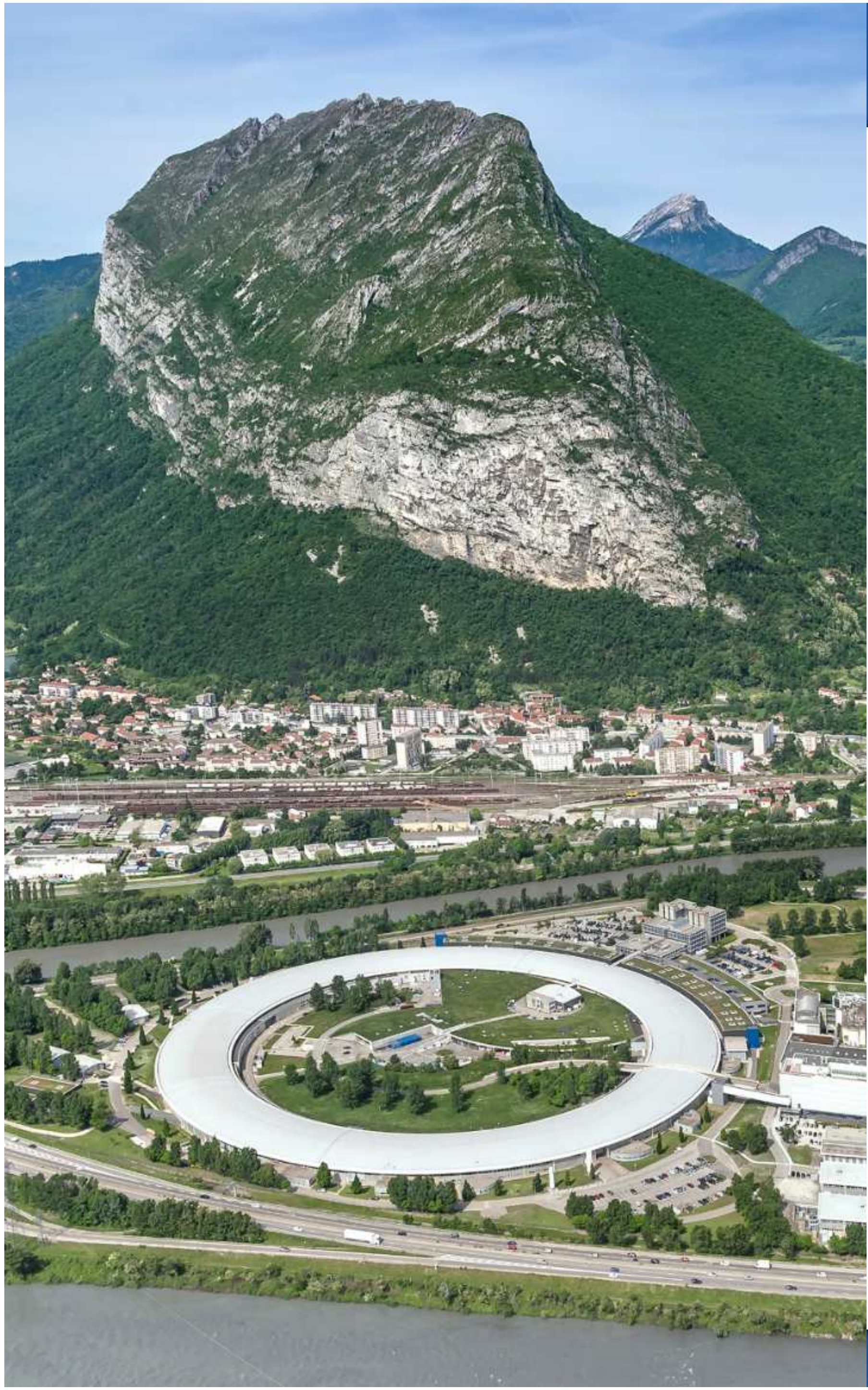

X-Ray Diffraction under Extreme Conditions using diamond anvil cell

Gaston Garbarino

European Synchrotron Radiation Facility
Grenoble, France

Outline

- Introduction
- How to generate and measure high pressure (using DAC)
- High pressure at ESRF
- Example of a high pressure beamline (ID27 @ ESRF)
- Scientific examples of high pressure experiments

Outline

- **Introduction**
- How to generate and measure high pressure (using DAC)
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- Scientific examples of high pressure experiments

Introduction

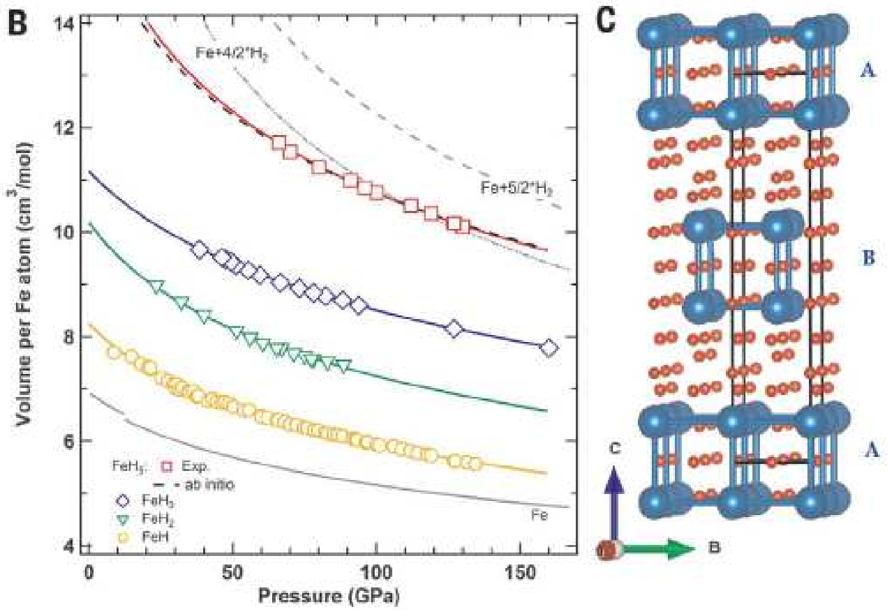
‘Science at Extreme Conditions’: multidisciplinary research

HIGH-PRESSURE PHYSICS

Pépin *et al.*, *Science* **357**, 382–385 (2017)

Synthesis of FeH_5: A layered structure with atomic hydrogen slabs

C. M. Pépin,[1,2]* G. Geneste,[1] A. Dewaele,[1] M. Mezouar,[3] P. Loubeyre[1]*

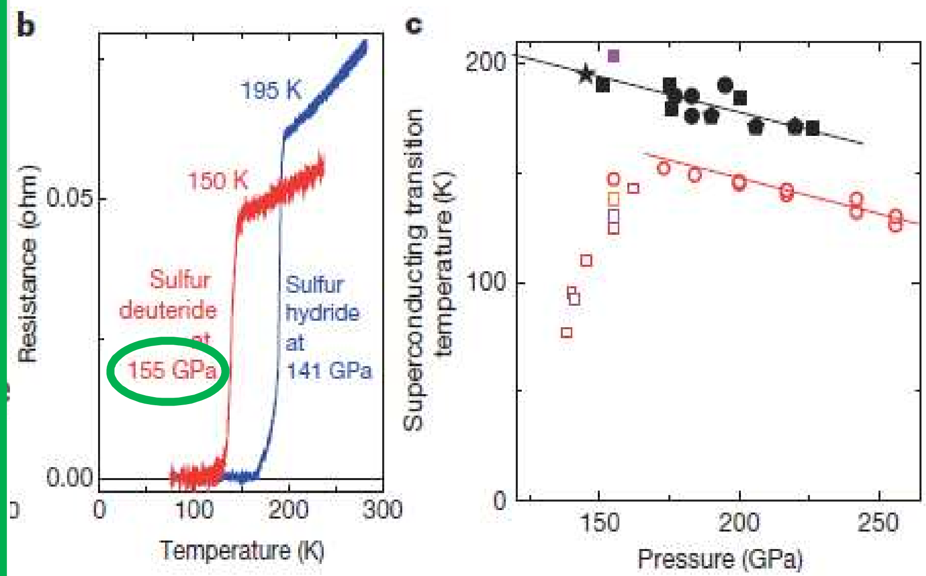


LETTER

doi:10.1038/nature14964

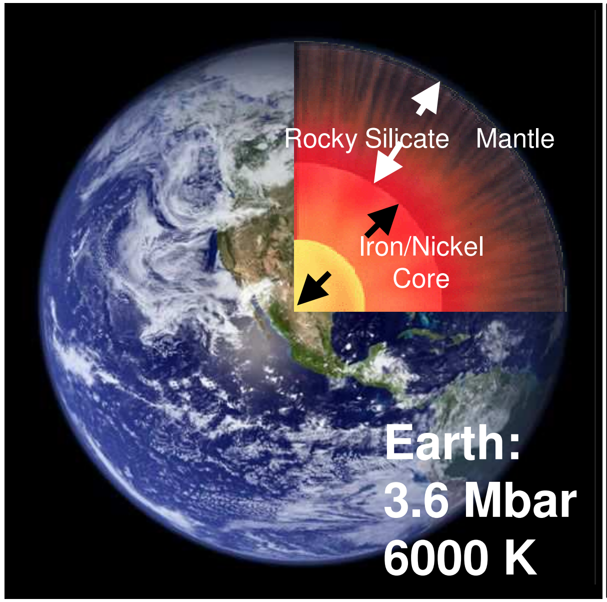
Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

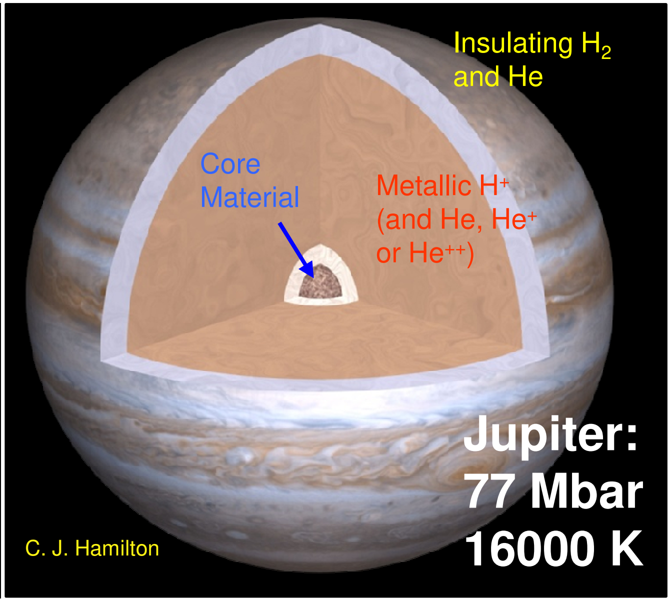
A. P. Drozdov[1]*, M. I. Eremets[1]*, I. A. Troyan[1], V. Ksenofontov[2] & S. I. Shylin[2]

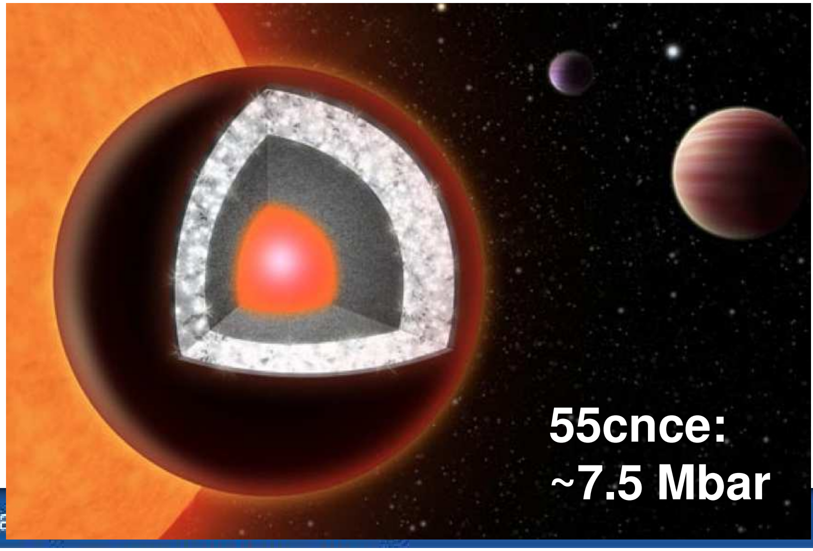


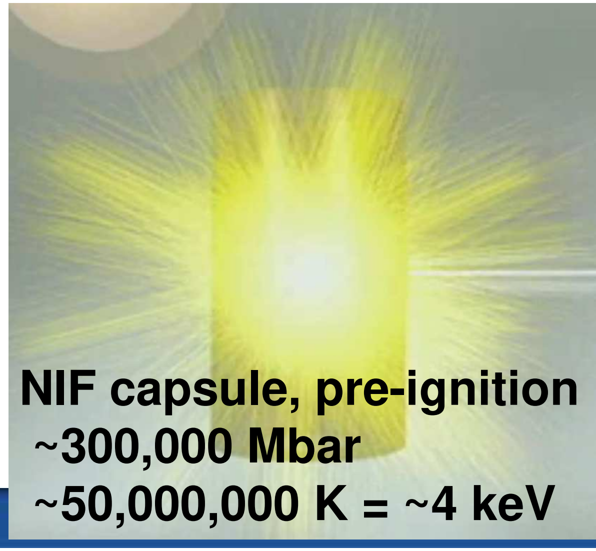
Introduction

Matter at extreme *P, T* are found throughout our universe







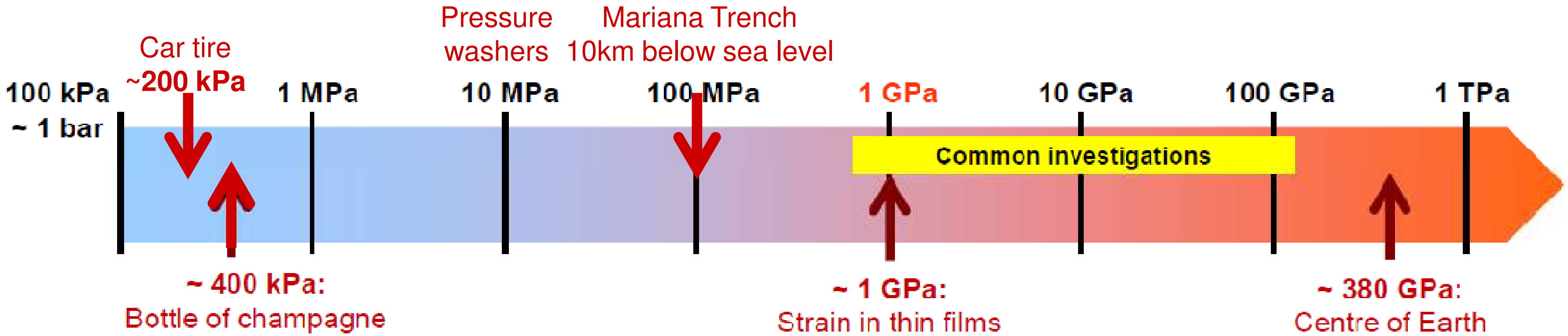


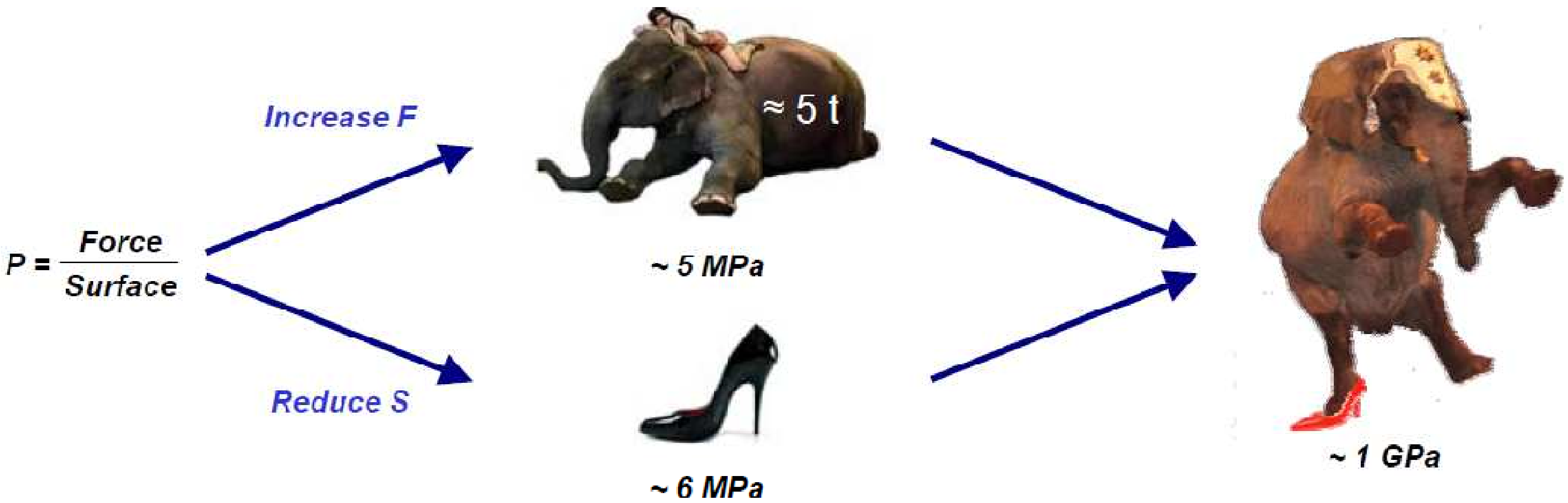
What is high-pressure?

High pressure units

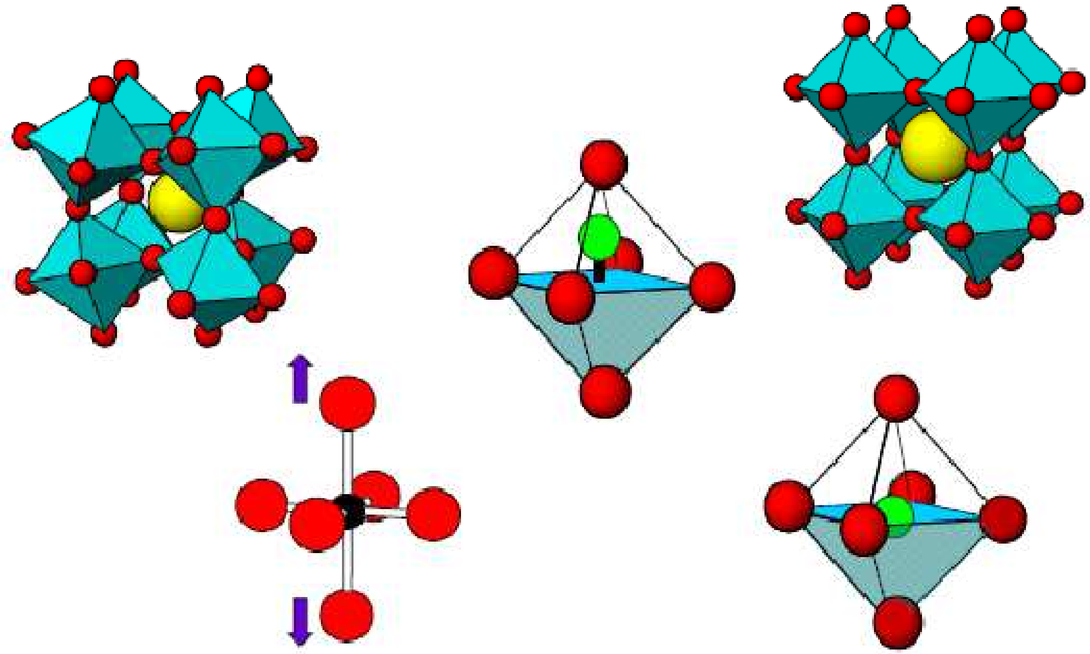
1 **bar** = 1 kg/cm^2 = 1013 hPa = 10^2 kPa = 10^{-1} MPa = 10^{-4} **GPa**
50 GPa = 500 kbar = 500 t/cm2

1GPa = 10.000bar ~ 10.000atm ~< 20km deep in Earth





What is the effect of high pressure?



<u>High pressure:</u>

Strong modification of interatomic distances and bond angles
Modification / Tuning of coupling and physical properties
“Clean” parameter because it acts only on interatomic distances
Important changes in volume (chemical bonding)
0 to 700 K $\rightarrow \Delta V/V0 \sim 1$ %
1 bar to 100 GPa $\rightarrow \Delta V/V0 \approx 25$ %

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Experimental aspects

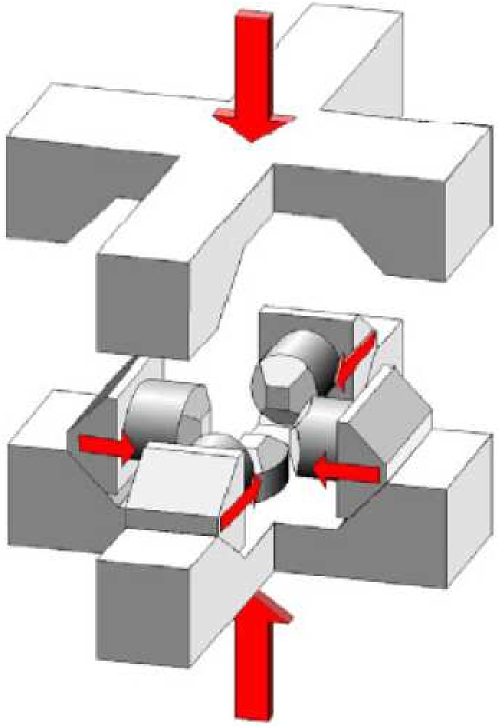
~ 1 GPa

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

1) Large volume cells
2) Diamond anvil cells
3) Shock / laser driven compression
4) …

1.1) Multi anvil cell



Large Volume multi-anvil Press on ID06 – 50 mm^3
- **P < 20 GPa, T<2500 K**

Credit S. Klotz

Experimental aspects

~ 1 GPa

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

1) Large volume cells
2) Diamond anvil cells
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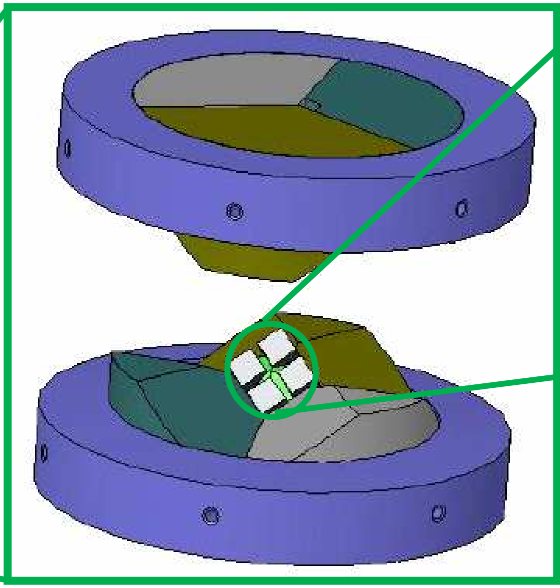
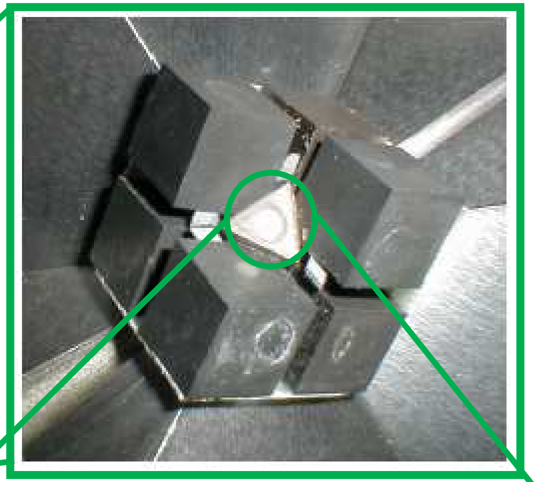
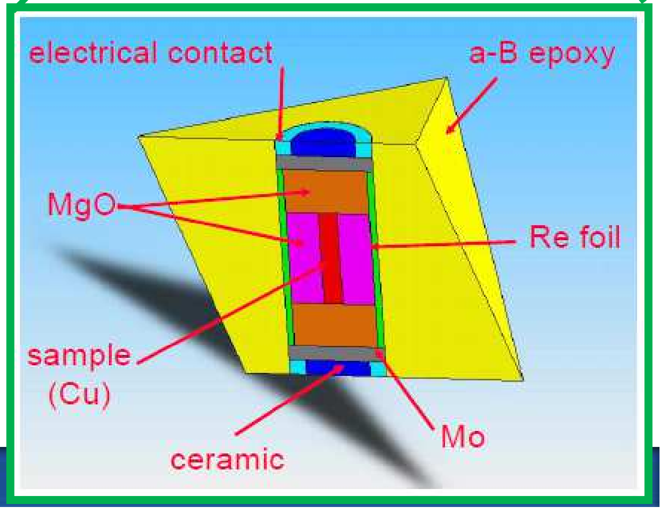
4) …

1.1) Multi anvil cell







Credit S. Klotz

Experimental aspects

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

~ 1 GPa

1) Large volume cells
2) Diamond anvil cells
3) Shock / laser driven compression
4) …

1.1) Multi anvil cell

P_{max}=30 GPa (Misasa, Japan)

Record P ~ 100GPa

Eiji Ito, Gabriel Gwanmesia, R.C. Liebermann

Credit S. Klotz

Experimental aspects

~ 1 GPa

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

1) Large volume cells
2) Diamond anvil cells
3) Shock / laser driven compression
4) …

1.2) Paris-Edinburgh cell

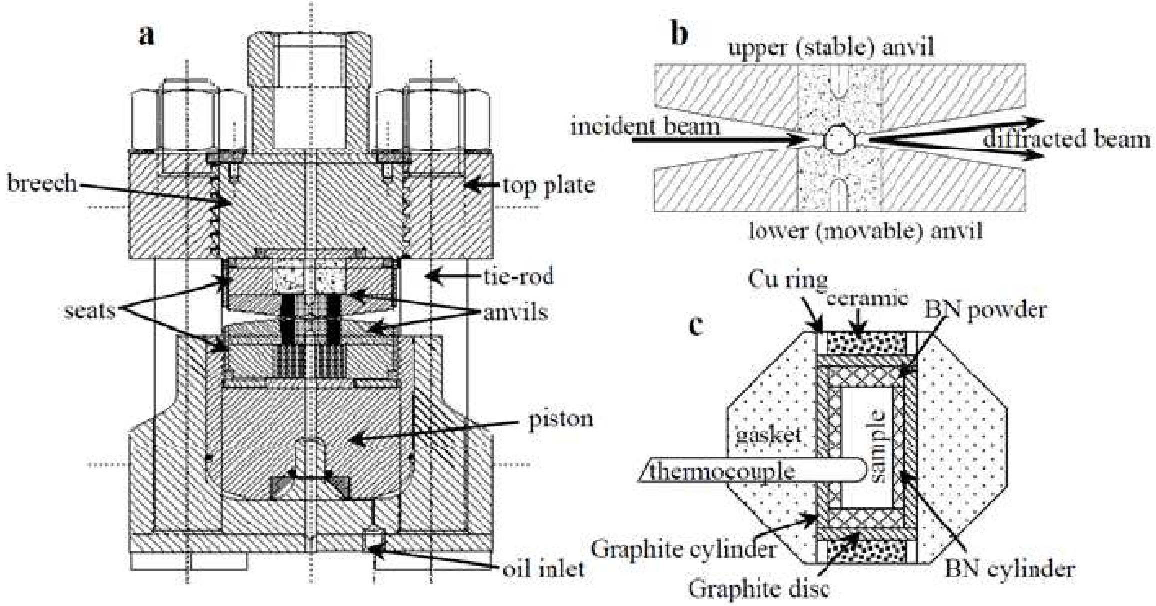


Figure 1: Cross-section of Paris-Edinburgh press (**a**), anvils/sample ensemble (**b**) and sample (**c**).

Paris-Edinburgh Press on ID27 and BM23 – 2 mm^3

P < 17 GPa, T<1800 K

Experimental aspects

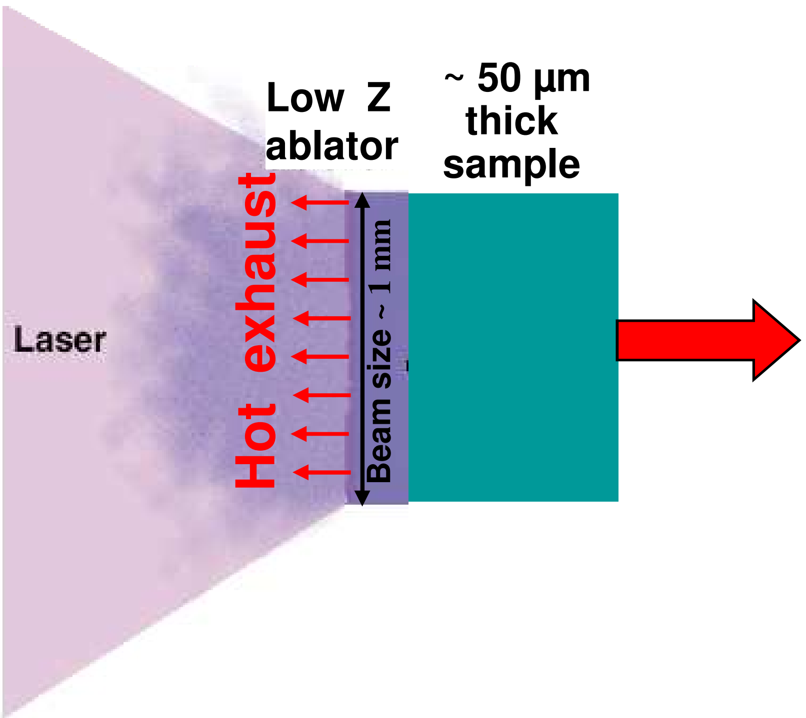
~ 1 GPa

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

1) Large volume cells
2) Diamond anvil cells
3) Shock / laser driven compression
4) …

3) Laser driven compression

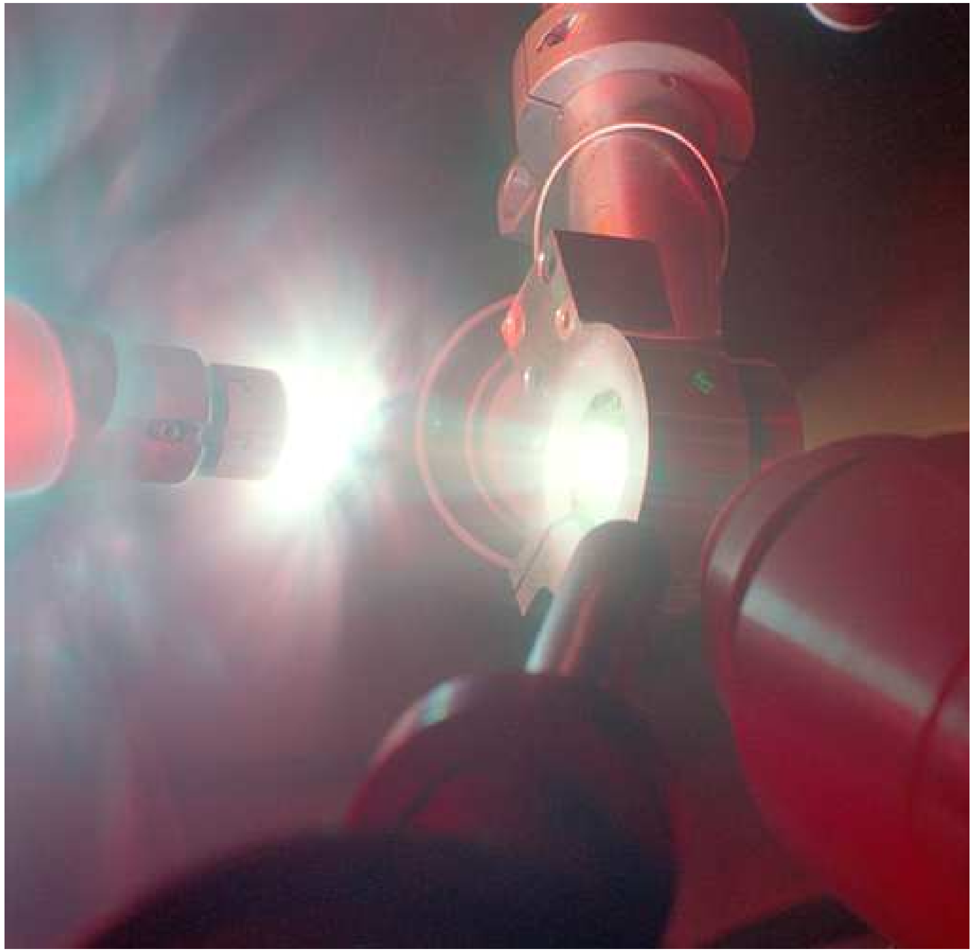


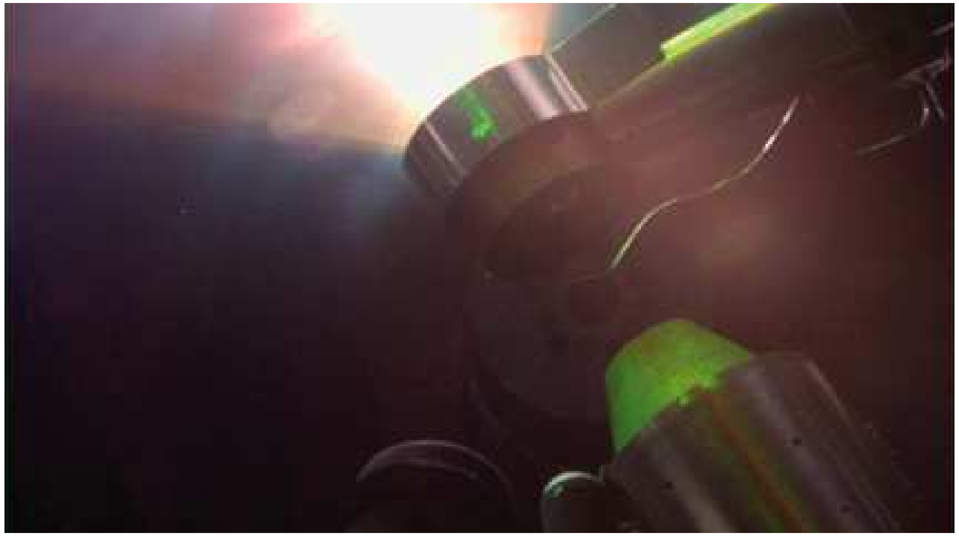
Compression (shocked, or ramped)

F_{net}, acceleration, due to the rocket effect

Credit J. Eggert

High pressures result from the rocket effect generated by laser-induced ablation.





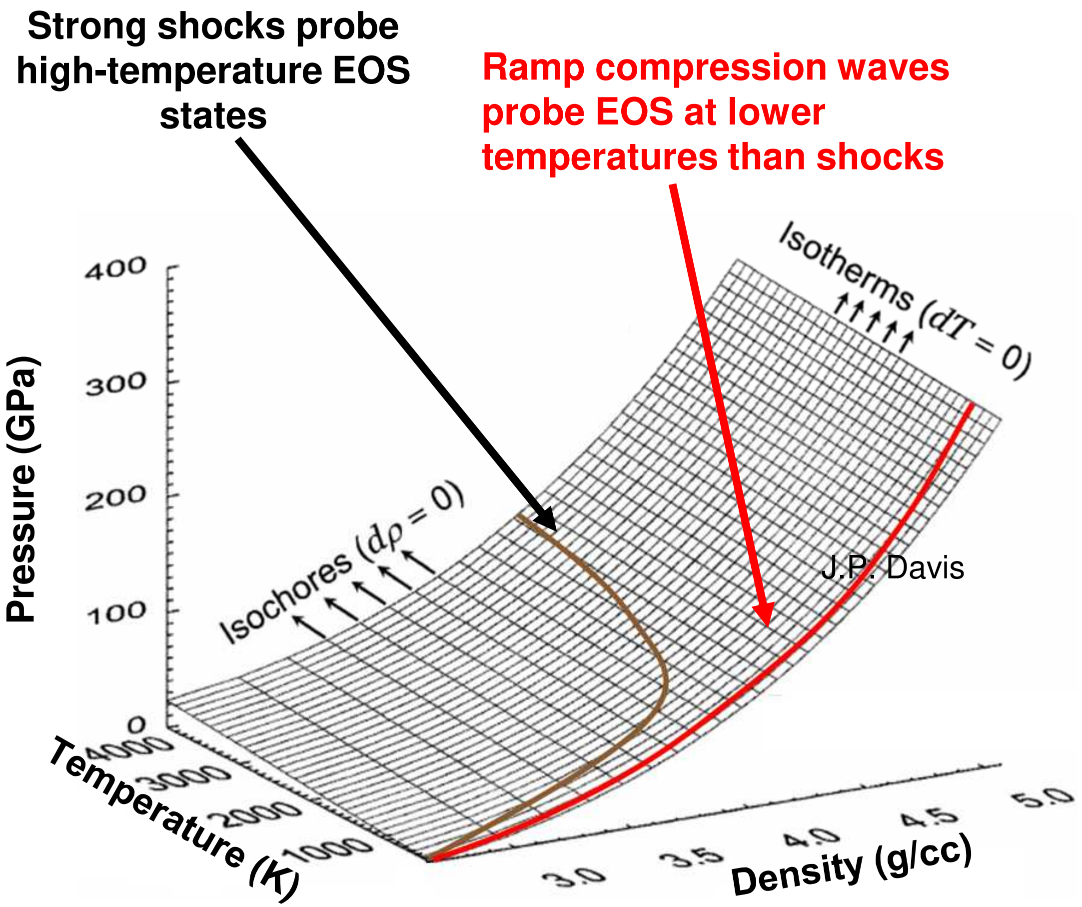
Time-integrated photos of shots at the Omega laser (60 beams, 30 kJ) at University of Rochester Credit J. Eggert

Experimental aspects

High pressures result from the rocket effect generated by laser-induced ablation.

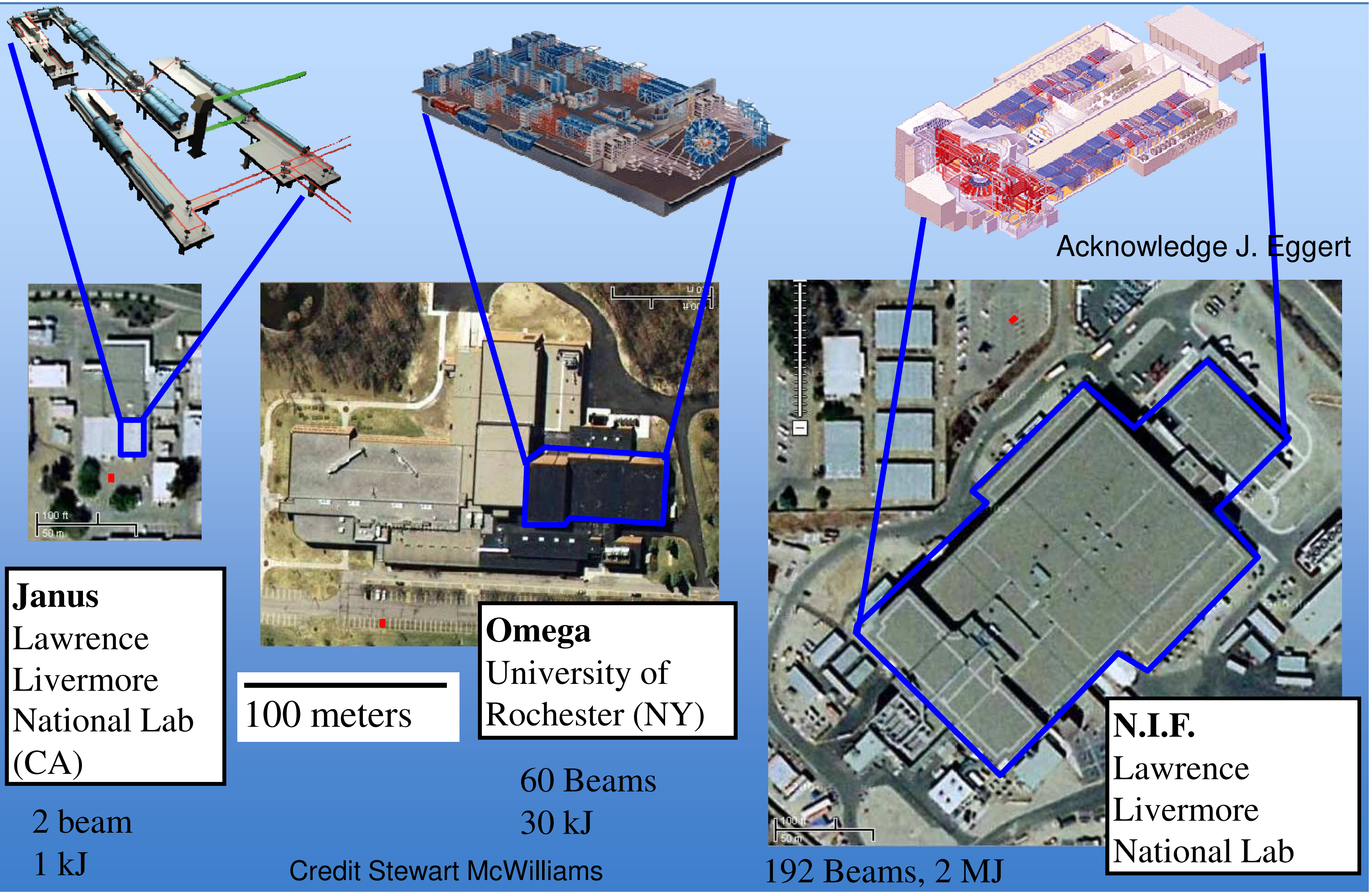
In order to study the physics of extreme compression we need to keep temperature low.

Ramp and shock compressions follow different paths on EOS surface.



Credit J. Eggert

Laser-induced ablation facilities



Experimental aspects

A Common Definition for “High-Energy Density” is 10^{11} J/m^3 = 1 Mbar

High-Energy Density allows us to clump high temperatures and high densities together.

Extreme Compression Physics: $\rho/\rho_0 > 2$

Material	Pressure at 2-Fold Comp (GPa)
H_2	18
Mg	~120
Pb	180
Sn	180
Al	240
Zn	~250
Ag	~460
Ta	470
Cu	~500
Mo	~640
Au	~810
W	~820
Diamond	900

Credit J. Eggert

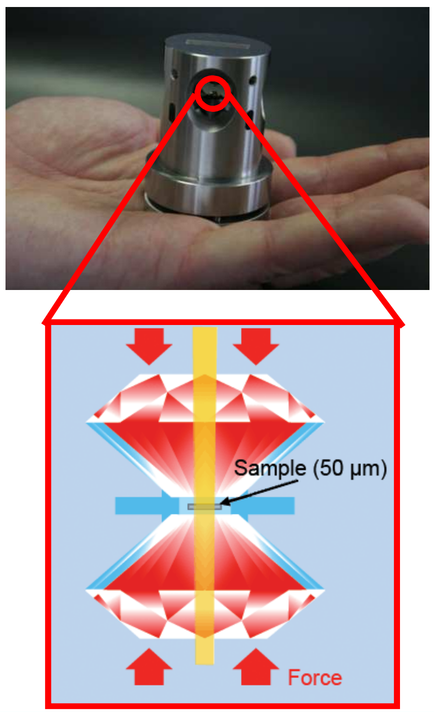
Experimental aspects

More elegant ways to apply high-pressure …

$$P = \frac{Force}{Surface}$$

1) Large volume cells
2) Diamond anvil cells
3) Shock / laser driven compression
4) …

2) Diamond anvil cell



High pressure apparatus at ESRF

Large Volume multi-anvil Press on ID06 **50 mm^3**

Paris-Edinburgh Press on ID27 and BM2 **2 mm^3**

Diamond Anvil Cell P > 300 GPa **>10^{-3} mm^3**
3K < T < ~7000K

Record P: **0.6 TPa** Occelli, Loubeyre et al, to be published
1TPa Dubrovinskaia et al., Sci. Adv. 2, 341 (2016)

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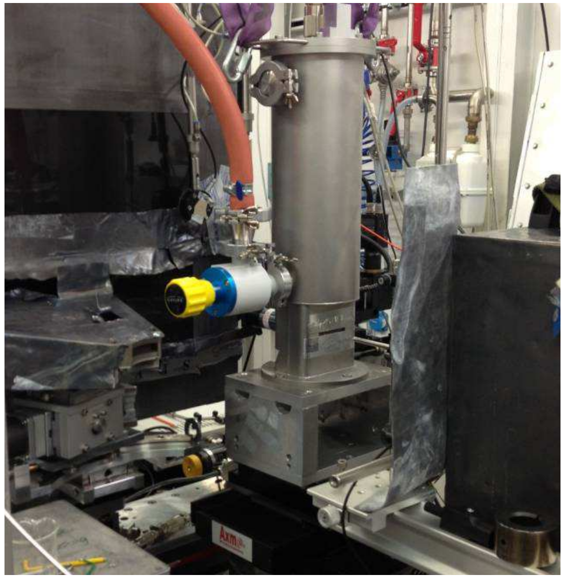
Diamond Anvil Cell

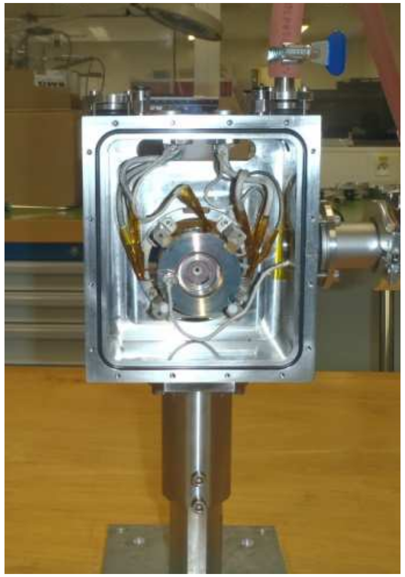
LeToullec type DAC (P~200GPa)

Magnetic field (H < 8-17 T)

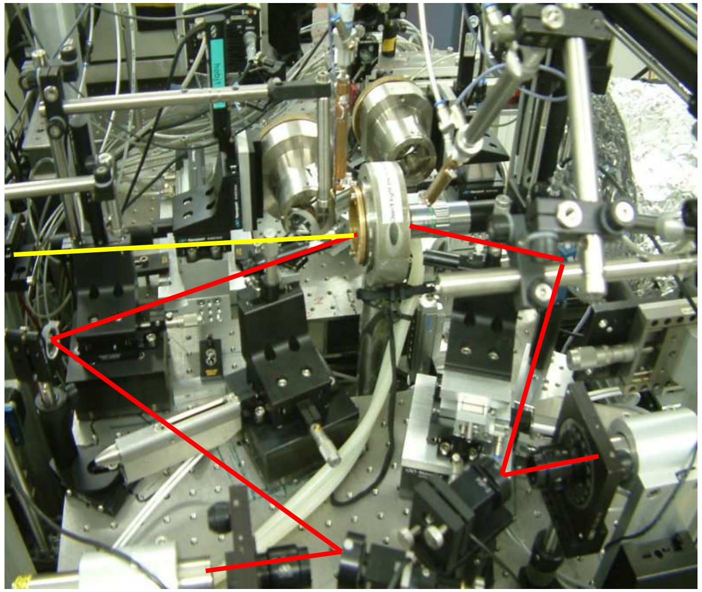
Cryostat (T > 2.7 K)



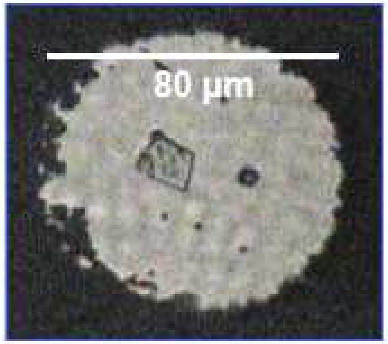
Resistive heating (T < 1300 K)



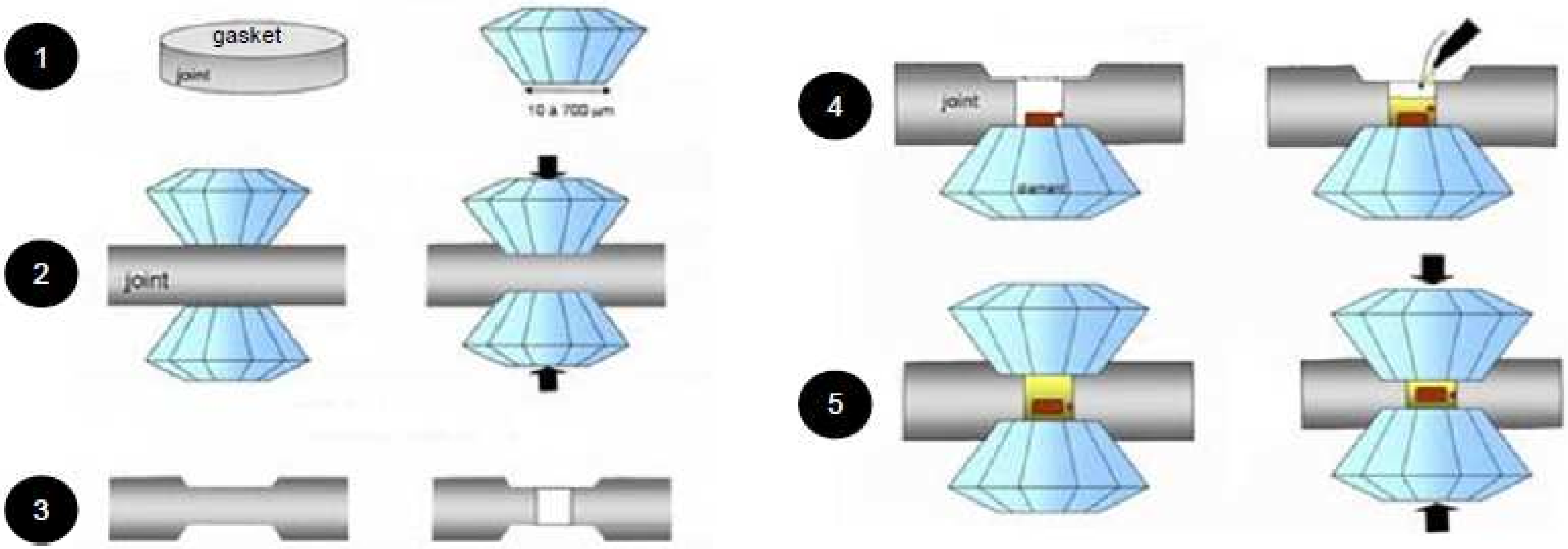
Laser heating (T > 5000 K)



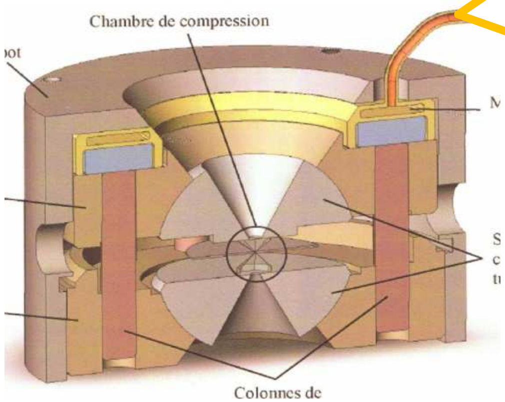
Diamond Anvil Cell



Important aspects: gasket material and pressure transmitting medium



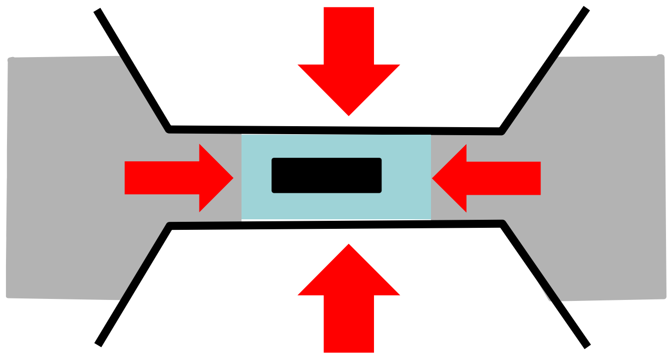
Diamond Anvil Cell



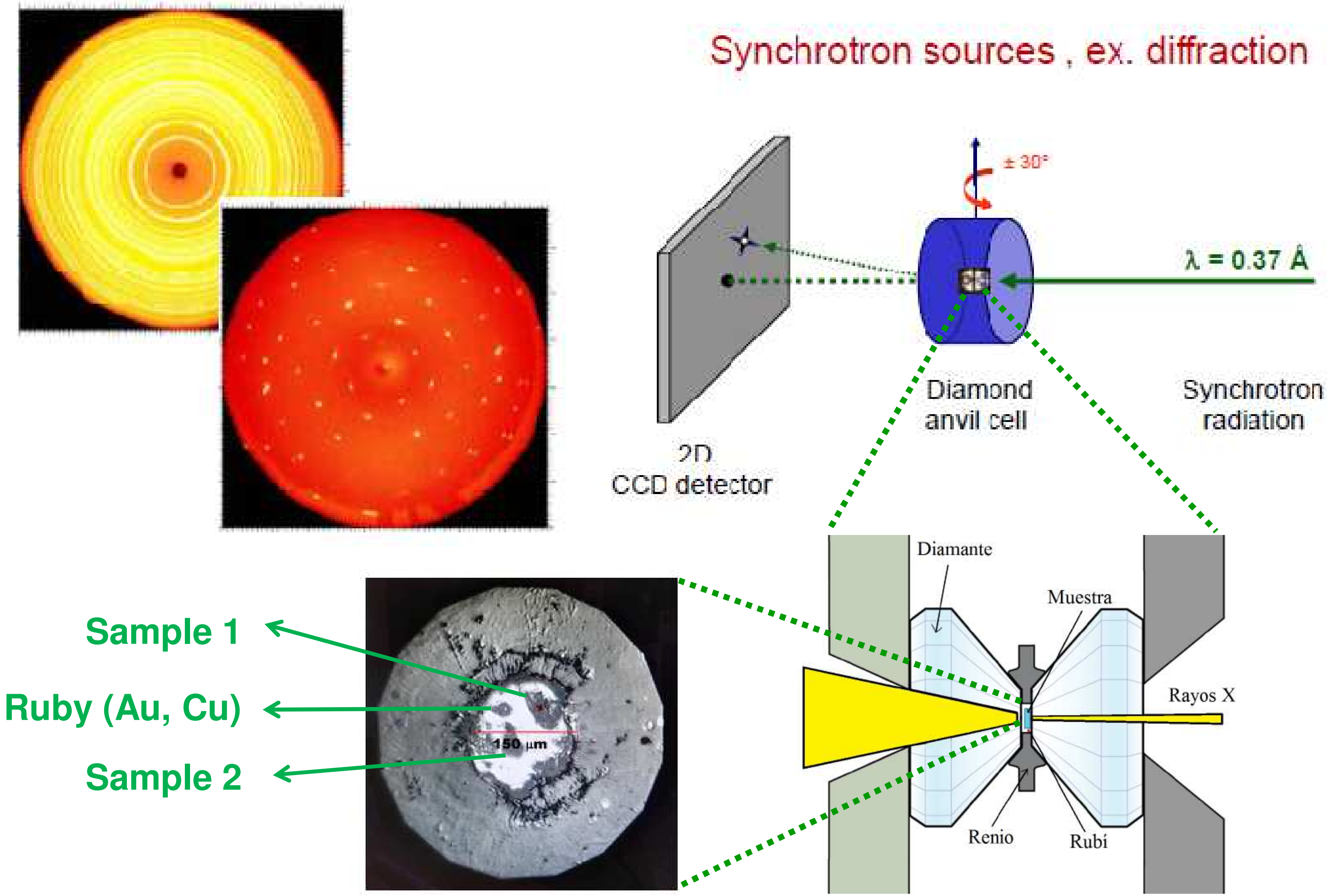
Pressurized gas on the membrane change the load on the diamonds

Pressure driver
manual / automatic

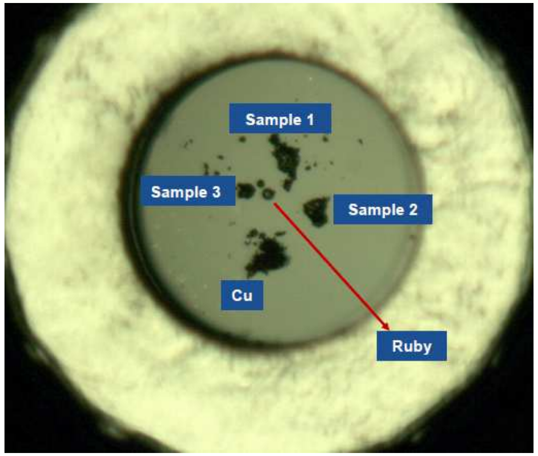
gasket



XRD using a DAC

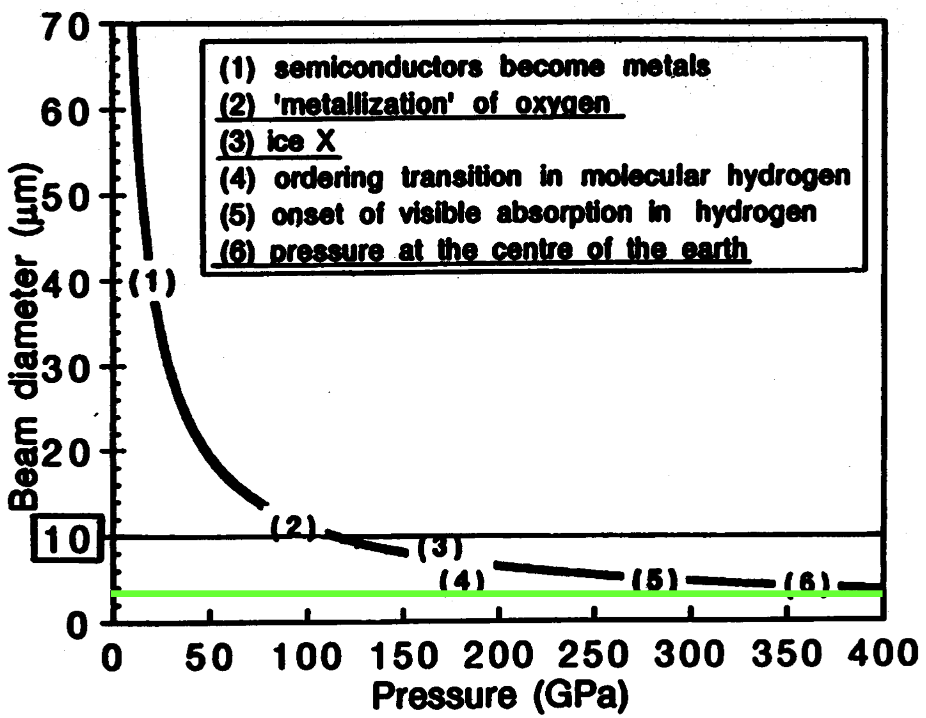


Diamond Anvil Cell + X rays



<100μm = 0.1mm

Need of very intense and very small X-ray beam.



XRD using a DAC

X-Ray Diffraction

High resolution ADXRD on single crystals, powders, liquids, amorphous

Acquisition with rotation ($\pm$35 deg, 1 axis or 2 axis), fixed

Analysis using Crysalis, Jana, ShelX, Fullprof, GSAS

Development software to analyze liquid/amorphous

Diamond anvil cell

P < 2 Mbar

Low temperature

Helium flow cryostat T > 3K

“No” mechanical vibrations

High temperature

Resistive heating (external, T<700K)

Resistive heating (external, T<1200K)

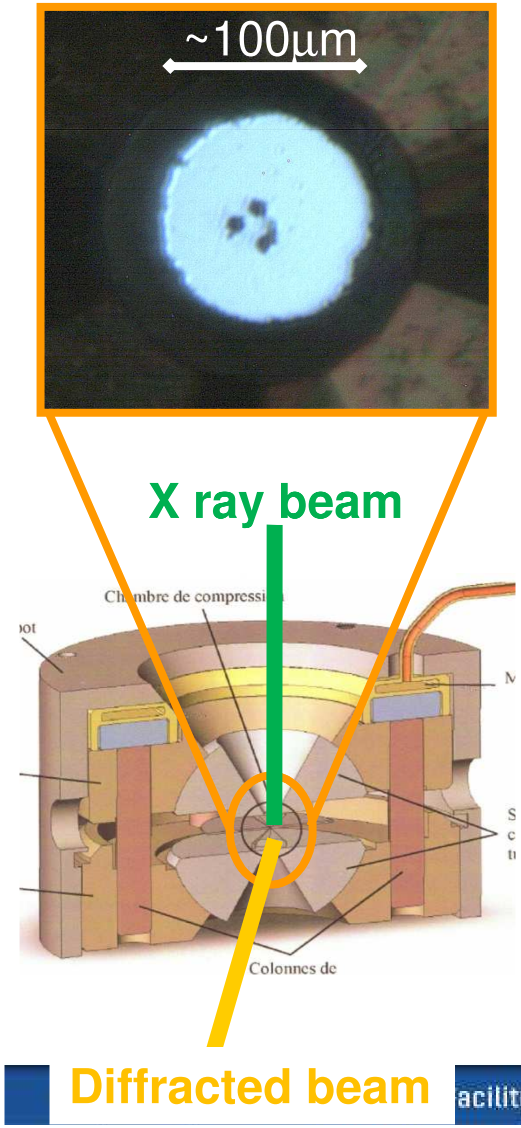
Laser heating (T>1000K)

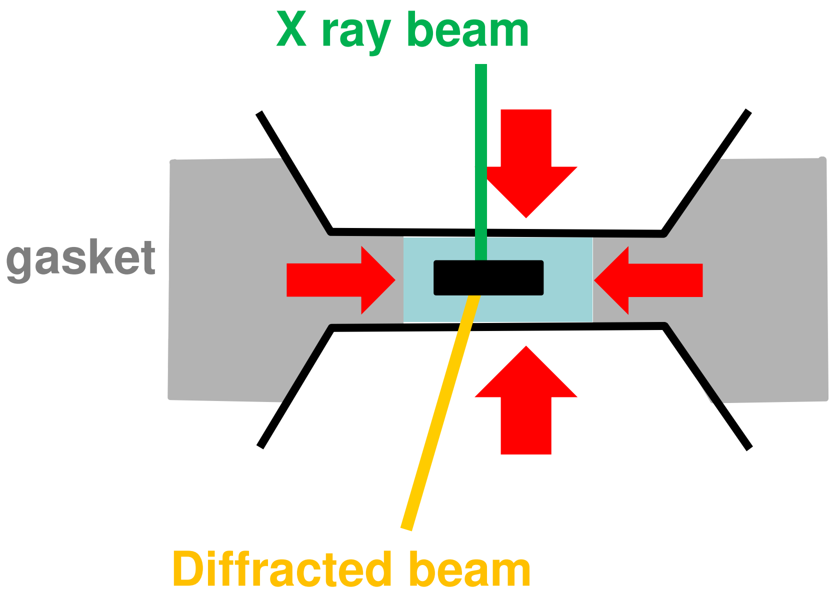
XRD using a DAC

Important technical aspects:

- gasket material: P - T range, chemical reactivity …

ST ST (in general)
Re (high T - very high P)
Be (X ray beam through gasket)
composite (X ray beam through gasket / insulator)
Cu (low pressure)
Inconel (low pressure)



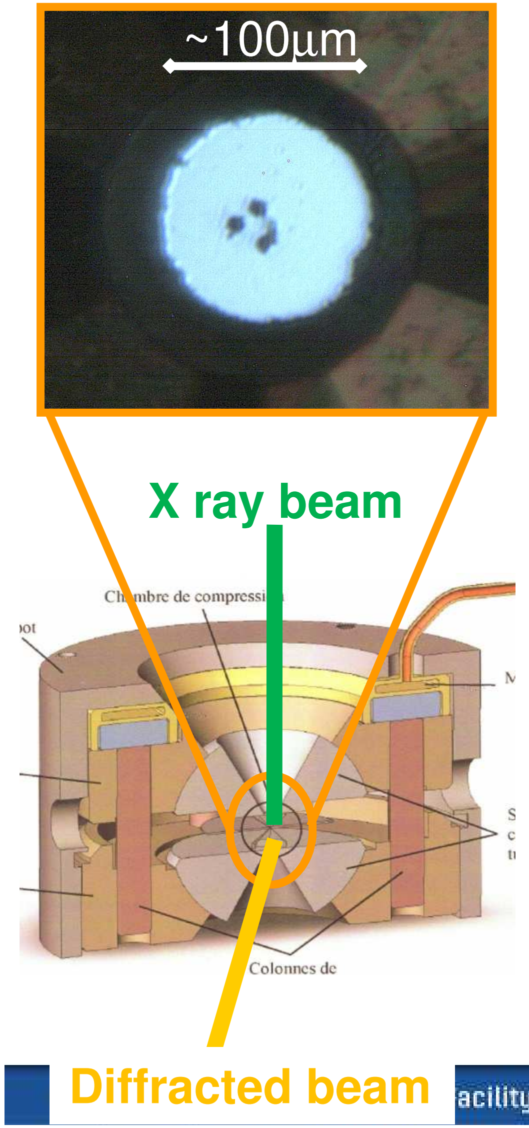


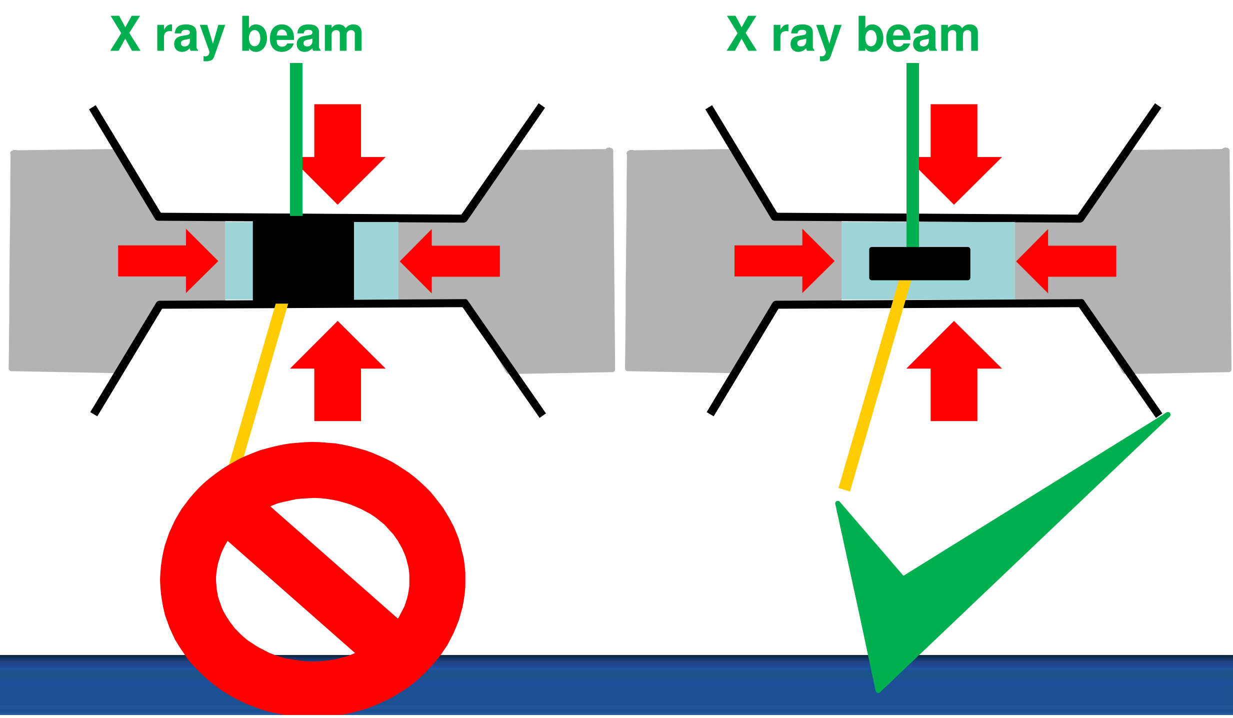
XRD using a DAC

Important technical aspects:

- gasket material

- sample dimensions
  - keep hydrostatic conditions through experiment
  - absorption (high Z samples)
  - signal to background ratio (low Z samples)



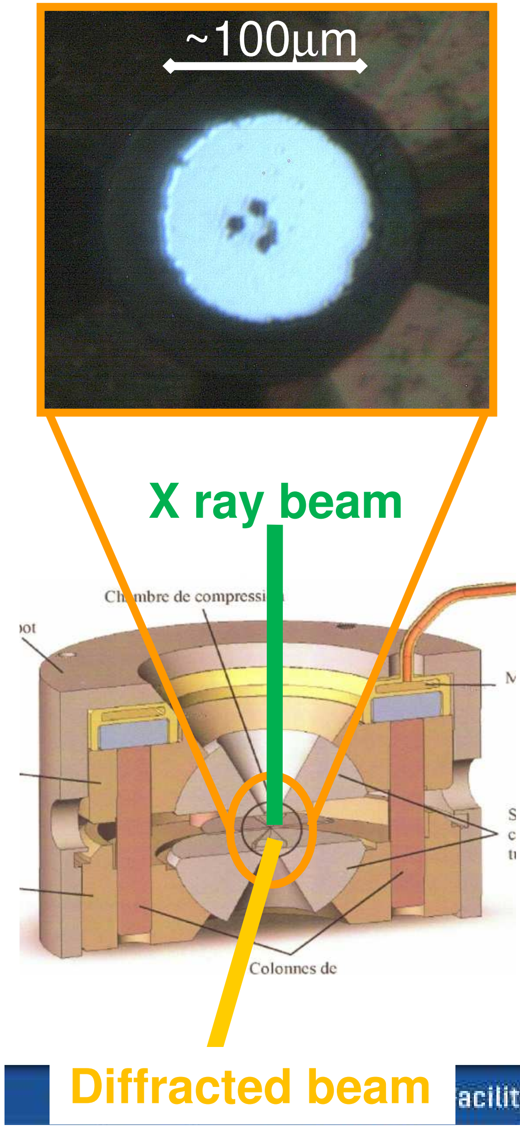


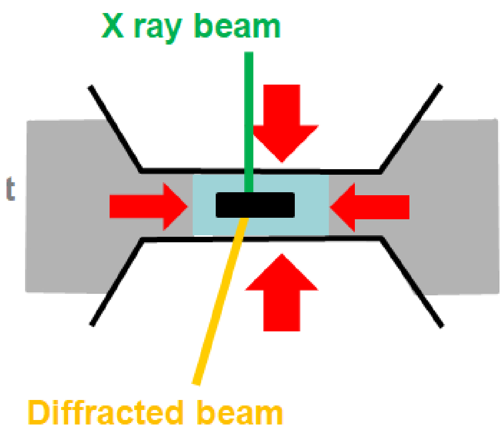
XRD using a DAC

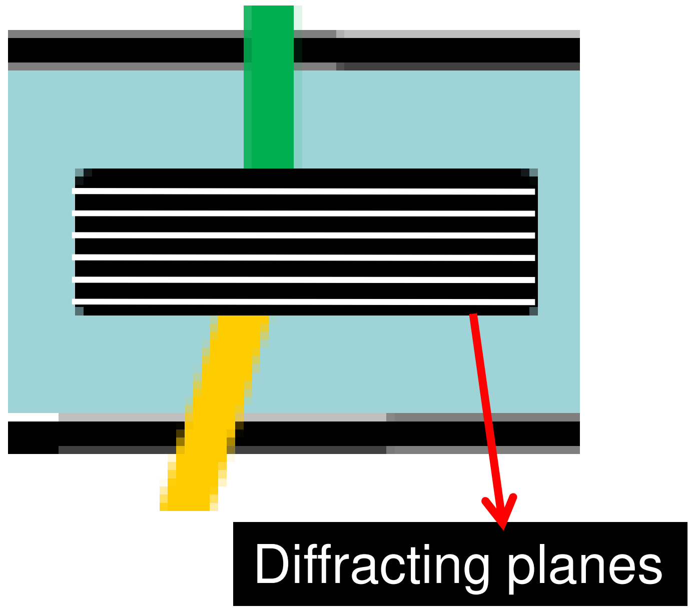
Important technical aspects:

- gasket material

- sample dimensions
  - keep hydrostatic conditions through experiment
  - absorption (high Z samples)
  - signal to background ratio (low Z samples)
  - small coverage of reciprocal space (30-40%)
  - crystal: orientation!!



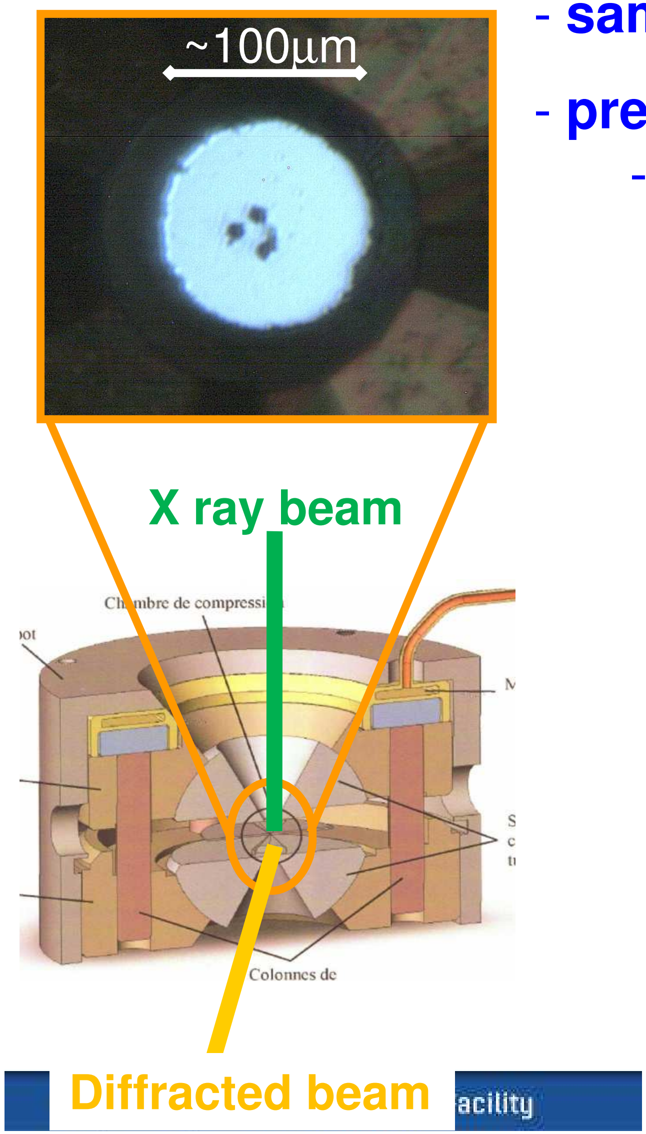


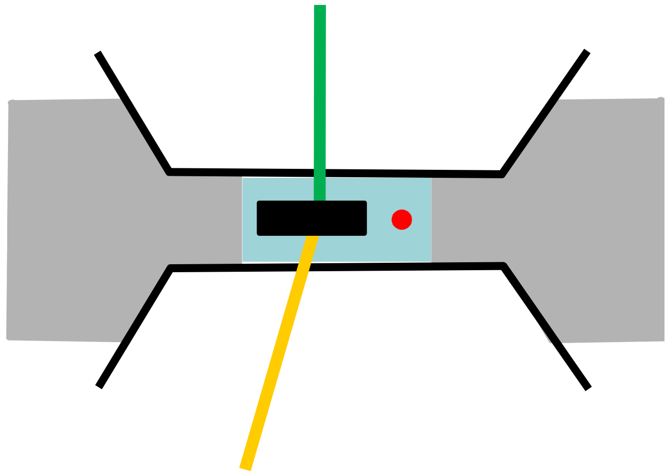


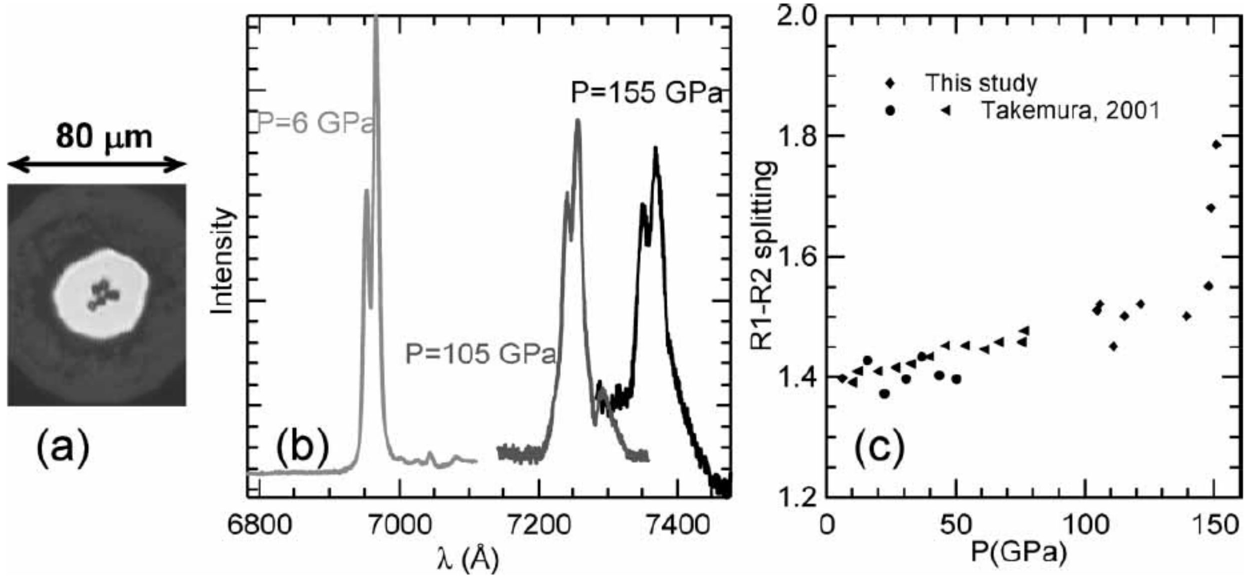
XRD using a DAC

Important technical aspects:

- gasket material
- sample dimensions
- pressure measurement
    - ruby



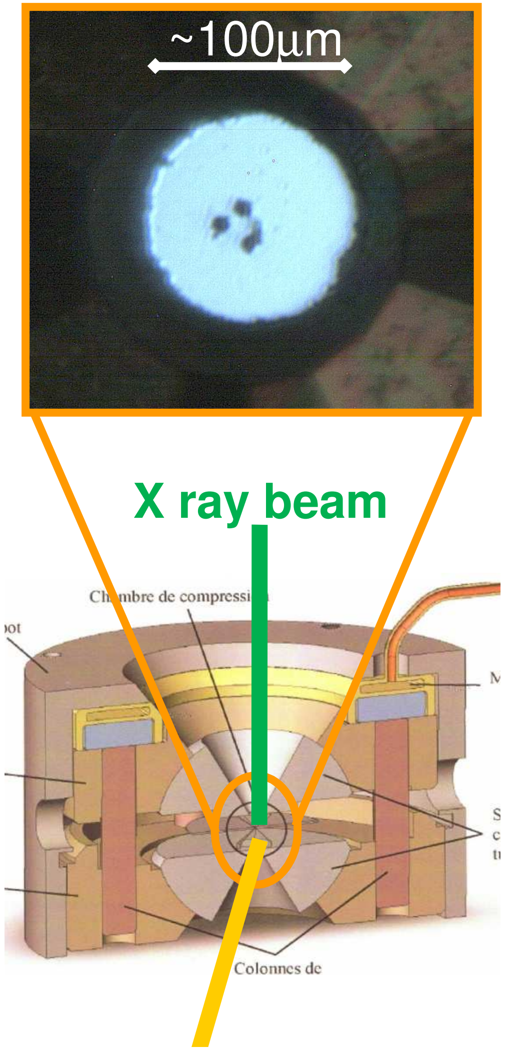


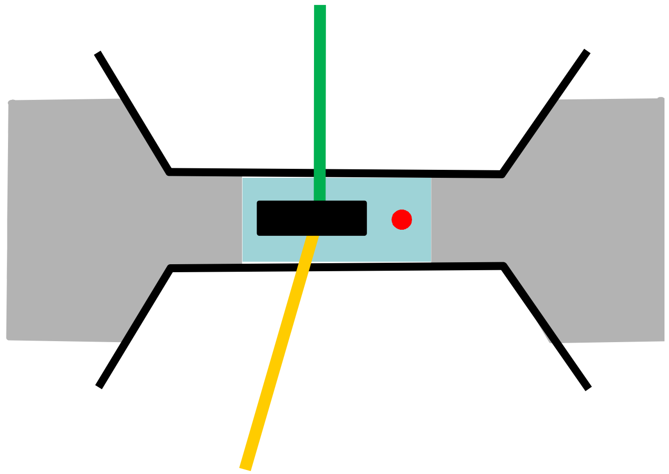


XRD using a DAC

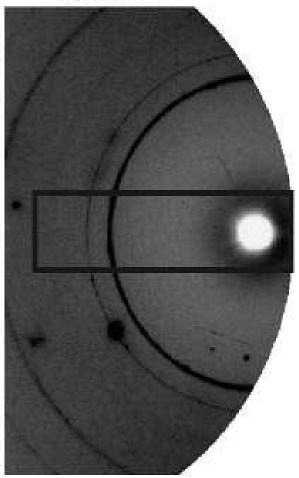
Important technical aspects:

- gasket material
- sample dimensions
- pressure measurement
    - ruby
    - metal (known EoS)
    - salt (known EoS)
    - diamond Raman mode
    - pressure transmitting medium EoS

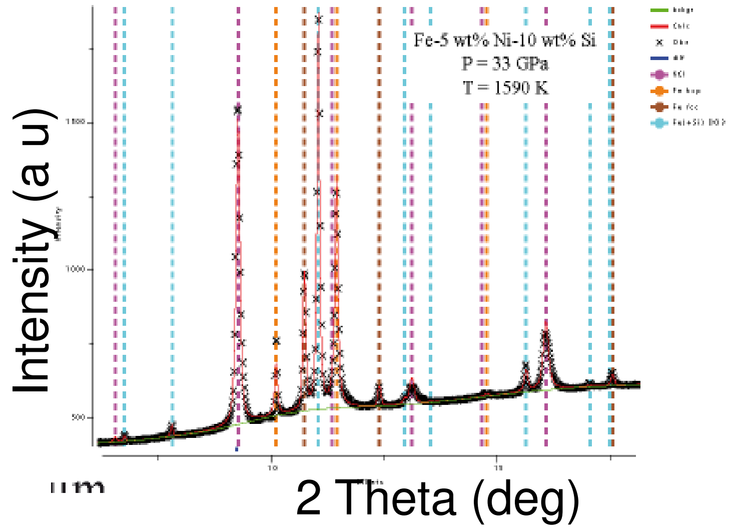




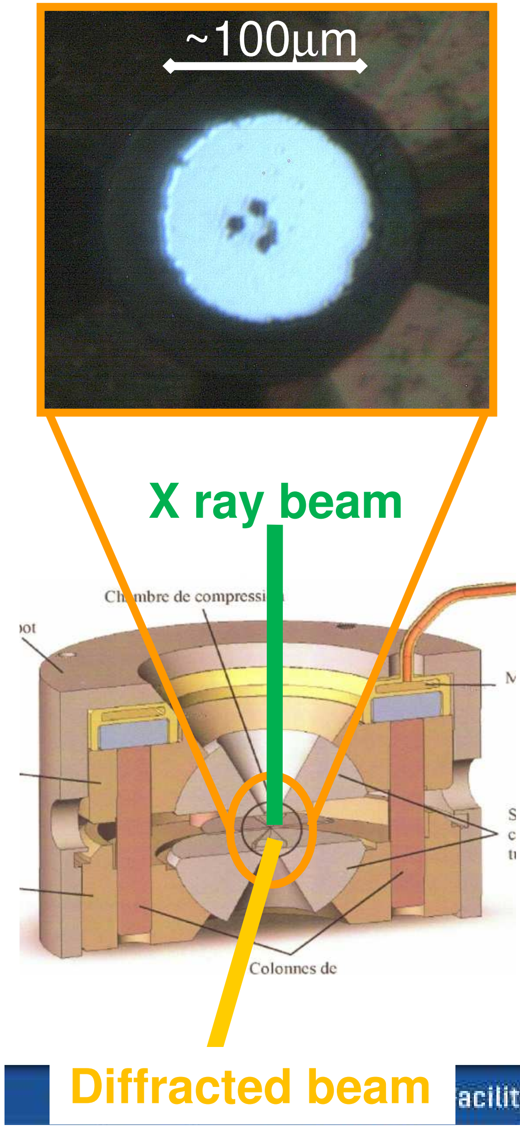
2920 K



Fe-5%wt Ni-15%wt Si ; P =

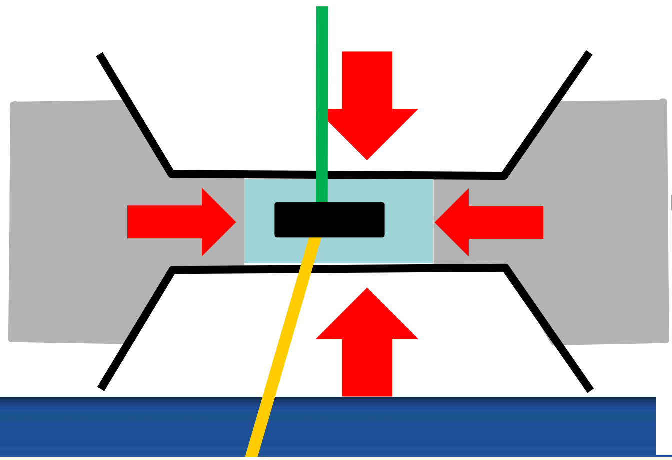


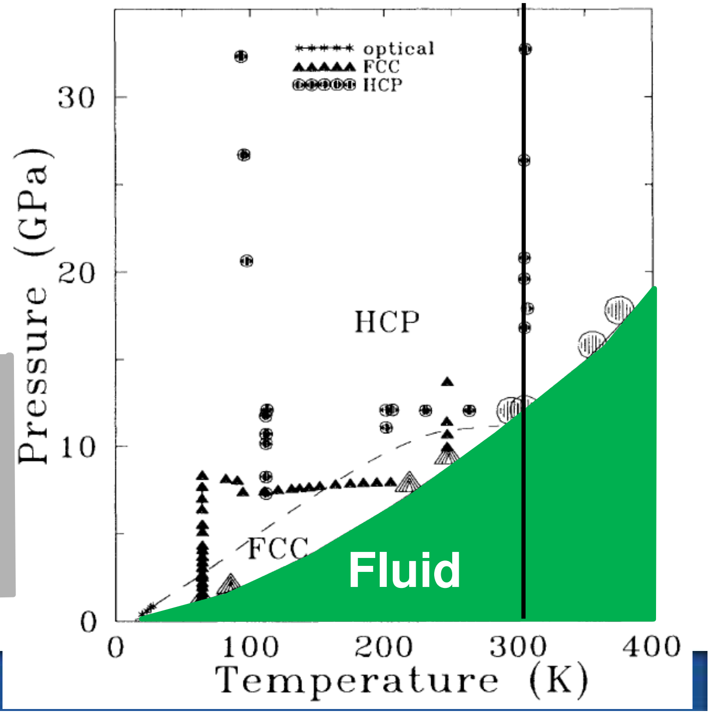
XRD using a DAC



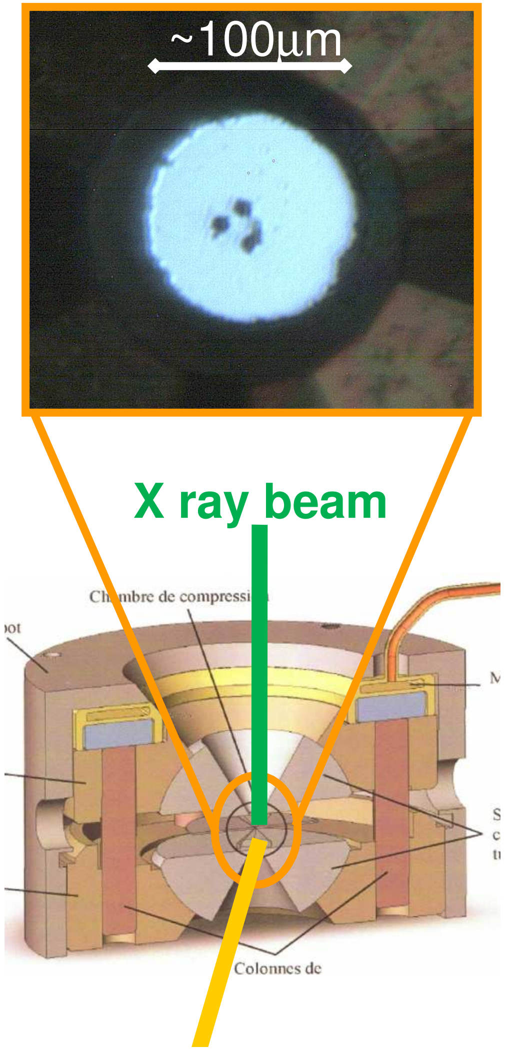
Important technical aspects:

- **gasket material**
- **sample dimensions**
- **pressure measurement**
- **pressure transmitting medium**
  - **Best hydrostatic conditions if PTM is liquid**
    - **not always the case at low temperature**
  - **- He** **Room T - Low T**





XRD using a DAC



Important technical aspects:

- **gasket material**
- **sample dimensions**
- **pressure measurement**
- **pressure transmitting medium**

Best hydrostatic conditions if PTM is liquid

not always the case at low temperature

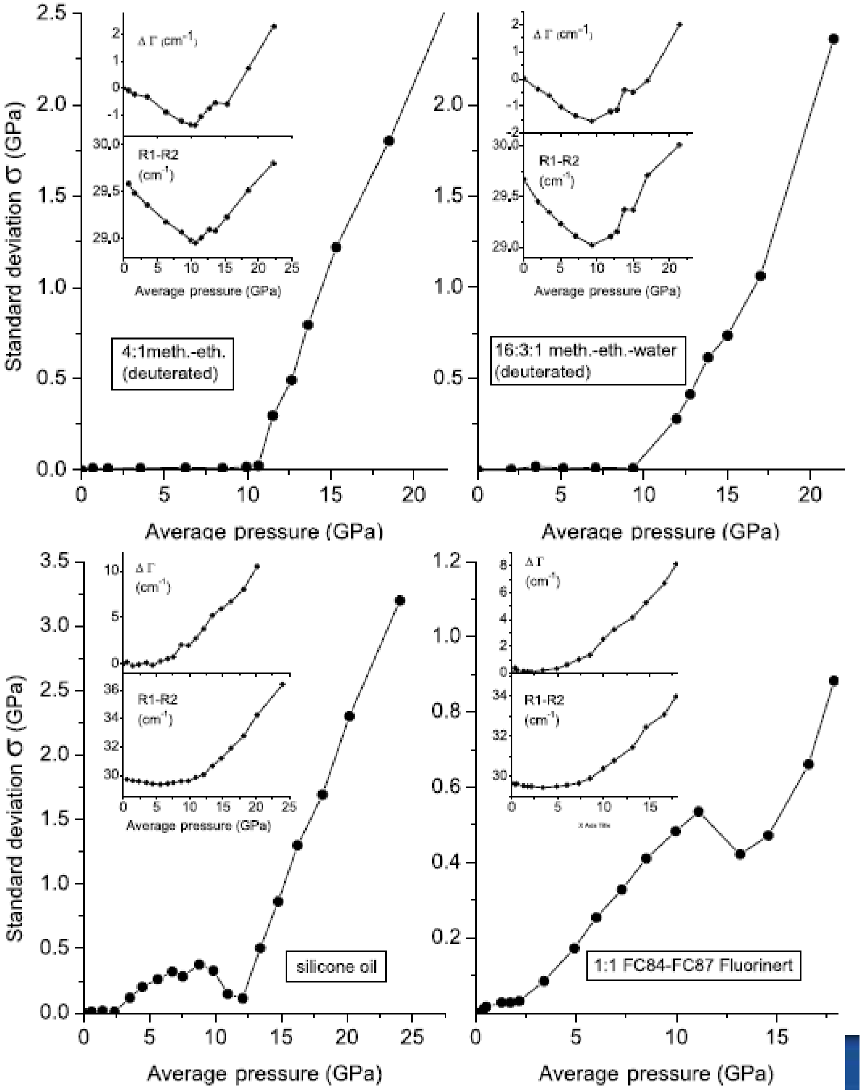
- He	Room T - Low T
- Ne, Ar, N_2, H_2, O_2 …	Room T - High T
- Mix Eth:Meth:Water	Room T - Low T
- Oil	Room T - Low T
- Mother liquid	Room T - Low T
- Salts	High T

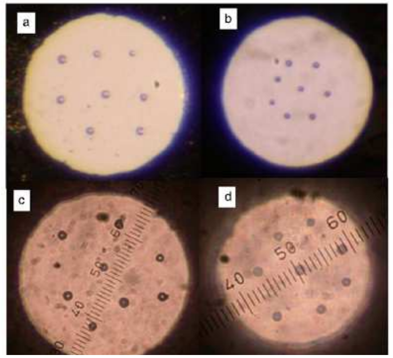
XRD using a DAC

Hydrostatic limits of 11 pressure transmitting media

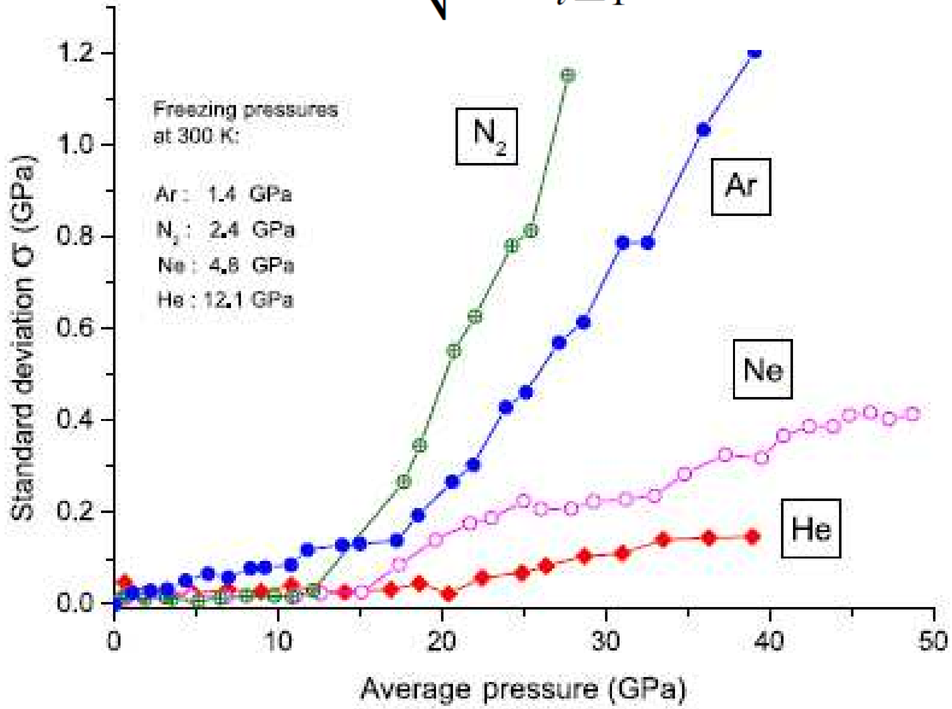
J. Phys. D: Appl. Phys. 42 (2009) 075413 (7pp)

S Klotz, J-C Chervin, P Munsch, and G Le Marchand





$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - \bar{P})^2}$$



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- Scientific examples of high pressure experiments

ESRF High Pressure Activity

ID06, ID15B, ID27 : X-ray Diffraction – Structure, Crystallography, Strain, Deformation, …

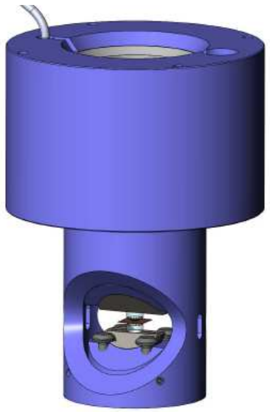
ID18: Nuclear Resonance Scattering - Magnetism, Phonons

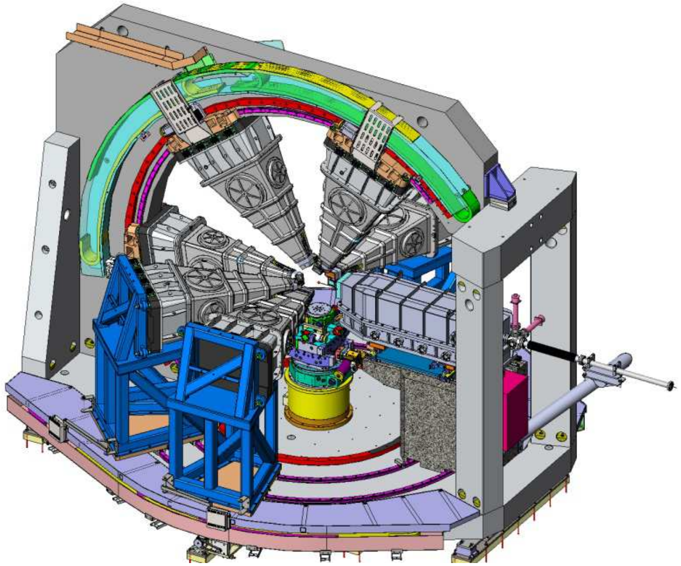
ID20: Resonant Inelastic X-ray Scattering - Electronic and Magnetic Structure

ID28: Inelastic X-ray Scattering, Diffuse Scattering – Phonons

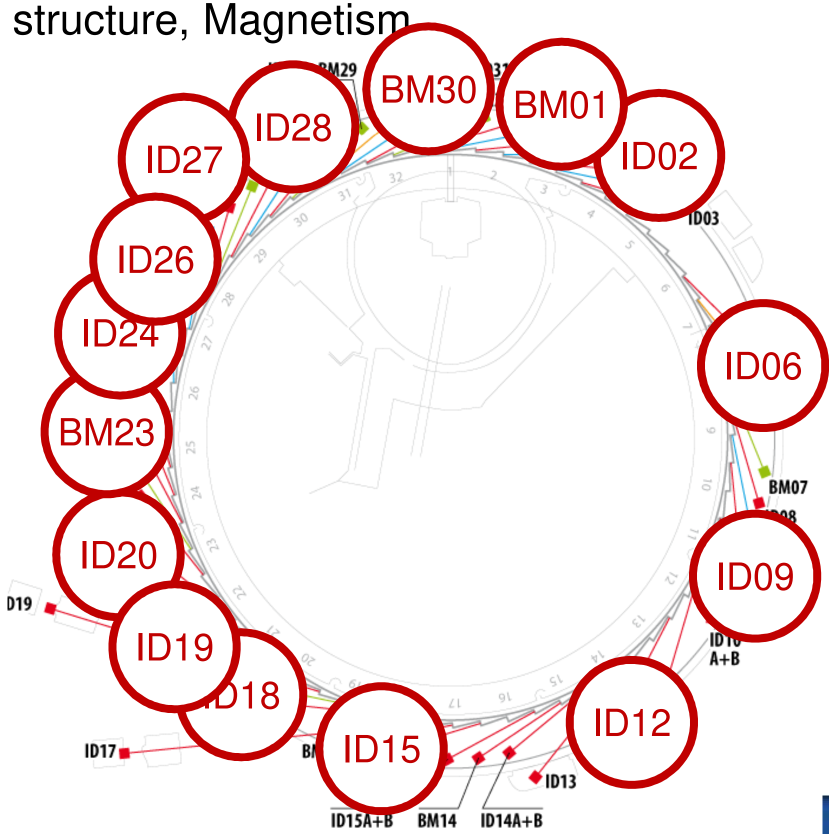
ID12, BM23, ID24: XAS, XMCD - Local and electronic structure, Magnetism

ID02, ID26, BM01, BM30, ID09B, ID19, ….





ID20: 72 Analysers and Panoramic DAC



ESRF High Pressure Laboratory

USER DEDICATED SPACE FOR DAC PREPARATION:

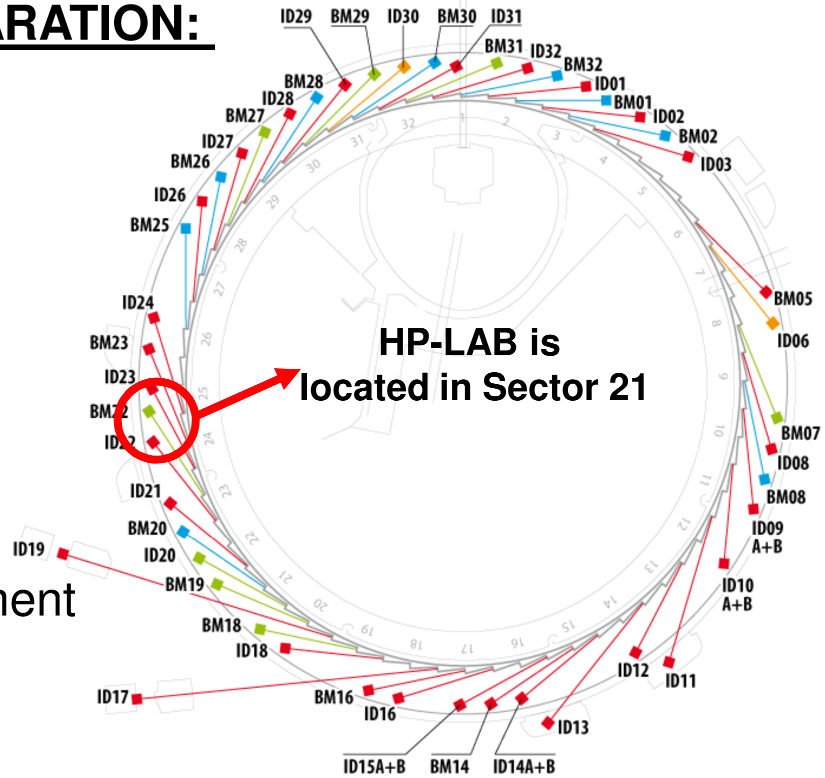
- From **diamond purchase** to **sample loaded**

HP-LAB PURPOSES:

- **SERVICE** to extreme condition experiments at the ESRF beam lines

- **LOAN POOL** with all equipment for DAC experiments

- **DEVELOPMENT** of extreme condition equipment requested from beamlines



Jeroen Jacobs

ESRF High Pressure Laboratory

AVAILABLE SPACE: FOUR DEDICATED ROOMS

- user dedicated space (21.0.12, 21.0.13)
- super-user space (21.0.09)
- gas loading space (21.0.11)

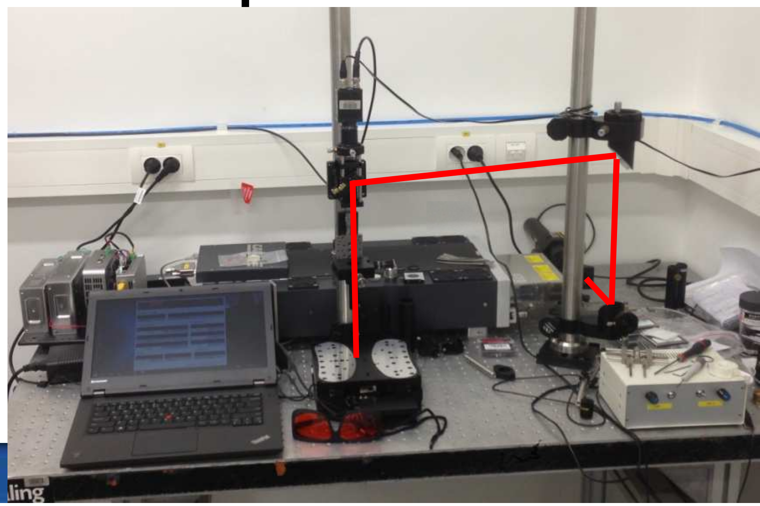
AVAILABLE EQUIPEMENT:

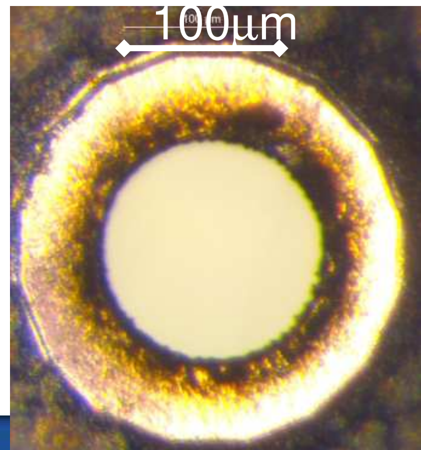
- Microscopes
- Spectrometer I for ruby fluorescense measurement
- Indentation “stage”
- Gas loading machine
- Laser drilling machine

SOON

- Femtosecond laser drilling machine to improve cutting quality

Very positive impact on the quality data produced at the ESRF





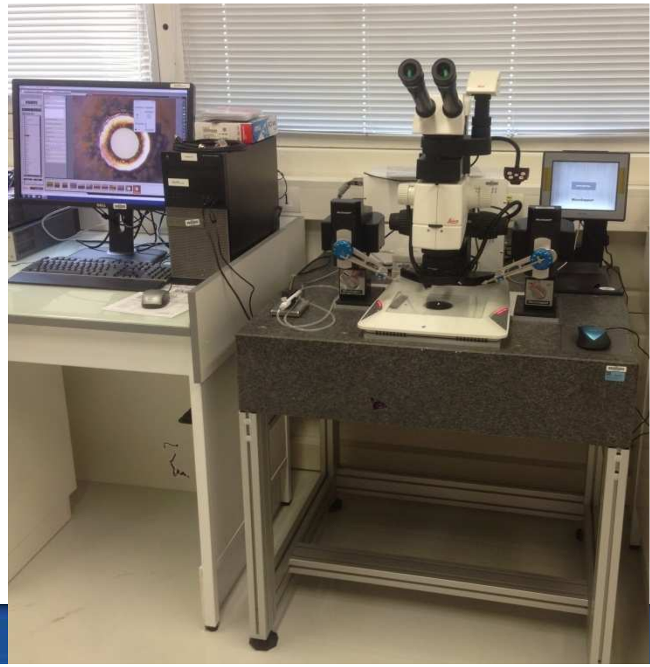
ESRF High Pressure Laboratory

AVAILABLE SPACE: FOUR DEDICATED ROOMS

- user dedicated space

AVAILABLE EQUIPEMENT:

- Be manipulation glove box
- Mouse controlled Micromanipulator
- Oven (120C under vacuum)
- Preparation space dedicated to HP-lab staff

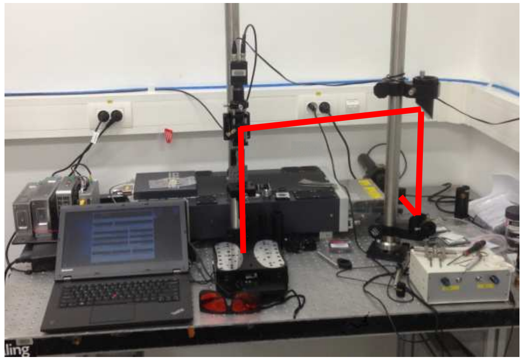


ESRF High Pressure Capabilities

Importance of high level offline and online equipments to perform the most challenging DAC loadings and experiments on-site

High pressure laboratory

+



Laser drilling

+

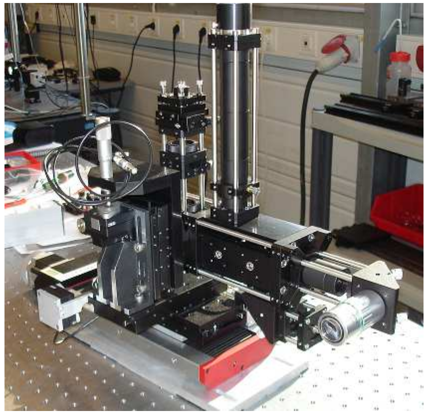
Sample manipulation

Inert atmosphere
sample manipulation
and preparation

+

Gas loading

+



Off-line characterization
Raman spectroscopy, laser annealing,
magnetic and transport prop …

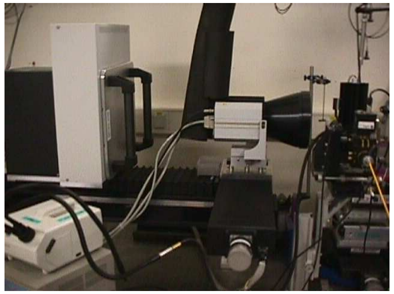
Outline

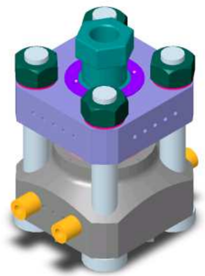
- Introduction
- How to generate and measure high pressure (using DAC)
- High pressure at ESRF
- **Example of a high pressure beamline (ID27 @ ESRF)**
- Scientific examples of high pressure experiments

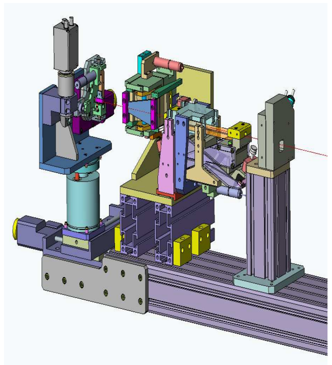
ID27 at ESRF (Grenoble, France)

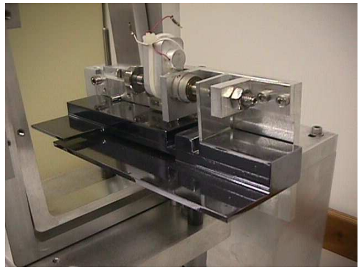
Very intense micro-focused beam
(2 microns) using two KB mirrors
at short wavelengths: 0.15<λ<0.4 Å

ESRF
6 GeV



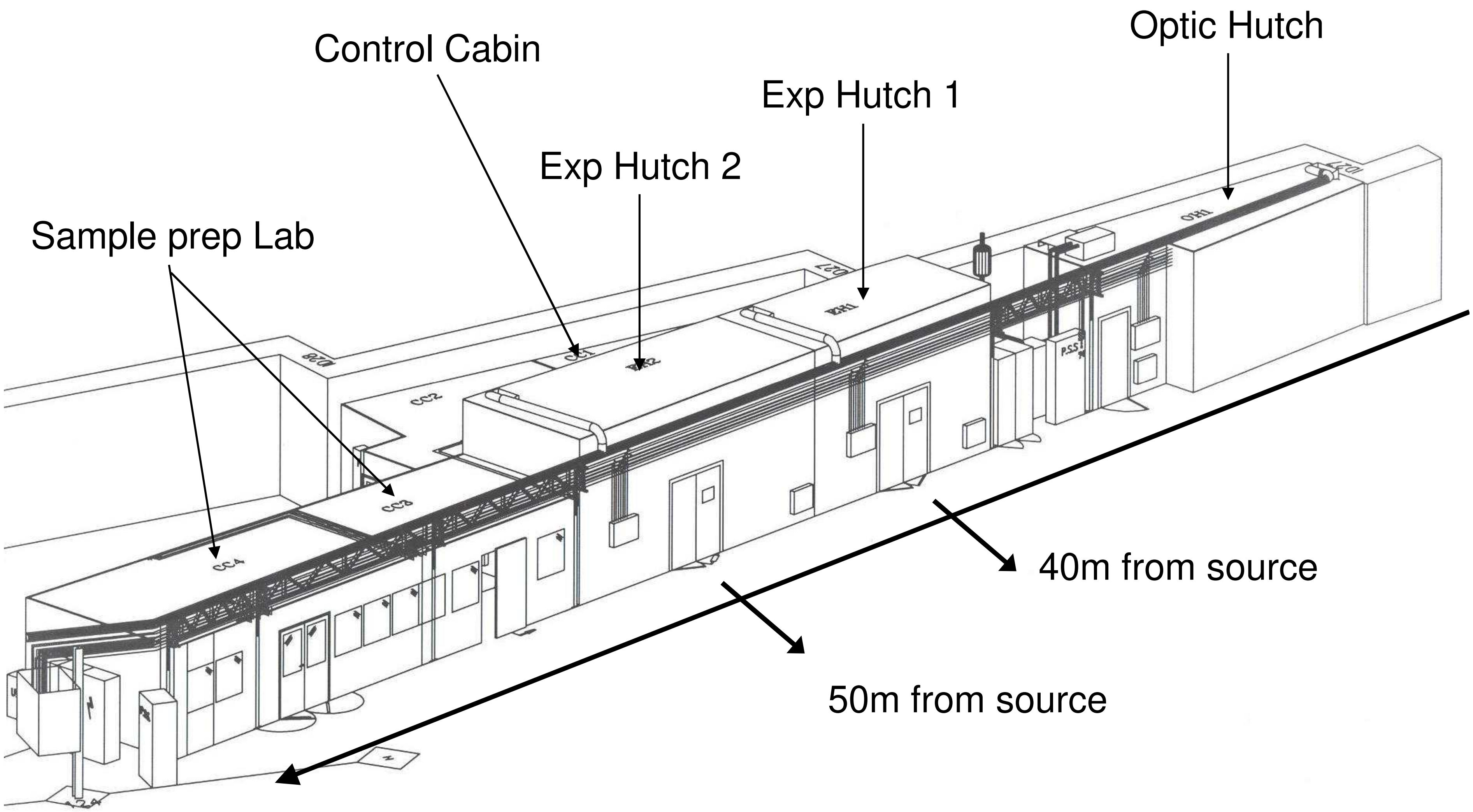






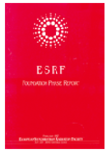
Detectors | Sample environment | Mirrors | Monochromator | X-ray Source

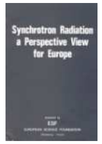
ID27 at ESRF (Grenoble, France)

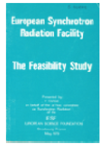


ESRF : More than 20 years of success and excellence

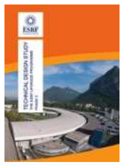




- **1988** **12 member states sign the creation of the ESRF**
- **1992** **1st electron beam in the storage ring**
- **1994** **Inauguration : 15 beamlines**
  In time and within budget
- **1998** **40 beamlines**
  In time and within budget
- **2009-2015** **Upgrade Programme Phase I**
  In time and within budget
- **2012** New design for the storage ring
- **2015 - 2022** ***Upgrade Programme Phase II***
  18 month shutdown from 12/2018

Upgrade Programme Phase II

World-wide efforts to improve the SR beam parameters

Users strongly benefit by any of the following improvements:

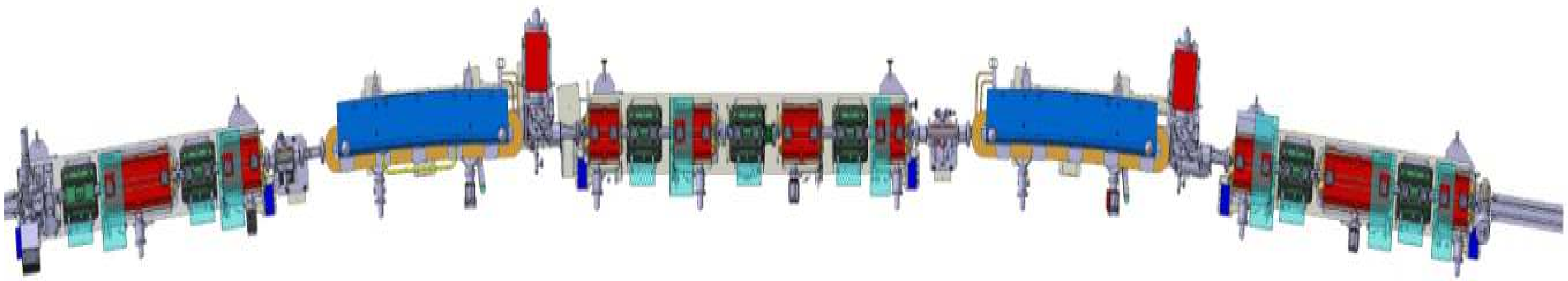
Vertical **e**mittance	=> diffraction limit reached routinely everywhere
Beam current	=> close to the limits imposed by the BLs
Bunch length	=> costly solutions (e.g. SC Crab Cavities)
Energy **s**pread	=> no solutions exist for a significant decrease (< 0.05-0.1%) IN SR

Horizontal emittance => large potential for reduction

Upgrade Programme Phase II

today's synchrotron radiation sources

double bend achromat (DBA - ESRF)



What do we do today to make $\epsilon_{\mathbf{x}} \propto \mathbf{E^2} \cdot \theta^{\mathbf{3}} \cdot \mathbf{\Gamma}$ small ?

➔ many cells ➔ large storage rings
- ESRF: 32; APS: 40; SPring-8: 48 NSLS II: 30

➔ damping wigglers
- PETRA III; NSLS II

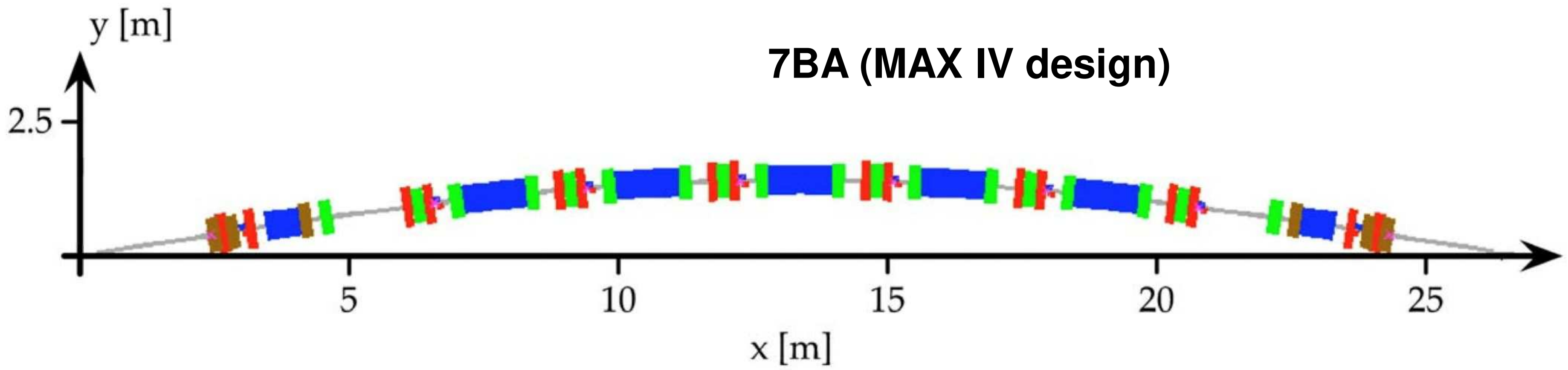
Upgrade Programme Phase II

Next step

What can be done to make $\epsilon_{\mathbf{x}} \propto \mathbf{E^2} \cdot \theta^{\mathbf{3}} \cdot \mathbf{\Gamma}$ small ?

multi-bend achromat (MBA) **D. Einfeld**

7BA (MAX IV design)



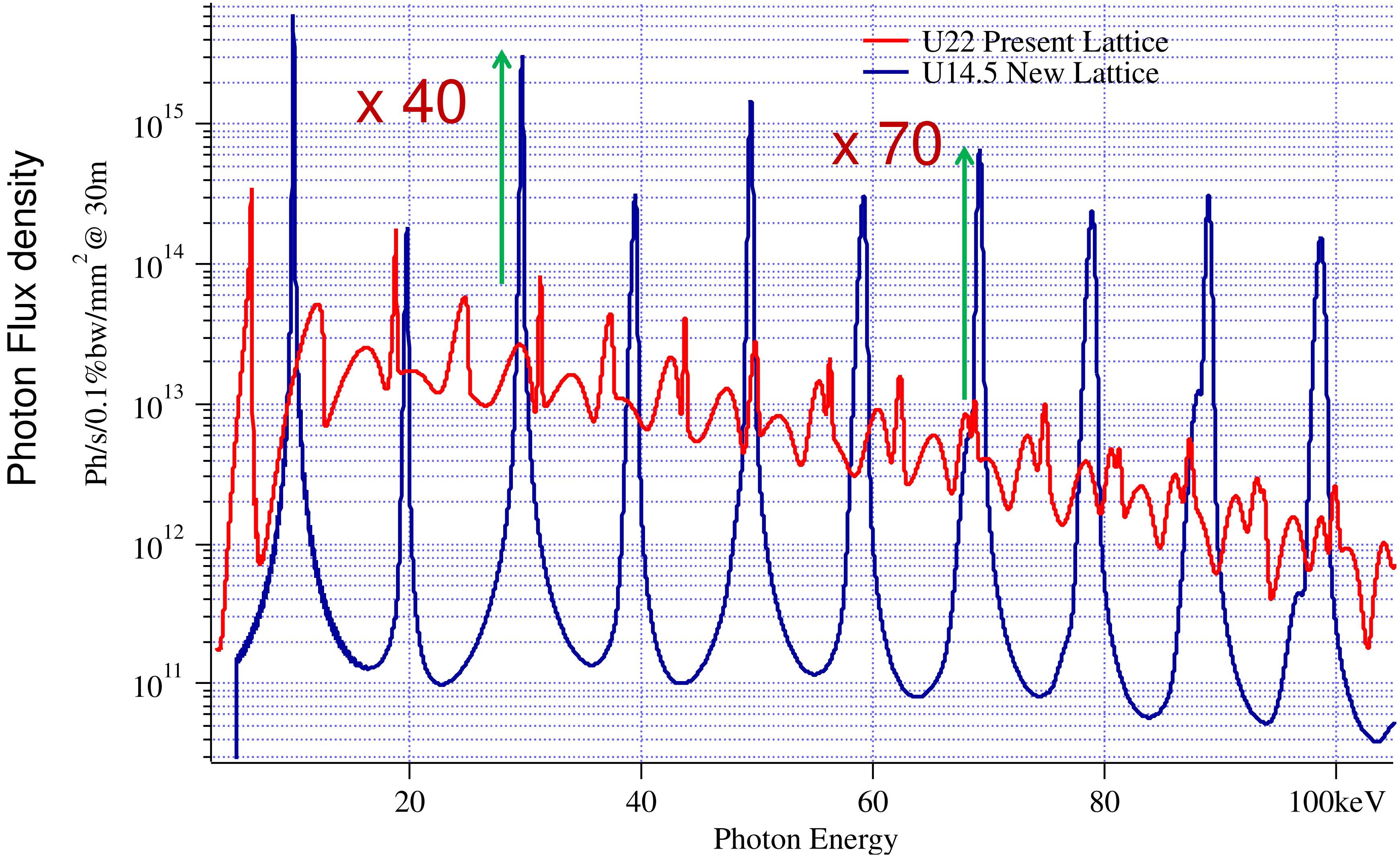
➔ **many small bending magnets per cell**

Upgrade Programme Phase II

ESRF

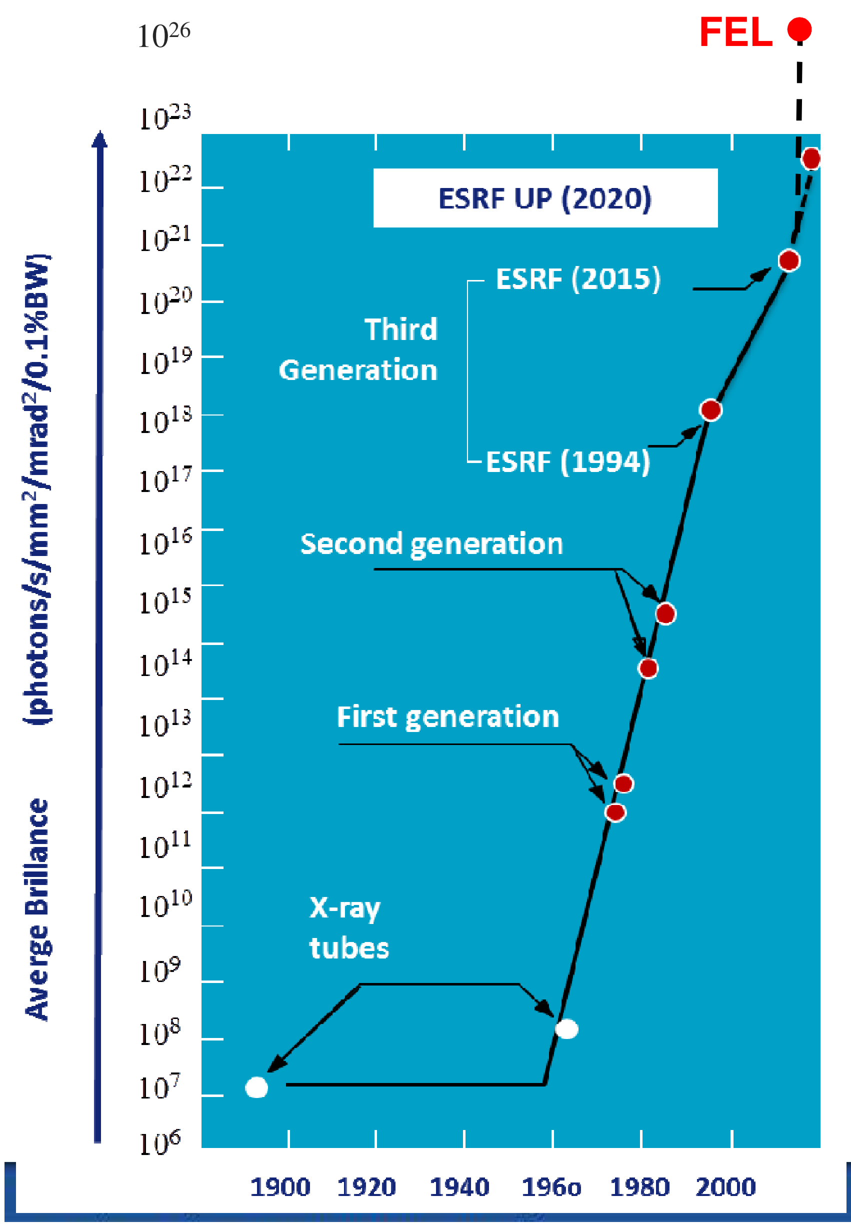
U22 Min. gap 6 mm, K_{max}=1.7
U14.5 Min. gap 4 mm, K_{max}=1.7 (CPMU)

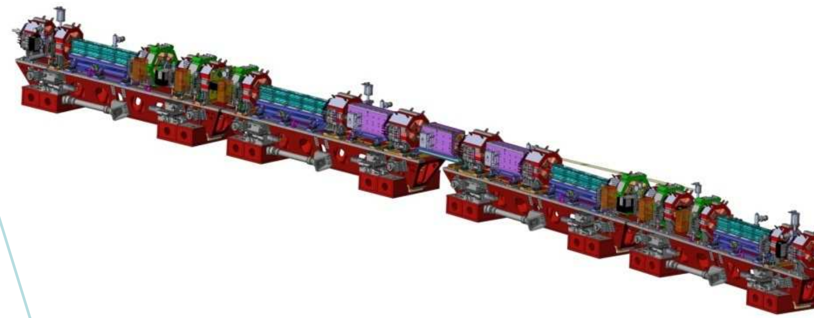
Increased Flux



Upgrade Programme Phase II

THE EXTREMELY BRILLIANT SOURCE - EBS





Horizontal emittance

ε_x= 4 nm

↓

ε_x= 0.15 nm

ID27: x 50 monochromatic flux, x 5 10^3 pink beam

ID16: x 30 in flux at ultimate 10nm focus (nanoprobe BL)

ID10: x 40 in coherent flux (soft matter BL)

ID31: x 10^3 in focused high energy beam (interfaces BL)

ID29: x 10^5 in flux density at the sample (MX BL)

…….. etc

Upgrade Programme Phase II

Future of the ID27 beamline

The reconstruction of ID27 is approved by the ESRF management

Objective:

Build a unique state-of-the-art beamline to:

→ **fully exploit the outstanding performance of the new storage ring**

→ **address the multiple challenges defined in the scientific and technical case**

Upgrade Programme Phase II

Future of the ID27 beamline

Four key areas identified:

- Materials at and beyond the current limits of static pressures and high temperatures
  → **High spatial resolution (down to 150 nm)**
- Structure and chemistry of low *Z* melts and glasses at extreme conditions
  → **High Flux (pink beam operation)**
- Fast melting, kinetics of chemical reactions
  → **Time resolution (down to micro-second)**
- Rheology of materials by fast X-ray imaging
  → **High coherent beam fraction**

Upgrade Programme Phase II

Future of the ID27 beamline

- The **new ID27 beamline** will be unique in the world in terms of **photon flux** and focusing capabilities at high X-ray energies**: x100 (monochromatic) to x5000 (pink beam).**

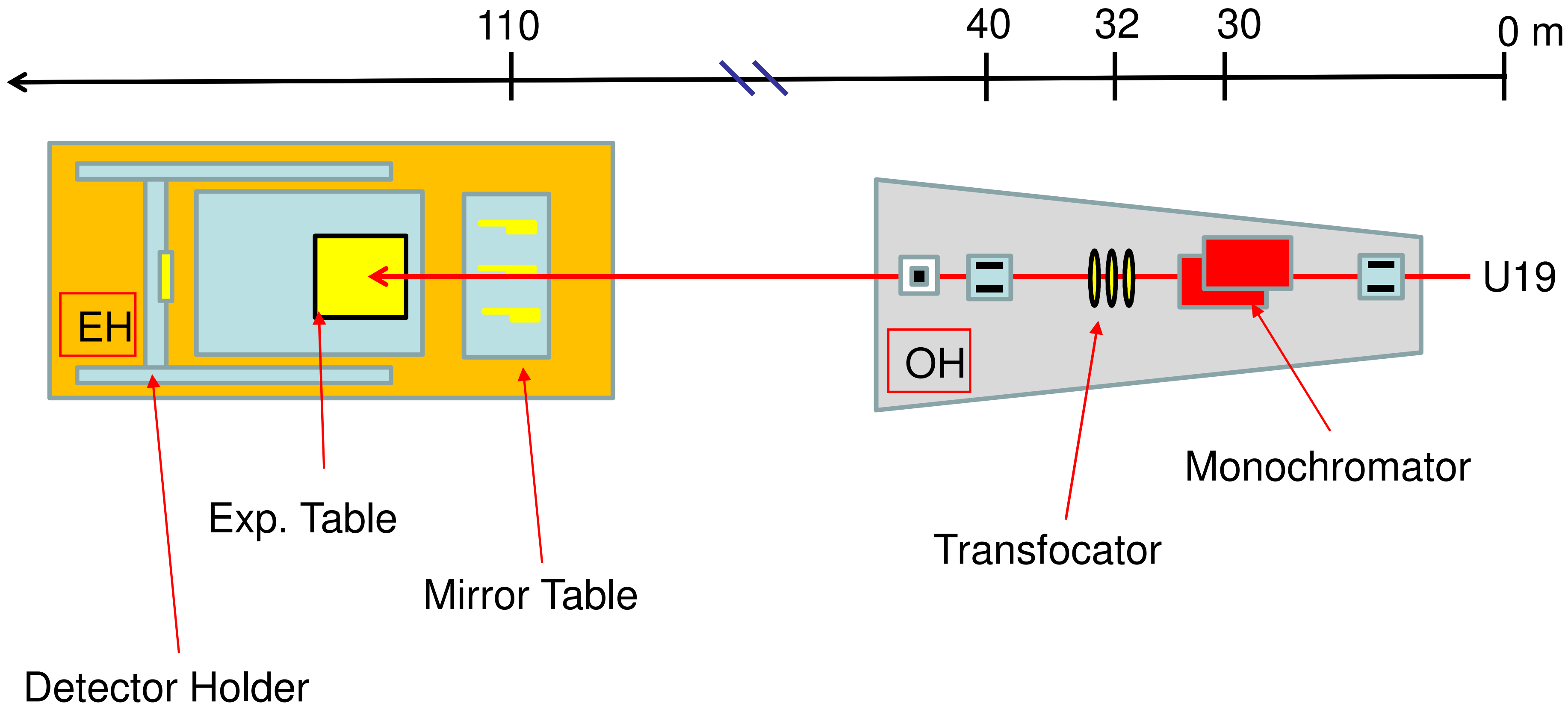
- It will offer flexible energy bandwidth and beam spot sizes to cover all the key areas identified in the scientific case: **10<E<70 keV; beamsize from 150nm to 5 mm**

- The new instrument **will complement ID15B and ID6LVP**, the two existing high pressure diffraction beamlines.

- It will enable **micro-second time resolved** studies to **bridge the gap between static and laser driven dynamic compression experiments**.

Upgrade Programme Phase II

Future of the ID27 beamline
Preliminary id27 beamline layout

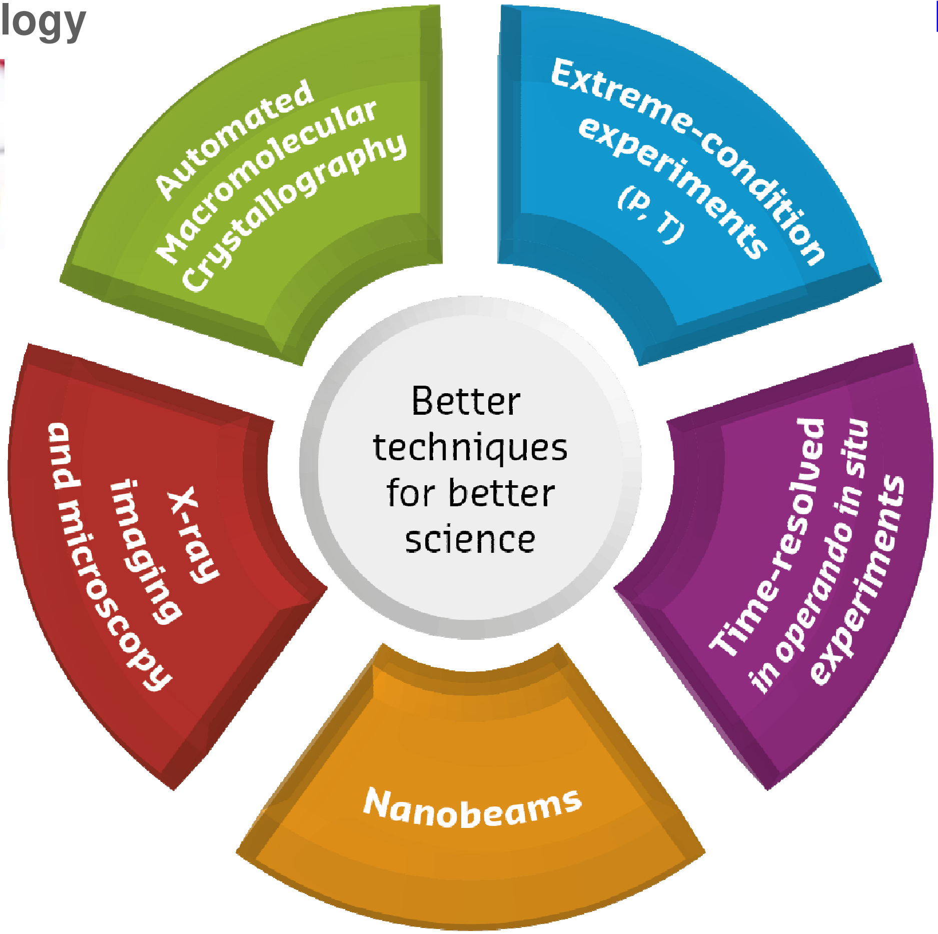


Upgrade Programme Phase II

Science case

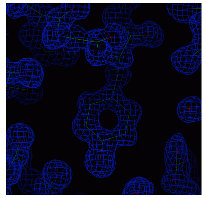
Health,
Structural biology

Earth science,
New materials



Medicine,
Paleontology,
Cultural heritage

Chemistry,
Energy, Materials,
Ultra fast biology



Nanosciences
Information technology

List of beamlines @ ESRF

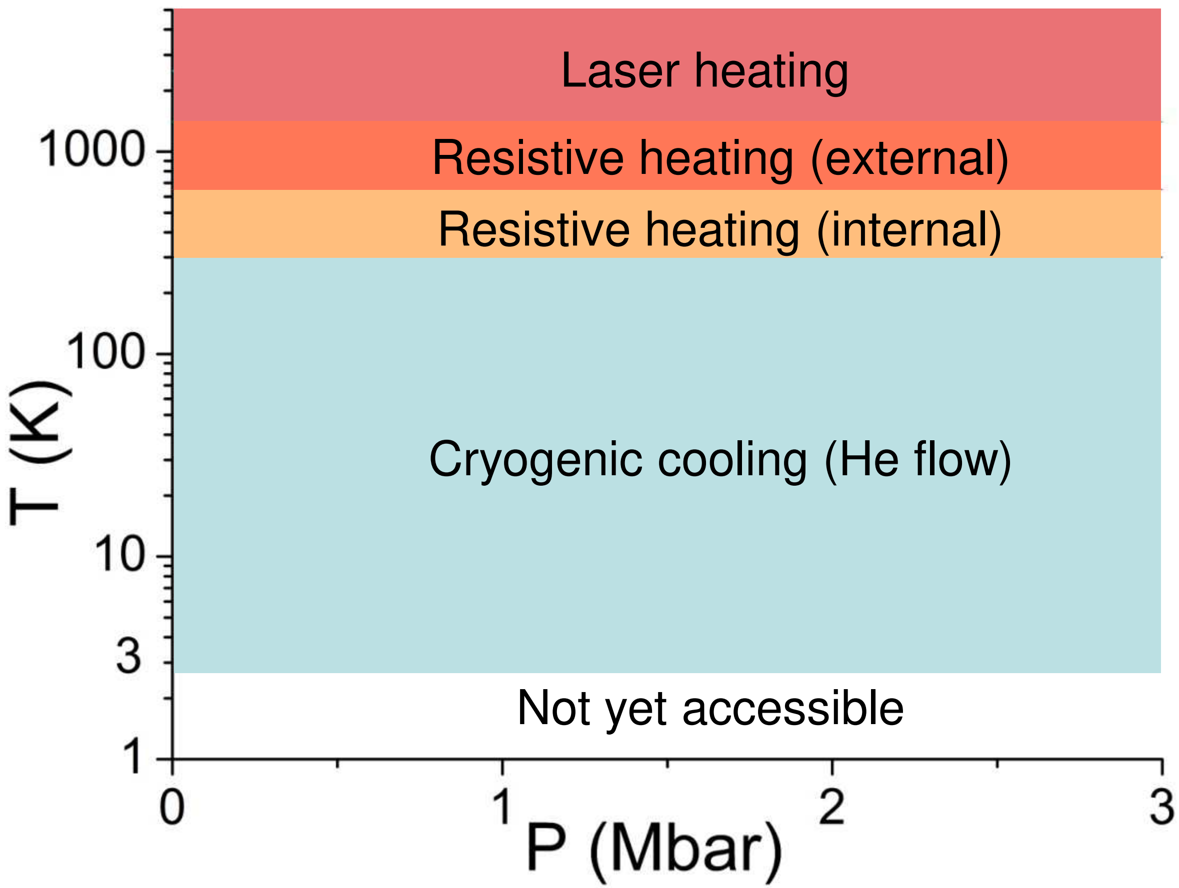
ID01	Anomalous scattering
ID02	High brilliance
ID03	Surface diffraction
ID06	XRD Large Volume Press
ID09	Biology
ID10	Coherence beamline XPCS
ID11	Material science
ID12	Circular polarisation
ID13	Microfocus
ID14	Protein crystallography
ID15	High energy diffraction / High pressure
ID16	NINA
ID17	Medical
ID18	Nuclear scattering
ID19	Microtomography – Topography
ID20	Magnetic scattering
ID21	X-ray microscopy
ID22	Microfluorescence
ID23	Macromolecular crystallography
ID24	Dispersive EXAFS
ID26	X-ray absorption and emission
ID27	High pressure
ID28	Inelastic scattering
ID29	Biology (MAD)
ID31	Powder diffraction
ID32	Spectroscopy using polarised soft X-rays
BM05	Optics
BM23	Absorption spectroscopy

BM01	Swiss-Norwegian	Absorption and diffraction
BM02	D2AM (France)	Materials science
BM08	GILDA (Italy)	Absorption and diffraction
BM14	(EMBL)	Structural biology (MAD)
BM16	(Spain)	Structural biology (MAD)
BM20	ROBL (Germany)	Radiochemistry
BM25	SPLINE (Spain)	Absorption and diffraction
BM26	DUBBLE (Netherlands, Belgium)	Multipurpose
BM28	XMAS (UK)	Magnetic scattering
BM30	FIP (France)	Structural biology
BM30	FAME (France)	Environment (EXAFS)
BM32	IF (France)	Surfaces and interfaces

Pressure + Temperature

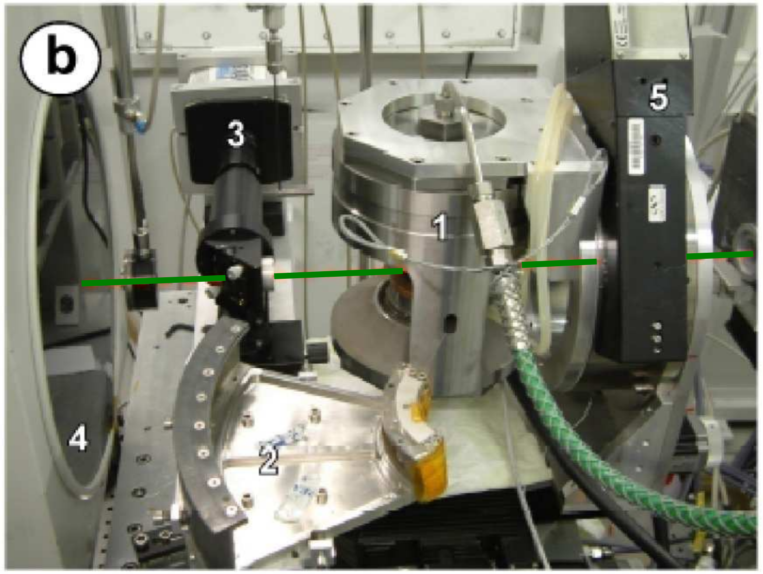
Available Pressure - Temperature domain using Membrane driven Diamond Anvil Cell

In-situ (Membrane driven) — **Pressure Control** (Diamond Anvil Cell)



ID27 – EH1

- **X-Ray Diffraction/Viscosity/Density/Tomography on powders-liquids-amorphous samples**
- **Paris-Edinburgh large volume cell**
- The only monochromatic large volume cell
- Pressure up to **17 GPa** on **5mm³** sample volume
- High temperature **T<2300 K**



RoToPEC

Device requirements:

1) Designed for synchrotron experiments: operate 24/24h, 6/7 days

2) Continuous He flow cryostat No vibrations, sample <50μm

3) For high pressure (high magnetic field) experiment: DAC weight ~ 500g

4) Minimum possible temperature: Two heat exchangers: $T_{MIN} = 2.1K$

5) Excellent thermal homogeneity and stability on first Heat exchanger $\Delta T/T<10^{-3}$

6) Fast colling and heating rates (designed for synchrotrons)

7) Compact, light, easy and user friendly (automation) to operate

8) Also suitable for inelastic, absorption, X ray experiments

and complementary measurements: optical spectroscopies, transport, magnetic ...

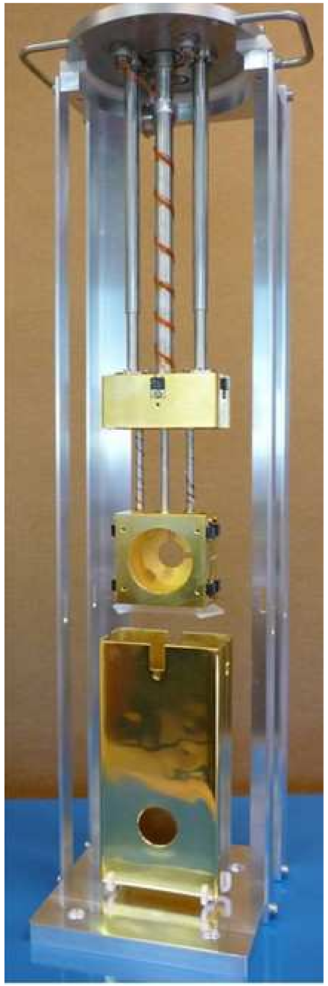
9) HP-XRD CRYSTALS: Sphere of confusion <2um under rotation of ±35°

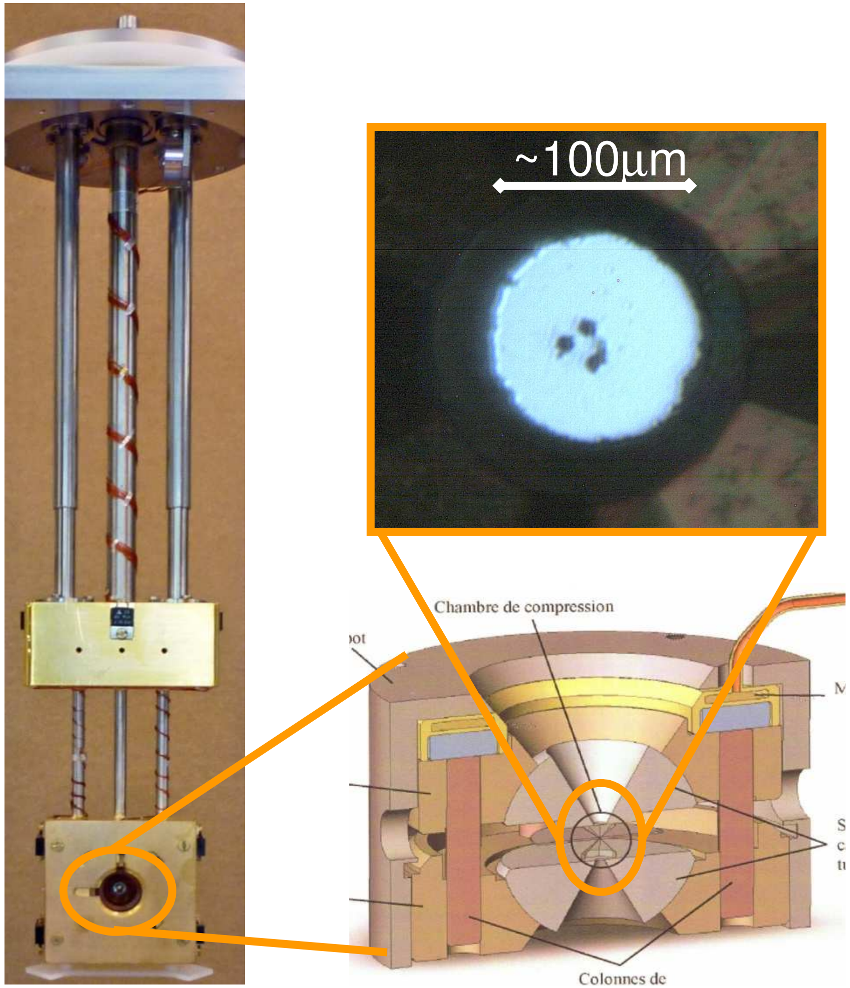
10) HP-XMCD at low energy: Amagnetic materials

Low Temperature XRD at HP

- Membrane driven Diamond Anvil Cell
- P < 200GPa = 2Mbar = 2 10^6 atm
- Helium flow Cryostat (**T** ≥ **2.5K**)

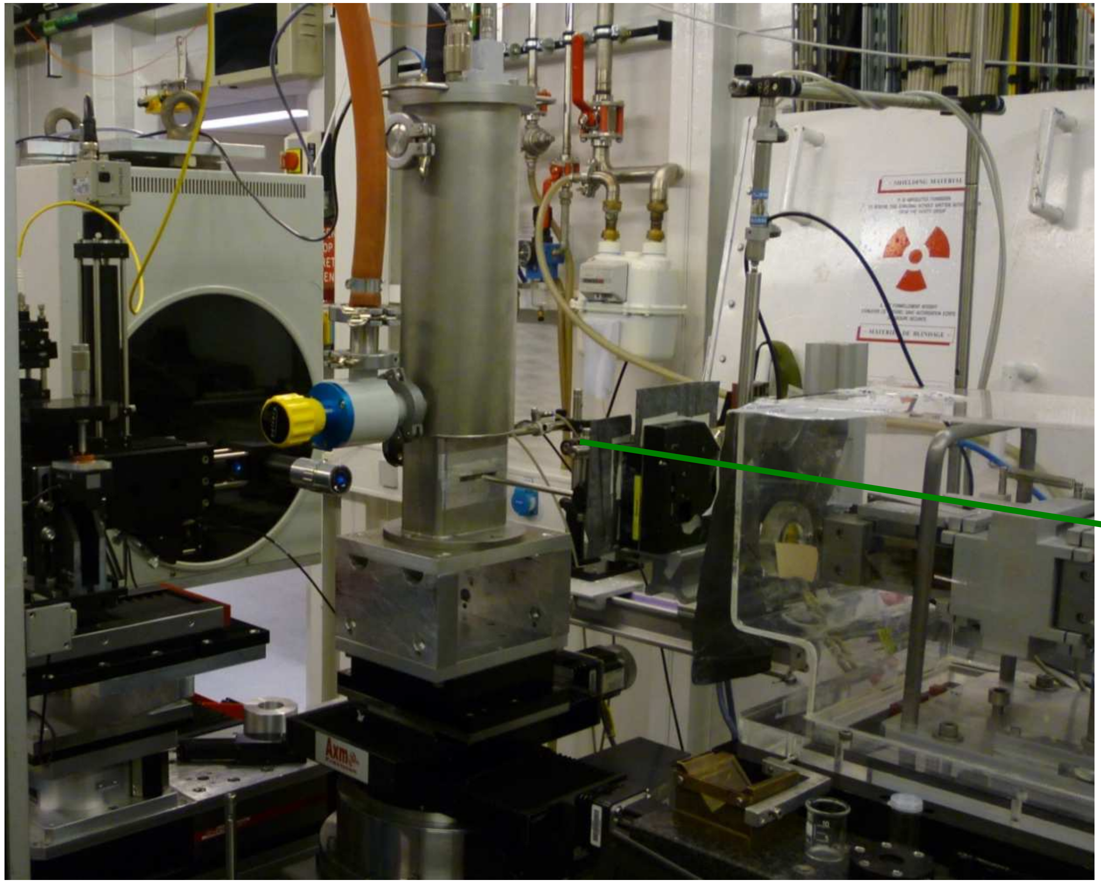
ESRF: ID27, ID15b





Low Temperature XRD at HP

- **X-Ray Diffraction on single crystals and powders with DAC**
- **Diamond anvil cell**
- Accessible PT domain for in situ powder XRD: **P>300GPa; T>2.5K**
(helium flow cryostats)



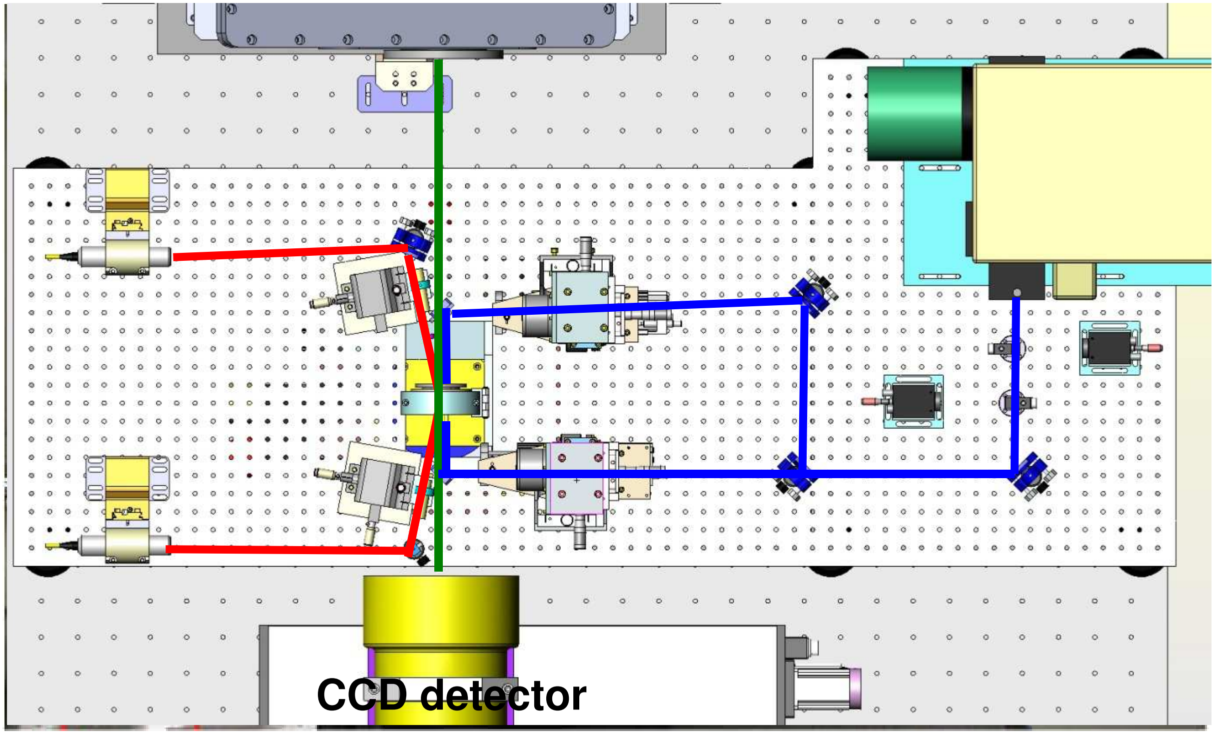
High Temperature XRD at HP

- **X-Ray Diffraction on single crystals and powders with DAC**
- **Diamond anvil cell**
- Accessible PT domain for in situ powder XRD: **P>300GPa; T>5000 K**

(YAG, CO_2 lasers)

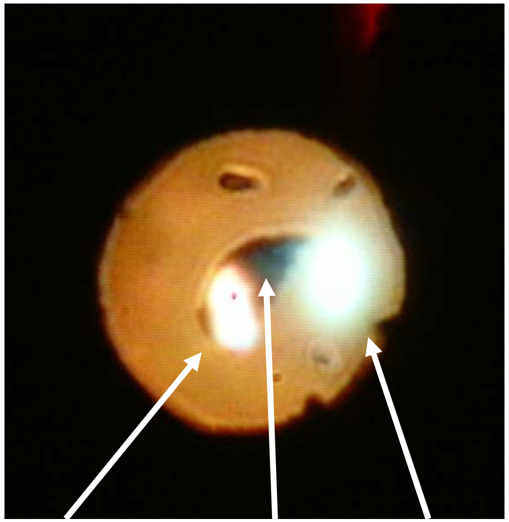
ESRF: ID27

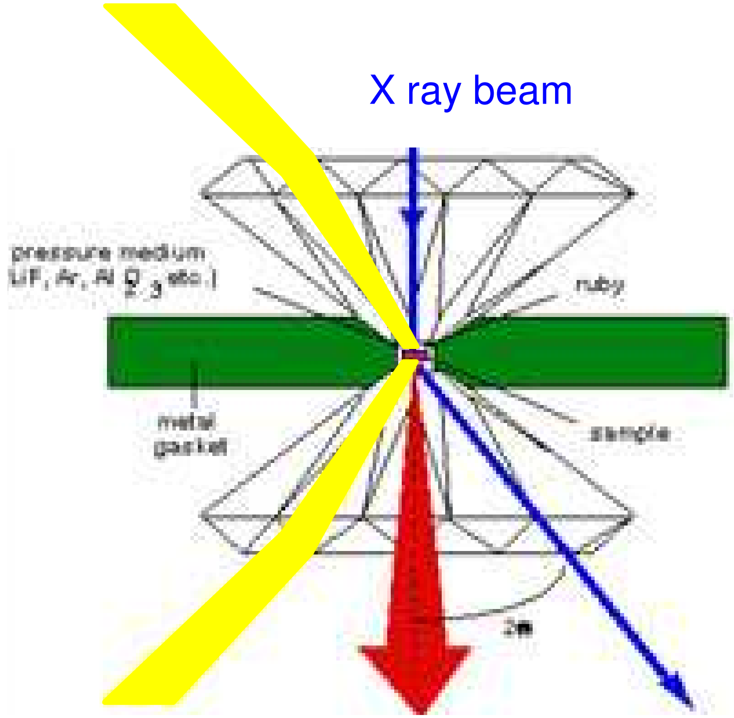
Laser beam
X-ray beam
Sample Imaging and T measurement



High Temperature XRD at HP

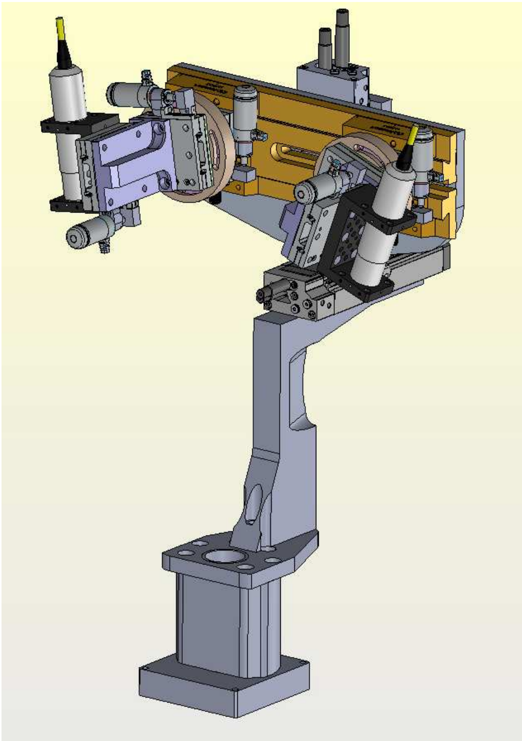
Difficulty to take diffraction pattern at the hot spot

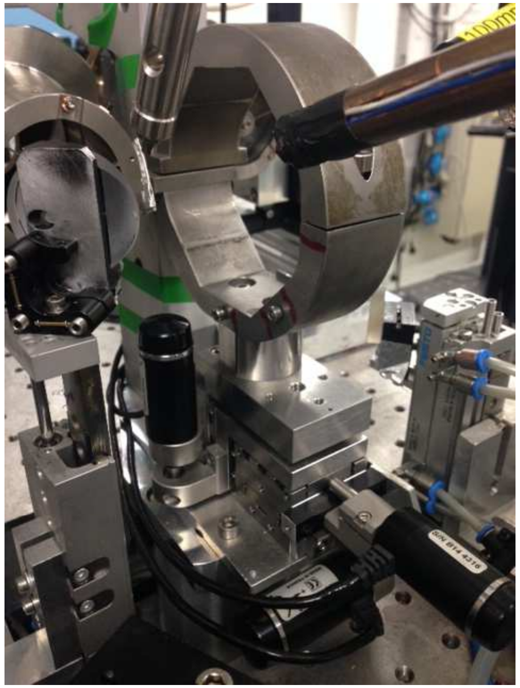




High Temperature XRD at HP

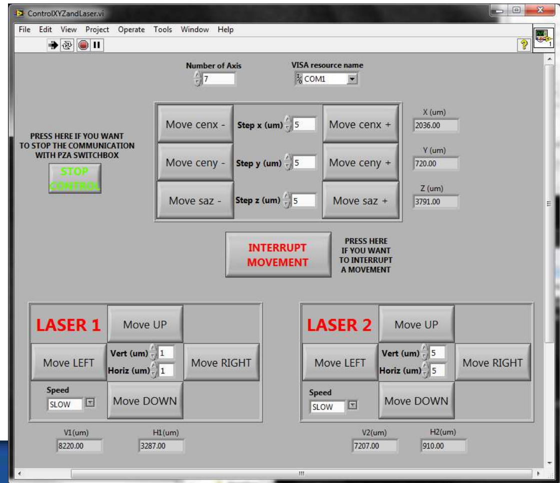
ESRF: ID27





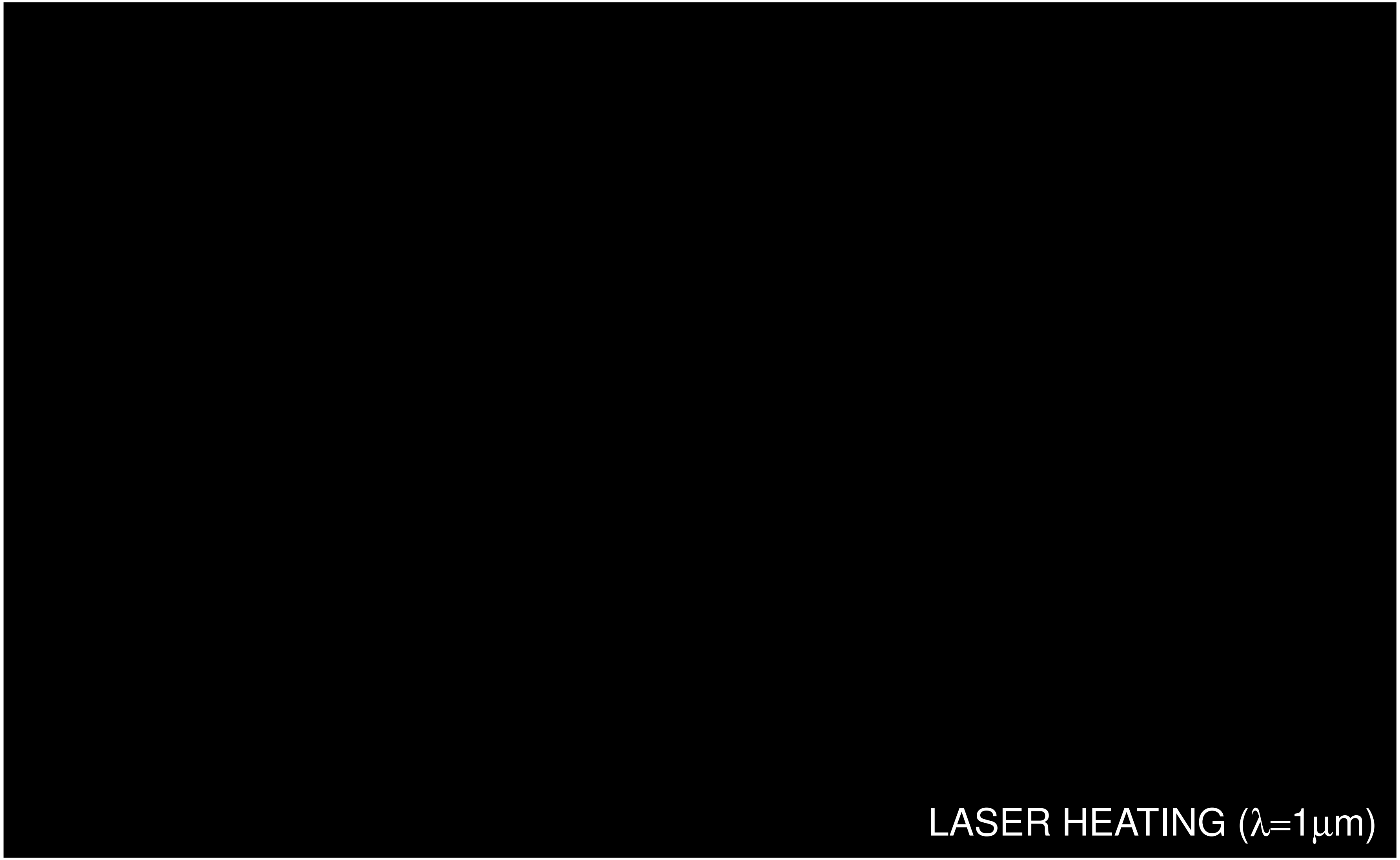
Second design of vertical laser heating developed at ID27

- simplified version but with the same number of "degrees of freedom"
- Labview software development
- available for users since end 2015
- possibility to install on other beamlines



X ray diffraction at HP-HT

ESRF: ID27



Collaboration **G. Weck** (CEA), **F. Datchi** (IMPMC), **ID27 team** (ESRF)

Outline

- Introduction
- How to generate and measure high pressure (using DAC)
- High pressure at ESRF
- Example of a high pressure beamline (ID27 @ ESRF)
- **Scientific examples of high pressure experiments**

Liquid and glassy states at HP

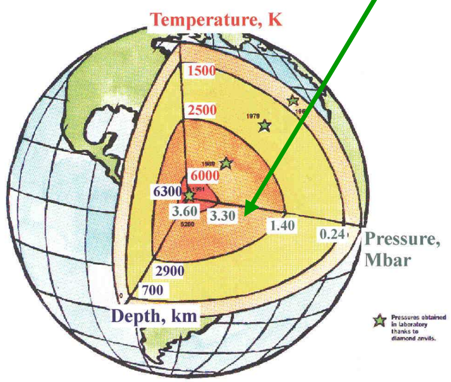
Physics, chemistry and biology

•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

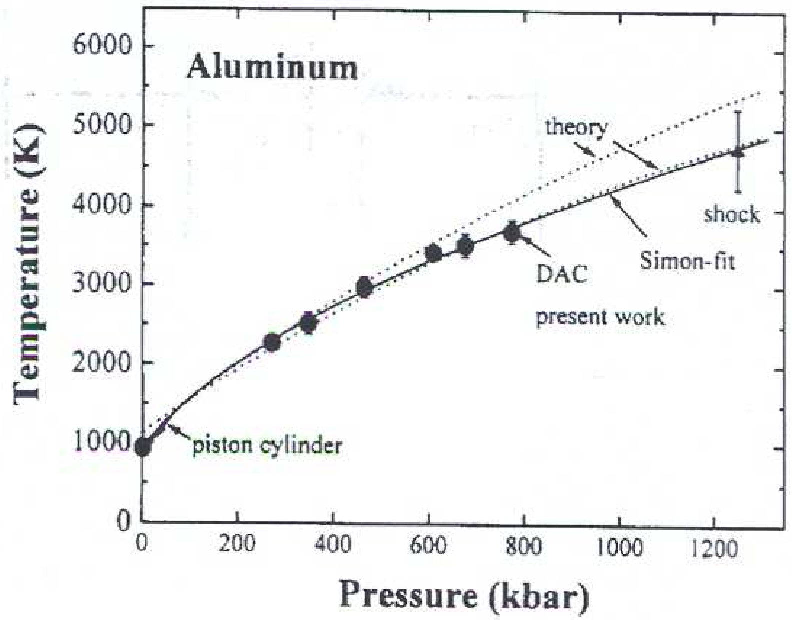
•Effect of light elements

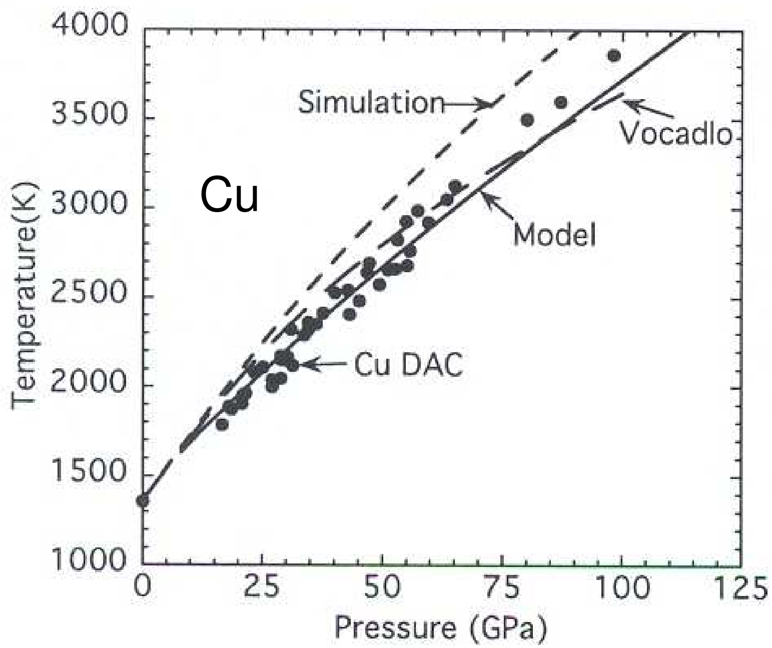
•Water in the Earth's upper mantle

•Magmas...

Melting at HP

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



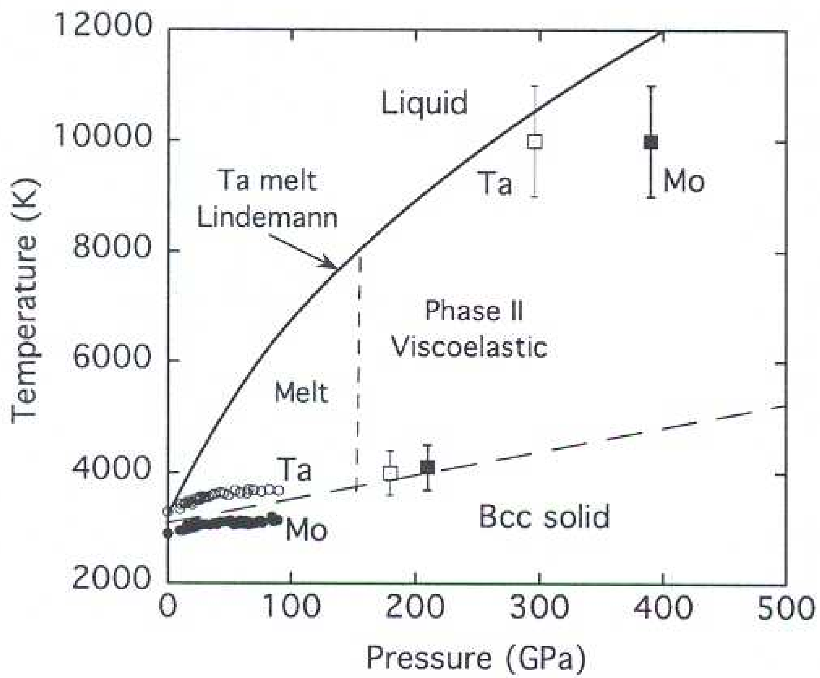


Ref. : Al: R. Boehler, M. Ross, EPSL, 153, 223(1997)
Cu: M. Ross, R. Boehler, D. Errandonea, PRB, 76, 184117(2007)

Melting at HP

But also some fundamental disagreements:

Most famous: Iron but also other transition metals such as Ta, W, Mo, Fe…



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

Why???

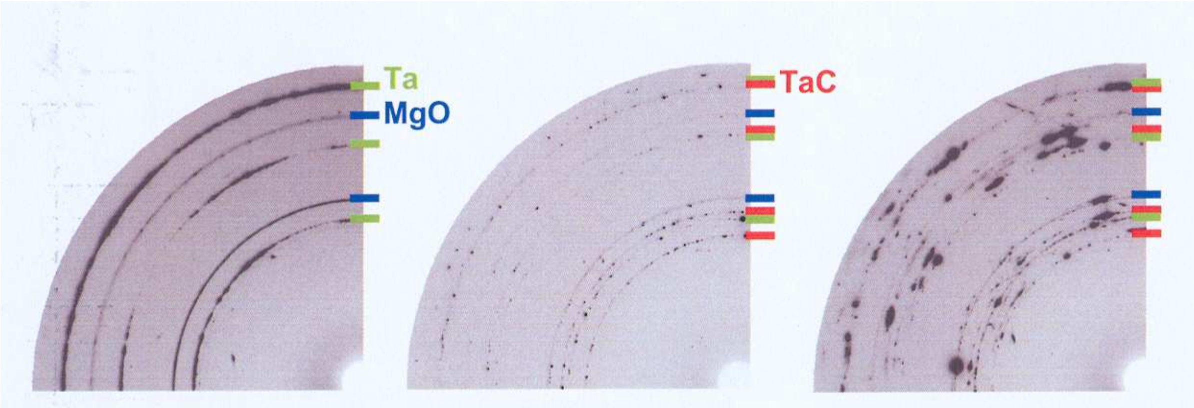
↓

Reaction with diamonds
Synthesis of carbides

….

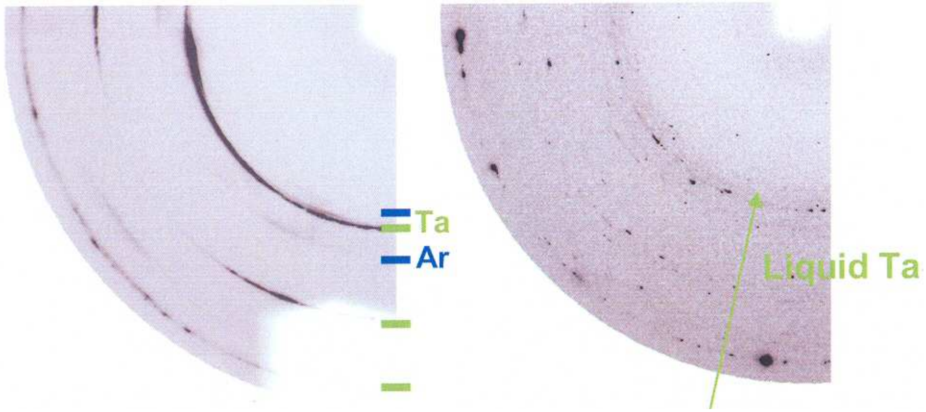
Melting of Ta @ HP

Ta in MgO (pressure medium)

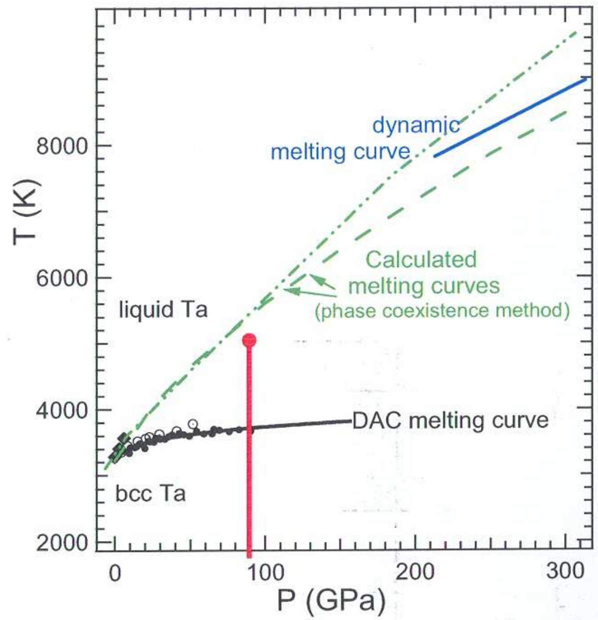


Before heating During heating After heating: ~ 50% of Ta transformed into TaC

Ta in argon (pressure medium) Al_2O_3 coated diamonds
Still some traces of TaC but much less than without coating

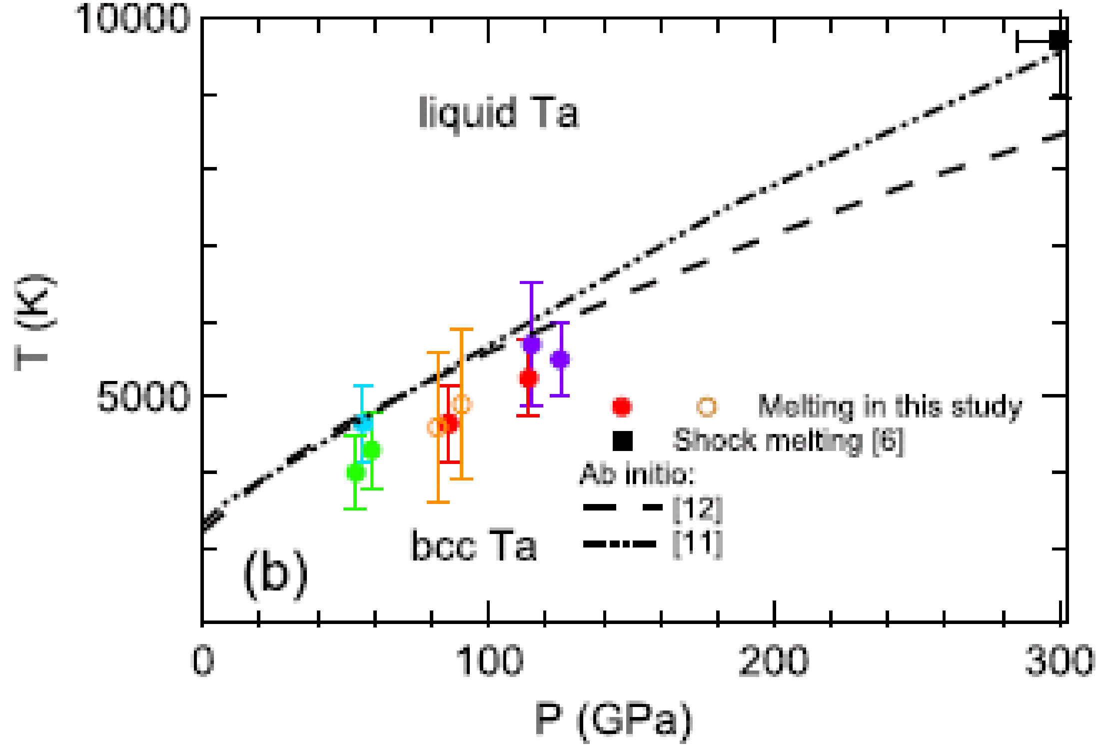


Before heating During heating



Dewaele et al, Phys. Rev. Lett. 104, 255701 (2010)

Melting of Ta @ HP



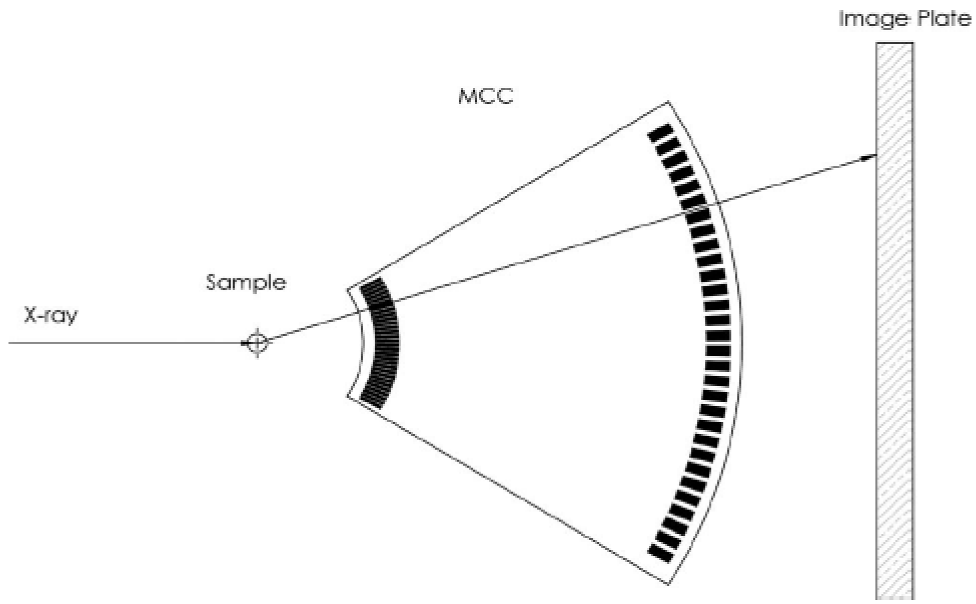
Melting curve of Ta in good agreement with theory and shock data

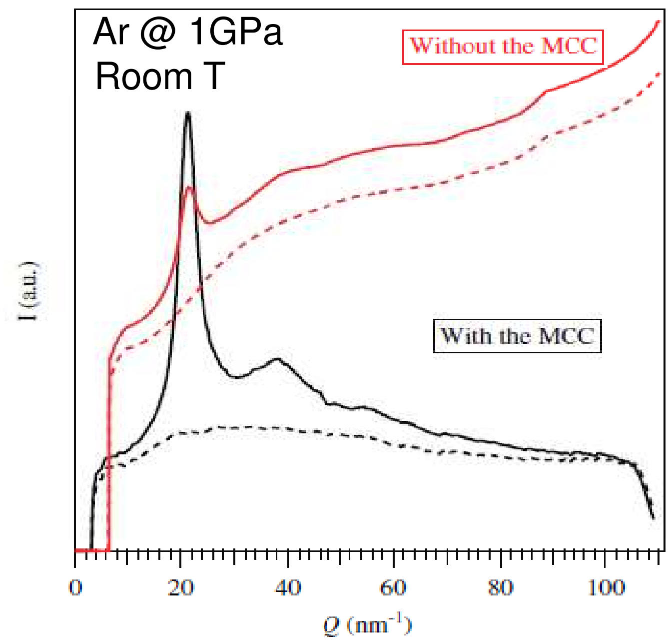
Used pressure medium: MgO, Ar, Ne, NaCl, Al_2O_3, KCl

Dewaele et al, Phys. Rev. Lett. 104, 255701 (2010)

XRD of Dense Low Z Fluids

STRUCTURE FACTOR OF LOW Z LIQUIDS AT EXTREME CONDITIONS:
THE MULTICHANNEL COLLIMATOR (SOLLER SLITS)





Strategy:

Couple DAC with Multi-Channel Collimator to reduce Compton diffusion of diamonds

- **Partnership ID27 - CEA - IMPMC (LTP)**

G. Weck, G Garbarino et al., Rev. Sci. Instrum. 84 p 063901 (2013)

XRD of Dense Low Z Fluids

DE LA RECHERCHE À L'INDUSTRIE
cea

G. Weck
P. Loubeyre

IMPMC - INSTITUT DE MINÉRALOGIE ET DE PHYSIQUE DES MILIEUX CONDENSÉS

F. Datchi
S. Ninet
J. A. Queyroux
M. Saitta

ID27
ESRF

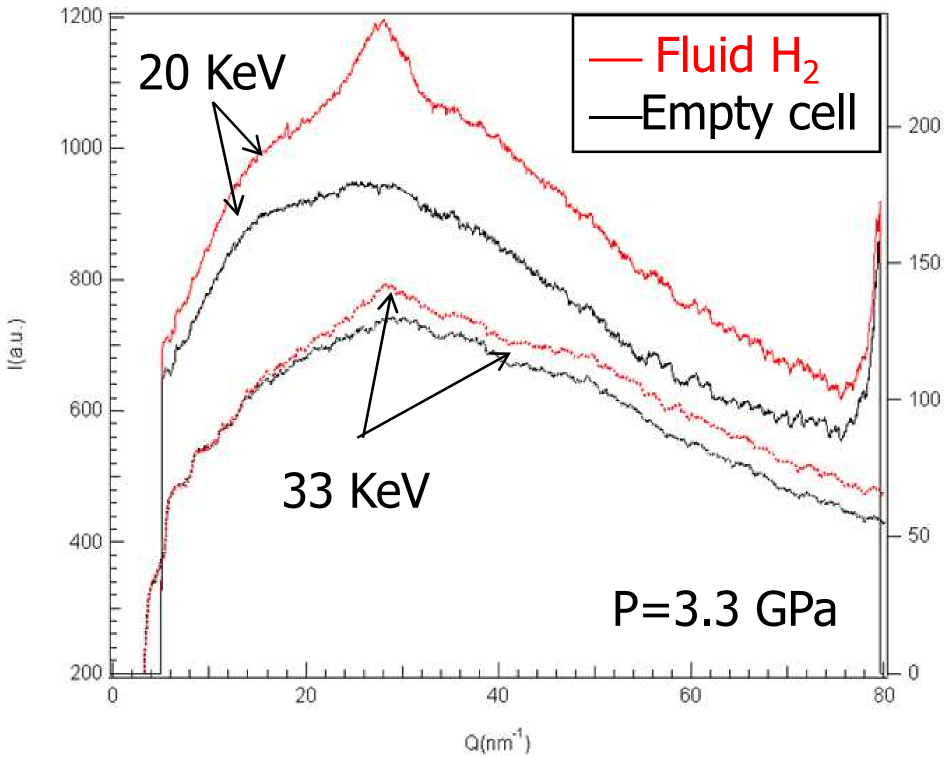
M. MEZOUAR
G. GARBARINO
S. BAUCHAU
F. DEVOTO

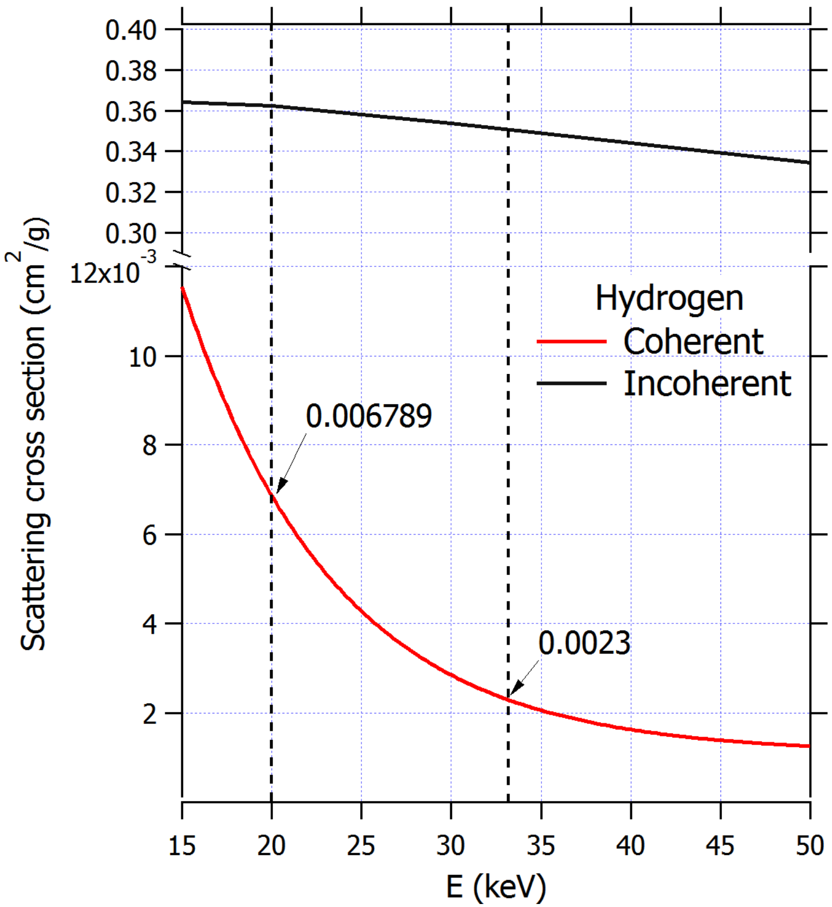
ESRF Long Term Project (2011-2014)
+ Projet ANR « MOFLEX » (2014-2017)

PROJET FINANCÉ PAR L'ANR - PROJECT FUNDED BY THE ANR
ANR

Fluid H_2 / D_2 (Z = 1) @ HP

STRUCTURE FACTOR OF LOW Z LIQUIDS AT EXTREME CONDITIONS:
THE MULTICHANNEL COLLIMATOR (SOLLER SLITS) AND ENERGY INFLUENCE





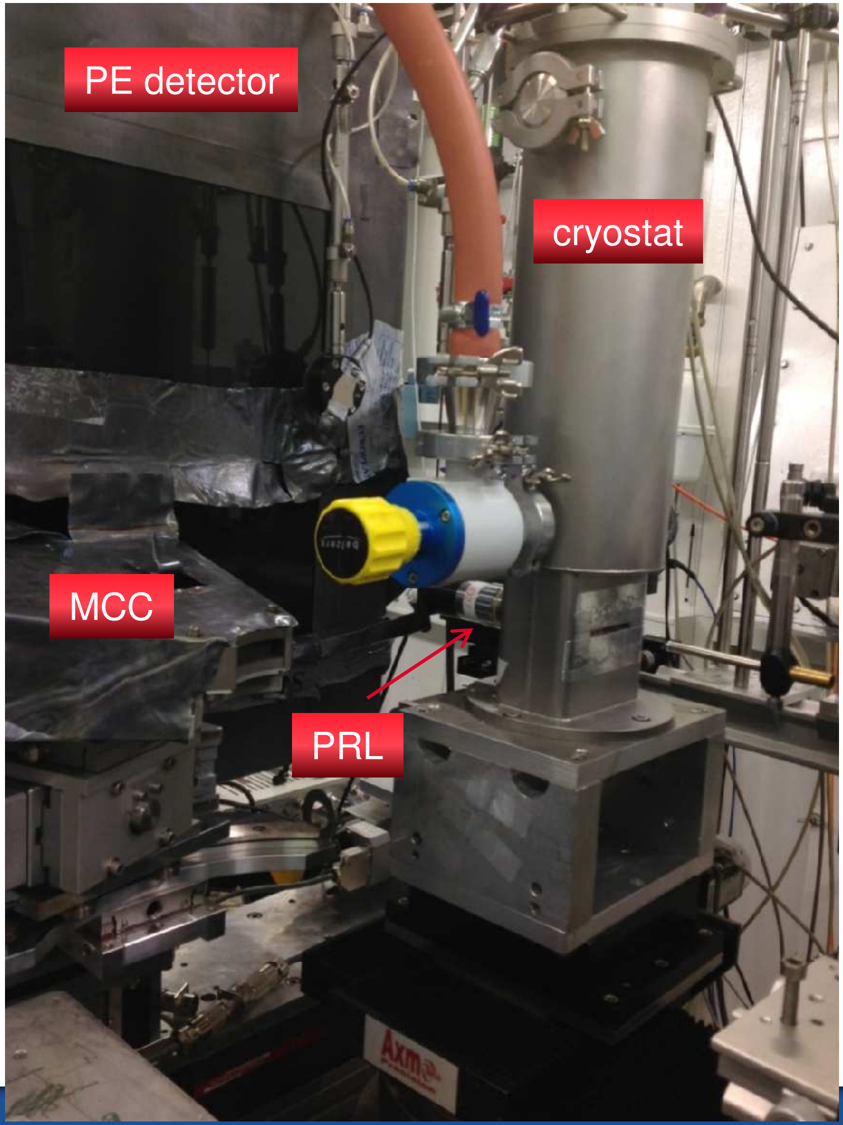
Fluid H_2 / D_2 (Z = 1) @ HP

STRUCTURE FACTOR OF LOW Z LIQUIDS AT EXTREME CONDITIONS:
THE MULTICHANNEL COLLIMATOR (SOLLER SLITS) AND ENERGY INFLUENCE

Perkin-Elmer Flat panel

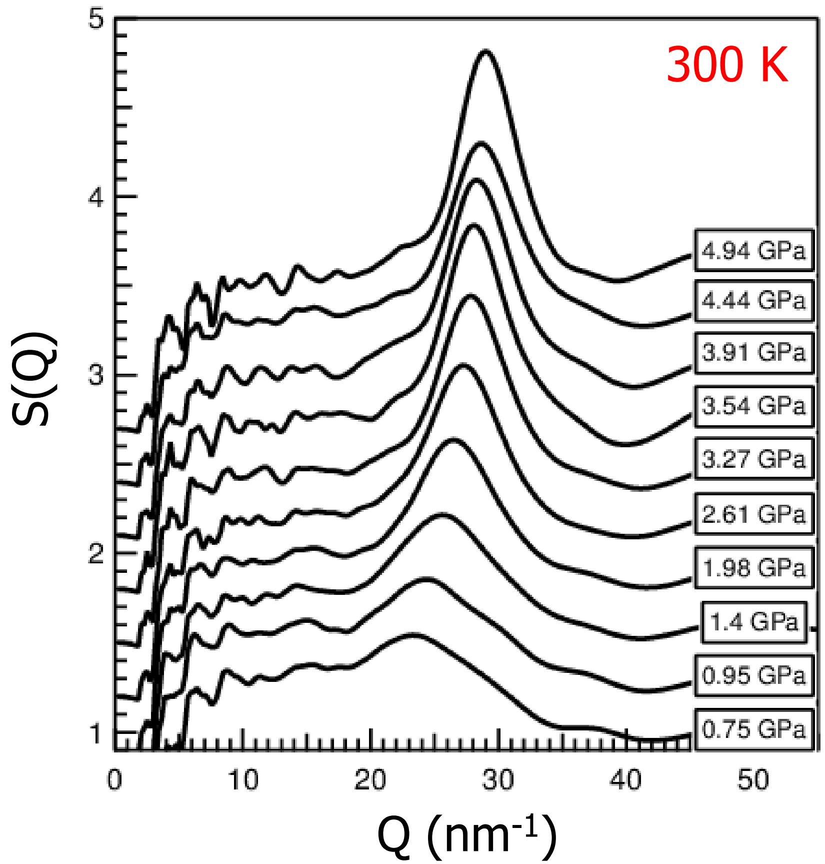
$E_{X\text{-}rays}$=20 or 33 KeV

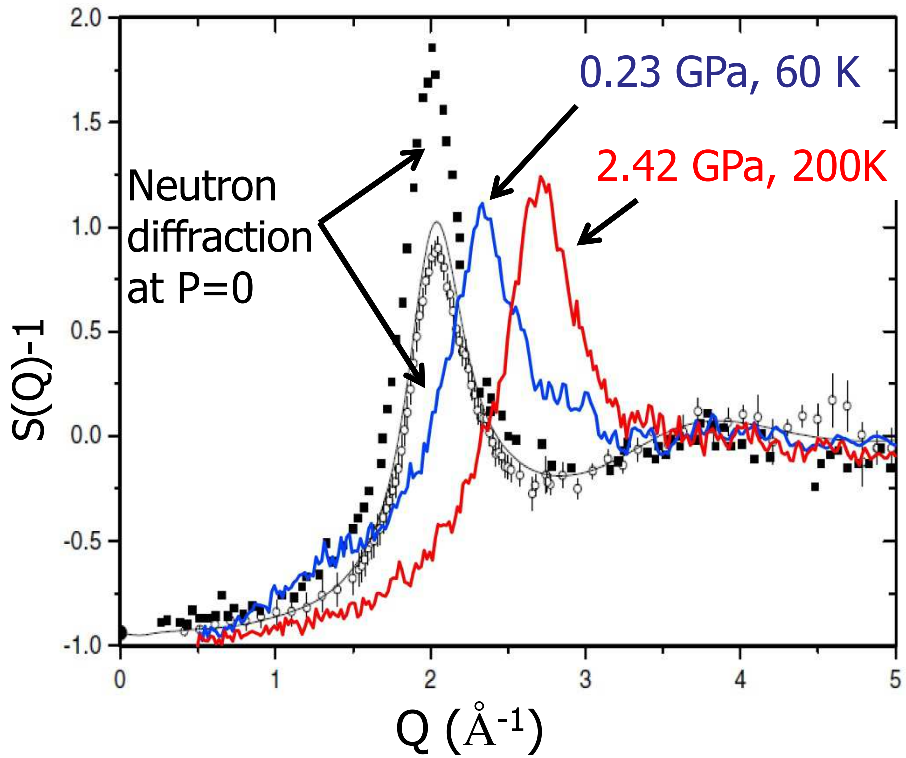
T from 50K to 300K using ID27 cryostat



Strategic partnership ID27 - CEA - IMPMC (LTP)

Fluid H_2 / D_2 (Z = 1) @ HP

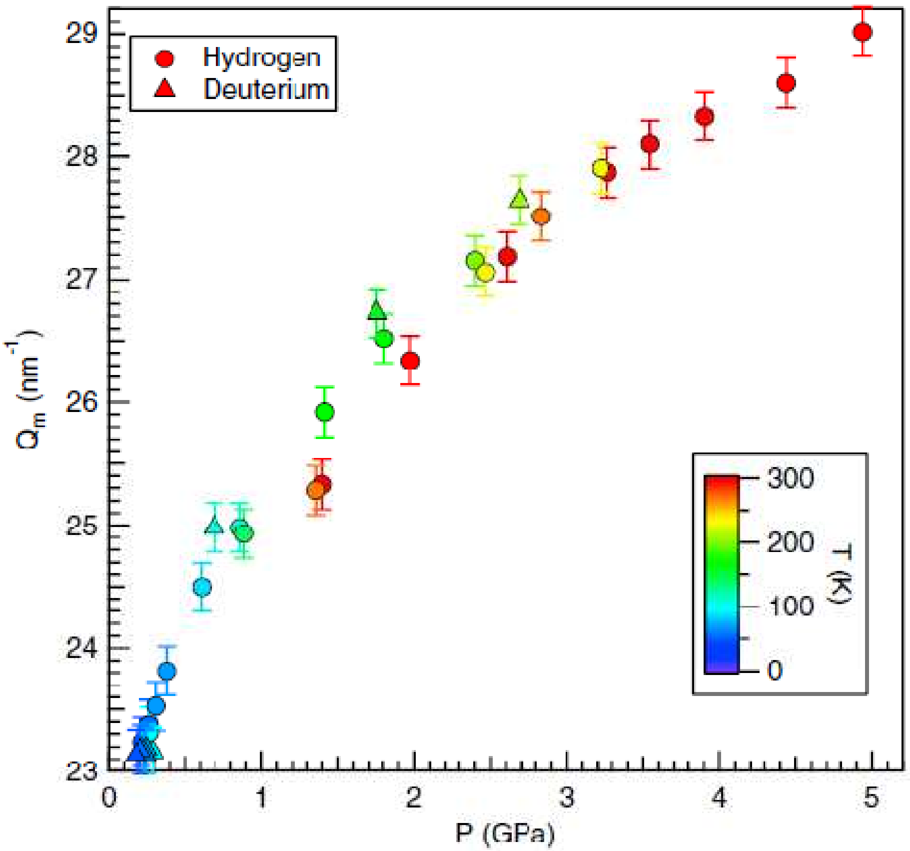


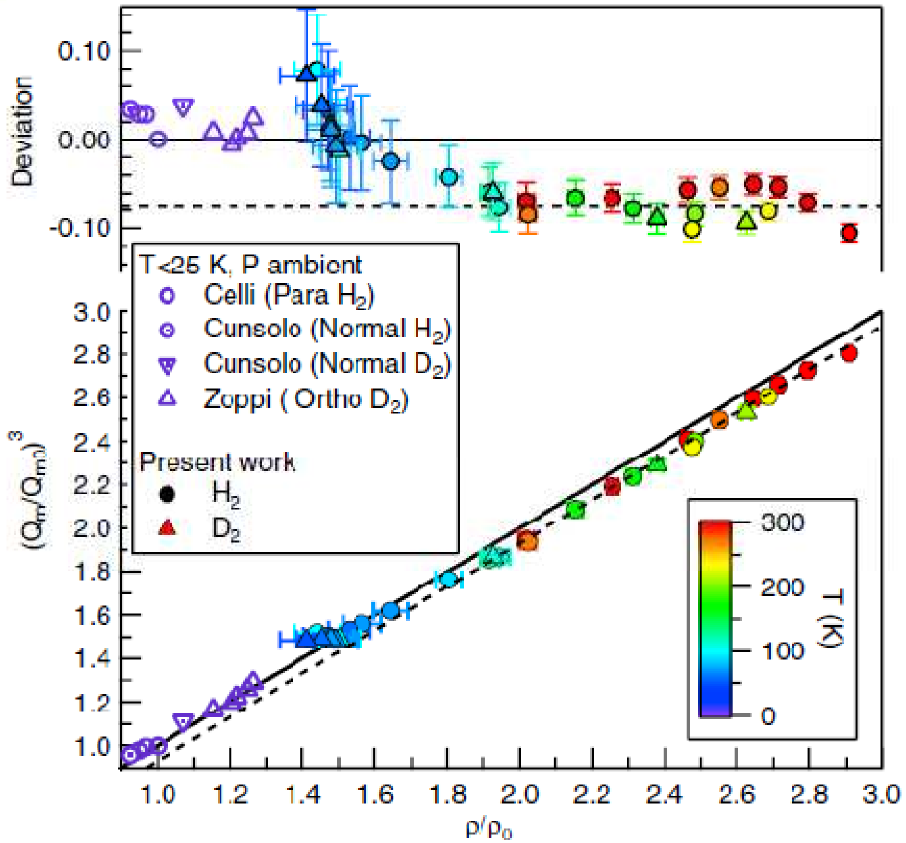


➔ **S(Q) becomes more structured with pressure**
➔ **The First-Sharp Diffraction Peak (FSDP) shifts with P and T**
➔ **Compares very well with neutron diffraction at P=0**

Weck et al, PRB 91 p 180204 (2015)

Fluid H_2 / D_2 (Z = 1) @ HP



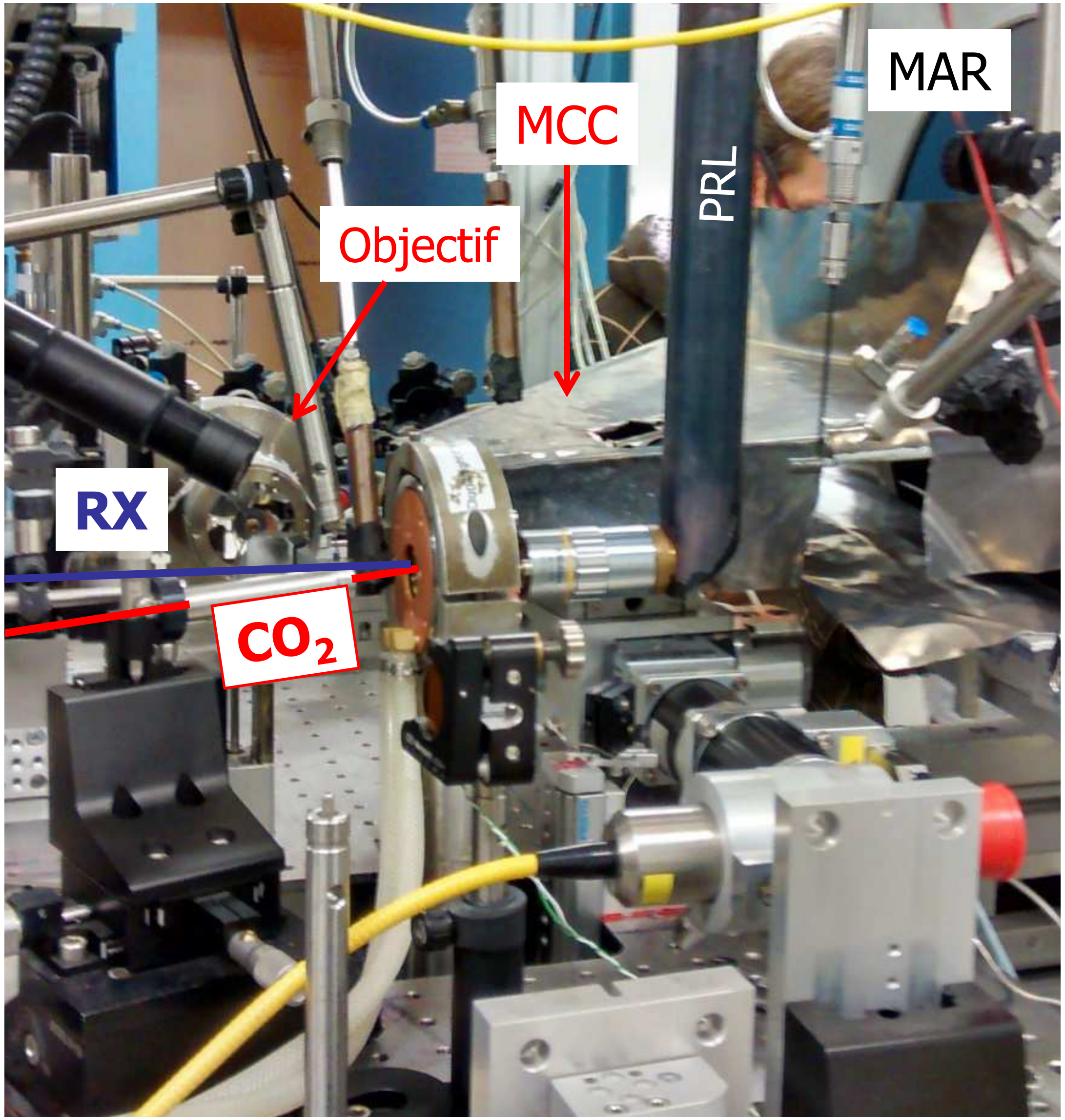


➔ **Isotopic shift of the Q_m between H_2 and D_2** due to density effect

➔ **Pseudotransition between two liquids**, possibly due to a change in the zero-point motional renormalization of the interaction from anharmonic to harmonic

➔ **Extension of the experimental studies in liquid H_2 up to Mbar range** seems very encouraging (signal/background ratio will only be reduced by a factor 5)

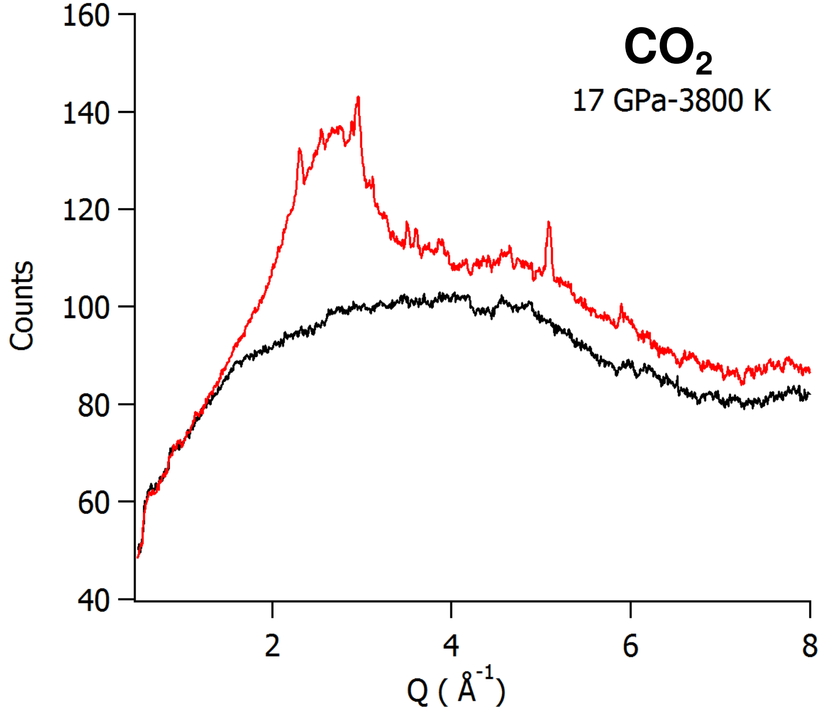
Fluid CO_2 @ HP



- Extension to other fluid systems: CO_2, H_2O, NH_3… couples directly with CO_2 laser (λ=10.6μm)

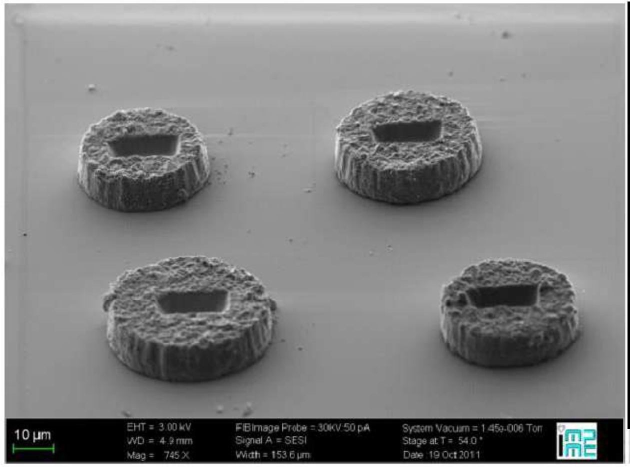
- One sided laser heating

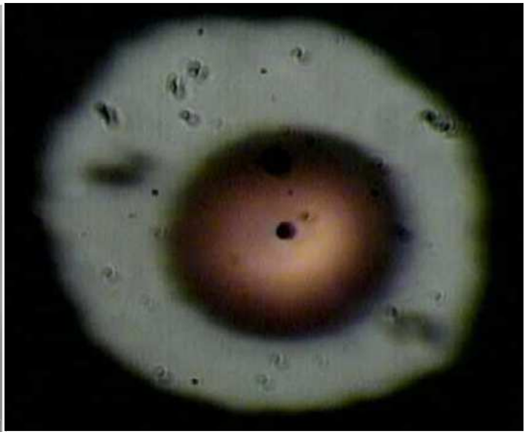
- No need of absorber



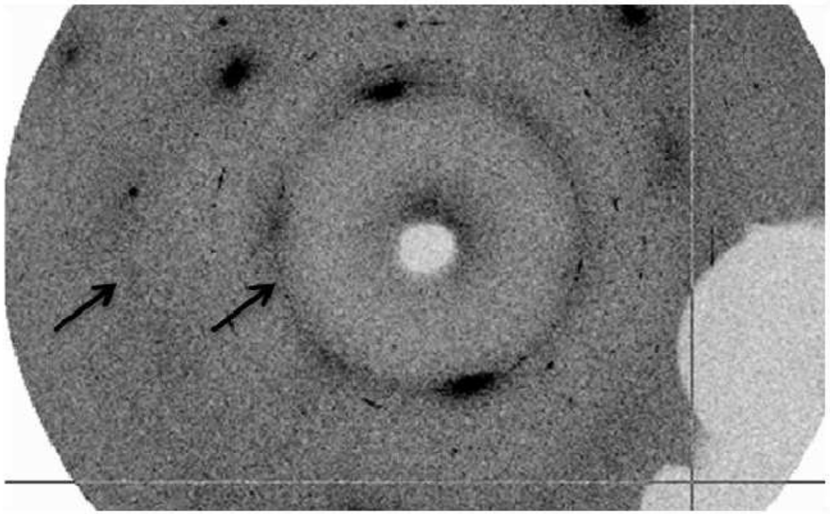
F. Datchi, G Weck, S. Ninet et al

Fluid N_2, Xe, Au … @ HP

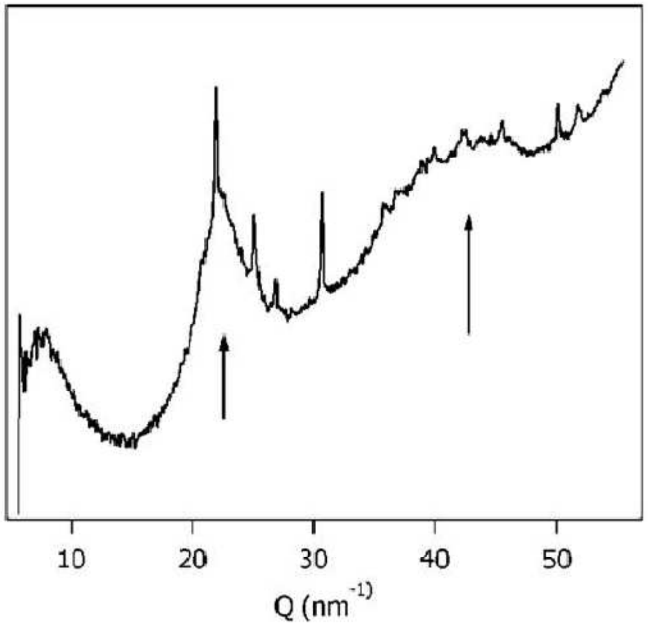




- Extension to other fluid systems: N_2, Au… does not couple directly with CO_2 neither YAG laser
- Need of absorber (B doped C machined by FIB)
- Two sided YAG laser heating
- Vertical laser heating only possibility as MCC horizontal plane



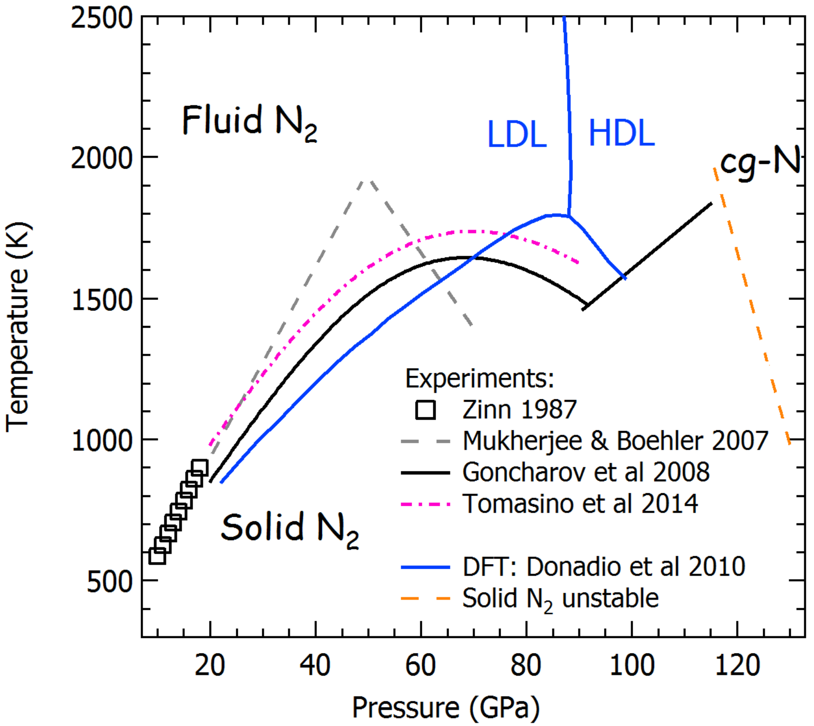
Xe, 21GPa, 3200K



Fluid N_2 @ HP

Motivation:

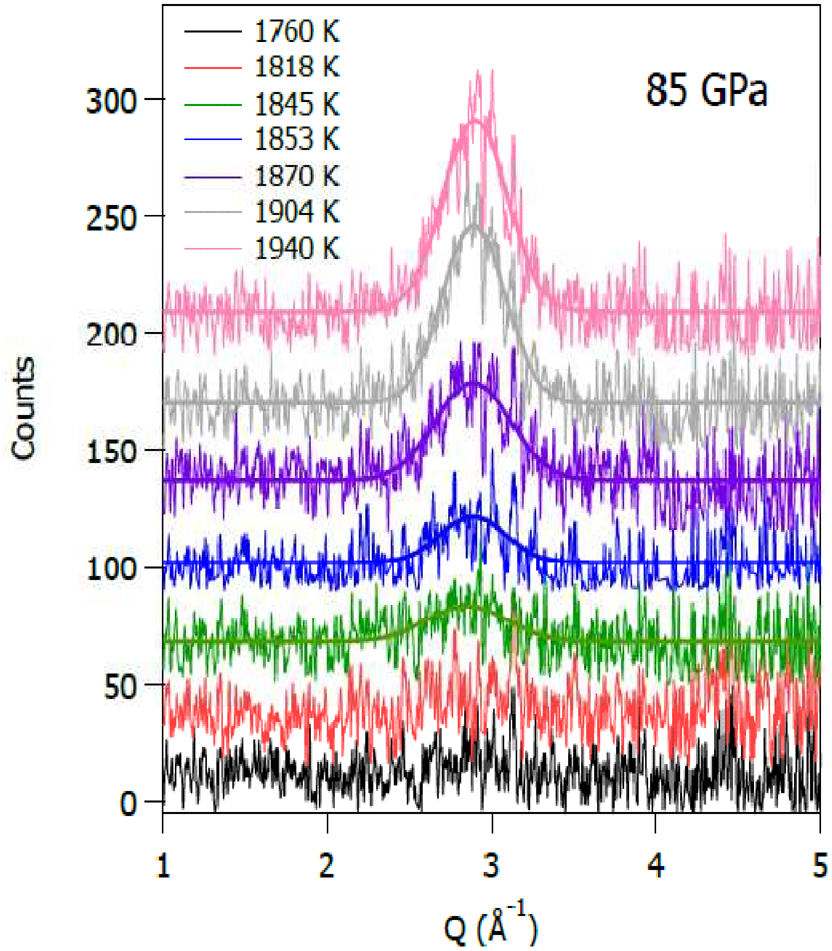
- Ab initio prediction of a liquid-liquid phase transition at P~90 GPa
- Different experimental melting curves reported (Raman, Speckle)
- Observation of a maximum in the melting curve
- No structural data in the liquid state

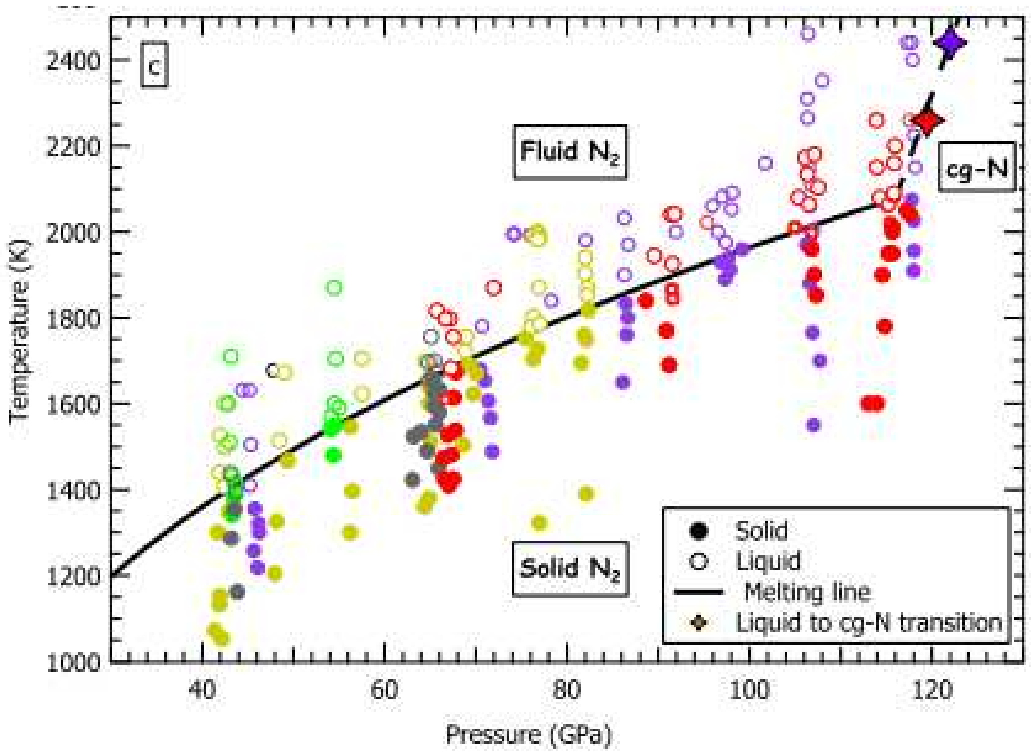


Challenges:

Nitrogen:
-is a light element
-does not absorb YAG radiation

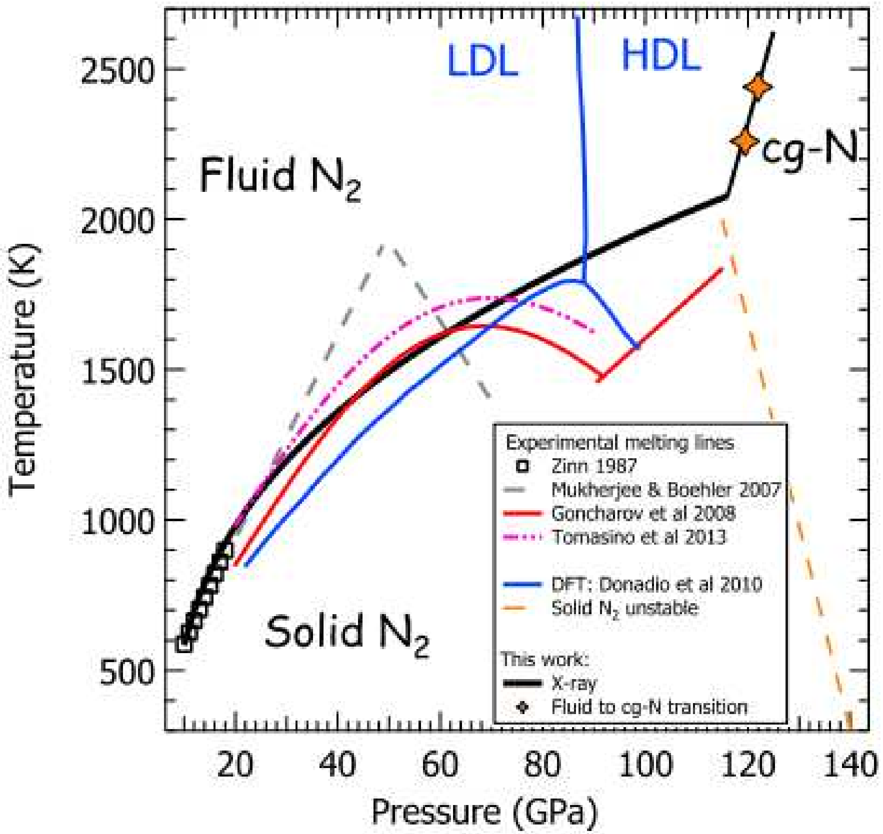
Fluid N_2 @ HP





Possible to extend the melting curve of N_2 up to Mbar pressure range obtained during LTP - HD 463

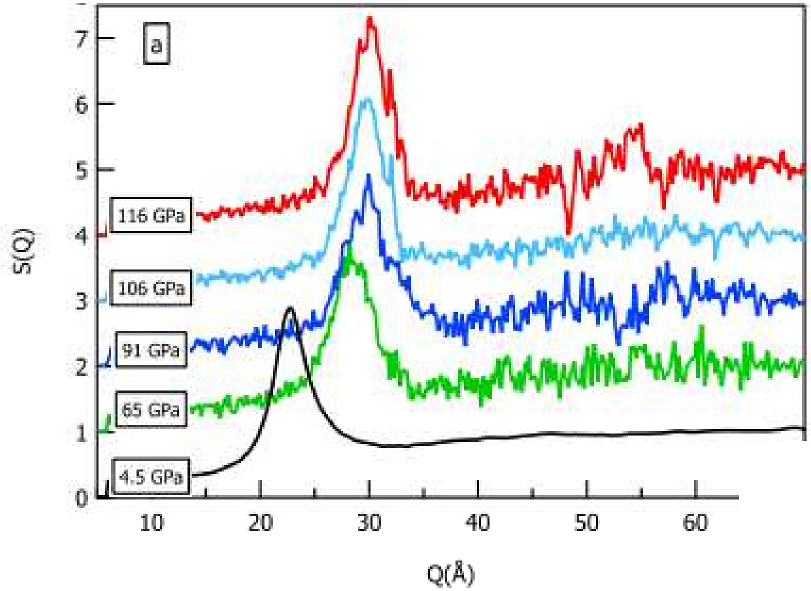
Fluid N_2 @ HP



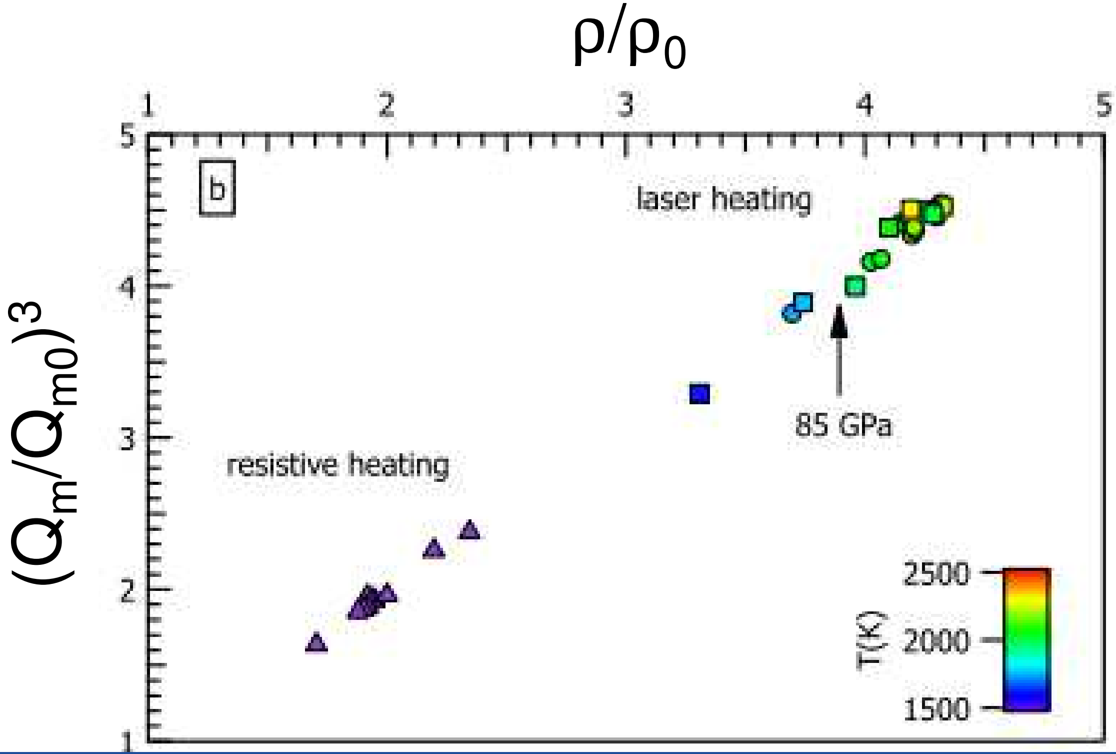
In contrast with literature data, we do not observe a **maximum in melting curve** which would correspond to a **LDL to HDL transition** up to 120 GPa

At **P>120 GPa**, we observed a **strong increase of the slope of the melting curve** indicative of a **first-order phase transition in the solid**

Fluid N_2 @ HP



The **absence of discontinuity** in the pressure evolution of the structure factor first peak confirms the **absence of LDL to HDL transition**



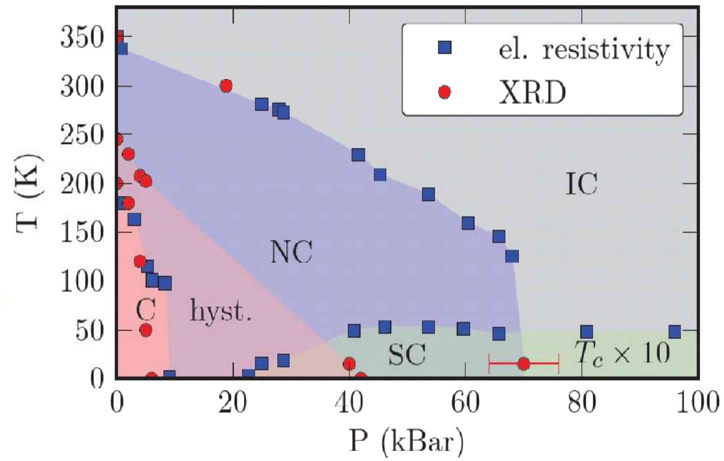
G. Weck et al, PRL(2017)

CDW: $1T\text{-}TaS_2$

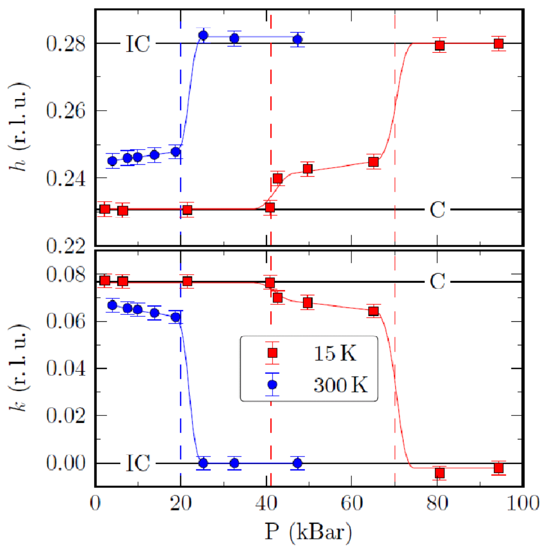
From Mott state to superconductivity in $1T\text{-}TaS_2$

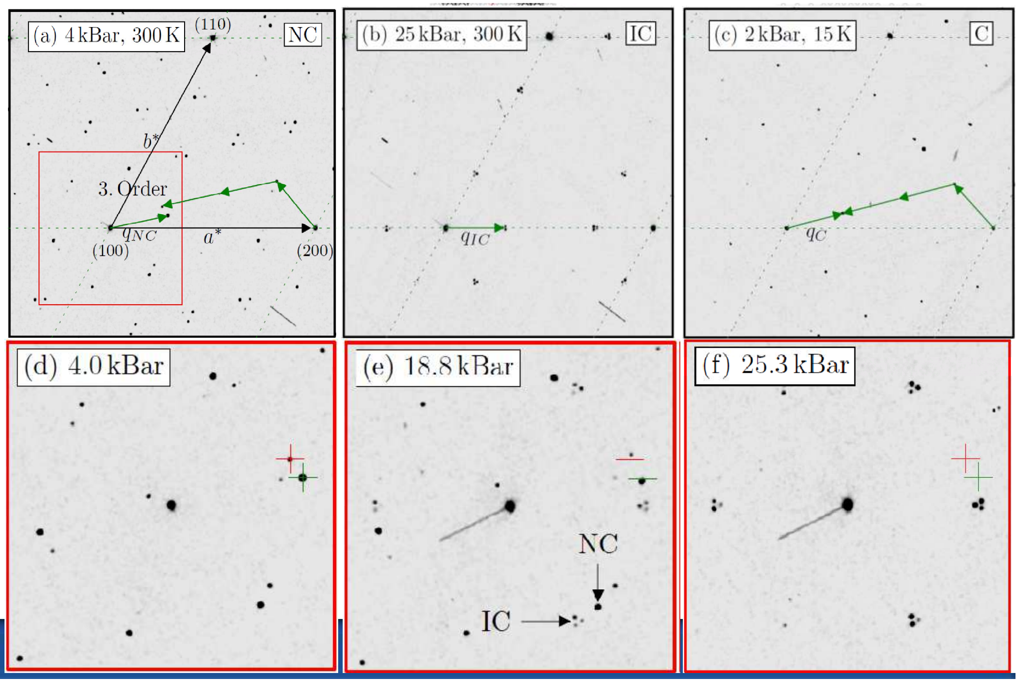
B. SIPOS[1]*, A. F. KUSMARTSEVA[1]*, A. AKRAP[1], H. BERGER[1], L. FORRÓ[1] AND E. TUTIŠ[2]
[1] Ecole Polytechnique Fédérale de Lausanne, IPMC, CH-1015 Lausanne, Switzerland
[2] Institute of Physics, Bijenička c. 46, Zagreb, Croatia
* e-mail: bsipos@gmail.com; anna.kusmartseva@ed.ac.uk

nature materials 2008



- **XRD at high pressure and low temperature** on single crystals of $1T\text{-}TaS_2$
- Confirm the proposed phase diagram from R(T)
- No collapse of CDW domains





T. Ritschel et al., PRB (2013)

Superconductors with iron in tetrahedral coordination

05/2006 **LaFePO**

T_C ~ **6K**

(Hosono's group *JACS* *128, 10012*)

03/2008 **LaFeAs(O,F)**

T=26K

(Hosono's group *JACS* *130, 3296)*

Highest T_C

$Gd_{1-x}Th_xFeAsO$

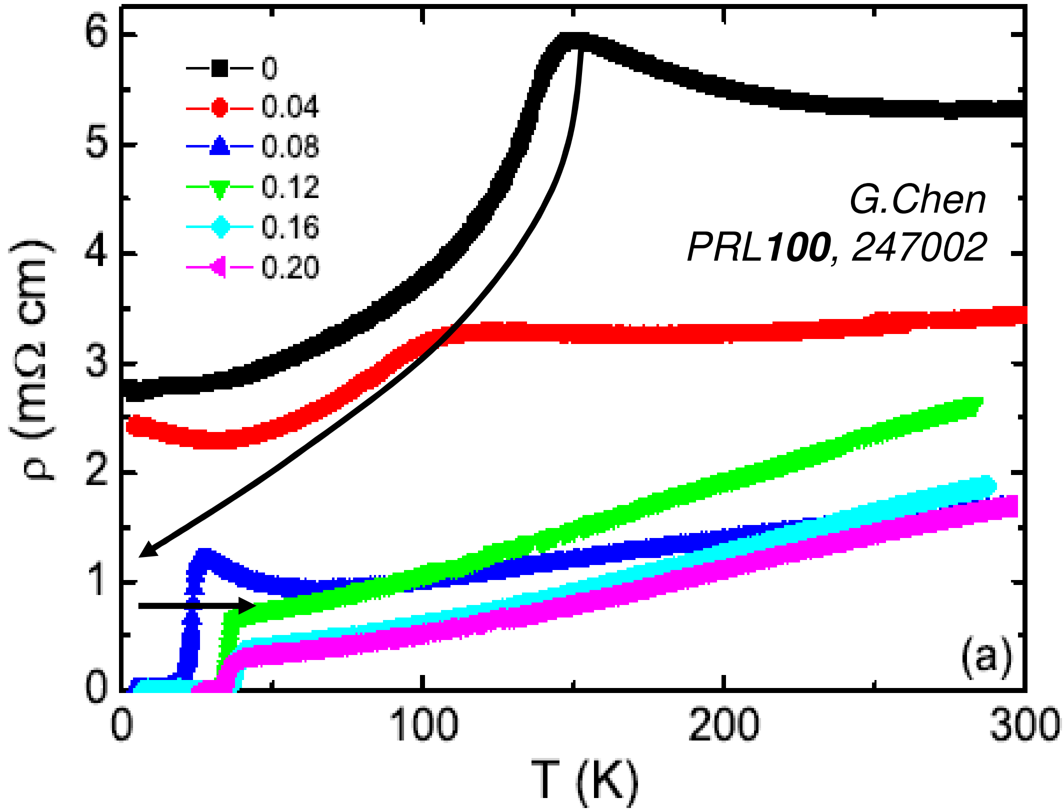
(EPL 83, 67006)

T_C = 56K **$Sm_{1-x}Sr_xFeAsF$**

(arXiv:0811.0761)

$SmFeAsO_{1-x}F_x$

(Chin. Phys. Lett. 25, 2215)



Search
webofknowledge
"**Fe based superconductor**"
More 1000papers

Why so much interest in this superconductors?

ε - Fe

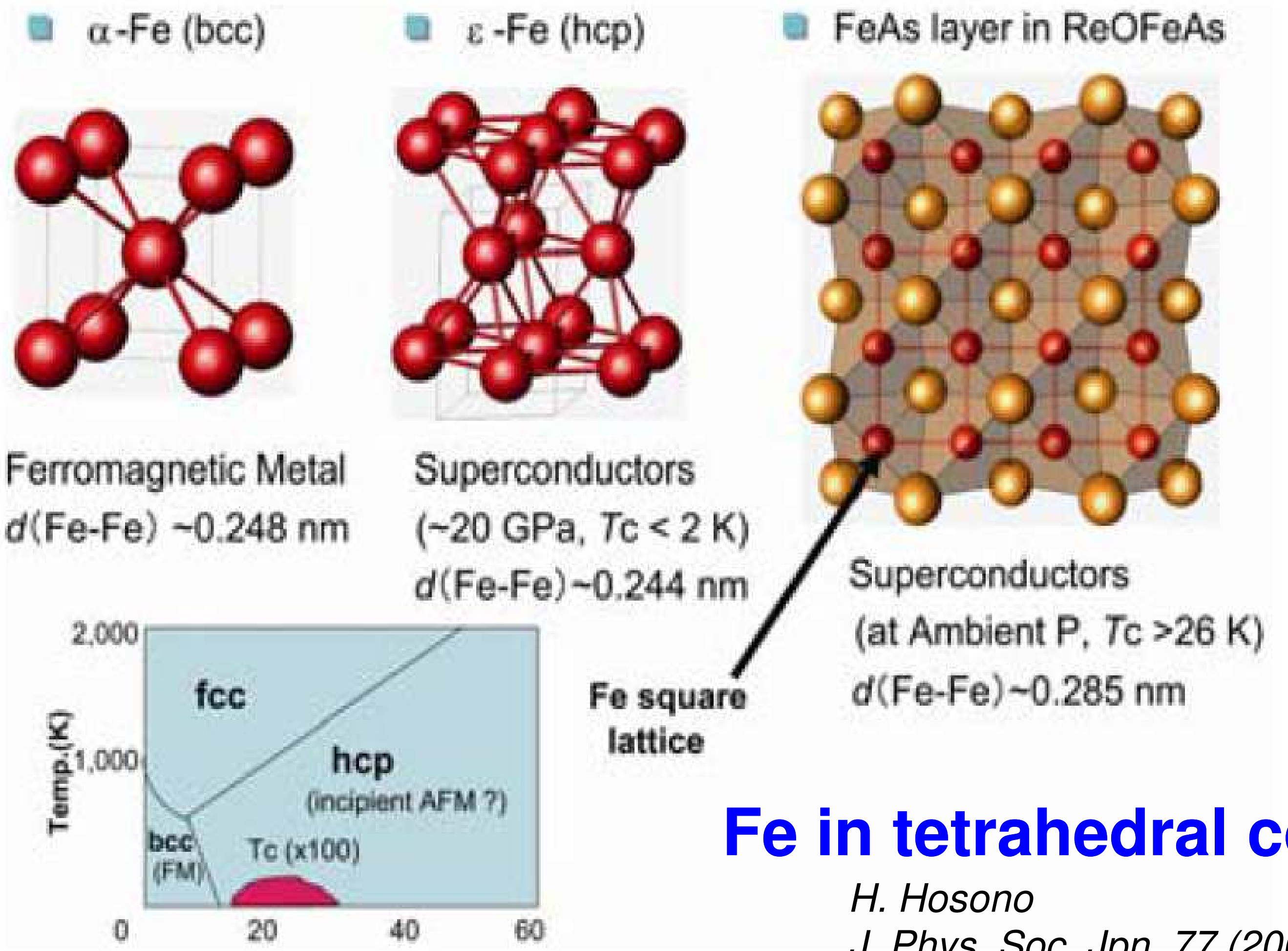
T_C < 2K P~20GPa

(S. Saxena and O. Littlewood, Nature 2001)

LnFeAs(O,F)

T_C < 56K

(Hosono's group *JACS 2008)*



Fe in tetrahedral coordination

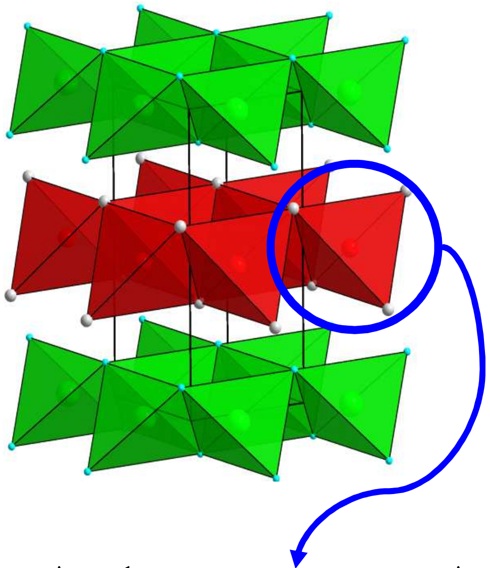
H. Hosono

J. Phys. Soc. Jpn. 77 (2008) Suppl. C

Superconductors with iron in tetrahedral coordination

Crystal structure: tetragonal, space group P4/nmm or I4/mmm

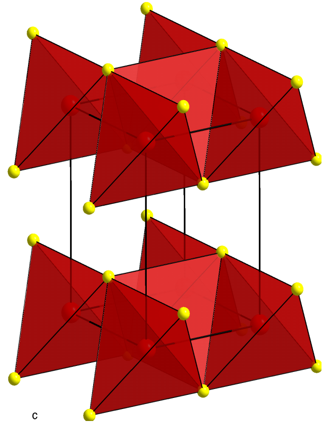
LnFeAsO
1111



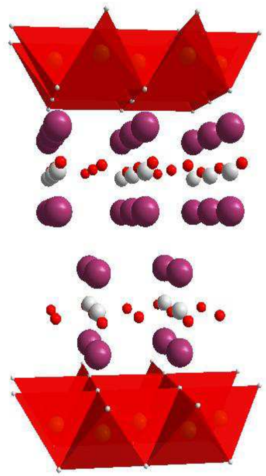
Many families

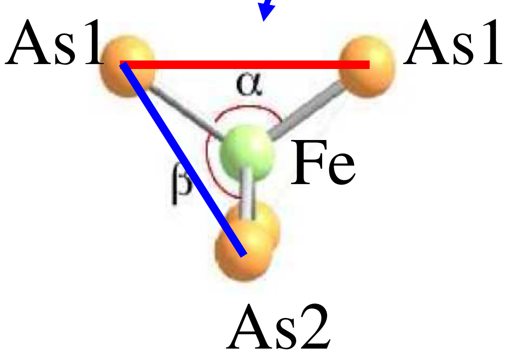
FeSe	**11**
AFeAs	**111**
Æ(FeAs)$_2$	**122**
LnOFeAs	**1111**
$Sr_4V_2O_6Fe_2As_2$	**42622**
$(CaFeAsPt)_{10}Pt_4As_8$	**1048**
…..	

$FeSe_{1-x}$
11



$Sr_4V_2O_6Fe_2As_2$
42622





- $FeAs_4$ tetrahedron is the common unit in all "families"
- Non distorted structure α(x2) = β(x4) = 109.471°

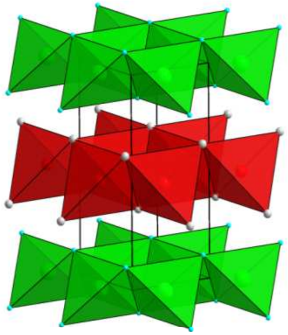
  d(As1-As1) = d(As1-As2)

- Distorted structure α >/< β

Superconductors with iron in tetrahedral coordination

Crystal structure: tetragonal, space group P4/nmm or I4/mmm

LnFeAsO
1111



Many families

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LnOFeAs	**1111**
$Sr_4V_2O_6Fe_2As_2$	**42622**
$(CaFeAsPt)_{10}Pt_4As_8$	**1048**
…..	

Major drawback: pnictogen / chalcogen atoms

High interest to look for isostructural compounds without pnictogen/chalcogen

Already various examples exist:

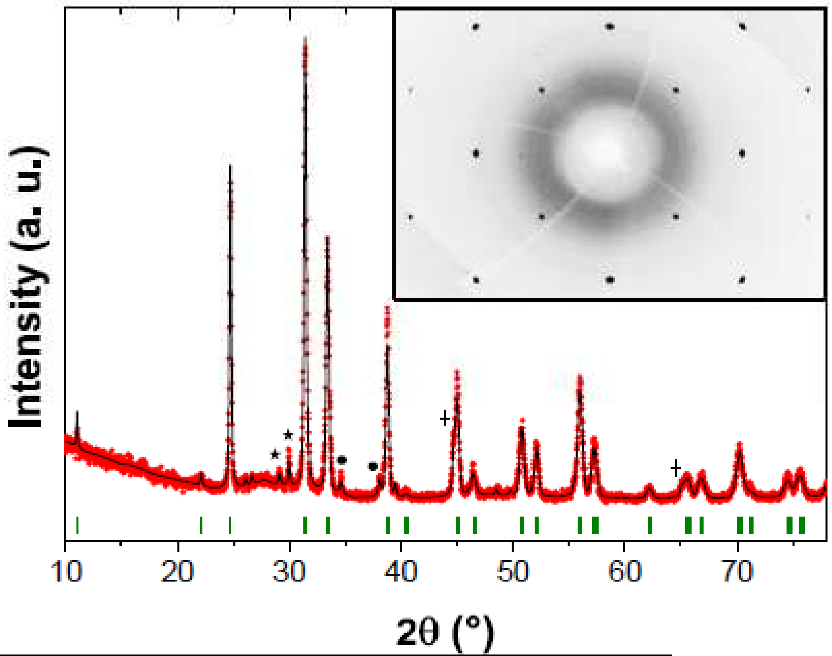
MgFeGe (isostructural LiFeAs)
YFe_2Ge_2 (SC @ T<2K)

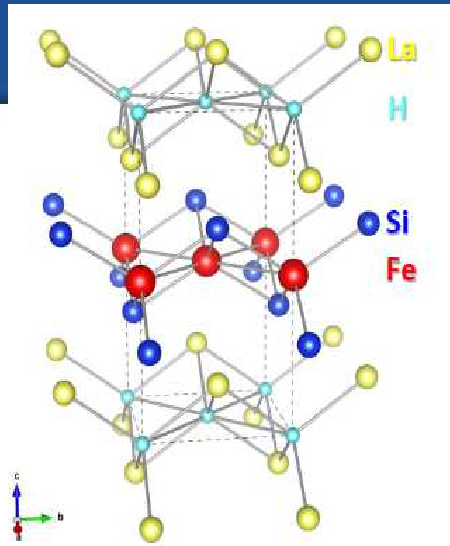
H substitution favor SC
on $LaFeAsO_{1-x}H_x$

R. Welter, et al Solid State Comm. (1998)
X. Liu, et al , Phys Rev. B (2012).
H. Jeschke, et al Phys. Rev. B (2013).
Y. Zou, et al; Phys Stat Solidi RRL (2014).
J. Chen, et al Phys. Rev. Lett. (2016).
H. Kim, et al Phil Mag (2015).
S. Iimura, et al; Nat. Commun (2012).

Synthesis of LaFeSiH

- **We synthesized LaFeSiH by hydrogenation of LaFeSi**
- **The crystal structure is isostructural with LaFeAsO**





293K - $P4/nmm$ (#129, origin 2)
$a = 4.0270(1)$Å $c = 8.0374(8)$Å

	Wyckoff pos.	x	y	z
La	$2c$	1/4	1/4	0.6722(1)
Fe	$2a$	3/4	1/4	0
Si	$2c$	1/4	1/4	0.1500(5)
H	$2b$	3/4	1/4	1/2

	a (Å)	*c* (Å)
LaFeSi	4.098	7.133
LaFeSiH	4.027	8.037

DFT calculations confirmed that the 2b position is a very stable position for the H atom.

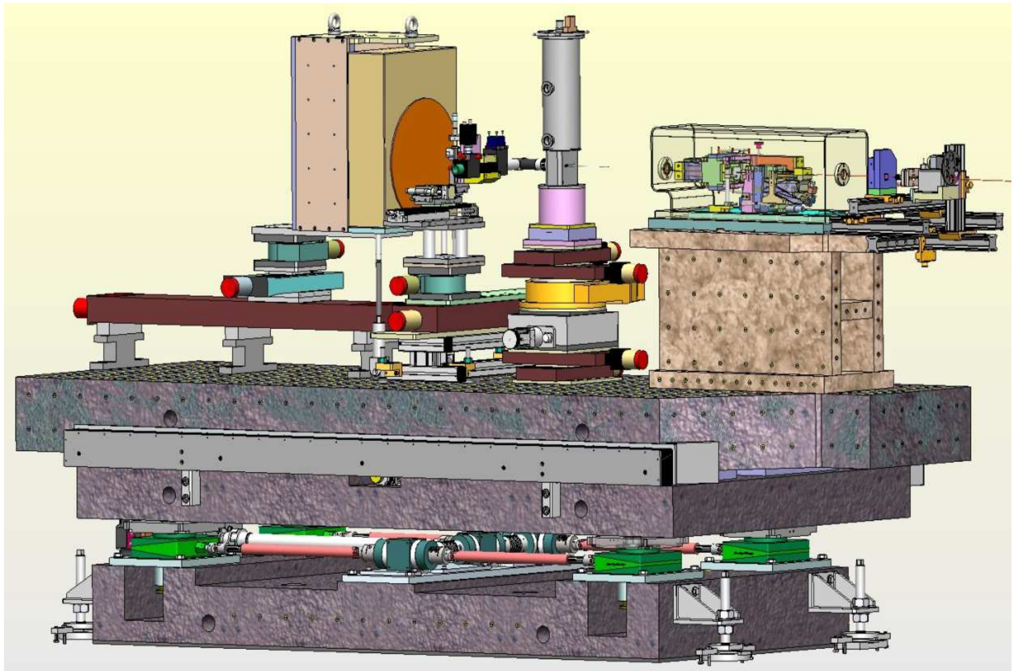
E. Gaudin, B. Chevalier, A. Cano, S. Tencé — *ICMCB, CNRS, Univ. Bordeaux, Pessac, France*
A. Sulpice, M. Núñez-Regueiro[3] — *Institut Néel, CNRS, UGA, Grenoble, France*
F. Bernardini — *CNR-IOM-Cagliari Cagliari, Italy*

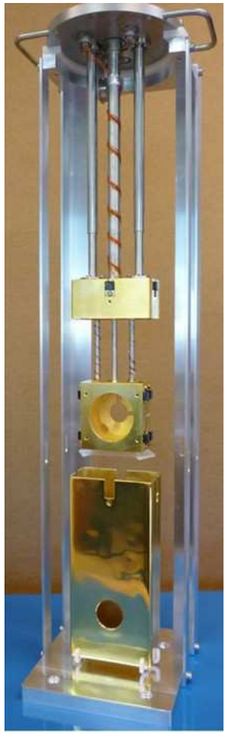
Experimental: Structure under High Pressure

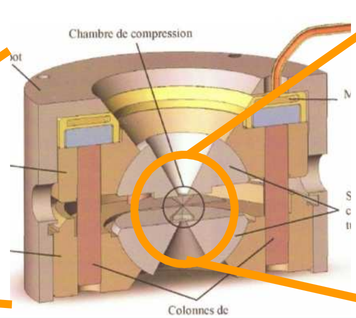
X ray diffraction at HP-LT

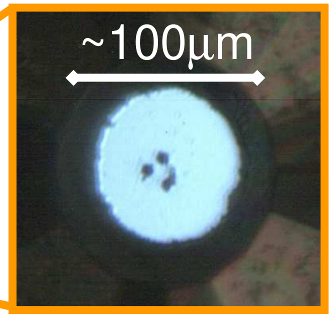
- Angular dispersive XRD, λ=0.3738A
- Membrane driven Diamond Anvil Cell
- P < 200GPa = 2Mbar = 2 10^6 atm
- Helium flow Cryostat (**T ≥ 3K)**

ID27 beamline
ESRF (Grenoble, France)









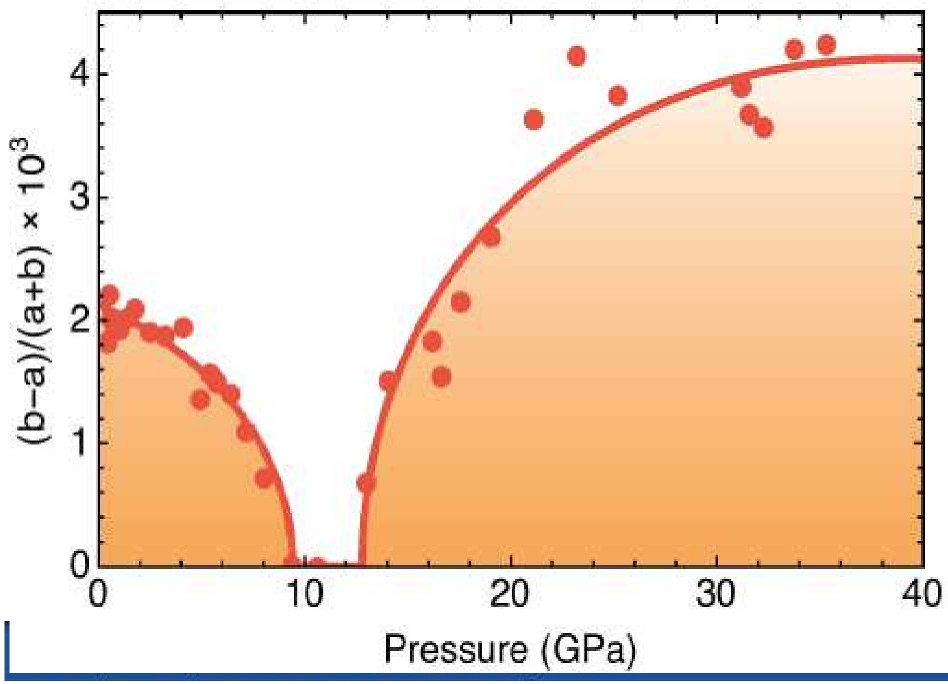
Crystal structure under P and low T

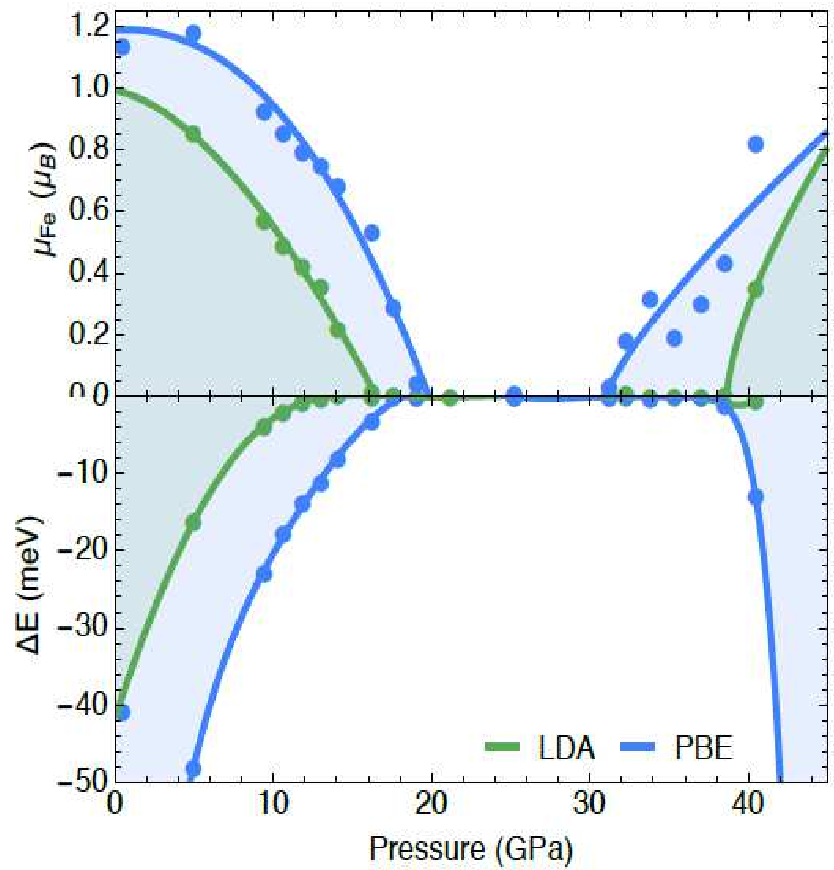
- **We observed orthorhombic distortion at 15K**
- **We studied the evolution of the distortion under pressure**
- **Using DFT calculation we confirm distortion and analyze magnetic structu**

15K - $Cmma$ (#67)

$a = 5.6831(6)$Å $b = 5.7039(6)$Å $c = 7.9728(6)$Å

	Wyckoff pos.	x	y	z
La	$4g$	0	1/4	0.1747(3)
Fe	$4b$	1/4	0	0
Si	$4g$	0	1/4	0.655(1)
H	$4a$	1/4	0	0

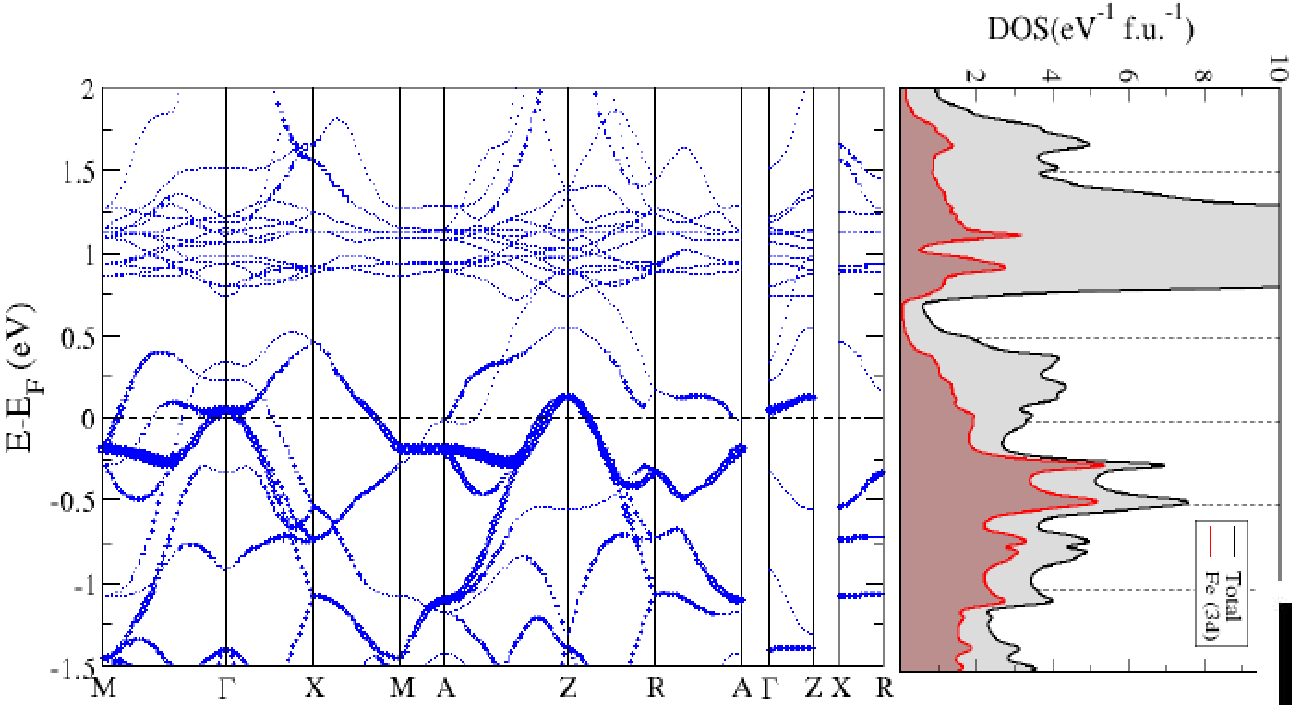


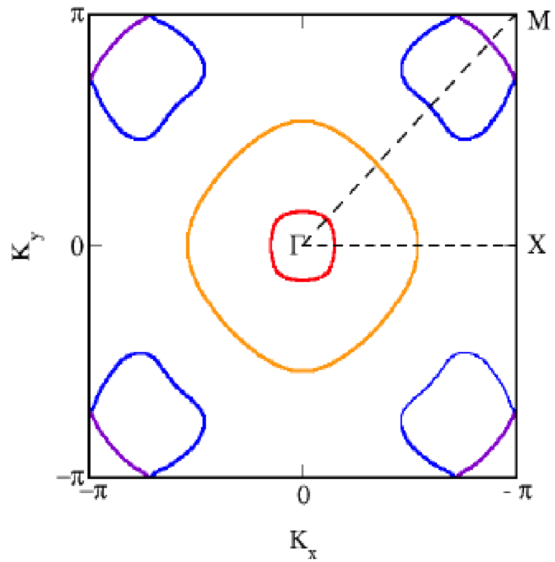


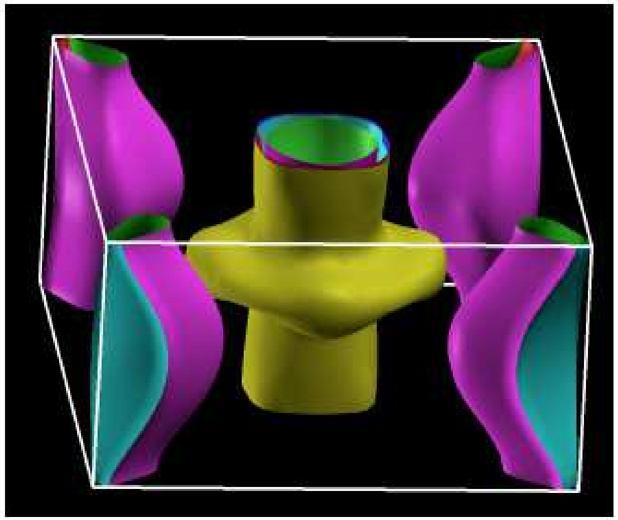
	checkerboard	FM	double-stripe	single-stripe
ΔE (meV/Fe)	-5.71	-11.11	-11.26	**-44.56**
μ_{Fe} (μ_{B})	0.90	0.65	1.04	1.16

Electronic structure

- **Using experimental atomic position, we calculated the band structure**







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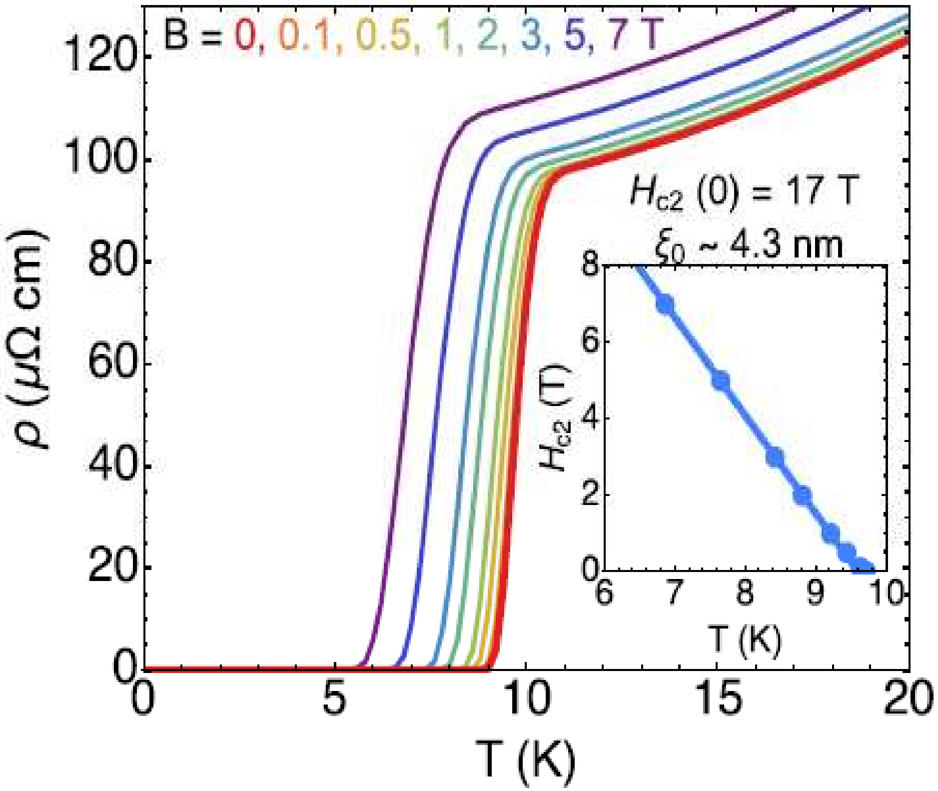
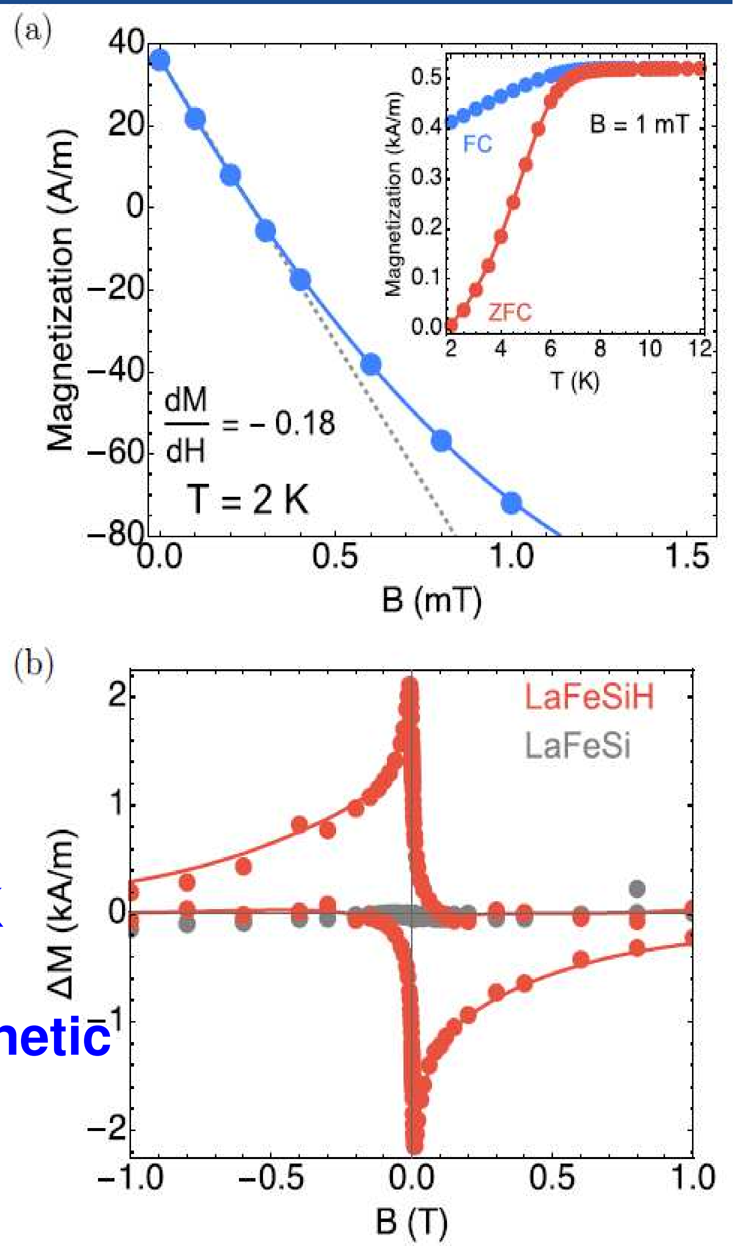
F. Barnardini et al, PRB - RC (2018)

Superconductivity





Resistivity measurements show ρ=0Ω T< 10K

Magnetization measurements show a diamagnetic response for T<10K

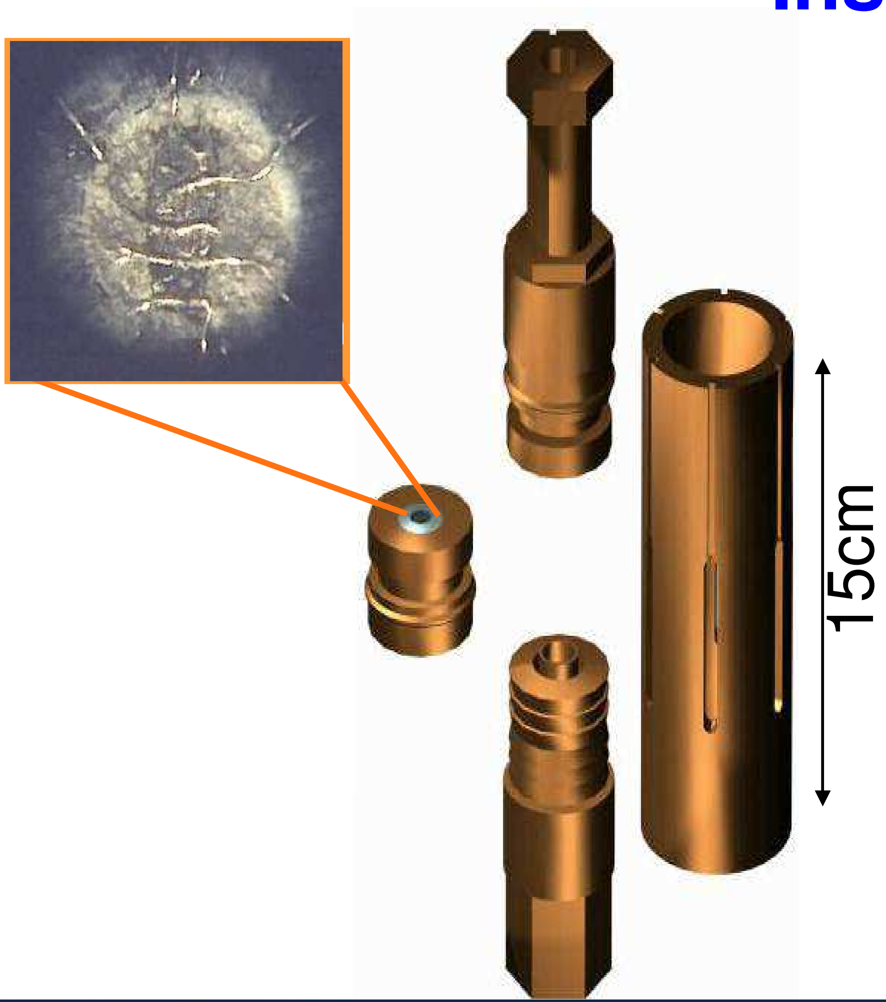
F. Barnardini et al, PRB - RC (2018)

Experimental: Resistance under High Pressure

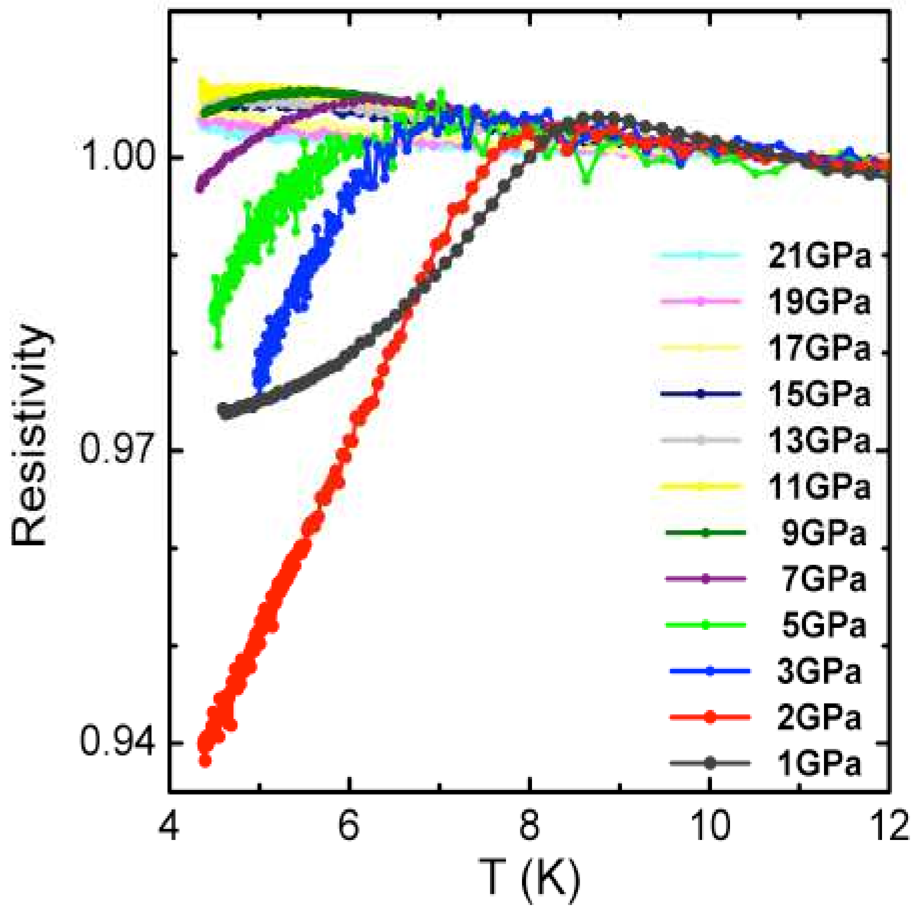
Resistance - ac Susceptibilty

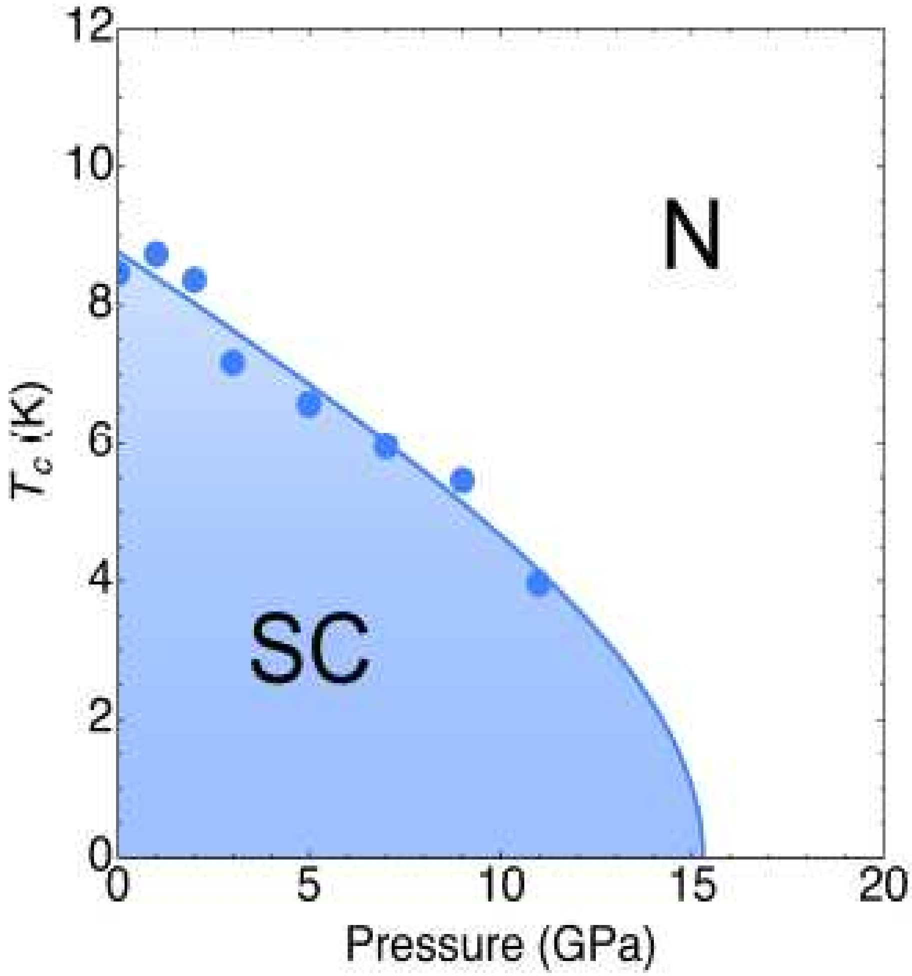
• Quasi-hydrostatic cell (P<30 GPa)   Temperature: 2K < T < 300K

Institut Néel (Grenoble, France)



Superconductivity

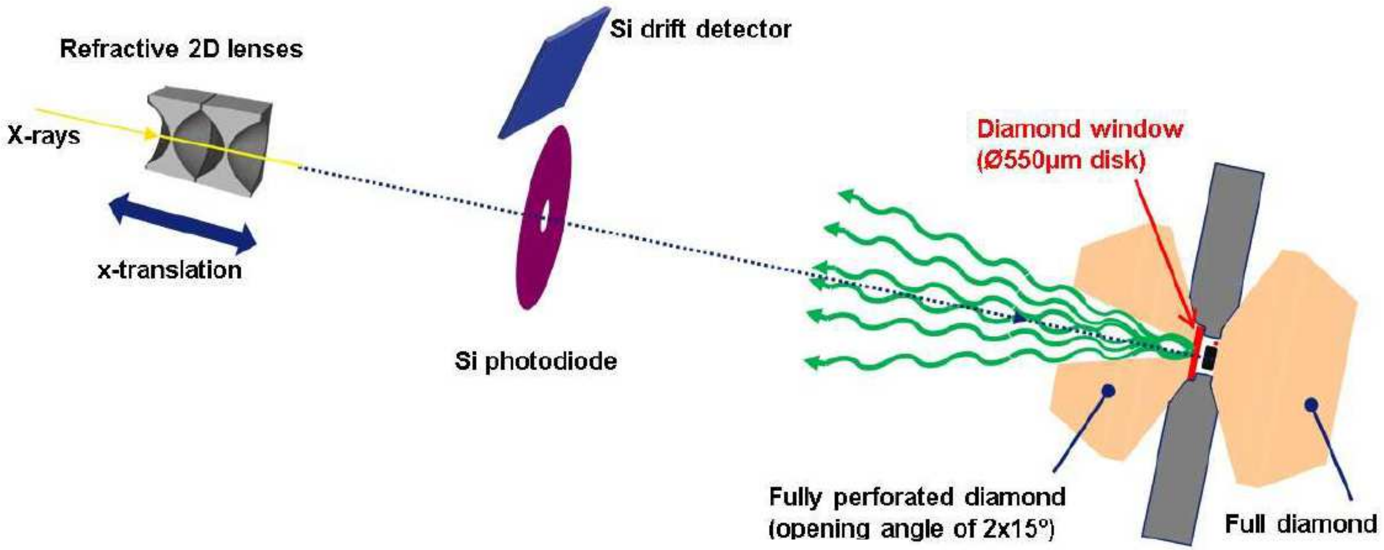


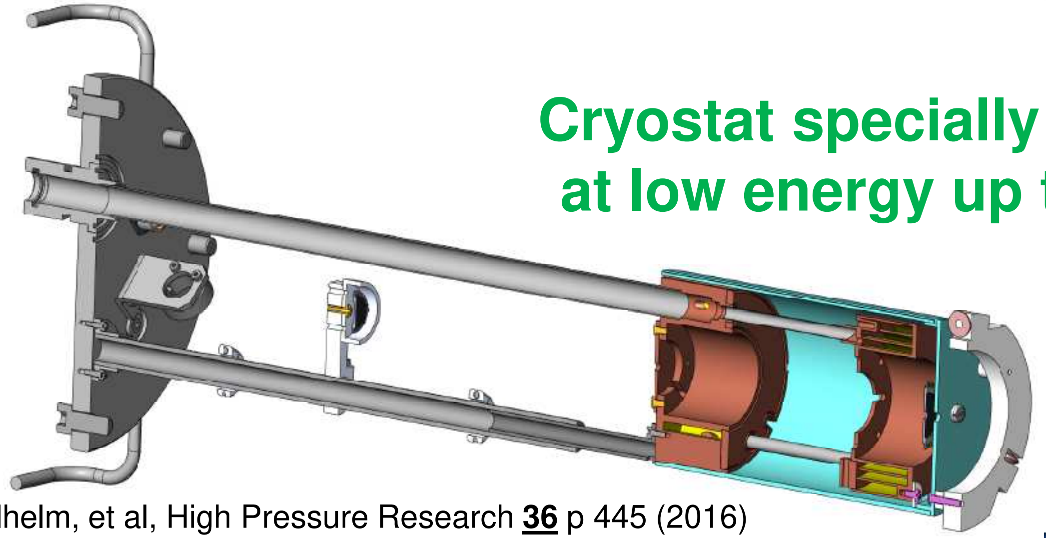


- **External pressure induce a reduction of $T_{C\ Onset}$ and a complete disappearance of the superconducting state for P>15GPa and no reentrance has been observed**

XMCD AT Low Energy and High Pressure

The ESRF beamline ID12 is a beamline dedicated to polarization dependent X-ray spectroscopy in photon energy range from 2 to 15 keV





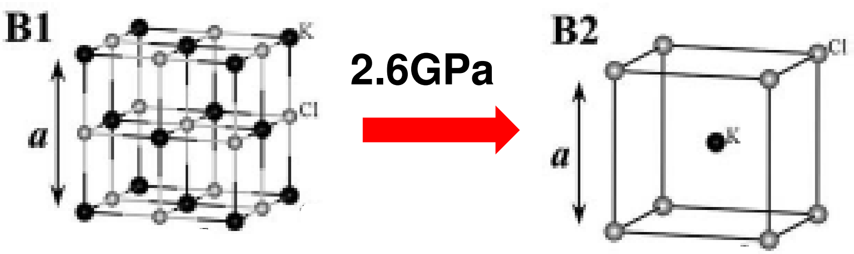
Cryostat specially designed for XMCD at low energy up to 7T and below 3K

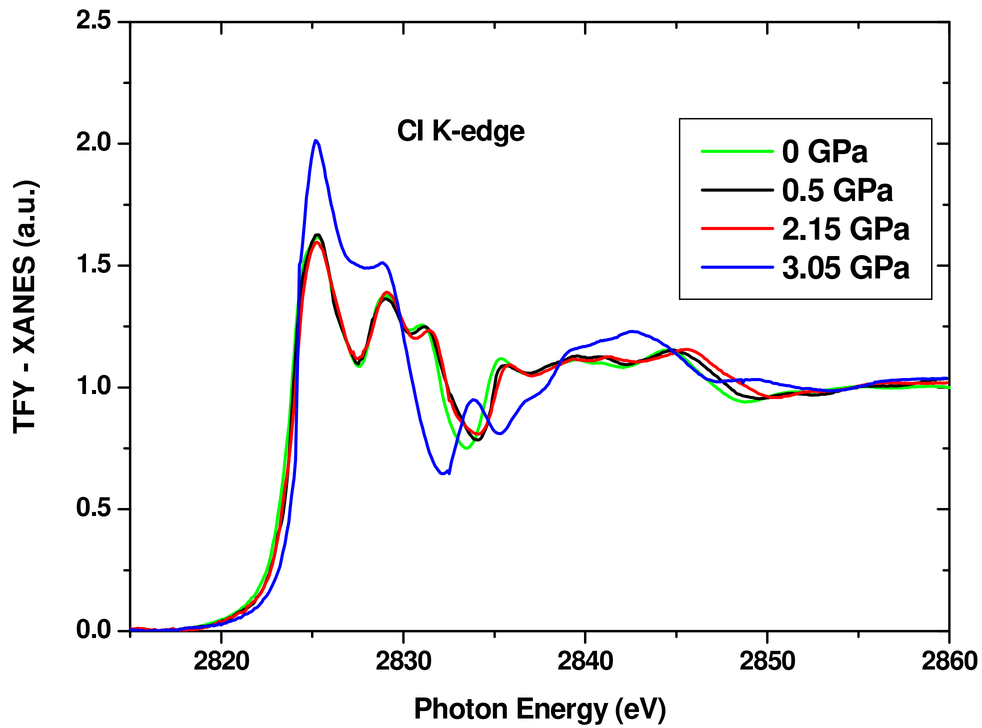
Main Heat Exchanger
T_{MIN}= 2.4K, T_{DAC}= 2.5K

Wilhelm, et al, High Pressure Research **36** p 445 (2016)

XMCD AT Low Energy and High Pressure

KCl → B1(NaCl-type) - B2(CsCl-type) structural phase transition (≈2.6GPa) studied using Cl K-edge XANES



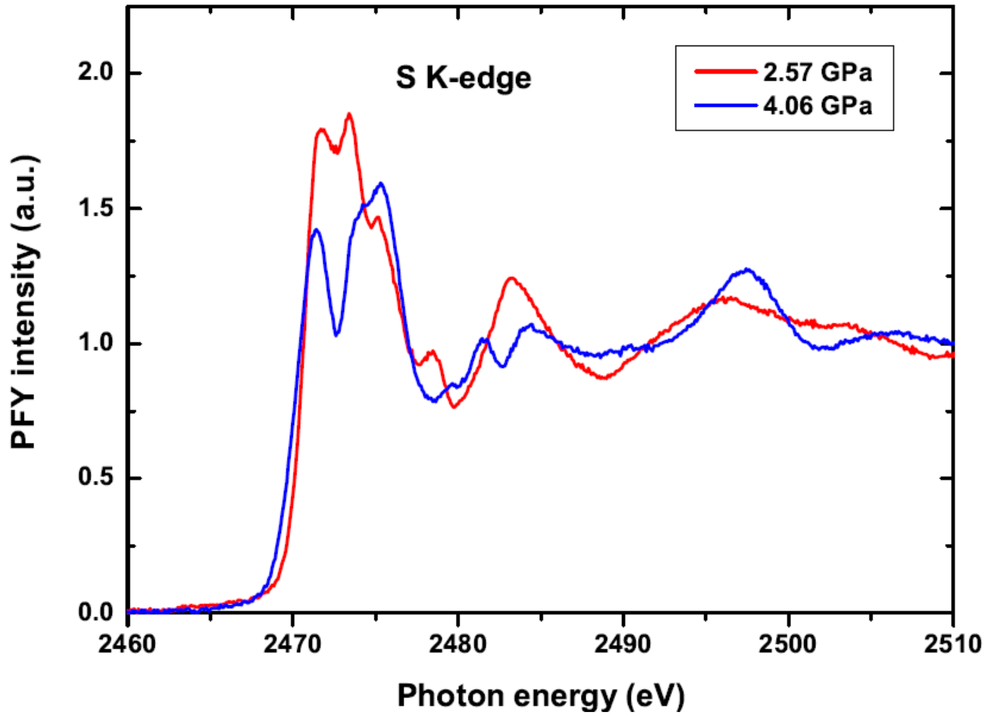


Wilhelm, et al, High Pressure Research **36** p 445 (2016)

XMCD AT Low Energy and High Pressure

CdS → B1(NaCl-type) - B2(CsCl-type) structural phase transition (≈3GPa) studied using S K-edge XANES

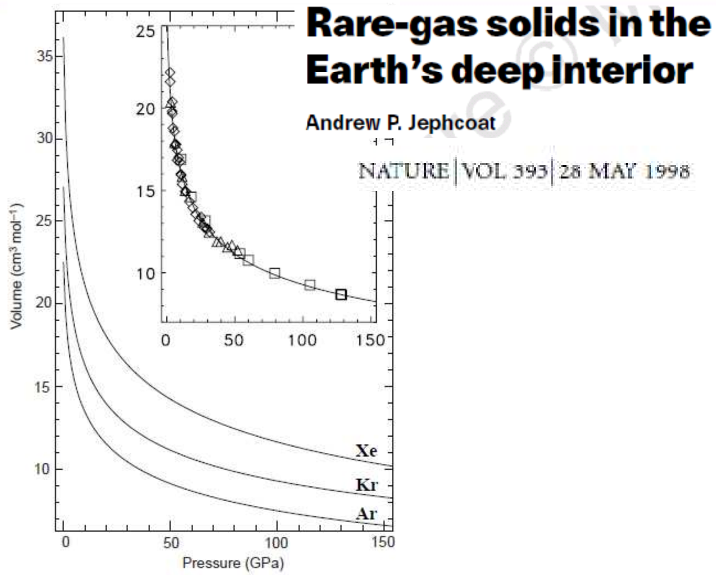
EXAMPLE: CdS Phase transition



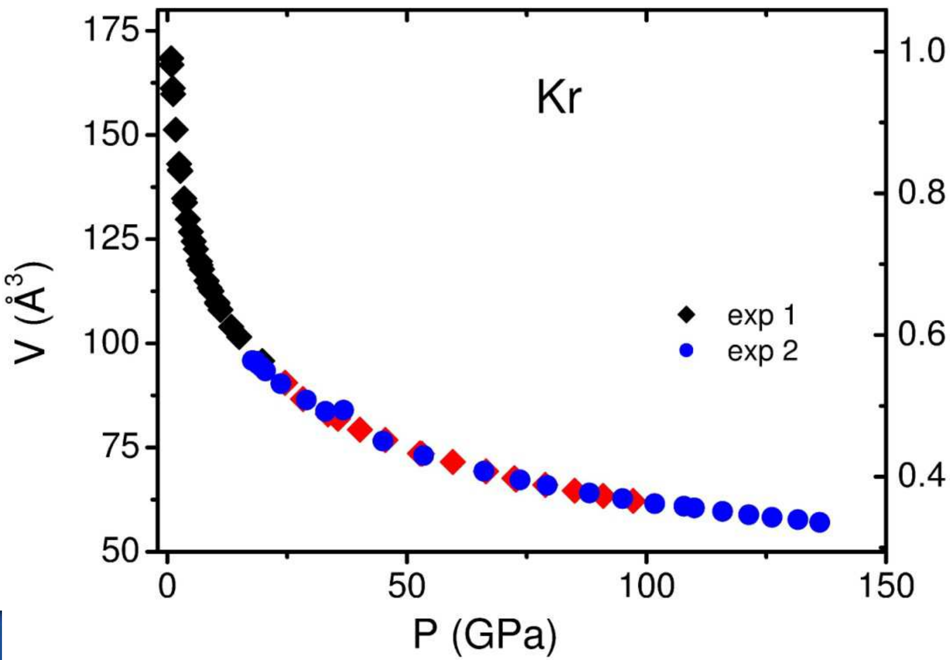
Studies on Nobel gases

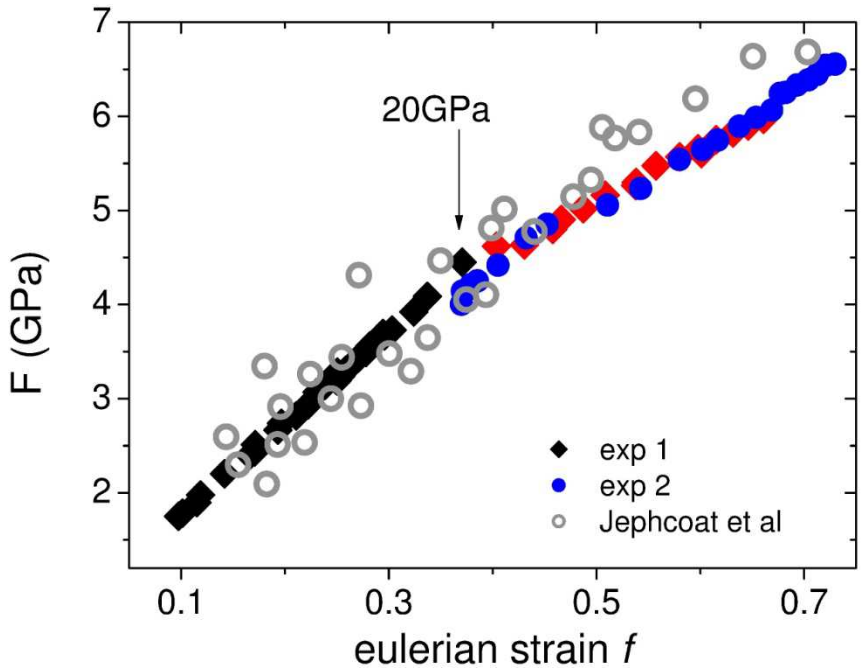
Rare (noble) gases unique trace-elemental and isotopic system for constraining the formation and evolution of the solid Earth and its atmosphere

- Missing Krypton
- Equation of State not well stablished
- Origin in anomalies in V vs P



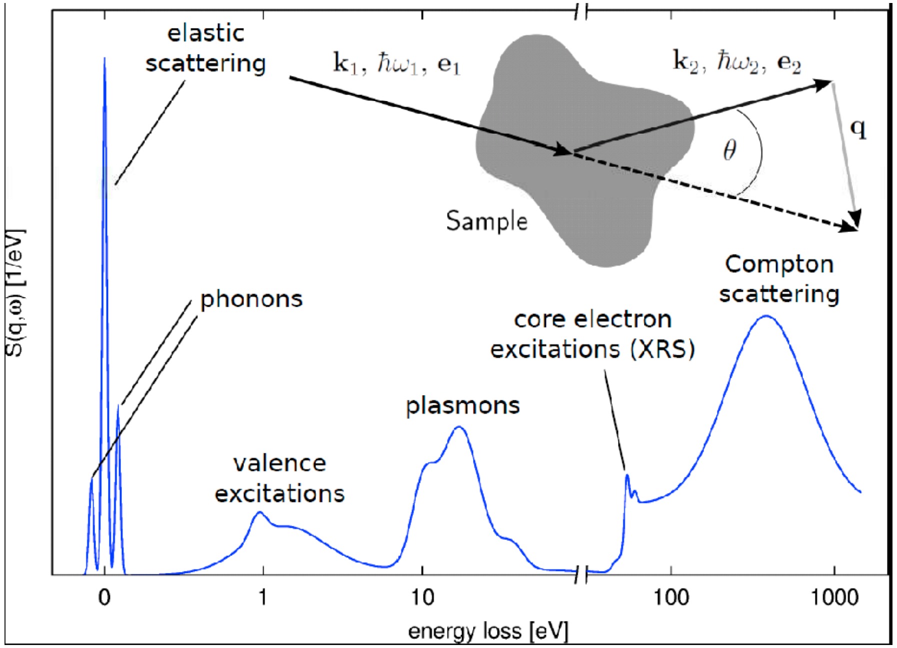
Credits to Rosa, Jacobs loading



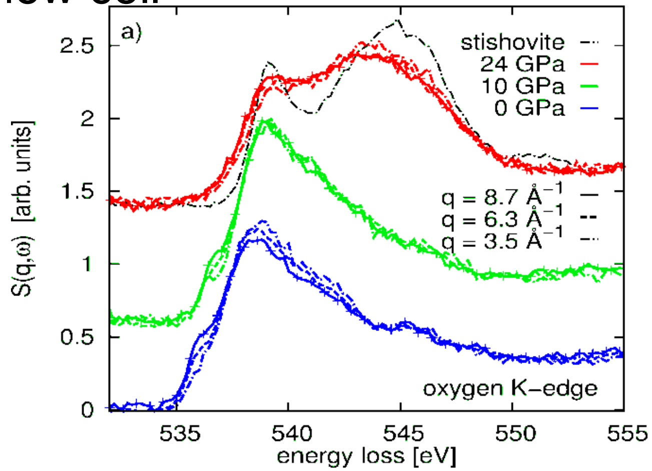


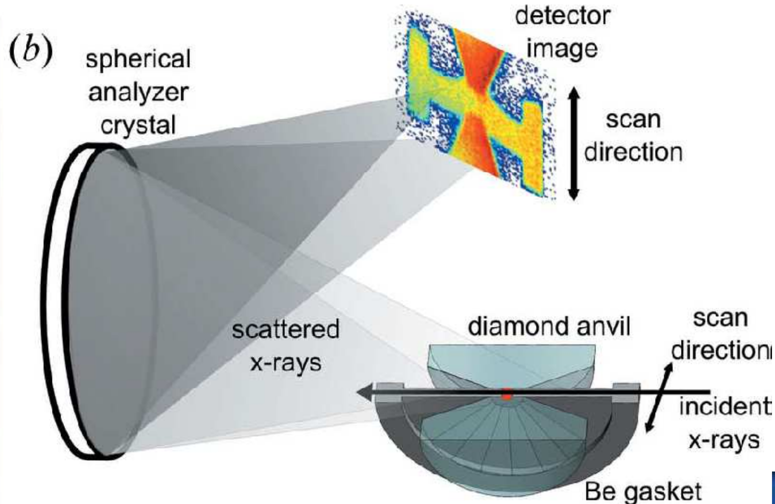
Be Manipulation + Specific DAC

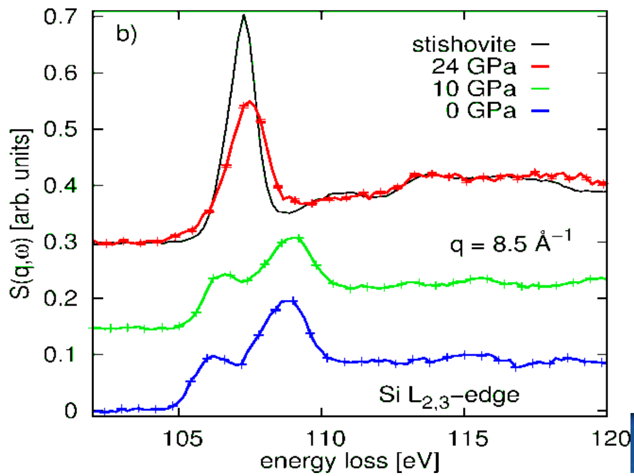
ID20 Raman X ray scattering



- Specially dedicated panoramic DAC develop at HP Lab (Jacobs) in order to satisfy restrictions of angular opening, sample-diamond-X ray beam geometry
- Be manipulation setup
- Project of new cell

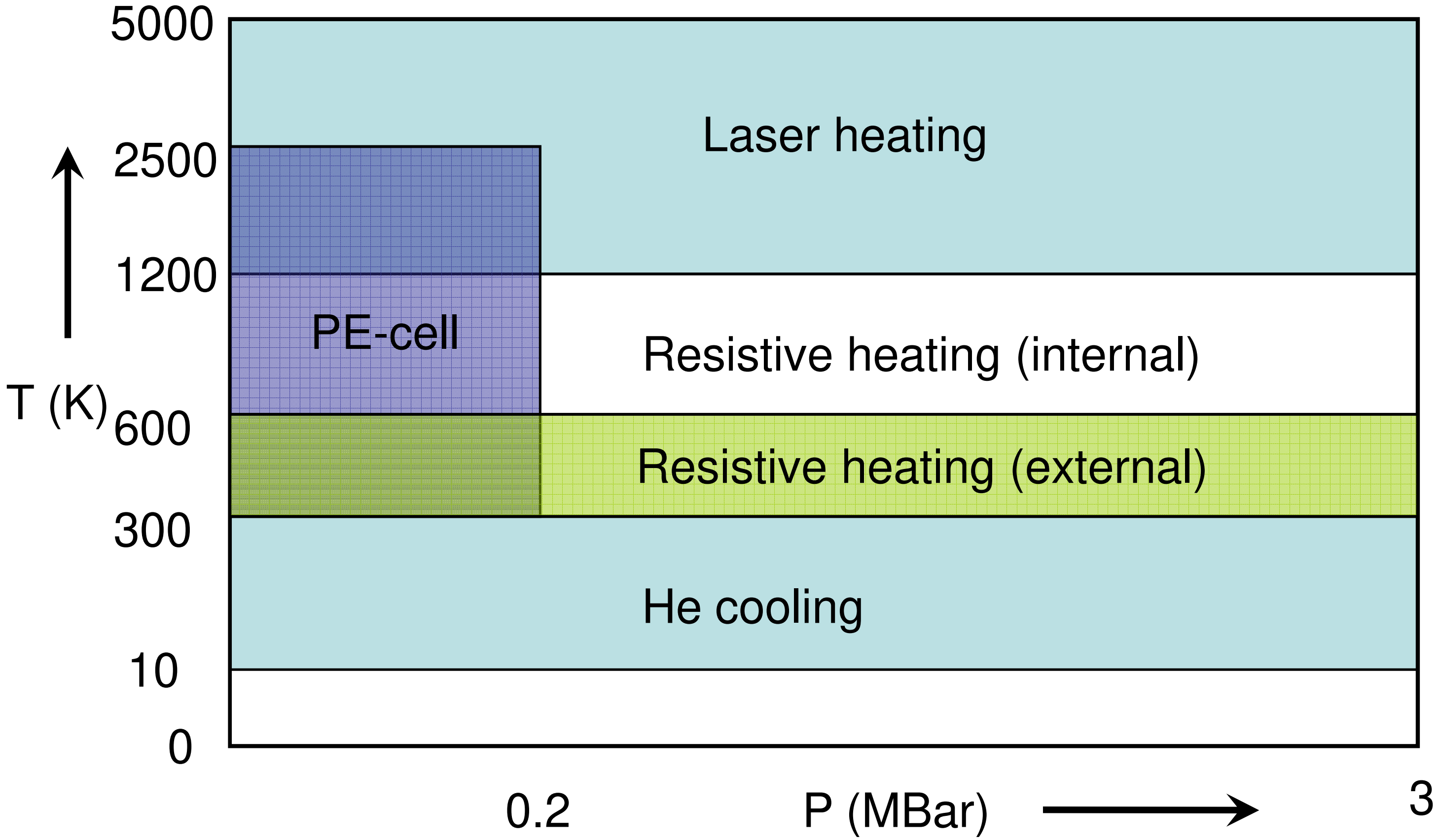






Summary

Temperature vs. Pressure diagram – HP/HT technologies
Using DAC + LVP + Synchrotron radiation



+ Time resolution

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Merci beaucoup de votre attention

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