Research with Synchrotron Radiation

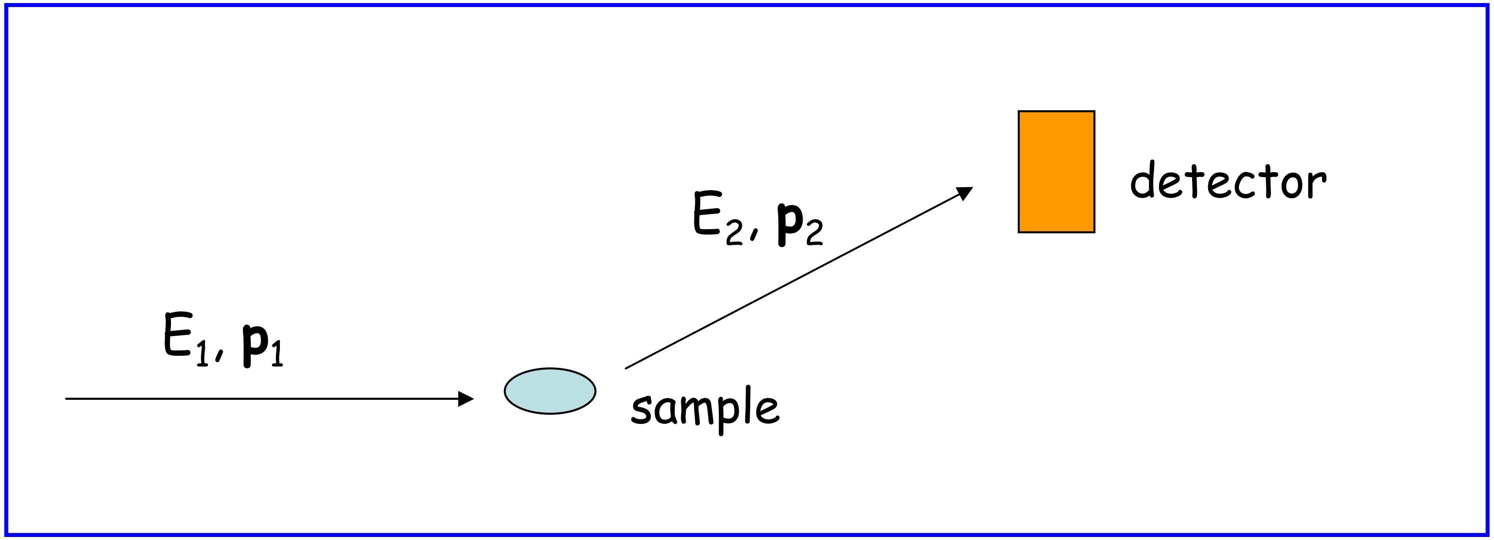
Part II

Ralf Röhlsberger

- Principles of structure determination
- Experiments at Storage Rings
  - Diffraction/Scattering
  - Spectroscopy
  - Imaging
- Experiments at Free Electron Lasers

Experiments with Synchrotron Radiation

Reveal the structure and dynamics of matter by performing scattering experiments with photons

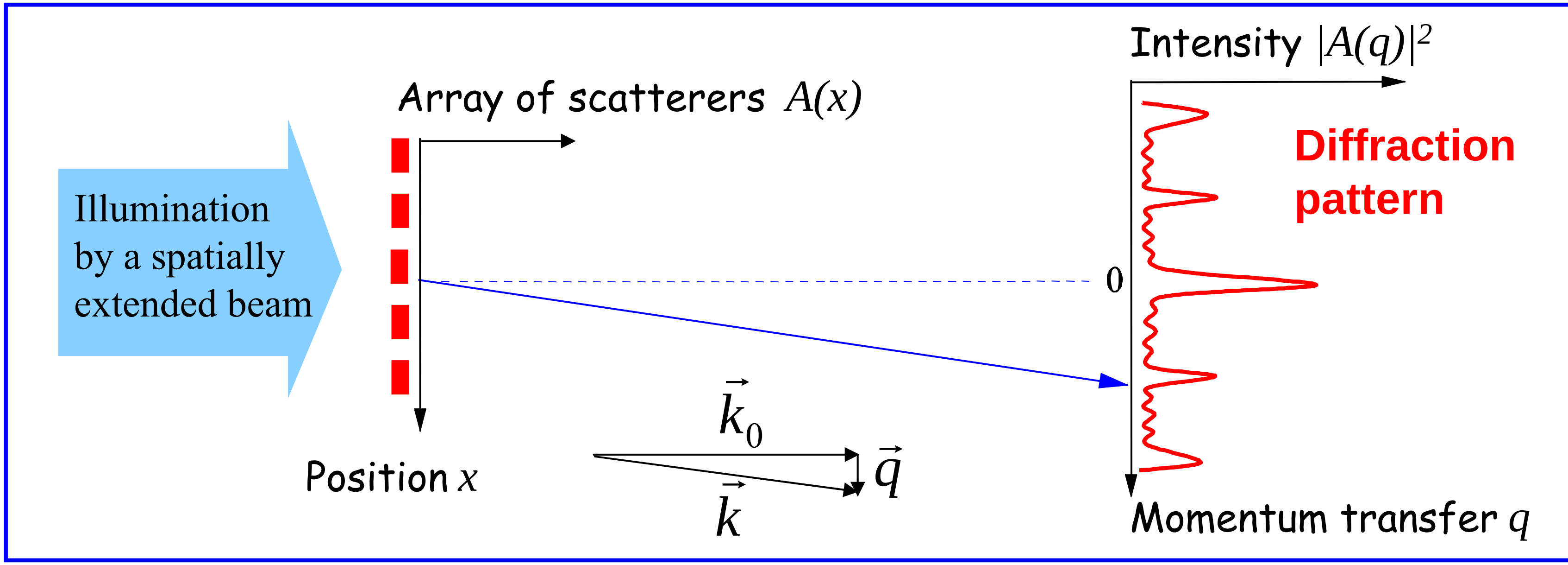


Analyze the distribution of scattered photons in reciprocal space → Diffraction

… in real space → Imaging

Analyze the energy spectrum of scattered photons → Spectroscopy

Principles of structure determination



$\vec{q} = \vec{k} - \vec{k}_0$ momentum transfer

Relation between $A(x)$ and $A(q)$:

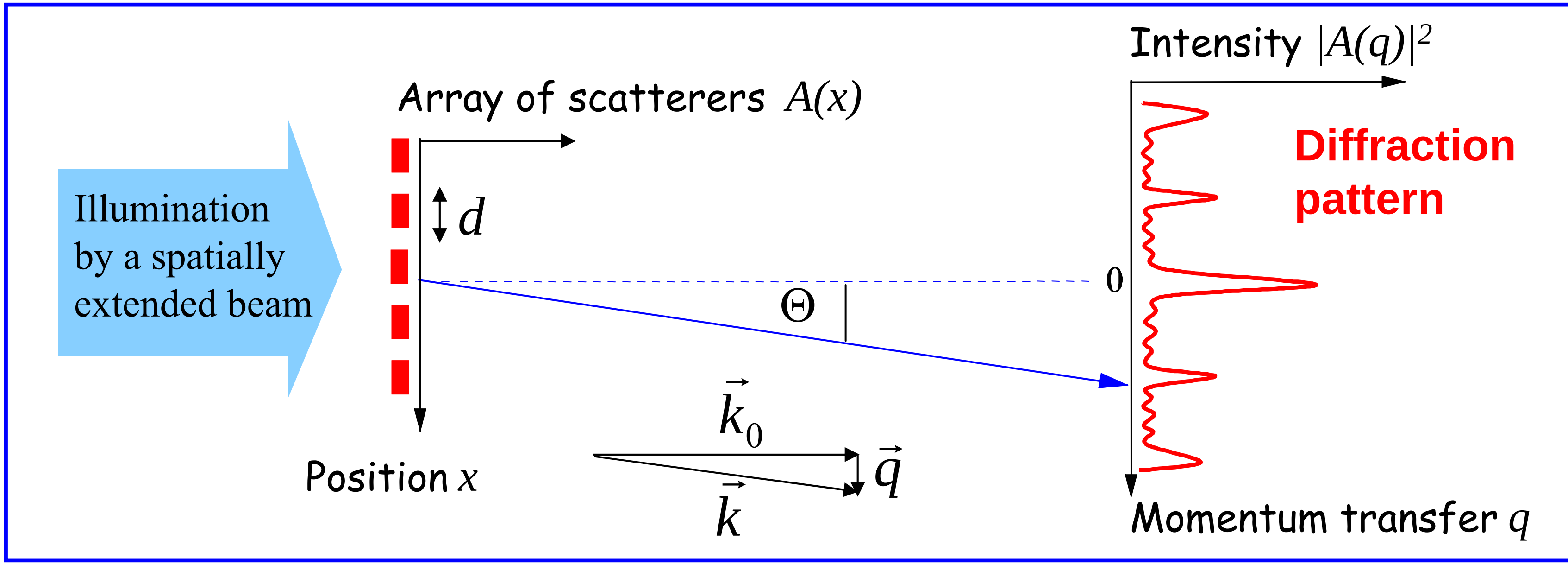
$$A(q) = \int A(x)\, e^{iqx}\, dx \quad (1)$$

Task: Determine $A(x)$ from measured $|A(q)|^2$

Problem: Eq. (1) cannot be simply inverted, because the phase is lost

(Phase problem of crystallography)

Principles of structure determination

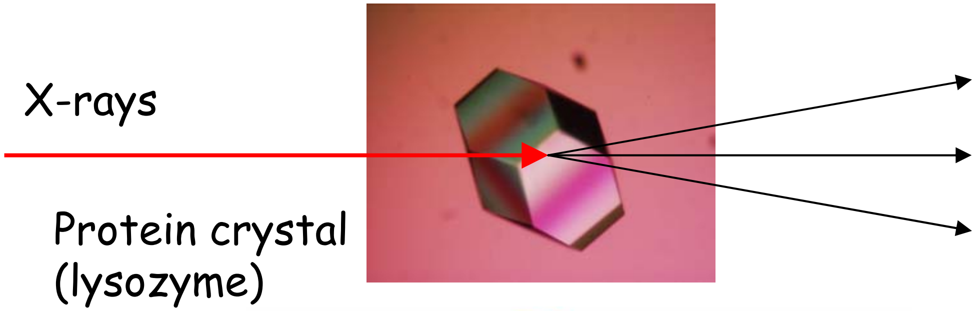


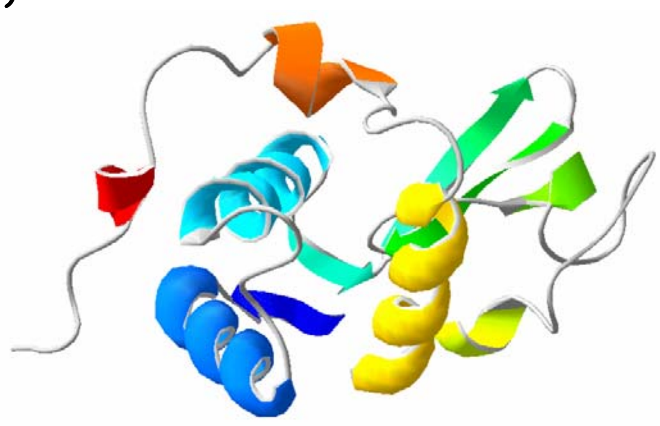
Position of diffraction peaks given by Bragg's equation:

$$n\lambda = 2d\sin\Theta$$

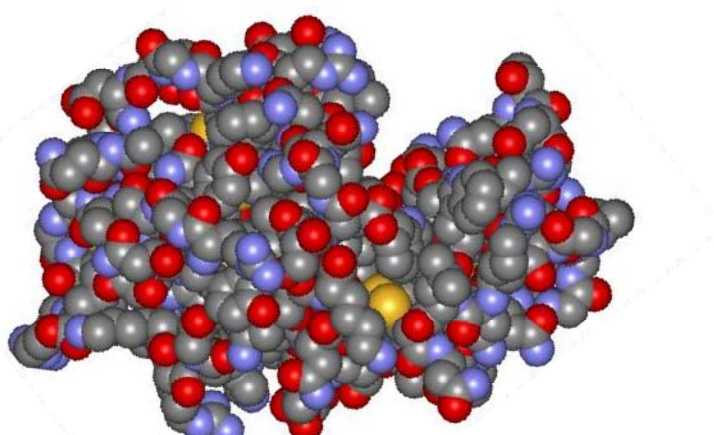
Diffraction Experiments

Protein crystallography

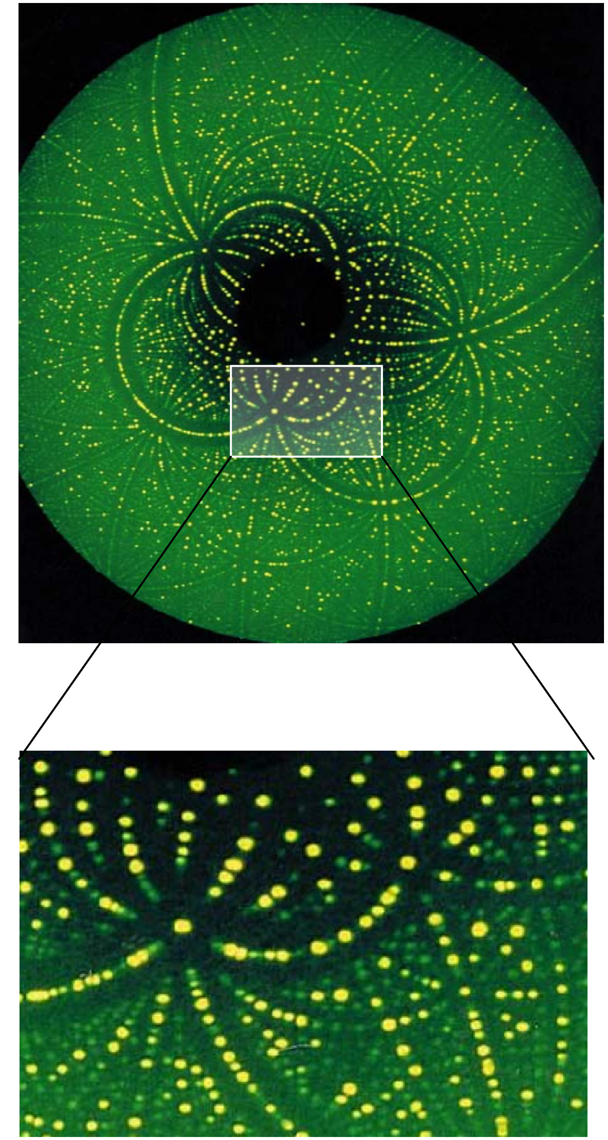




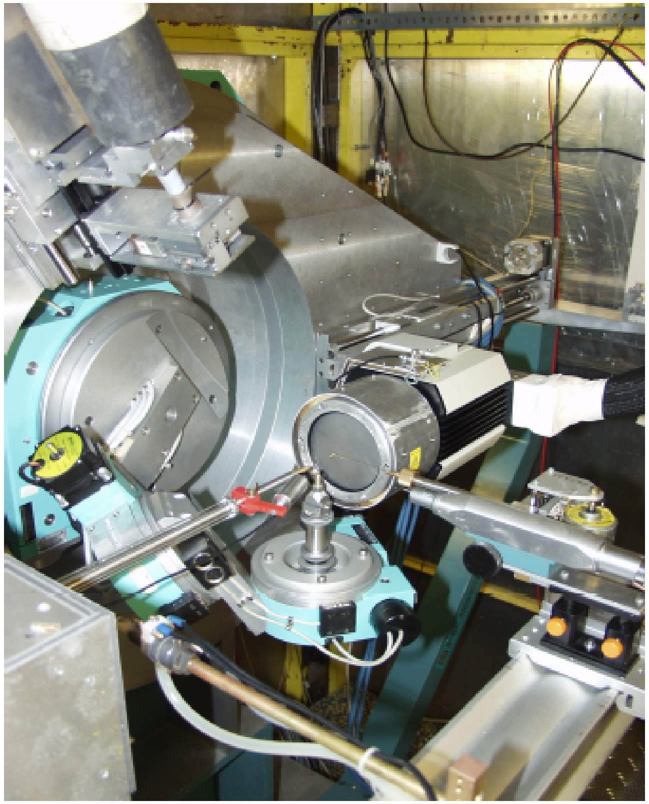
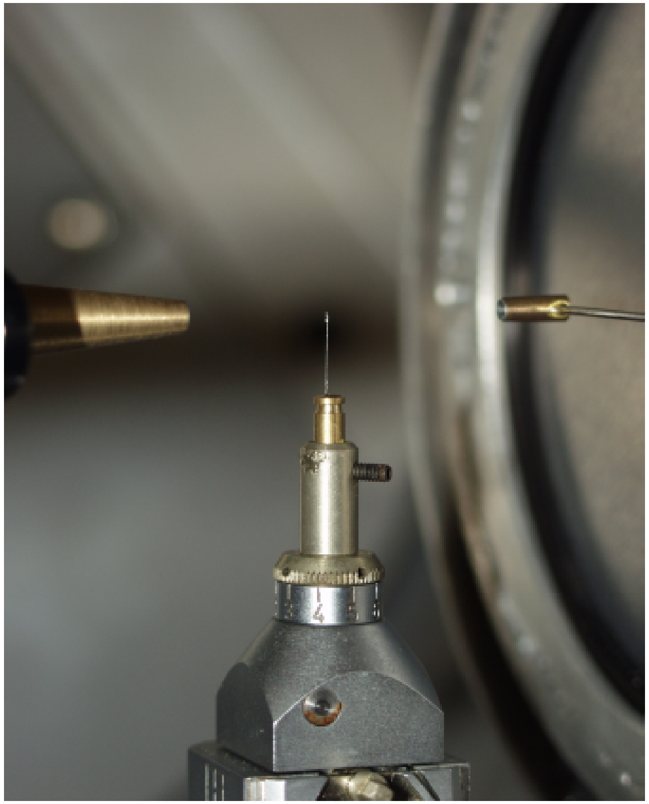
Carbon: Grey
Nitrogen: Blue
Oxygen: Red
Sulphur: Yellow



Diffraction pattern



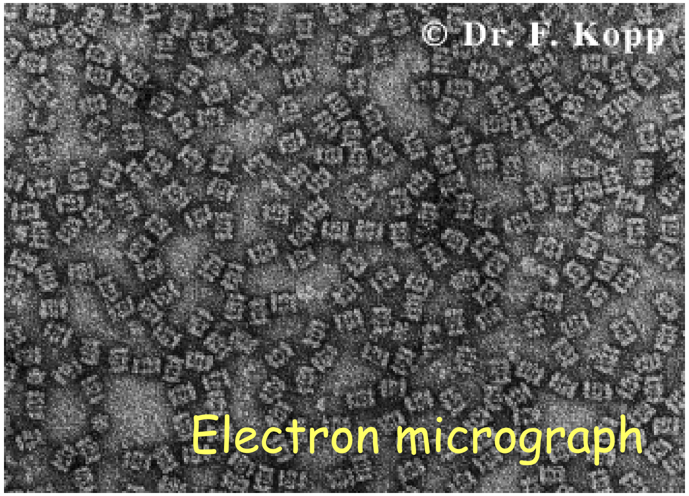
Single crystal diffractometers

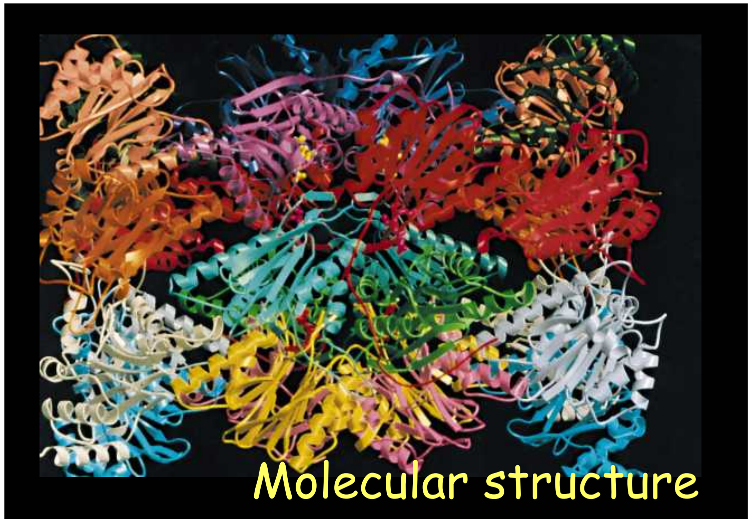



Single crystal diffractometer in κ-geometry with CCD and scintillation counter. Crystal mounted on a glass fiber. The κ-diffractometer has 3 rotations for the crystal and one for the detector.

The proteasome

(cuts proteins into peptides and amino acids)





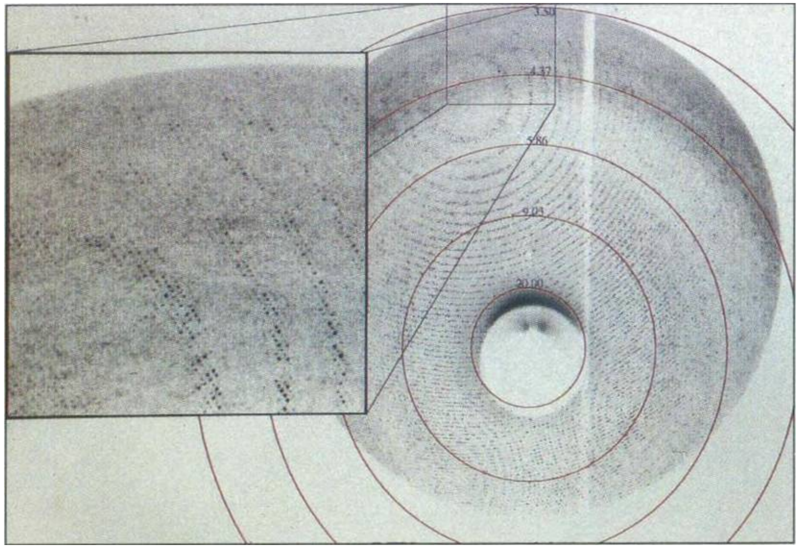
The ribosome

(synthesis of proteins)

The 30S subunit of the ecoli ribosome

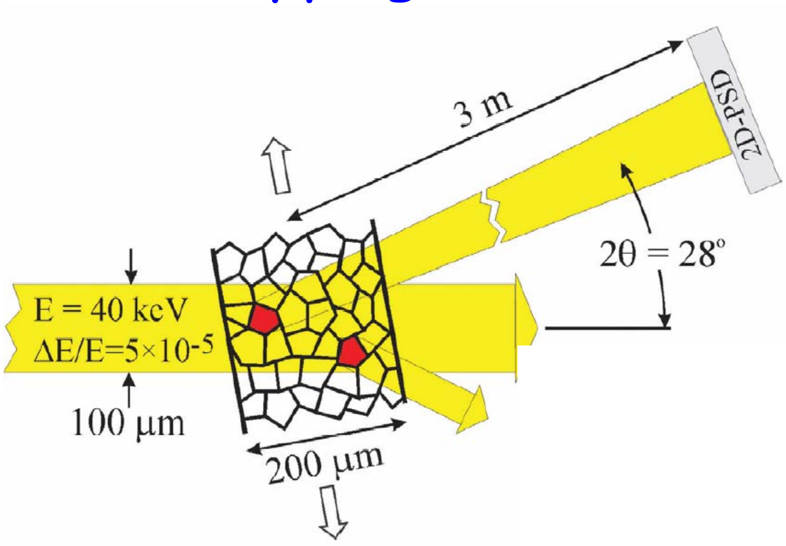
Extremely large complexes (e.g., viruses)

Example: Blue Tongue Virus



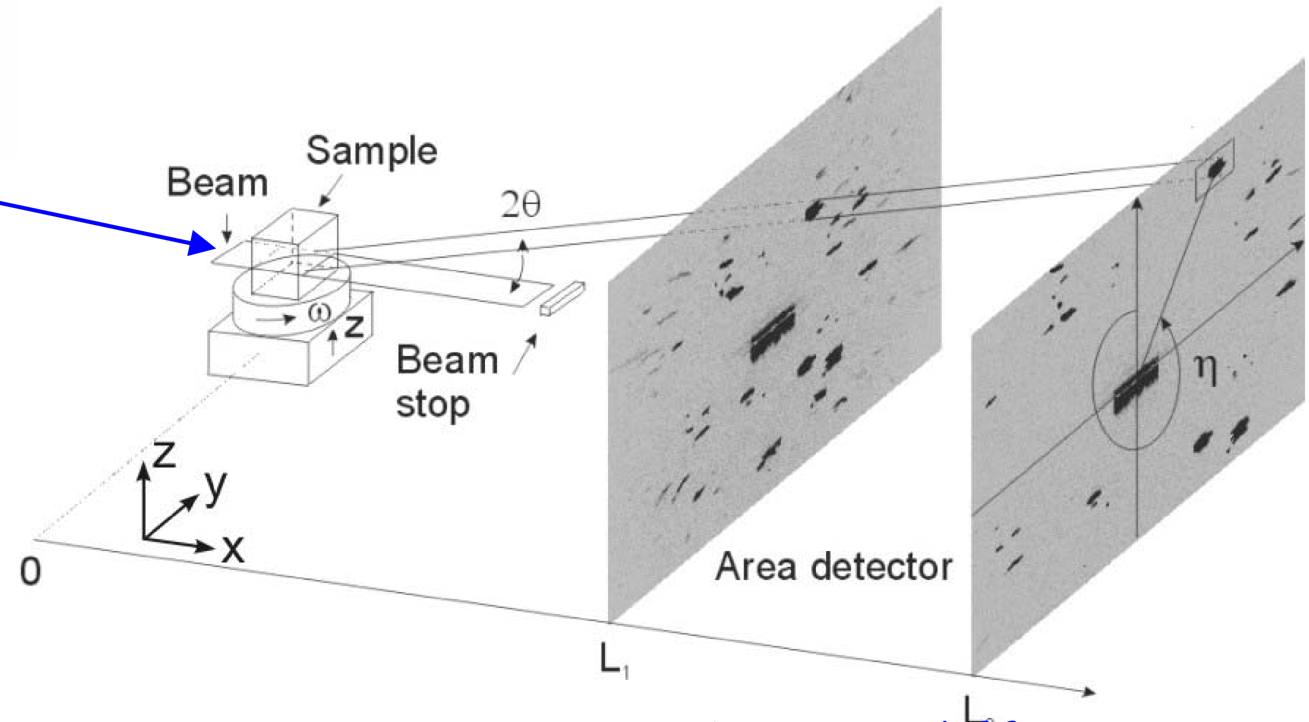
J.M. Grimes et al., Nature 395, 470-478 (1998)

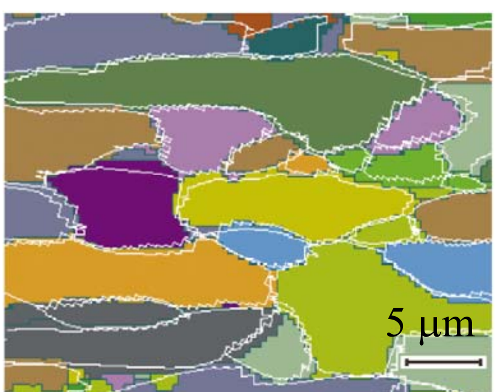
Grain mapping of metals and alloys



How does the microstructure of a material change upon mechanical load and deformations ?

Grain properties to be determined: position, morphology, orientation, deformation



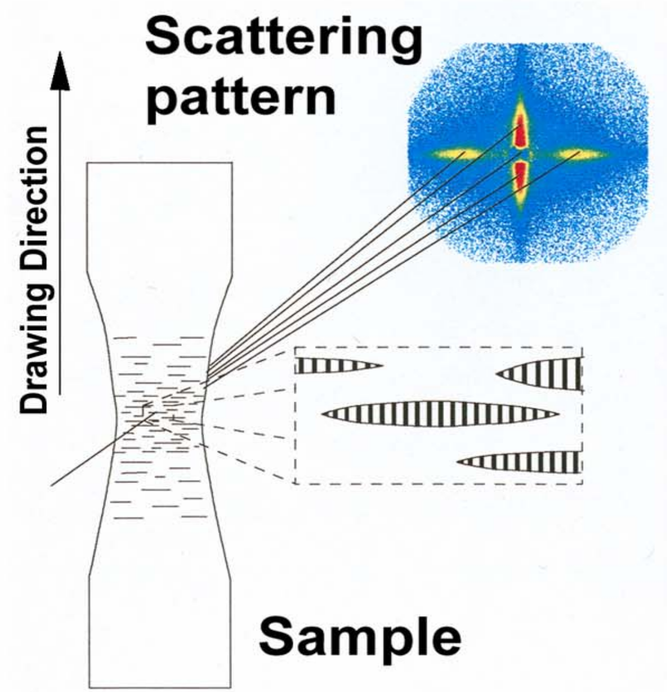


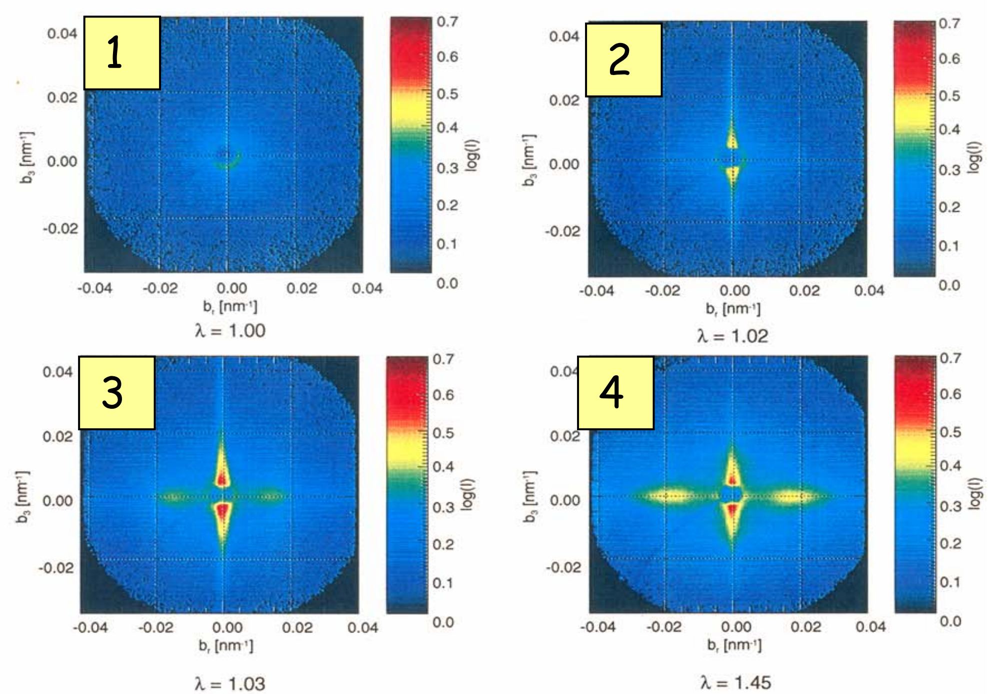
3D X-ray diffraction microscopy

H. F. Poulsen et al., J. Appl. Cryst. 34, 751 (2001)

Small angle x-ray scattering (SAXS)

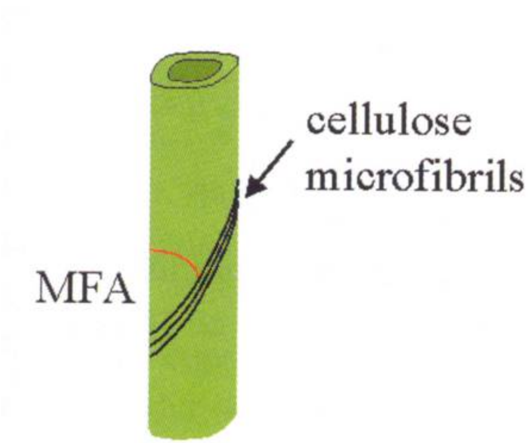
Craze formation in polycarbonate upon elongation below the glass transition temperature

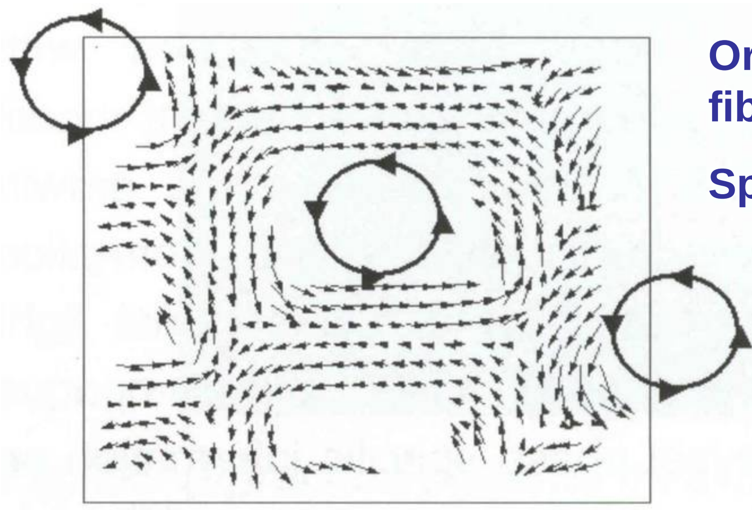




1 → 4 : increasing elongation

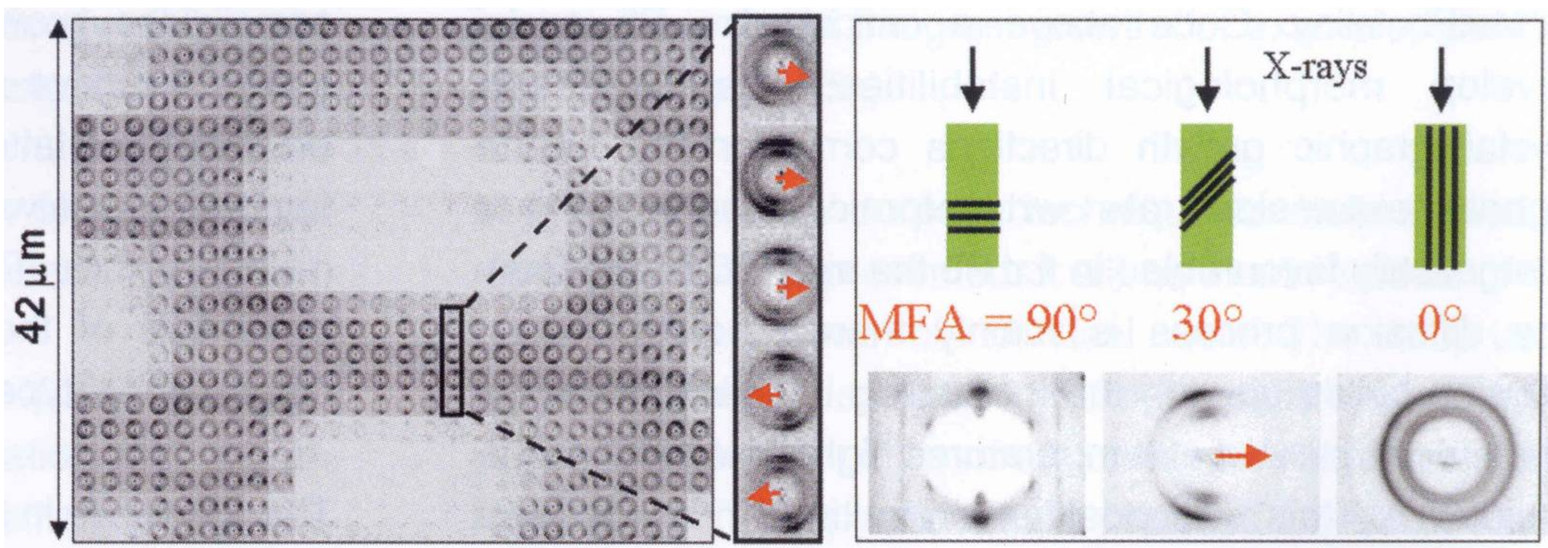
μSAXS : SAXS with a microfocused beam





Orientation of micro fibrils in wood cells.

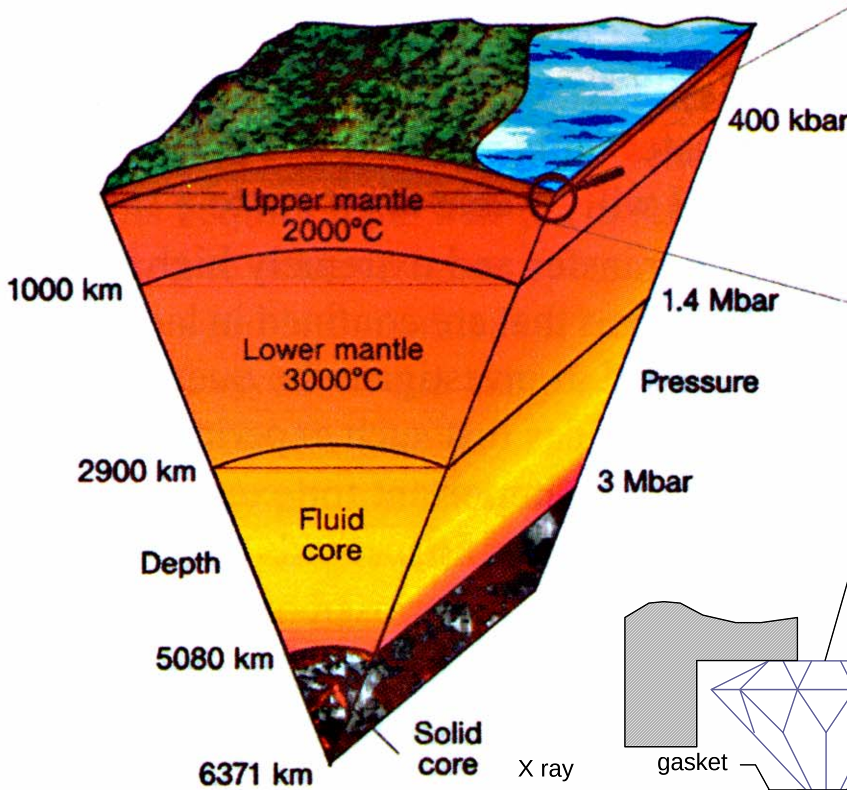
Spatial resolution: 2 μm

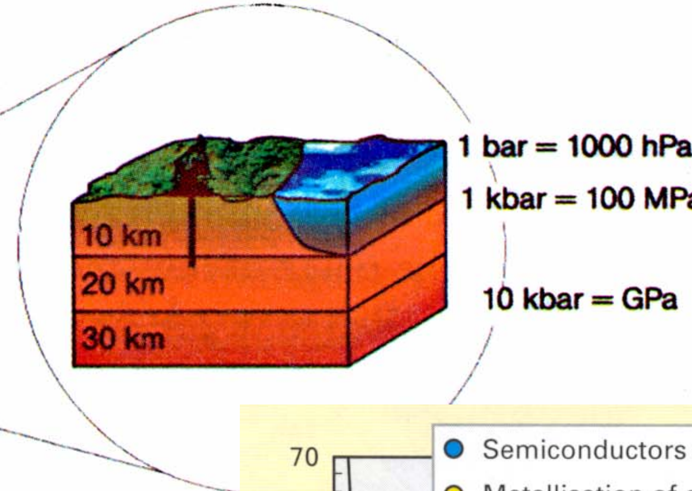


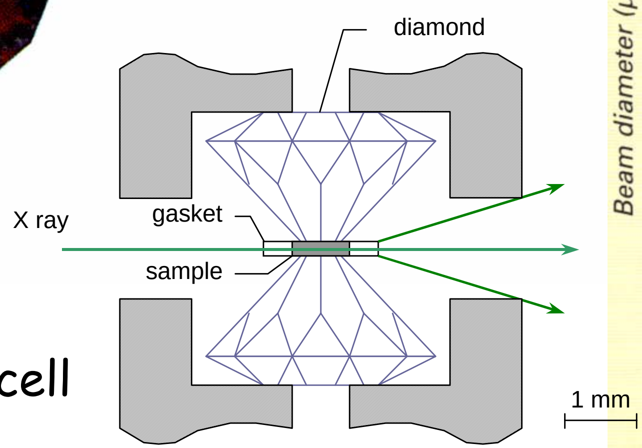
Collection of SAXS patterns: From these pattern the orinetation of the fibrils is derived

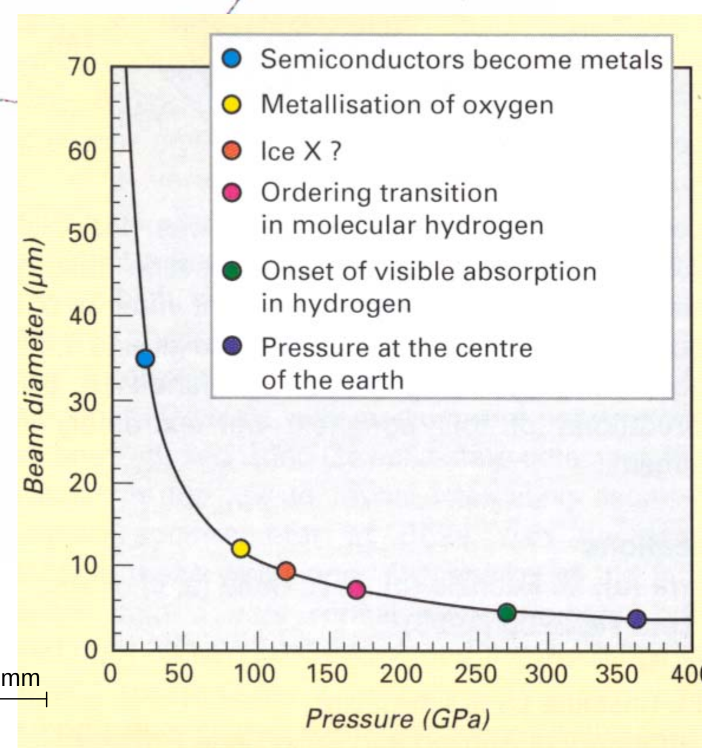
X-ray scattering under high pressure

Research in geophysics









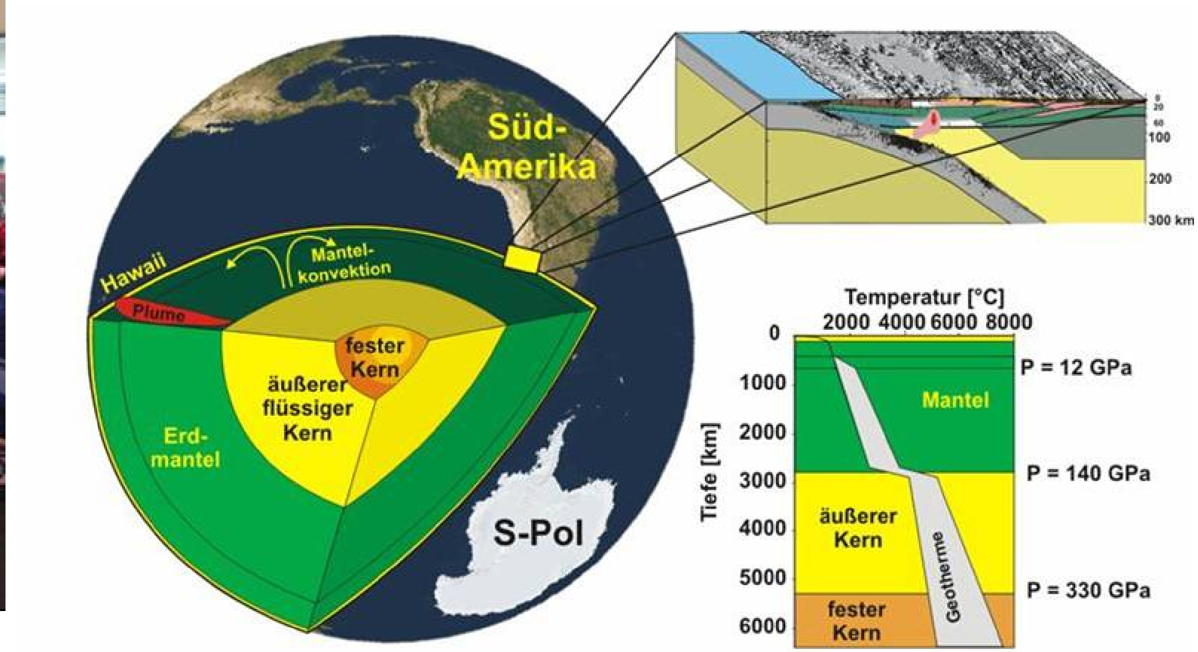
Diamond anvil cell

X-ray scattering under high pressure

GFZ (GeoForschungs Zentrum Potsdam) @ DESY

1750 t press for in situ studies of large sample volumes.
Maximum pressure: ~ 25GPa
Temperature: > 2000K

Study of material under the conditions of the earths lower mantle.



X-ray reflection from surfaces

Index of refraction

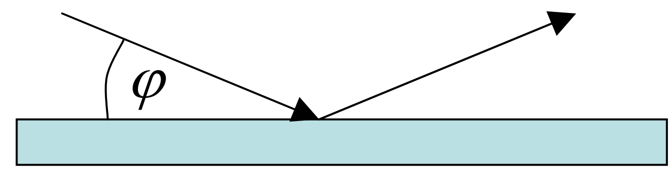
$$n = 1 - \delta$$

$$\delta = \frac{\rho_e r_0 \lambda^2}{4\pi}, \quad \rho_e \equiv \text{ electron density}$$

$$\approx 10^{-5} - 10^{-6} \quad \text{for} \quad \lambda = 0.1\,\text{nm}$$

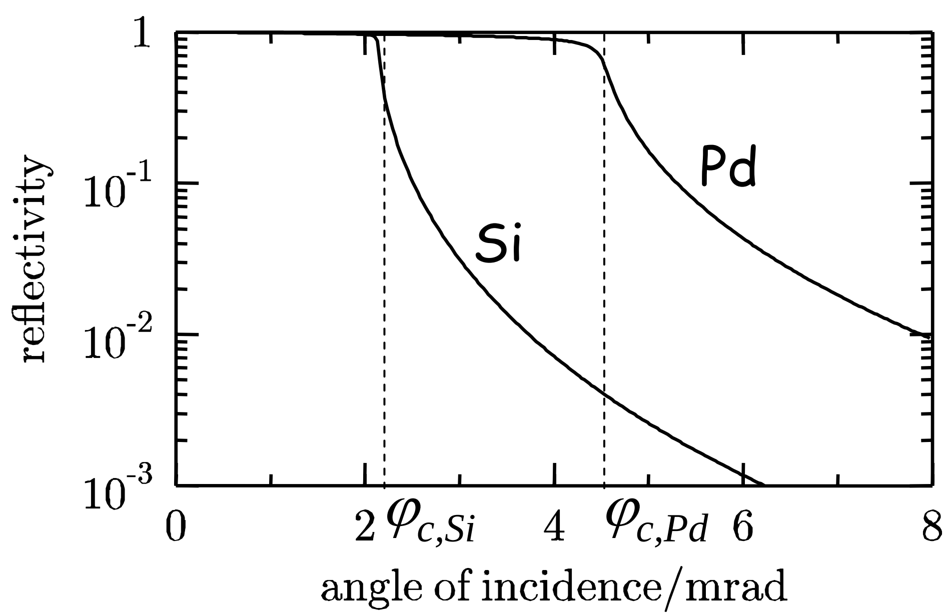
For x-rays, every medium is optically thinner than vacuum !

X-rays incident on a surface below the critical angle are totally reflected



Critical angle of total reflection

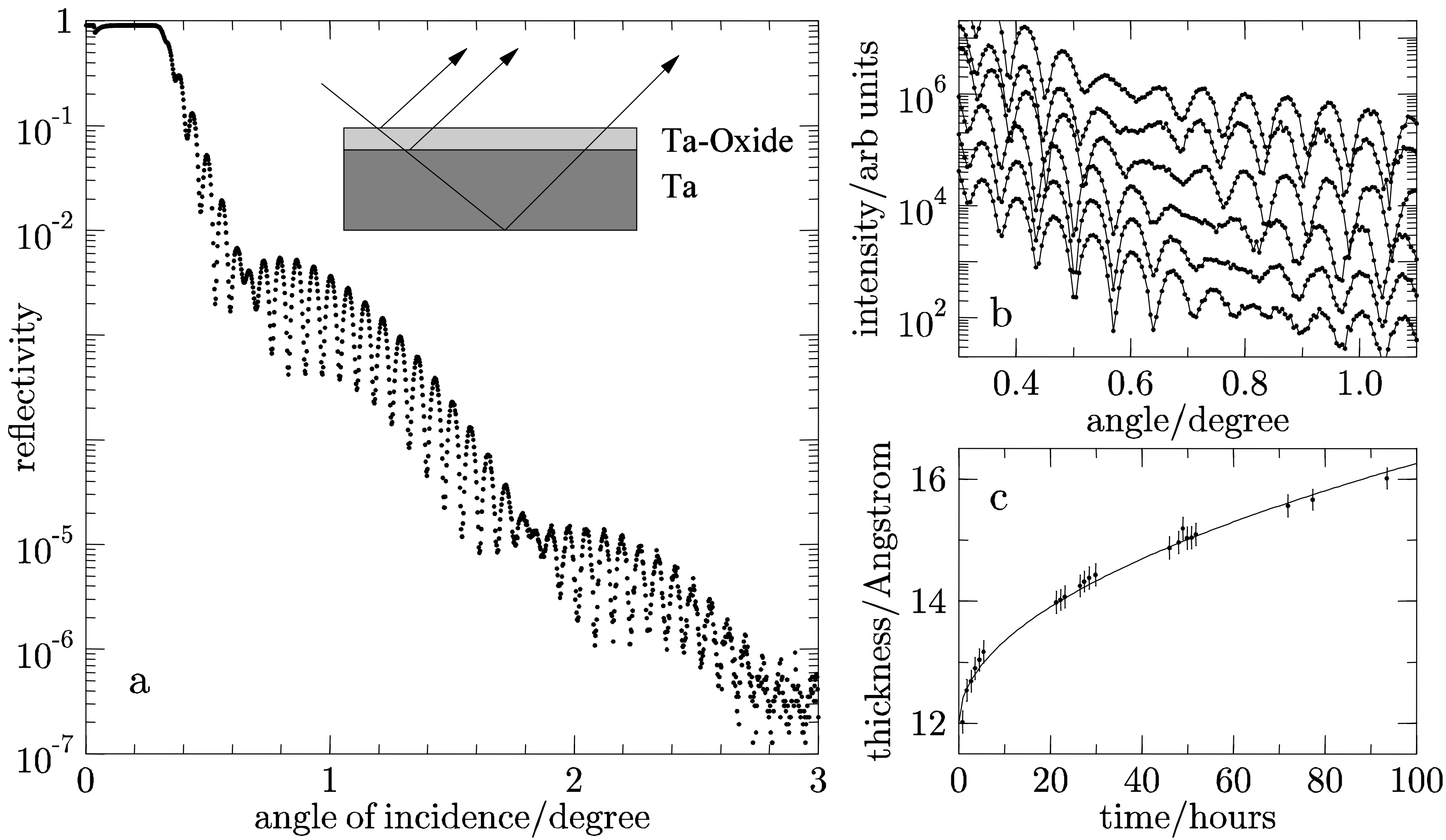
$$\varphi_c = \sqrt{2\delta}$$



For angles $\varphi < \varphi_c$ the penetration depth of hard x-rays is only a few nm.

X-rays can be used for the study of structures at surfaces

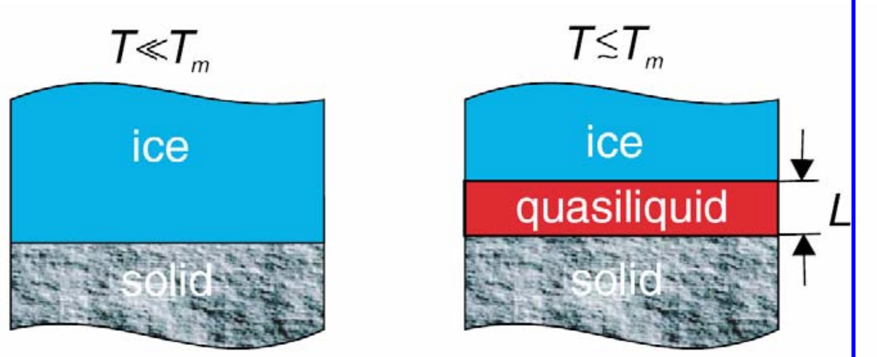
Monitoring the growth of oxide layers: Ta_2O_5 on Ta



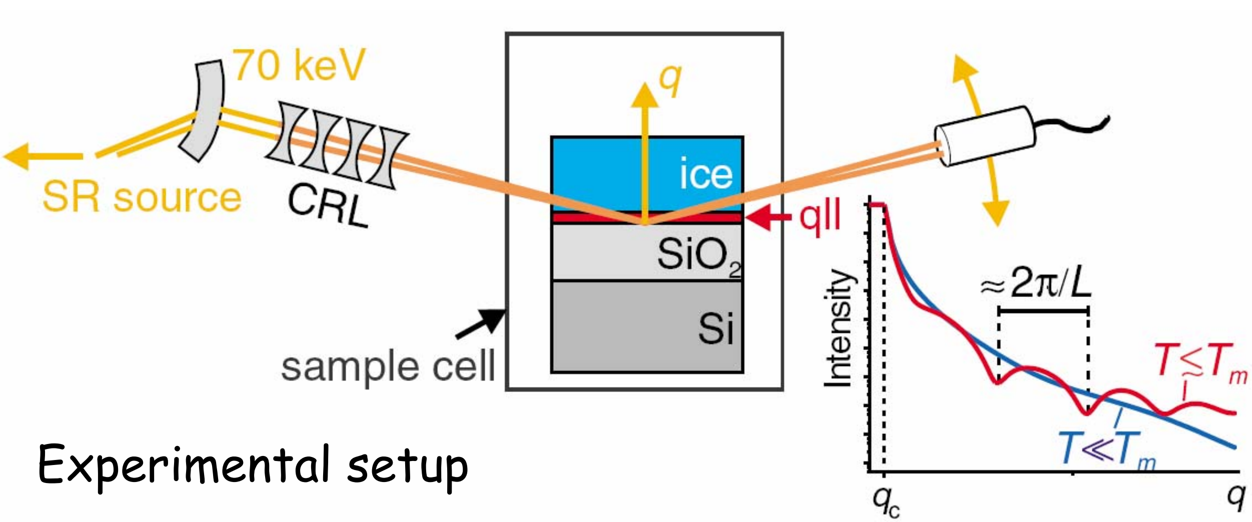
T. Klein, Diploma Thesis, University of Rostock (2001)

Interfacial Melting of Ice in Contact with SiO_2

Hypothesis

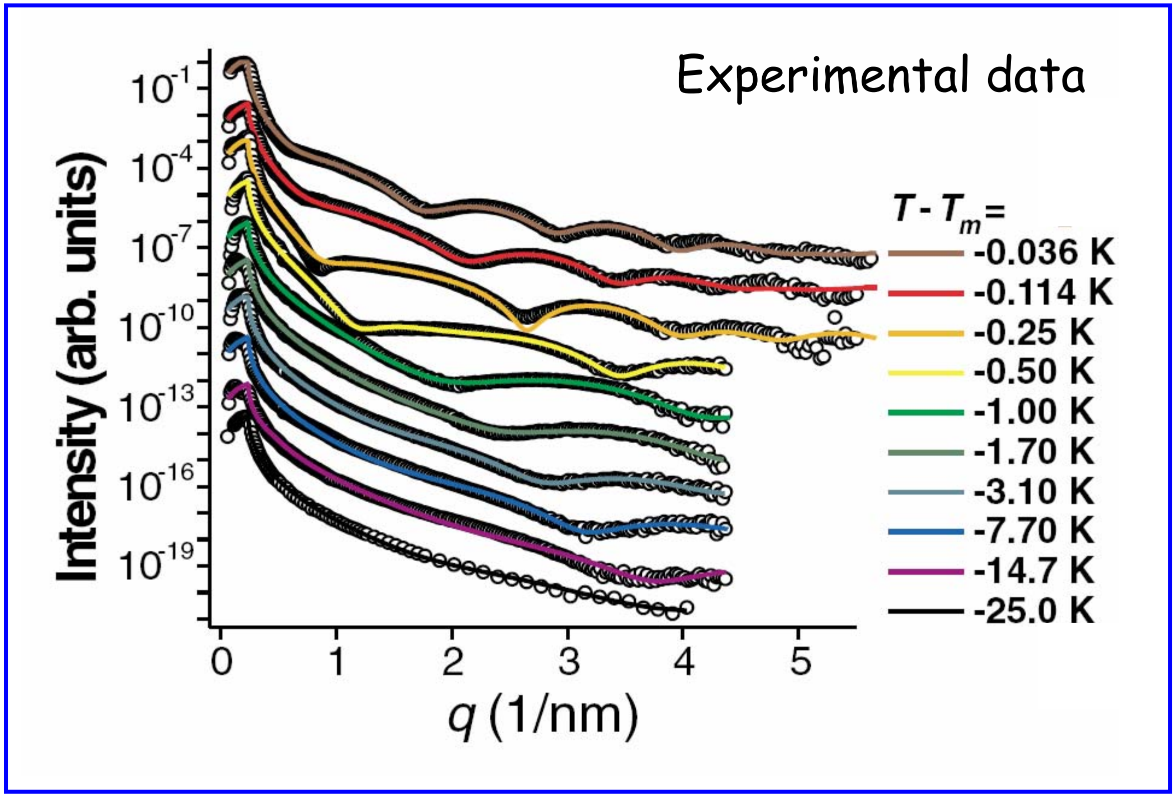


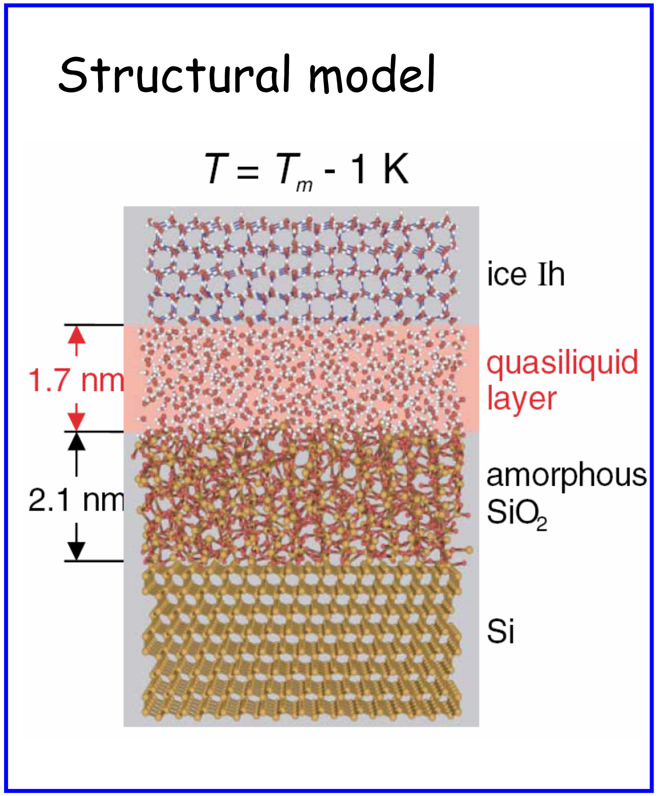
S. Engemann et al., Phys. Rev. Lett. 92, 205701 (2004)



Experimental setup

Interfacial Melting of Ice in Contact with SiO_2

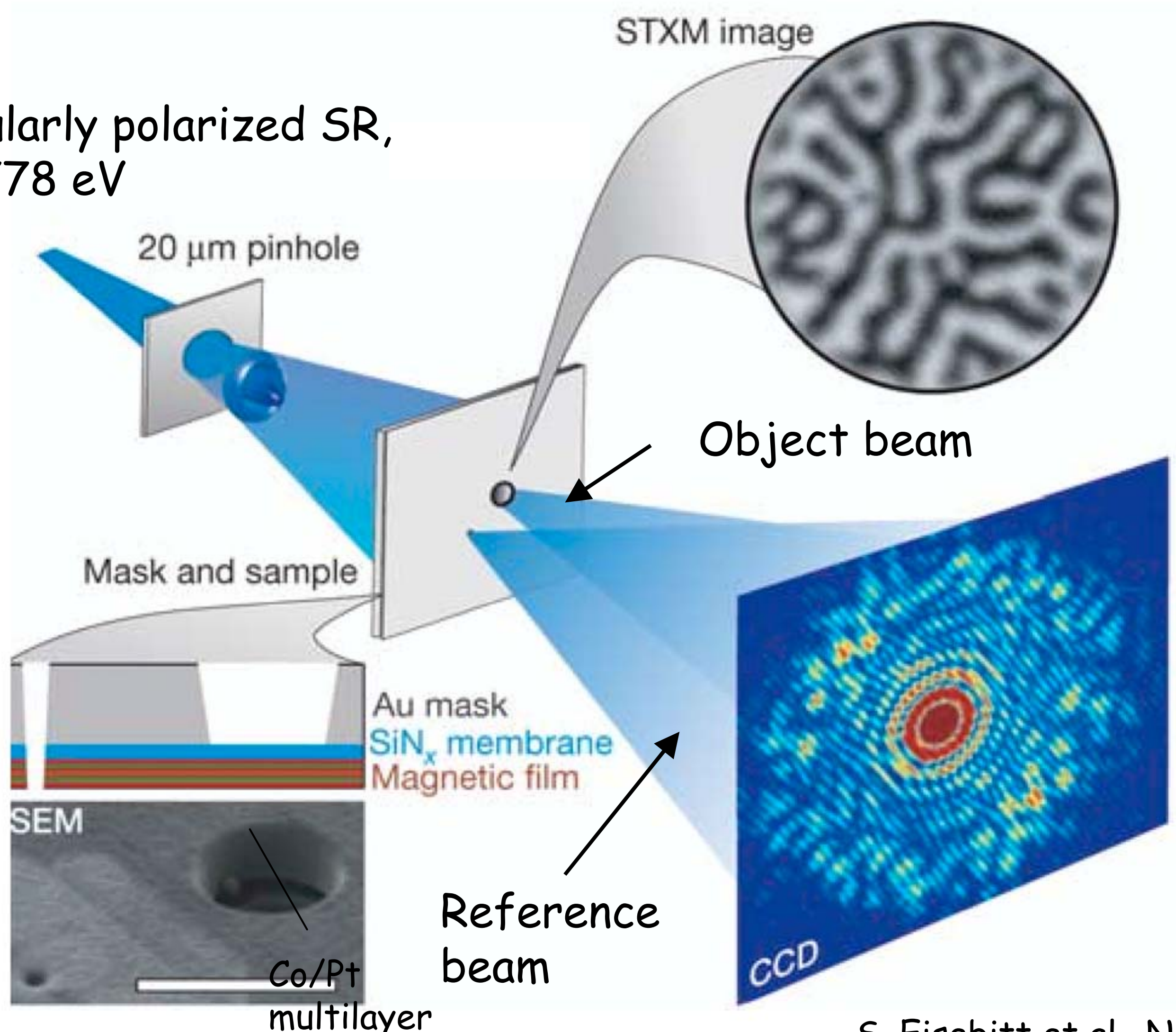




Exploiting the coherence of x-rays:

Imaging of magnetic domains via x-ray holography

Circularly polarized SR,
E = 778 eV



S. Eisebitt et al., Nature 432, 885 (2004)

Spectroscopy

Absorption spectroscopy

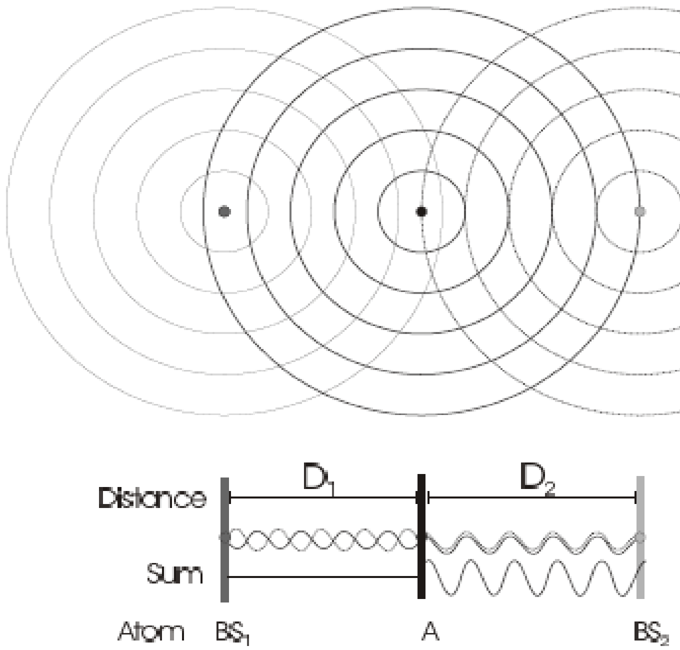
Photons are resonantly absorbed near an absorption edge

The outgoing photoelectron is scattered by the surrounding atoms

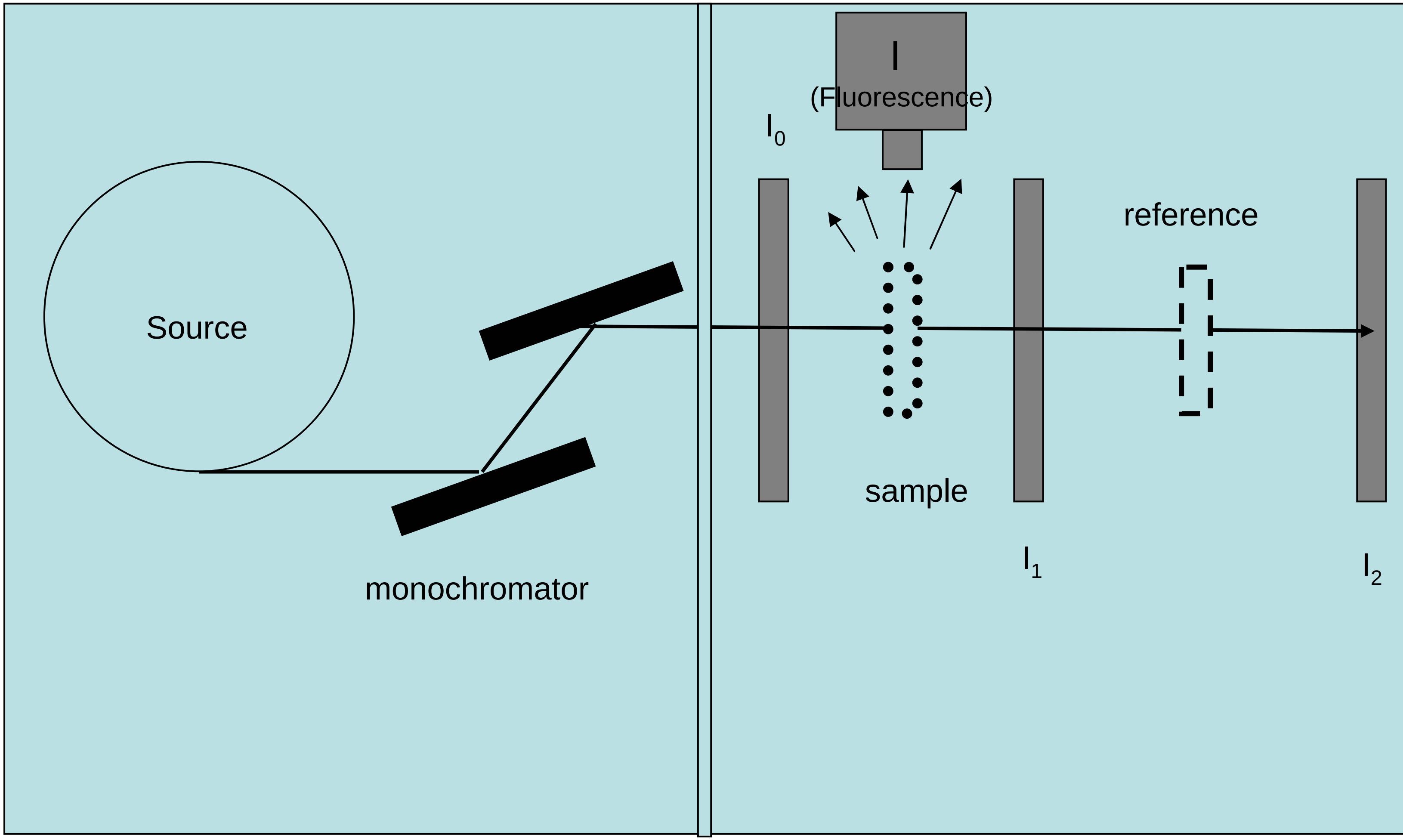
Interference of the outgoing electron wave with the backscattered electron waves

→ Modulation of the cross section as function of energy

→ Information on the distance of neighbouring atoms



Absorption spectroscopy: Experimental setup



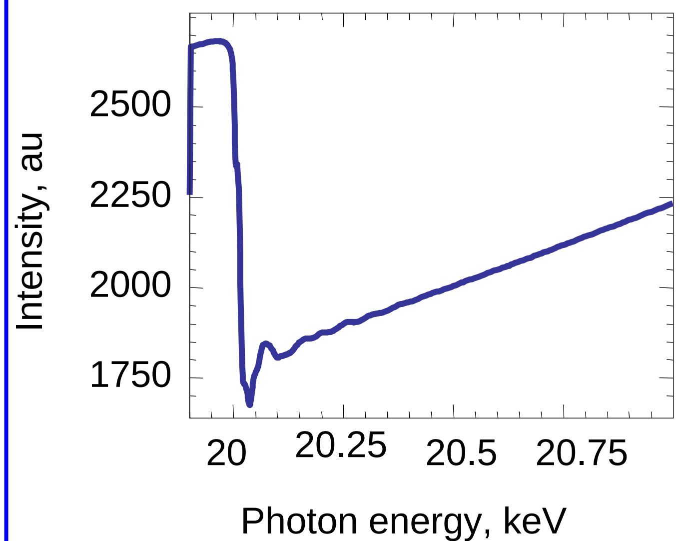
Features of X-ray absorption spectroscopy

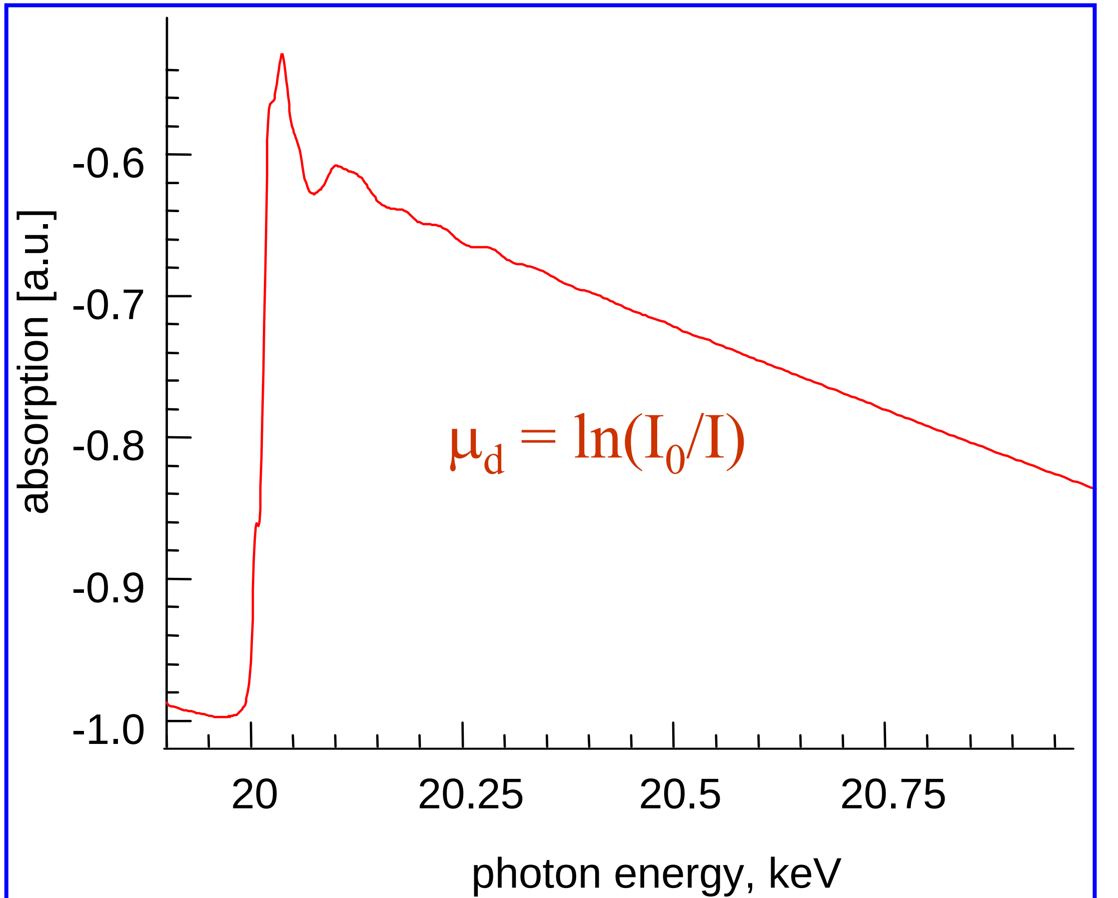
Measured absorption signal (Mo metal) :

μ = linear absorption coefficent

$I = I_0 * exp(-\mu d)$

(Lambert's law)

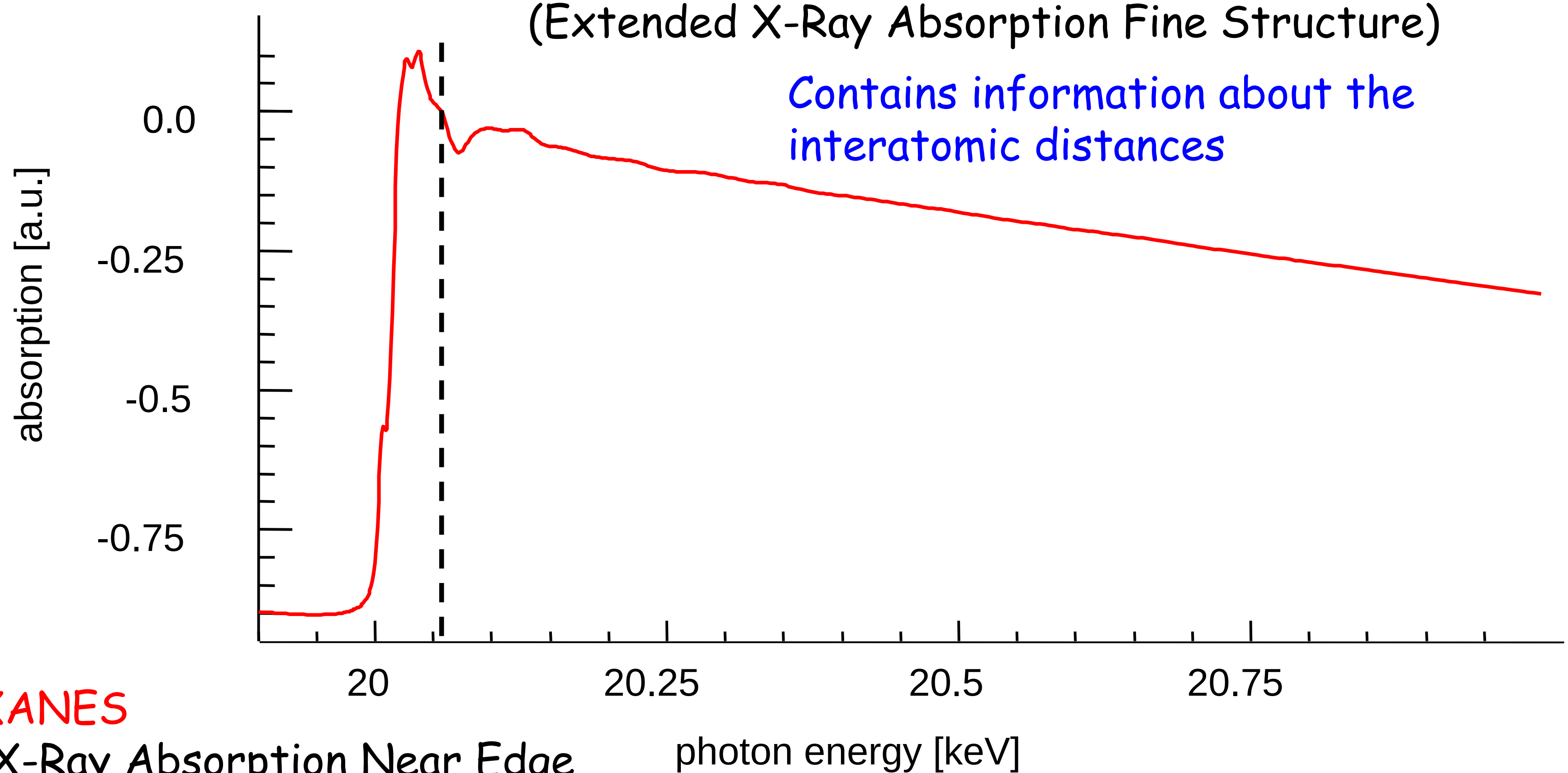




Regions in the XAS spectra

EXAFS
(Extended X-Ray Absorption Fine Structure)

Contains information about the interatomic distances



XANES
(X-Ray Absorption Near Edge Structure)
NEXAFS
(Near Edge X-Ray Absorption Fine Structure)

Contains information about the chemical binding state of the absorbing atoms

Spectroscopy at DORIS III

- Techniques:
- **absorption spectroscopy**
- photoemission
- luminescence
- soft X-ray spectroscopy
- micro-fluorescence and micro-XAFS

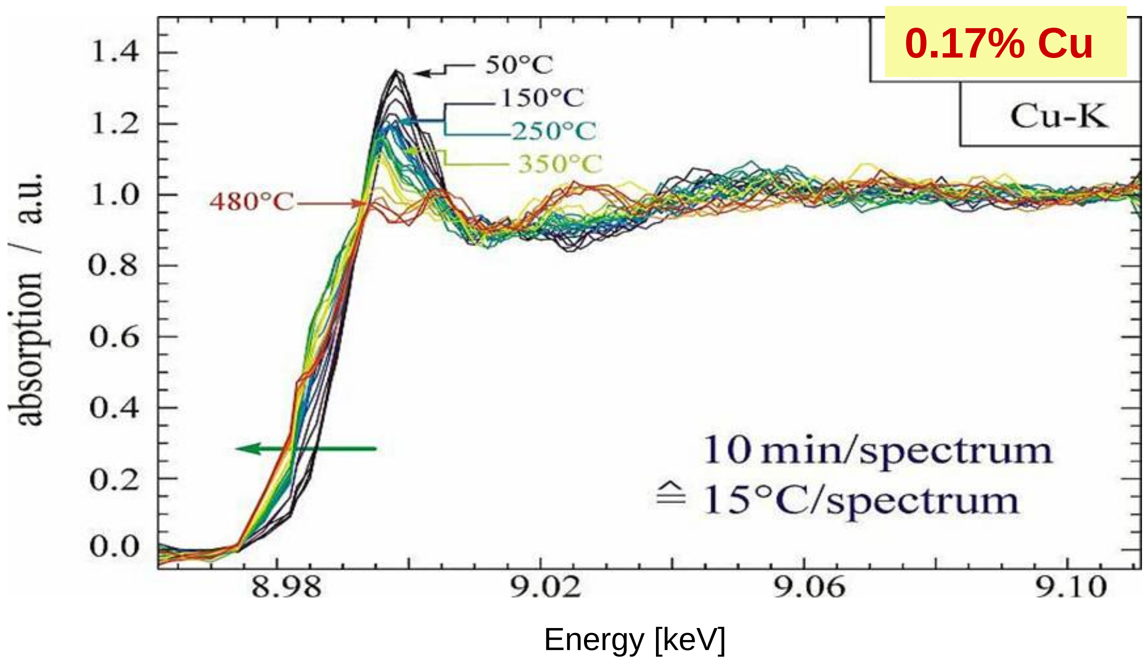
Fields of application:
- surfaces
- atoms/molecules/clusters
- catalysis/chemistry
- materials science
- geo-/environmental science

Example:

In situ study on $Cu/Fe(Fe/Cr)_2O_4$ for water gas shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

Use catalyzer to reduce reaction temperature



Evolution of spectra under catalytic conditions during heating

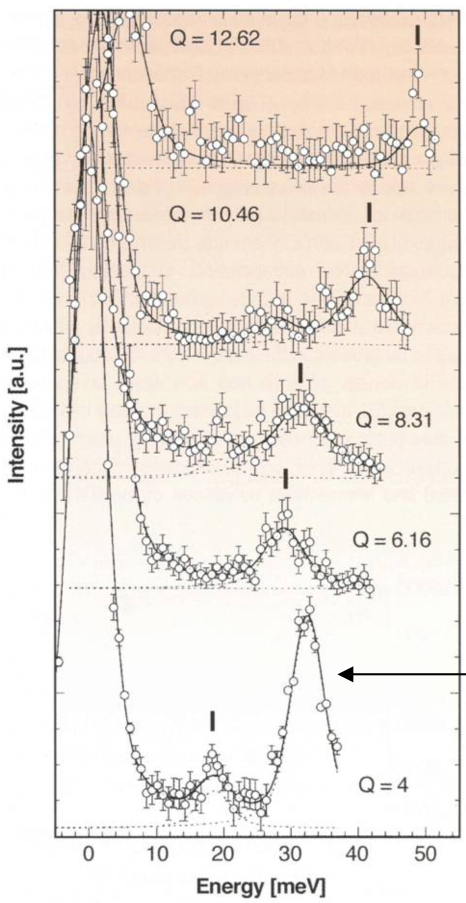
- **intermediate stable Cu(I)-Phase**
- **stability depends on Cu-concentration**

P. Kappen et al.,
J. Catal. 198(2001) 56-65

Inelastic x-ray scattering under high pressure

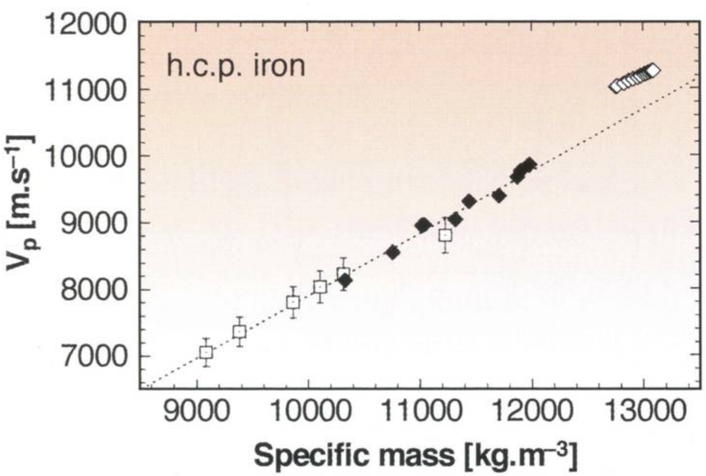
X-rays change energy due to interaction with phonons

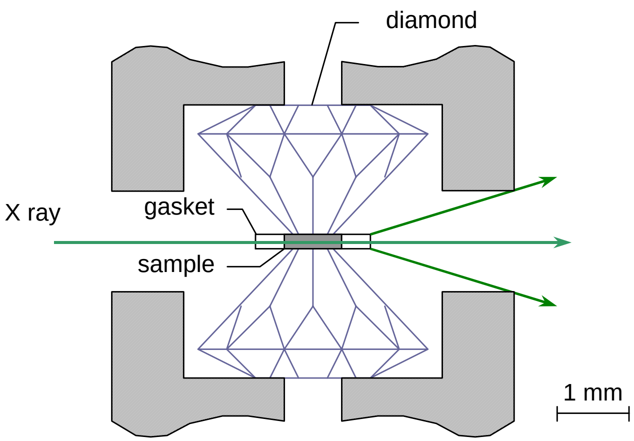
Example: Determine the speed of sound in Fe under pressure



P = 28 GPa

Peaks are due to phonons





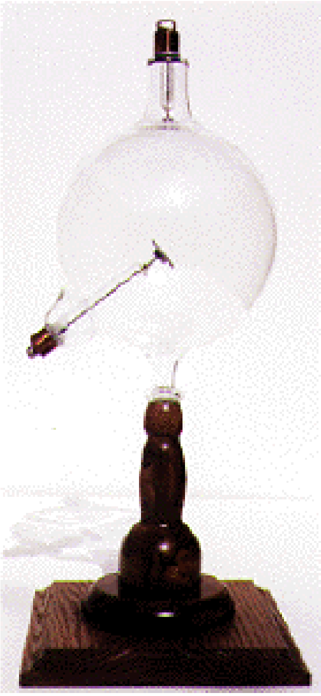
G. Fiquet et al., Science (2000)

Imaging

First imaging experiment

The easiest scattering experiment is the transmission through a material

First commercial x-ray tube



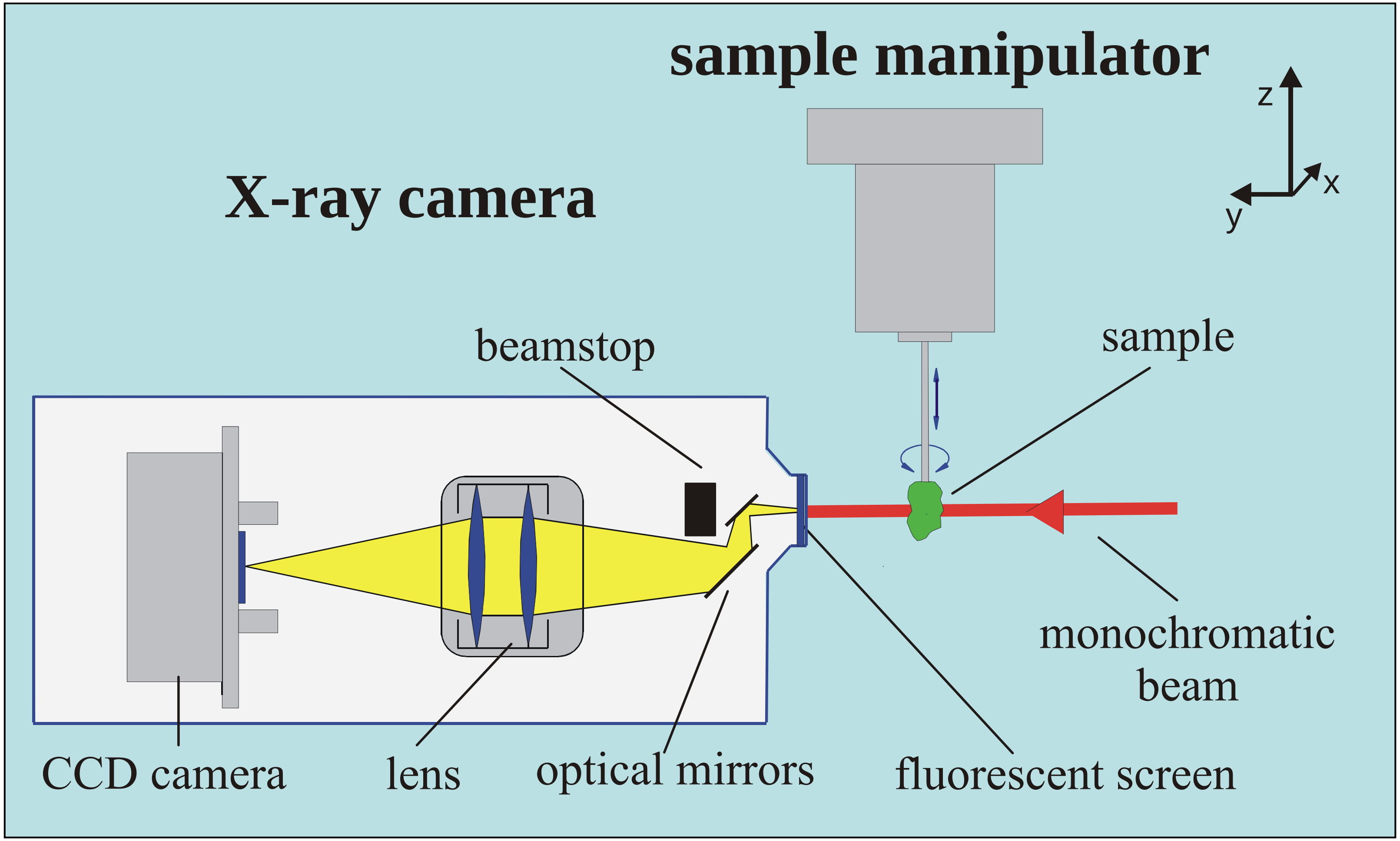
Imaging with x-rays

1895: Discovery of x-rays by W. C. Röntgen

Detector: photographic plate

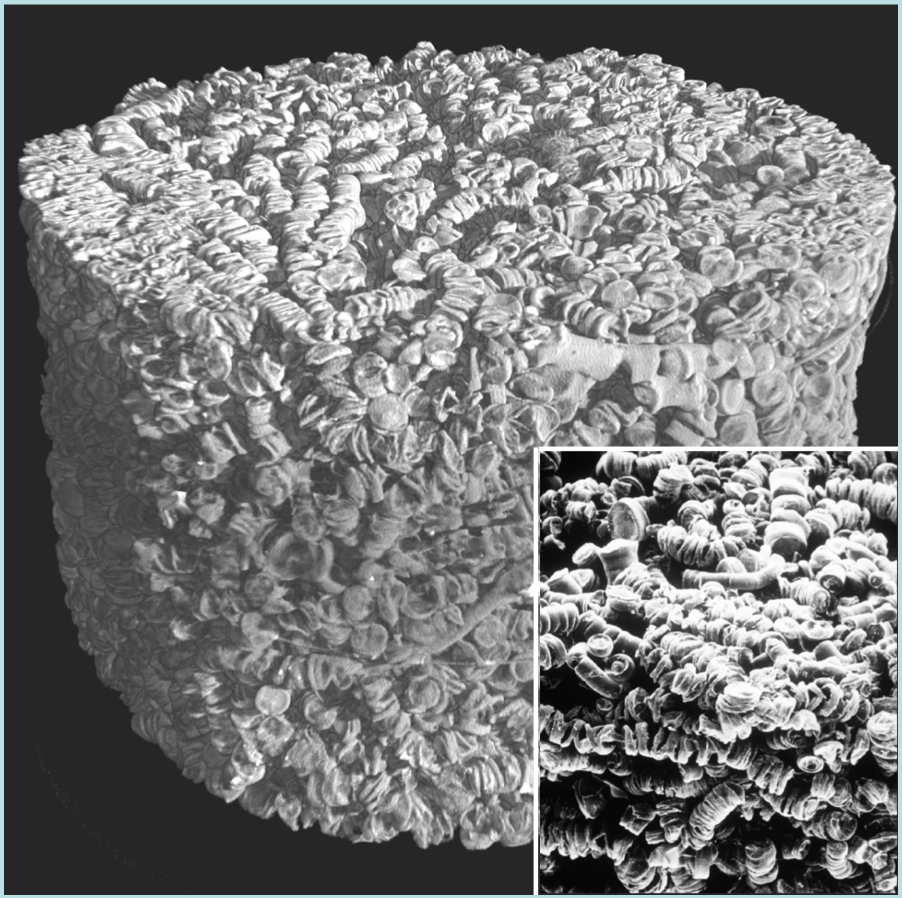
Exposure time: 5 min

Microtomography at DORIS III



Tomography of porous PLGA scaffold

Biodegradable polyester scaffolds as cellular microenvironment for biological tissue engineering



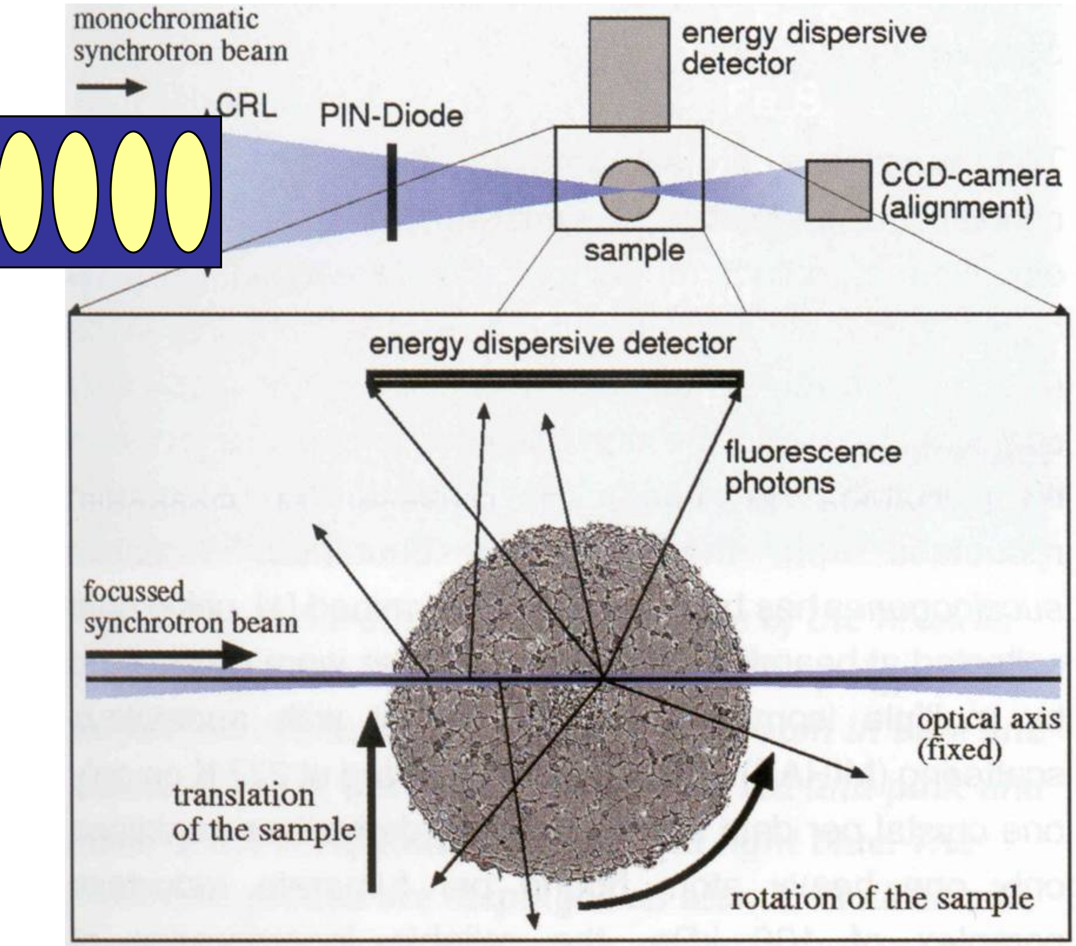
μCT at BW2 using 9 keV
sample diameter: 5 mm

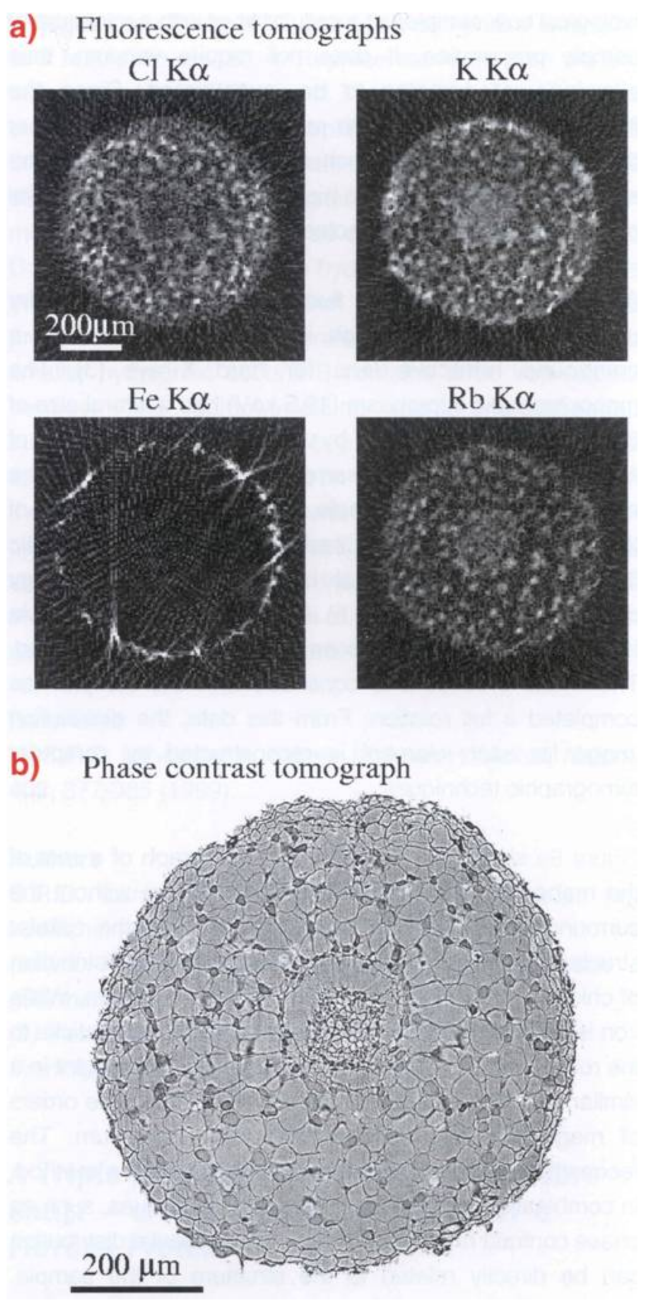
slice (2 x 2 mm²)
spatial resolution: 5.4 μm

Micro fluorescence tomography:

Analysis of elemental distributions

Example: Root of mahagoni tree

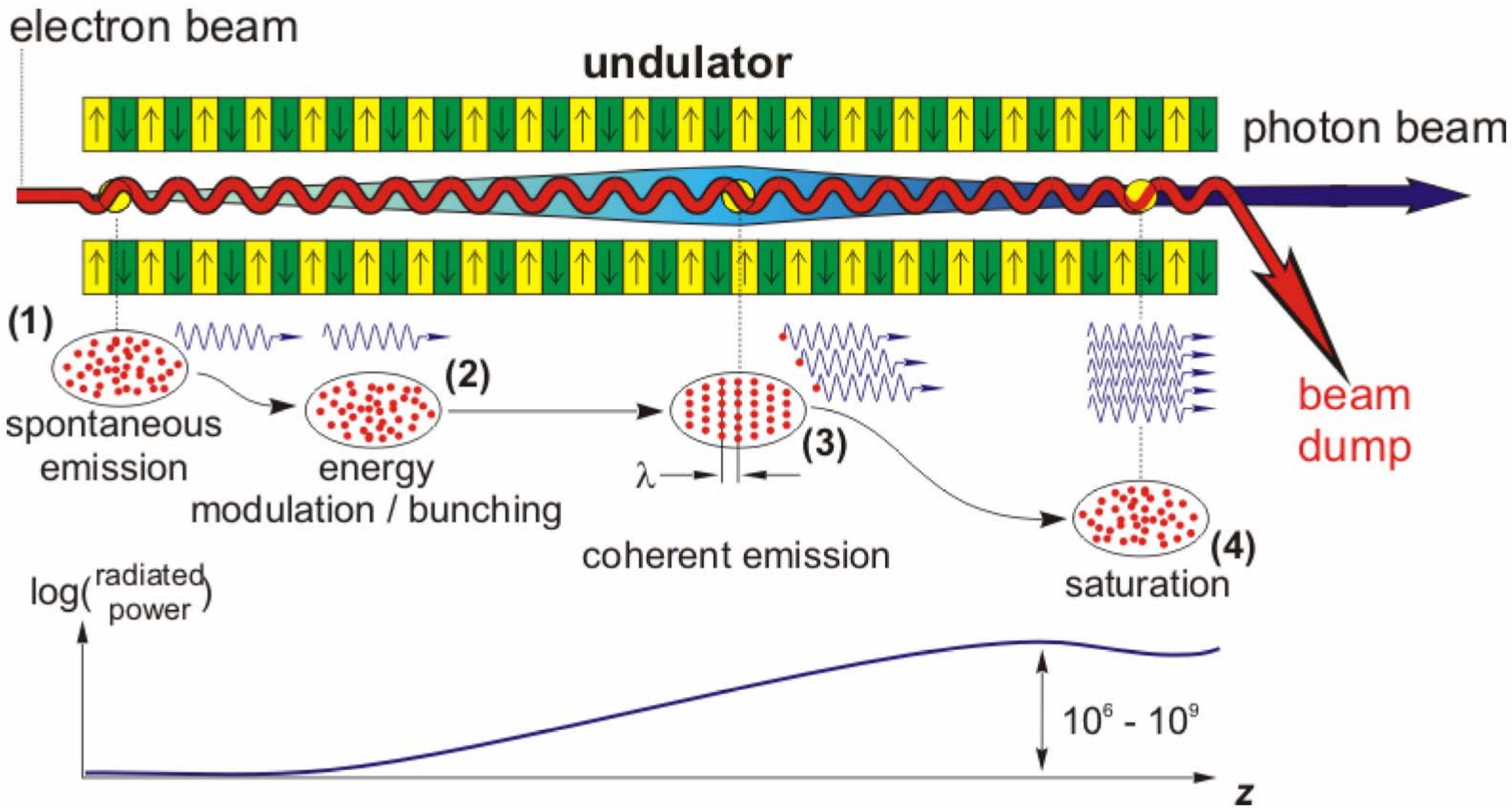




Lengeler et al. JSR, 6, 1153-1167 (1999)

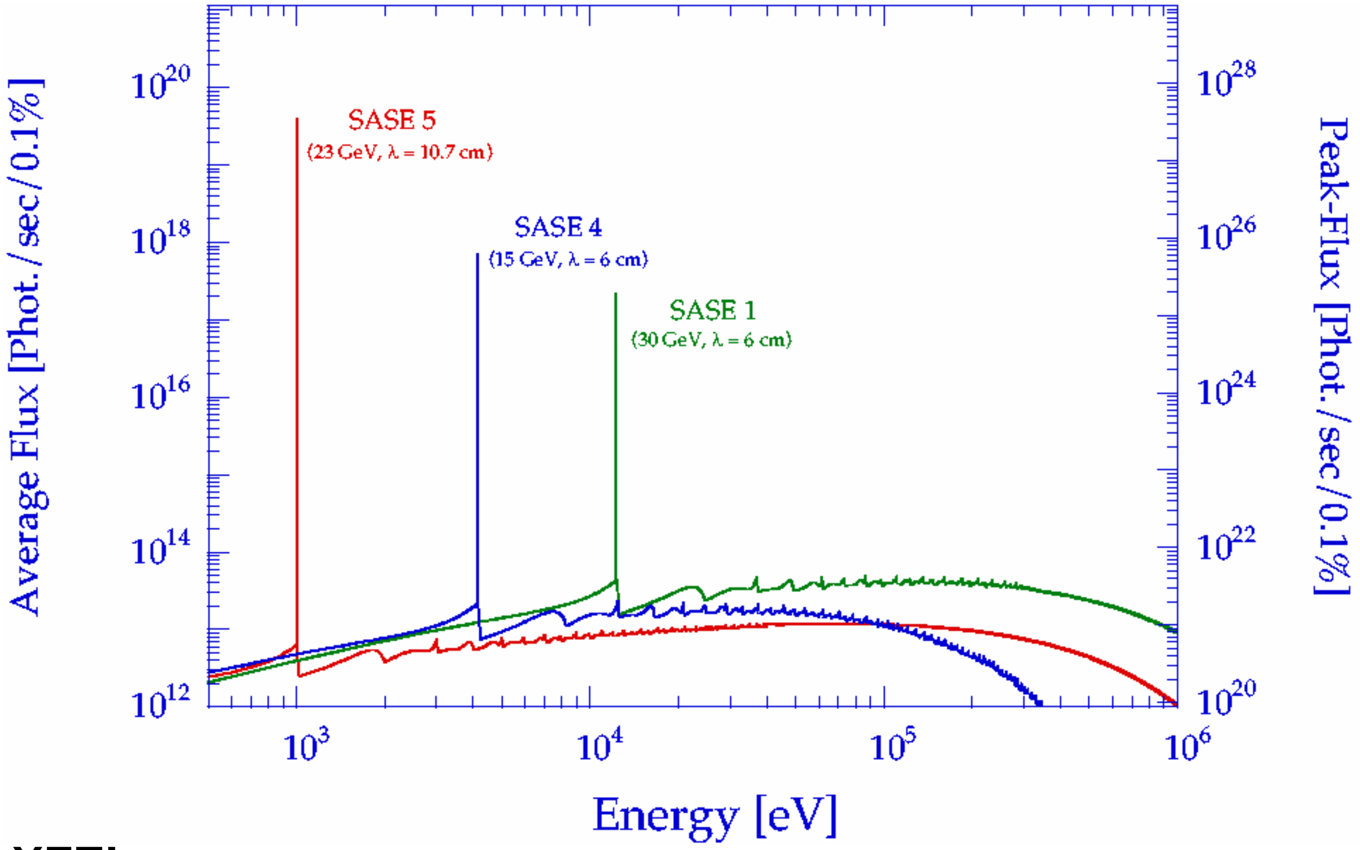
Experiments at Free-Electron Lasers

Generation of ultrashort, coherent light pulses via Self-Amplified Stimulated Emission (SASE)



Low gain	Exponential gain	Saturation

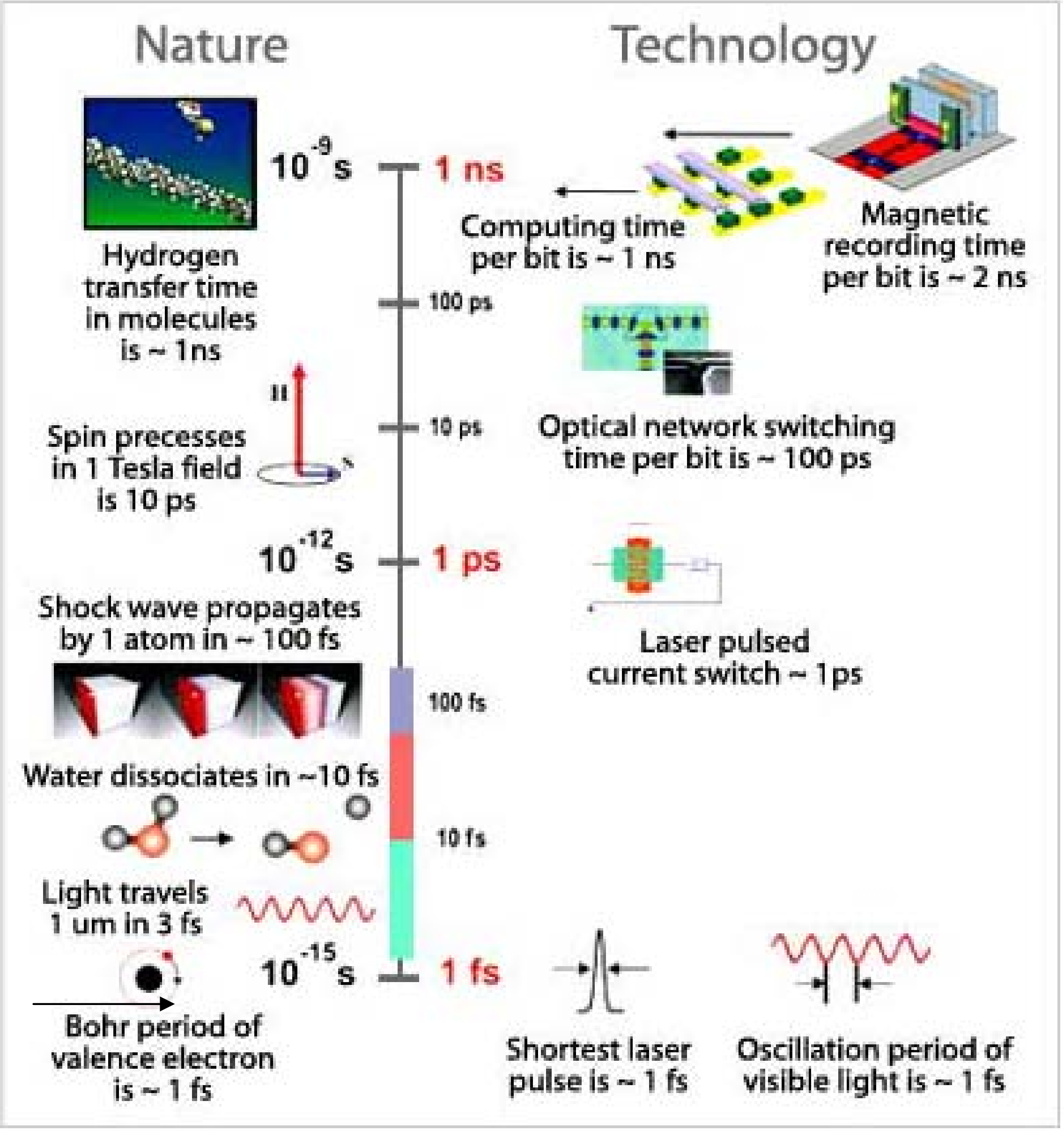
Characteristics of XFEL radiation



XFEL:

- **10^{12}-10^{13} photons/pulse**
- **100 fs pulse length**
- **intrinsic energy resolution: 0.1%**
- **from single pulse to ~40000 pulses/s**

Examples for ultrafast processes

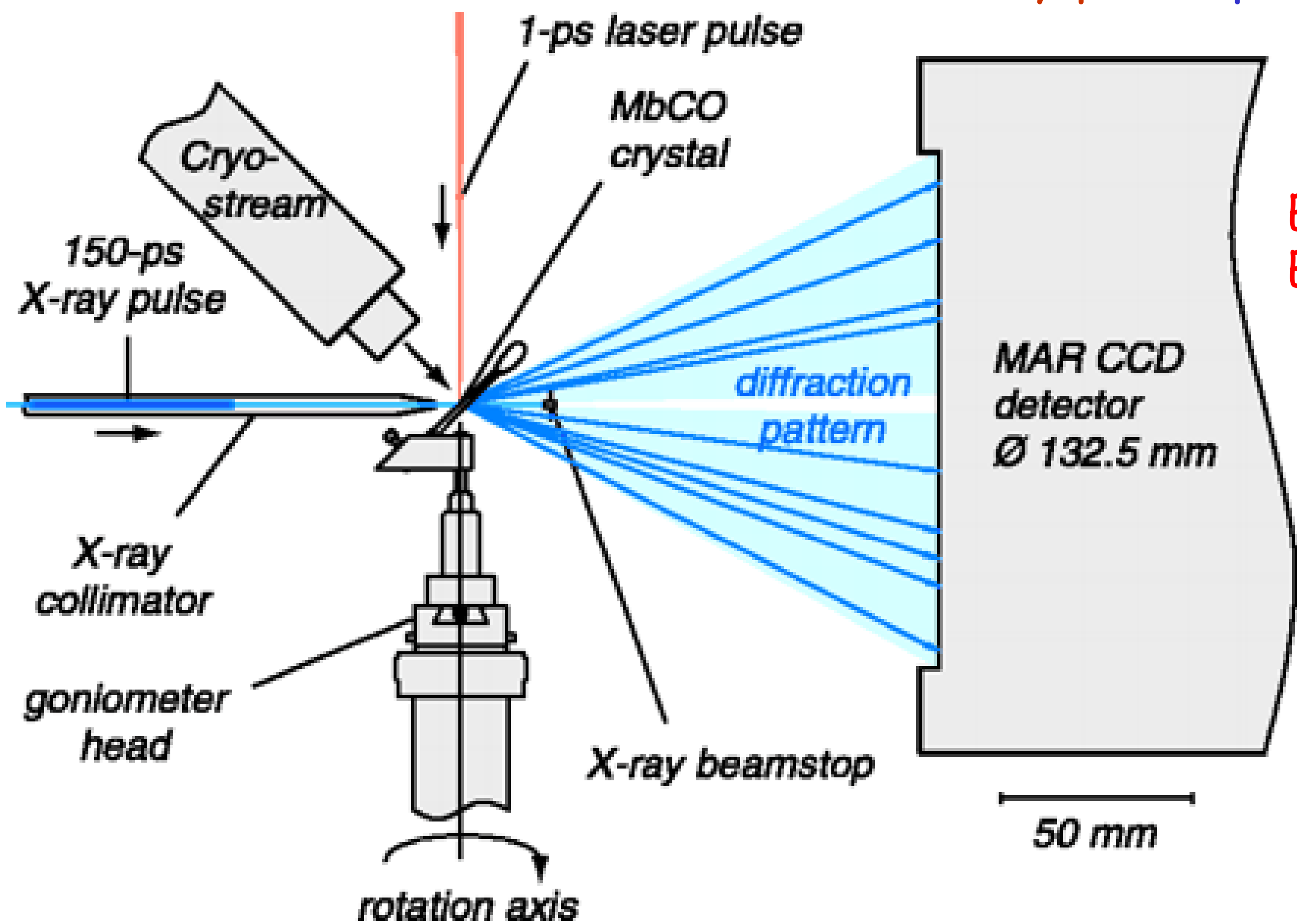


Fast processes can be studied with femtosecond (optical) lasers, but correlation with structural information on the atomic scale is only possible with x-rays !!

Time resolved investigation of the photo ionization of CO-myoglobin

- pump-probe technique
- X-ray crystallography

Variable delay between laser pump pulse and X-ray probe pulse.

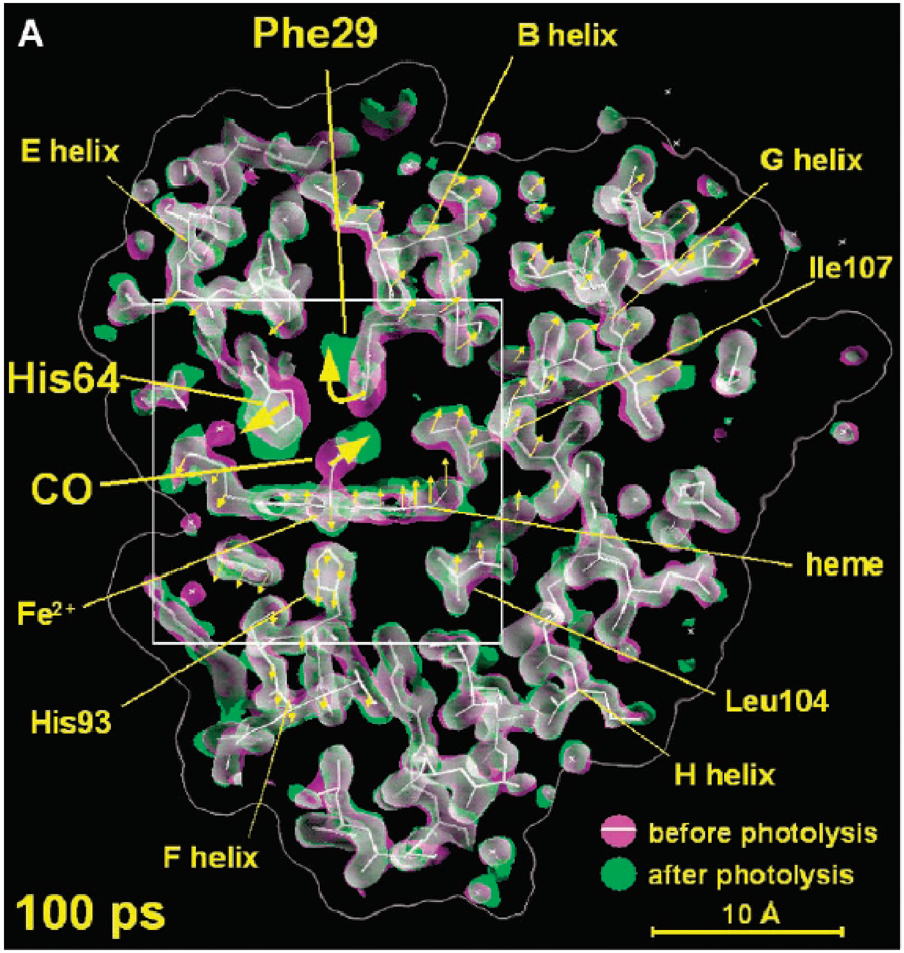


Experiment at ESRF, ID9

Schotte et al., Science 300(2003)1944

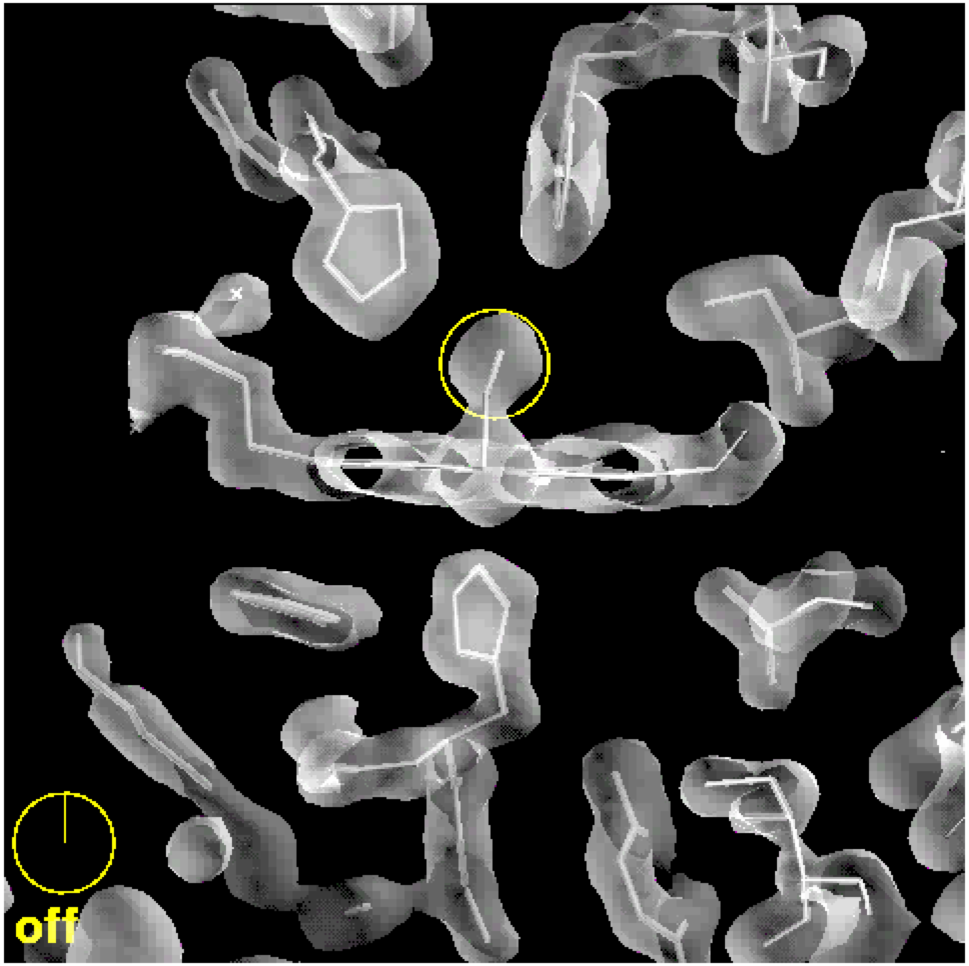
Time resolved crystallography

Structural changes during photolysis of CO-Myoglobin



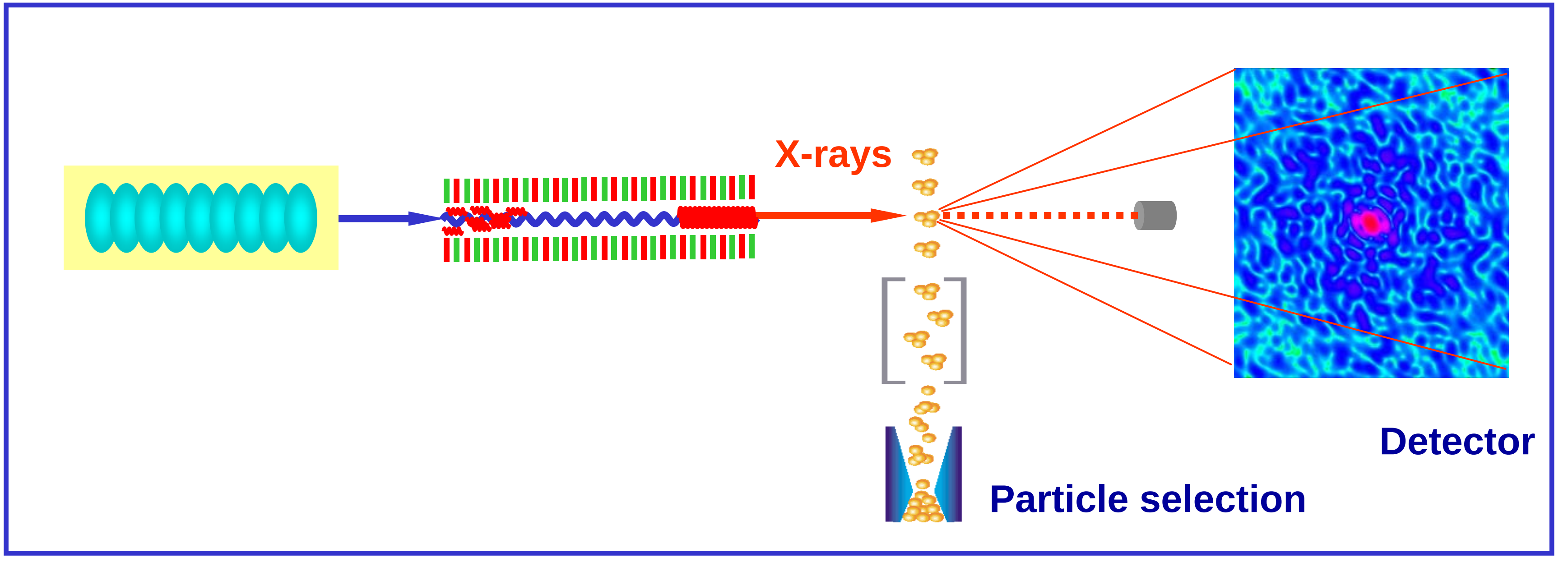
Time resolved crystallography

Structural changes during photolysis of CO-Myoglobin



XFEL: 1000 times better time resolution than today

A dream: Single - molecule diffraction



Potential for biomolecular imaging with femtosecond X-ray pulses

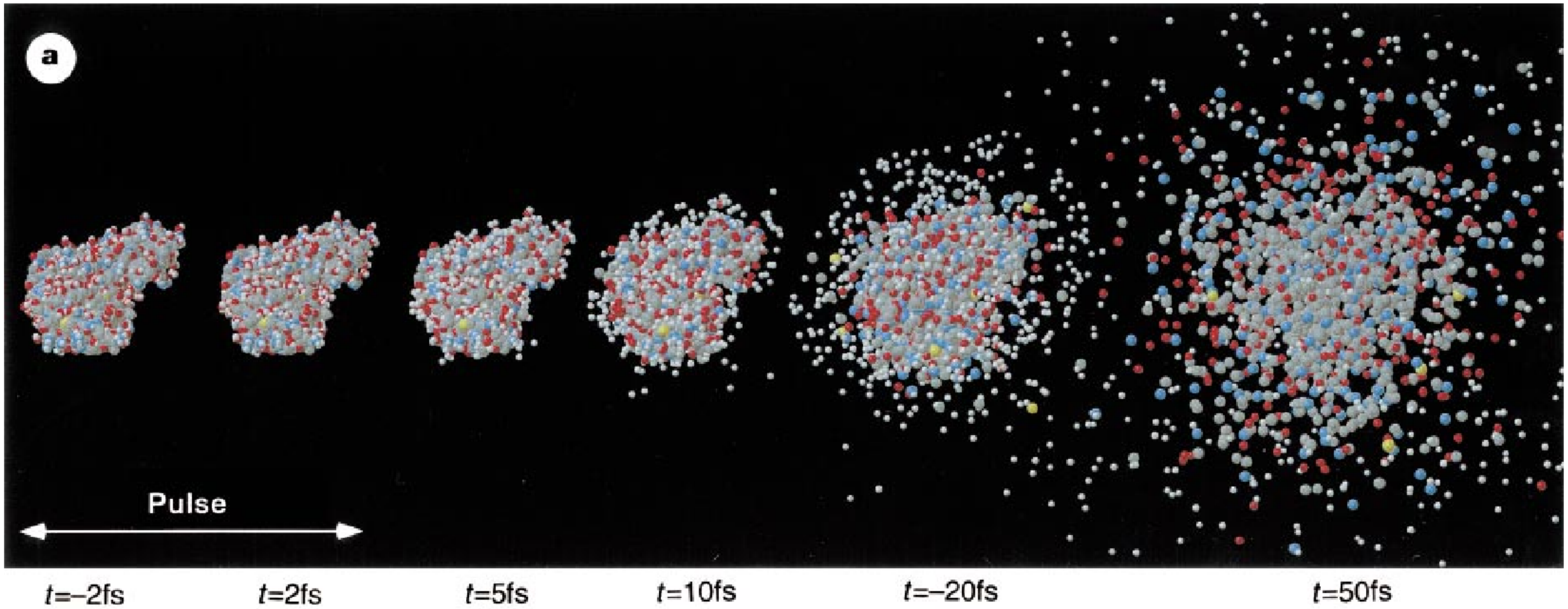
Richard Neutze*, Remco Wouts*, David van der Spoel*, Edgar Weckert†‡ & Janos Hajdu*

* *Department of Biochemistry, Biomedical Centre, Box 576, Uppsala University, S-75123 Uppsala, Sweden*
† *Institut für Kristallographie, Universität Karlsruhe, Kaiserstrasse 12, D-76128 , Germany*

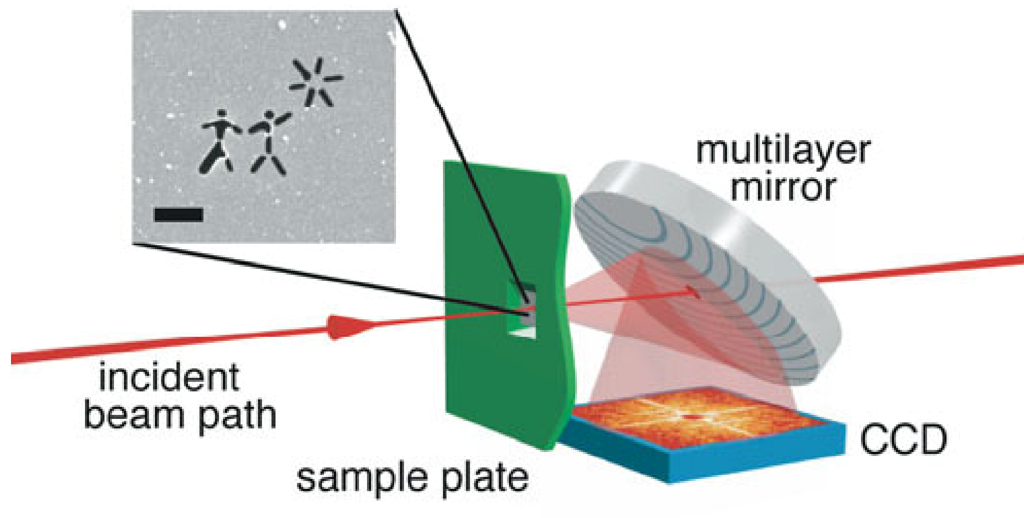
Nature 406, 752 (2000)

Theoretical calculations

Explosion of a biomolecule (T4 lysozyme) after exposure to a 2-fs XFEL pulse (E = 12 keV)

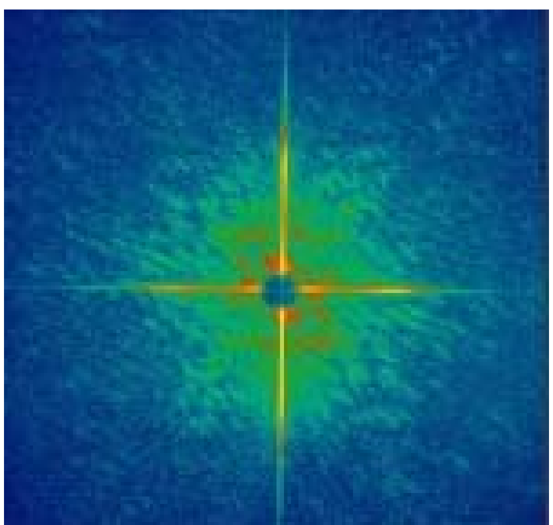


First demonstration of ultrafast coherent X-ray diffraction

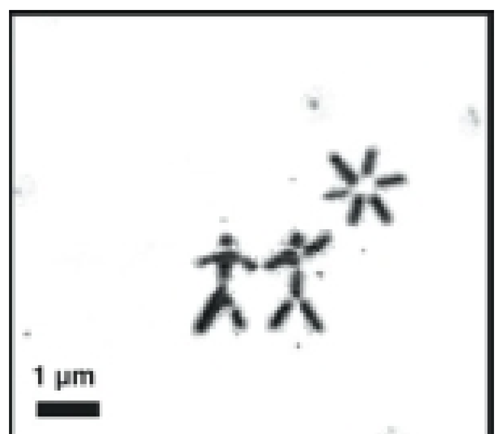


Incident FEL pulse:
30 fs, 32 nm,
3 x 10^{13} W cm^{-2}

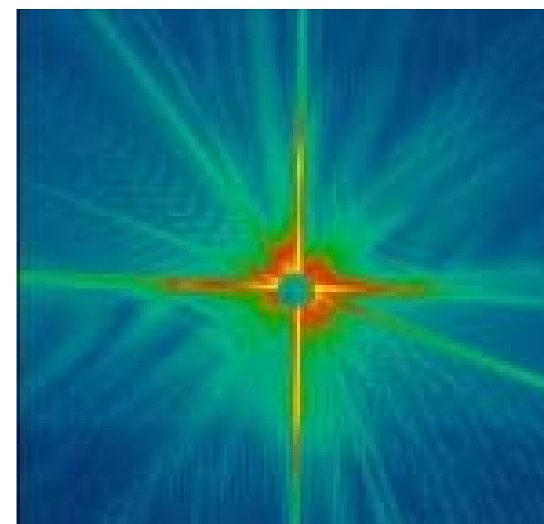
Pulse #1: Diffraction pattern



Reconstructed image



Pulse #2 sees structure destroyed by pulse #1



H. Chapman et al. Nature Physics 2, 839 (2006)

Conclusion: Structure diffracts the x-rays before being destroyed !