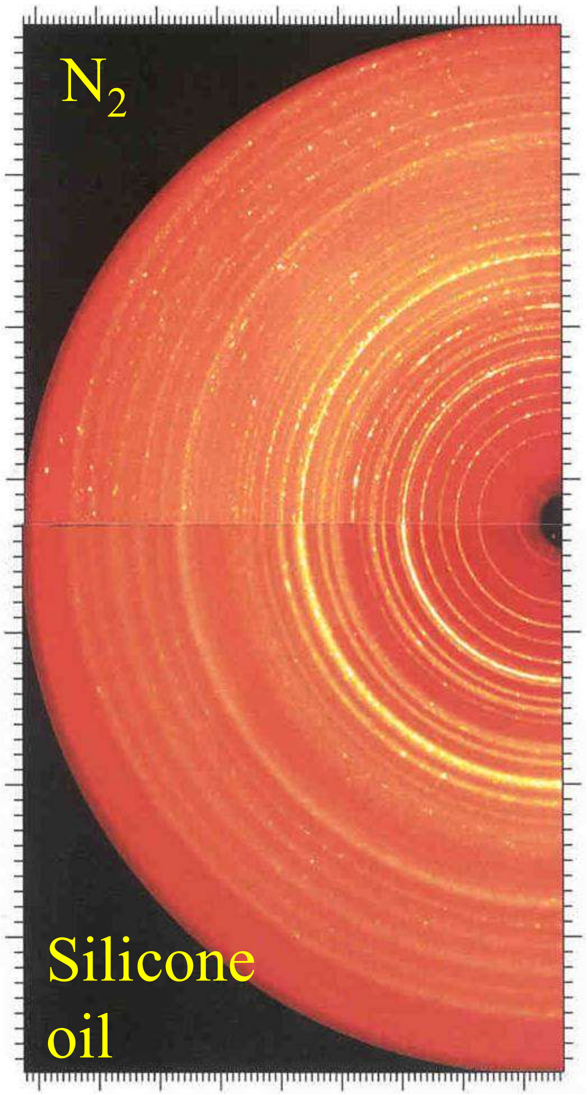
- Undesired X-ray effects (radiation damage)
- EDX instead of ADX
- X-ray background coming from HP cells (elastic and inelastic)

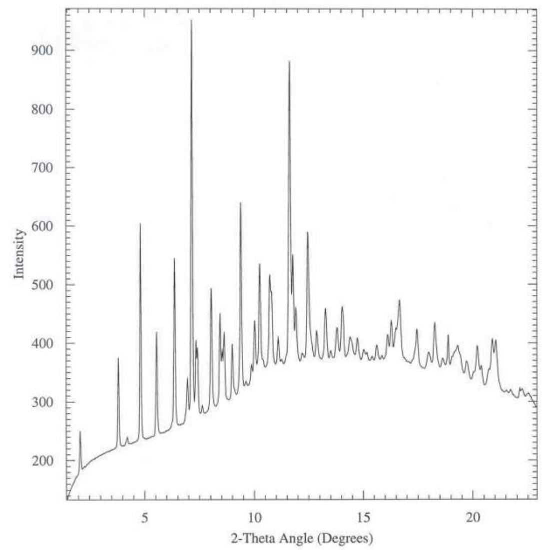
Diffraction geometry

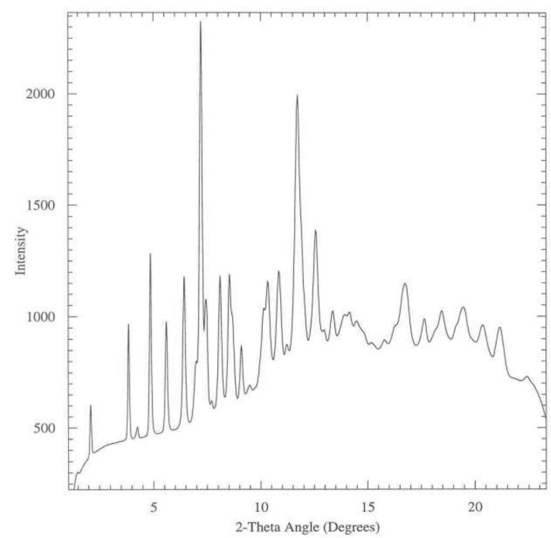


Example: $IrSe_2$ in different pressure media

Data quality - Non hydrostatic conditions





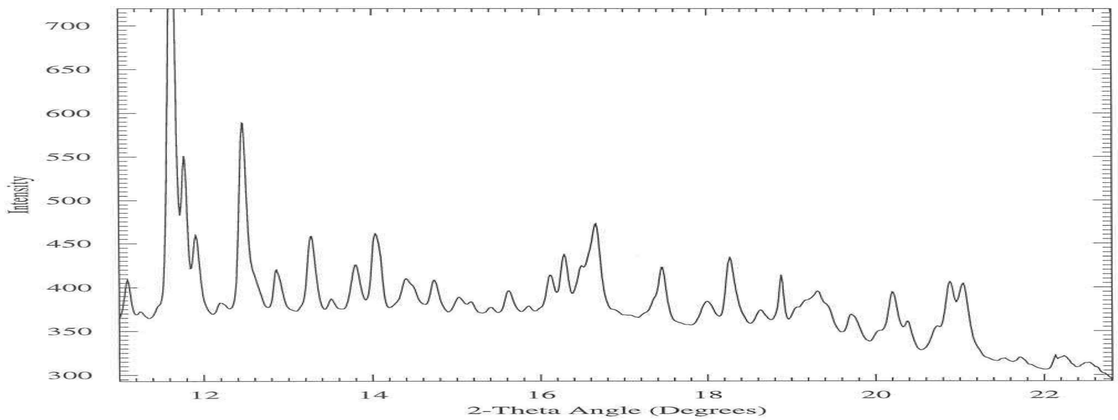


$IrSe_2$ in N_2 and in silicone oil at P=33 GPa

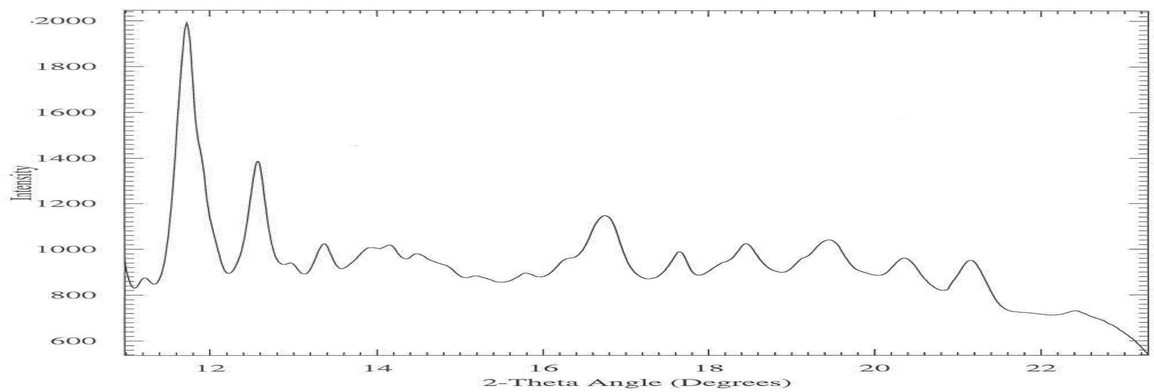
Ref.: C. Soulard, P.E. Petit, Nantes (France)

Very important peak broadening when silicone oil is used as pressure medium (same effect with eth.-meth. mixture)

Suitable for refinement

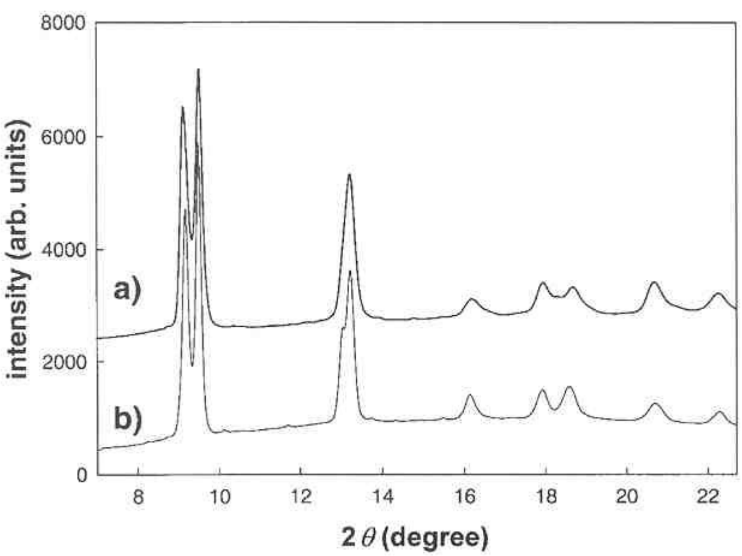


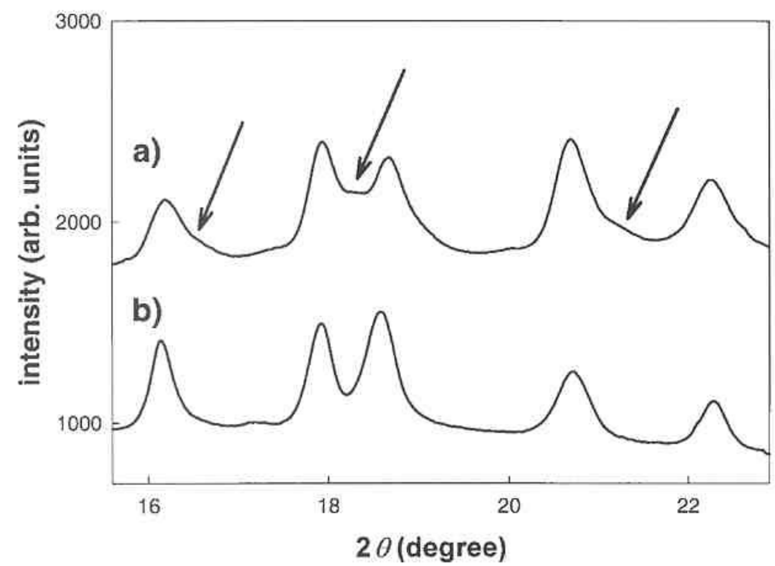
Not suitable for refinement



In some cases, non hydrostatic conditions can induce metastable phases

GaSb in a DAC at P=12 GPa without pressure medium (a) and in N_2 (b)



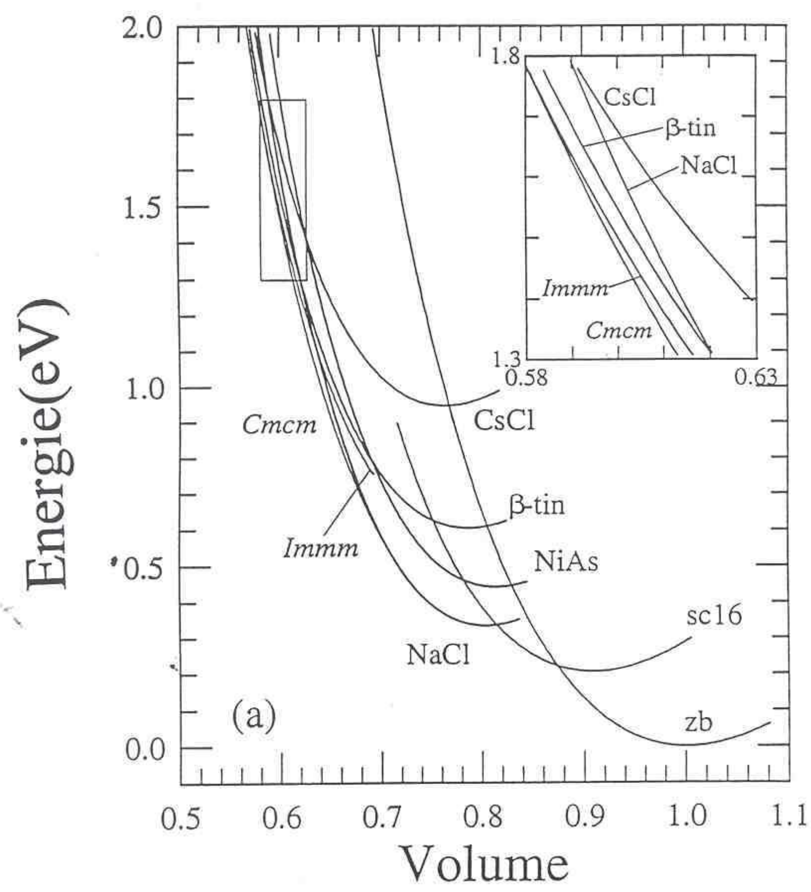


(a) Othorhombic distortion (Imma)
(b) β-tin structure

Gibbs free energy G(P,T, ε_{NH})

Additional non hydrostatic terms can stabilize metastable phases.

Ab initio calculation- InP -



Ref.: Mujica et al., PRB

Data quality - Non hydrostatic conditions

Which pressure medium?

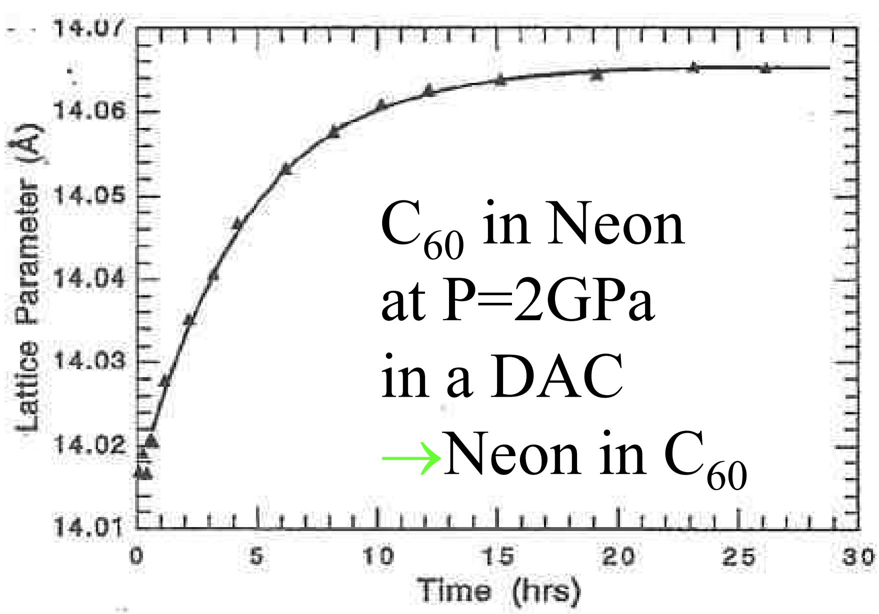
P < 8 GPa; silicone oil, Eth. Meth. Mixture are "OK"

P < 30 GPa: Ar or N_2

P < 50 GPa: Ne

P > 50 GPa: He

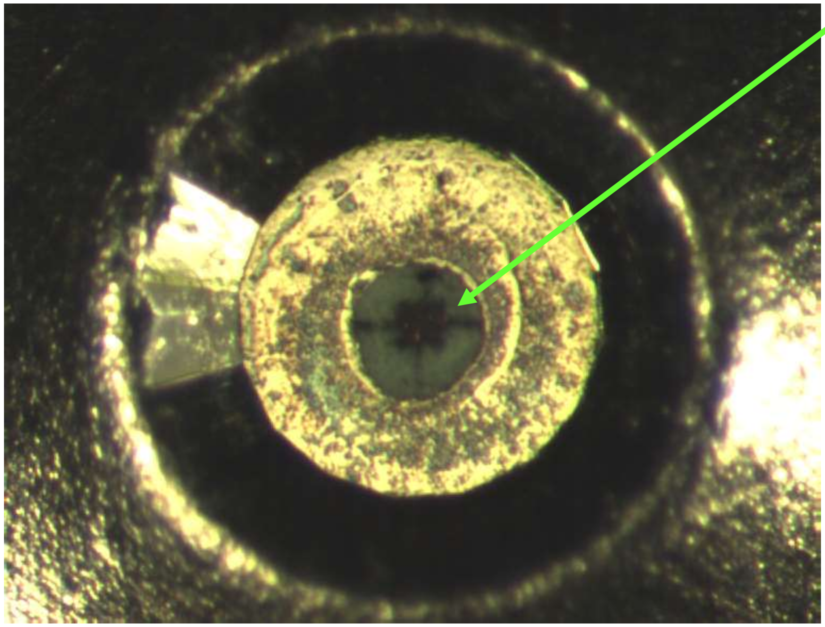
With one noticeable exception: cage structures (Clathrates; Zeolites)



Ref: J. Shirber et al., PRB,51 (1995)

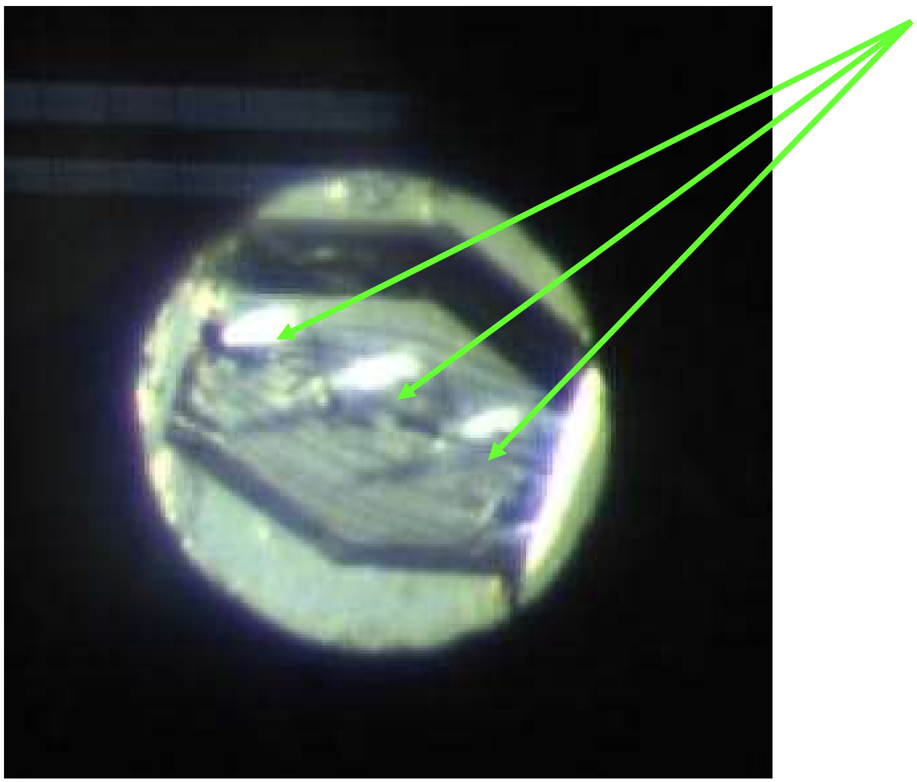
Undesired X-ray effects

Photochemical reactions



CuOHF
+
Eth. Meth.
+
Beam
=
?

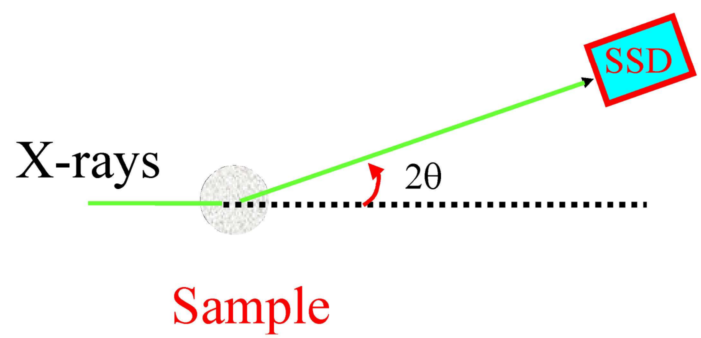
Radiation damage on a protein single crystal (lysozyme)

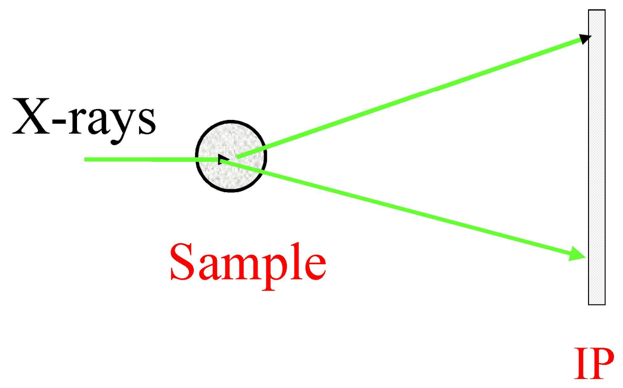


Beam impacts
slow degradation
process (free radicals
propagation)

EDX versus ADX

Which XRD technique to use?





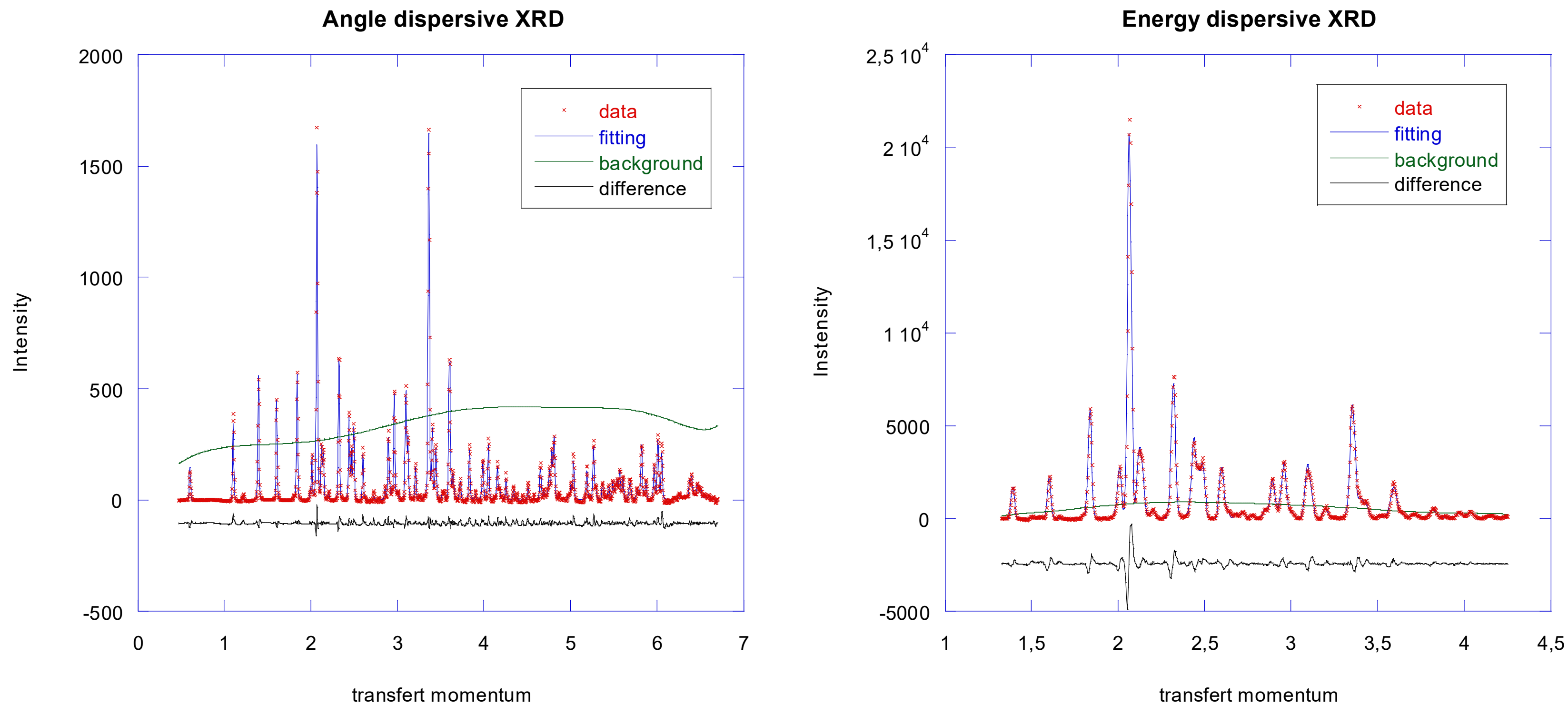
$2d\sin\theta=\lambda$
θ is fixed
λ Varies
Spatial selectivity
<u>But</u> intensities are not reliable
and poor energy resolution

$2d\sin\theta=\lambda$
λ is fixed
θ Varies
Reliable intensities and high resolution
<u>But</u> no spatial selectivity
→High background

EDX versus ADX

$IrSe_2$ in a DAC

Ref.: C. Soulard, P.E. Petit, Nantes (France)



EDX is suitable for Le Bail fitting of unit cells
BUT not suitable to extract structure solutions

Background reduction

- At high static pressures, the pressure cell always produces a high elastic and inelastic X-ray background

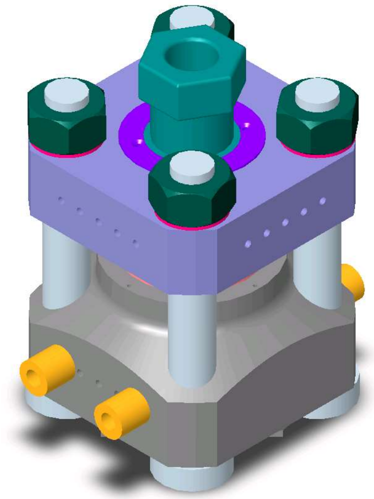
- It is crucial to collect the « cleanest » diffraction patterns

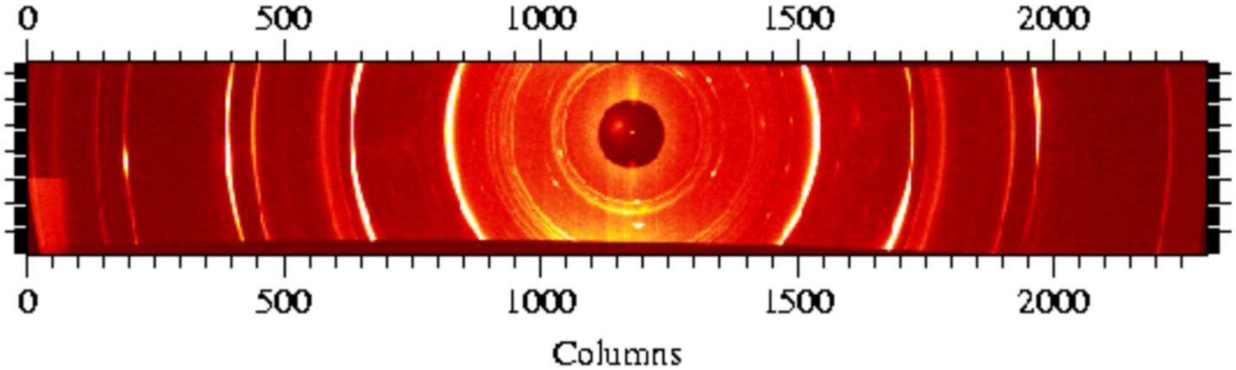
How to reduce the HP cell background?

Paris-Edinburgh cell:

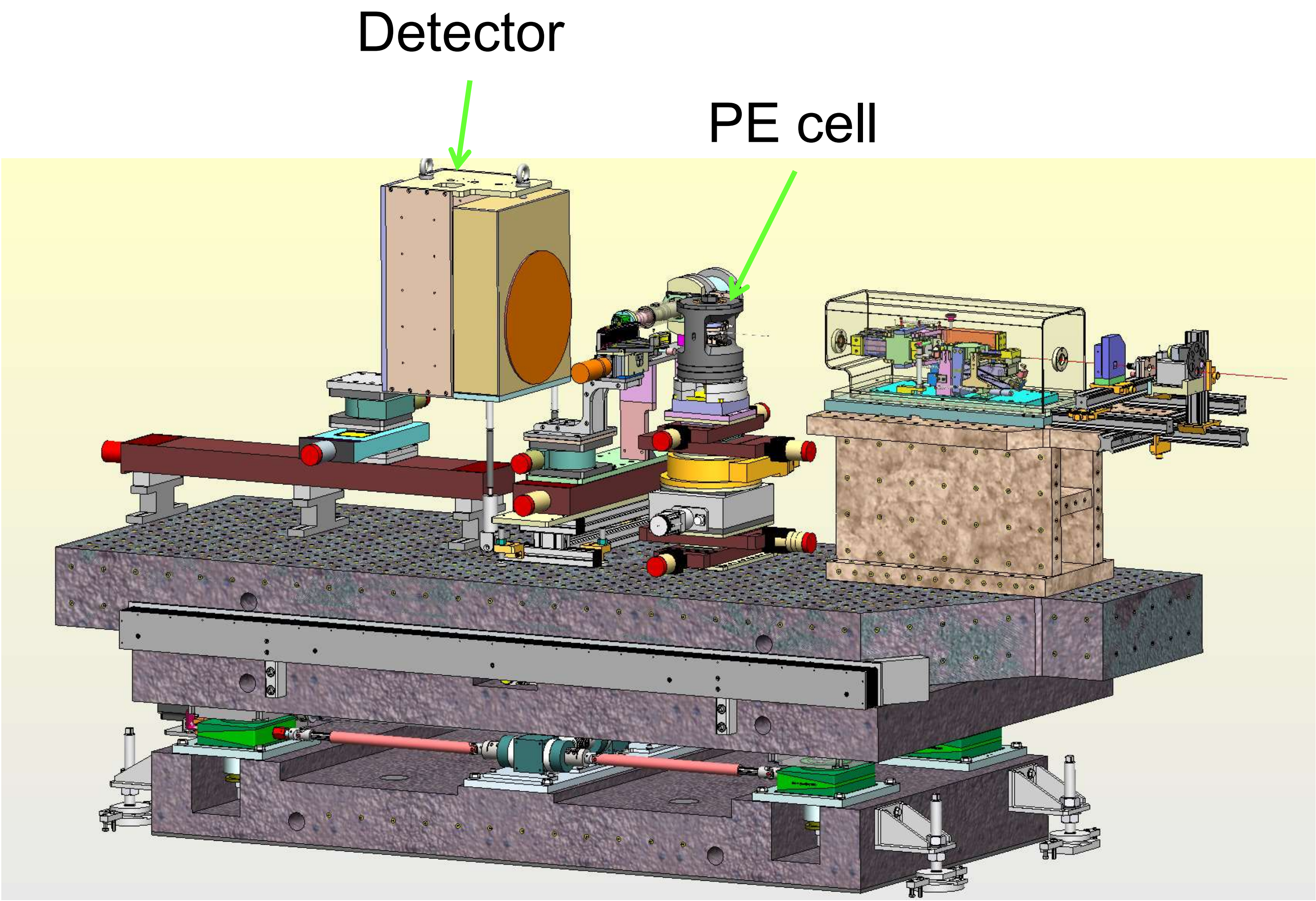
- Pressure up to 17 GPa on 2 mm^3 sample volume
- Resistive heating up to 1800 K

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

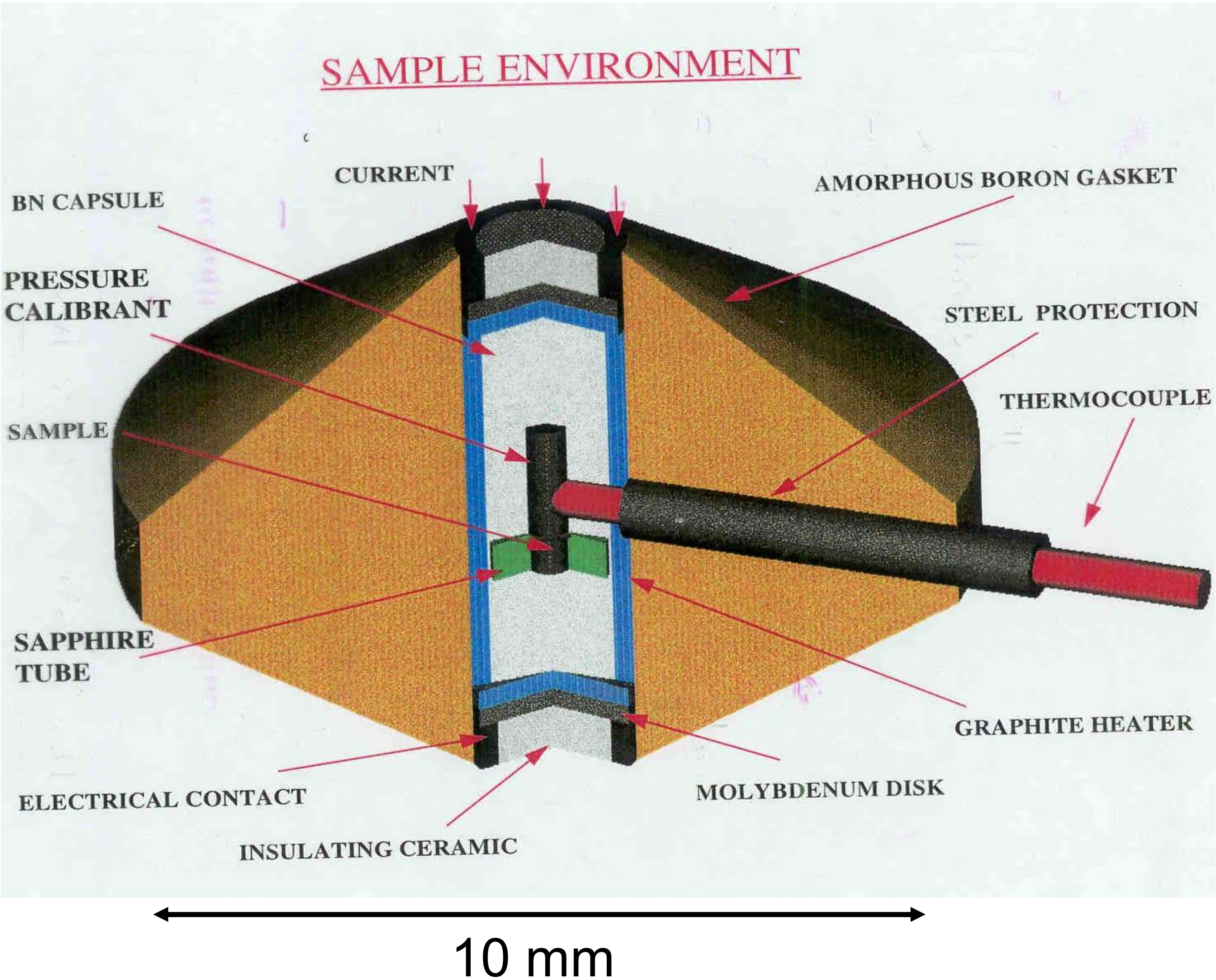




Background reduction



Paris-Edinburgh setup



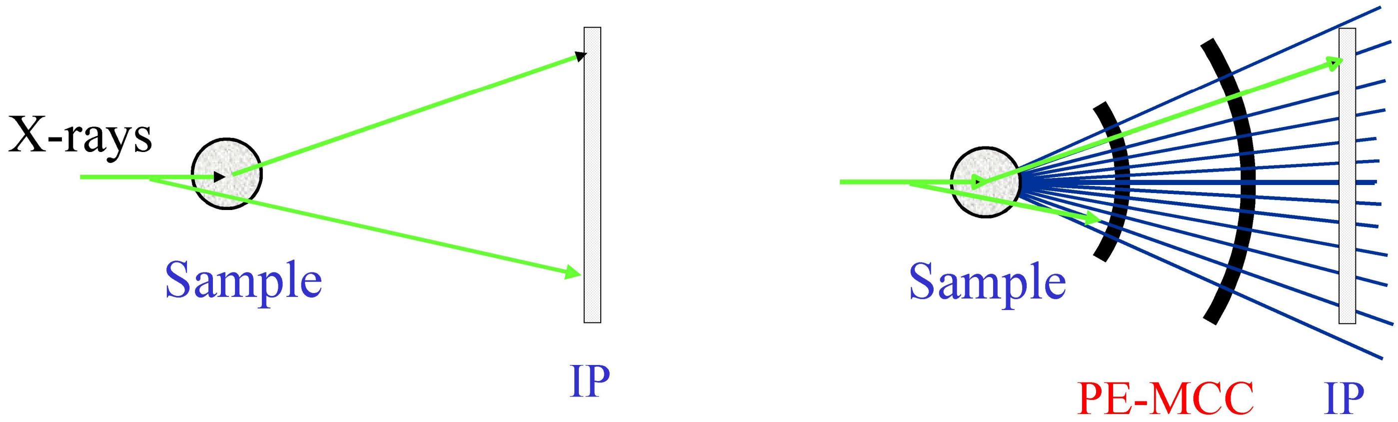
Soller slits system

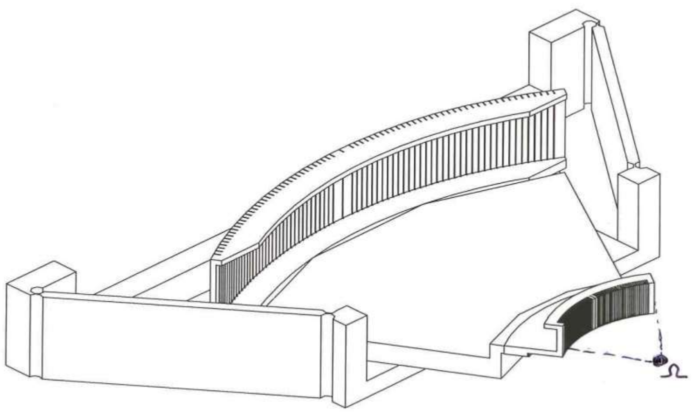
In monochromatic mode the high background coming from the large volume cell (boron gasket, graphite heater, h-BN) strongly deteriorates the data quality.

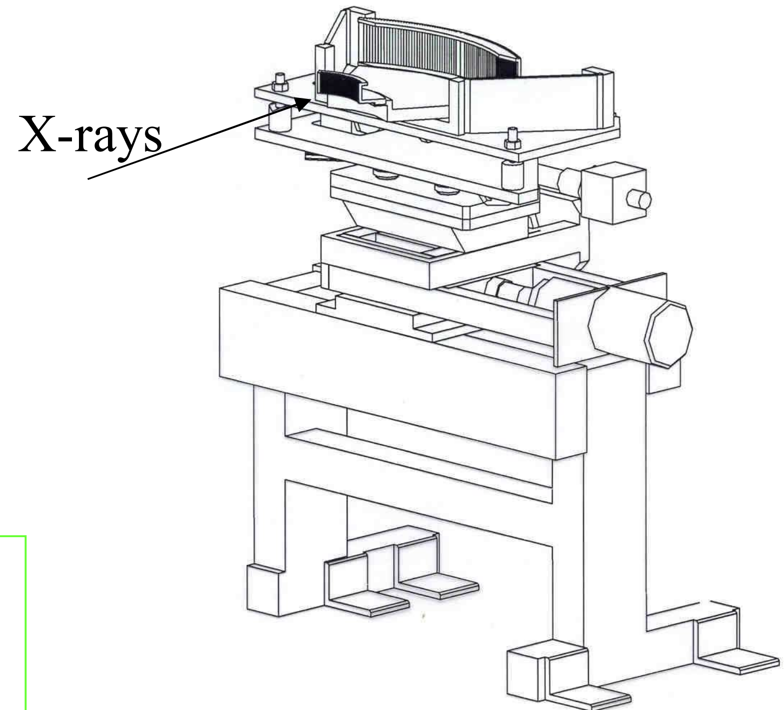
When sample/cell signal <<1; high photon flux is not enough

⇒ Most of the LV presses work in EDX mode

Alternative ⇒ Soller slits system



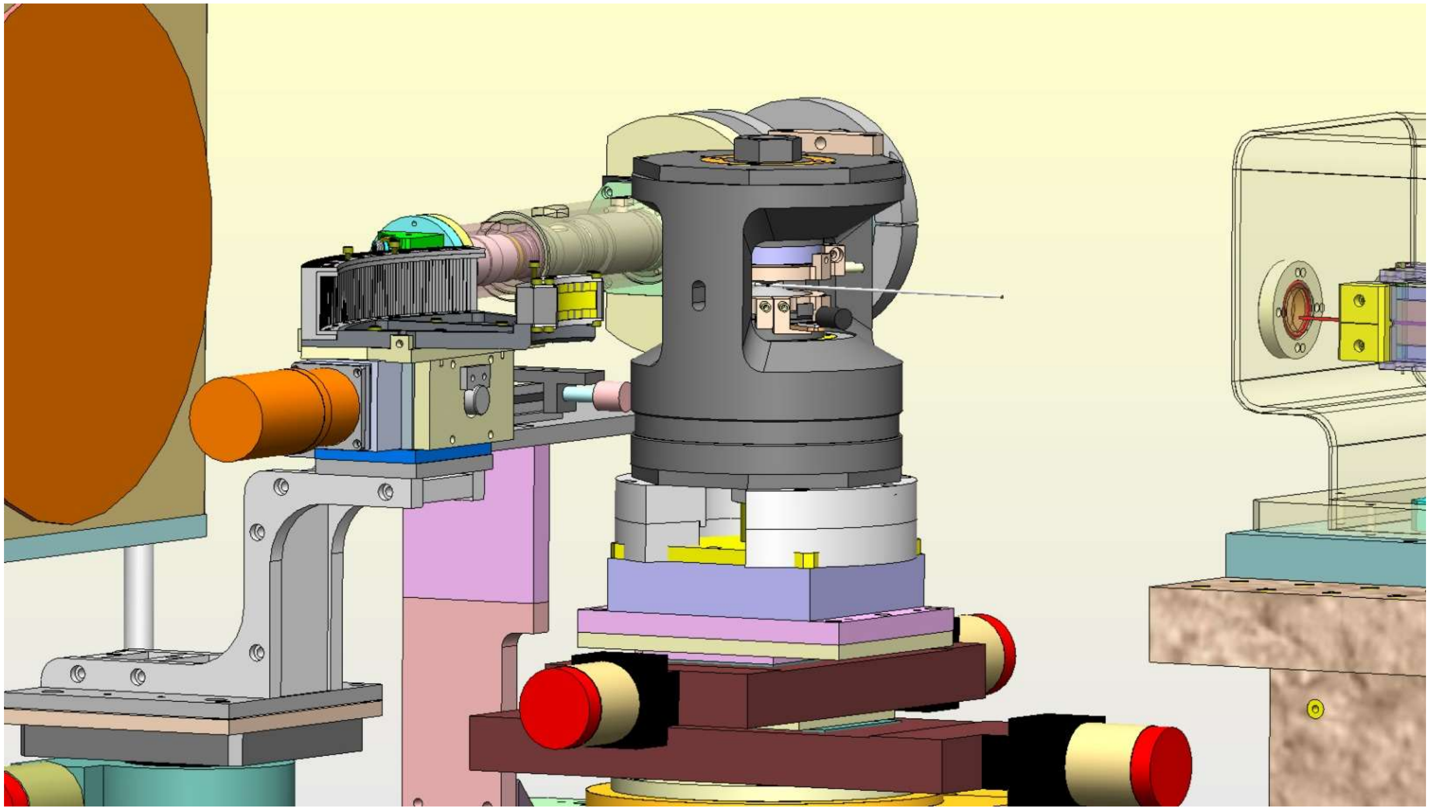




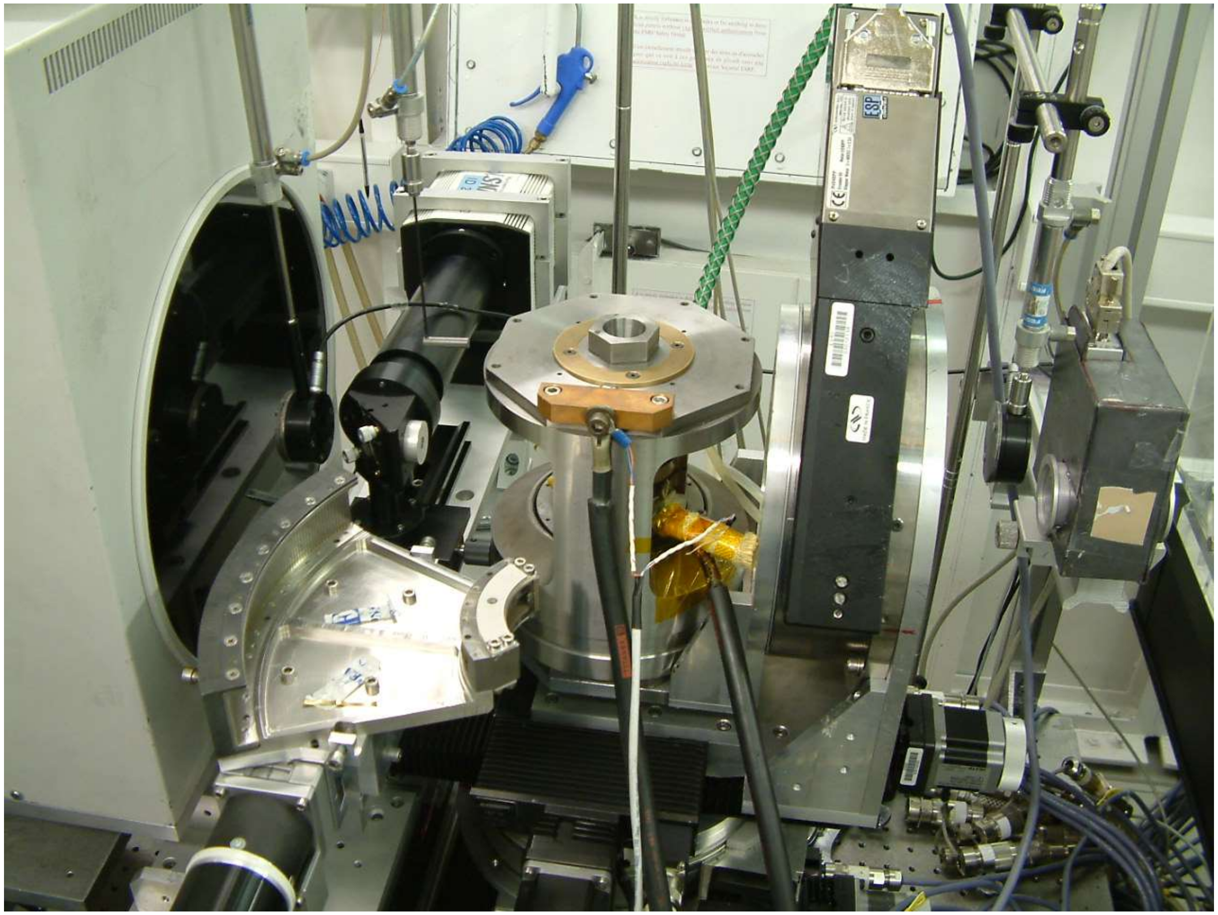
Front slits: 100 microns
Back slits: 300 microns
Ω= Sample position
Sphere of confusion = 3 microns
Oscillation angle=0.8°

2 degrees of freedom only
(1 translation, 1 rotation)
⇒Easy to align

Soller slits system

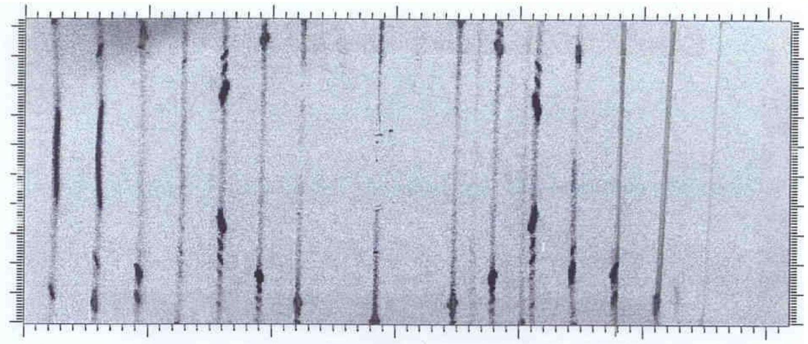


Soller slits system

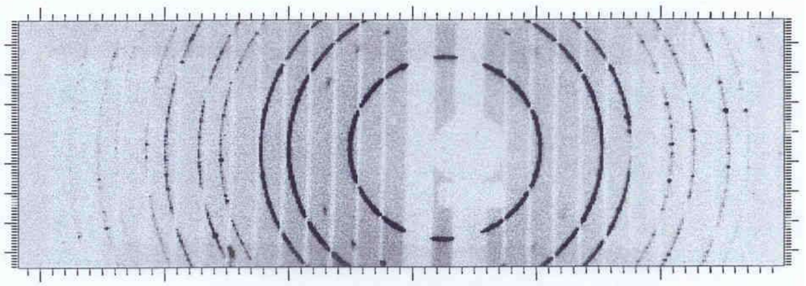


Soller slits system

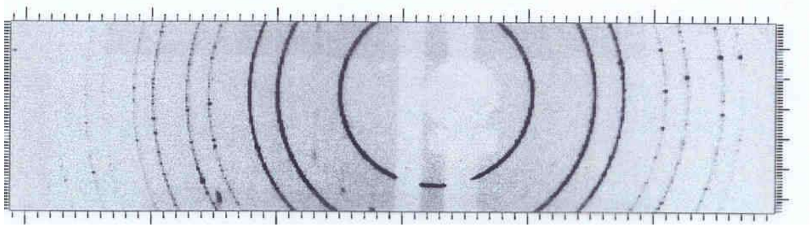
Ω=0°

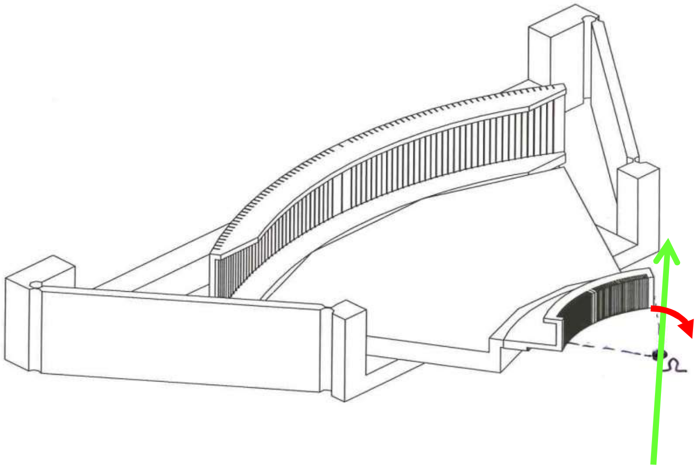


Ω=0.7°



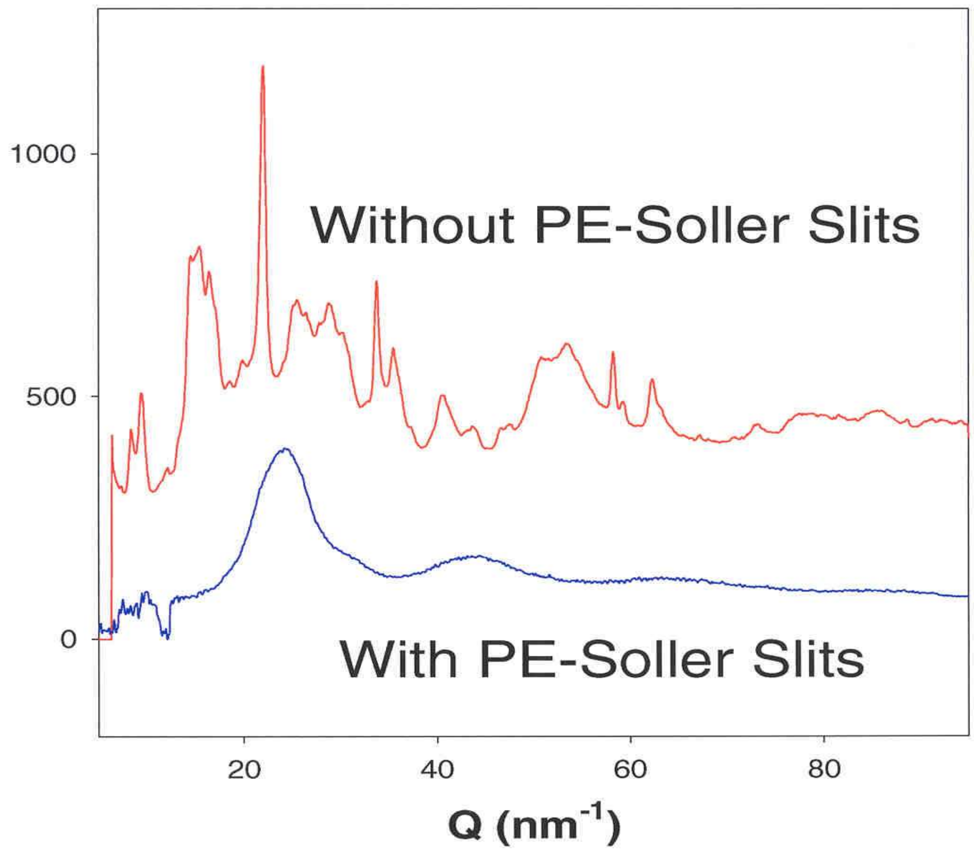
Ω=0.8°





Background reduction

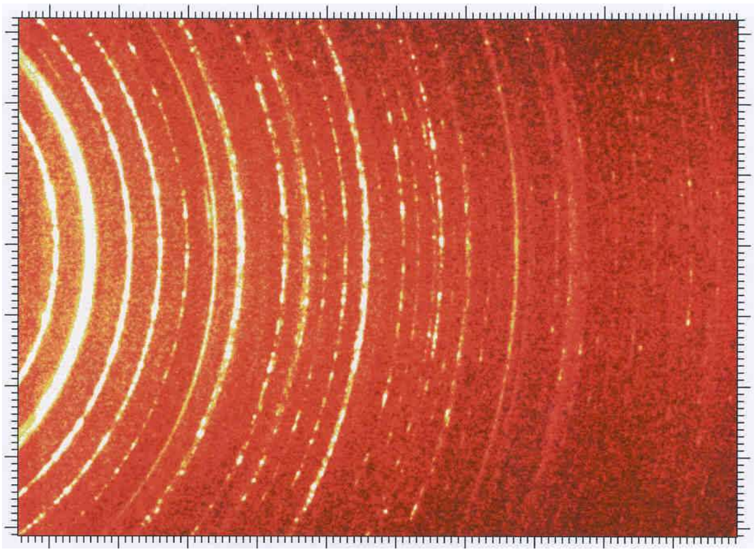
Liquid tin at P=4 GPa and T=750 K

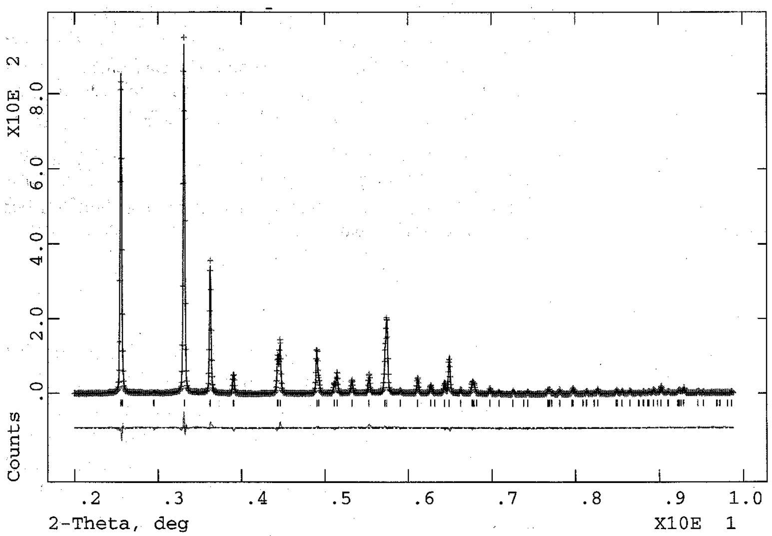


Spectacular improvement of signal to noise ratio!

The soller slits system is also routinely used for powder X-ray dffraction

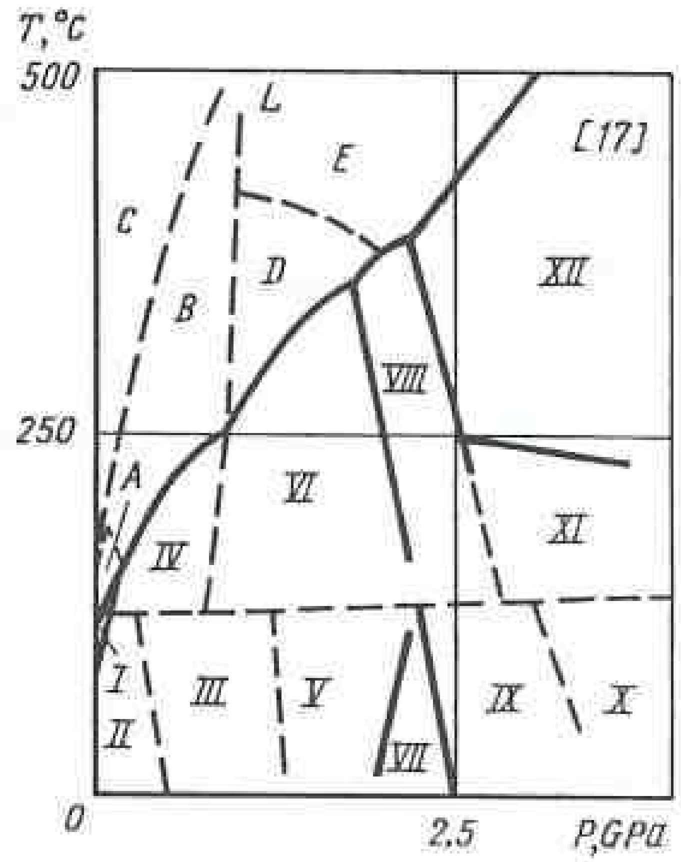
Polymeric sulfur at P=3GPa
and T=550 K





"In situ" versus "quenched" - Sulfur -

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



- Phase diagram based on "quenching" experiments

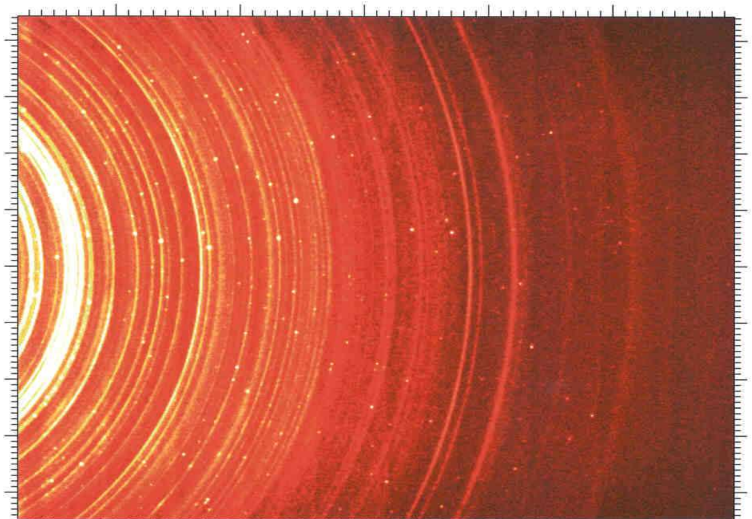
- 12 solid phases identified
(Only 3 with known structures, I, II, XII)

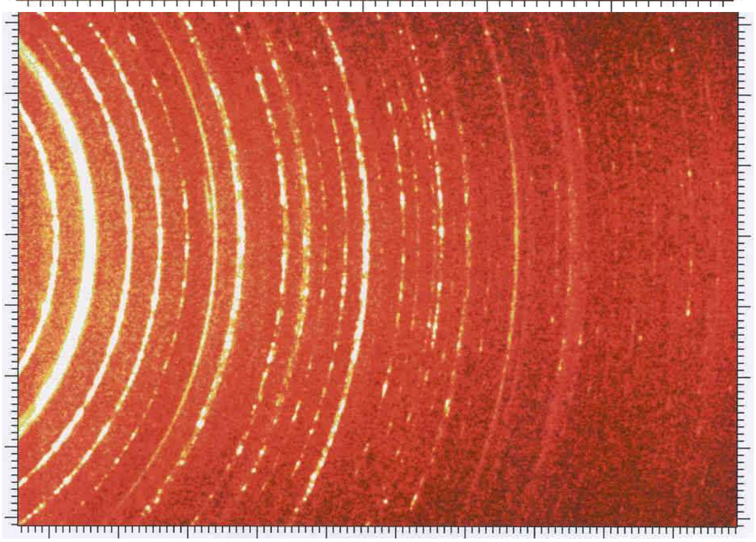
Question:

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

→In situ investigation at high P and T

"In situ" versus "quenched" - Sulfur -

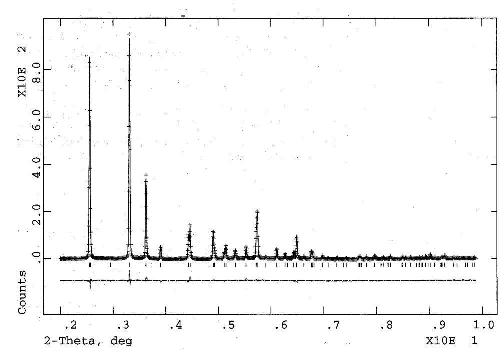


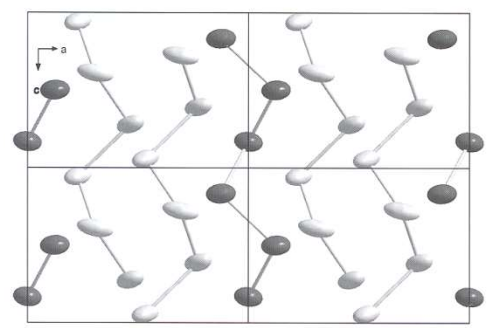


At RT-RP, Orthorhombic Fddd based on S_8 rings (molecular units)

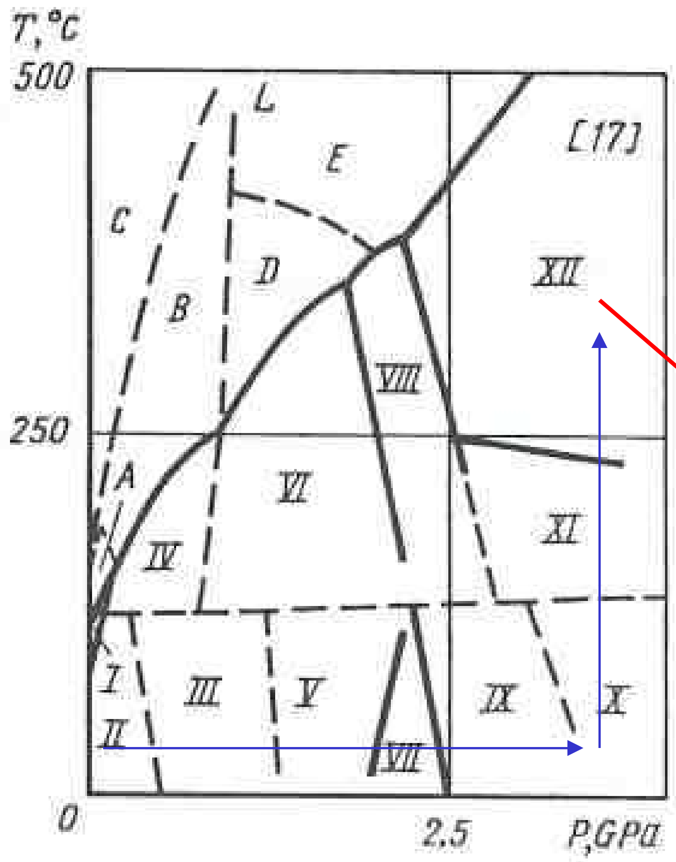
P=3GPa T=600K

Hexagonal $P3_221$



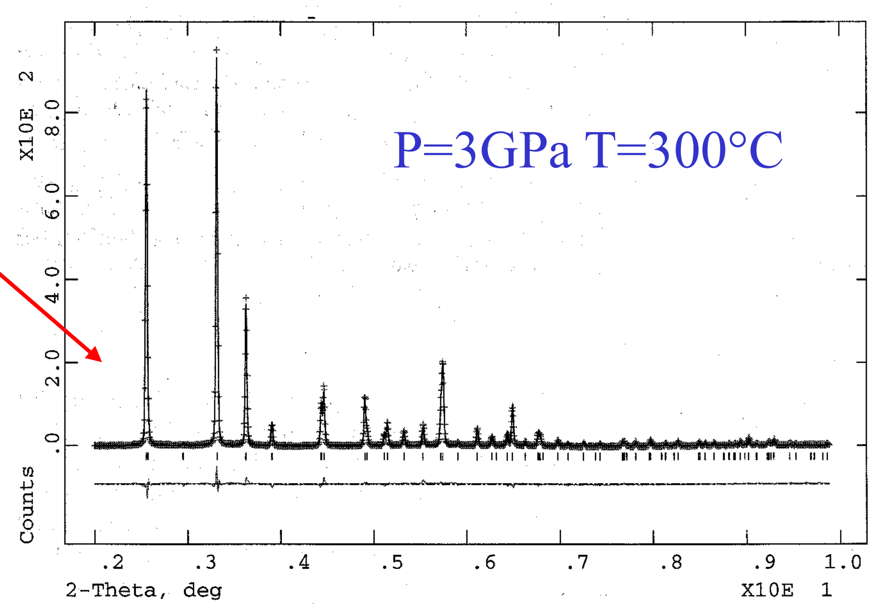


"In situ" versus "quenched" - Sulfur -

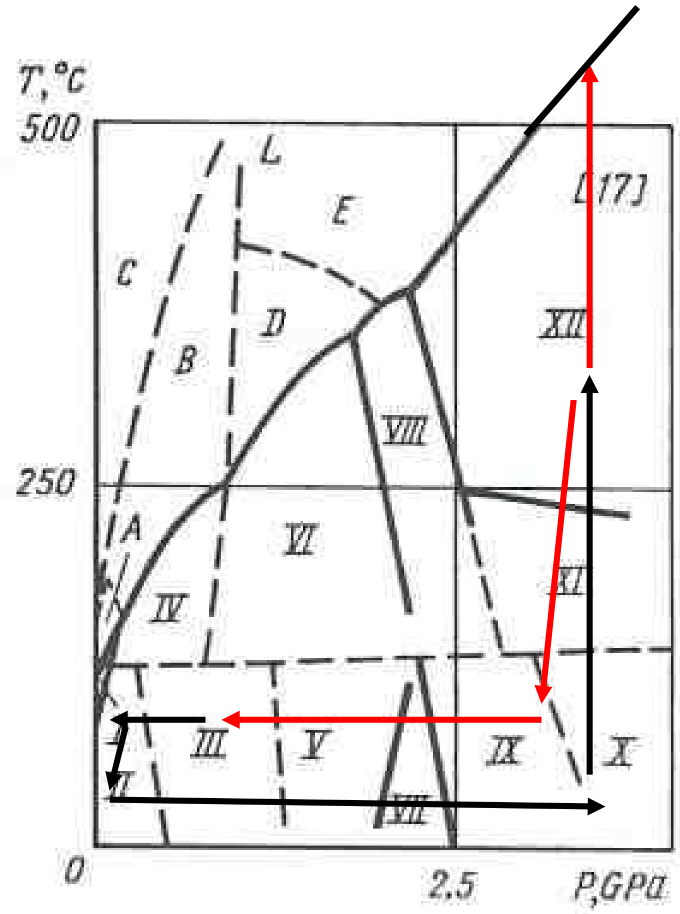


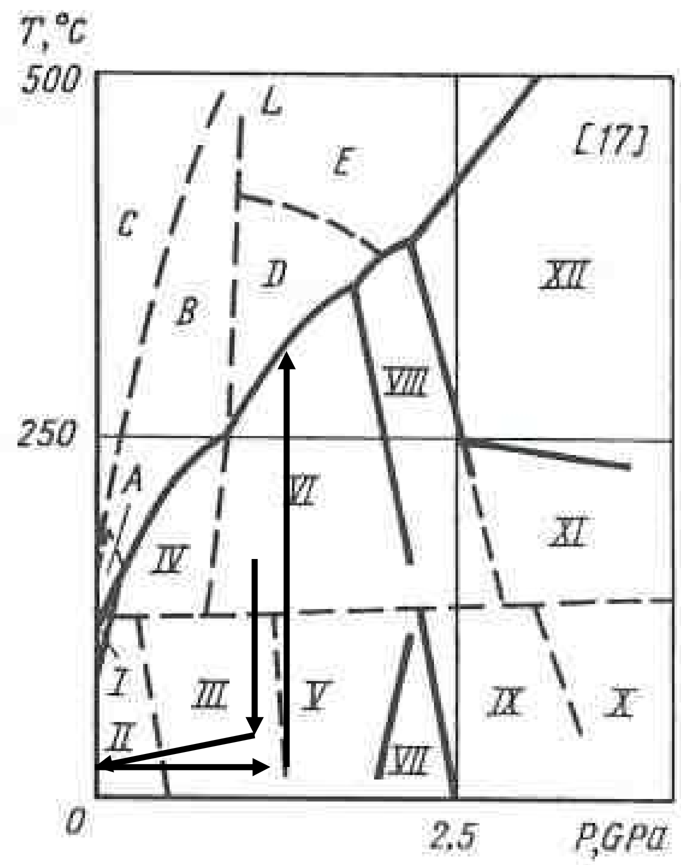
Direct Transformation

Ortho. Fddd → Hexagonal $P3_221$



Phase XII previously identified as monoclinic P2

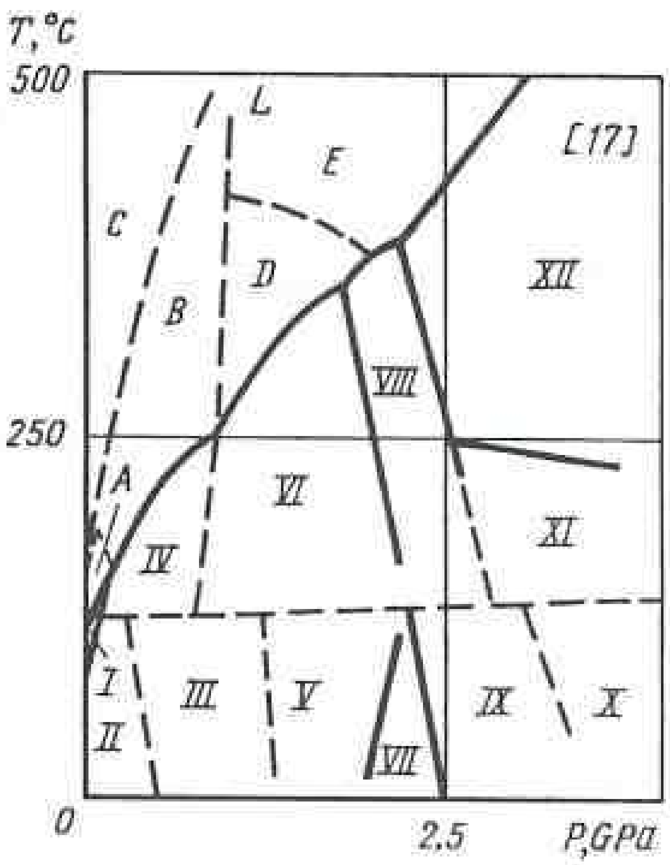




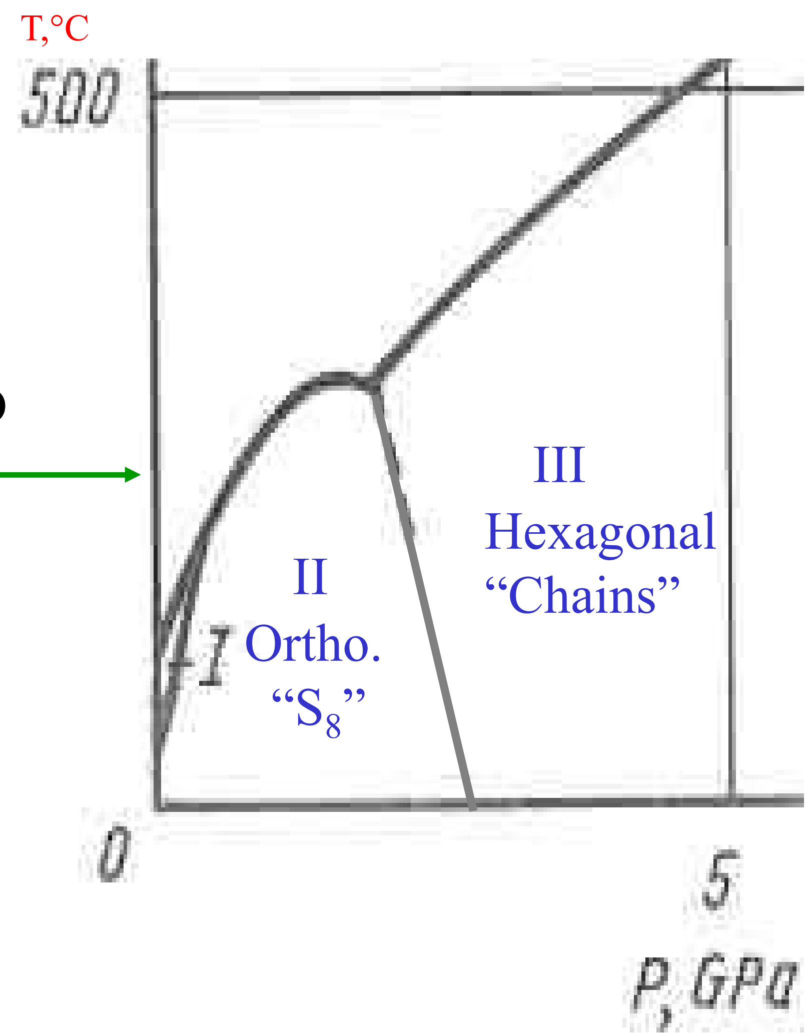
$P3_221$ (Hexagonal)

Fddd (Orthorhombic)

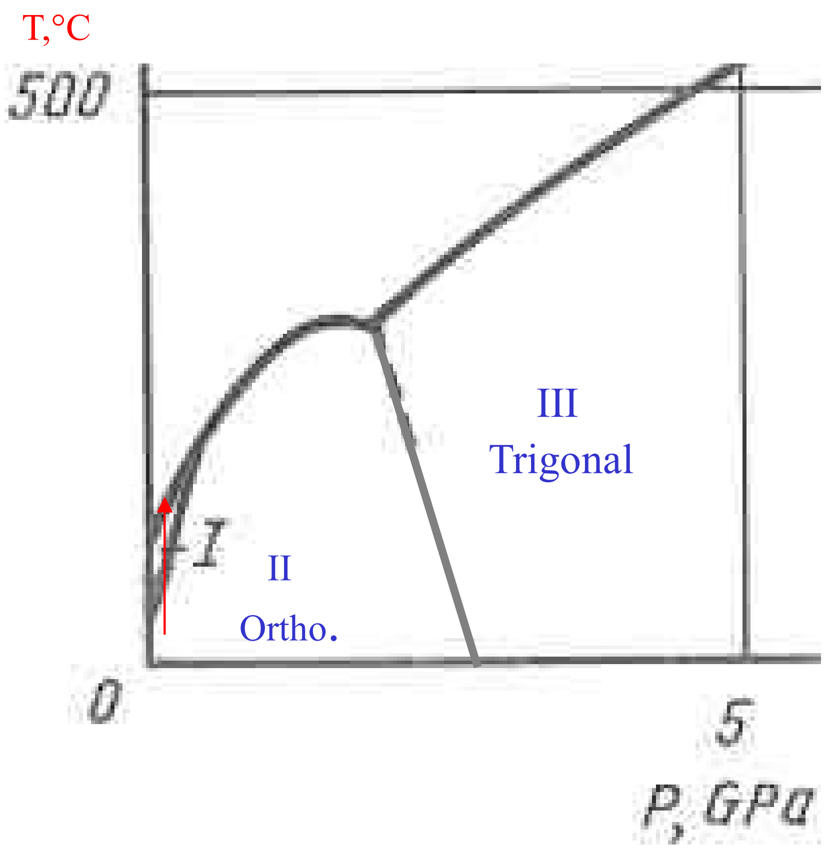
$P3_221$ kinetically inhibited at pressures below 1.5 GPa


T,°C
500
250
0
2.5
P,GPa
[17]
L
E
C
D
B
A
XII
VIII
VI
XI
IV
I
II
III
V
VII
IX
X

In situ XRD


T,°C
500
0
5
P, GPa
I
II
Ortho.
“S_8”
III
Hexagonal
“Chains”

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



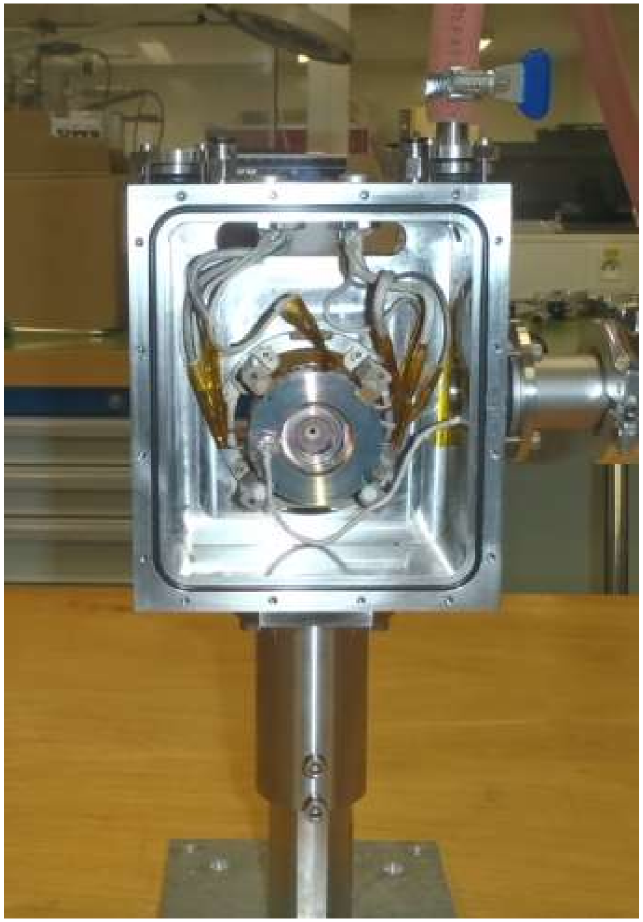
Phase I is monoclinic with space group P21/c. This phase exists in a very narrow P-T domain below the melting curve.

Question:
Is it a stable or metastable phase?

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

Resistively heated diamond anvil cell

Resistive heating system



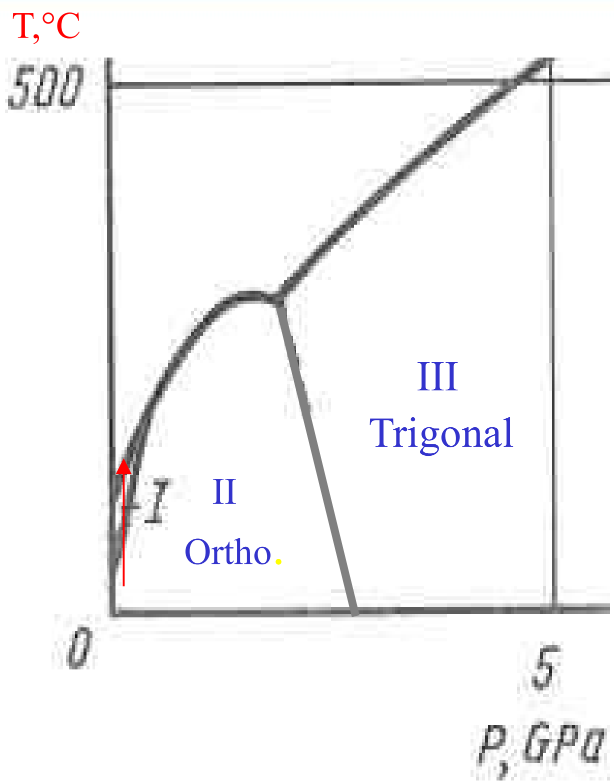
Main Features:

•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

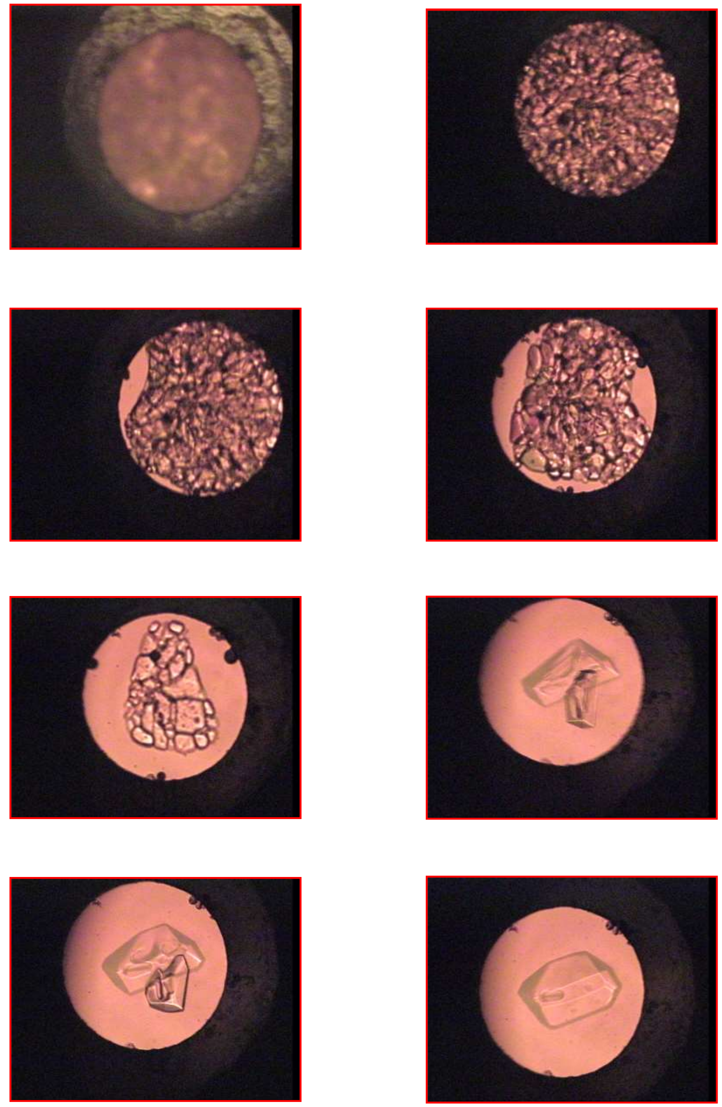


Isobaric growth of sulfur I at P=0.3 GPa

T=90°C

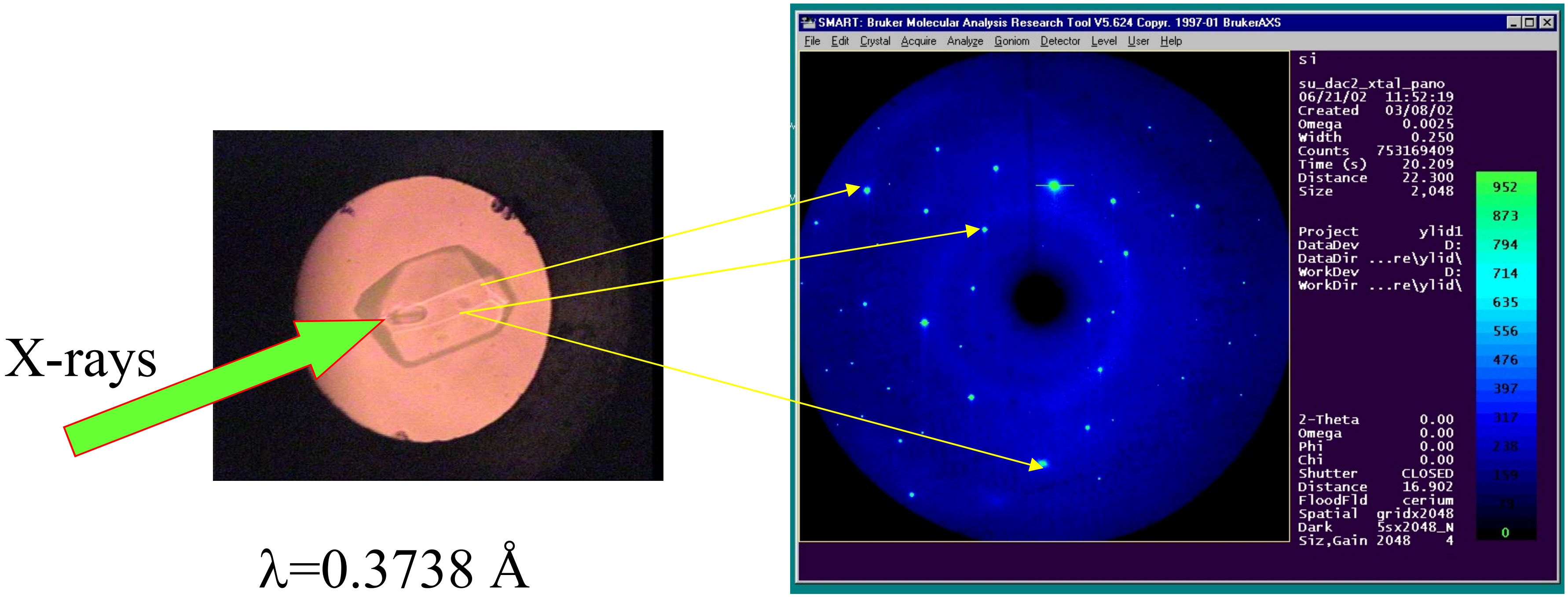
T=110°C

T=112°C



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

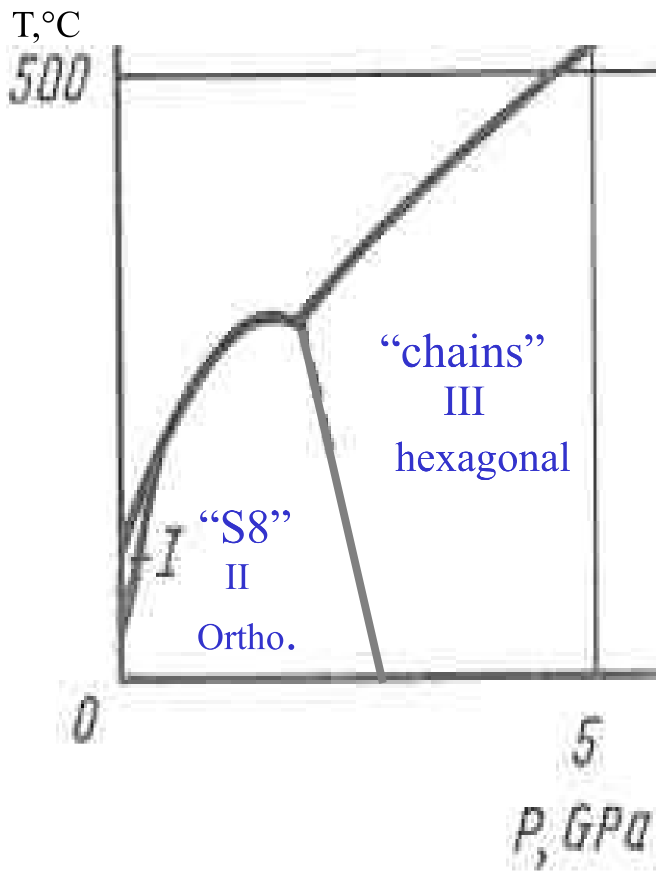
"In situ" versus "quenched" - Sulfur -



λ=0.3738 Å

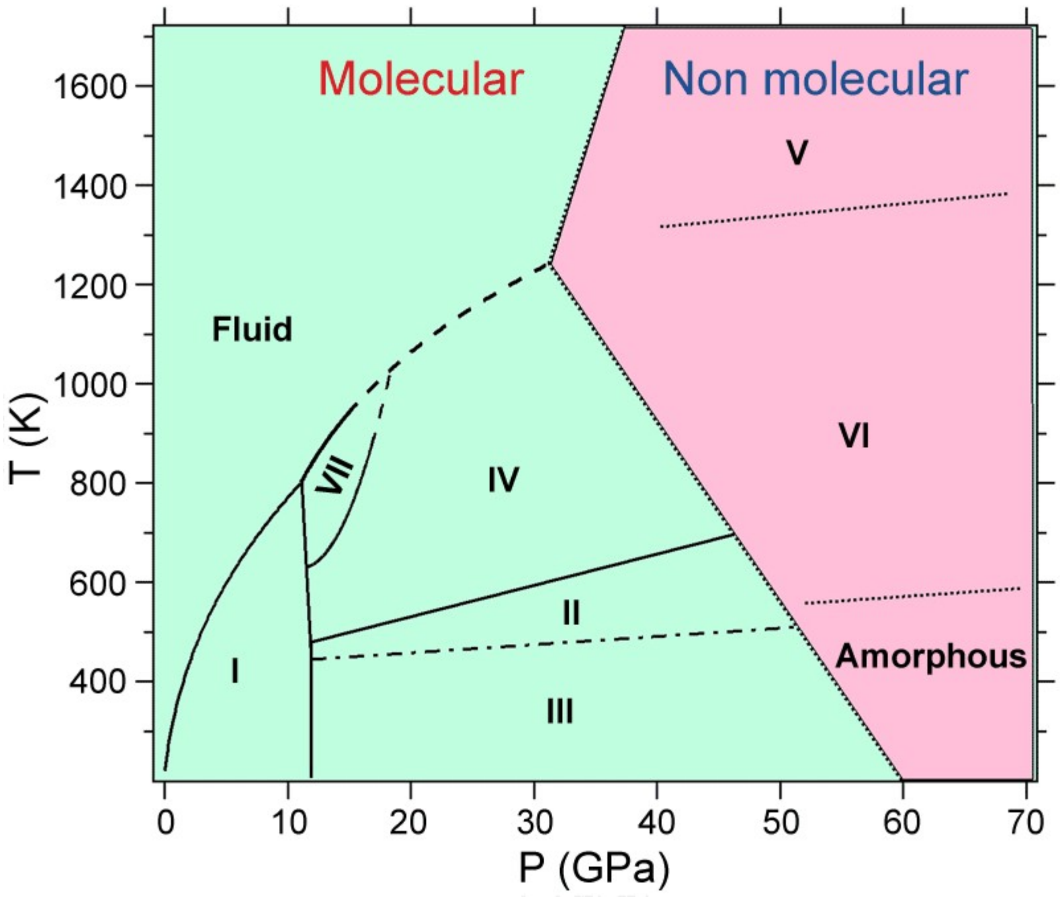
monoclinic P21/c symmetry
NOT orthorombic Fddd

"In situ" versus "quenched" - Sulfur -



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

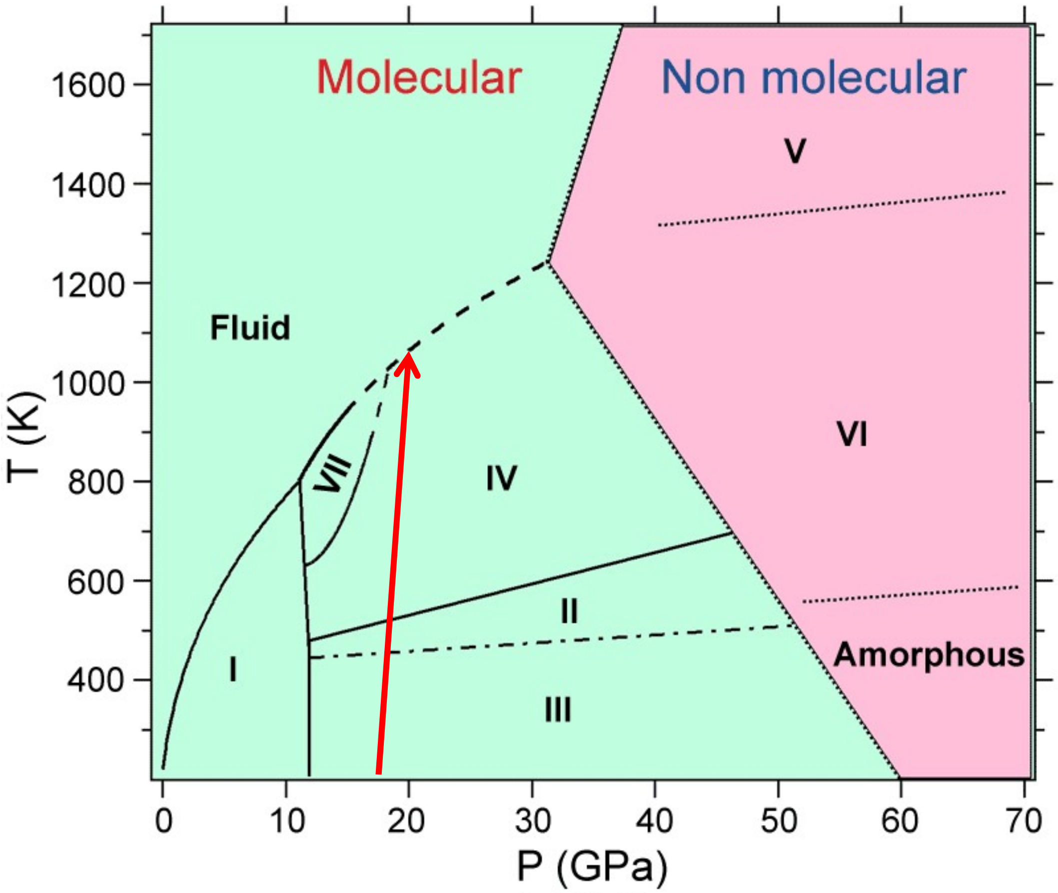
The phase diagram of CO_2



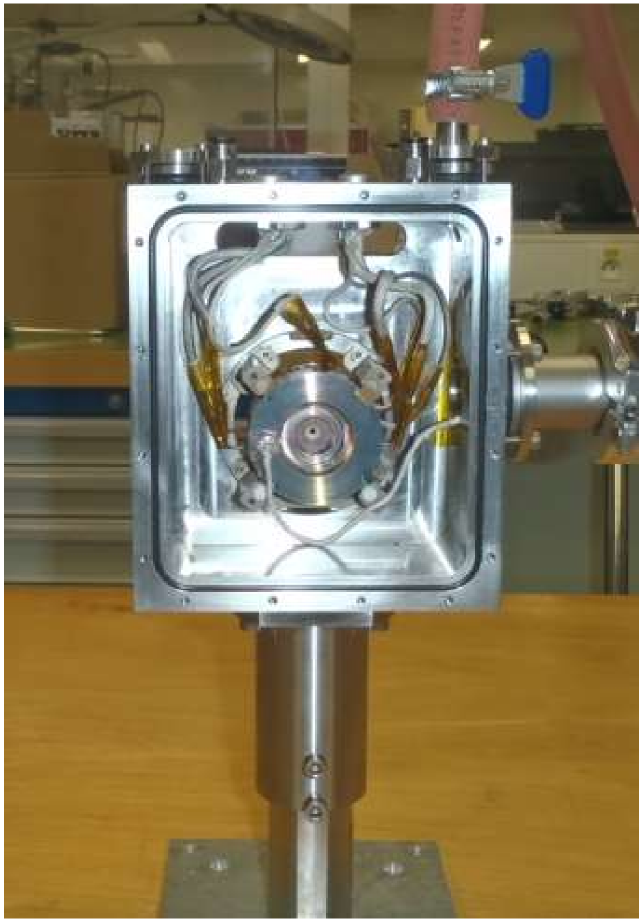
Motivation

- Understand the evolution of molecular bonds at high density
- Structure of phase IV controversial Molecular/non-molecular character?
- Structure of polymeric phase V unknown

Structure of phase IV?



Resistive heating system



<u>Main Features:</u>

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

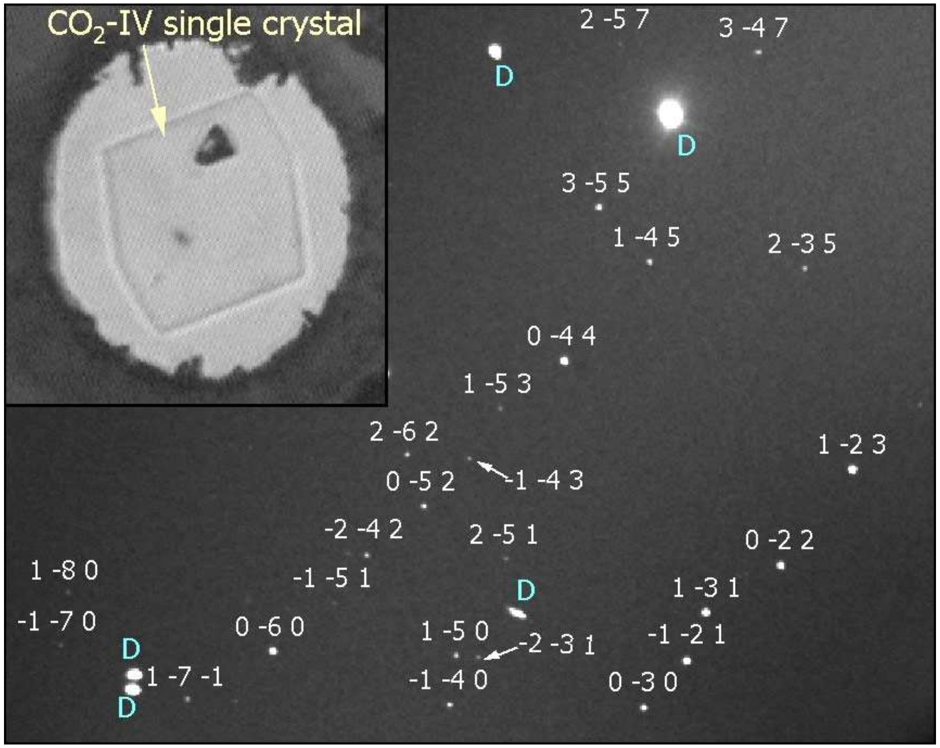
• Max T : 1300 K

• Very good P and T stability

→ 1300 K (2K) for 72 hours

•Similarly to sulfur, a single crystal of CO_2 IV was grown

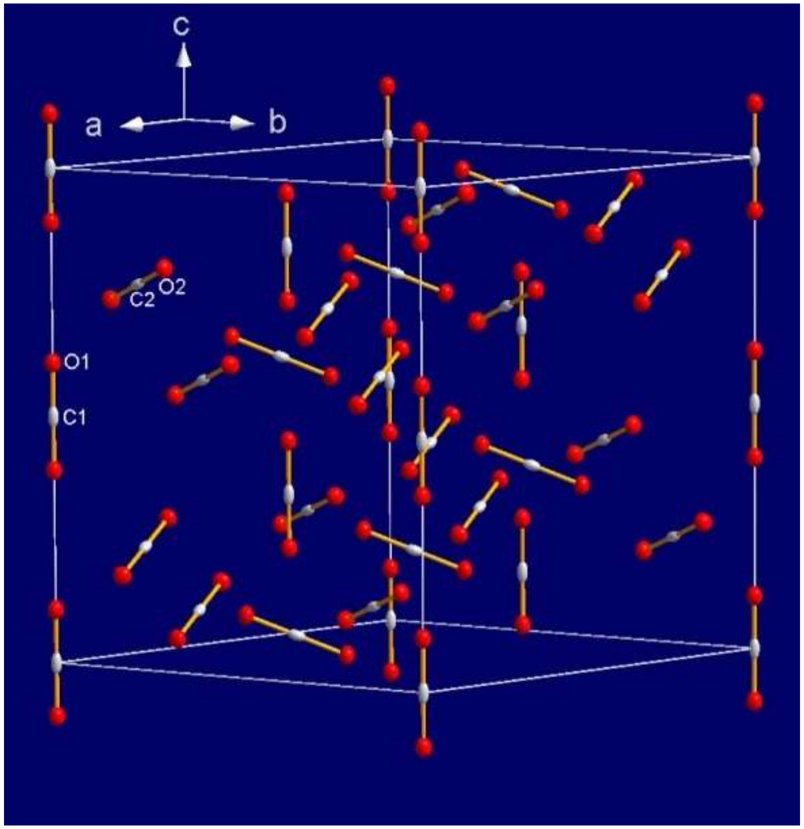
•SXD patterns collected *in situ* at P=20 GPa and T=830 K



From high quality SXD data:

- CO_2 IV is rhombohedral, space group R-3c and not orthorhombic Pbcn.

- CO_2 is still a purely molecular system



Ref: Datchi et al., PRL, 103, 185701(2009)

Solving the structure of Polymeric CO_2-V

Polymeric Carbon Dioxide was discovered in 1999

VOLUME 83, NUMBER 26 PHYSICAL REVIEW LETTERS 27 DECEMBER 1999

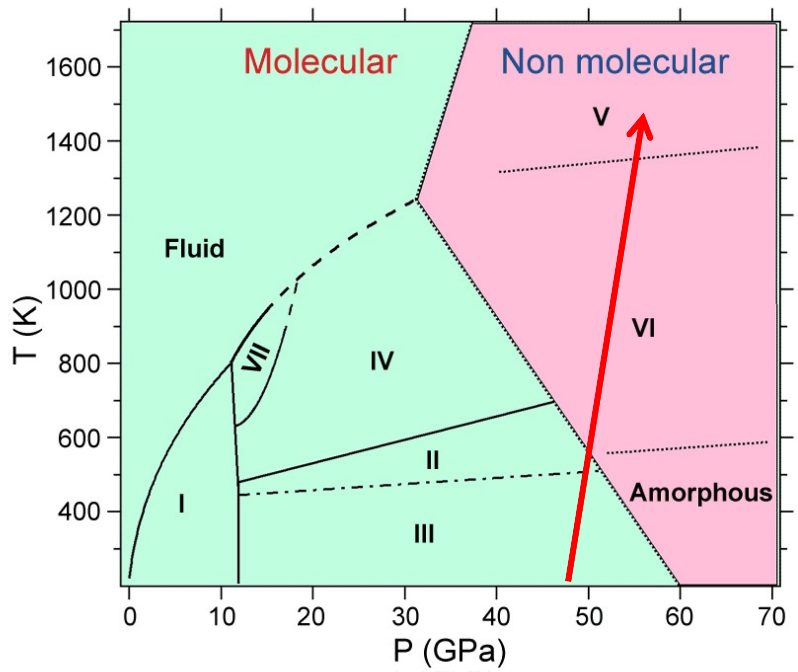
Crystal Structure of Carbon Dioxide at High Pressure: "Superhard" Polymeric Carbon Dioxide

C. S. Yoo,[1] H. Cynn,[1] F. Gygi,[1] G. Galli,[1] V. Iota,[1] M. Nicol,[2] S. Carlson,[3] D. Häusermann,[3] and C. Mailhiot[1]

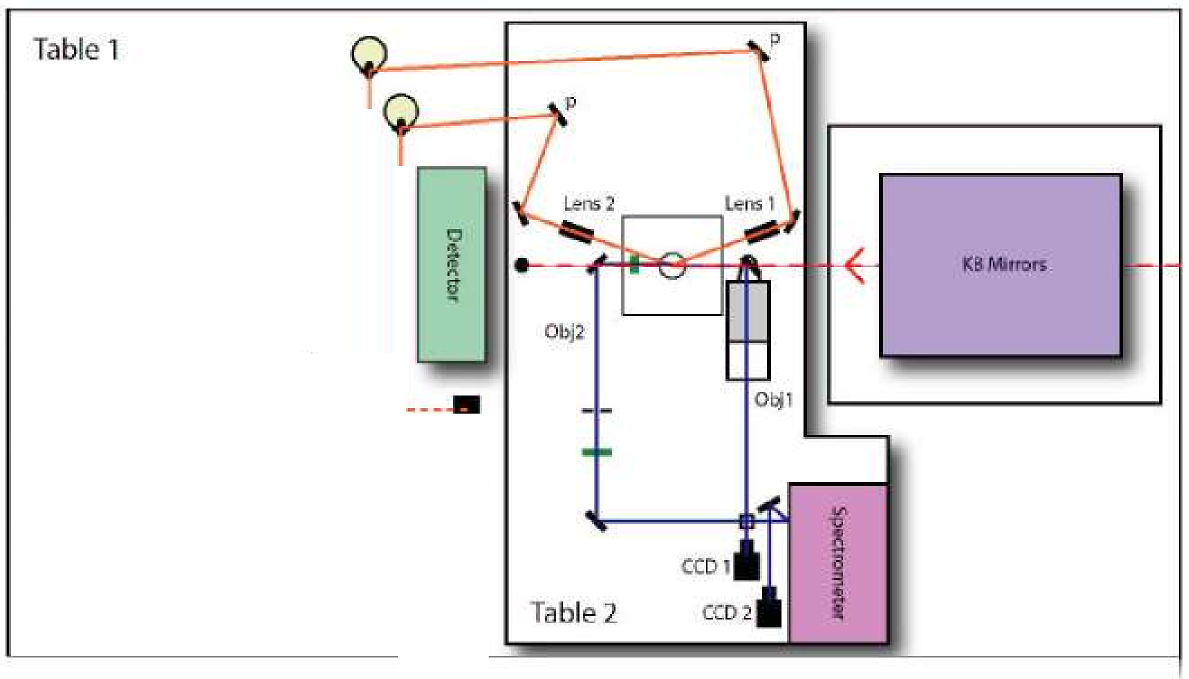
5 MARCH 1999 VOL 283 SCIENCE www.sciencemag.org

Structure of CO2- V?

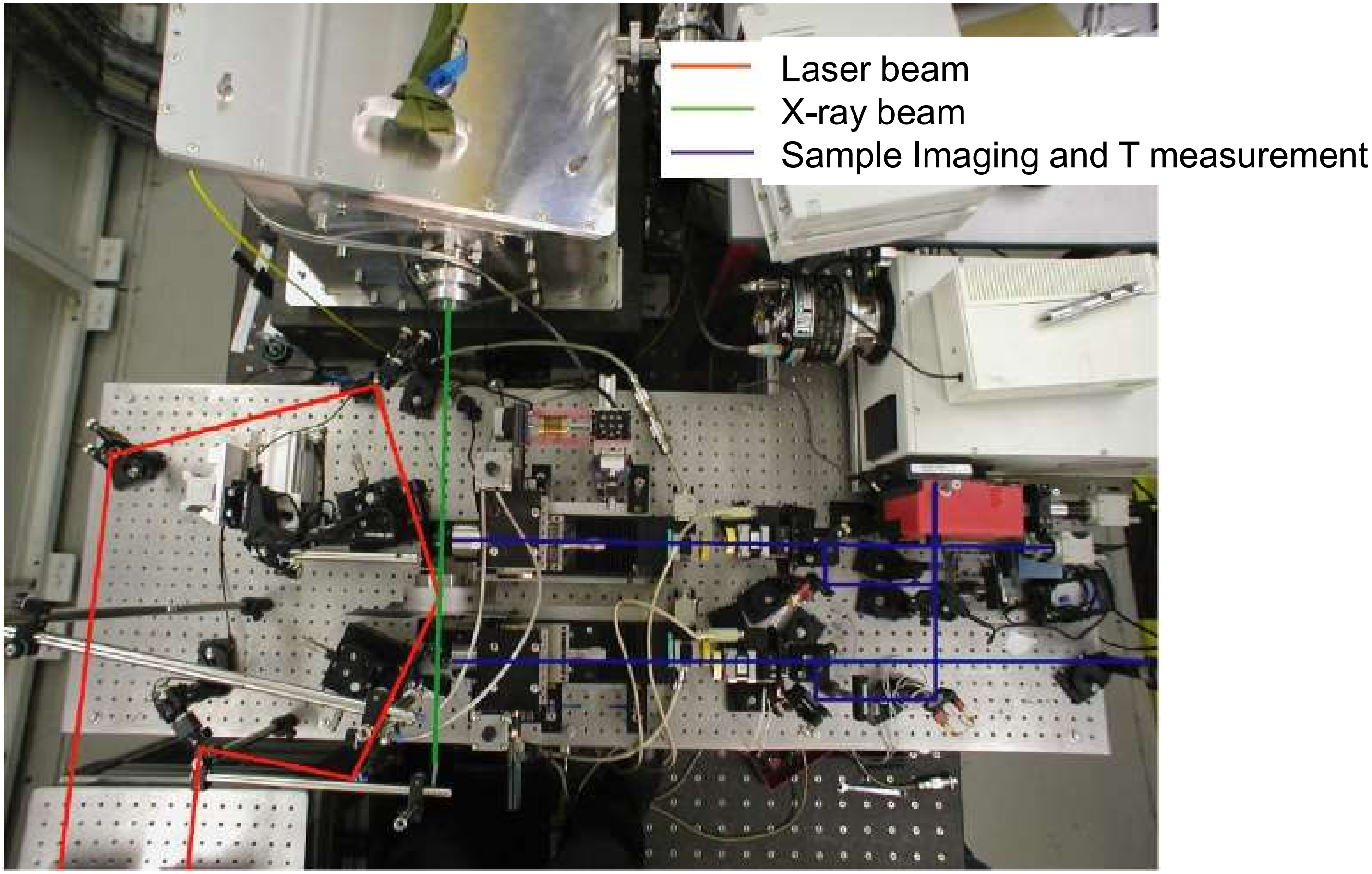
PT conditions beyond the PT limits of the resistive DAC



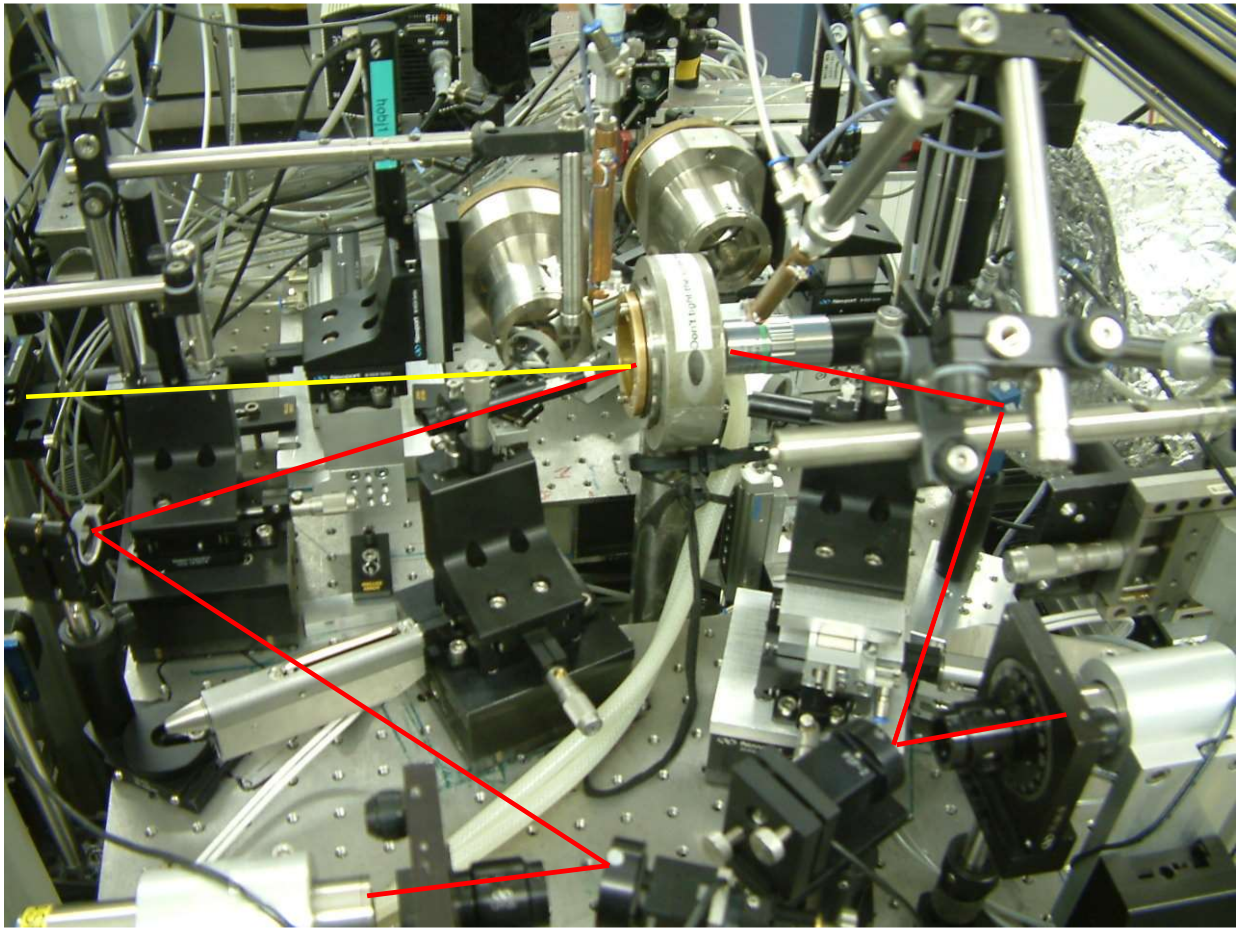
Accessible PT domain for in situ powder XRD: P>2 Mbar; T>5000 K



Double-sided laser heating system at ID27

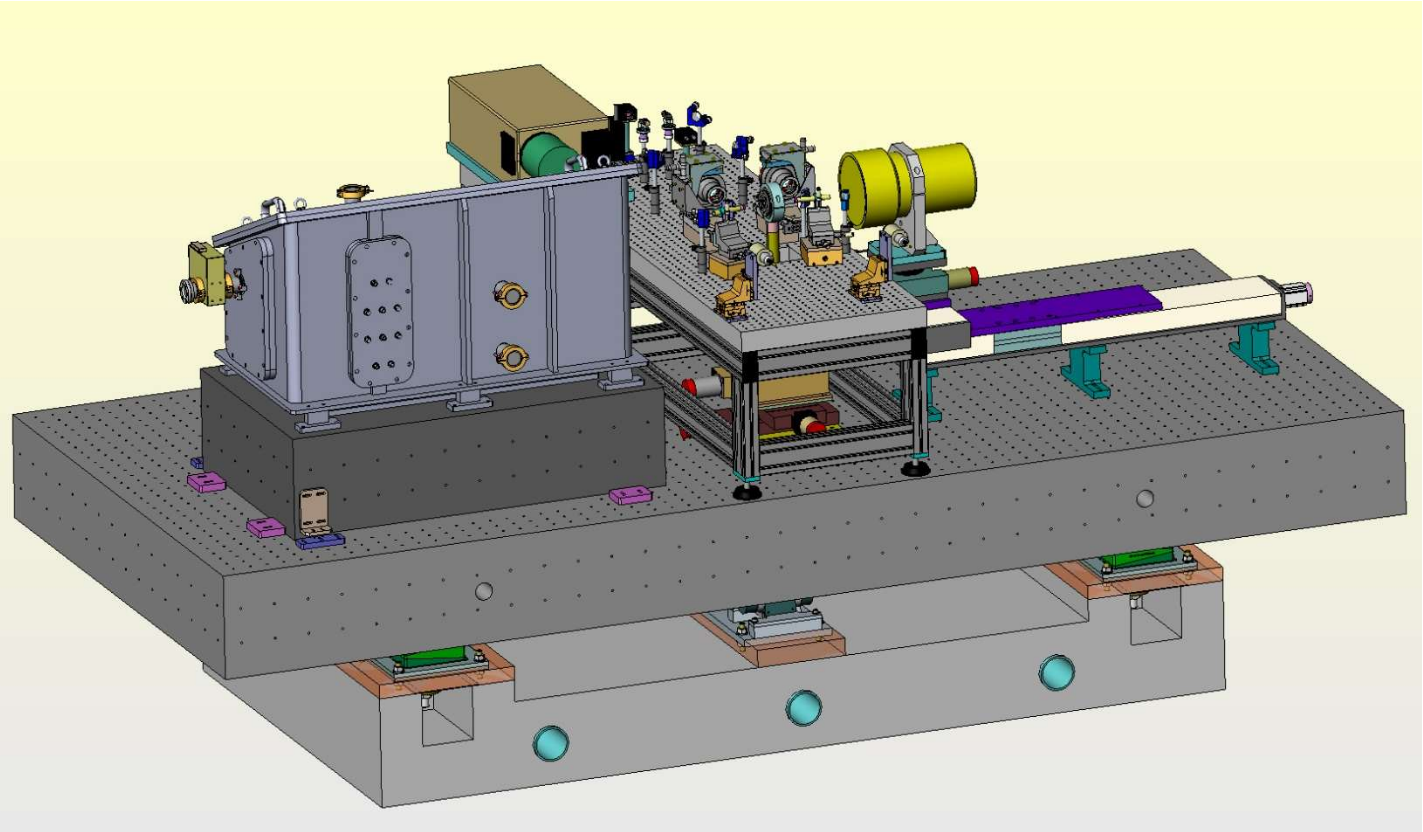


Double-sided laser heating system at ID27

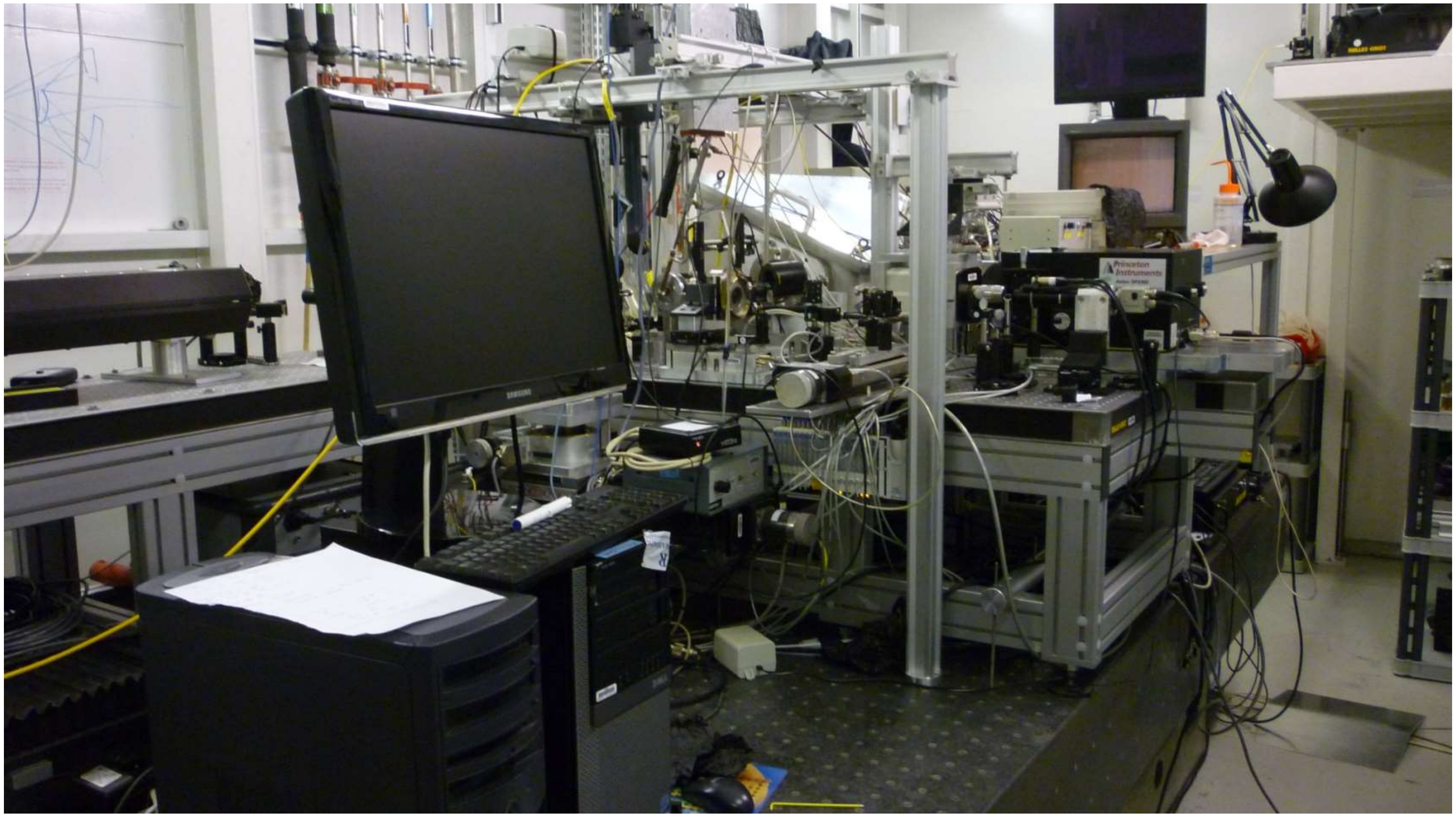


Double-sided laser heating system at ID27

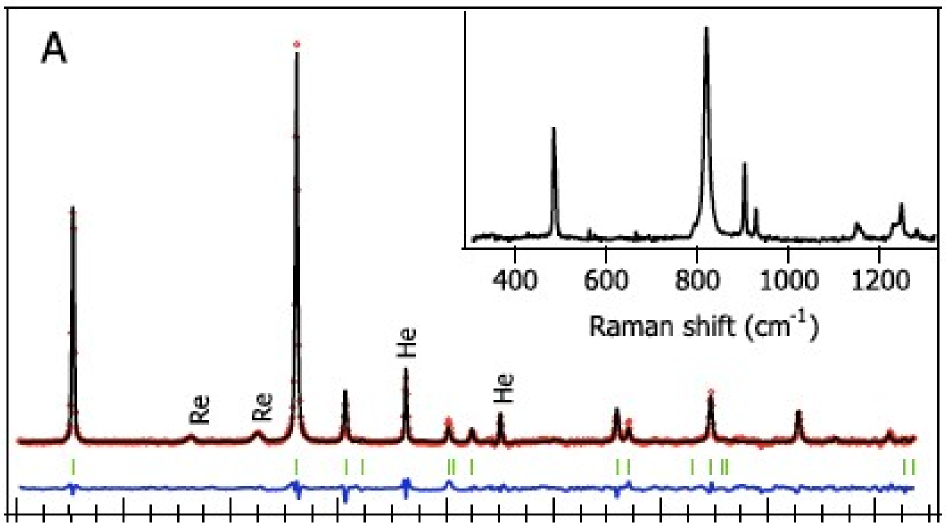
Dedicated experimental hutch – The system is mounted on a high stability 5 tons granite table – High mechanical stability

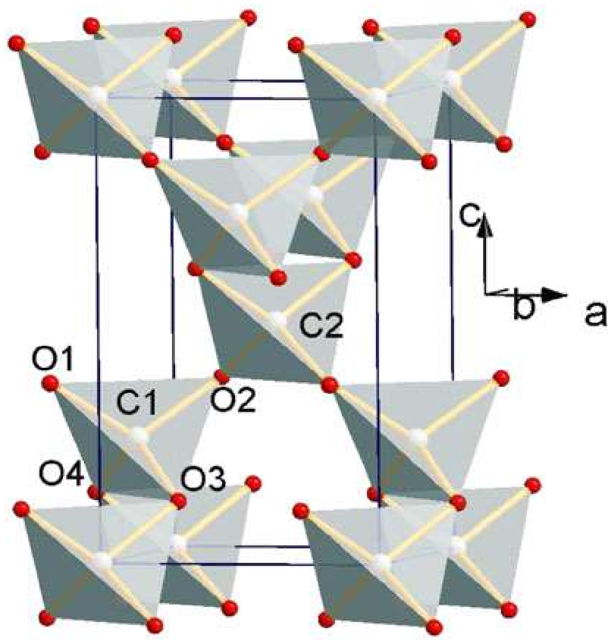


Double-sided laser heating system at ID27



High quality powder pattern of CO_2 V





Structure identified as β-cristobalite (tetragonal; *I*-42*d*)
- Not othorhombic $P2_12_12_1$

Ref: Datchi et al., PRL, 108, 125701(2012)

Formation of cubic BC2N and BC5

- Economy of super-abrasive materials
- Synthesis of cubic BC_2N and BC_5 with remarkable physical properties

V. L. Solozhenko, O. O. Kurakevych, LPMTM, Paris, France
D. Andrault, LVM, Clermont-Ferrand, France
Y. Le Godec, IMPMC, Paris, France

Economy of super-abrasive materials

- The economy of super-abrasive materials are essentially oriented toward the machining and polishing industry.

- In Y2010, the annual production of synthetic diamonds is estimated ~650 million carats

- The annual production of synthetic diamond and c-BN represents ~1 billion US dollars

- This market is growing at an annual rate of 12%

Formation of cubic BC2N and BC5

However

Diamond and c-BN are far from being perfect abrasive materials

⇒Diamond is thermally and chemically unstable in presence of oxygen

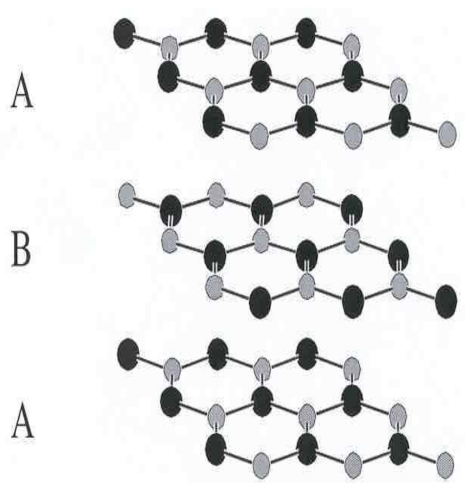
Major problem for the machining of ferrous materials (steel)

⇒c-BN: thermally and chemically stable but not as hard as diamond

Formation of cubic BC2N and BC5

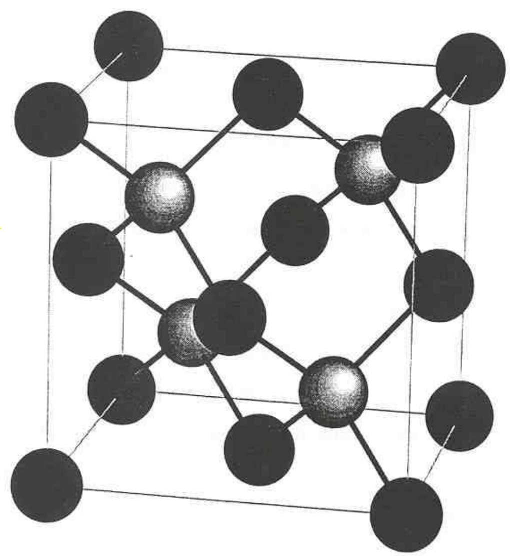
In some cases, the synthesis of superhard phases is very difficult to make using chemical methods due to phase separation problems.

⇒Use of HP-HT techniques in laser-heated DACs



Graphite-like structure

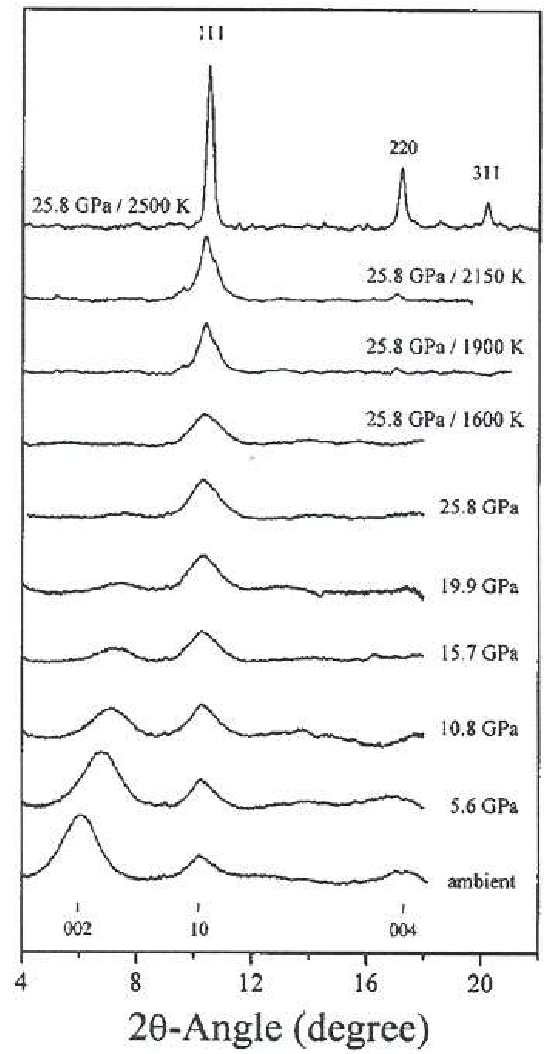
HP, HT



Diamond-like structure

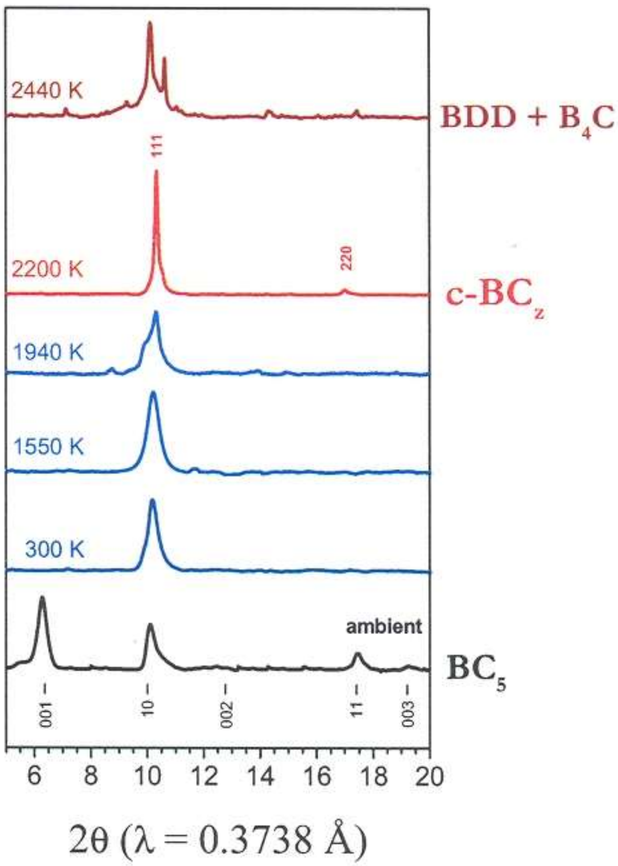
Formation of cubic BC2N and BC5

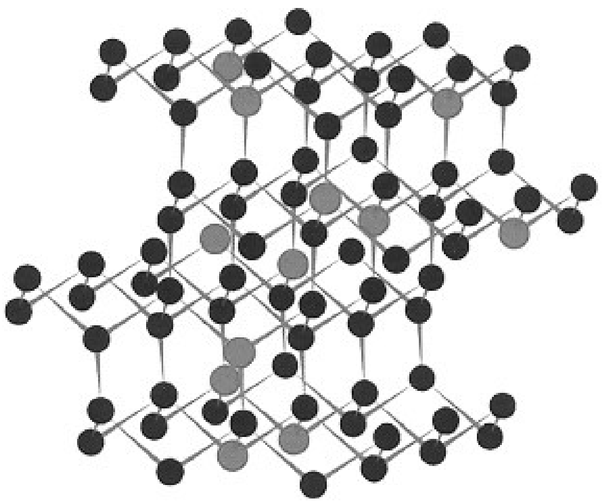
Formation of c-BC2N from g-BC2N in the laser heated diamond anvil cell at P=25 GPa and T=2500 K



Reference: V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, D.C. Rubie, Synthesis of cubic BC2N, a new superhard phase, Appl. Phys. Lett., 78, 1385 (2001)

Formation of cubic BC2N and BC5





$g\text{-}BC_5 \rightarrow c\text{-}BC_5$ at P=20 GPa and T=2200 K

Super-hard Cubic BC_2N and BC_5

Outstanding mechanical properties

Table 1 Mechanical properties of superhard phases of the B–C–N system.

	Vickers hardness (GPa)	Nanohardness (GPa)	Fracture toughness (MPa $m^{0.5}$)
c-BC_5	71[†]	73[†]	9.5[†]
B_4C	38[36*]		3-4[37*]
cBN	62[24*]	55[24*]	2.8[24*]; 6.8[24†]
c-BC_2N	76[12,24†]	75[12,24†]	4.5[24†]
diamond	115[25*]		5.3[25*†]

Cubic BC_2N and BC_5 respectively second and third in hardness after diamond and thermally stable up to 1900 K in oxygen atmosphere

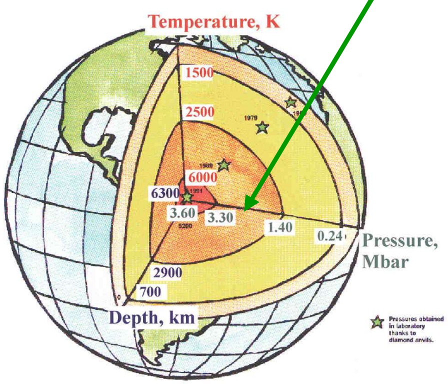
Physics, chemistry and biology

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

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

•Melting curves

Liquid Fe



Geophysics

•Determination of planets cores structures

•Effect of light elements

•Water in the Earth's upper mantle

•Magmas...

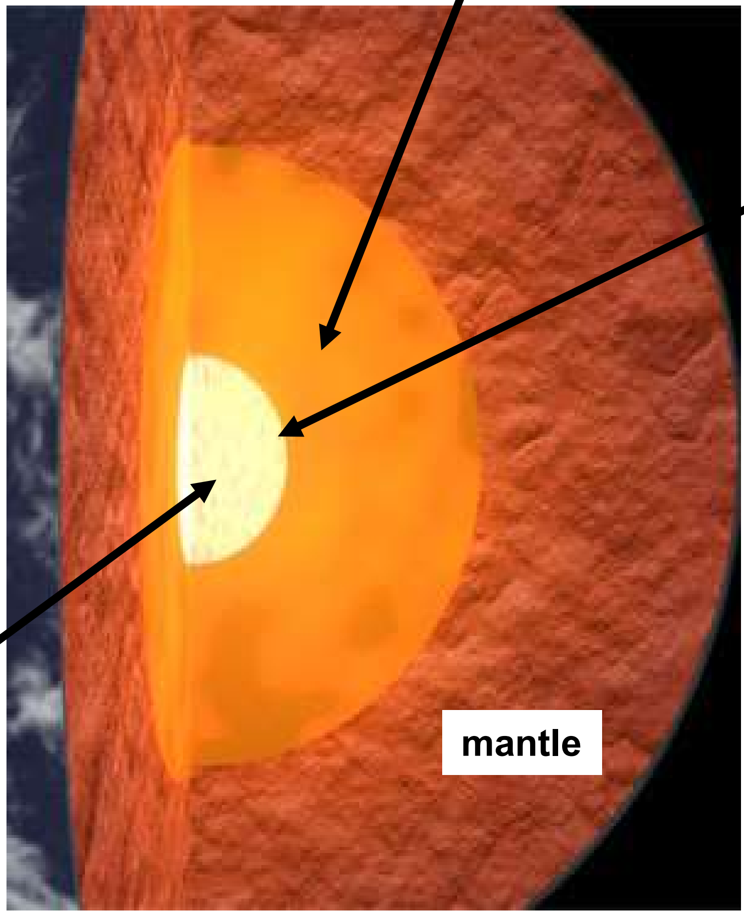
MELTING CURVE OF IRON TO 200 GPA

- 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



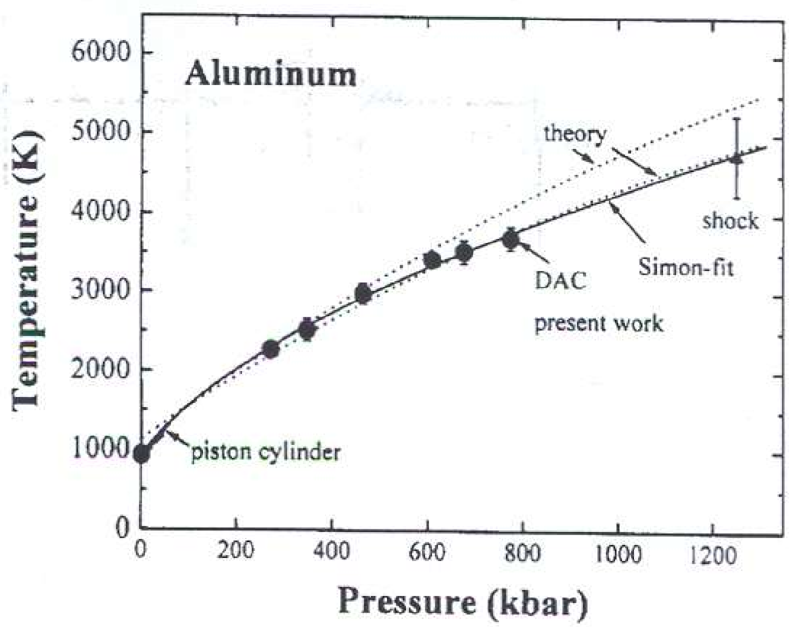
Melting at HP

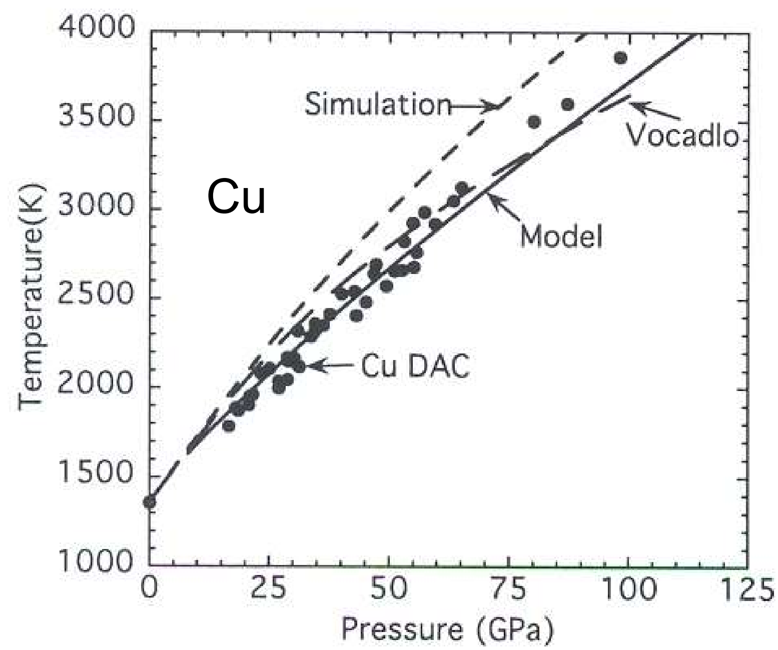
Two classical experimental methods

1. Optical measurements in the laser heated diamond anvil cell (speckle)
2. Melting induced by shock compression

Ab-initio calculations

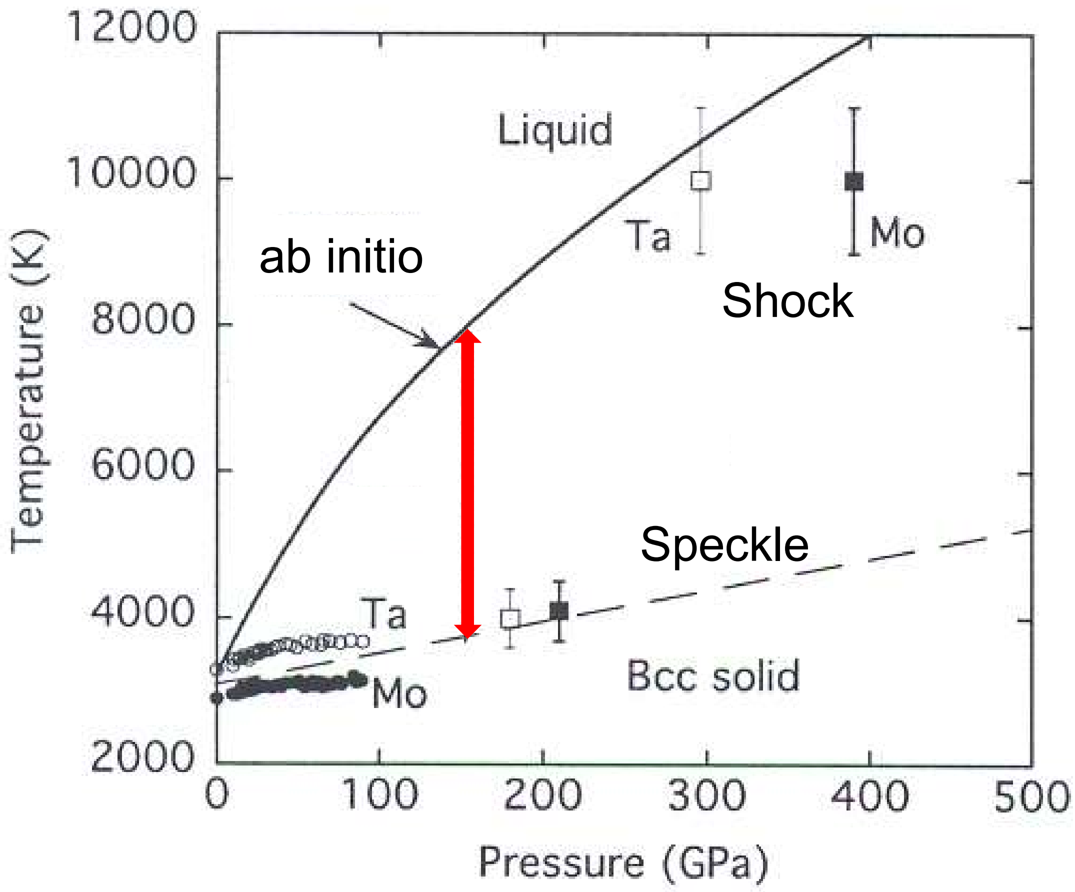
Good agreement between DAC, shock compression and theory for several systems: i.e. Al, Cu



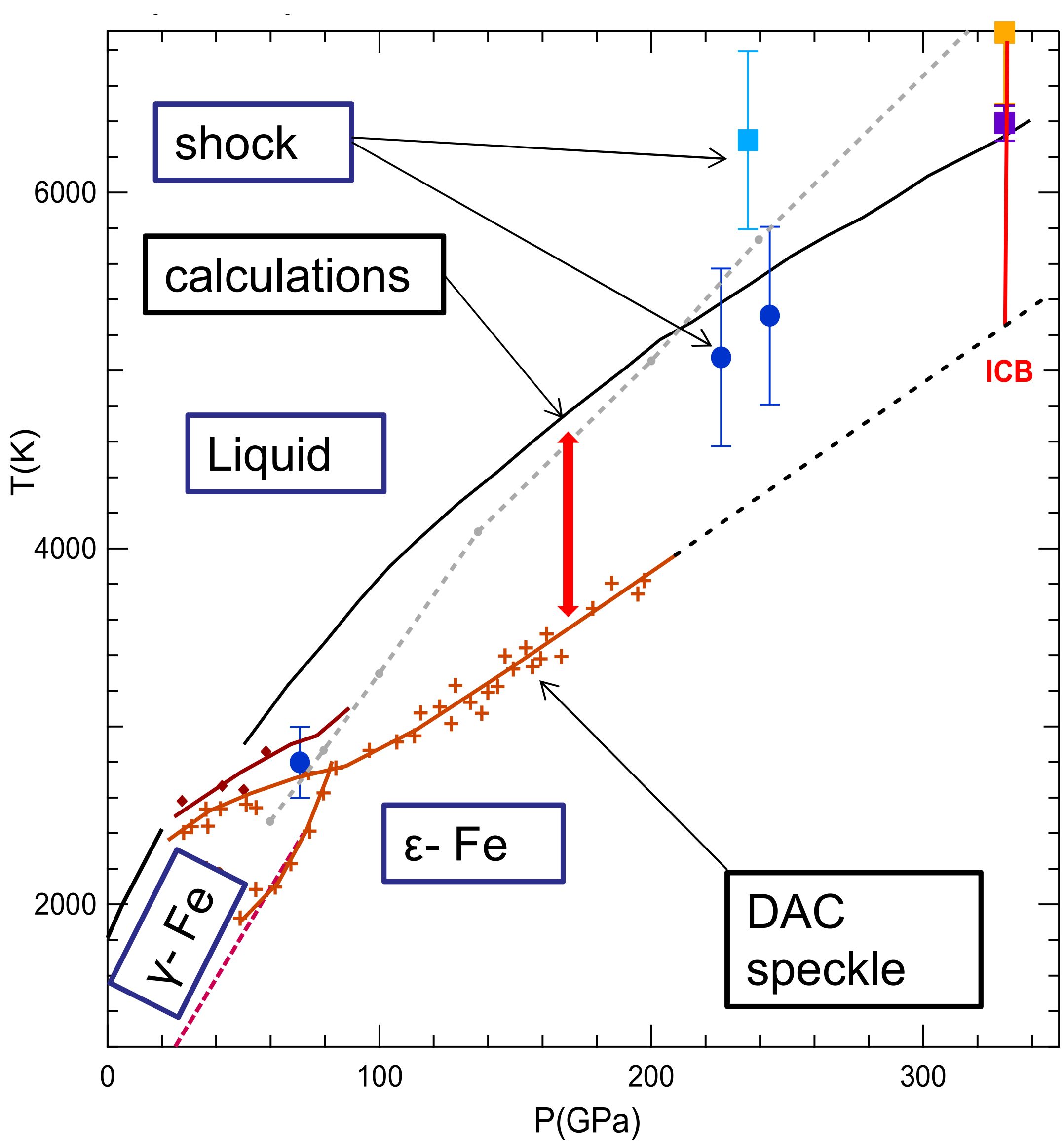


Ref. :
Al : R. Boehler, M. Ross, EPSL, 153, 223 (1997)
Cu: M. Ross, R. Boehler, D. Errandonea, PRB, 76, 184117 (2007)

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

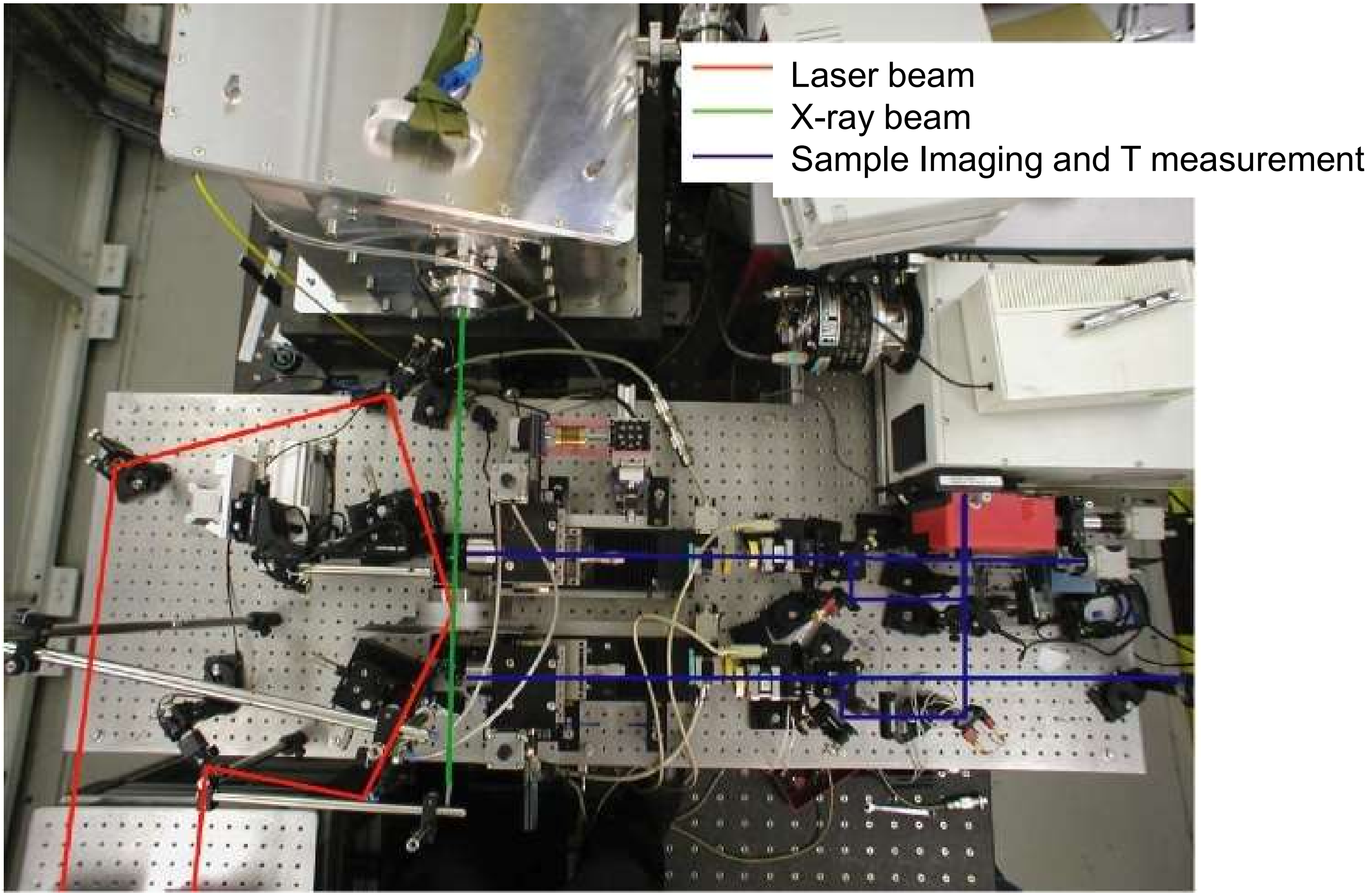
Also very important:

-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

Double-sided laser heating system at ID27

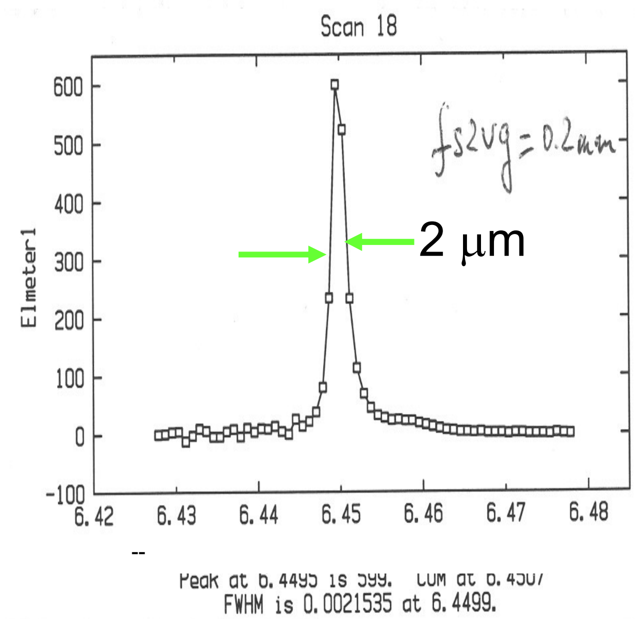
Accessible PT domain for in situ powder XRD: P>2 Mbar; T>5000 K



- Main features:

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

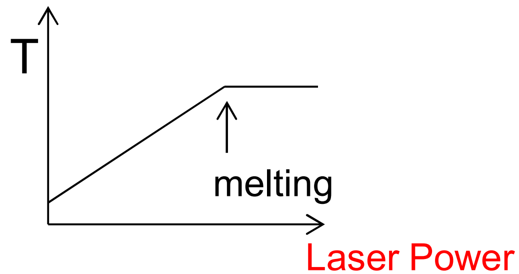
-The temperature increment is ~30 K

-The typical collection time is ~2 seconds

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

In static 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

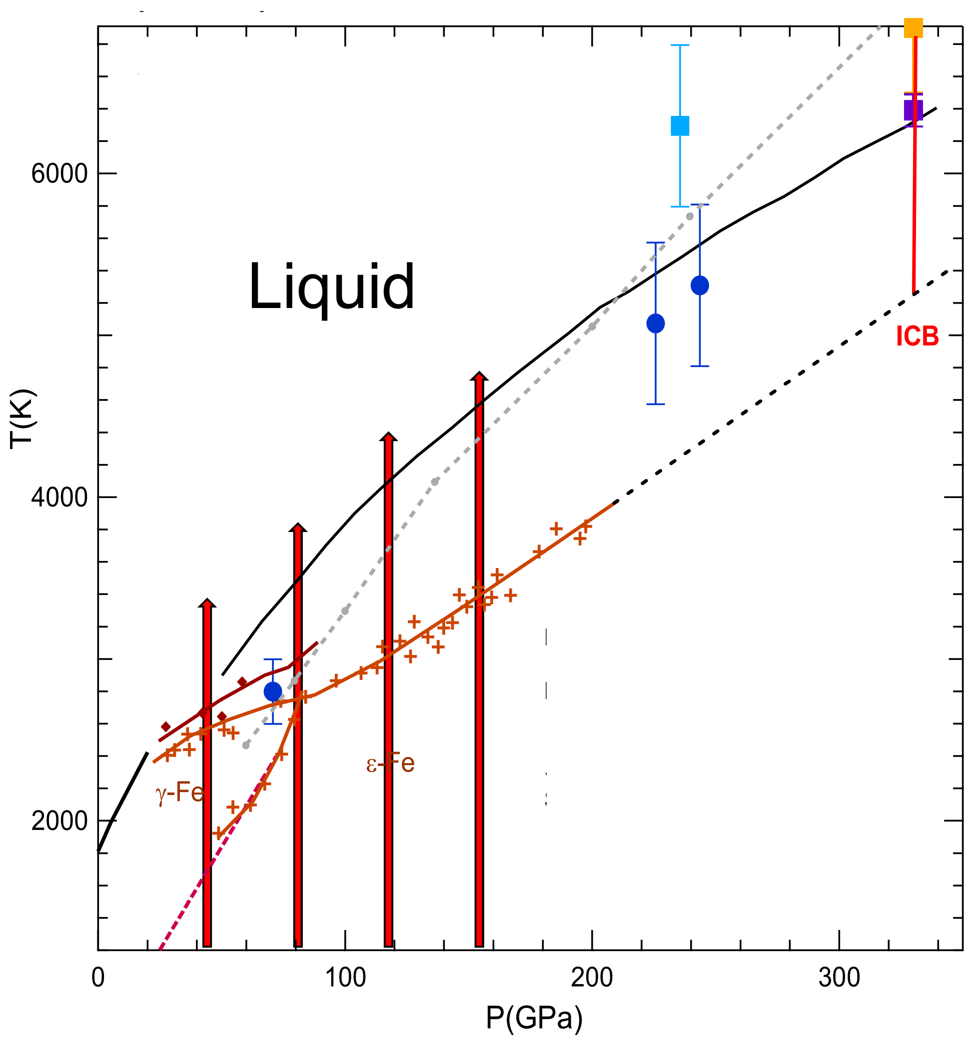


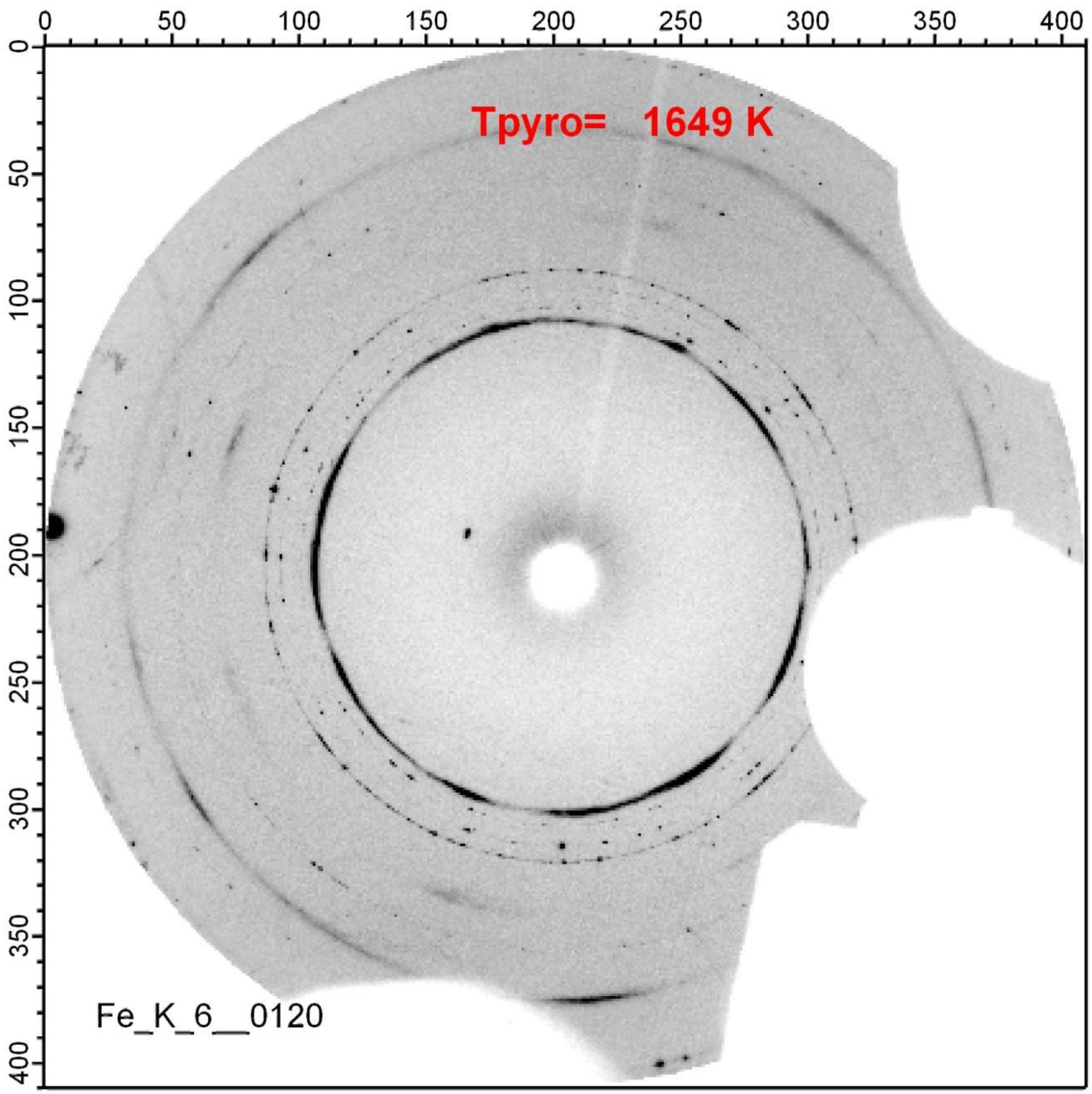
2. The “fast” sample recrystallisation observed using *in situ* XRD or the fast sample surface movement observed using the speckle method

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





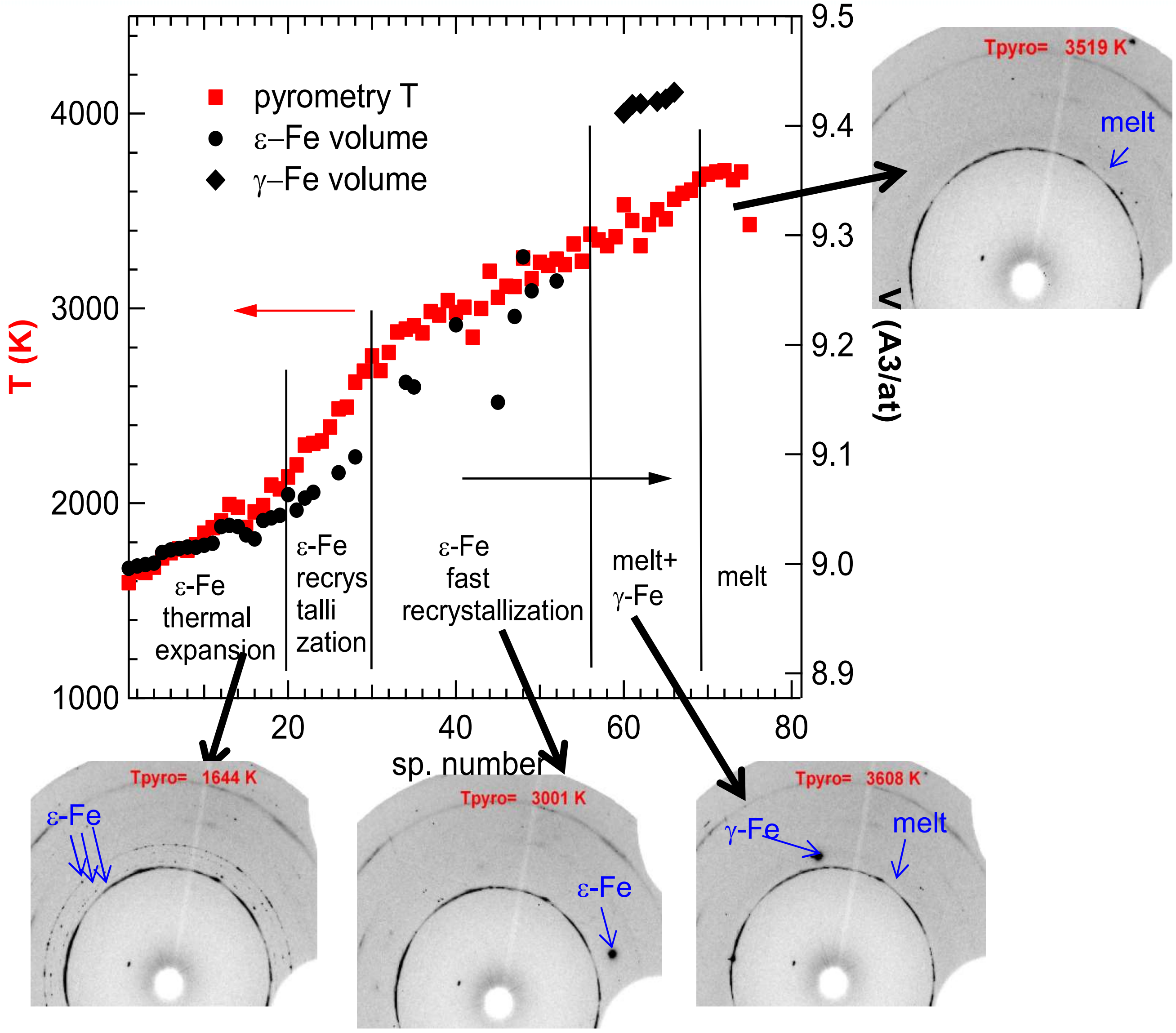
Gradual T increase at P~80 GPa

t=2 sec.

4 regimes:

- Thermal expansion
- Recrystallization
- Fast recrystallization
- Melting

Melting of iron at ~80 GPa

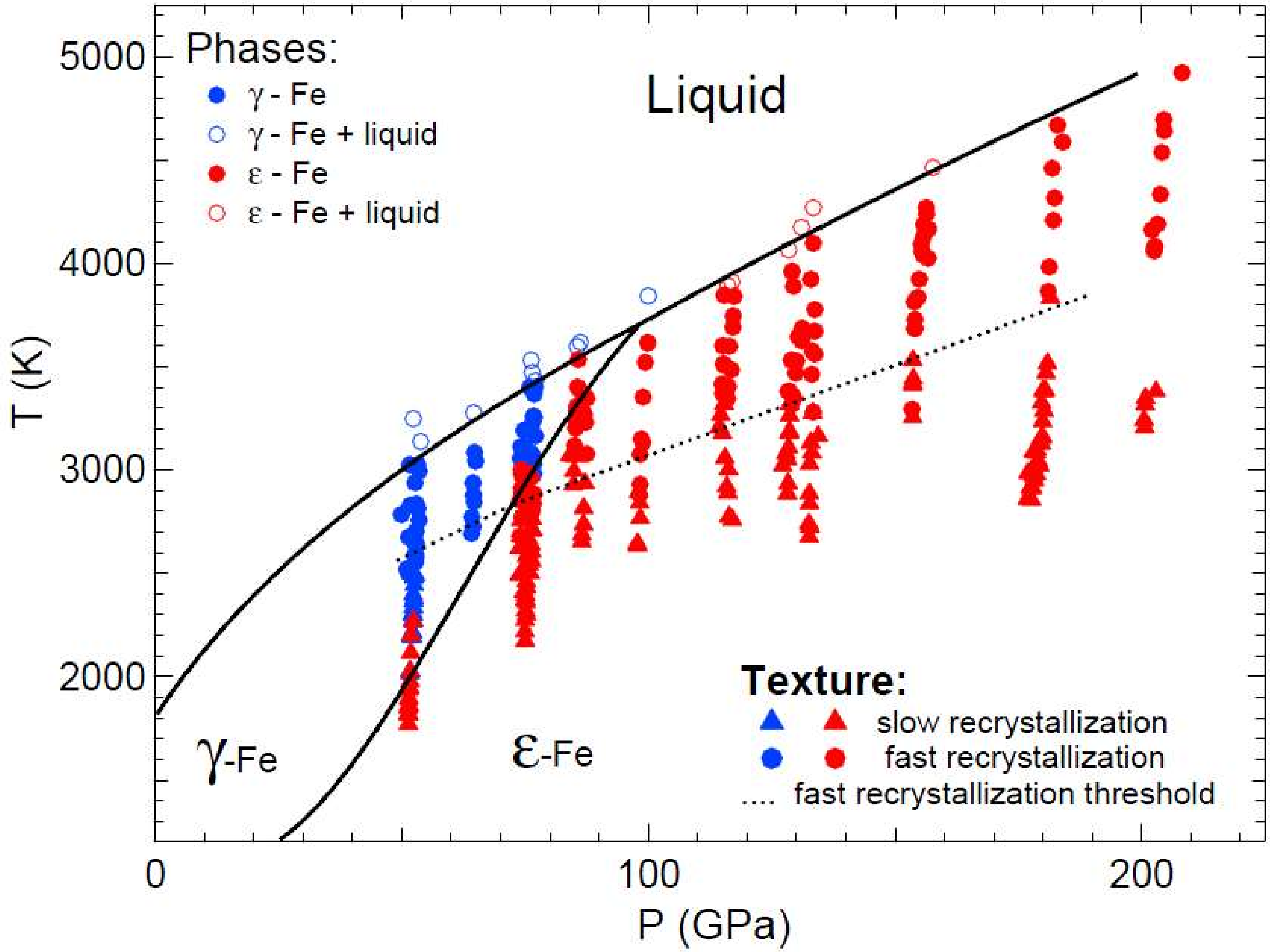


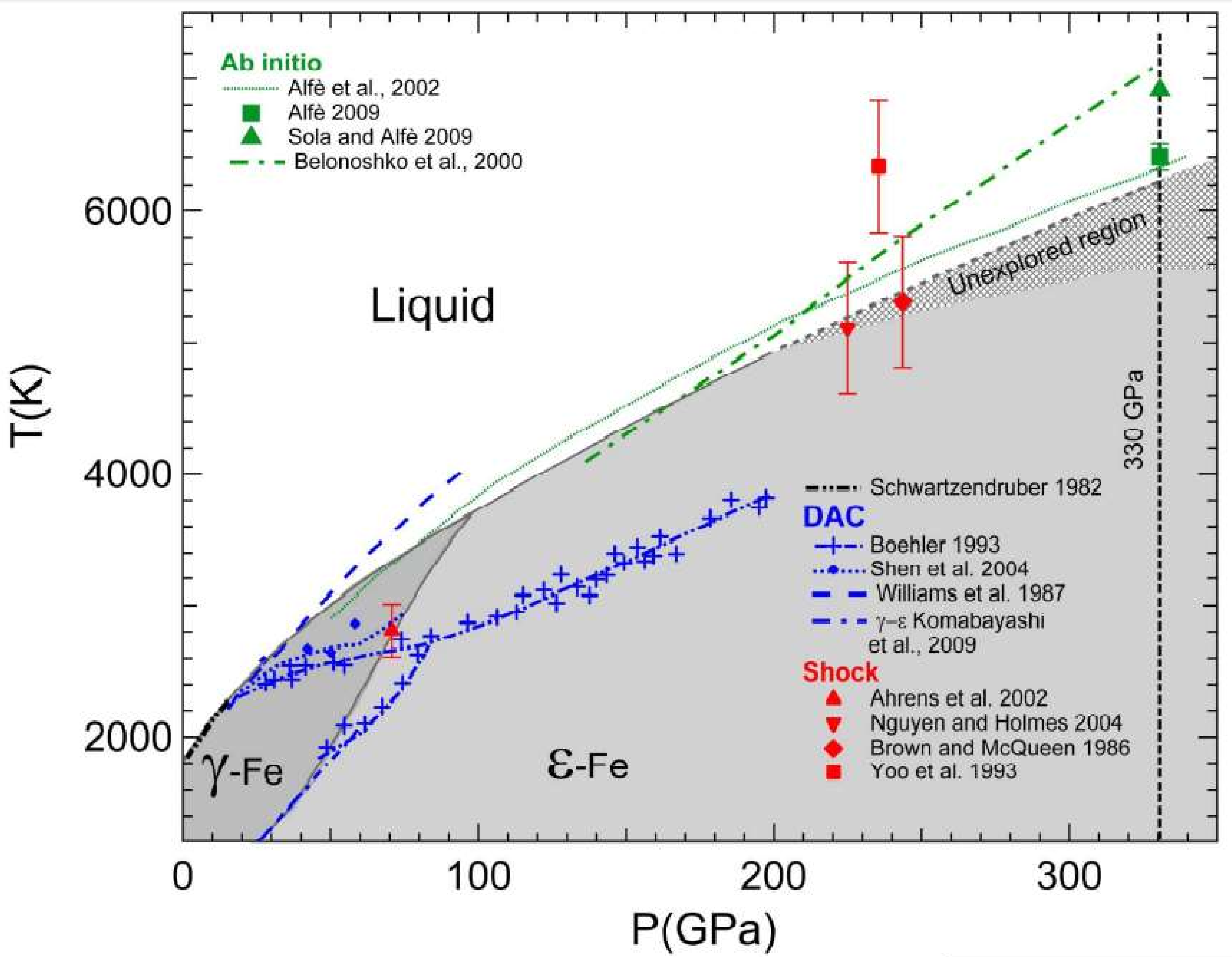
Assessment of melting criteria

1. Melting without “plateau” is observed

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

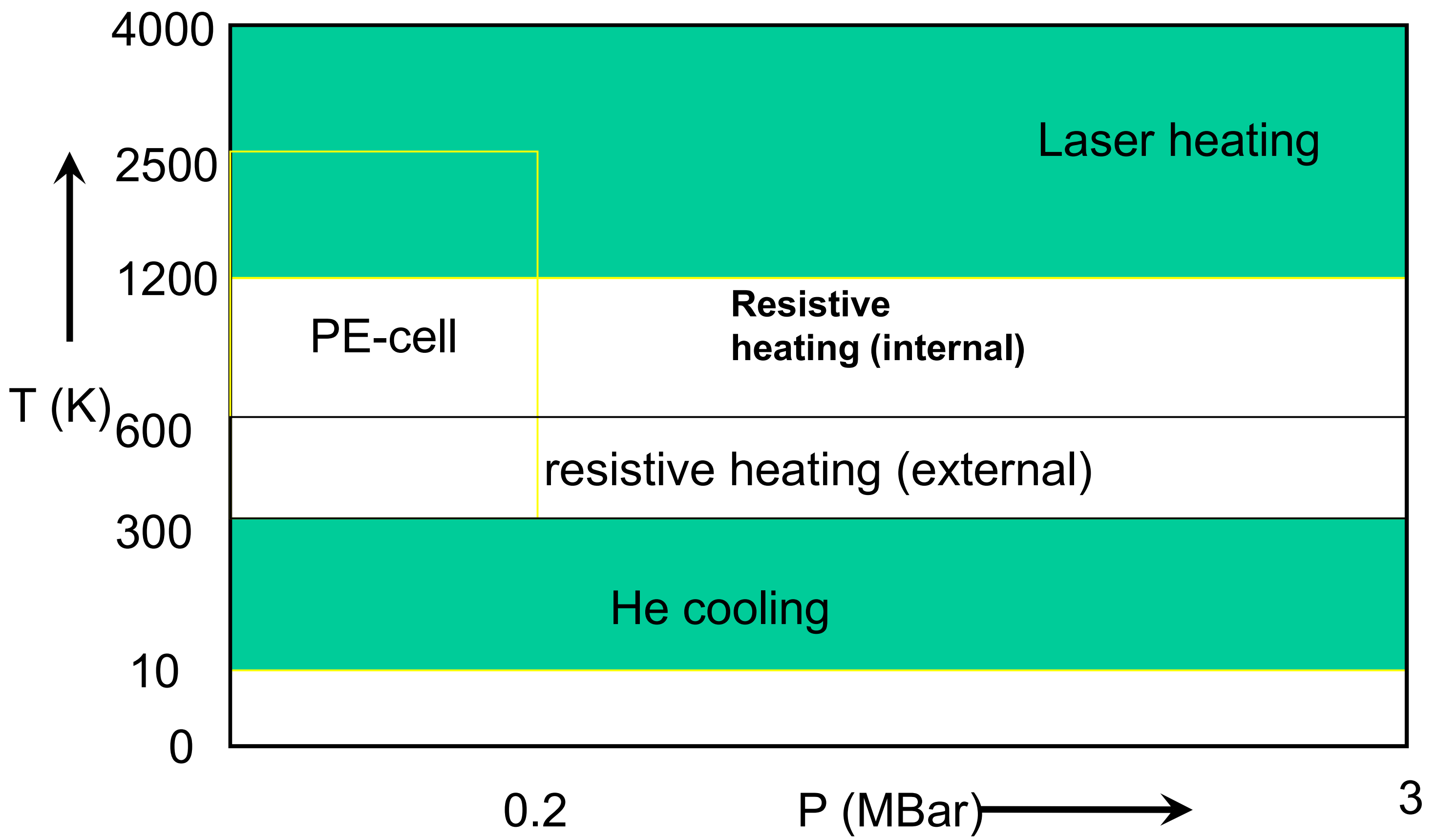
3. Onset of X-ray diffuse scattering : OK


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


Ab initio
Alfè et al., 2002
Alfè 2009
Sola and Alfè 2009
Belonoshko et al., 2000
6000
4000
2000
T(K)
Liquid
Unexplored region
330 GPa
Schwartzendruber 1982
DAC
Boehler 1993
Shen et al. 2004
Williams et al. 1987
γ–ε Komabayashi et al., 2009
Shock
Ahrens et al. 2002
Nguyen and Holmes 2004
Brown and McQueen 1986
Yoo et al. 1993
γ-Fe
ε-Fe
0
100
200
300
P(GPa)

Summary

Temperature vs. Pressure diagram – HP/HT technologies available at XRD beamlines



+ Time resolution