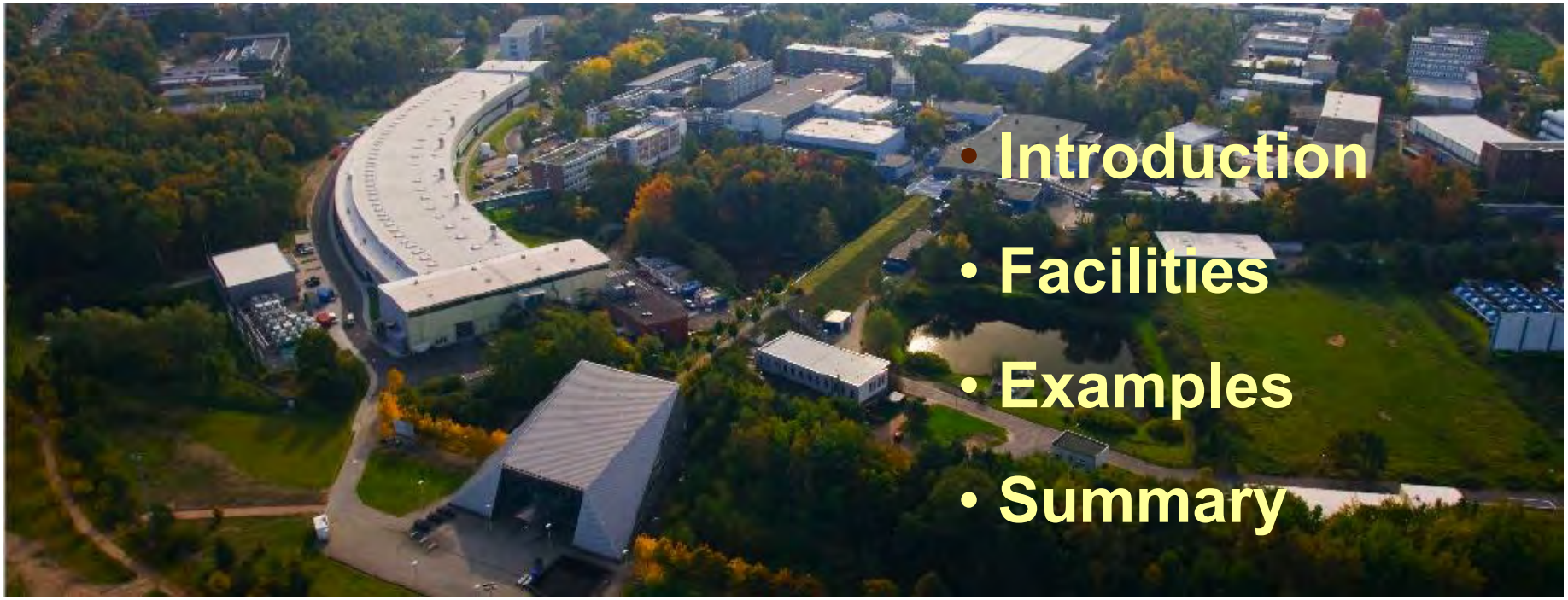
3rd generation synchrotron radiation investigations of advanced materials

Bulk metallic glasses



- Introduction
- Facilities
- Examples
- Summary

Hermann Franz

BNL Users Meeting 2014
May 18 - 21 2014

HELMHOLTZ | GEMEINSCHAFT

DESY

J. Bednarcik
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H.P. Liermann
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H. Lou
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Helmholtz Zhejiang University - DESY cooperation fund

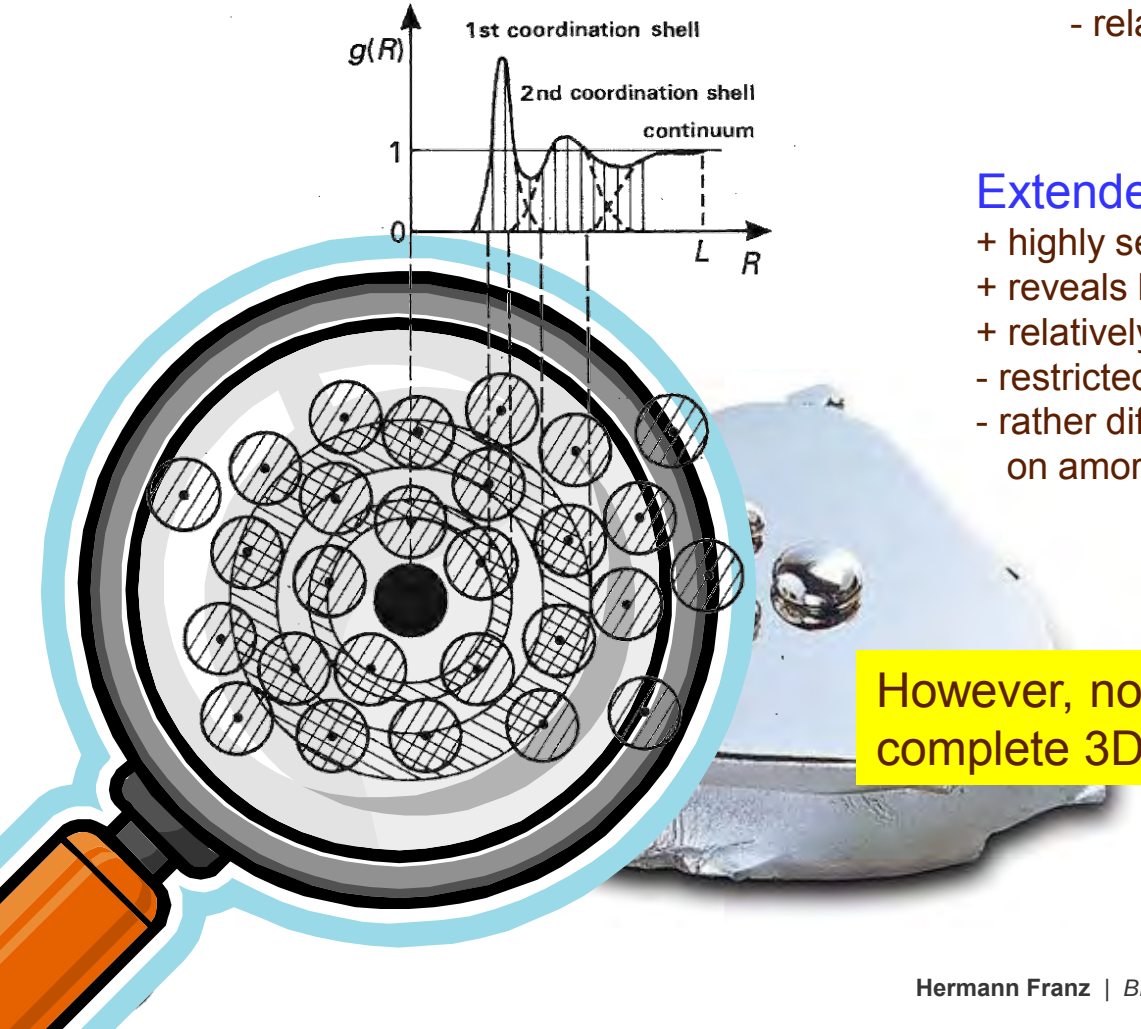
Structure determination of amorphous materials

X-ray diffraction using high energy photons

+ high penetration depths (mm-cm)
+ relatively fast, suitable for in-situ studies
- less sensitive to elements
- ASF depend on Q

Neutron diffraction

+ sensitive to different isotopes
+ ASF do not depend on Q
+ probes magnetic state of matter
- large sample volumes
- relatively slow, not suitable for in-situ studies



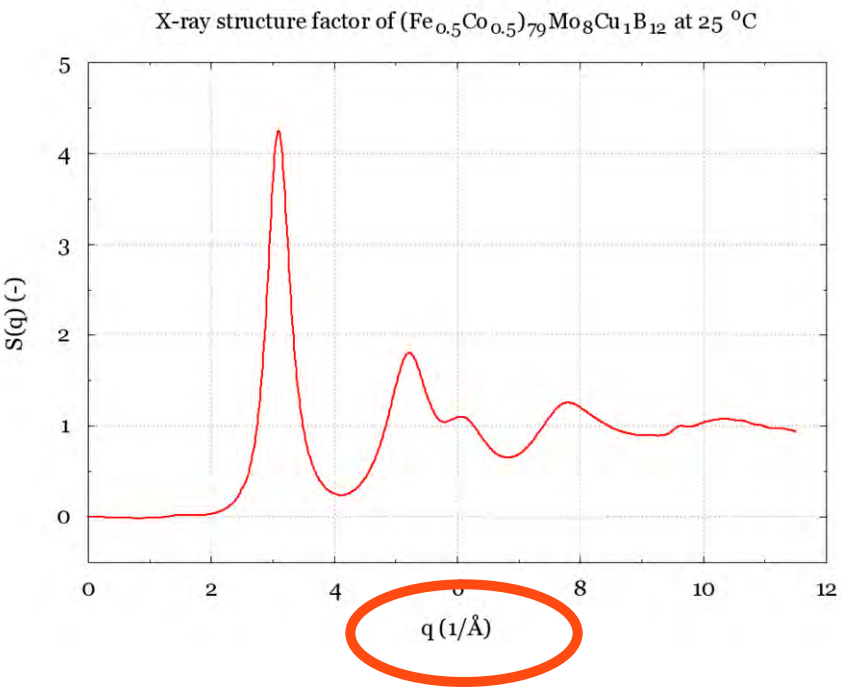
Extended X-ray Absorption Spectroscopy

+ highly sensitive to elements
+ reveals local atomic configuration
+ relatively fast, suitable for in-situ studies
- restricted sample size, geometry
- rather difficult to quantitatively analyze data on amorphous samples

However, none of these techniques gives a complete 3D image of amorphous structure ☹

Structure factor

- Measured intensities corrected for absorption, polarization, fluorescence, multiple scattering, Compton scattering
- Proper normalization based on weighted atomic scattering factors (Faber-Zimman formalism)



$$S(q) = 1 + \frac{I^{coh}(q) - \langle f^2 \rangle}{\langle f \rangle^2} \quad (1)$$

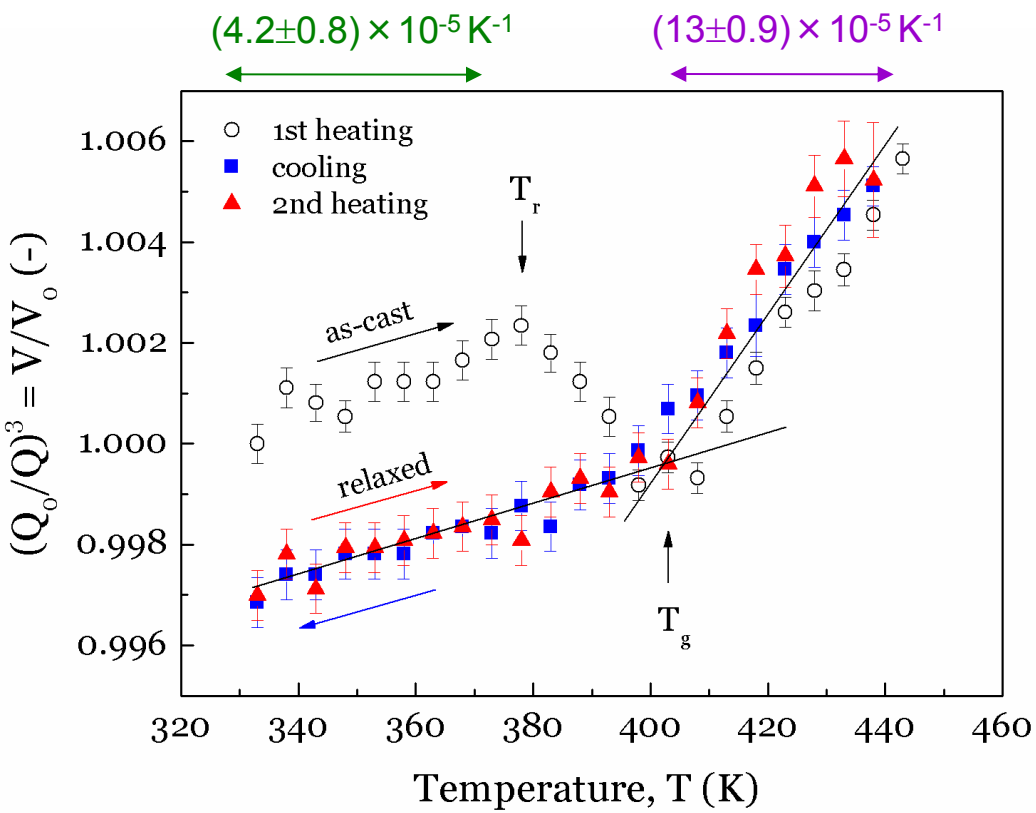
where $\langle f \rangle = \sum_{i=1}^{n} c_i f_i(q)$ and $\langle f^2 \rangle = \sum_{i=1}^{n} c_i f_i^2(q)$, in which c_i corresponds to the atomic fraction of the component i having X-ray atomic scattering factor $f_i(q)$. The reduced pair distribution function, $G(r)$, can be obtained through a sine Fourier transformation

$$G(r) = \frac{2}{\pi} \int_0^\infty q[S(q) - 1] \sin(qr)\, dq. \quad (2)$$

Thermal expansion from in-situ X-ray diffraction.

$La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Ni_5Co_5$ BMG

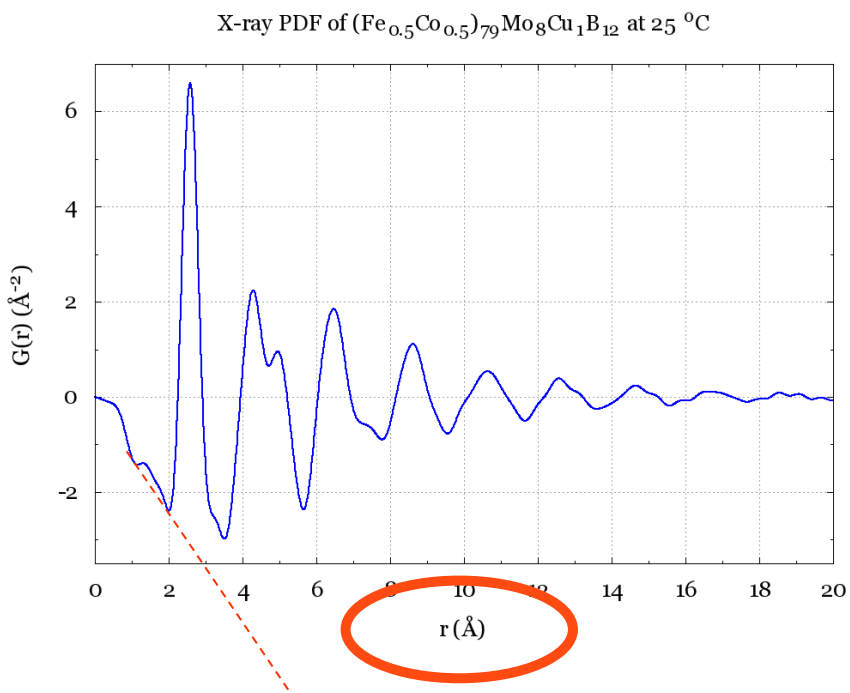
A.R. Yavari et al., Acta Materialia 53 (2005) 1611–1619



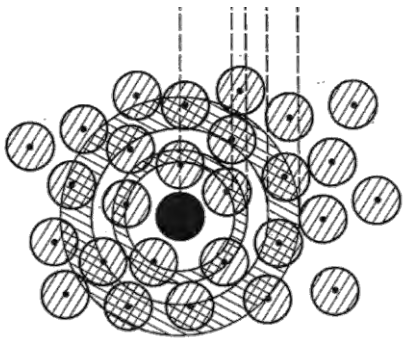
- Thermal cycling below crystallization temperature T_x reveals **hysteresis**
- Volume thermal expansion coefficient changes its value dramatically around **glass transition** T_g
- Thermal **expansion coefficient** for as-cast and thermally relaxed glass are similar

Pair Distribution Function

$$G(r) = 4\pi r\left[\rho(r) - \rho_0\right] = \frac{2}{\pi}\int_0^\infty q(S(q)-1)\sin(qr)dq$$



$$\rho_0 = -\frac{G(r)}{4\pi r}$$

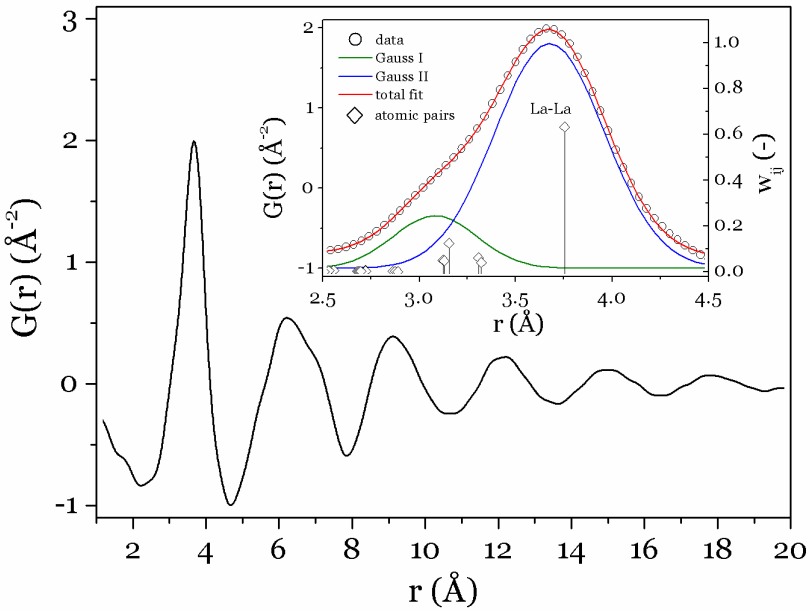


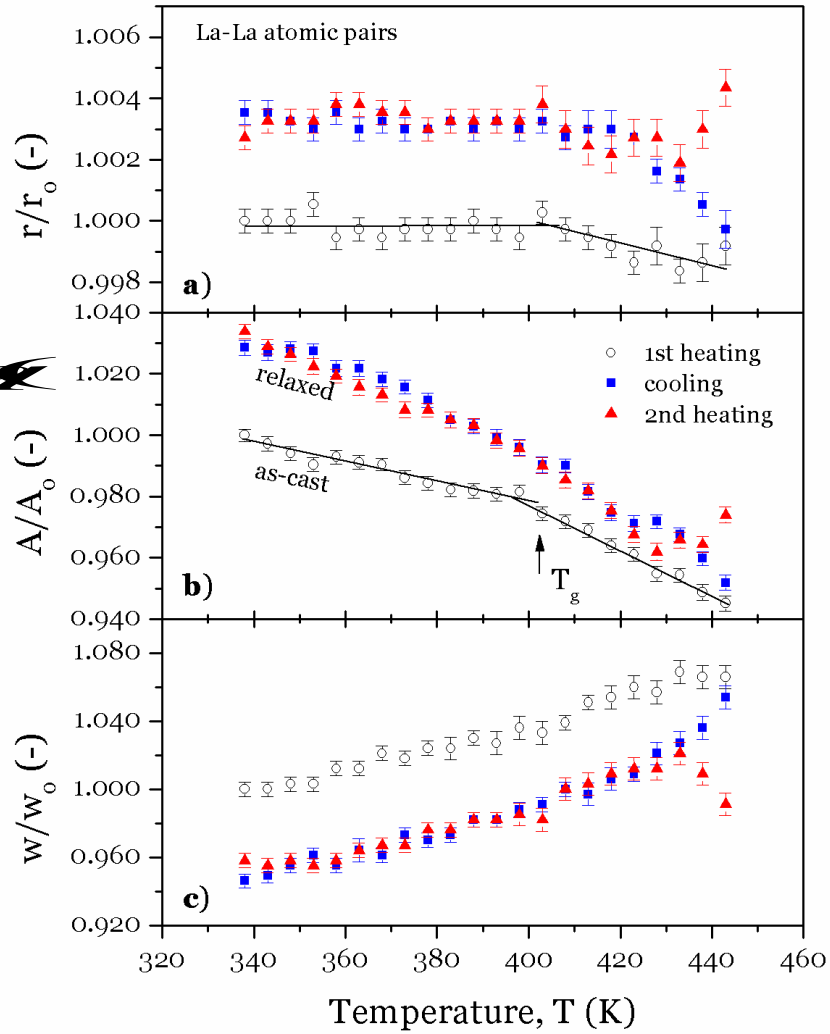
Real space analysis.

In $La_{62}Al_{14}(Cu_{5/6}Ag_{1/6})_{14}Ni_5Co_5$ BMG there are 21 partials !

La-La pairs are contributing with 64 %

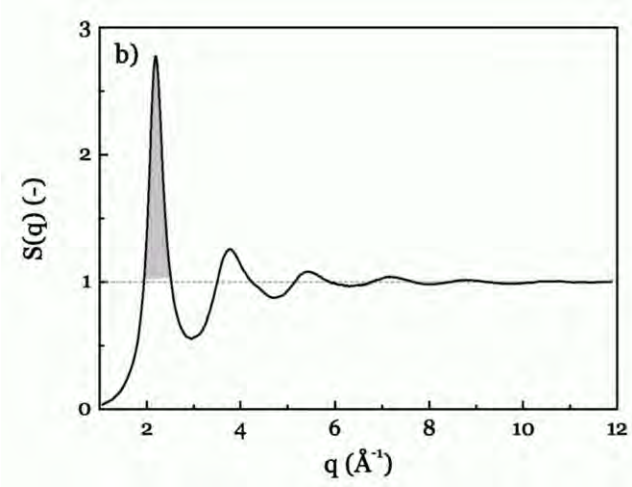
La-M pairs (M = Al,Cu,Ag,Ni,Co) -> 32 %





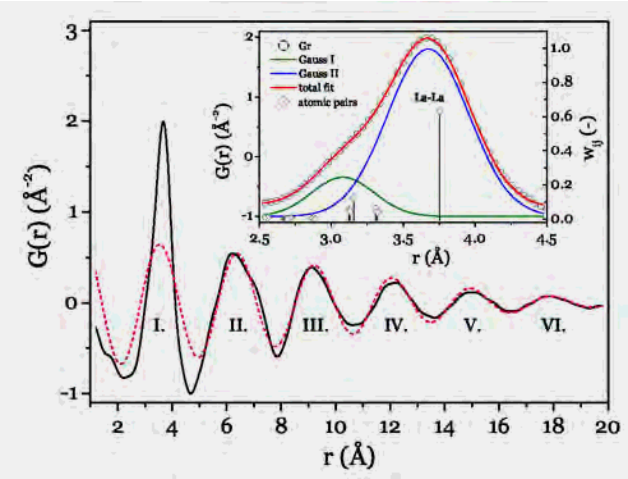
J. Bednarcik et al., J. Phys. Cond. Matt. (2011)

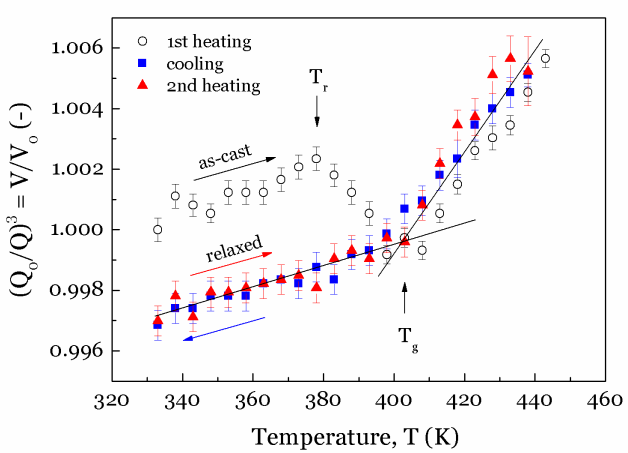
Reciprocal versus real space

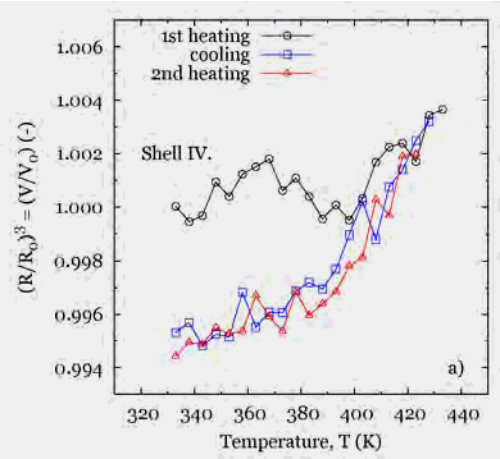


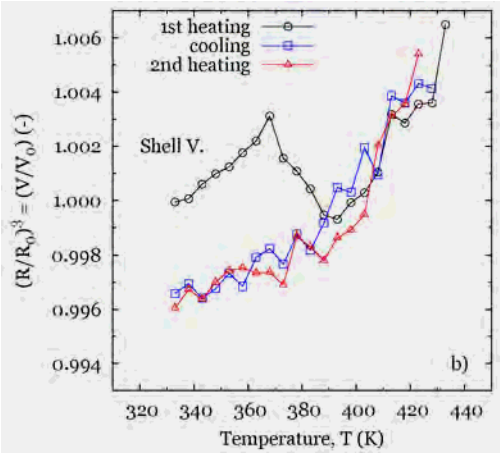
Thermal expansion based on reciprocal space analysis is more sensitive to long range inter atomic correlations.

On the other hand, real space analysis reveals correlations in the nearest atomic neighborhood.









J. Bednarcik et al., J. Phys. Cond. Matt. (2011)

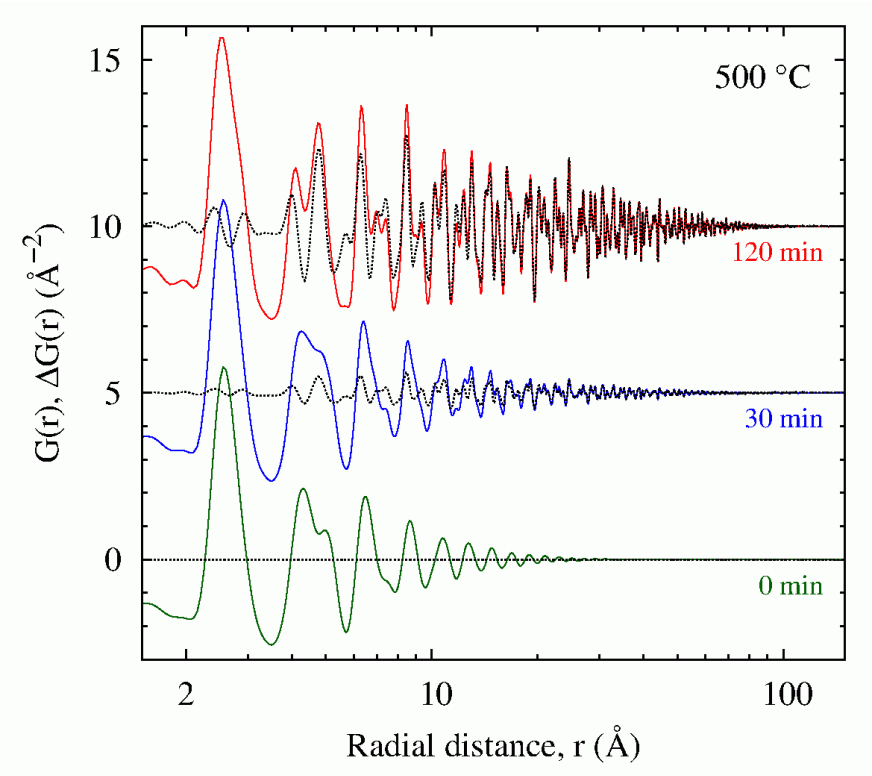
Kinetics of crystallization – real space

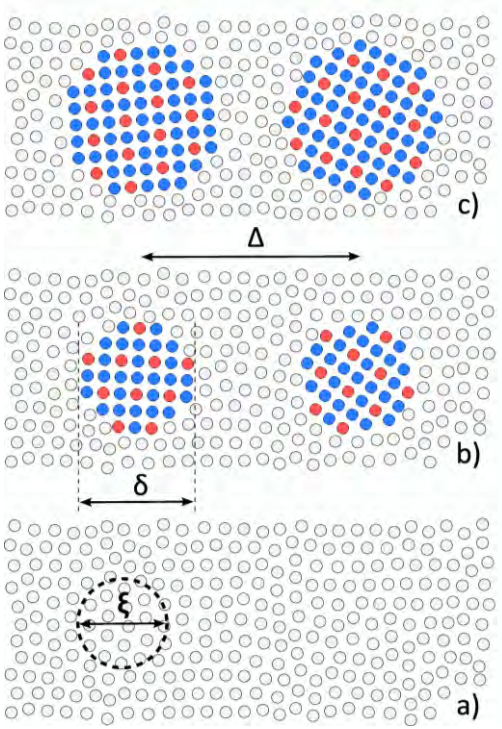
Maximum distance of still visible oscillations	<->	Average grain size
Crystalline fraction	<->	RMS of difference PDF

$$\Delta G(r)_t = G(r)_t - G(r)_{t=0}$$

where $G(r)_t$ and $G(r)_{t=0}$ are corresponding to the PDF at a given time t and reference time t = 0, respectively.

Degree of crystallization is revealed as an enhancement of long-range order correlations visible on PDF.

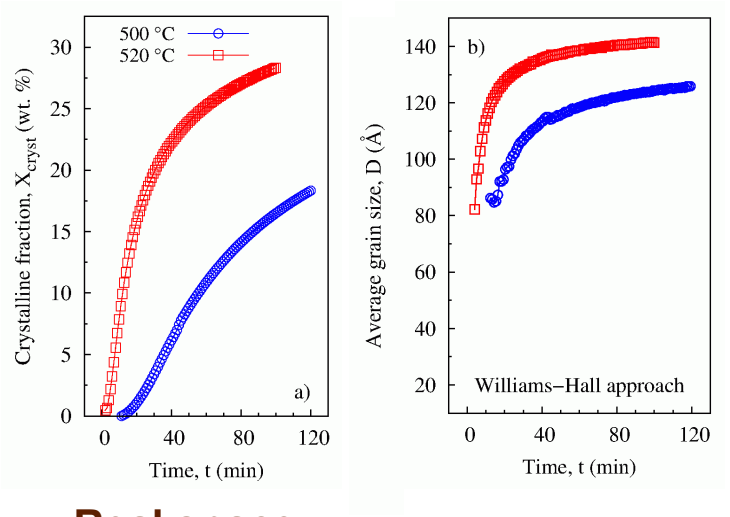




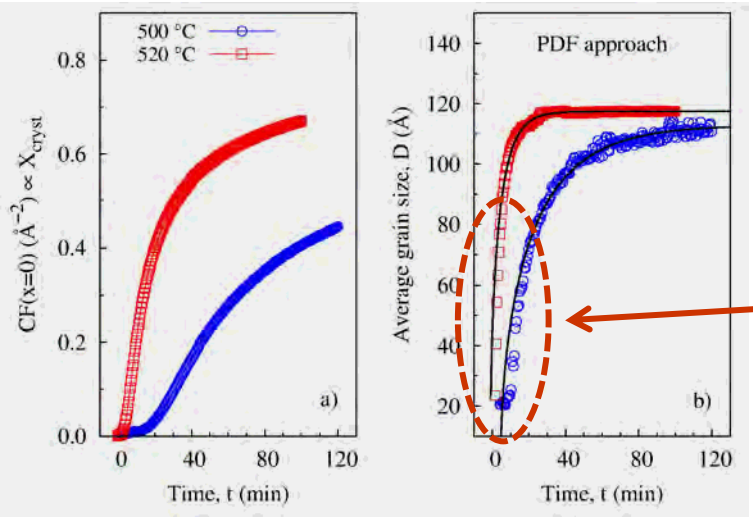
J. Bednarcik et al., PCCP (2014)

Conclusions

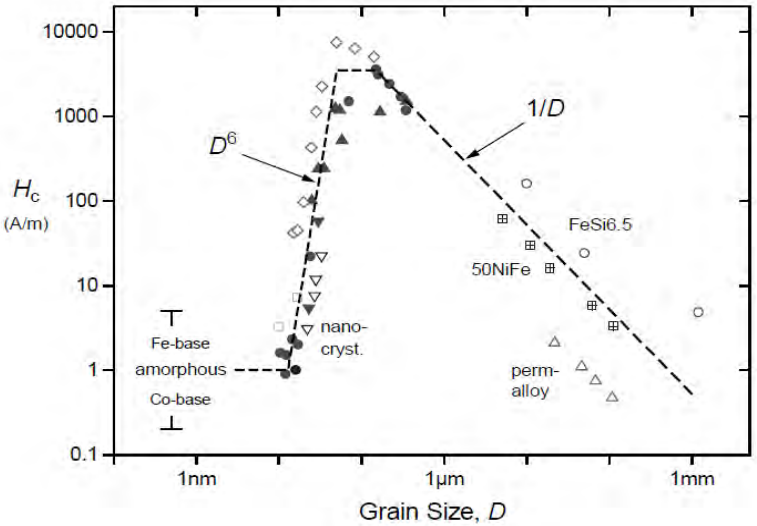
Reciprocal space



Real space



Coercivity H_c versus grain size D



G. Herzer, Proceedings of the NATO Advanced Study Insititute on Magnetic Hysteresis in Novel Materials, Mykonos, Greece, 1-12 July 1996

When comparing with the Williams-Hall method in reciprocal space, the **PDF method** offers much more resolving power to determine size of **ultra-fine particles** which are having grain sizes **well below 8 nm**.

Reverse Monte Carlo modeling

Diffraction:

The partial $g_{ij}(r)$ functions are calculated from the atomic coordinates and transformed to reciprocal space:

$$S_{ij}(Q) = \frac{4\pi\rho c_j}{Q}\int r \sin Qr (g_{ij}(r) - 1) dr$$

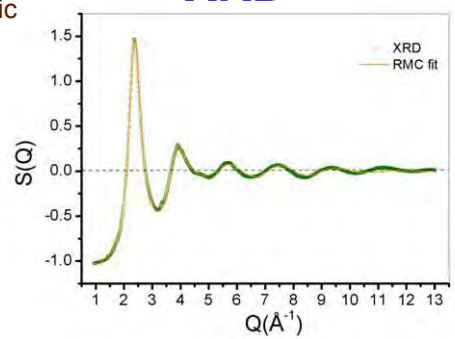
together with a weights (for ND $f(Q)=b$)

$$w_{ij} = \frac{(2-\delta_{ij}) c_i c_j f_i(Q) f_j(Q)}{\sum_{ij} c_i c_j f_i(Q) f_j(Q)}$$

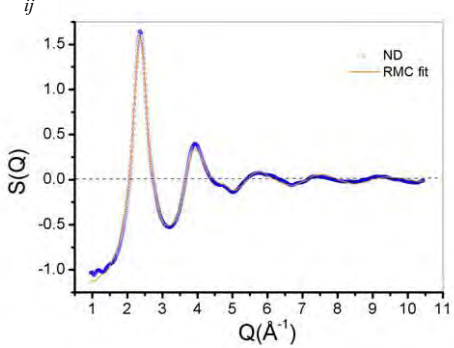
are combined in total structure factor

$$S^{RMC}(Q) = \sum_{ij} w_{ij}(Q) S_{ij}(Q)$$

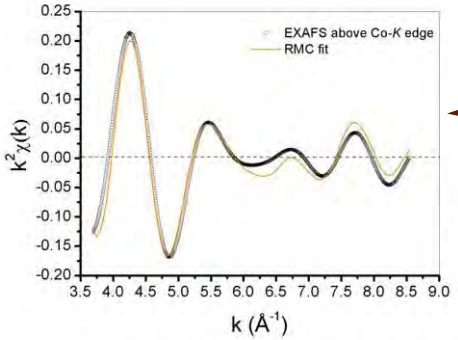
XRD



ND



EXAFS

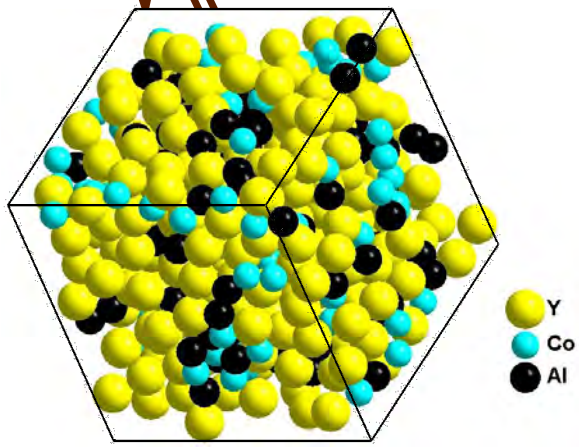


Move:

One particle is moved randomly taking into account applied constraints.

Settling:

Everything is repeated until ψ^2 begins to oscillate around a constant value.



EXAFS:

The model of EXAFS signal $\chi_i(k)$, at the absorption edge of i-type atoms can be calculated from the g_{ij}:

$$\chi_i(k) = \sum_j 4\pi c_j \rho \int_0^\infty r^2 \gamma_{ij}(r,k) g_{ij}(r) dr$$

while γ_{ij} is the atomic pair backscattering signal

$$\gamma_{ij}(r,k) = A_{ij}(k,r)\sin(2kr + \Phi_{ij}(kr))$$

Courtesy of Dr. K. Saksl

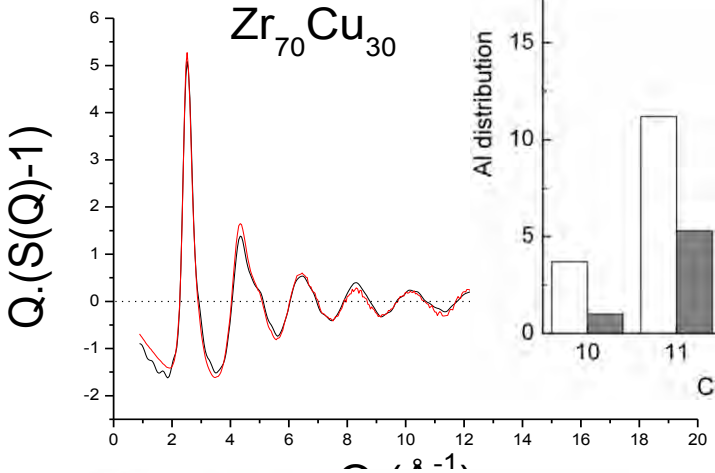
Acceptance of the move:

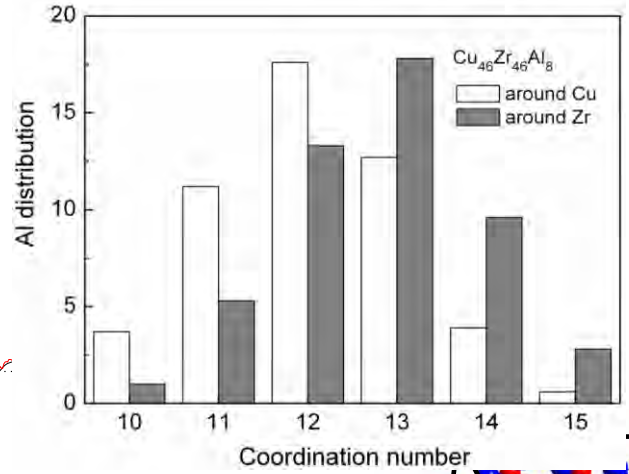
First the experiment-model difference is calculated

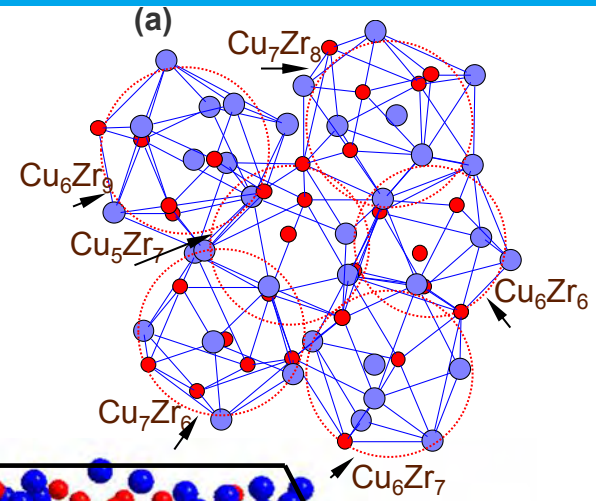
$$\psi^2 = \frac{1}{\delta}\sum_{i=1}^{m}\left[\zeta^{\exp} - \zeta^{RMC}\right]^2$$

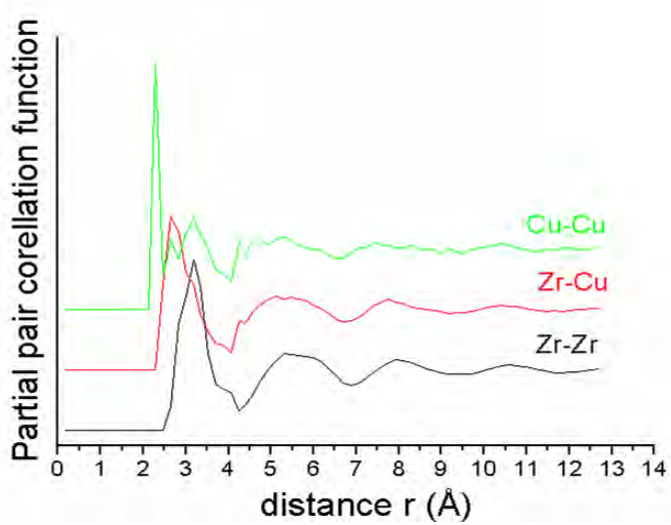
If $\psi^2_{n+1} < \psi^2_n$ the move is always accepted.
If $\psi^2_{n+1} > \psi^2_n$ the move is accepted with the probability $\exp[-(\psi^2_{n+1} - \psi^2_n)/2]$

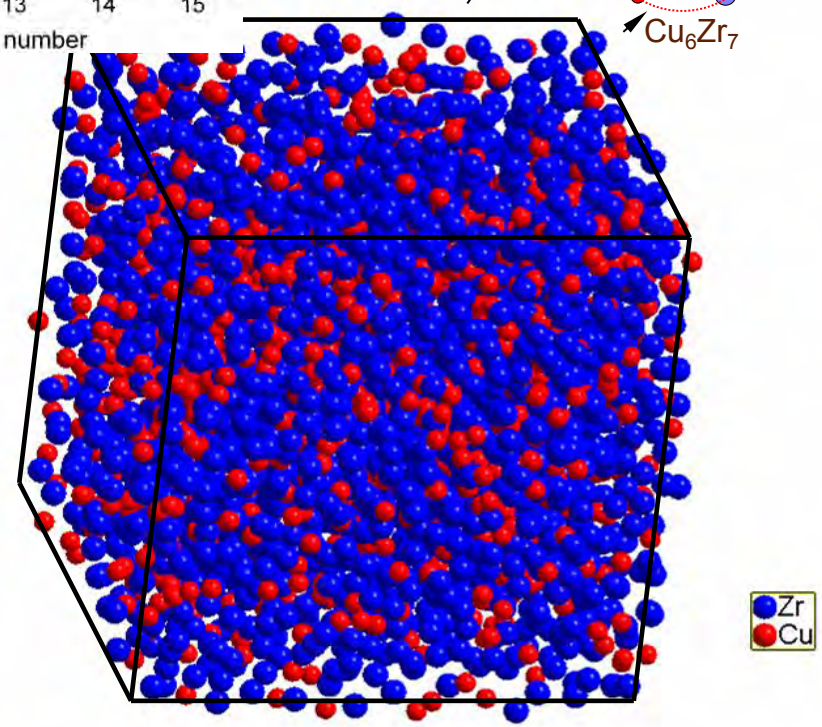
Reverse Monte Carlo results











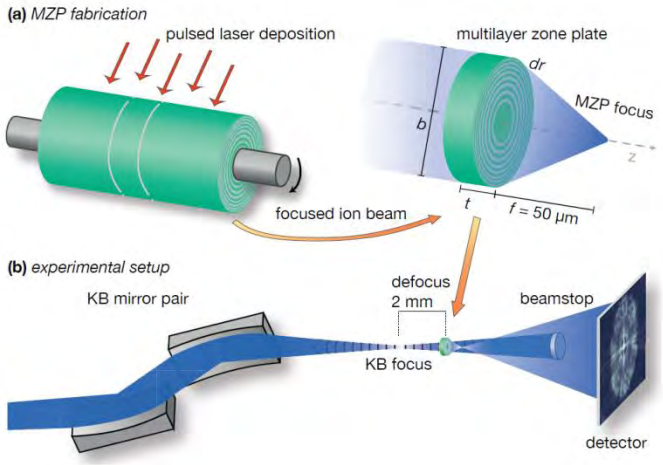
X.D. Wang et al. JAP (2008)

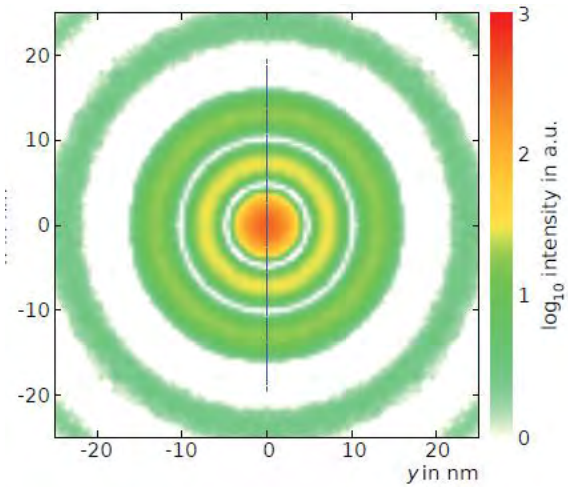
PETRA III: DESYs brilliant X-ray source

- particle energy:	6 GeV
- stored current:	100 mA (top-up)
- emittance:	1.0 nmrad
- circumferrence:	2304 m
- # of undulators:	14 (incl. canted)
- # of experiments:	30
- X-ray wavelength:	10 – 0.05 Å
- beamline length:	70-100 m
- annual operation:	5000 h

- built in 1978
- rebuilt as a synchrotron radiation source in 2007
- commissioning since 2009
- user operation since 2010
- largest storage ring of its kind

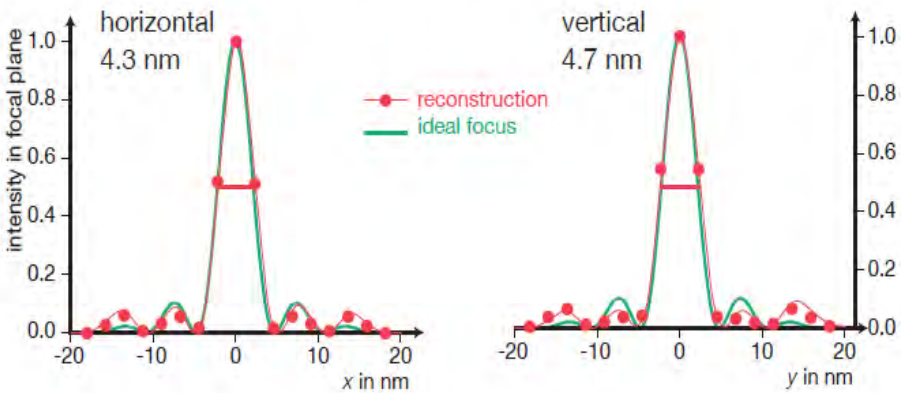
Sub-5 nm focus on beamline P10





- **Spherical MZP from Göttingen University**
- **Outermost zone width 5 nm**
- **W/Si structure grown on 0.9 µm W-wire**
- **"FIBed" to 0.7 µm thickness**
- **Intensity distribution in focal plane reconstructed from far-field detection**

reconstructed intensity profile in focal plane



F. Döring et al, Opt.Exp. (2013)

PETRA III Extension

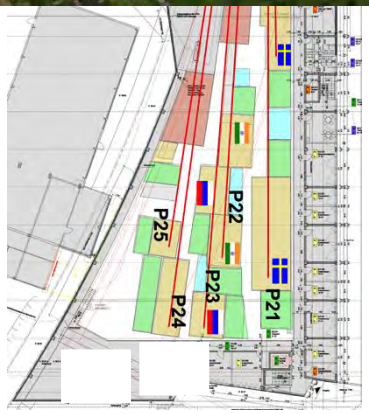
North

- damping wiggler straigh
- 4 straight sections (2m)

East

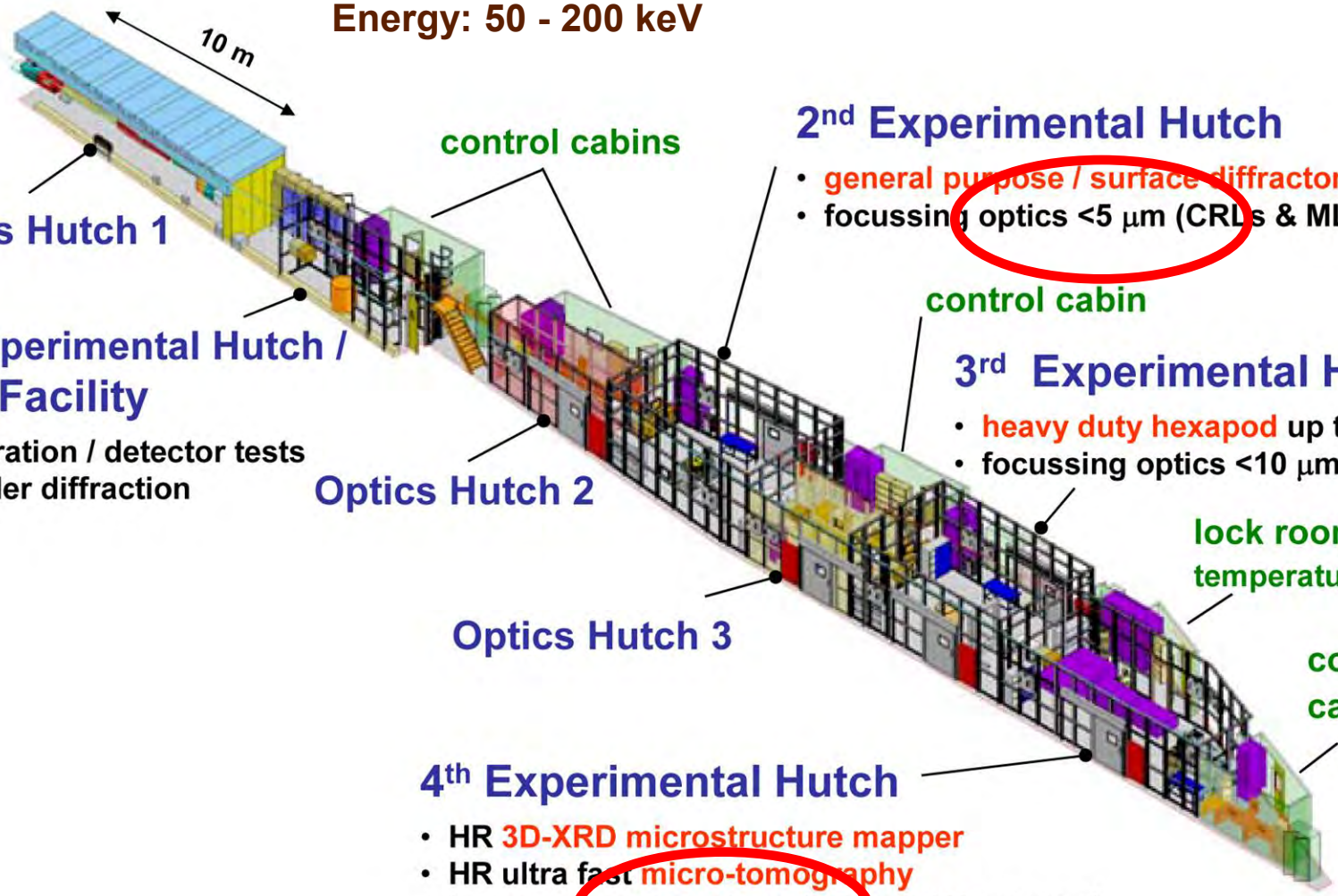
- Long straight section fo
- 4 straight sections (2m)

- **Design is in finalized**
-
-
-



P07 High Energy Materials Science beamline

Energy: 50 - 200 keV



Optics Hutch 1

1st Experimental Hutch / Test Facility

- calibration / detector tests
- powder diffraction

Optics Hutch 2

control cabins

2nd Experimental Hutch

- general purpose / surface diffractometer
- focussing optics <5 μm (CRLs & MLs)

control cabin

3rd Experimental Hutch

- heavy duty hexapod up to 1 t
- focussing optics <10 μm (CRLs)

lock room temperature

Optics Hutch 3

control cabin

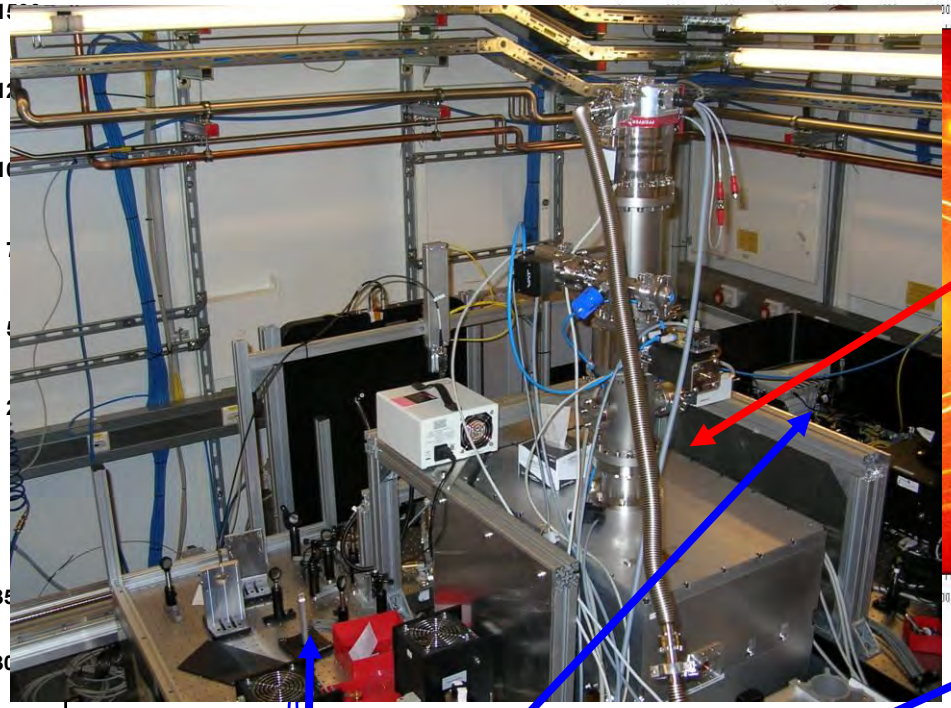
4th Experimental Hutch

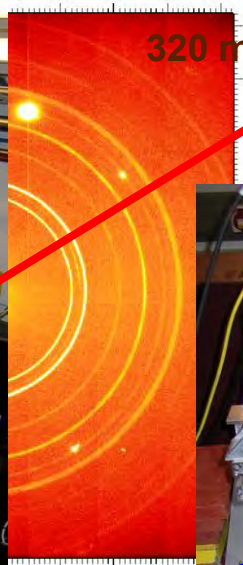
- HR 3D-XRD microstructure mapper
- HR ultra fast micro-tomography
- focussing optics <1 μm (CRLs & KB mirrors)

05

P02: Extreme conditions and powder diffraction

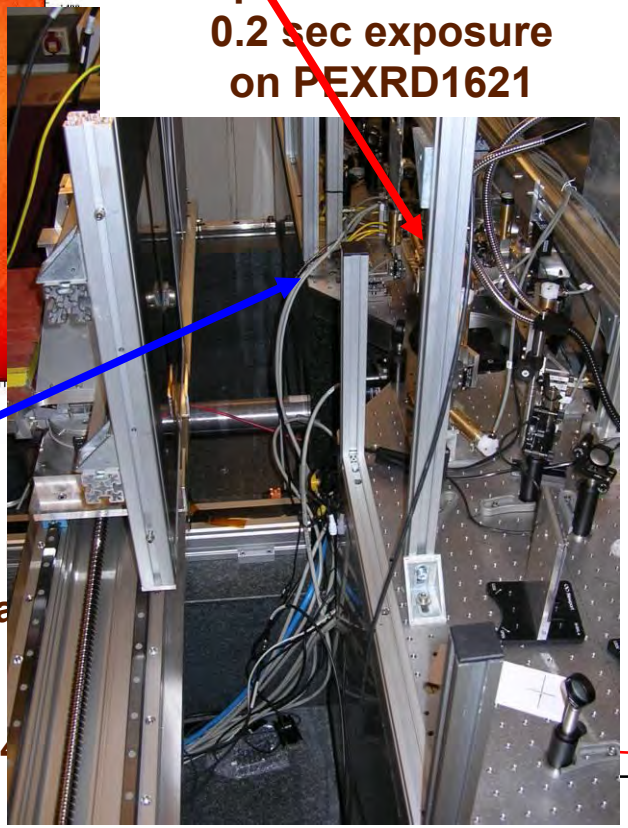
High pressure in diamond anvil cells with laser heating (H.P. Liermann)

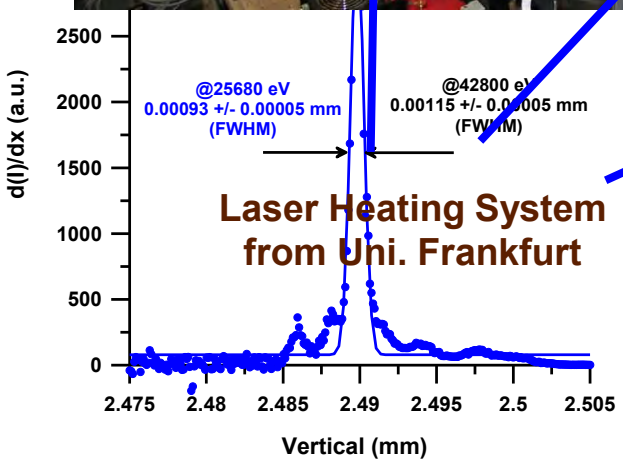




320 mm KB System from IDT

Fe-hcp at ~60 GPa in DAC
0.2 sec exposure
on PEXRD1621





Laser Heating System
from Uni. Frankfurt

Beam Energy = 25.7 keV (42.8

Grazing Incident Angle = 2 mra
(1.5 mrad)

Mirror Optical Length 280 mm

Entrance Aperture = 560 μm^2 (4
μm^2)

Net reflectivity 80%

3 x 10^{11} ph/sec (1 x 10^{11} ph/sec) in
the focal spot

2theta (degrees)

10

Equipment for materials investigations

IR-Lamp furnace 900° C

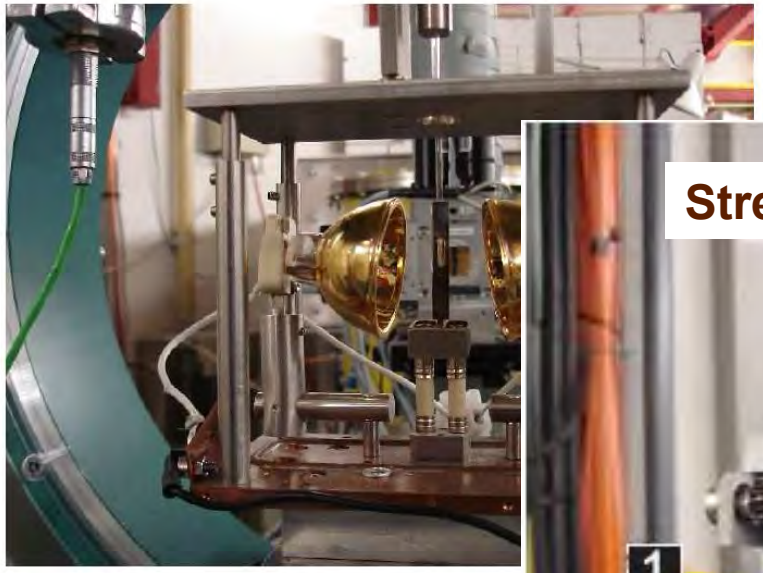
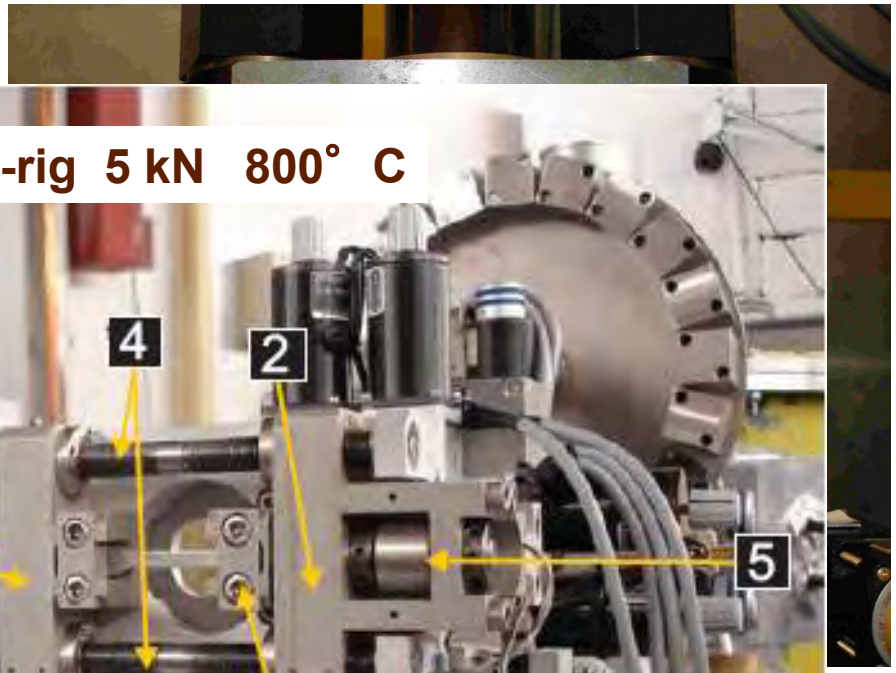
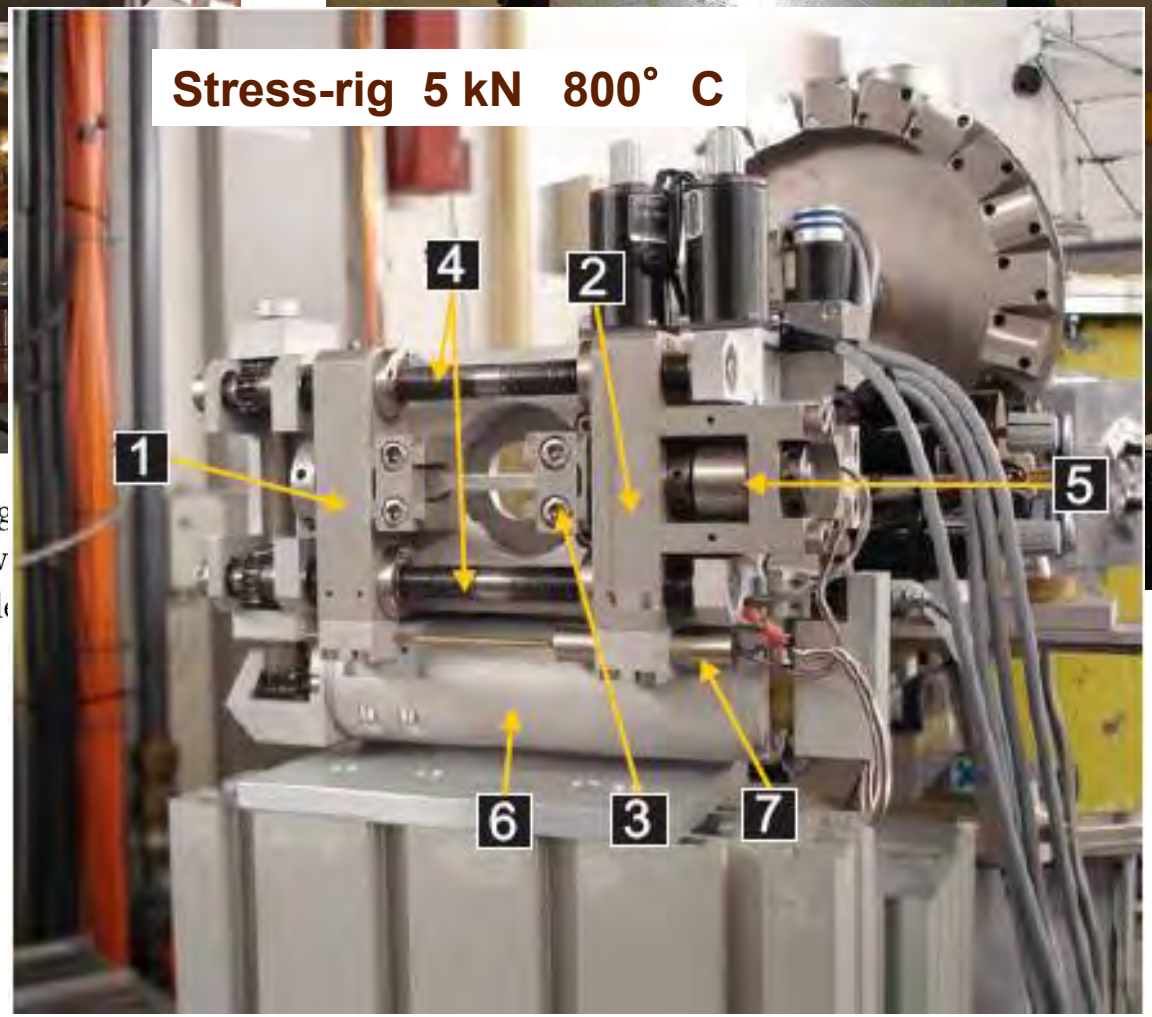


Figure 1: Detailed view showing
furnace. Black tube sitting betw
supports capillary with the sampl
a heat condenser.

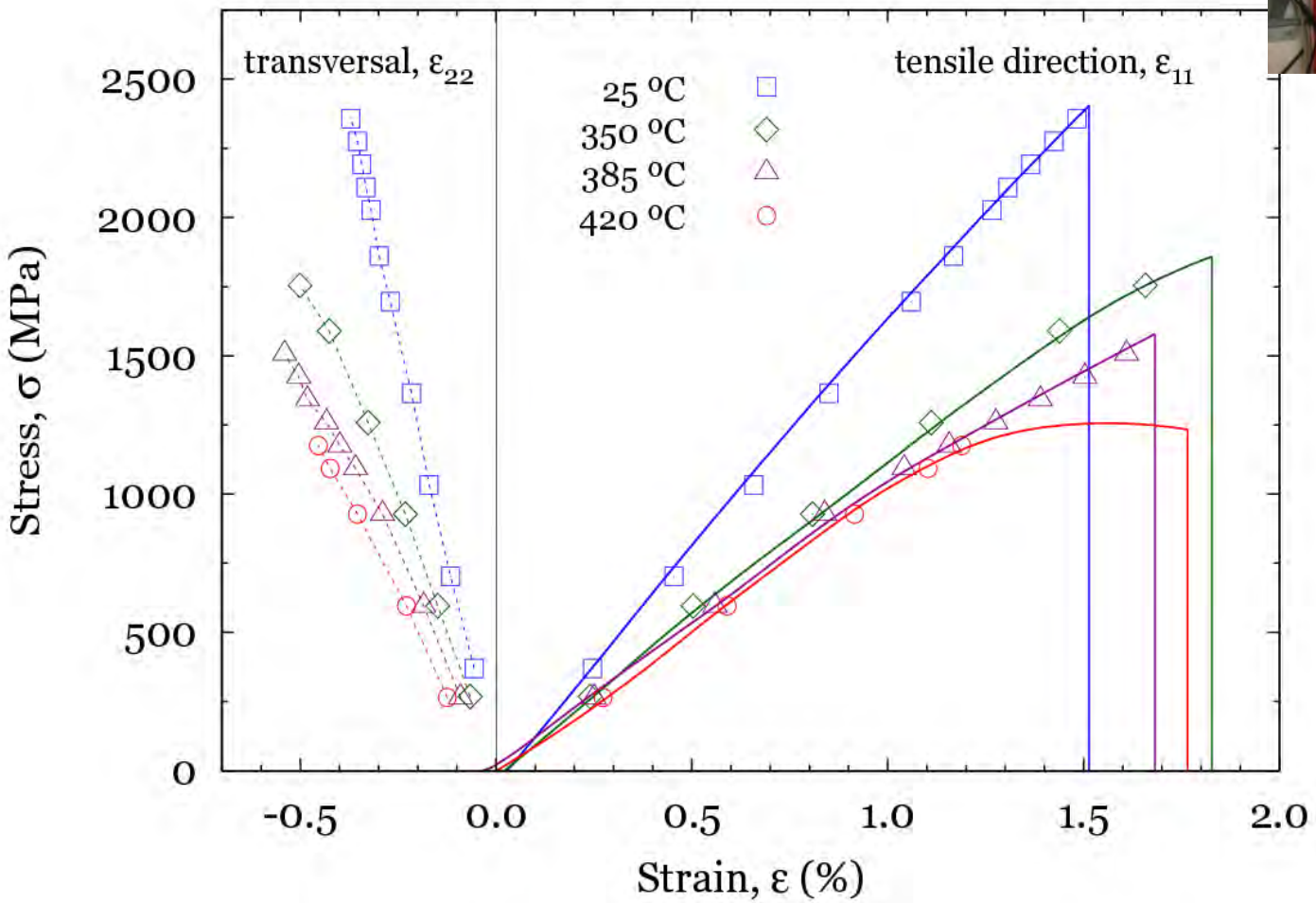
Paris-Edinburgh-Cell 7GPa 800° C



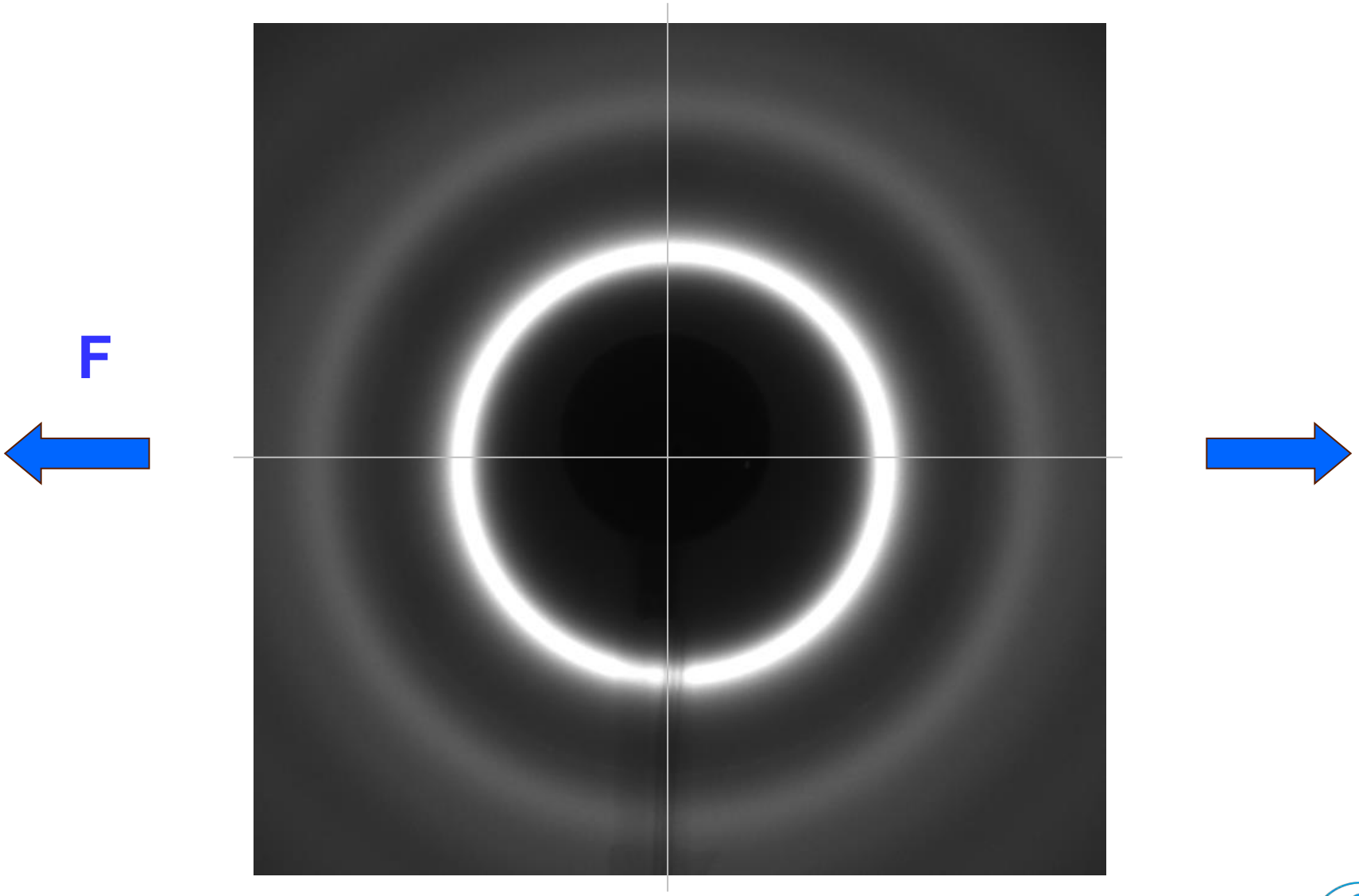
Stress-rig 5 kN 800° C



Metallic glass plastic deformation under tension

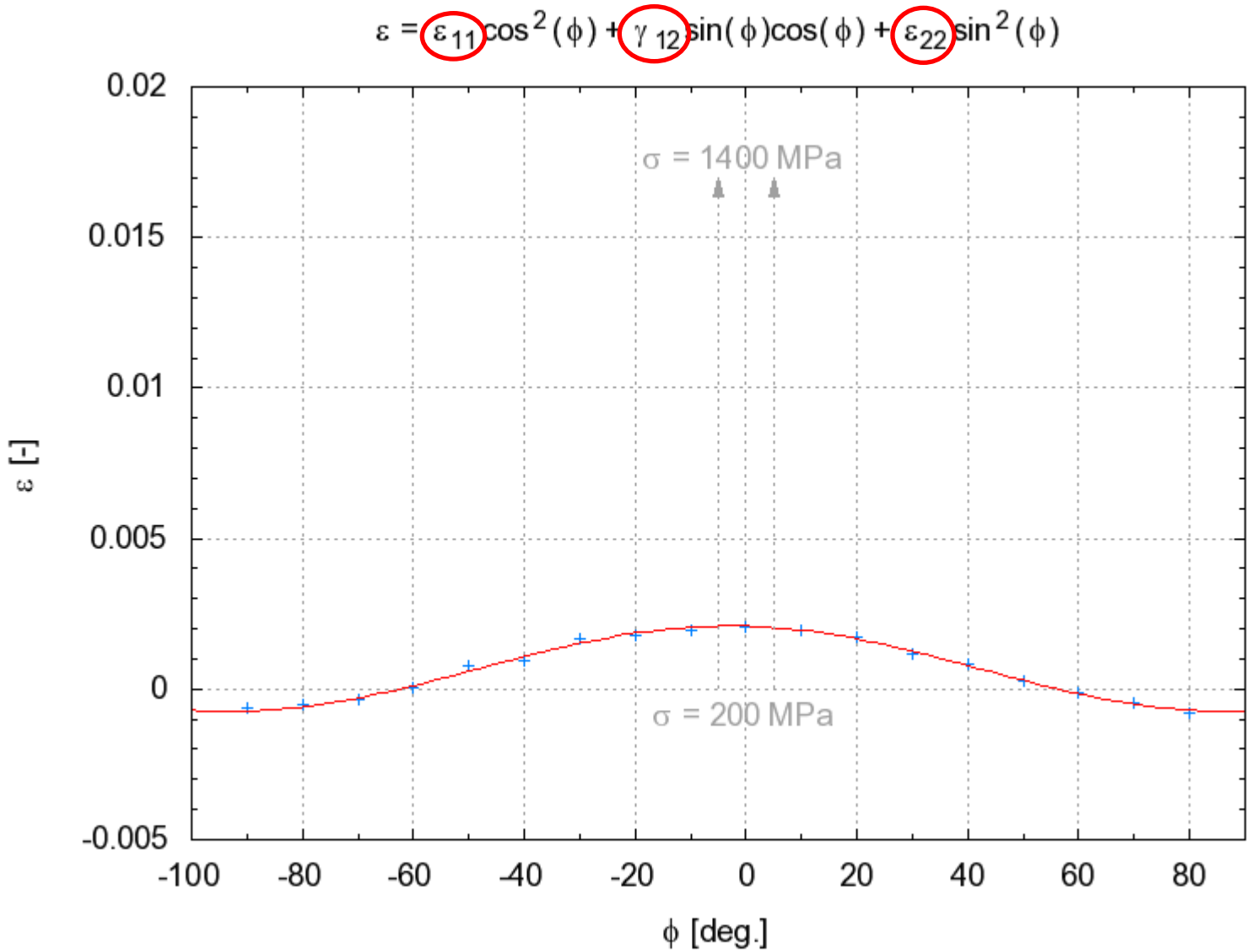


In-situ tensile experiments



Courtesy J. Bednarcik

Determination of tensor components



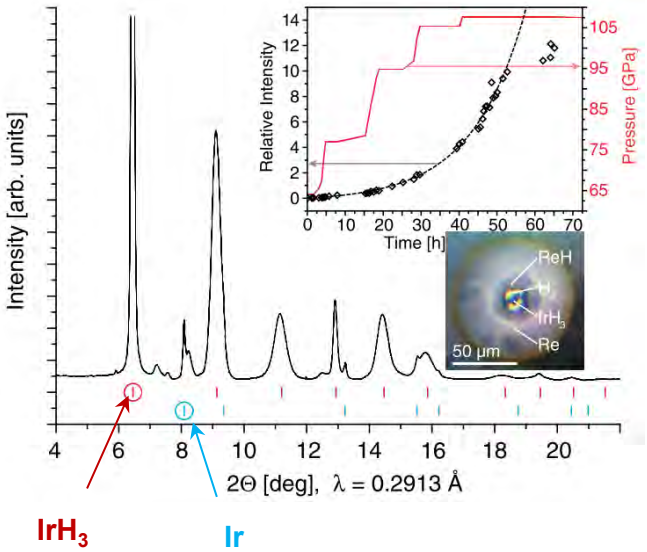
High-pressure as a route to material synthesis

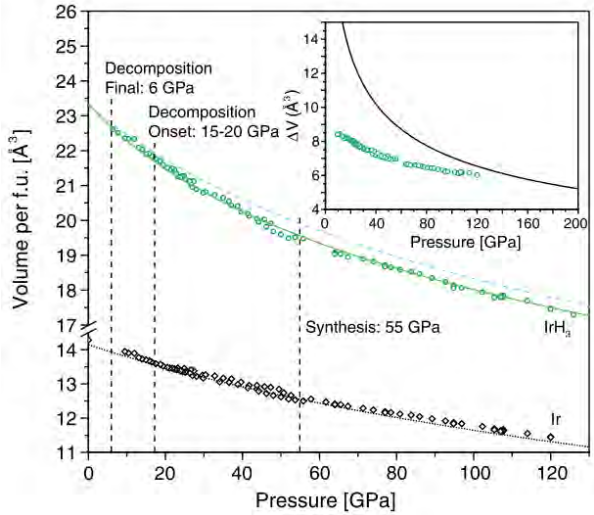
PRL 111, 215503 (2013) PHYSICAL REVIEW LETTERS week ending 22 NOVEMBER 2013

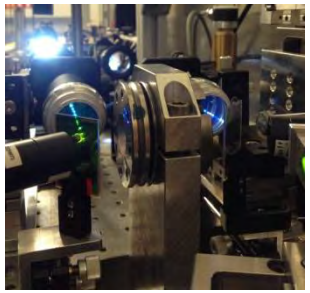
High-Pressure Synthesis and Characterization of Iridium Trihydride

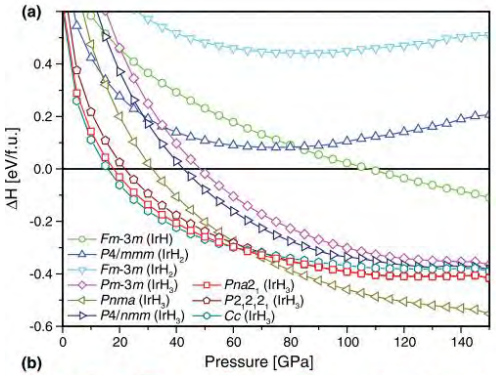
Thomas Scheler,[1] Miriam Marqués,[2] Zuzana Konôpková,[3] Christophe L. Guillaume,[1] Ross T. Howie,[1] and Eugene Gregoryanz[1,4]

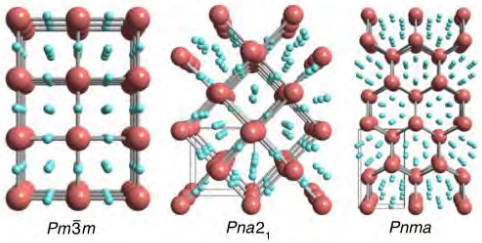
- ***First known non-interstitial noble metal hydride***
- ***IrH_3 stoichiometry => highest volumetric hydrogen content***











Pressure-Volume data of Ir and hydride -> EoS from 55 GPa after laser heating on decompression measured at P02

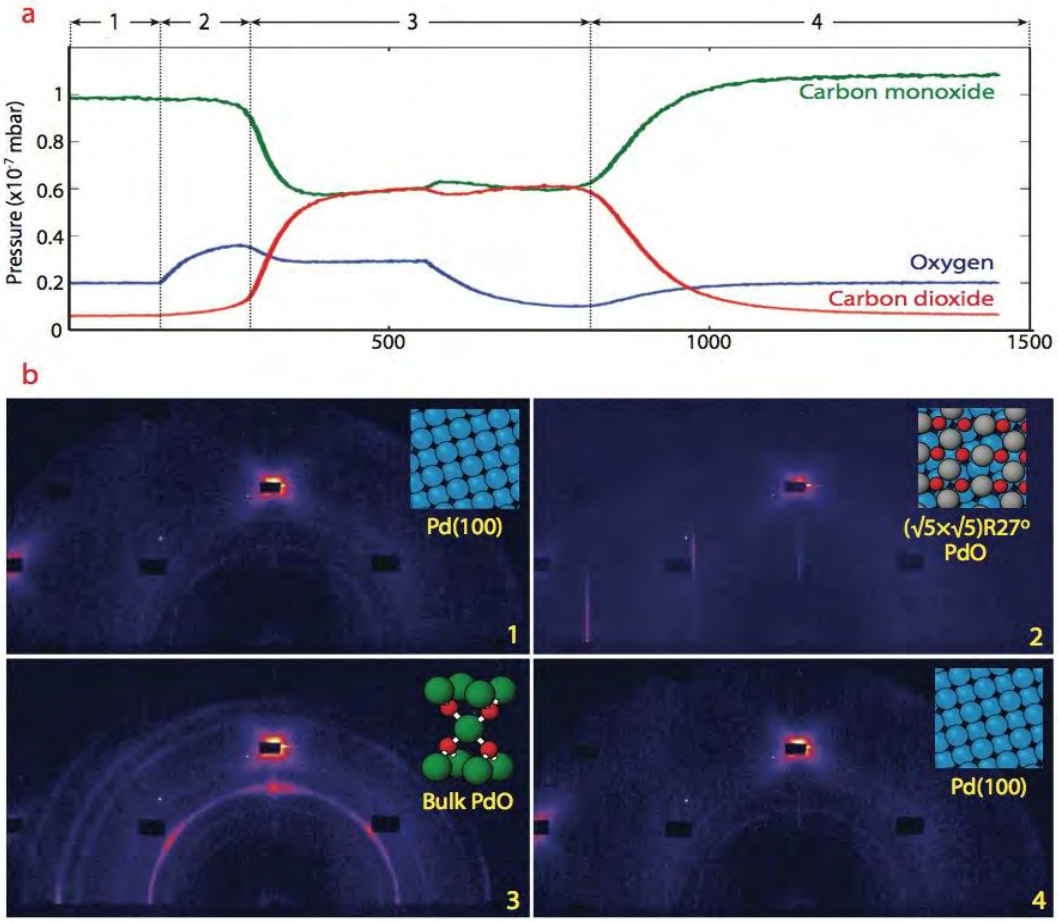
***Ab-initio* calculations to determine the position of hydrogen atoms -> reveals stoichiometry close to 3 & several competing structures with low enthalpies of formation (simulation and evaluation by T. Scheler and E. Gregoryanz, Edinburgh University).**

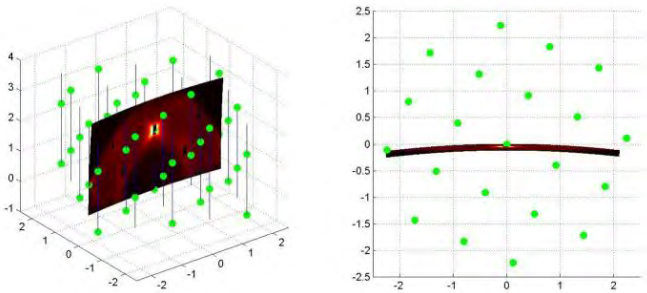
Surface Science: Catalysis

Sciencexpress

Röntgen Ångström Cluster

High-Energy Surface X-Ray Diffraction





Uta Hejral, Uta Rutt, O. Gutowski, A. Stierle, …

DESY

Summary

In-situ X-ray diffraction with high-energy photons

- powerful tool to characterize *in-situ* thermal and mechanical stability of materials
- allows measurement of thermal expansion as well as kinetics of transformations
- it is a non-destructive technique
- tiny structural changes due to external parameter changes can be observed
- real-space analysis can help identify the role of each element (difficult for many component systems)
- with PETRA III we have a world leading synchrotron radiation source to achieve very high spatial resolution (down to few nm) also in imaging