Structure of low Z liquids under extreme conditions: From dream to reality

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THE PROJECT TEAM

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

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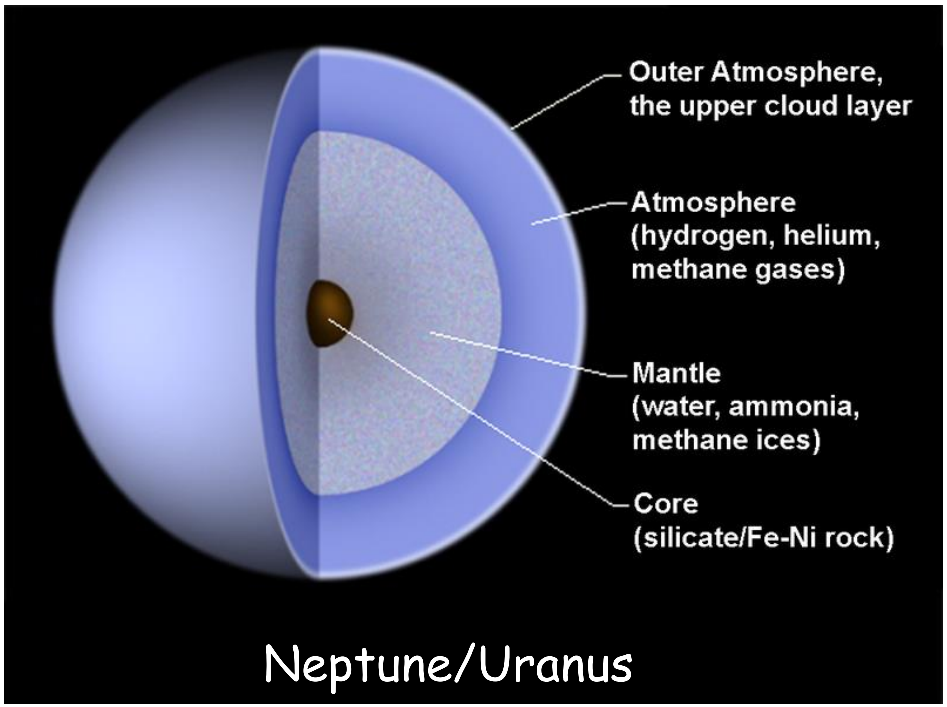
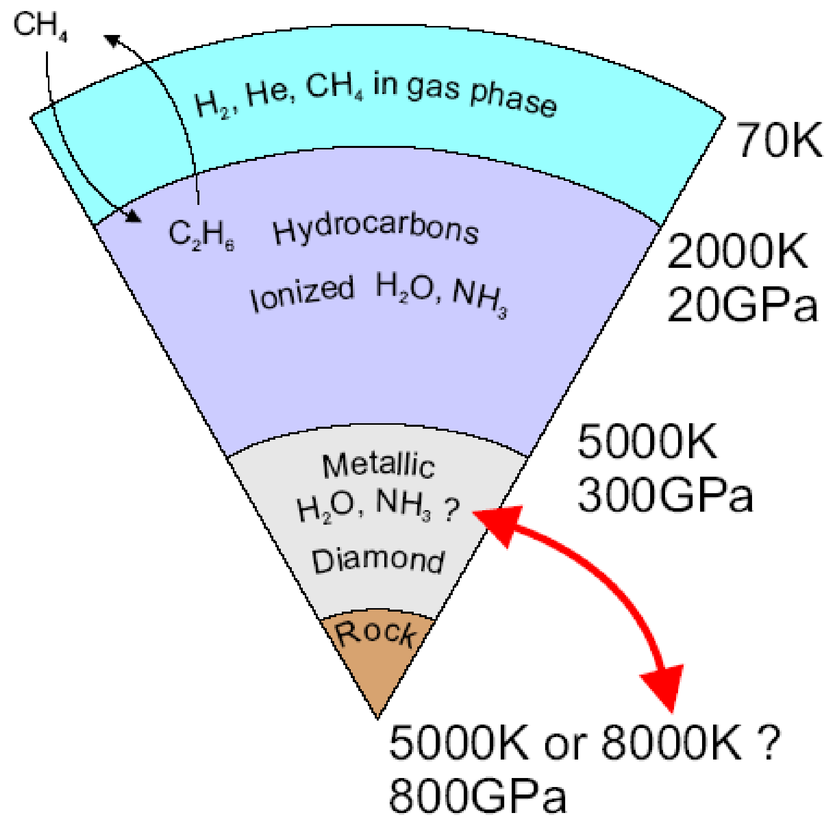
INTRODUCTION – WHY DO WE CARE?

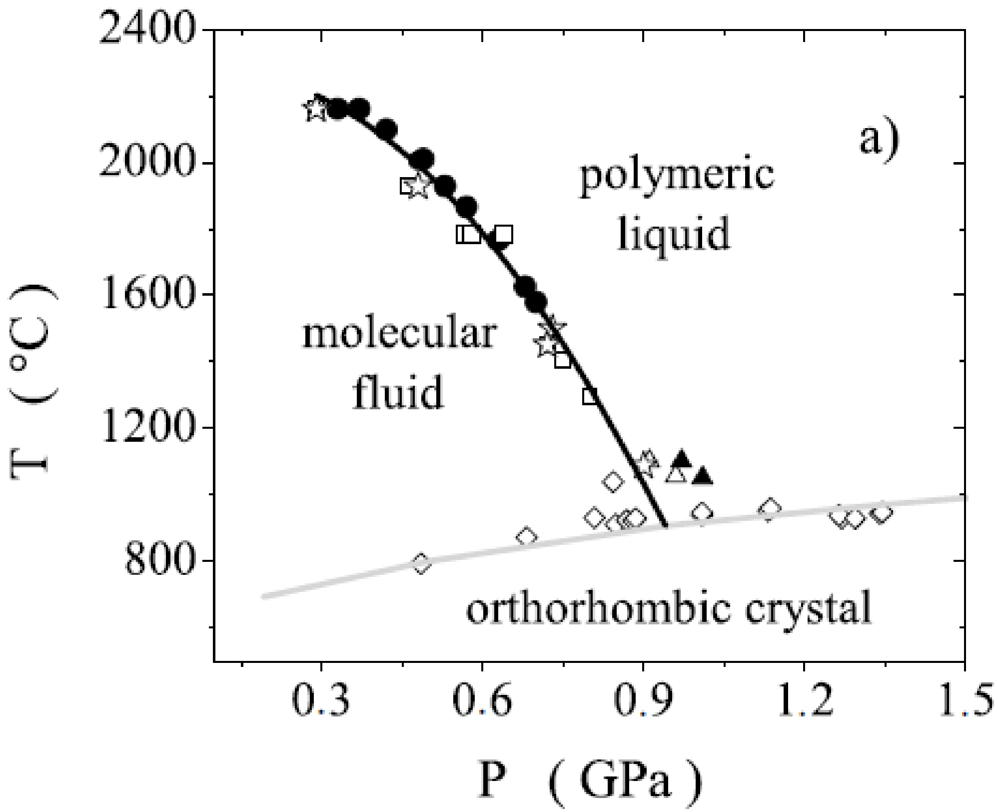
Simple molecular fluids are largely present in the Universe (giant planets) under extreme P-T conditions.





POLYMORPHISM IN DENSE FLUIDS

Liquid - liquid (first order) phase transition (LLT) in Phosphorous

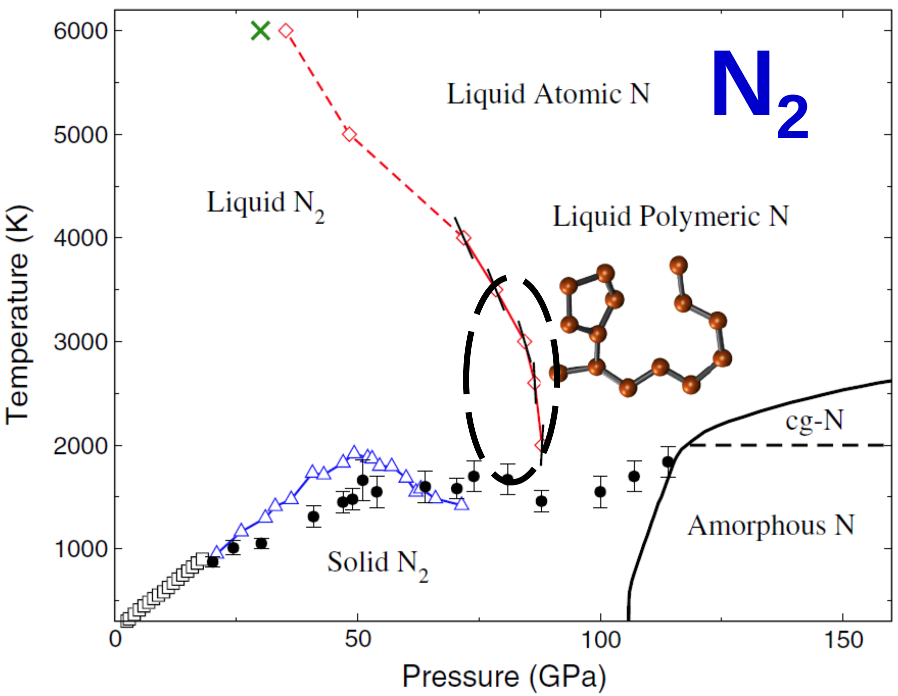


Katayama et al, Nature (2000)
Monaco et al, PRL (2003)
Katayama et al, Science (2004)

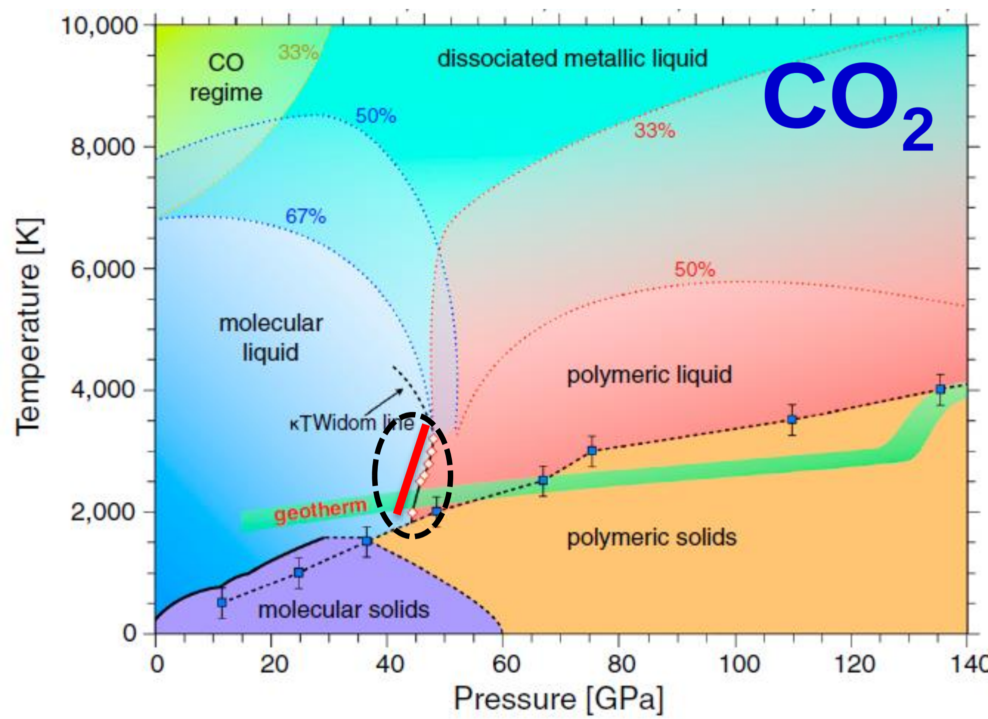
Are there LLTs present in other systems ?

POLYMORPHISM IN DENSE FLUIDS

Liquid - liquid (first order) phase transition (LLT) in N_2 and CO_2 (theory)



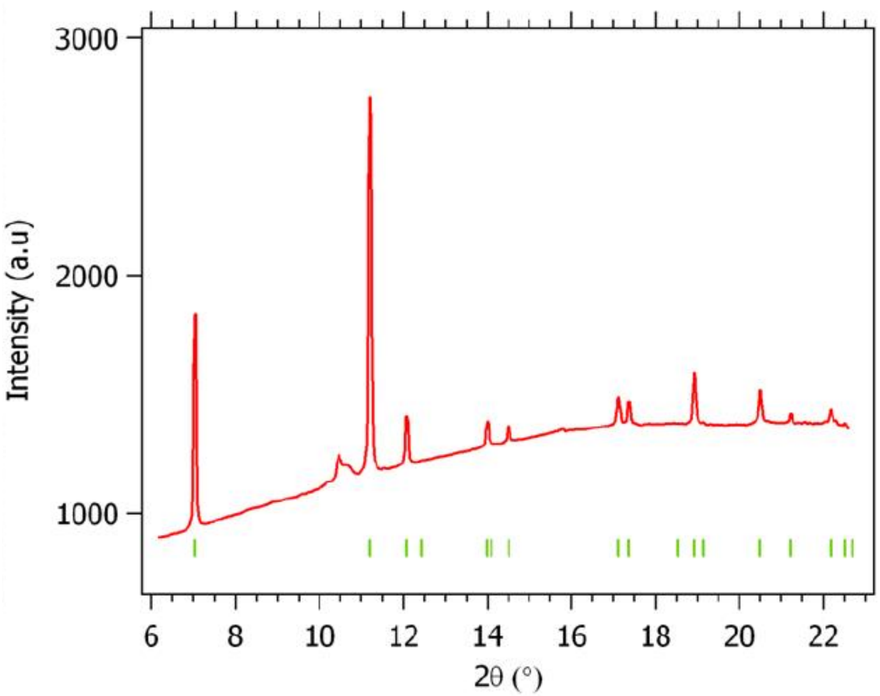
Bonev et al, PRL 2009

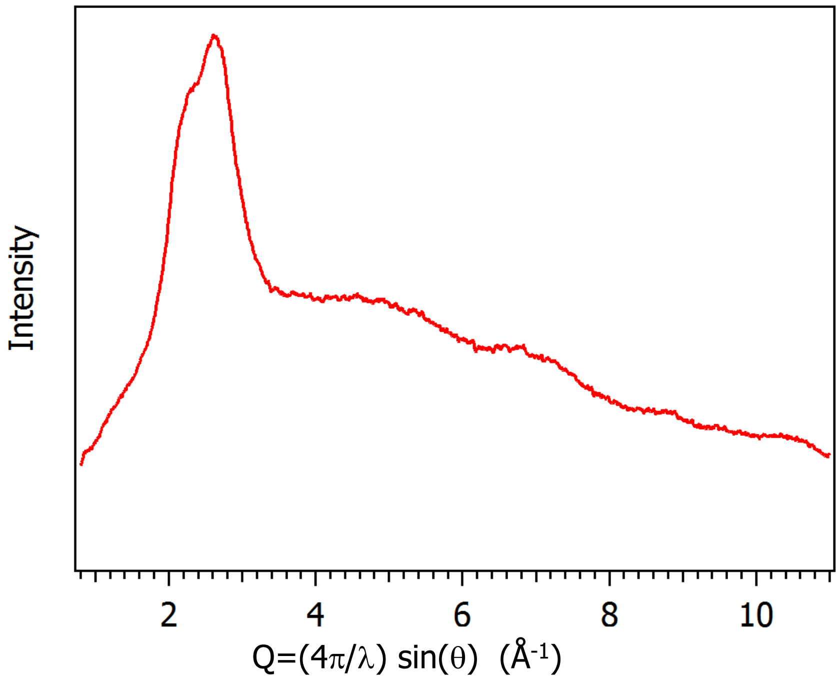


Boates et al, PNAS 2012

The DAC is needed to achieve these P-T conditions

X ray DIFFRACTION PATTERNS





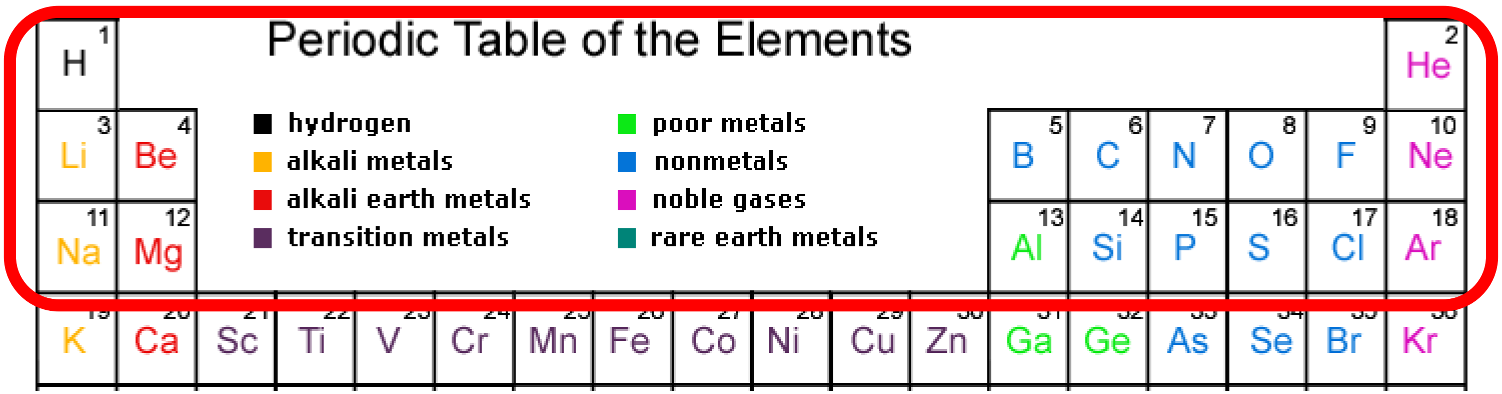
Crystals (ordered)

Fluids (disordered)

EXPERIMENTAL ISSUES

Low Z systems & small sample size (typ. ∅ 80 x 20um)

$$I \propto N \times Z^2$$

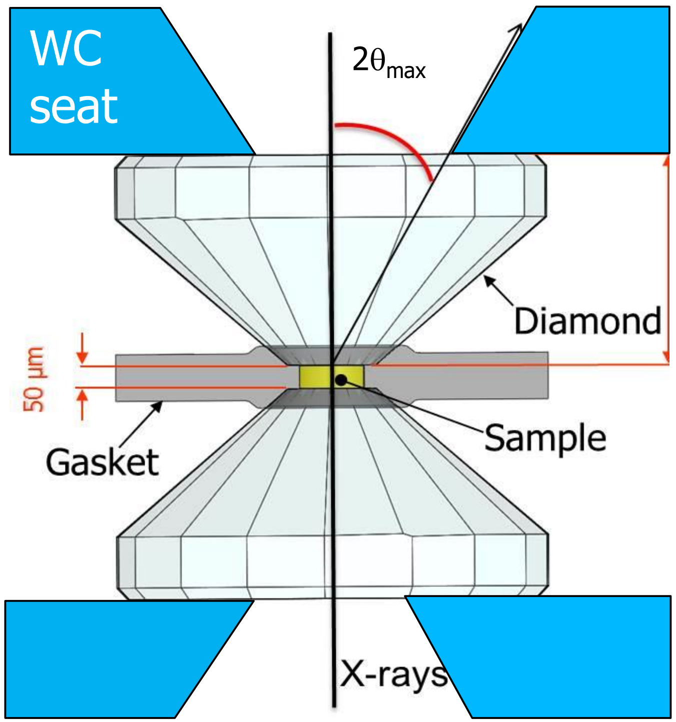


➔ **Very weak diffraction signal**

➔ **Need a very bright X ray source (synchrotron)**

The diffracted signal is truncated by the DAC aperture

➔ Loss of information at high Q (low r)



$$Q=(4\pi/\lambda)\sin(\theta)$$

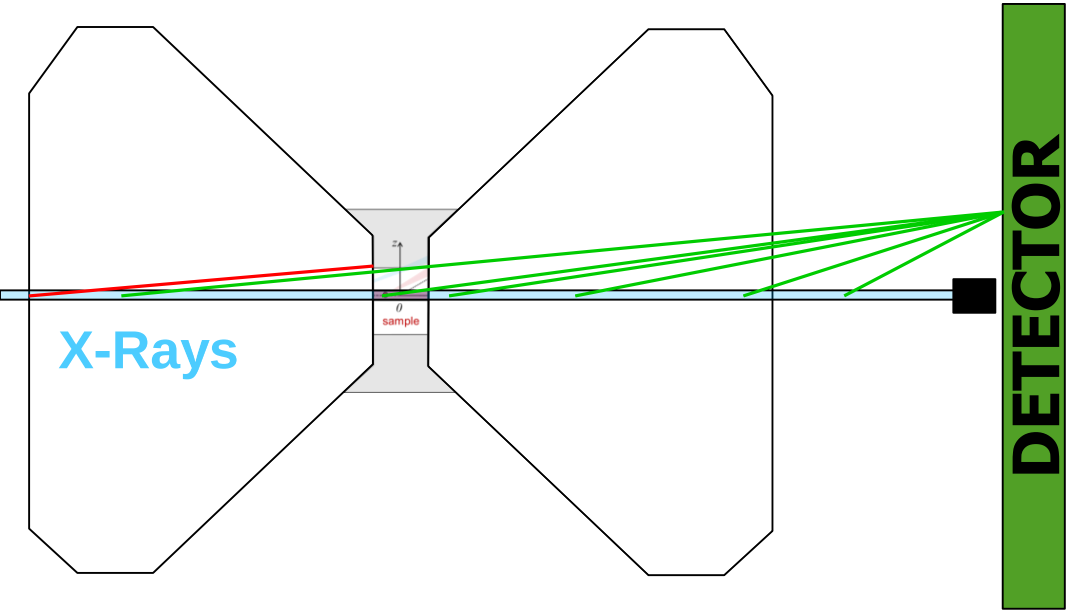
Use:

➔ larger aperture (Boehler-Almax anvils)

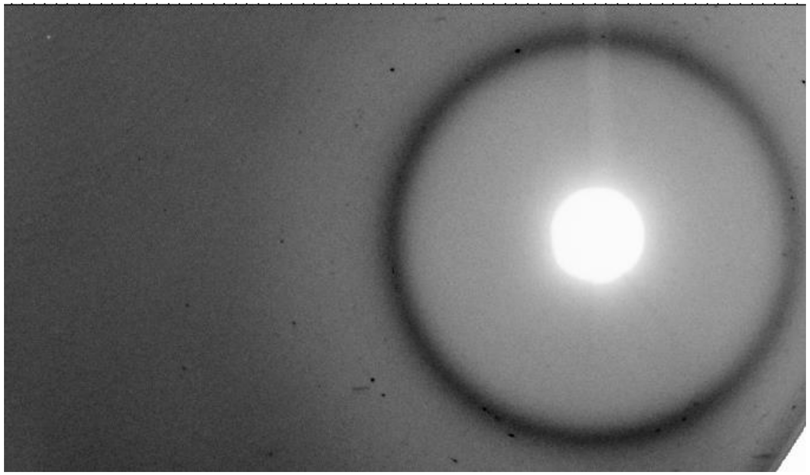
➔ smaller wavelength

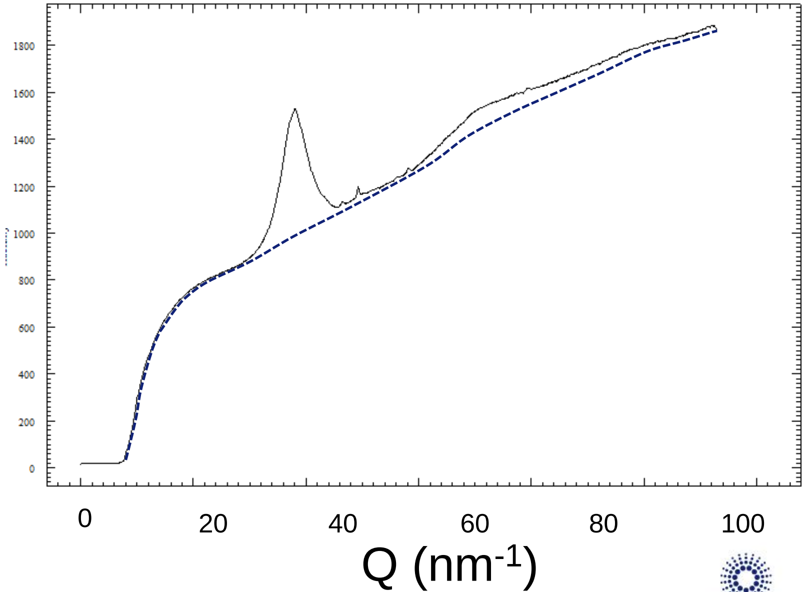
E(keV)	λ(Å)	$2\theta_{max}$ (°)	Q_{max}(Å^{-1})
33.17	0.3738	25	7.28
33.17	0.3738	35	10.1
60	0.2067	25	13.16
60	0.2067	35	18.28

EXPERIMENTAL CHALLENGE USING XRD



Potassium
P=3.1GPa, T=530K





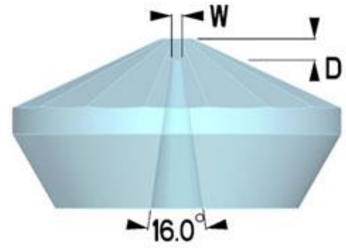
• A given point of detector sees the contribution from **sample + diamonds + air**

Diamond contributions: elastic and inelastic scattering

HOW TO REDUCE BACKGROUND

➔ Use smaller/perforated anvils

Anvils are more fragile:
limits P-T range

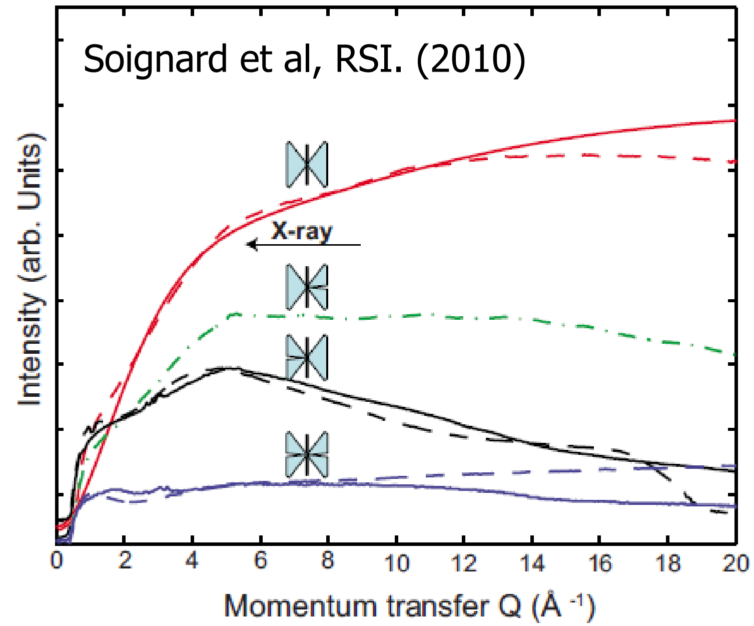


➔ Use energy-dispersive XRD

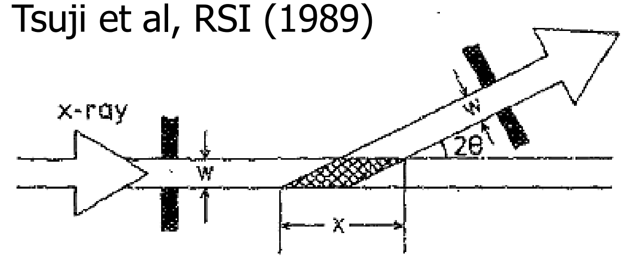
Long acquisition time

S(Q) has to be reconstructed

➔ Use a multichannel collimator

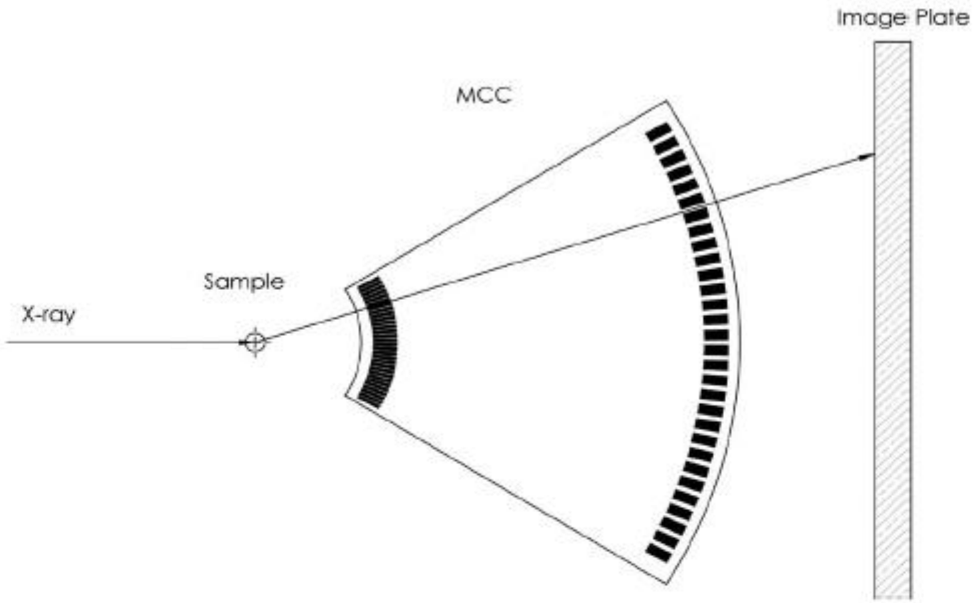


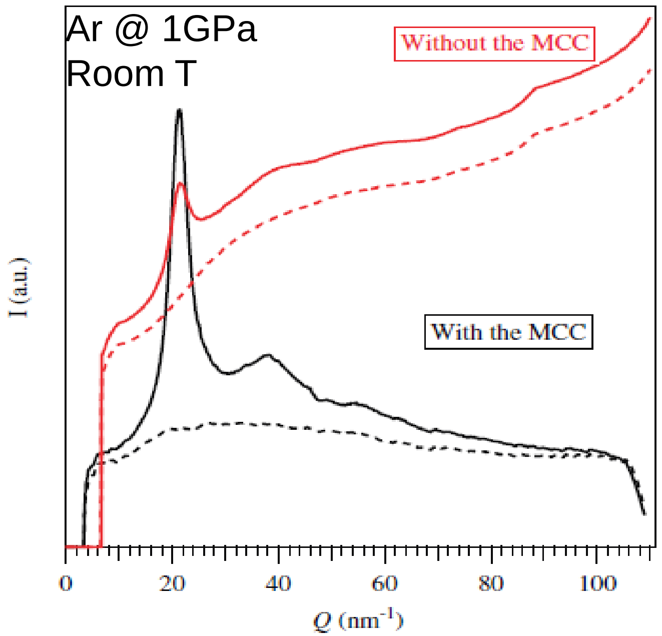
Tsuji et al, RSI (1989)



THE MULTICHANNEL COLLIMATOR (SOLLER SLITS)

X ray techniques



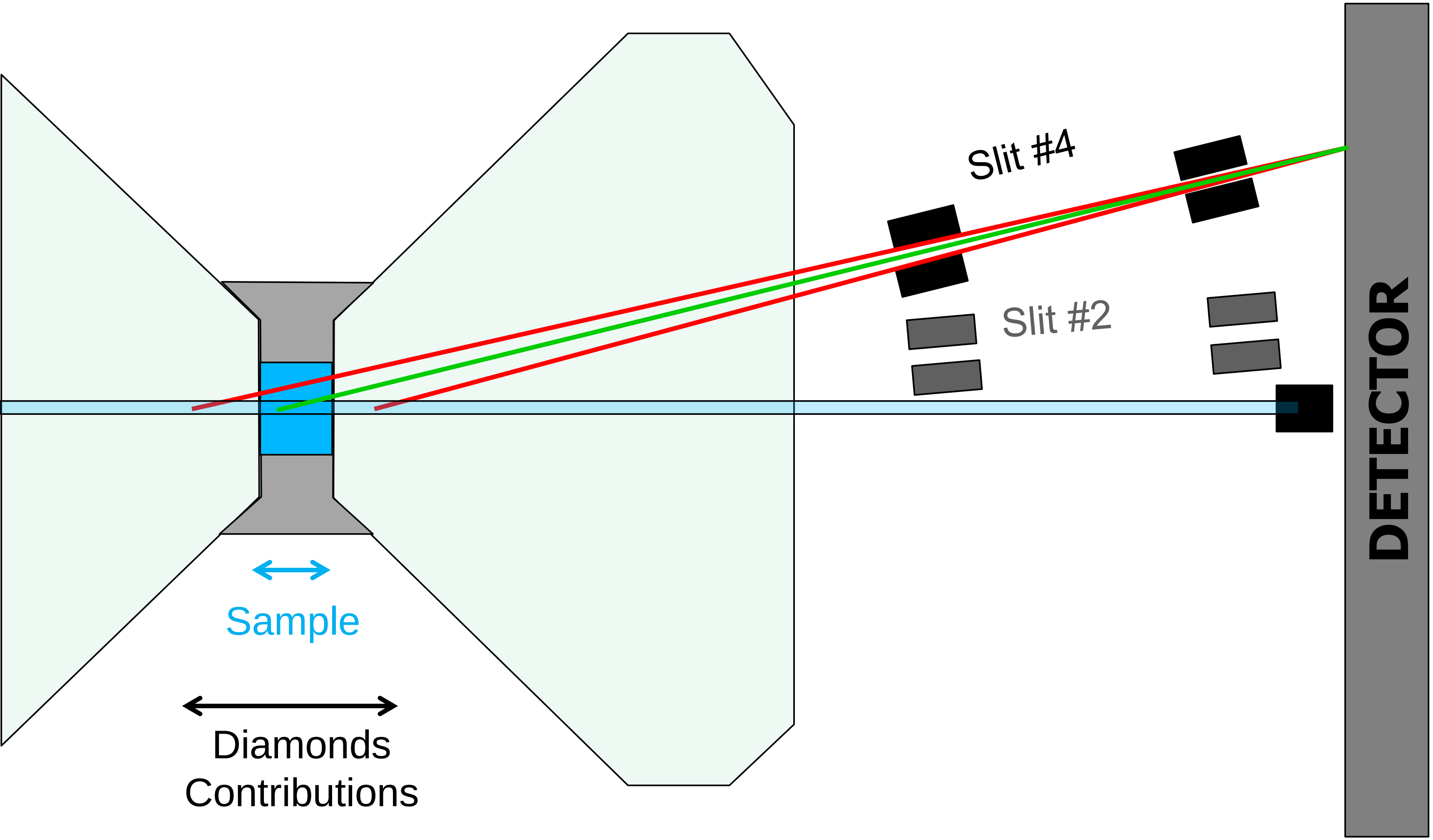


Our strategy:
Couple DAC with
Multi-Channel Collimator
to reduce Compton diffusion of diamonds

External and internal heaters: important improvement in Temperature metrology

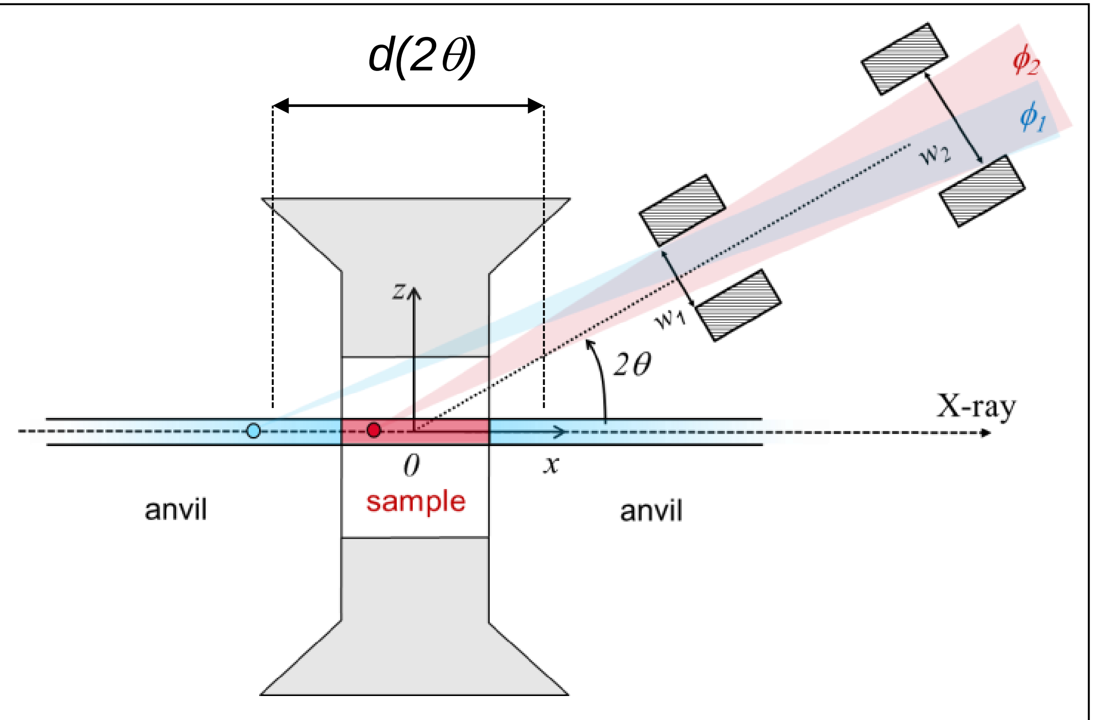
G. Weck, G Garbarino et al., Rev. Sci. Instrum. 84 p 063901 (2013)

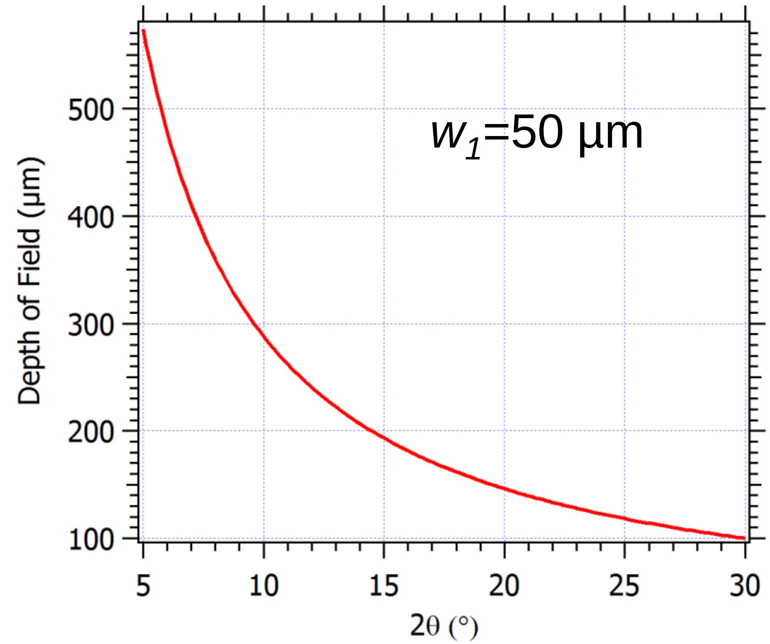
THE MULTICHANNEL COLLIMATOR (SOLLER SLITS)



The diamond contributions is drastically reduced

THE MULTICHANNEL COLLIMATOR (SOLLER SLITS)



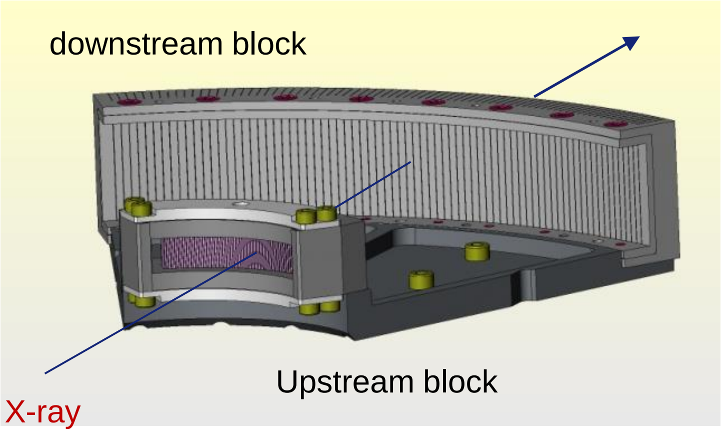


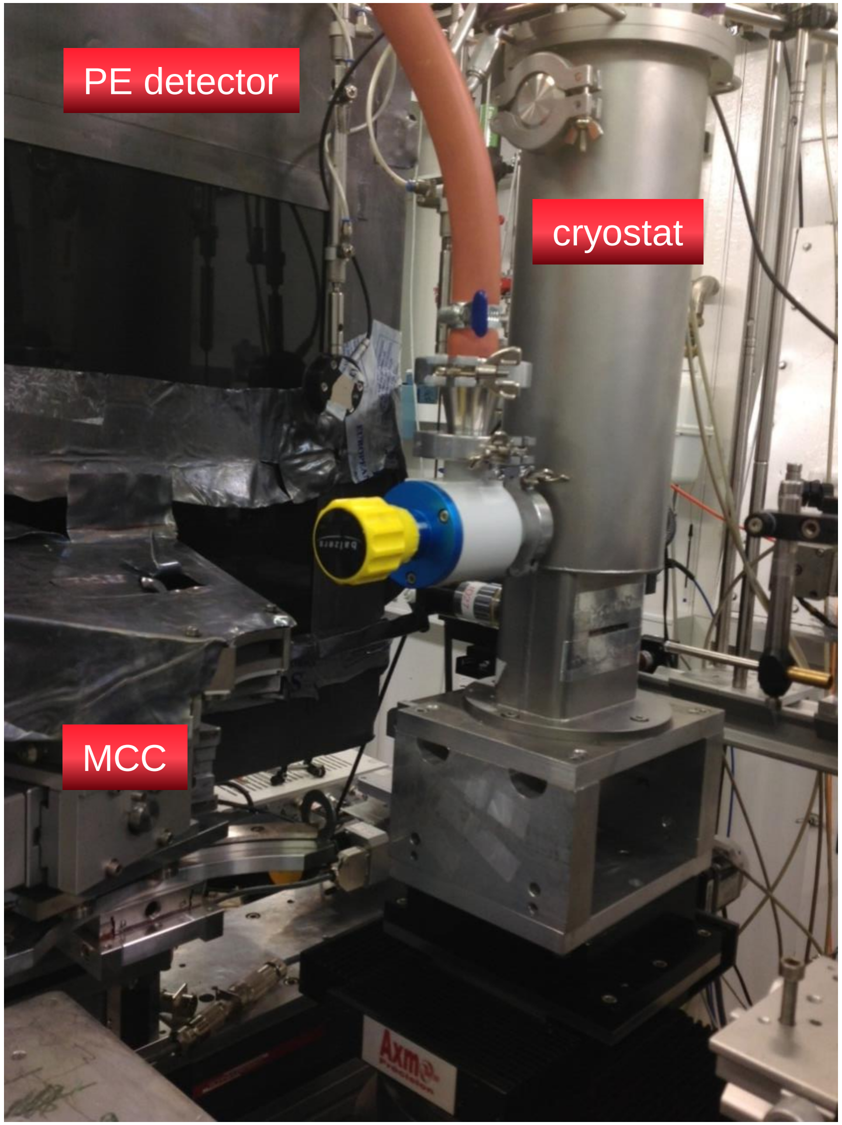
The “depth of field” along the beam is:

$$d(2\theta) \approx w_1/\sin(2\theta)$$

Covered angle= 60° (Horizontal) x 16° (Vertical). At 33 KeV, Q_{max}=145 nm^{-1}

MCC (SOLLER SLITS) AT ID27



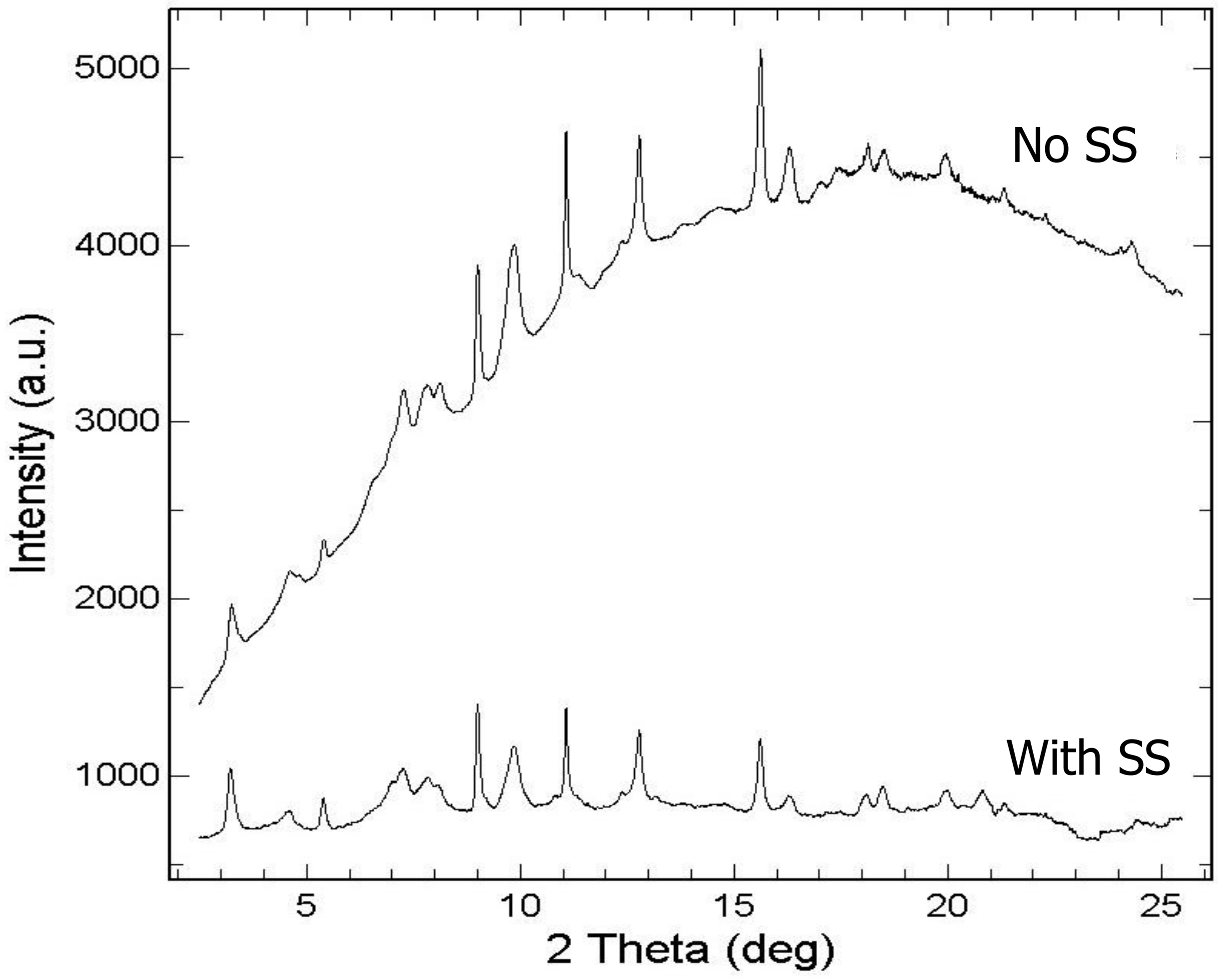


- Setup initially designed for the Paris-Edinburgh press.
- Upstream block: 75 slits of 50 μm at 50 mm of the sample
- Downstream block: 75 slits of 200 μm at 200 mm of the sample
- Angle between each slits = 0.8°.
- Total covered angle = 60°.
- Define with the X-ray beam a volume seen by the Detector

Morard et al. RSI 82 (2011)

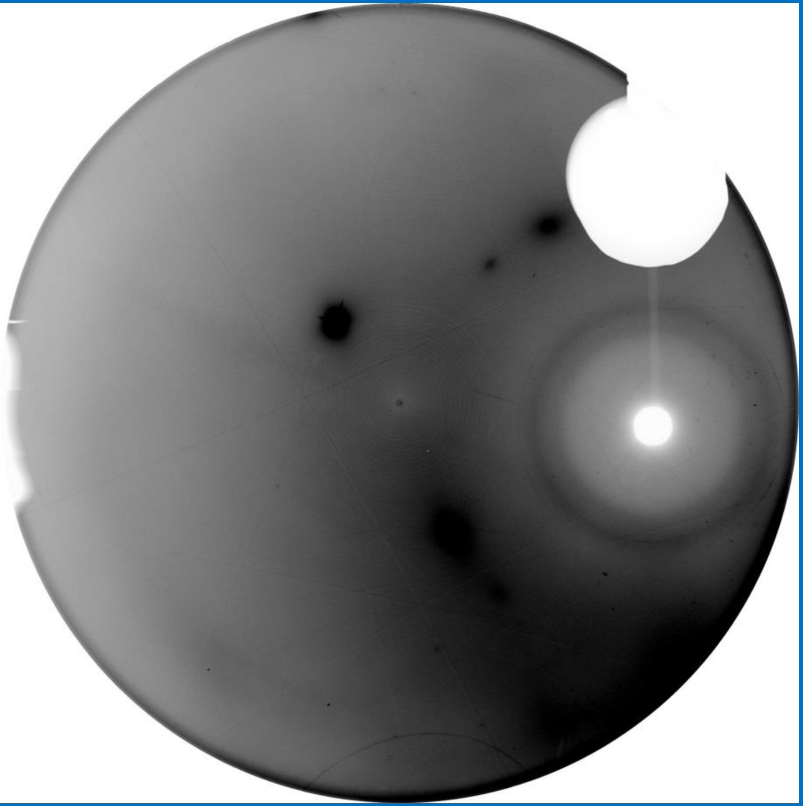
MCC EFFECT WITH THE DAC

$Na_{0.5}CO_2$ crystalline sample – MAR CCD



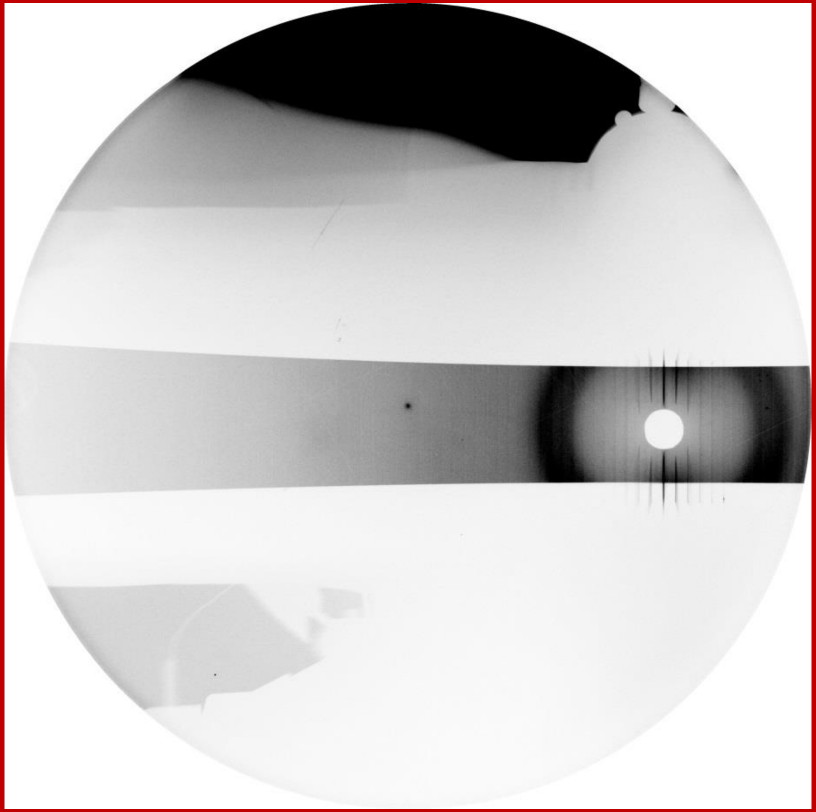
MCC EFFECT WITH THE DAC

CO_2 sample at 7.8 GPa, 710 K – MAR 345 IP



30 s

Without MCC



300 s

With MCC

MCC EFFECT WITH THE DAC

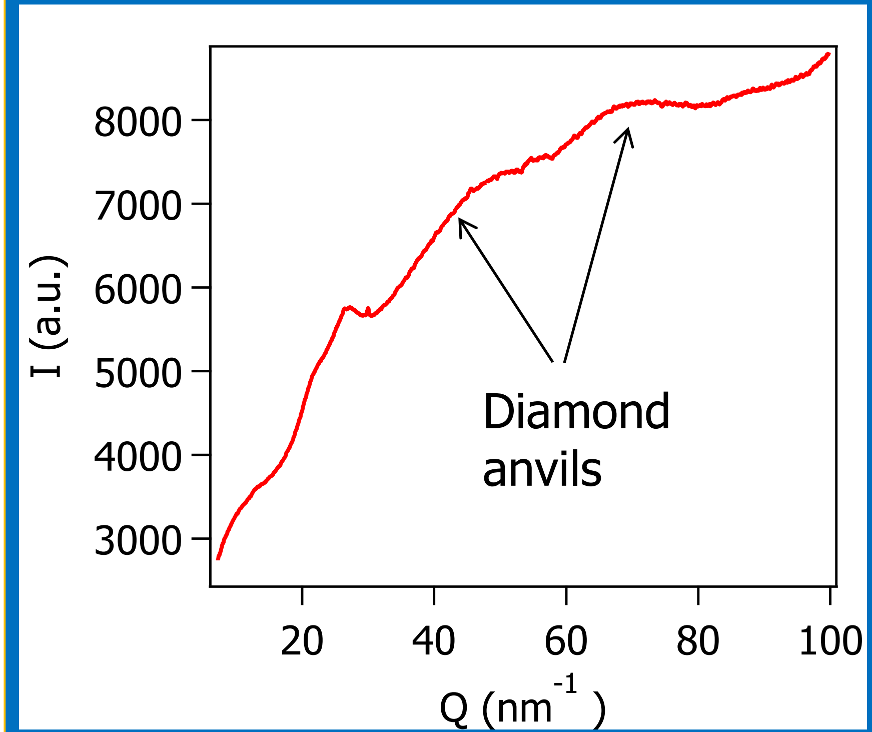
CO_2 sample at 7.8 GPa, 710 K – MAR 345 IP

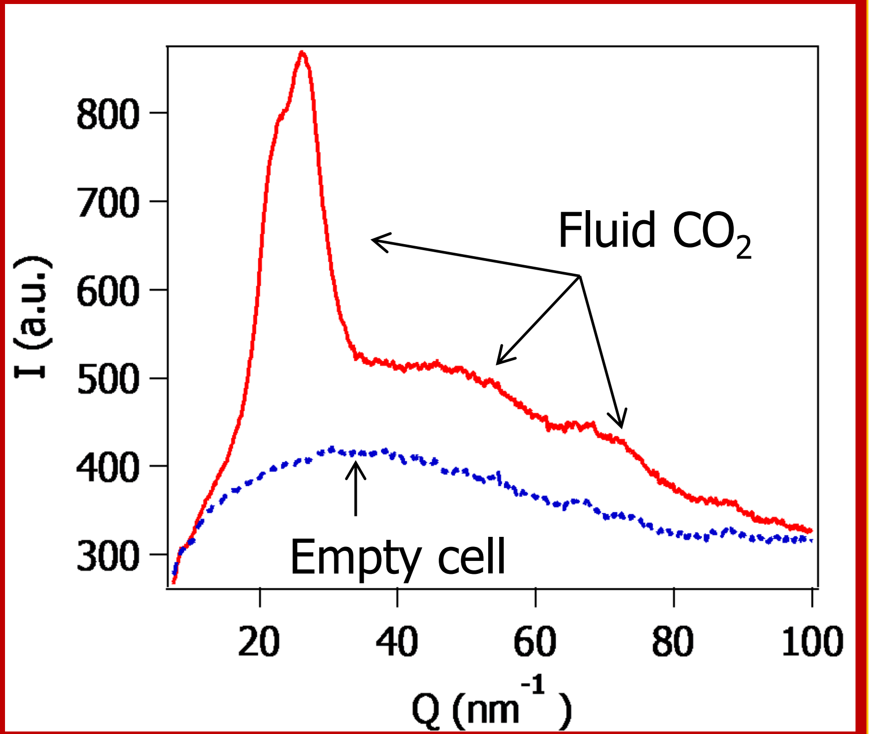
Without MCC

With MCC

MCC EFFECT WITH THE DAC

CO_2 sample at 7.8 GPa, 710 K – MAR 345 IP





The Compton signal of the anvils **is reduced by a factor of 100 at 20 nm^{-1}**, and by more than **400 at 80 nm^{-1}**

Without MCC | **With MCC**

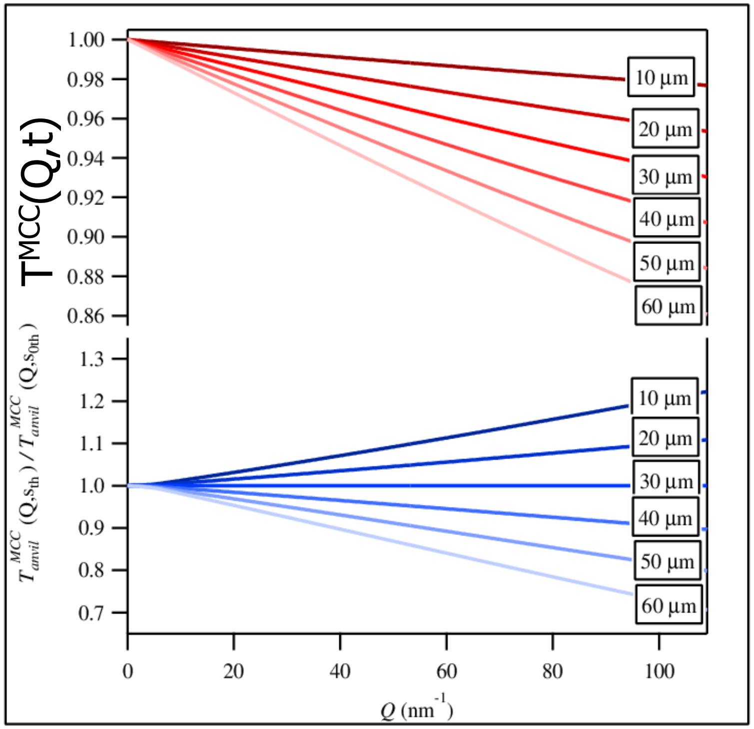
DATA ANALYSIS

➔ The measured signal $I^{meas}(Q)$ is analyzed using the method described in [Eggert et al, PRB 2002] to obtain *S(Q)* and *g(r)*. The method also allows to extract the density.

➔ The procedure has been modified to take into account the transmission of the MCC:

$$I^{meas}(Q) = T^{DAC}(Q) T^{MCC}_{Samp}(Q) I^{samp}(Q) + s I^{bkgd}(Q)$$

$$I^{bkgd}(Q) = T^{MCC}_{DAC}(Q) I^{anvil}(Q)$$

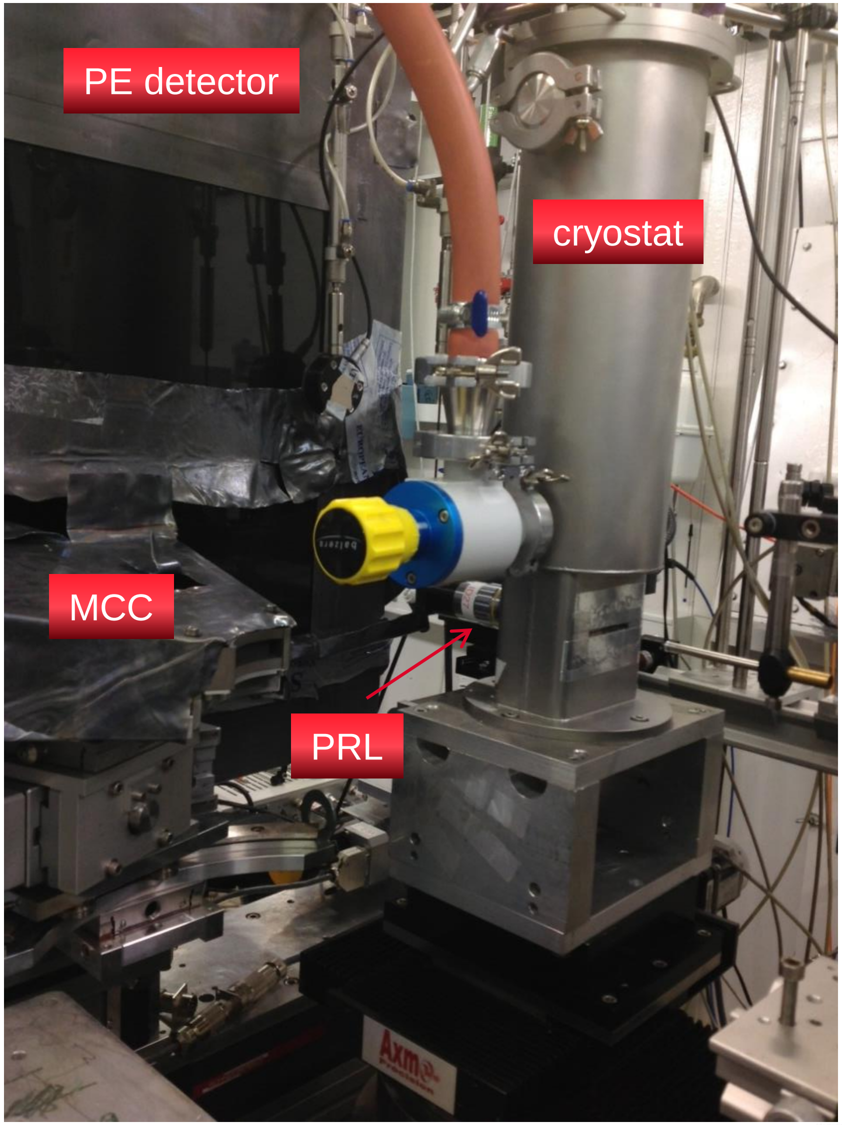


➔ T^{MCC} depends on Q and the sample thickness *t*, which varies with pressure. *t* was thus included as a fit parameter.

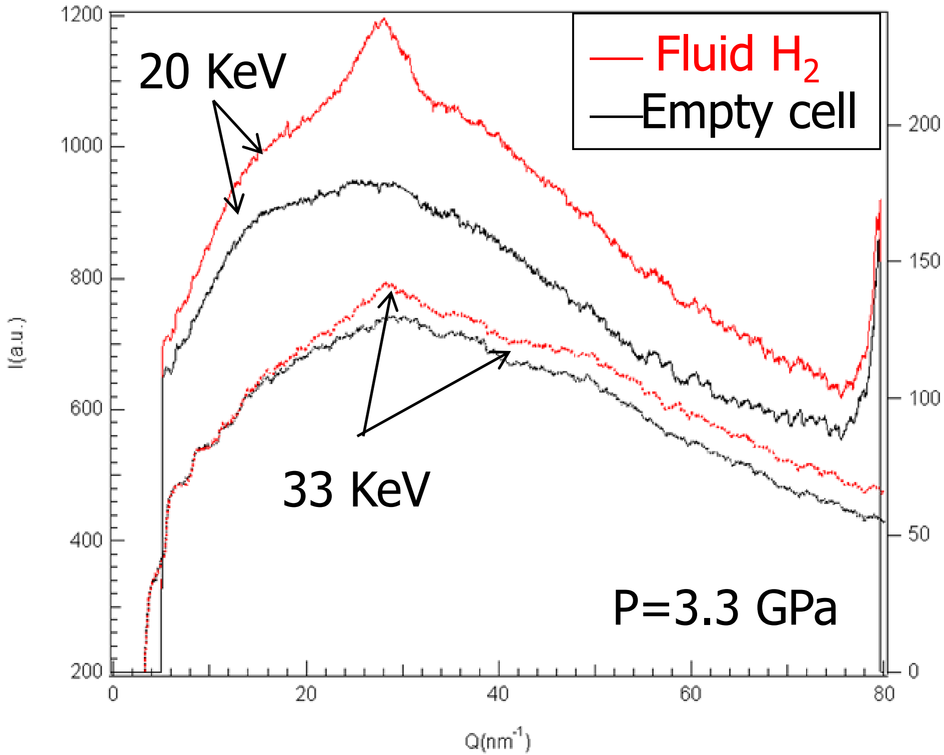
1) FLUID H_2 / D_2 (Z=1)

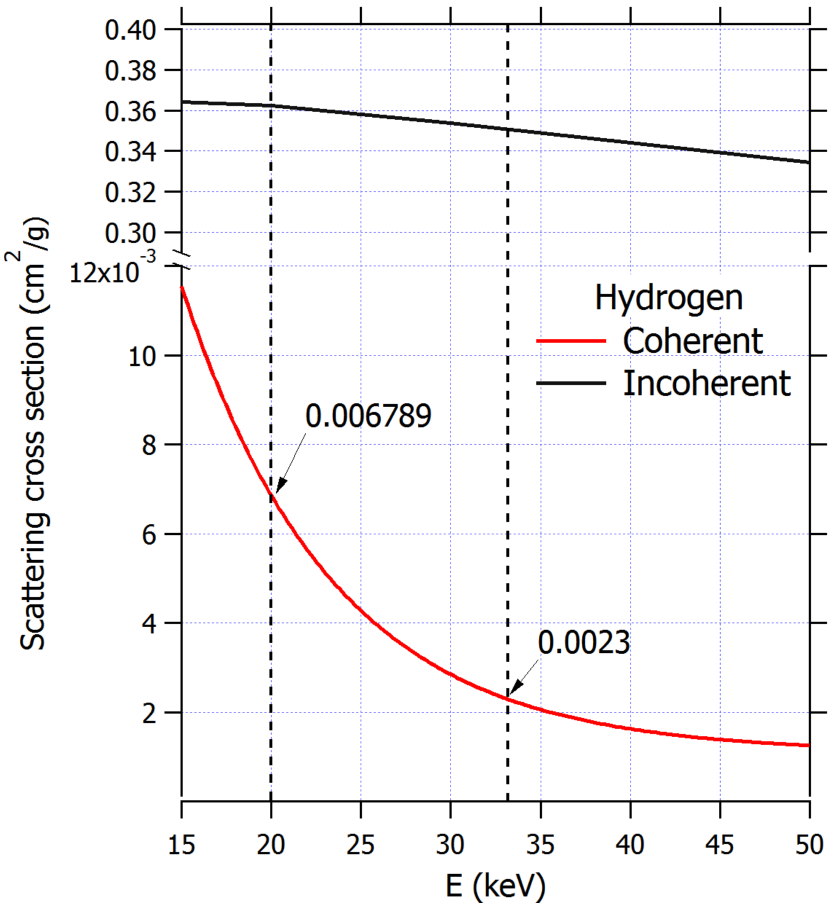
Z=1

- **Perkin-Elmer Flat panel**
- **$E_{X\text{-rays}}$=20 or 33 KeV**
- **T from 50 to 300 K using ID27 cryostat**

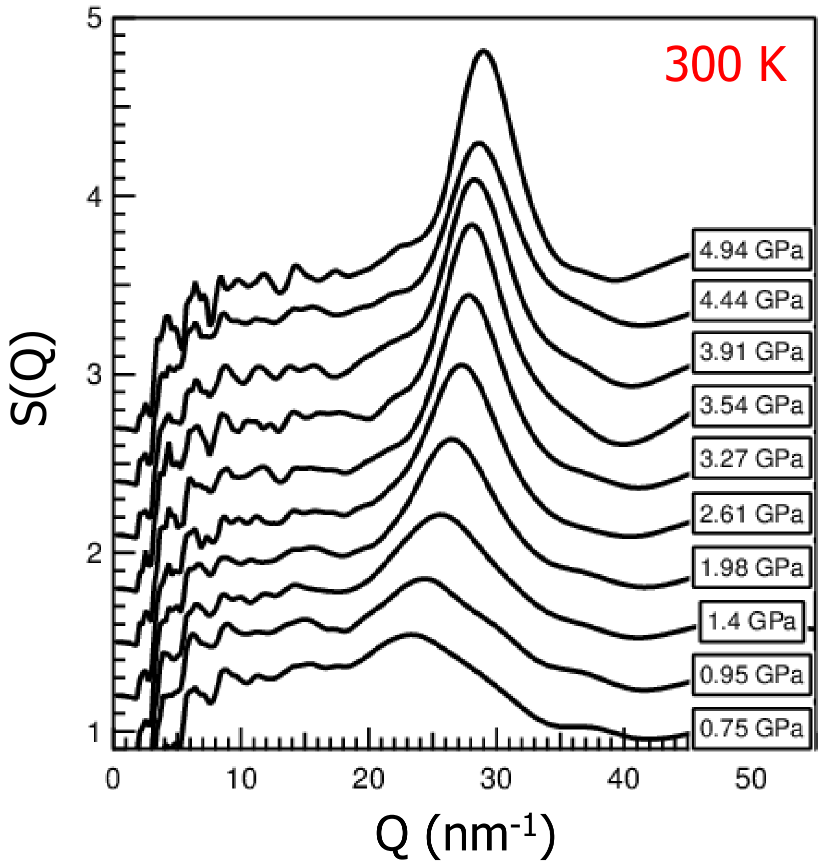


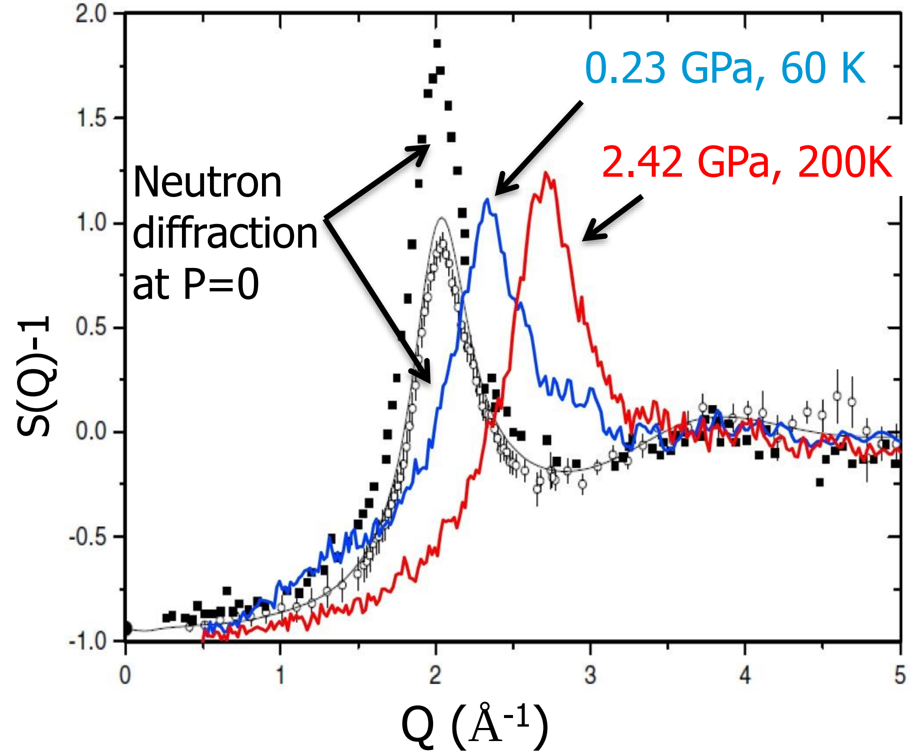
1) FLUID H_2 / D_2 (Z=1) – INFLUENCE OF THE ENERGY





1) FLUID H_2 / D_2 (Z=1)

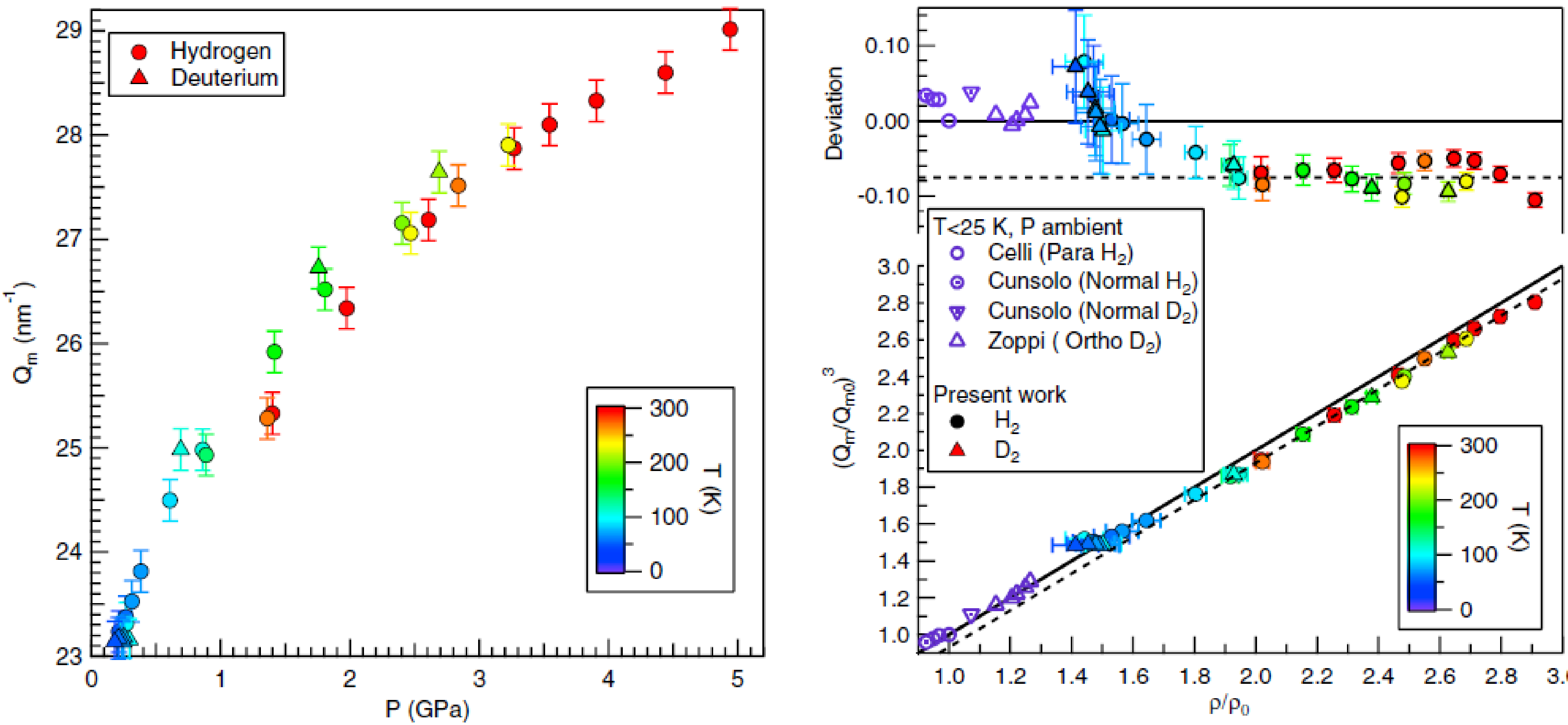




- ➔ **S(Q) becomes more structured with pressure**
- ➔ **The First-Sharp Diffraction Peak (FSDP) shifts with P and T**
- ➔ **Compares very well with neutron diffraction at P=0**

Weck et al, PRB 91 p 180204 (2015)

1) FLUID H_2 / D_2 (Z=1)

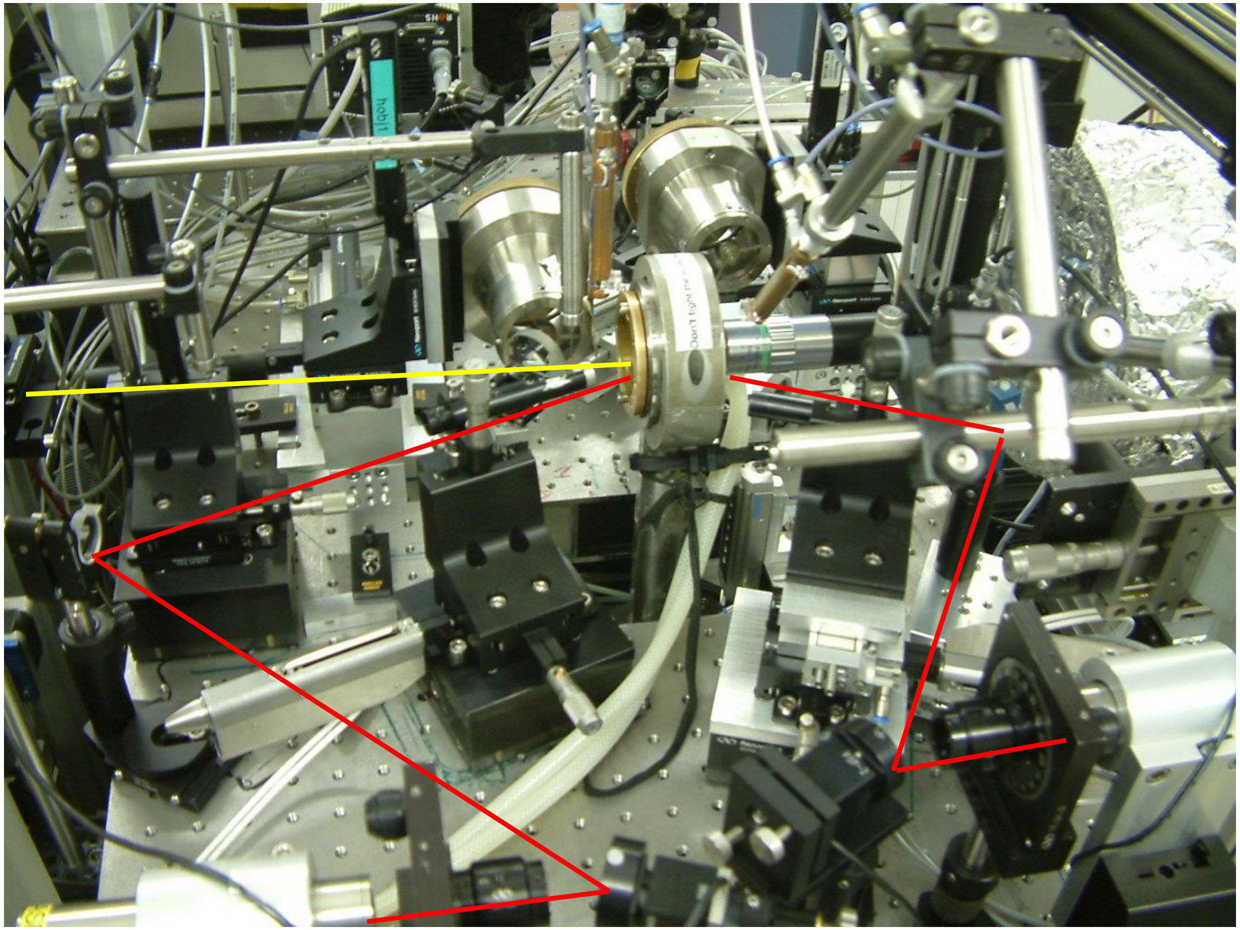


➔ **Isotopic shift of the Q_m between H_2 and D_2** due to density effect

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

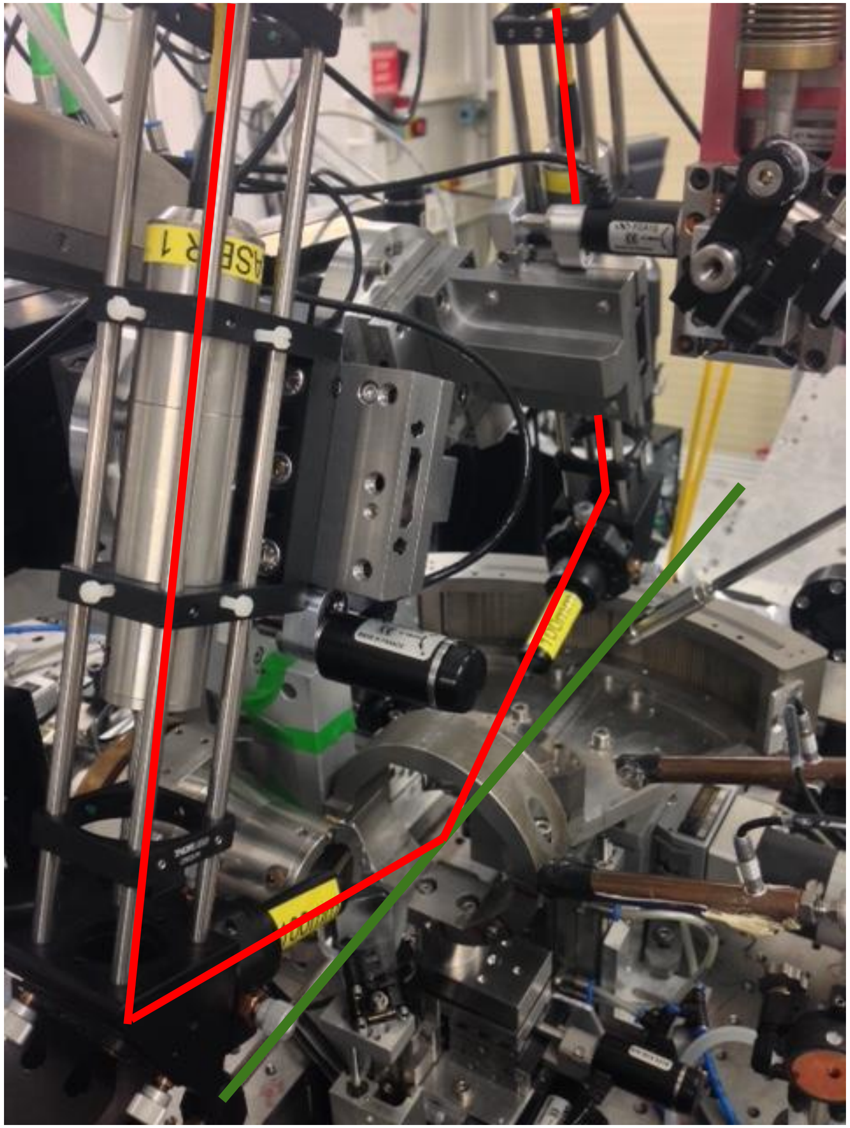
➔ **Extension of the experimental studies in liquid H_2 up to Mbar range** seems very encouraging (signal/background ratio will only be reduced by a factor 5)

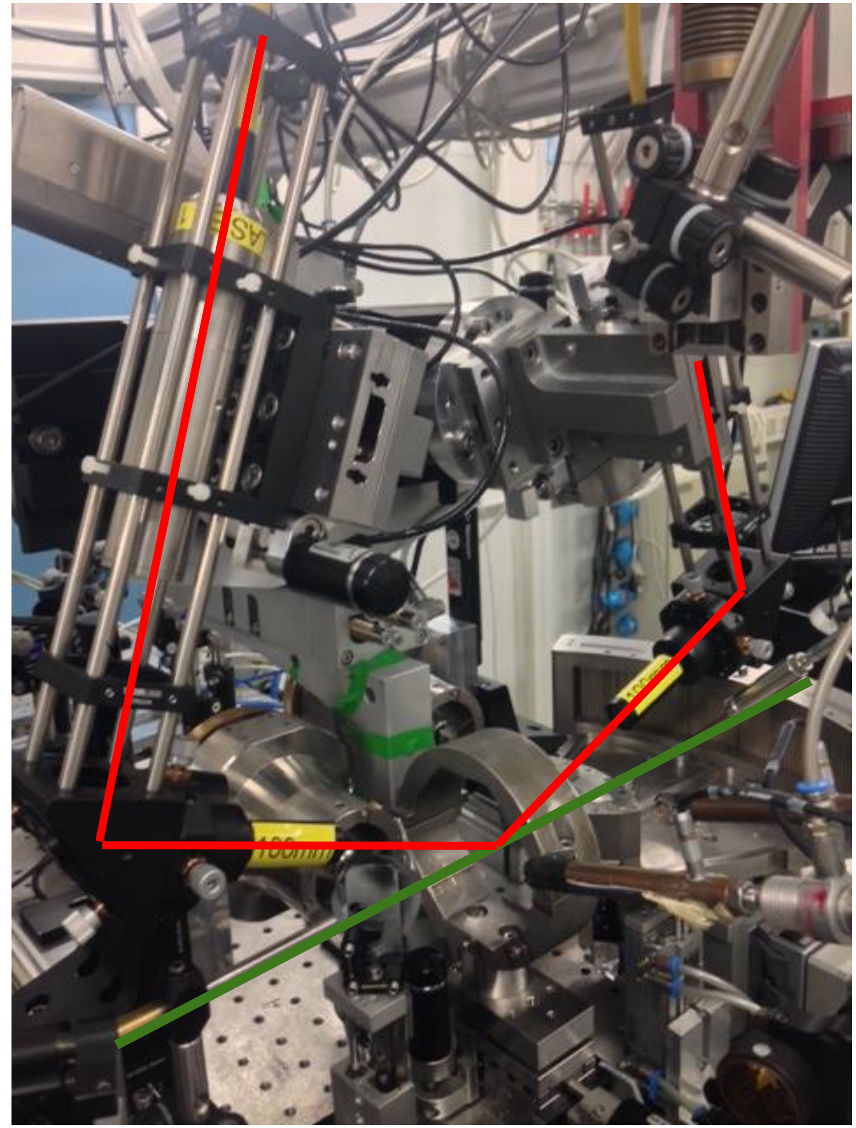
HORIZONTAL LASER HEATING SYSTEM



Not possible to rotate the DAC or insert additional devices (Soller slits)

VERTICAL LASER HEATING SYSTEM

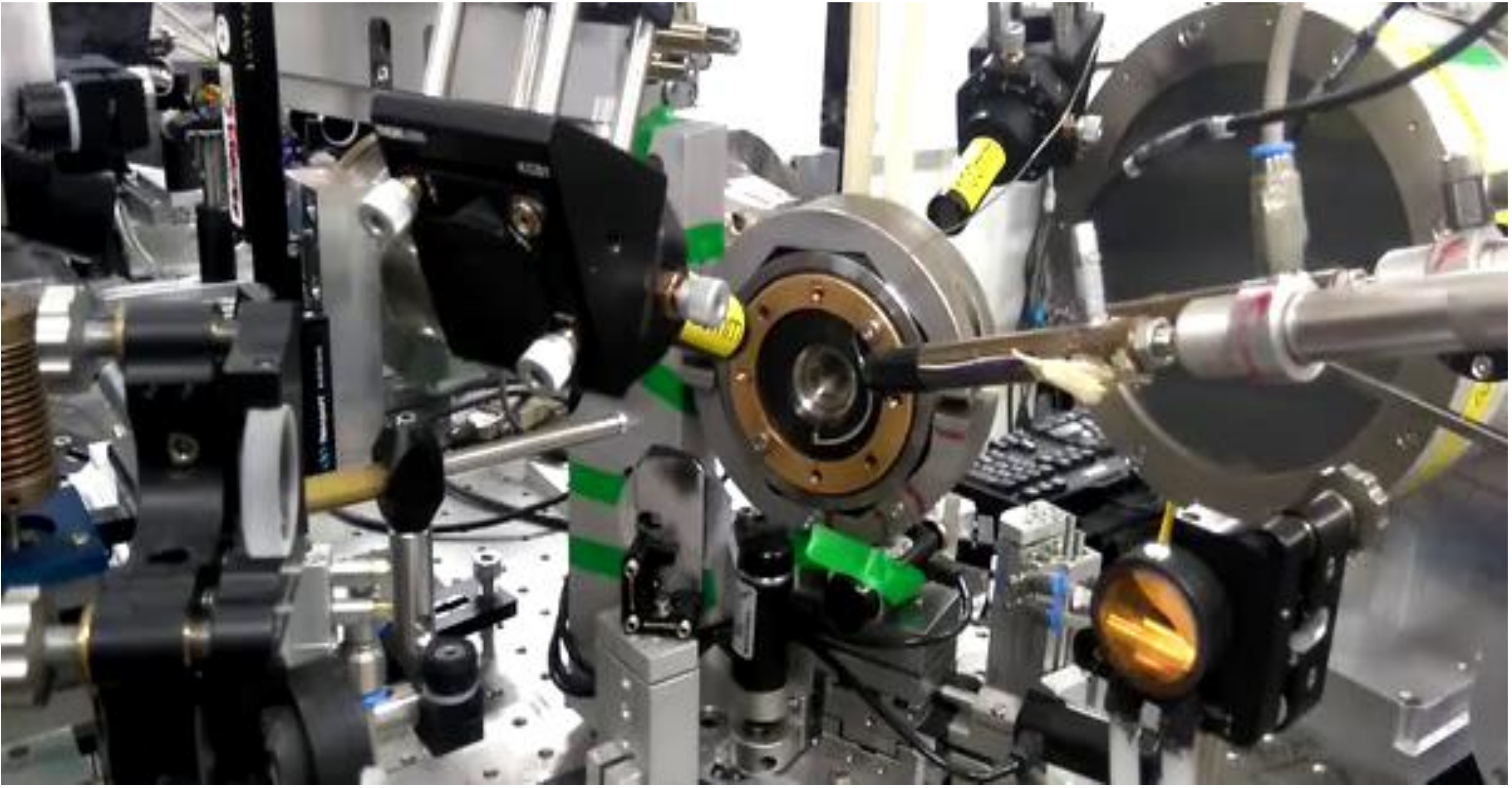




- The system can rotate → Single crystal XRD
- Additional devices can be introduced (Soller slits) → Liquid structures

XRD @ HP: VERTICAL LASER HEATING (λ=1μm)

EXAMPLE: SINGLE CRYSTAL COUPLED WITH LASER HEATING

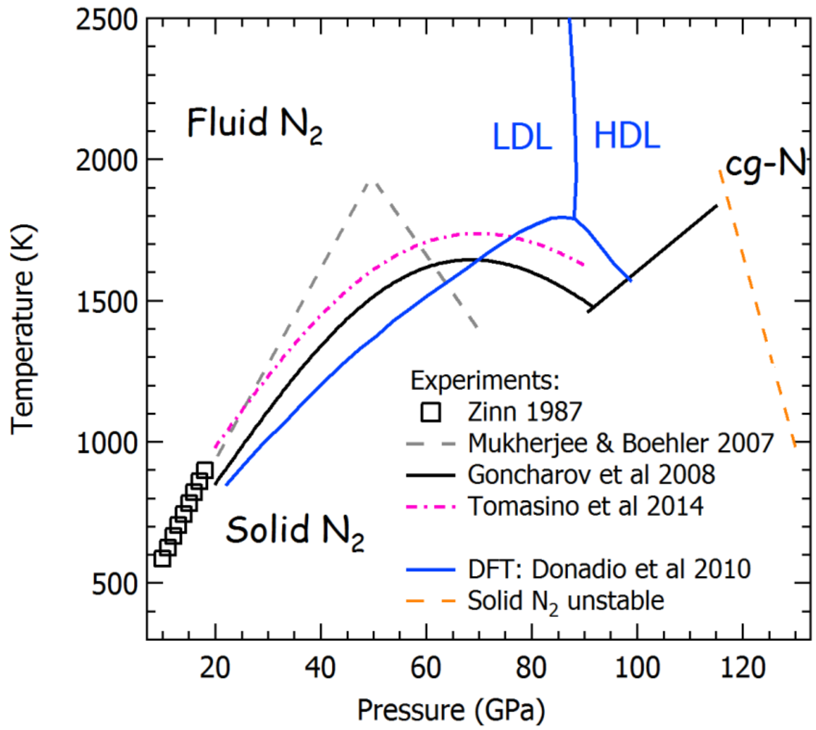


Courtesy Prof. Sebastien Merkel, Univ. Lille, France

MELTING CURVE AND STRUCTURE FACTOR OF N_2

Motivation:

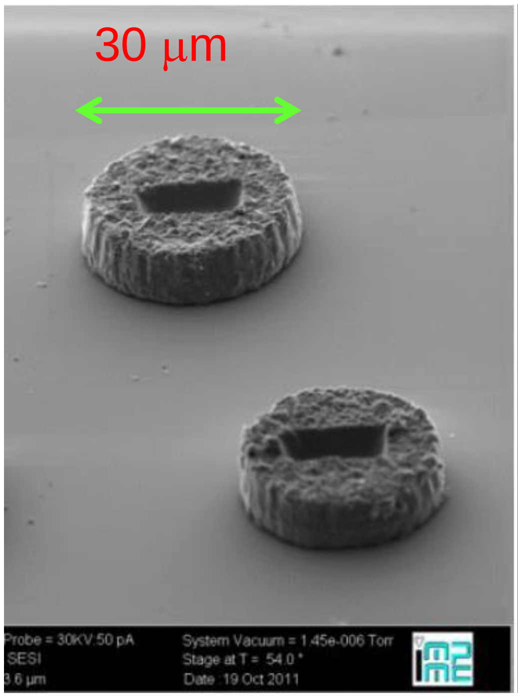
- Ab initio prediction of a liquid-liquid phase transition at P~90 GPa
- Different experimental melting curves reported (Raman, Speckle)
- Observation of a maximum in the melting curve
- No structural data in the liquid state

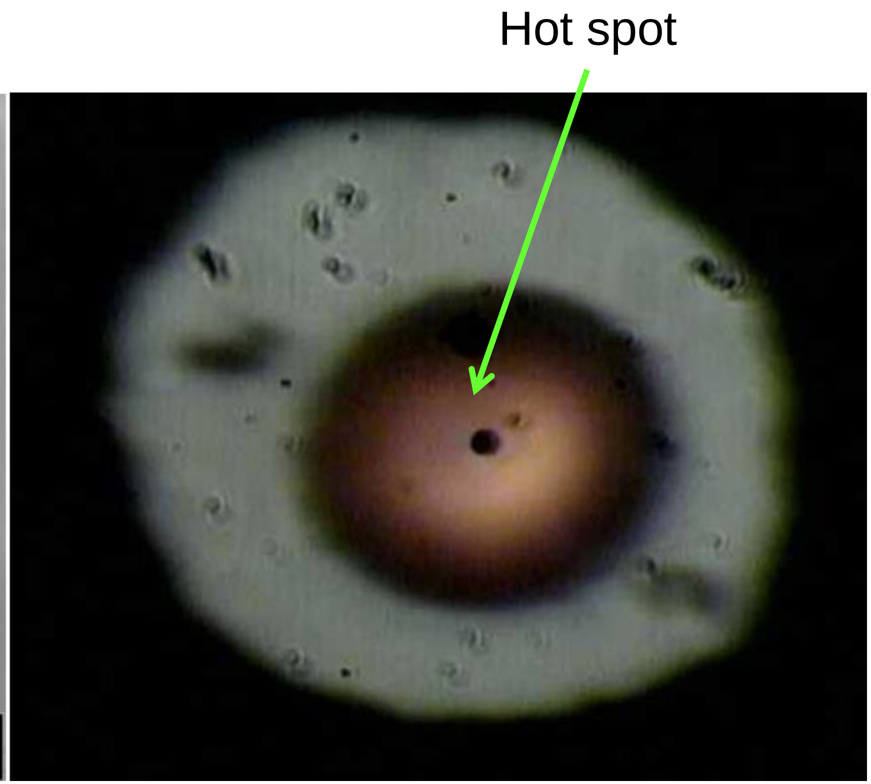


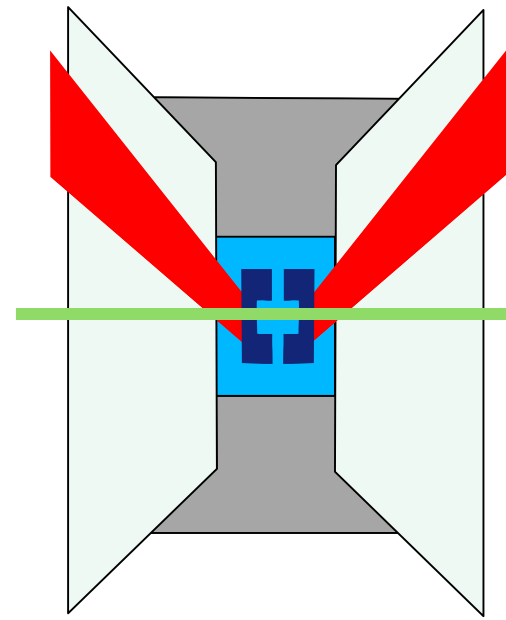
Challenges:

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

Confinement of N_2 in boron doped diamond micro-heaters (YAG absorber) machined using femto-laser and fast ion beam techniques





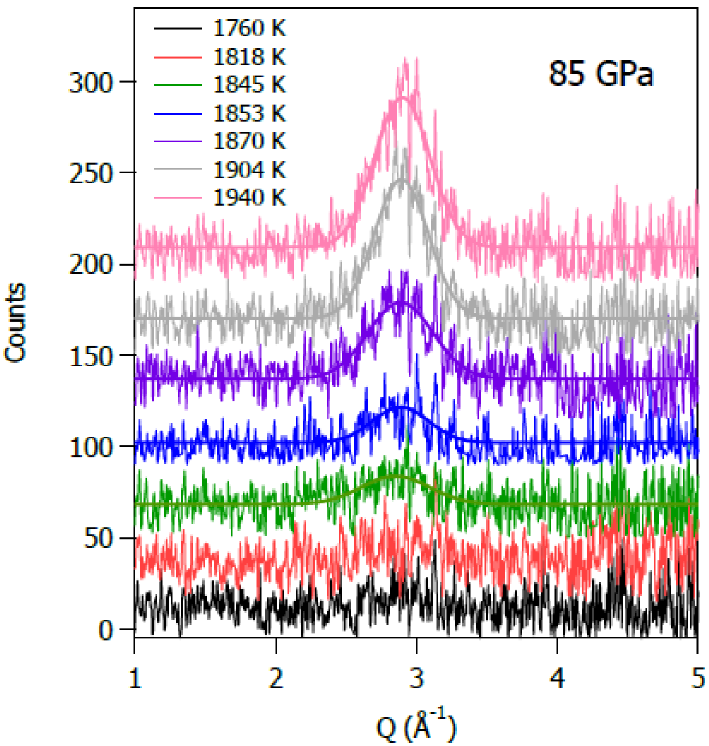


Homogeneous and stable heating conditions in the megabar regime

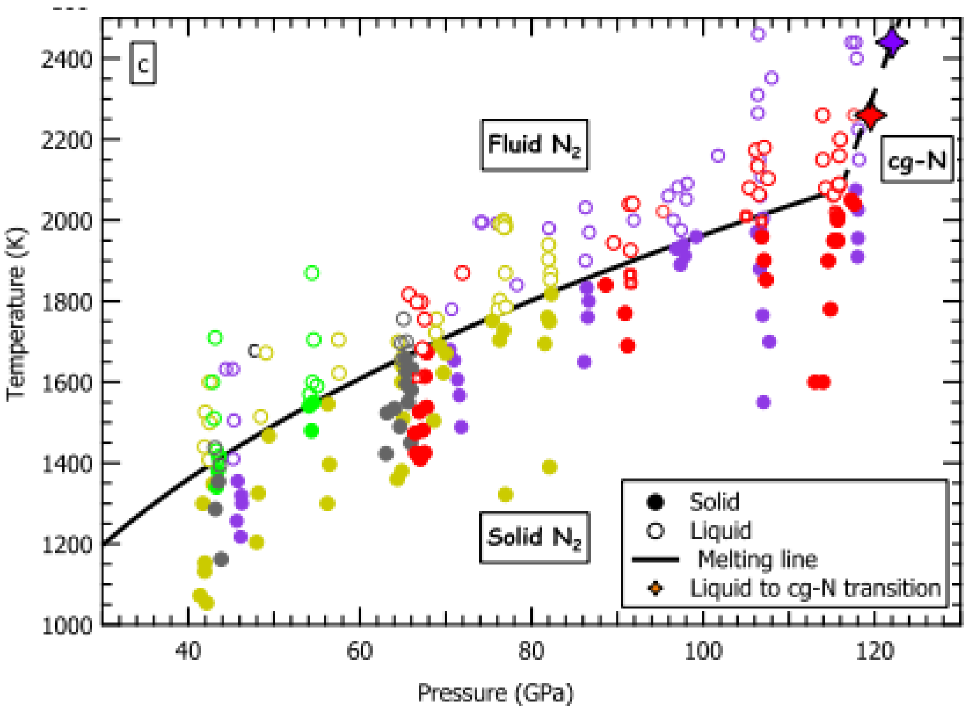
Weck et al, PRL 119 p 235701 (2017)

MELTING CRITERIA

Melting criteria: appearance of X-ray diffuse scattering of N_2

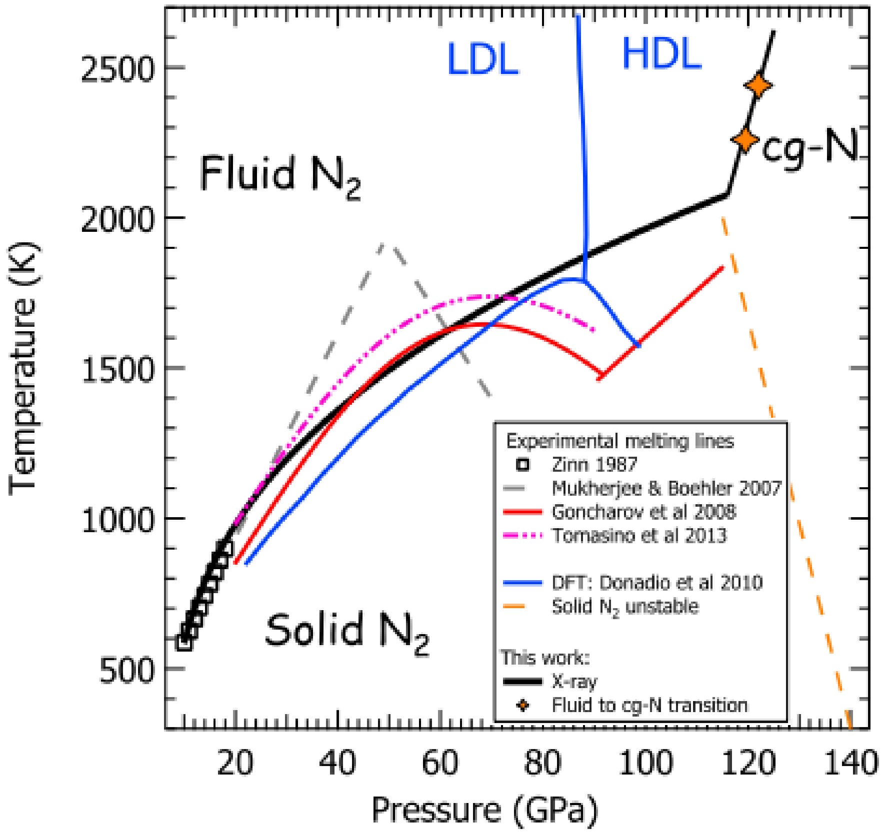


Melting curve of N_2



Weck et al, PRL <u>119</u> p 235701 (2017)

MELTING LINE

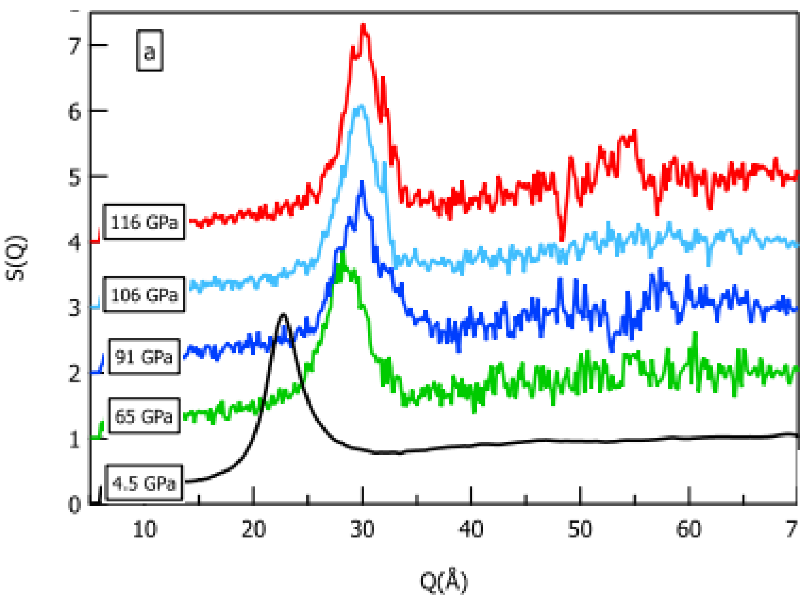


In contrast with literature data: we do not observe a maximum in t he melting curve which would correspond to a LDL to HDL transition up to 120 GPa

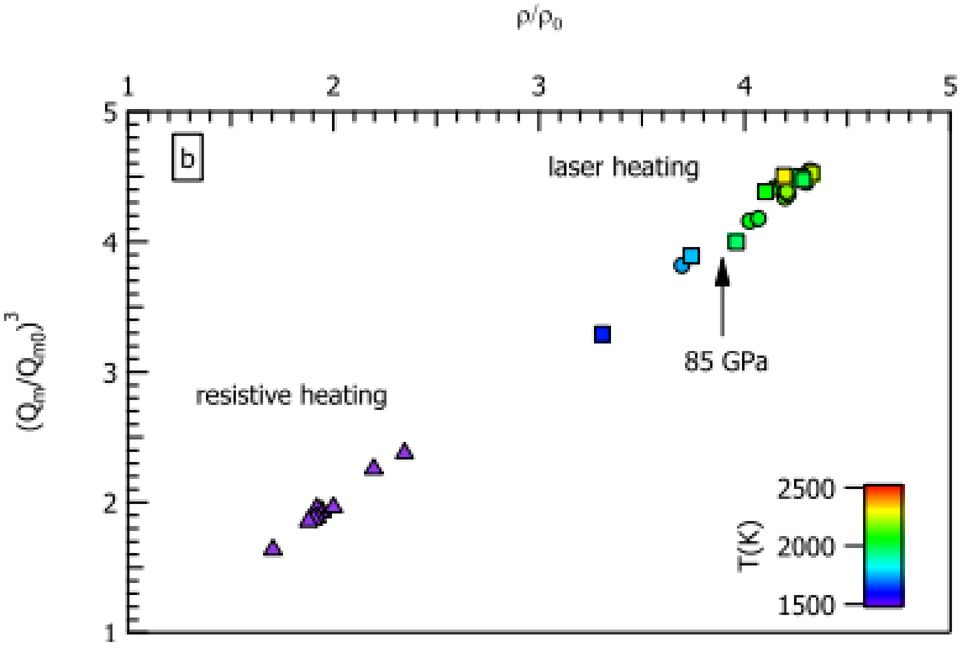
At P>120 GPa , we observed a strong increase of the slope of the melting curve indicative of a first-order phase transition in the solid

Weck et al, PRL 119 p 235701 (2017)

STRUCTURE FACTOR OF N_2



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



Weck et al, PRL 119 p 235701 (2017)

CONCLUSIONS

➔**We have implemented and tested a multichannel collimator for angle-dispersive x-ray diffraction with the DAC.**

➔**Large reduction of anvil signal which is necessary for quantitative studies of low-Z liquids at P>20 GPa.**

➔**First measurements of the liquid structure factor of CO_2, H_2 and alkali metals at HP using resistive heating or cryostat.**

➔**The analysis procedure from [Eggert et al, PRB 2002] has been updated to account for the transmission of the MCC. Allows to extract S(Q), g(r) and density at the same time.**

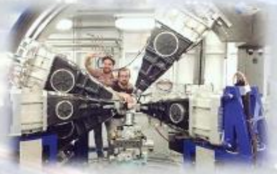
➔**This new set-up will also be useful for glasses, amorphous materials and even crystalline samples at very HP.**

➔ **CO_2 and YAG Laser heating are now feasible**

http://www.esrf.eu/
/high-pressure-school

Hands-on!
High pressure school at the ESRF.
17-21th June 2019

This school aims to give an introduction to high pressure research at synchrotron radiation facilities and to present the unique opportunities in this field with the ESRF-EBS (Extremely Brilliant Source) upgrade. It comprises lectures covering the basic principles of SR techniques used to explore matter at extreme conditions. The new capabilities of the EBS machine and the upgraded beamlines will be also presented in detail. Lectures will be completed with "hands-on" step by step practicals. We would like to promote a lively exchange between experts in the field and our future user community on instrumental developments to exploit the EBS upgrade.



Be ready! for the restart of the ESRF-EBS and next generation synchrotrons!

The EBS, together with beamline upgrades and technical advancements in high pressure instrumentation, will offer new and unique research opportunities for studies at extreme conditions.

1. Increase in brilliance ➡ more flux to study highly diluted and low Z elements
2. Lower horizontal emittance ➡ smaller beamsizes to probe matter at multi Mbar
3. Higher coherence fractions ➡ for better imaging

We will train you! in high P and high/low T techniques including the diamond anvil cell (resistively heated, laser-heated and cryogenic cooled), the autoclave, the Paris-Edinburgh press and the Large-volume-press. Lectures will be held in the morning. In the afternoon, small groups of 5 people will be trained in one technique step by step throughout the week.

Pre-registration will be opened early 2019 at the ESRF website.

Maximum 30 participants for practicals, 70 for lectures.
All participants are invited to present a POSTER.

Costs: estimated 250 € (accommodation and meals included)

Confirmed invited speakers / lectures:

Denis Andrault
Daniel Braithwaite
Leonid Dubrovinsky
Jochen Geck
Yann Le Godec
Federico Aiace Gorelli
Nicolas Guignot

Koen De Hantsetters
Nadege Hilairet
Tetsuo Irifune
Stefan Klotz
Yoshio Kono
Paul Loubeyre
Marion Louvel
Guillaume Morard

Gleb Pokrovski
Jean-Phillipe Perrillat
Chrystele Sanloup
Ilya Sergeev
Thomas Sheppard
Laurent Truche
Max Wilke

Main-Organizers: A. D. Rosa, G. Garbarino, J. Jacobs, Eva Jahn, Sonya Girodon
Co-organizers : V. Svitlyk, D. Sifre, R. Torchio, L. Henry, N. Sevelin, J-L. Hazemann
In-house Speakers: S. Pascarelli, F. Wilhelm, A. Chumakov, C. Sahle, M. Hanfland, L. Paolasini, W. Chrichton, D. Testemale, , M. Mezouar