Microscopy with Coherent X-Rays: Following Physical and Chemical Processes on the Nanoscale

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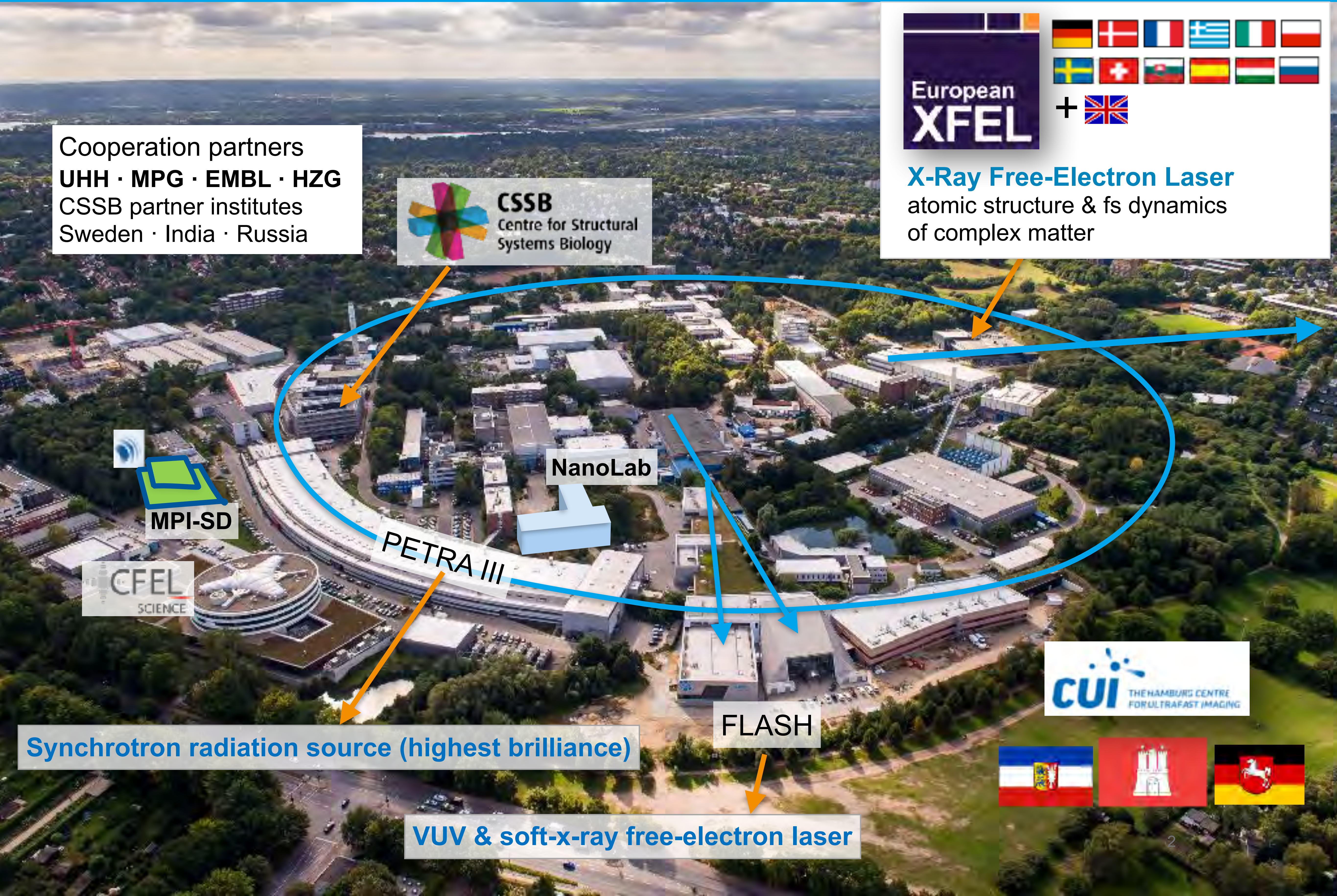
DESY Campus Hamburg



Cooperation partners

UHH · MPG · EMBL · HZG

CSSB partner institutes

Sweden · India · Russia

X-Ray Free-Electron Laser

atomic structure & fs dynamics of complex matter

Synchrotron radiation source (highest brilliance)

VUV & soft-x-ray free-electron laser

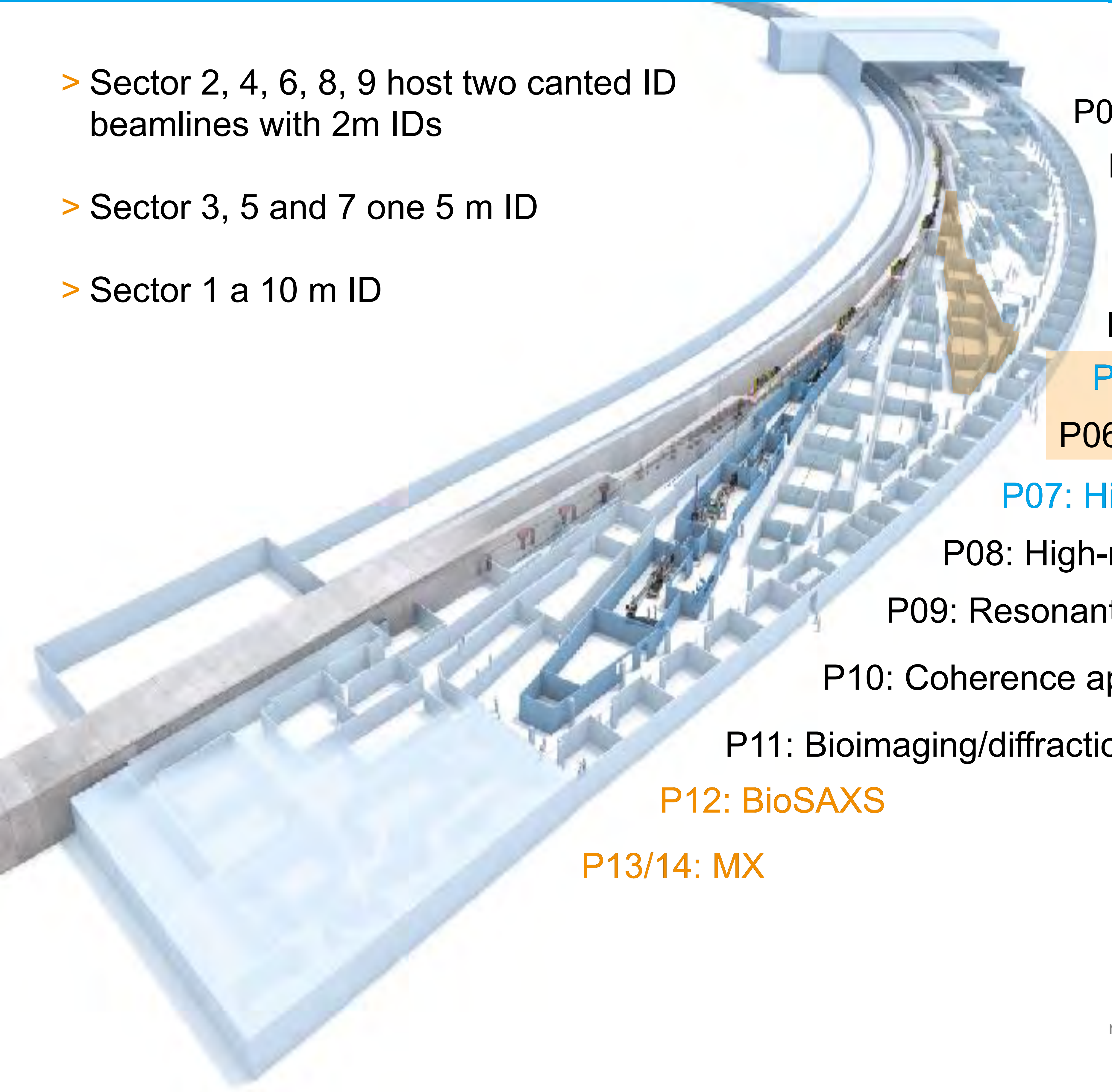
PETRA III: DESY's Brilliant Hard X-Ray Source

- **particle energy:** 6 GeV
- **stored current:** 100 mA (top-up)
- **emittance:** **1.1 nm rad**
- **circumference:** **2304 m**
- **# of undulators:** 25 (incl. canted)
- **# of experiments:** 50
- **X-ray wavelength:** 10 – 0.05 Å
- **annual operation:** 5000 h (for users)

- **built in 1978 for high-energy physics**
- **rebuilt as a synchrotron radiation source starting in 2007**
- **user operation since 2010**
- **extension added: March 2014 - April 2015**

Max von Laue Hall: 9 Sectors – 14 Beamlines

- Sector 2, 4, 6, 8, 9 host two canted ID beamlines with 2m IDs
- Sector 3, 5 and 7 one 5 m ID
- Sector 1 a 10 m ID



P01: Dynamics beamline, IXS, NRS

P02: Powder diffraction extreme conditions

P03: Micro-, nano-SAXS, WAXS

P04: Variable polarization XUV

P05: Micro-, nano-tomography

P06: Hard x-ray micro-, nanoprobe

P07: High energy materials science

P08: High-resolution diffraction

P09: Resonant scattering/diffraction

P10: Coherence applications

P11: Bioimaging/diffraction

P12: BioSAXS

P13/14: MX

Partly run by HZG

Run by EMBL

PETRA III Extension

PETRA III Experimental Hall ``Paul P. Ewald”

P65: X-ray Absorption Spectroscopy

P64: X-ray Absorption Spectroscopy

P61: High-energy x-ray engineering materials

© Edgar Weckert

PETRA III Experimental Hall ``Ada Yonath”

P 22 Nano spectroscopy 🇮🇳

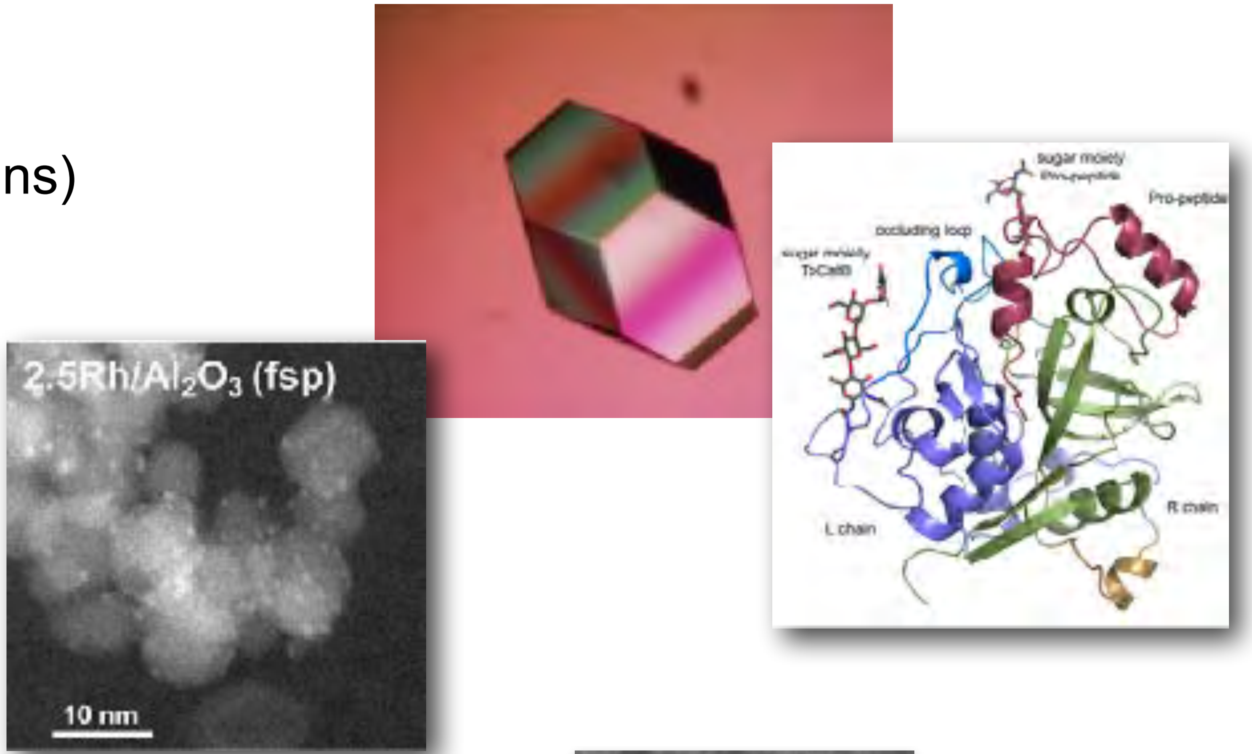
P 23 Nano diffraction 🇩🇪 🇷🇺

P 21 High-energy X-ray materials science 🇸🇪

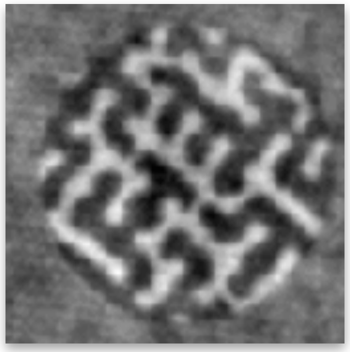
P 24 Chemical crystallography

PETRA III: Research Topics

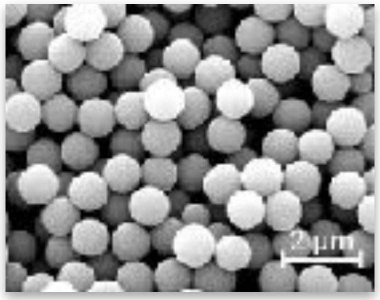
- Life sciences
  - structure of proteins (small crystals, membrane proteins)
  - cell physiology (e. g. photosynthesis)
  - drug design
- Chemistry (e. g. catalysis)
  - heterogenous catalysis on nanoscale
  - surface reactions
  - battery research (electro chemistry)



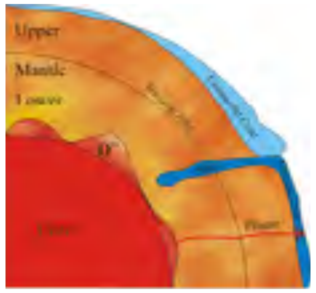
- Solid-state physics and chemistry
  - ordering of electronic degrees of freedom
  - single defects and structure and dynamics (e. g., domain boundaries)
  - magnetic thin films (electronic structure at surface and interfaces)
  - dynamics of strongly correlated electron systems
  - multiferroics
  - (photo-induced) phase transitions



- Soft matter
  - properties of colloids, complex fluids
  - glass transition



- Environmental science
  - environmental behavior of various elements (distribution and chemistry)
  - uptake of toxins by biological systems
- …



X-ray Microscopy

Broad field of applications:

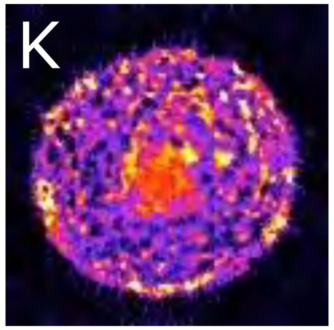
- Main advantage: large penetration depth
  - → *in-situ* and *operando* studies
  - → 3D bulk analysis without destructive sample preparation
- X-ray analytical contrasts: XRD, XAS, XRF, ...
  - → elemental, chemical, and structural information

Today: „mesoscopic gap“

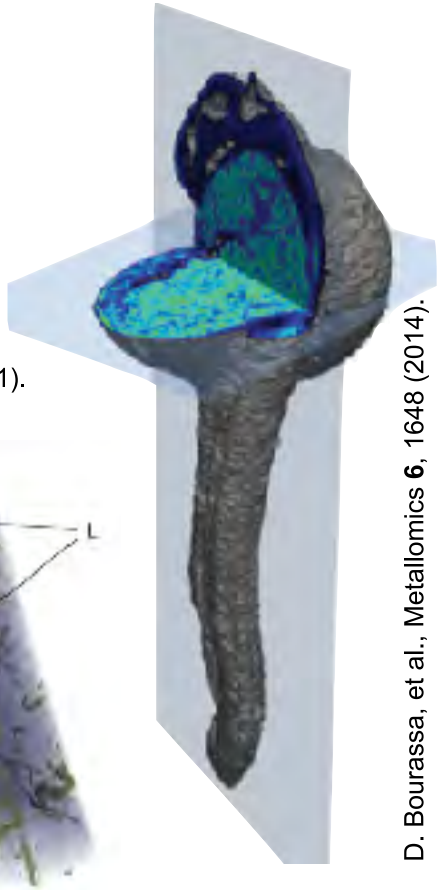
real-space resolution: down to about 10 nm

XRD and XAS: atomic scale

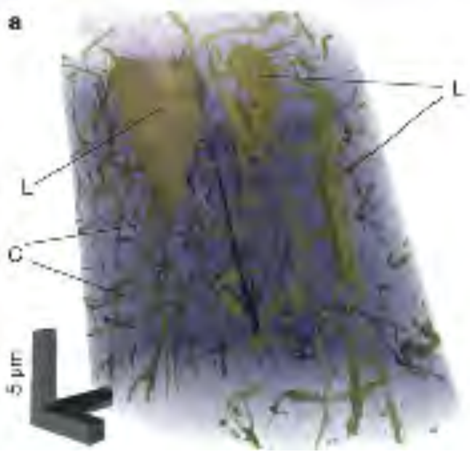
Many interesting physics and chemistry (e. g. catalysis) at the 1 - 10 nm scale!



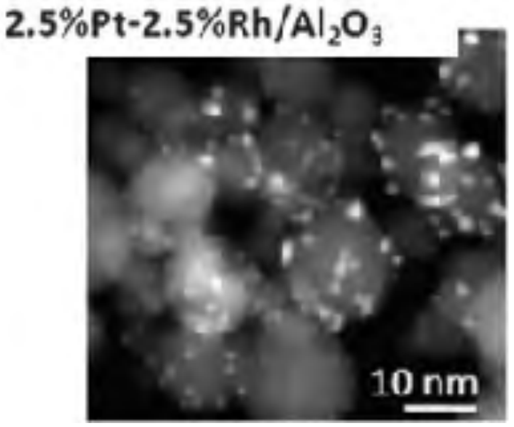
C. G. Schroer, APL **79**, 1912 (2001).



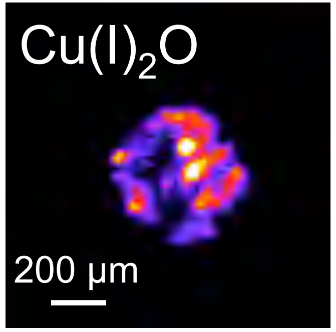
D. Bourassa, et al., Metallomics **6**, 1648 (2014).



M. Dierolf, et al., Nature **467**, 436 (2010).



catalysts



C. G. Schroer, et al., APL **82**, 3360 (2003).

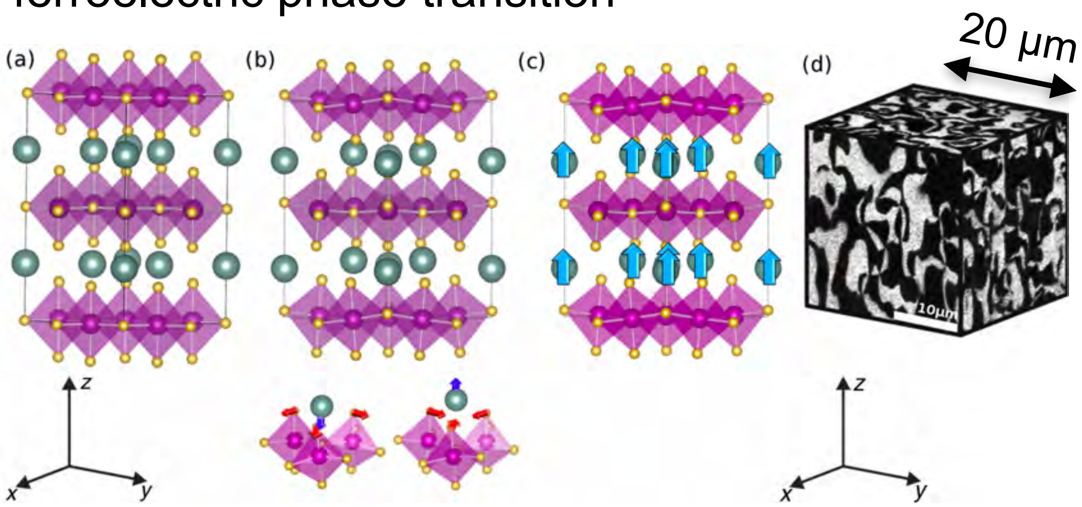
X-ray Microscopy

Many interesting physics and chemistry questions:

investigate local states:

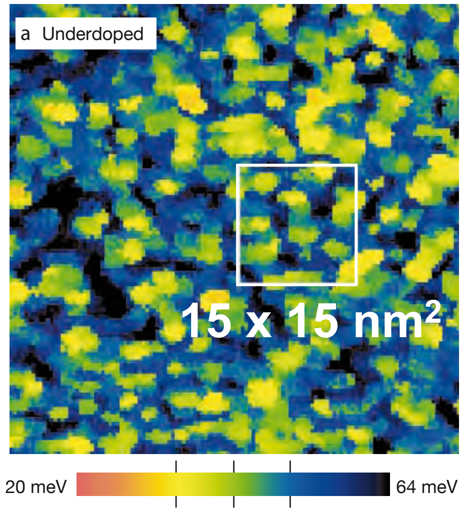
- individual defects (0D): changes in electron density, charge ordering
- (structural) domain boundaries (2D), e. g., in multiferroics
- mesoscopic dynamics at (solid-state) phase transitions
- catalytic nanoparticles (under reaction conditions)
- ...

ferroelectric phase transition



Griffin, et al., PRX **2**, 041022 (2012).

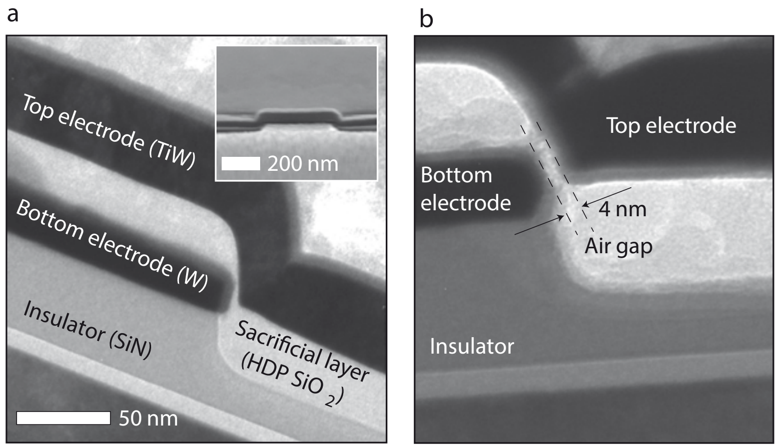
variation of supercond. gap



Lang, et al., Nature **415**, 412 (2002).

Mesoscale also very important for nanotechnology (e. g., defects in devices)!

nanoelectromechanical switch

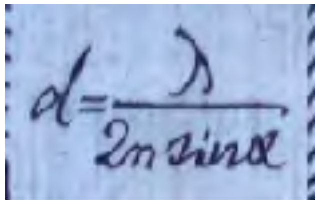


Lee, et al., Nature Nanotech. **8**, 36 (2012).

Current State of X-Ray Microscopy

Conventional x-ray microscopy

→ optics limit spatial resolution: diffraction limit



$$d=\frac{\lambda}{2n\sin\alpha}$$

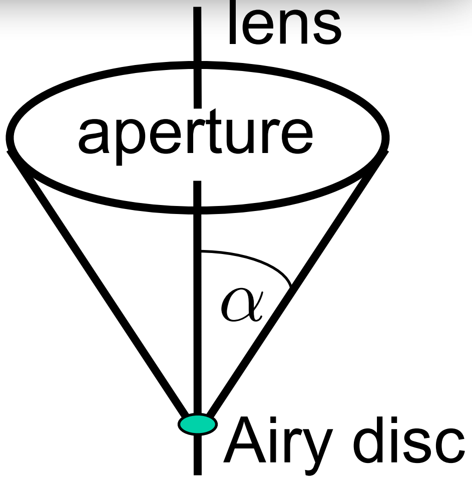
(typically: a few tens of nanometers)

optics are technology limited!

Theoretical extrapolation of x-ray optical performance to the atomic level.

[PRB **74**, 033405 (2006); H. Yan, et al., PRB **76**, 115438 (2007)]

Ernst Abbe



Coherent x-ray imaging techniques (CXDI, ptychography)

→ no imaging optic!

→ limited by statistics of far-field diffraction patterns ...

highest resolution: a few nanometers, focusing coherent beam

[PRL **101**, 090801 (2008); Y. Takahashi, et al., PRB **80**, 054103 (2009); A. Schropp, et al., APL **100**, 253112 (2012); D. A. Shapiro, et al., Nat. Phot. **8**, 765 (2014)]

Hard X-ray Scanning Microscopy at PETRA III

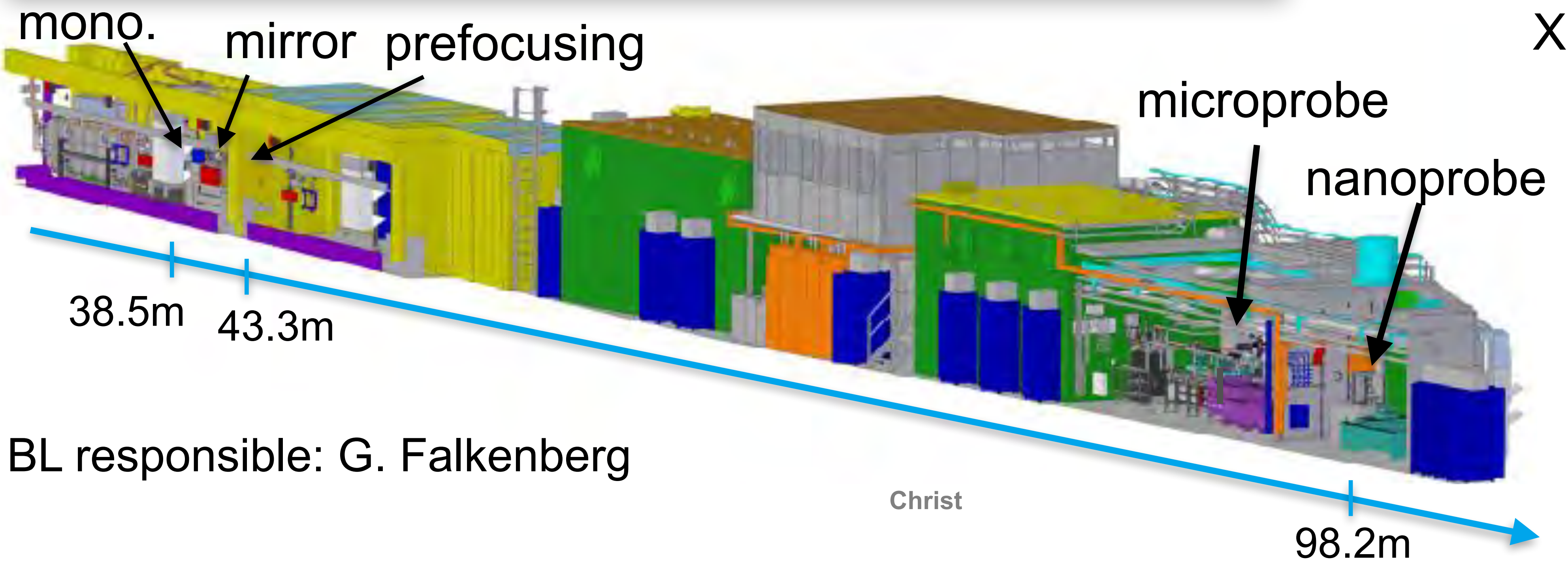
Microscope:

~98 m from source

different contrasts:

- fluorescence
- diffraction (SAXS, WAXS)
- absorption (XAS)
- ptychography & CXDI

spatial resolution:
down to < 50 nm
down to < 5 nm (CXDI)



X-ray energy:
10 - 50 keV

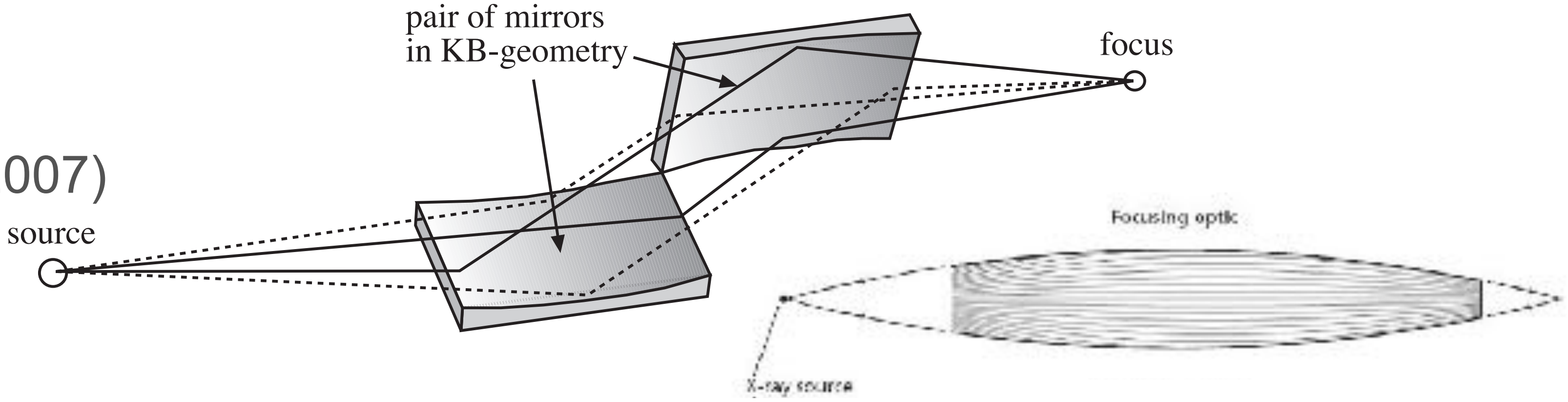
Nucl. Instrum. Meth. A **616** (2-3), 93 (2010).

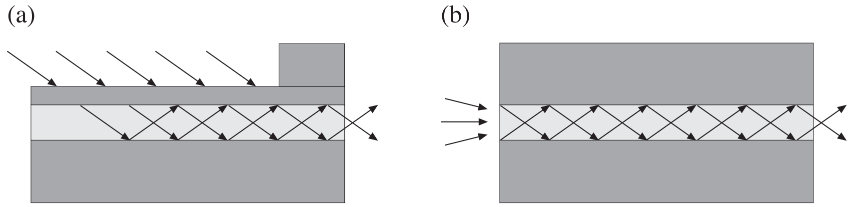
BL responsible: G. Falkenberg

Nanofocusing Optics

reflection:

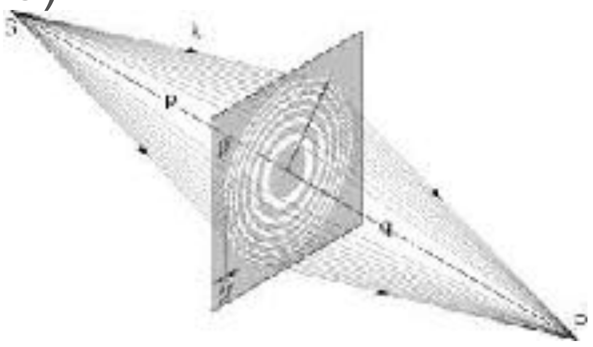
- mirrors (25 nm)
  H. Mimura, et al., APL **90**, 051903 (2007)
- capillaries
- wave guides (~10 nm)
  S. P. Krüger, et al., J. Synchrotron Rad. **19**, 227 (2012)

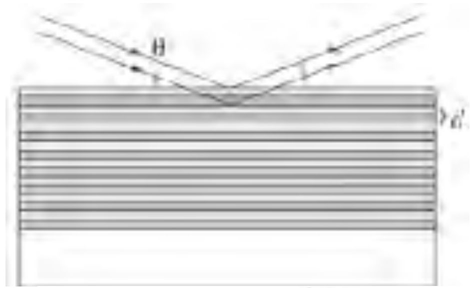


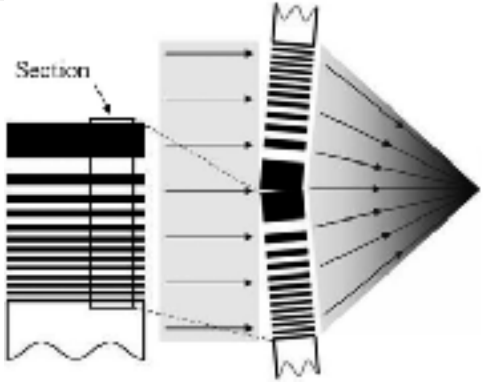


diffraction:

- Fresnel zone plates (< 10 nm)
  J. Vila-Comamala, et al., Ultramic. **109**, 1360 (2009)
- multilayer mirrors (7 nm)
  H. Mimura, et al., Nat. Phys. **6**, 122 (2010)
- multilayer Laue lenses (8 nm)
  A. Morgan, et al., Sci. Rep. **5**, 09892 (2015)
- bent crystals

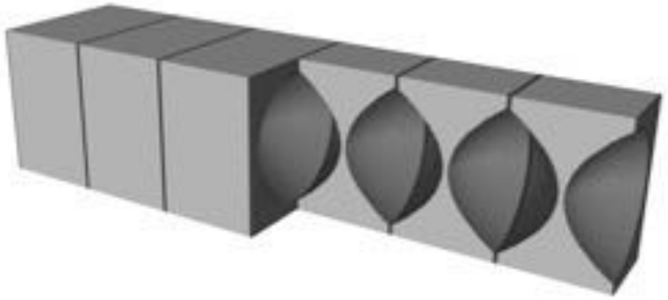






refraction:

- lenses (43 nm, 18 nm)
  C. G. Schroer, et al., AIP Conf. Ser. **1365**, 227 (2011)



Refraction

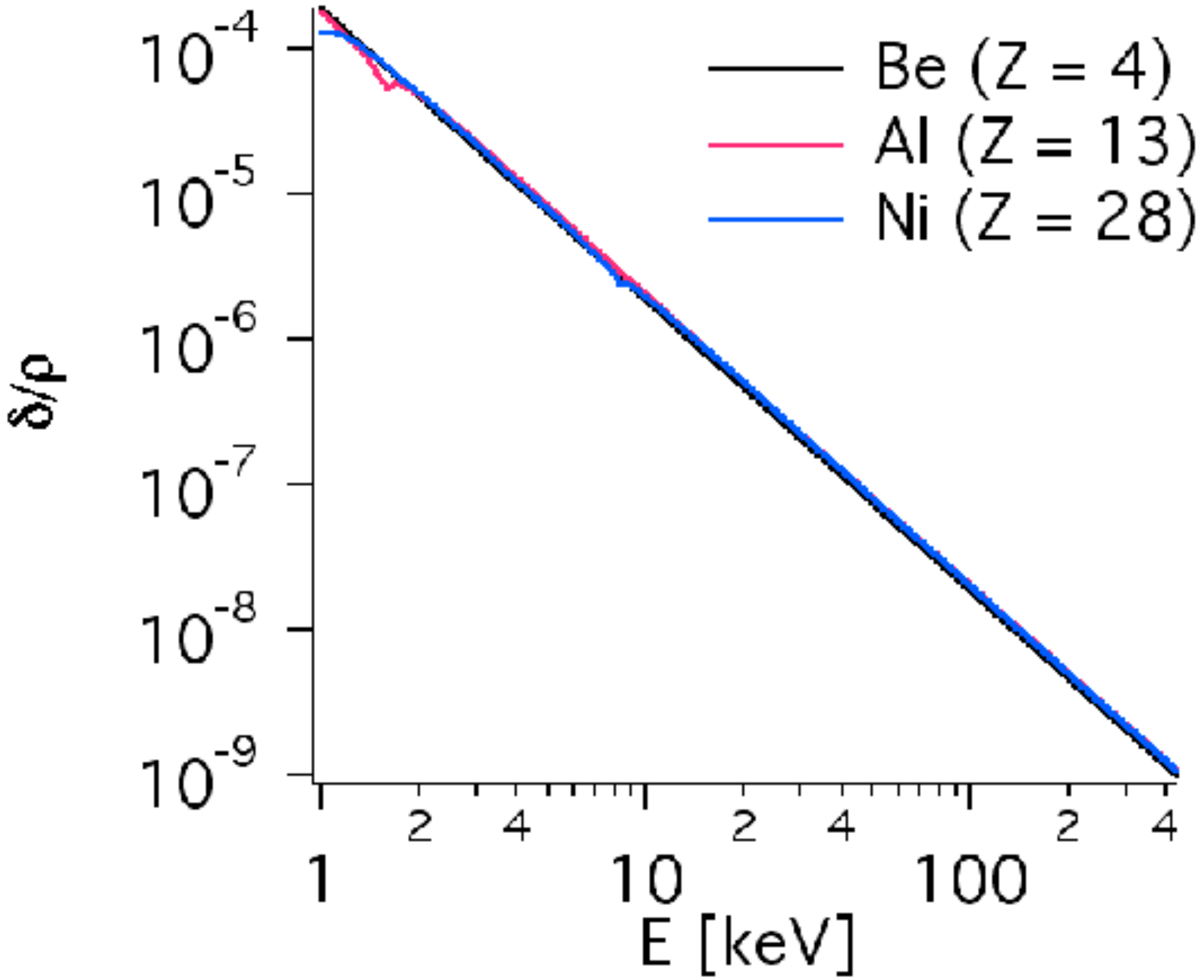
$$n = 1 - \delta + i\beta, \quad \delta > 0$$

Vacuum is optically denser than matter!

$$\delta = \frac{N_\mathrm{A}}{2\pi} r_0 \lambda^2 \rho \frac{Z + f'}{A}$$

specific refraction:

- independent of material
- very week



Absorption

$$n = 1 - \delta + i\beta, \quad \delta > 0$$

Lambert-Beer law:

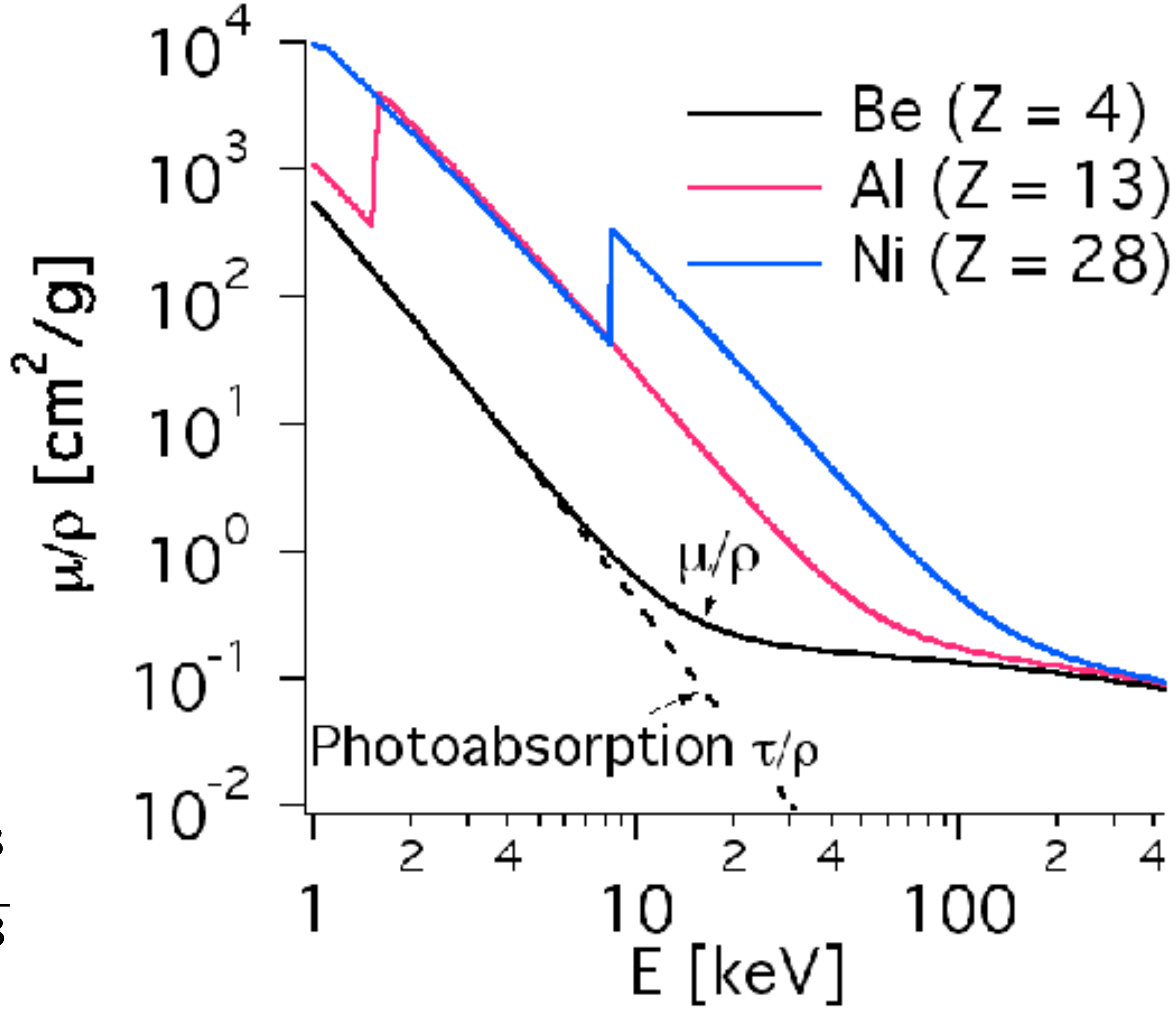
$$I(x) = I_0 e^{-\mu x}$$

attenuation coefficient μ:

$$\mu = \frac{4\pi\beta}{\lambda}$$

two main contributions:

- photoabsorption $\tau \propto \frac{Z^3}{E^3}$
- Compton scattering μ_C

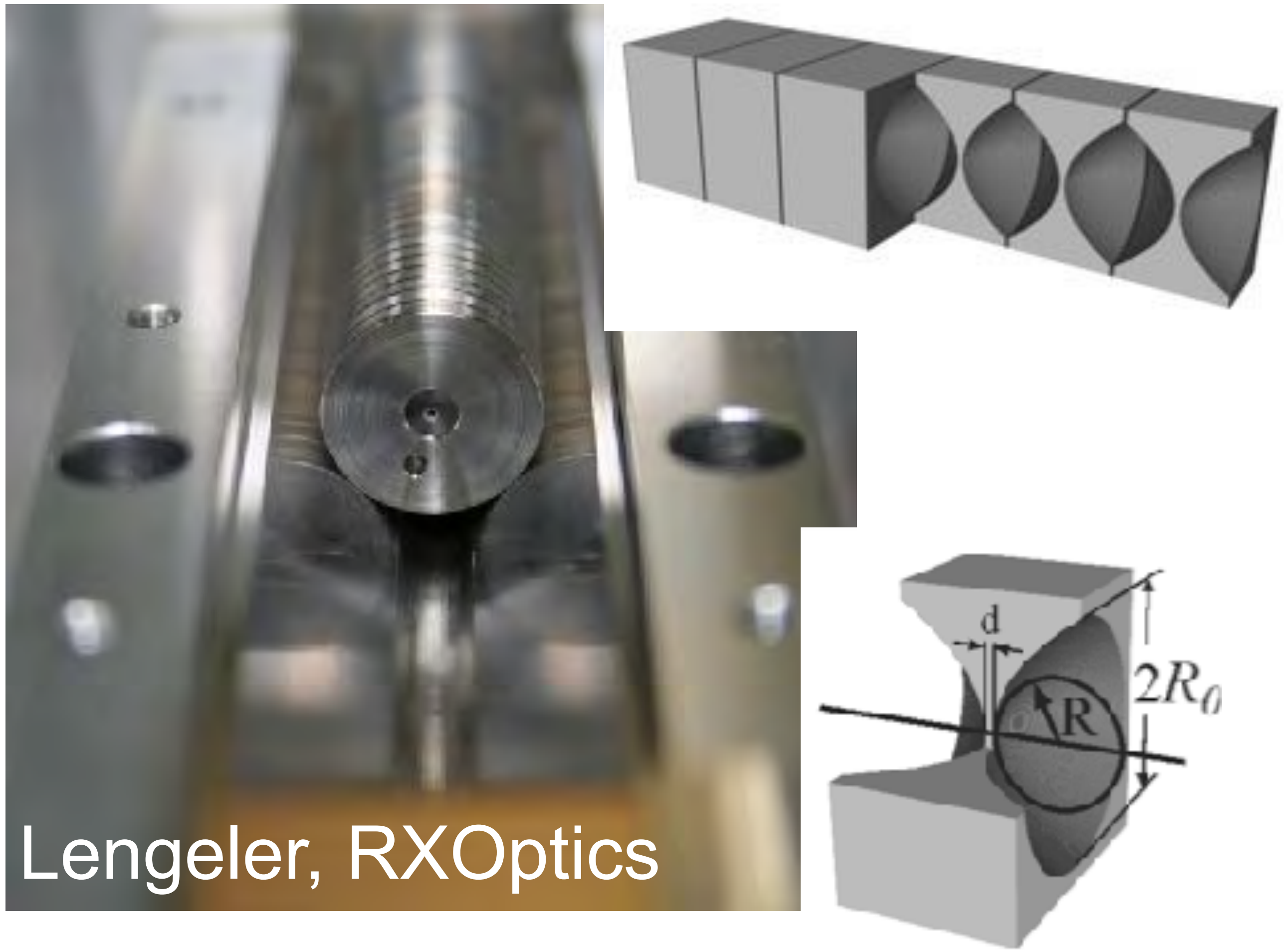


for comparison: $\mu_{glas} = 10^{-7}\ \mathrm{cm}^{-1}$ for visible light!

Refractive X-Ray Lenses

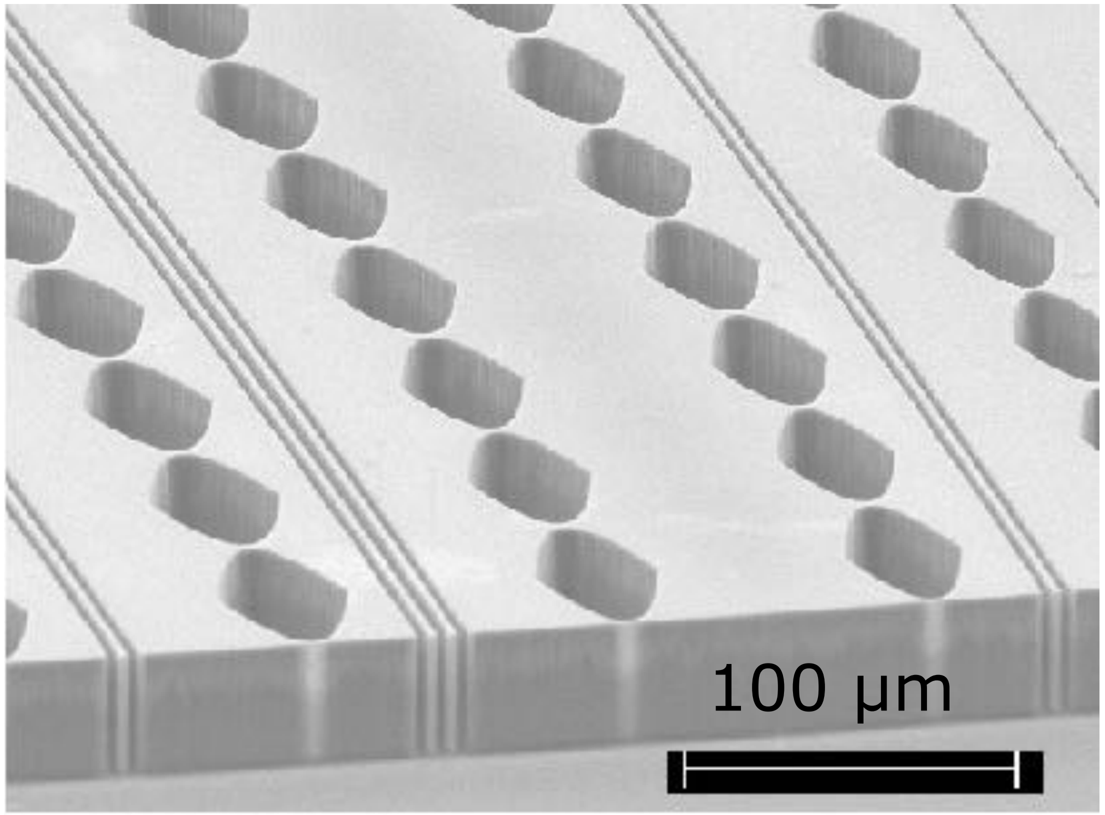
- first realized in 1996 (Snigirev et al.)
- a variety of refractive lenses have been developed since
- applied in full-field imaging and scanning microscopy
- most important to achieve optimal performance:

parabolic lens shape



Lengeler, RXOptics

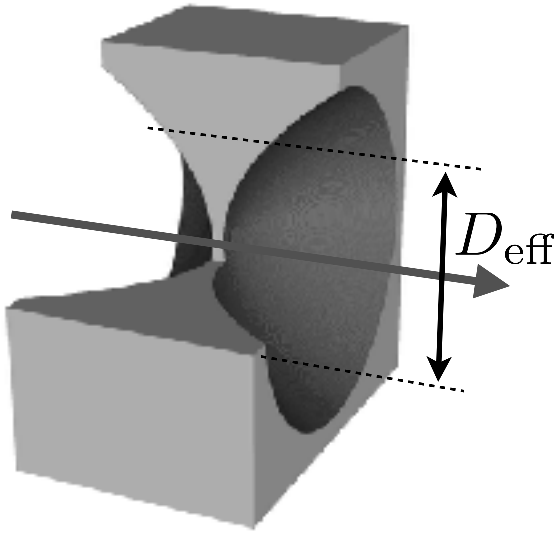
nanofocusing lenses

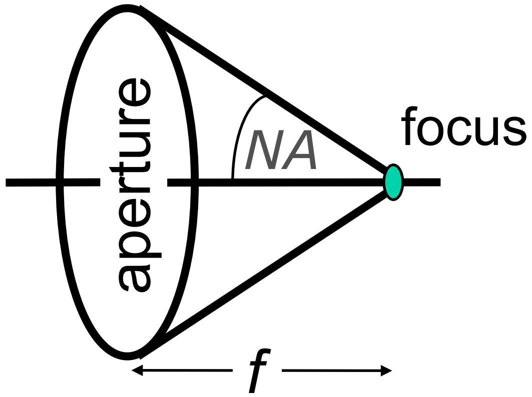


Nanofocus

Large focal length *f*: aperture limited by absorption

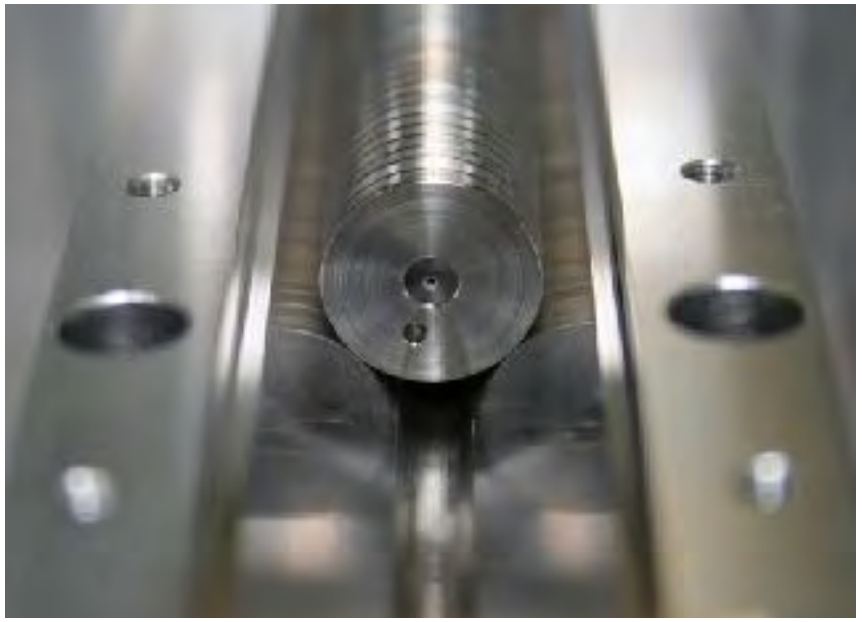
$$D_{\text{eff}} = 4\sqrt{\frac{f\delta}{\mu}} \propto \sqrt{f}$$





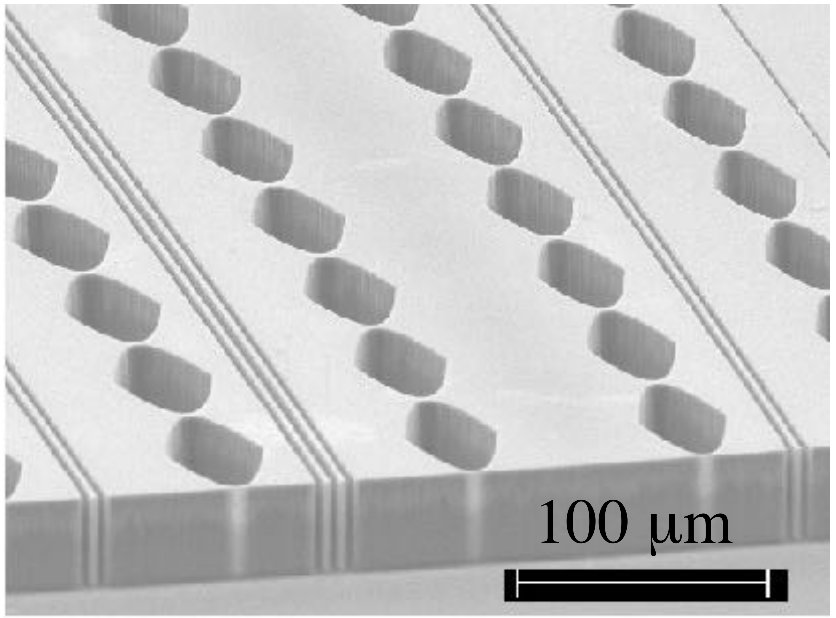
→ minimize μ/δ (⇒ small atomic number Z)

→ $NA = \frac{D_{\text{eff}}}{2f} \propto \frac{1}{\sqrt{f}}$ (⇒ minimize focal length *f*)

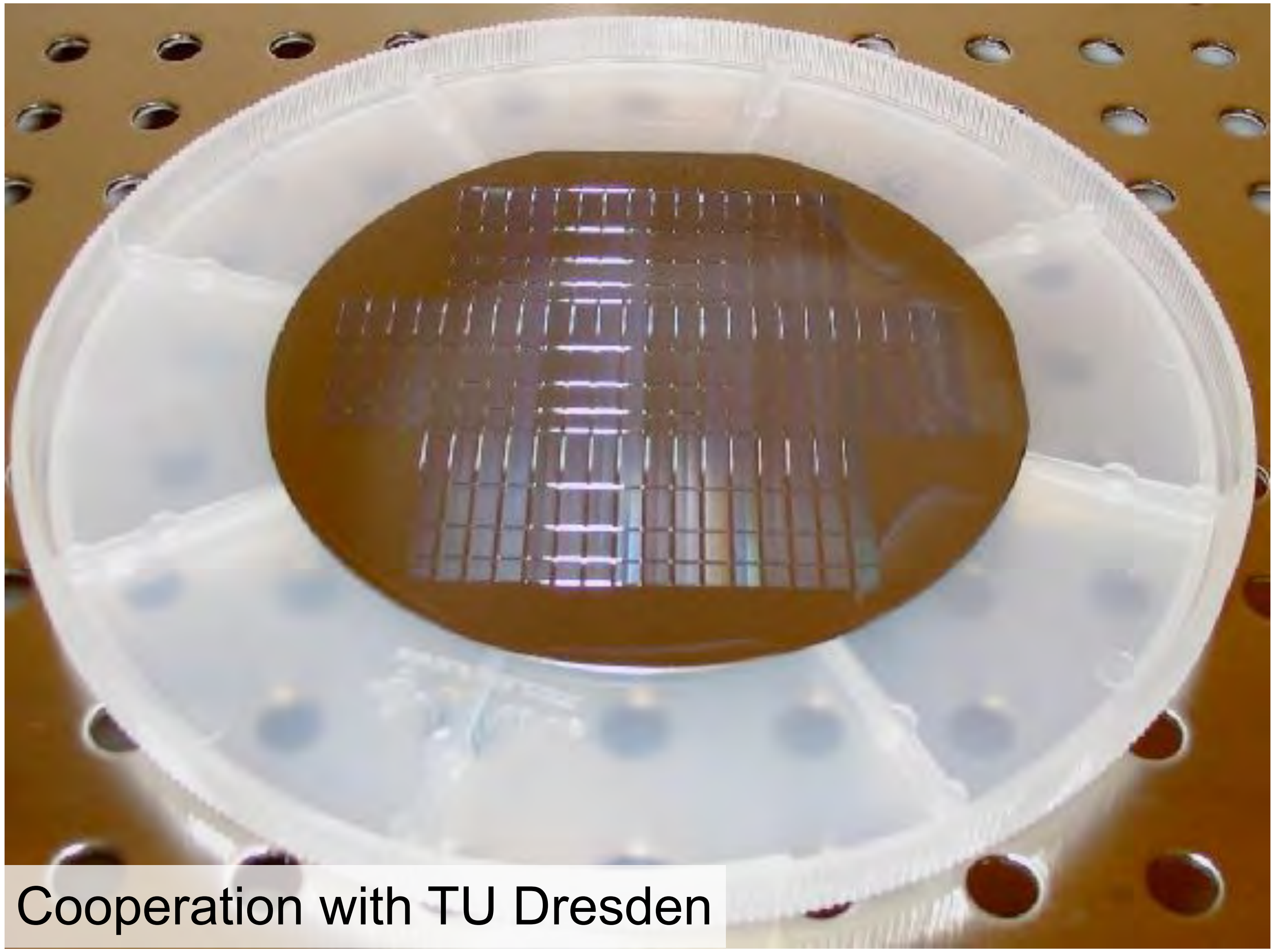


transition to nanofocusing lenses (NFLs)

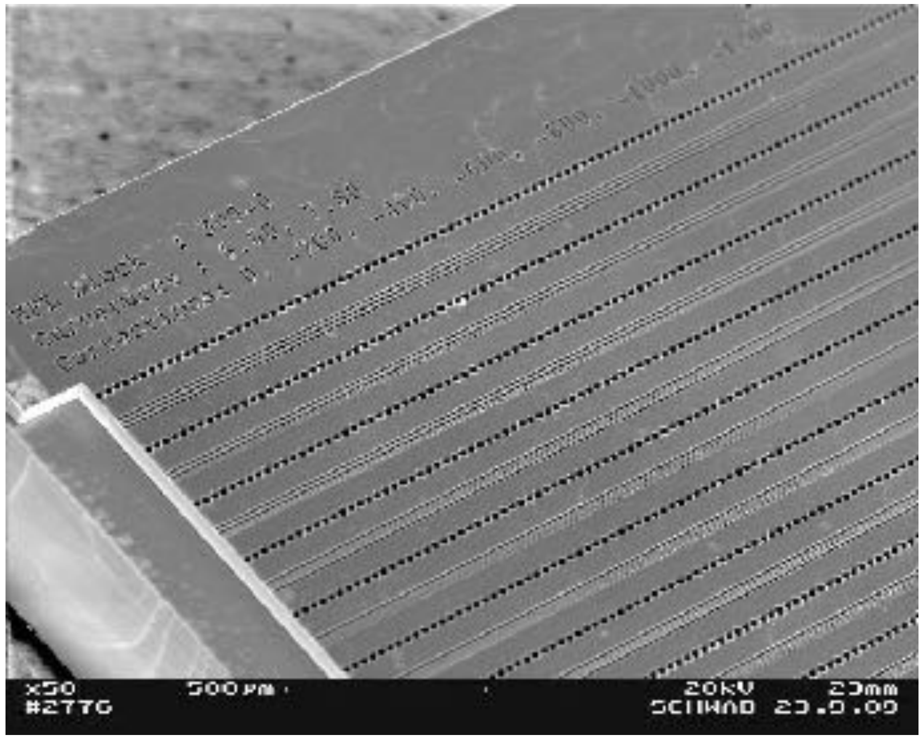
→

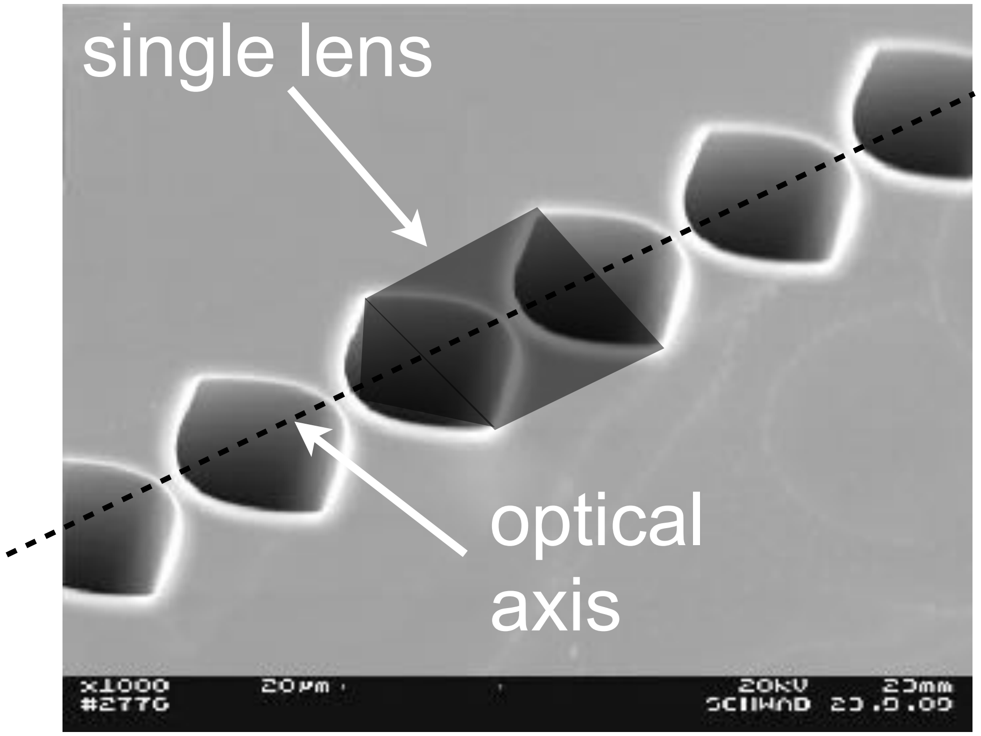


Nanofocusing Lenses (NFLs) Made of Silicon



Cooperation with TU Dresden





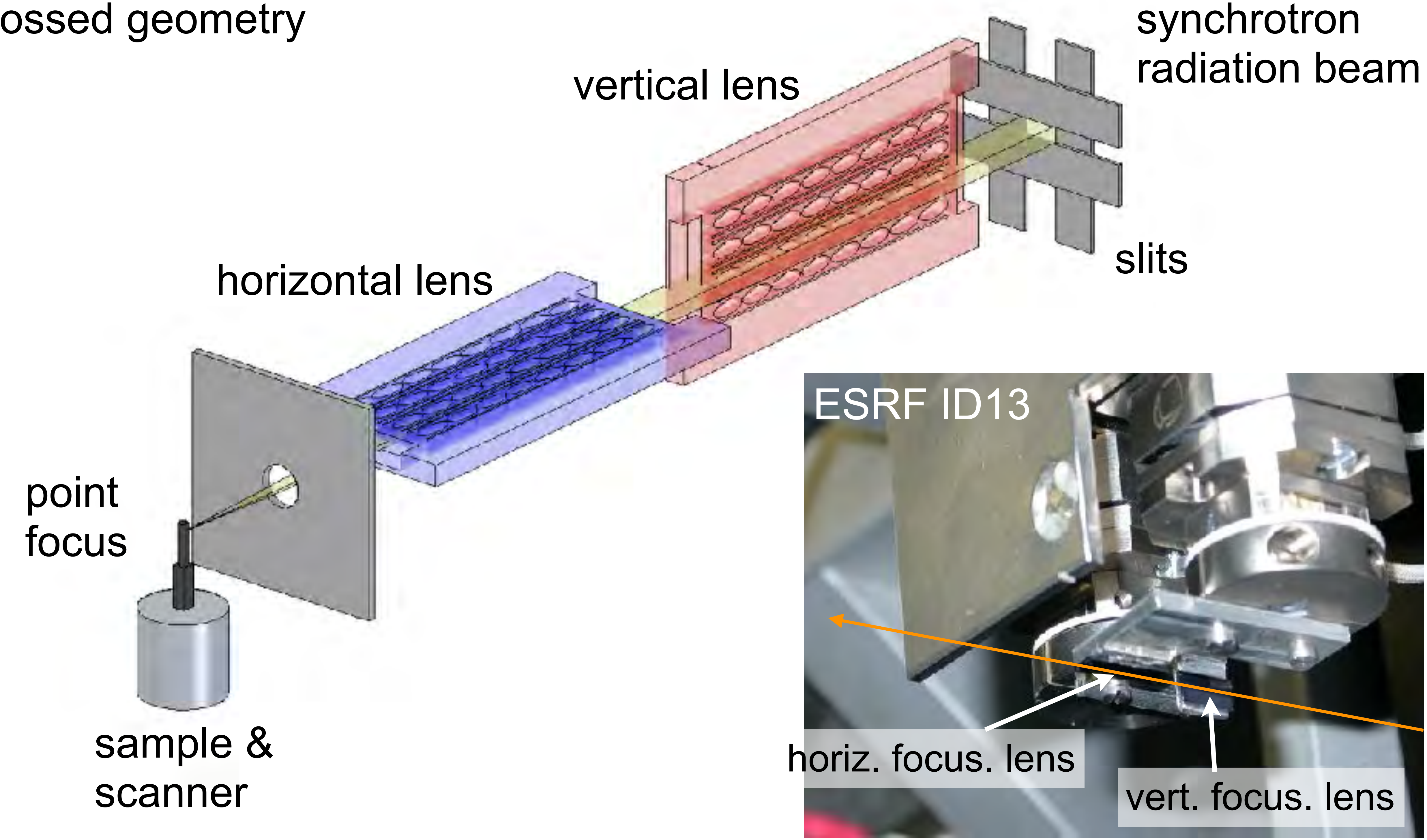
APL **82**, 1485 (2003).

3136 NFLs on wafer!
about 600000 single lenses!

→ high accuracy, reproducibility

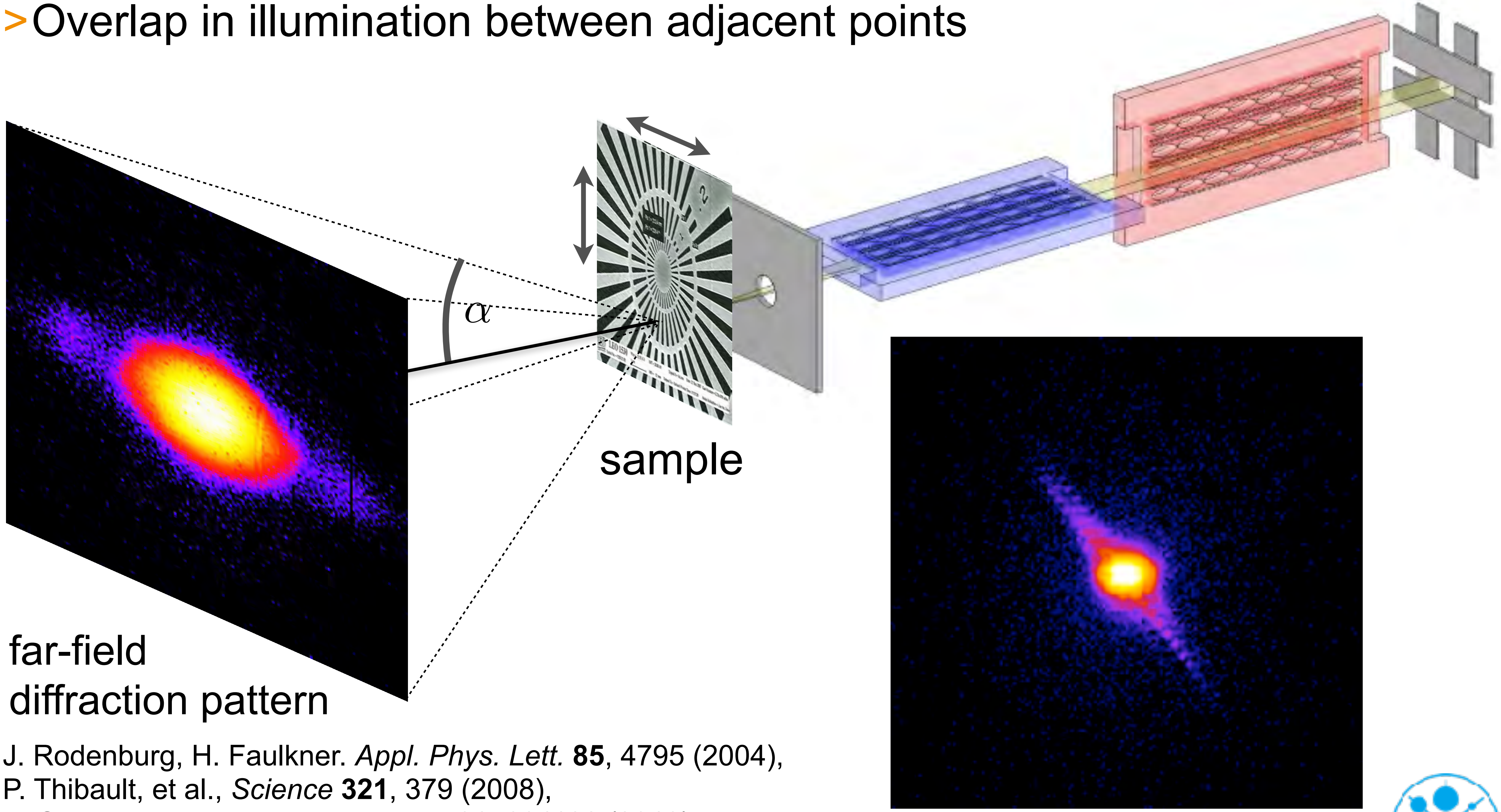
Nanofocusing Lenses (NFLs)

Point focus requires two lenses in crossed geometry



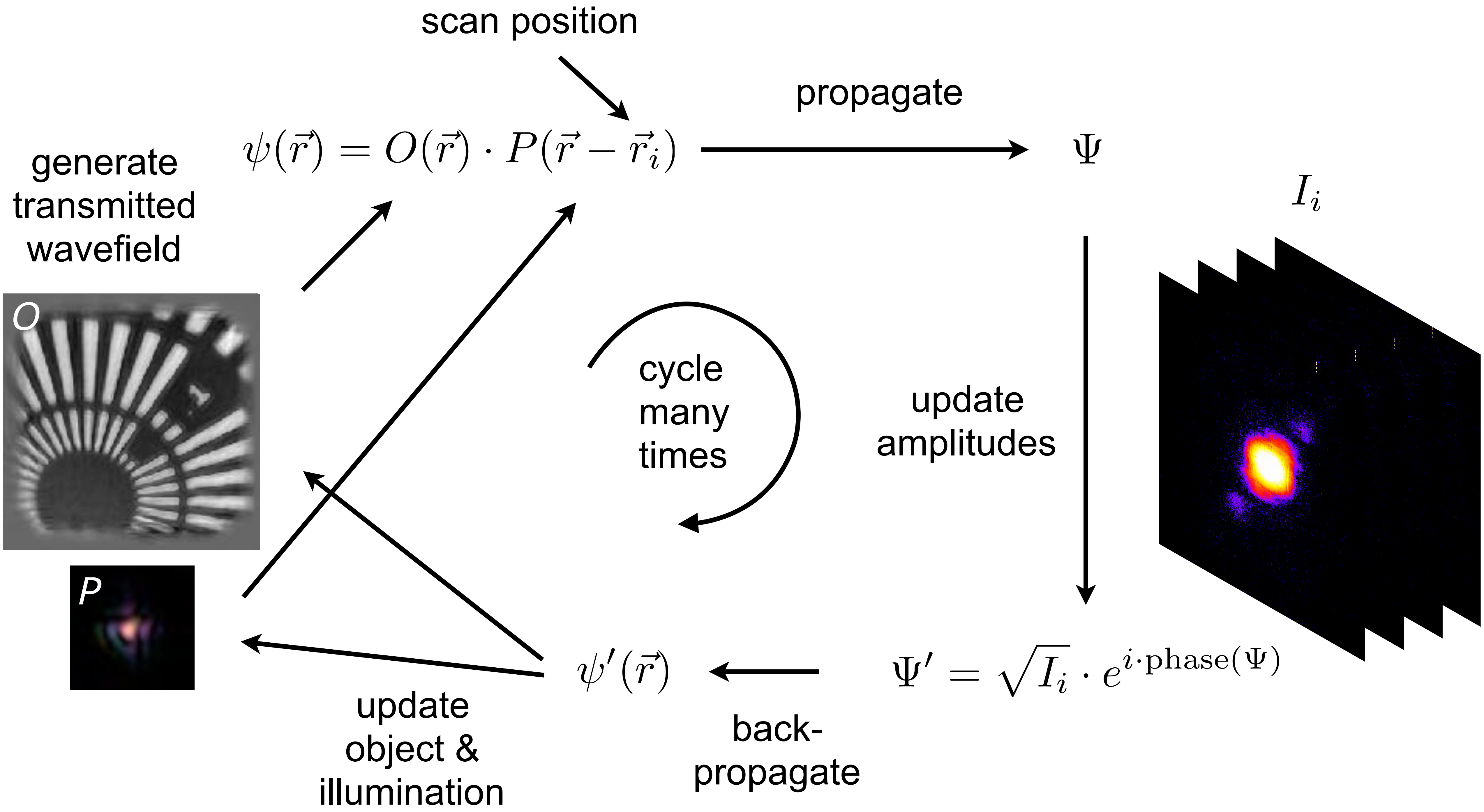
Scanning Coherent Diffraction Imaging: Ptychography

- Sample is raster scanned through confined beam
- At each position of scan: diffraction pattern is recorded
- Overlap in illumination between adjacent points



J. Rodenburg, H. Faulkner. *Appl. Phys. Lett.* **85**, 4795 (2004),
P. Thibault, et al., *Science* **321**, 379 (2008),
A. Schropp, et al., *Appl. Phys. Lett.* **96**, 091102 (2010),
M. Dierolf, et al., *Nature* **467**, 436 (2010).

Ptychography: Reconstruction



scan position

$$\psi(\vec{r}) = O(\vec{r}) \cdot P(\vec{r} - \vec{r}_i)$$

propagate

$$\Psi$$

$$I_i$$

generate transmitted wavefield

cycle many times

update amplitudes

$$\Psi' = \sqrt{I_i} \cdot e^{i \cdot \mathrm{phase}(\Psi)}$$

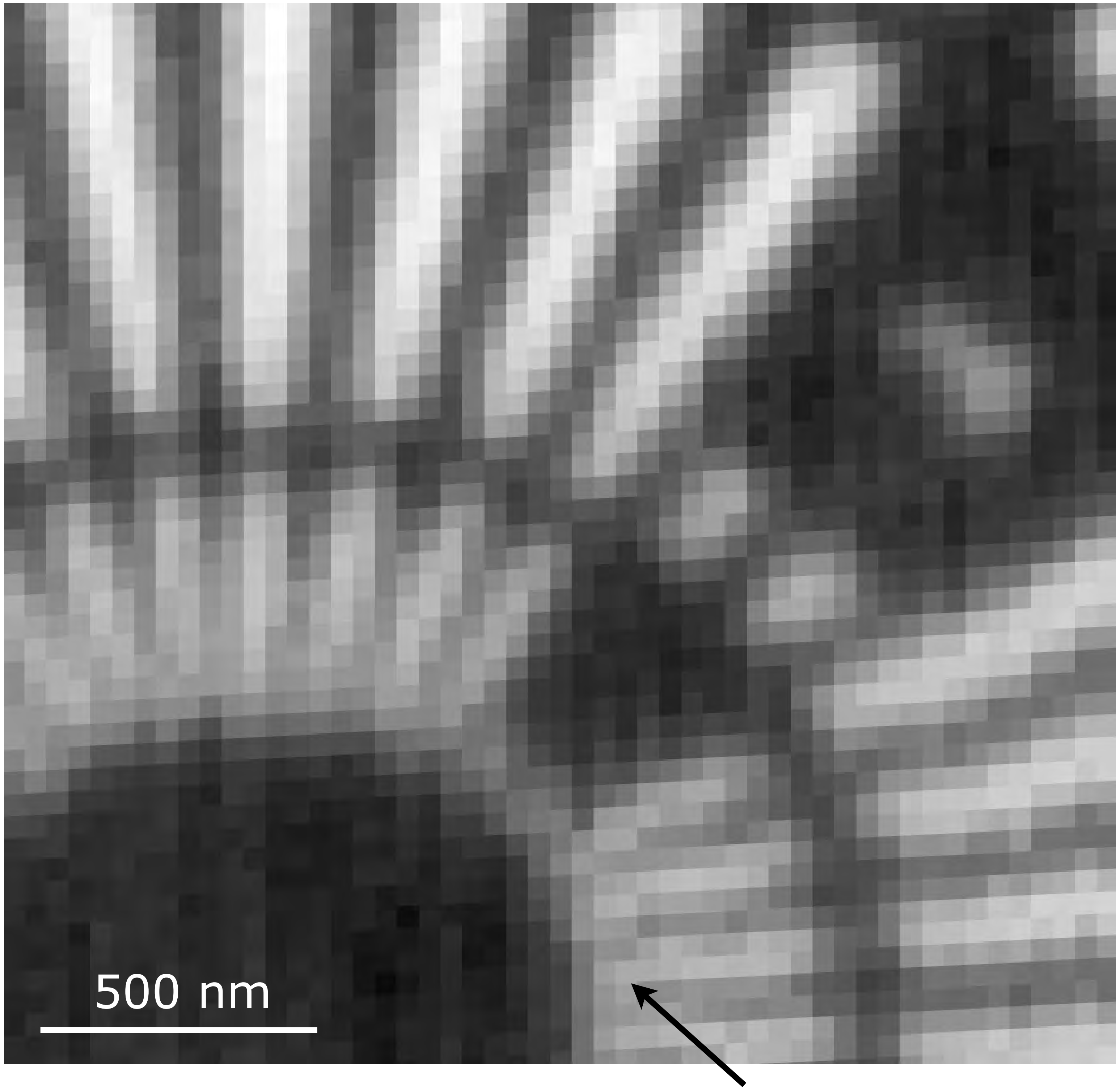
back-propagate

$$\psi'(\vec{r})$$

update object & illumination

Maiden & Rodenburg, Ultramicroscopy **109**, 1256 (2009).

Scanning Microscopy: Fluorescence Imaging



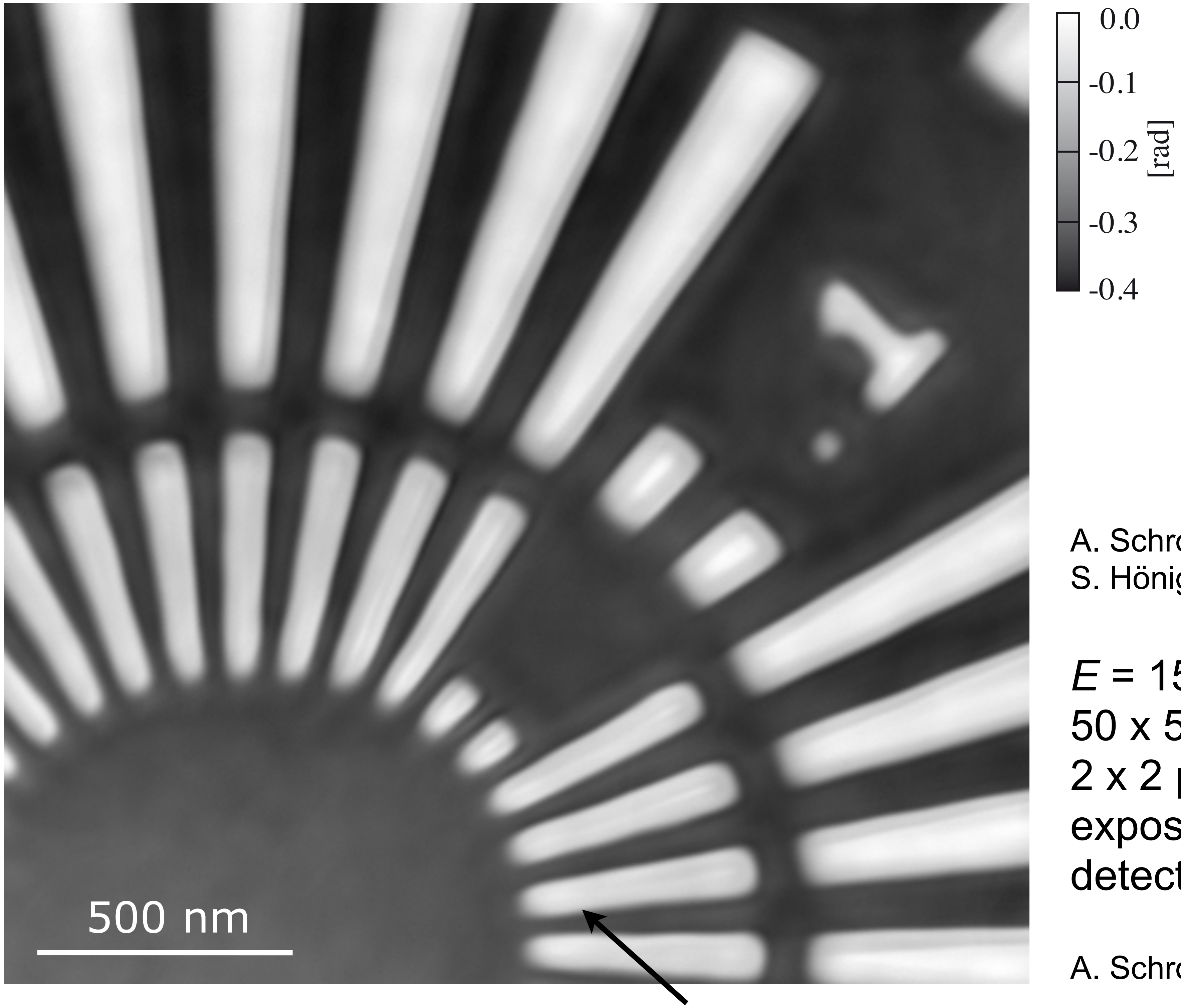
50 nm lines and spaces

Ta Lα fluorescence

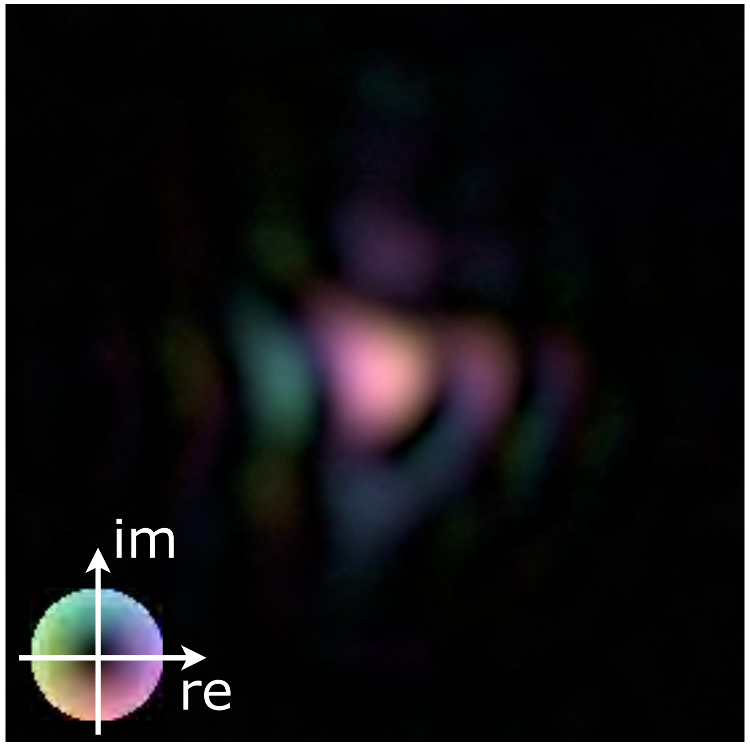
E = 15.25 keV
50 x 50 steps of 40 x 40 nm^2
2 x 2 μm^2 FOV
exposure: 1.5 s per point

A. Schropp, et al., APL **100**, 253112 (2012).

Scanning Microscopy: Ptychography



50 nm lines and spaces



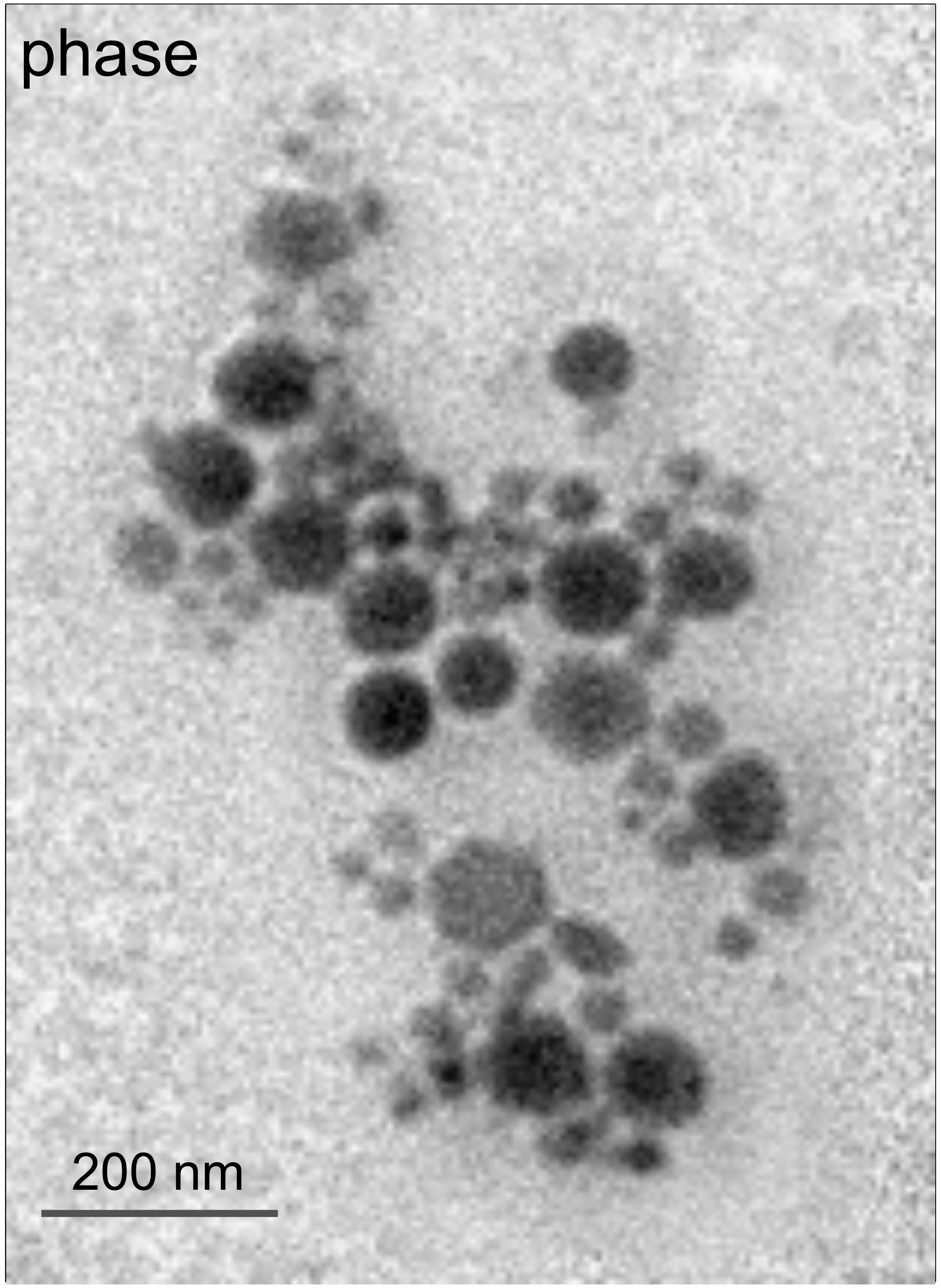
A. Schropp, et al., APL **96**, 091102 (2010),
S. Hönig, et al., Opt. Exp. **19**, 16325 (2011).

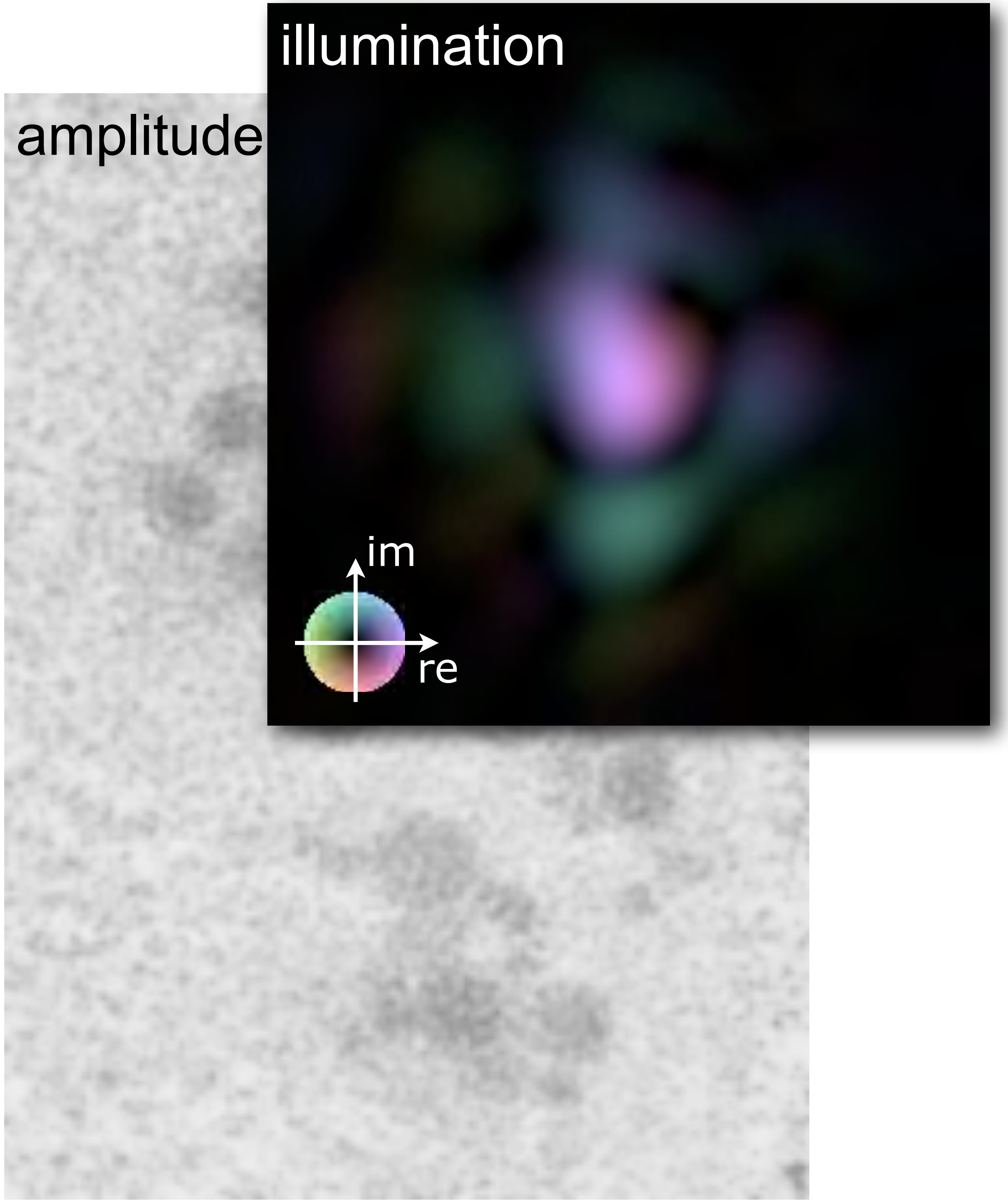
E = 15.25 keV
50 x 50 steps of 40 x 40 nm^2
2 x 2 µm^2 FOV
exposure: 1.5 s per point
detected fluence: 2.75·10^4 ph/nm^2

A. Schropp, et al., APL **100**, 253112 (2012).

Ptychography: Nanoparticles for Catalysis

Sample: Pd, Pt und Au particles

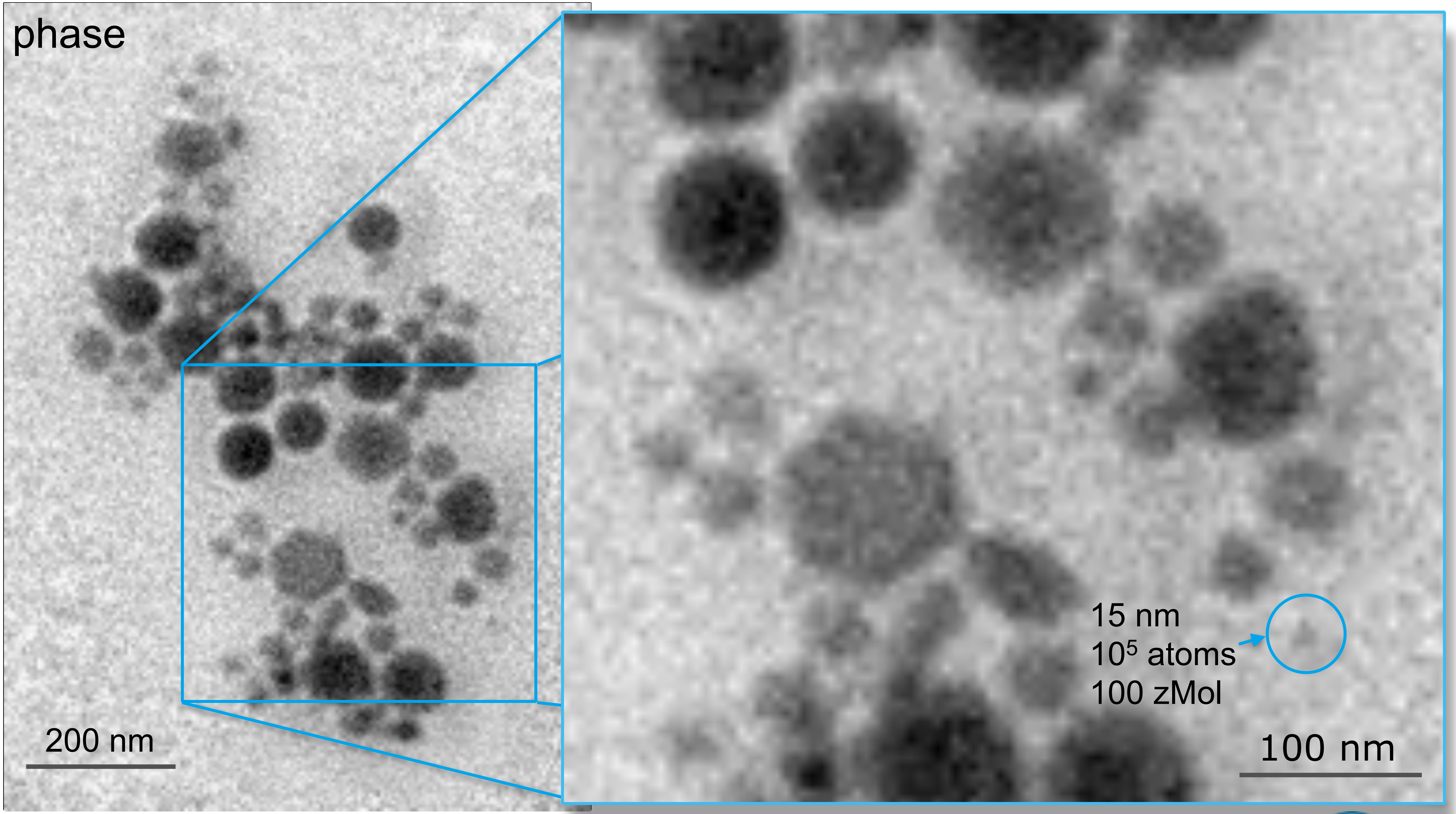




Collaboration with J. D. Grunwaldt, KIT and C. Damsgaard, DTU

Ptychography: Nanoparticles for Catalysis

Sample: Pd, Pt und Au particles

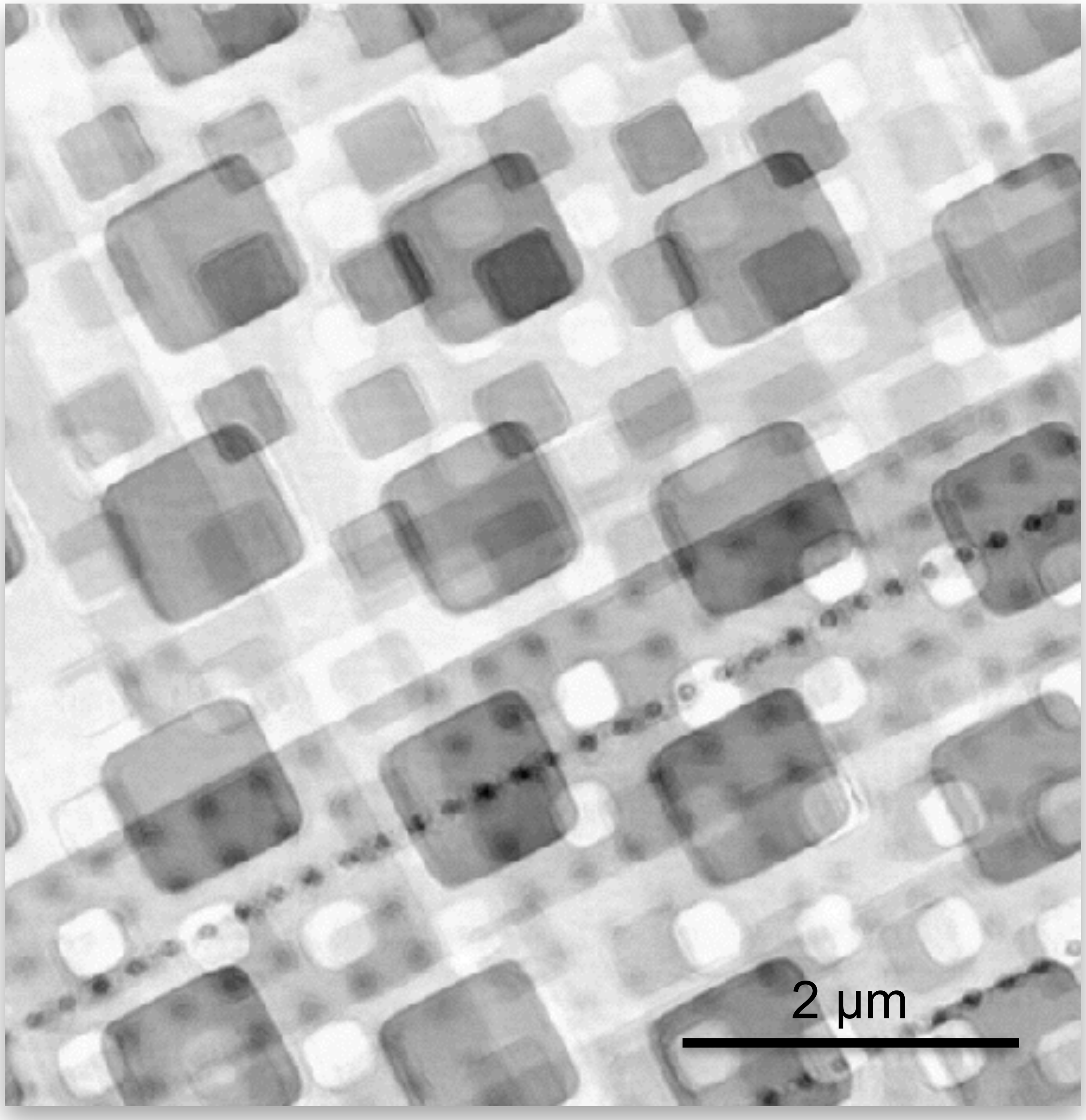


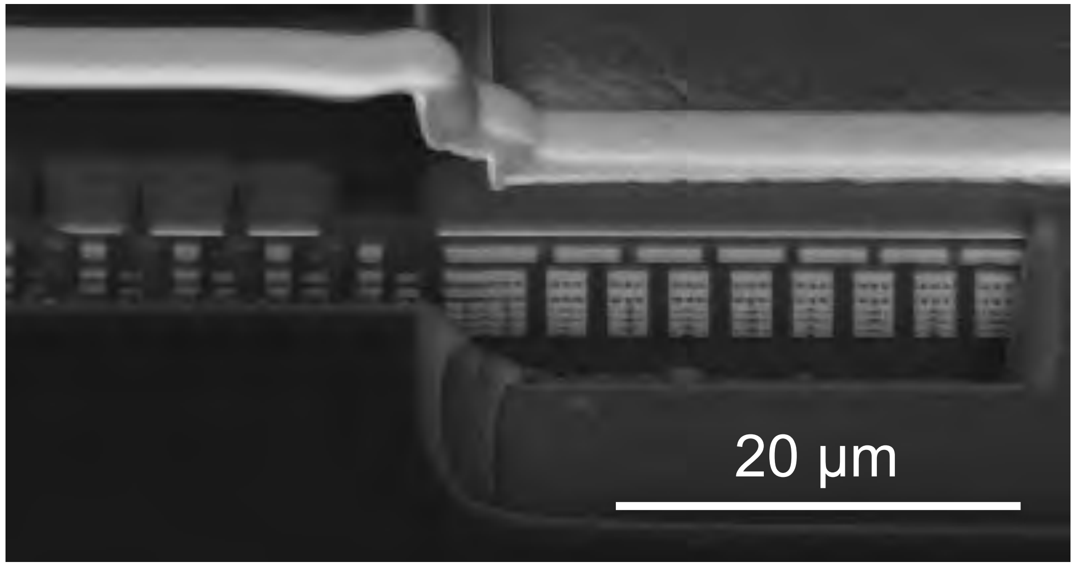
15 nm
10^5 atoms
100 zMol

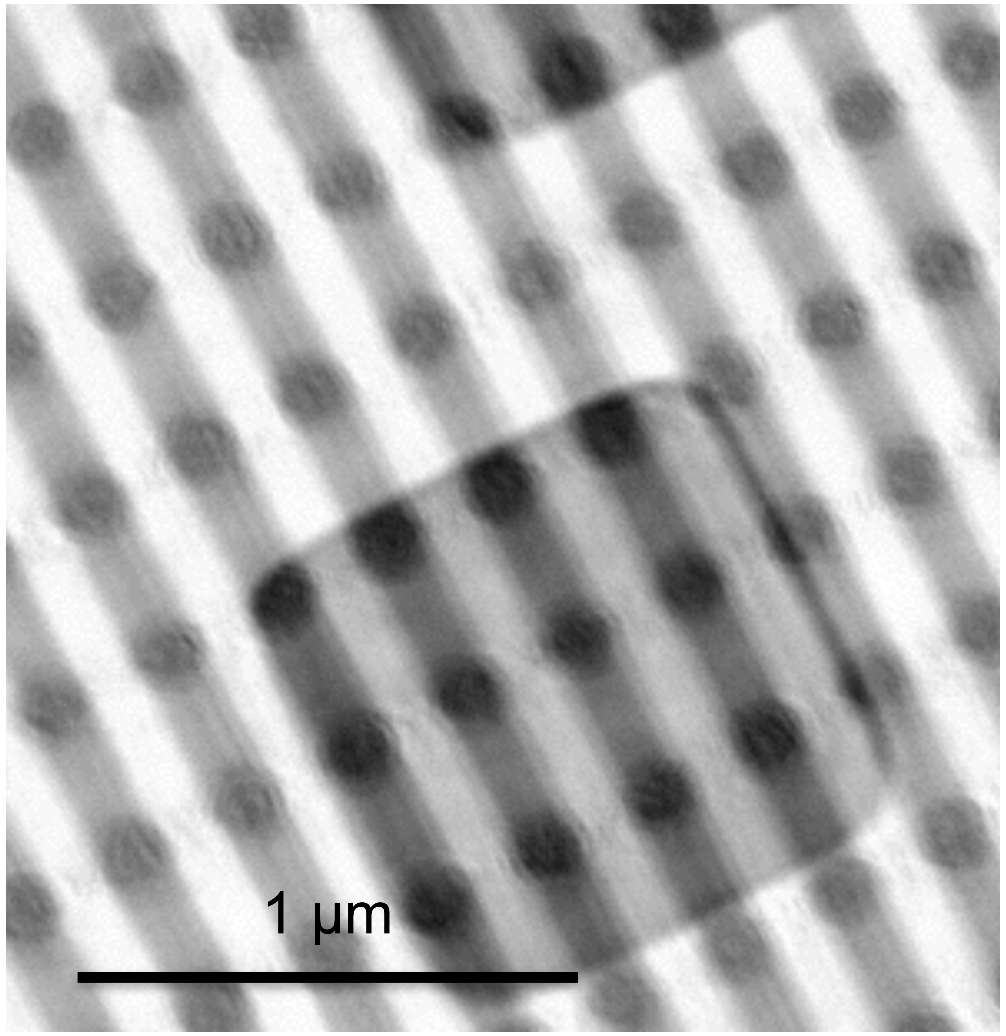
Collaboration with J. D. Grunwaldt, KIT and C. Damsgaard, DTU

In-situ Imaging of Nano-Electronic Devices

Currently at PETRA III:
Studies to image 3D structure of devices







No sample preparation:
front-end passivated chips

Collaboration with Infineon (Dresden)

Multimodal exploration of hierarchical structures

Example: high-speed scanning nano-XRF and ptychography enables exploration of hierarchical structures and multi-dimensional systems with high resolution and sensitivity

Fluid catalytic cracking

Combine

> ptychographic and
> fluorescence

tomography

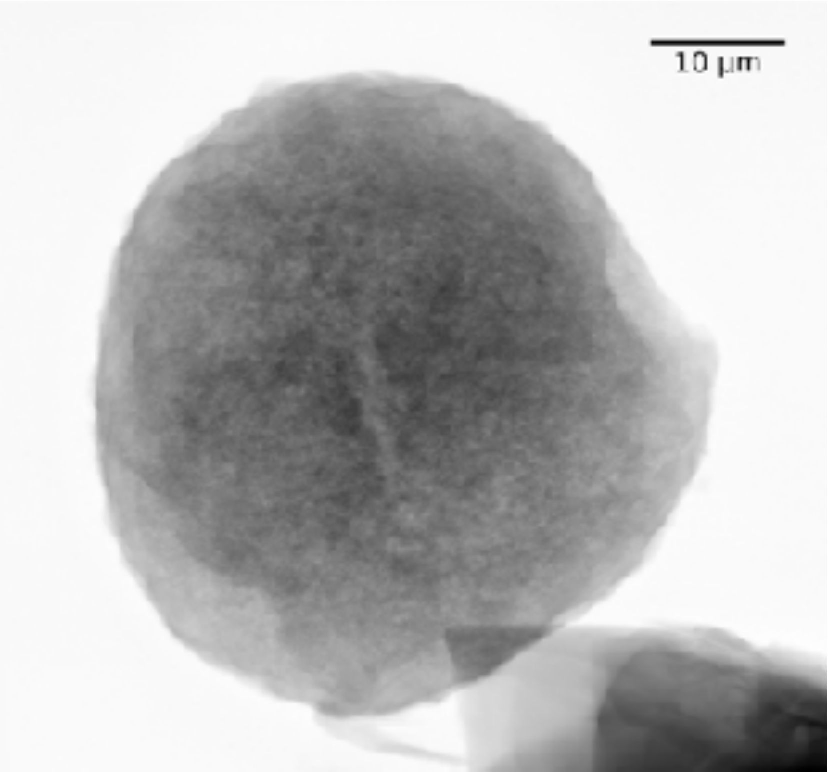
convert

high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils

to

more valuable gasoline, olefinic gases, and other products

Catalyst particle:



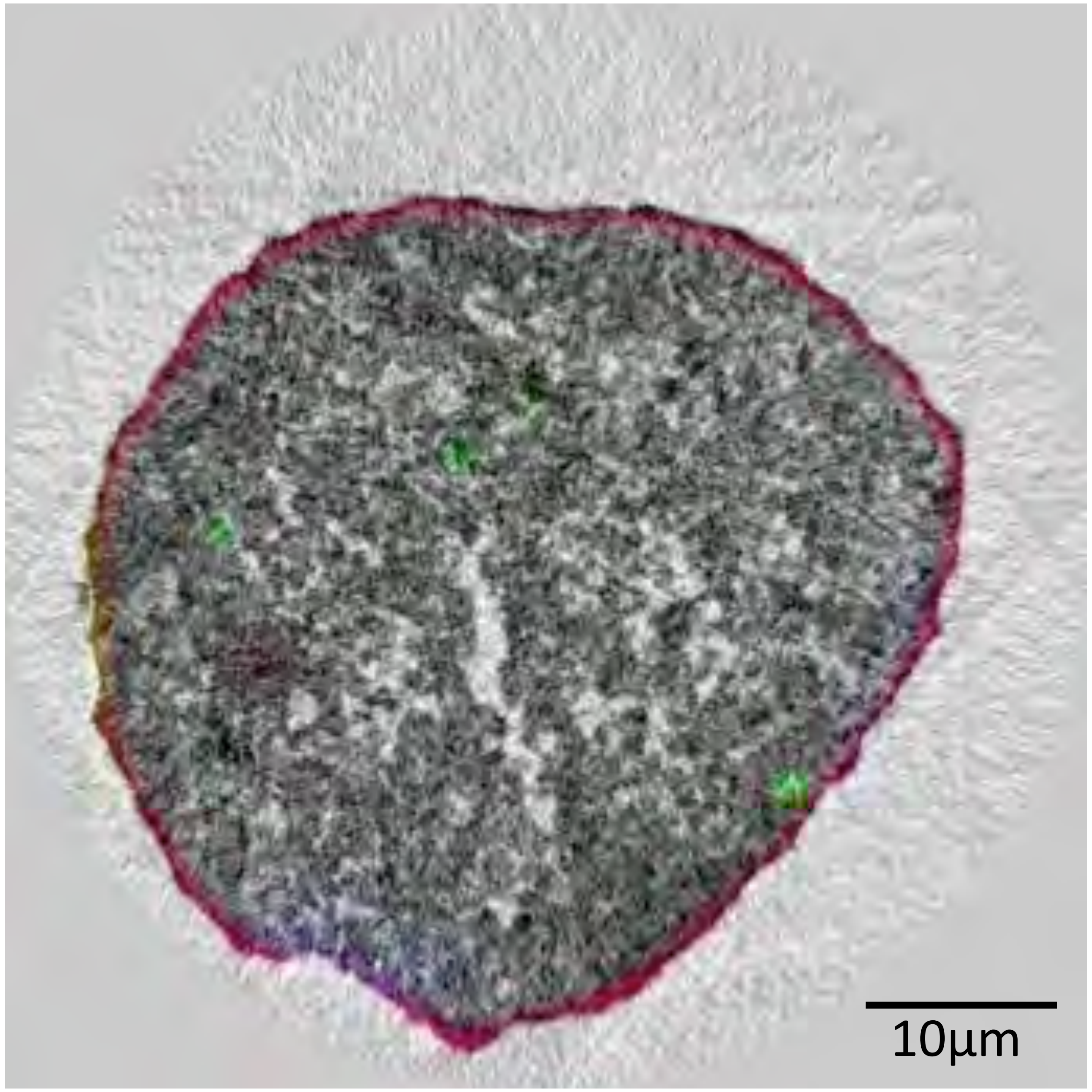
Zeolite in porous clay

J. Garrevoet, S. Kalirai, F. Meirer, *et al.*, unpublished

3D Structural and Spectroscopic Microscopy

Aged Fluid-Catalytic-Cracking Catalyst Particle

Tomographic reconstruction:



Simultaneous reconstruction of:

- element distribution:
  - 🔴 Fe
  - 🔵 Ni
  - 🟢 Ti
  - 🔵 Ga

  resolution: lateral beam size 300 nm
- electron density:
  resolution given by ptychography:
  ~ 100nm

Main result:

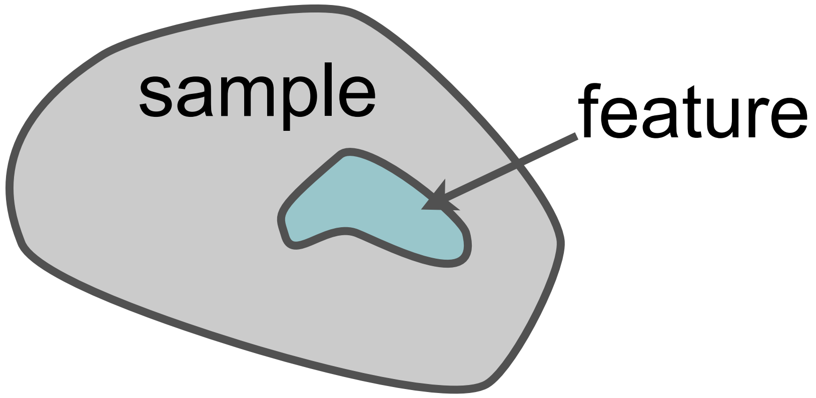
→ transport into particle clogged by Fe/Ni in feedstock

J. Garrevoet, S. Kalirai, F. Meirer, *et al.*, unpublished

Resolution and Contrast in CXDI and Ptychography

Ideal experiment:

- only scattering from object
- pure shot noise (no noise from detector)



Signal-to-background consideration:

When is a small feature detectable in the diffraction pattern?

i. e., when is the (heterodyne) contribution of the small feature above the noise level of the diffraction pattern?

Main result:

The feature can at best be detected if it could be imaged by itself (without the rest of the sample)! (Necessary condition)

$$I_c \cdot t \cdot \left(\frac{d\sigma}{d\Omega}\right)_d \Delta\Omega_d \geq \frac{\alpha^2}{4}$$

$\Delta\Omega_d$: size of Shannon pixel for given feature

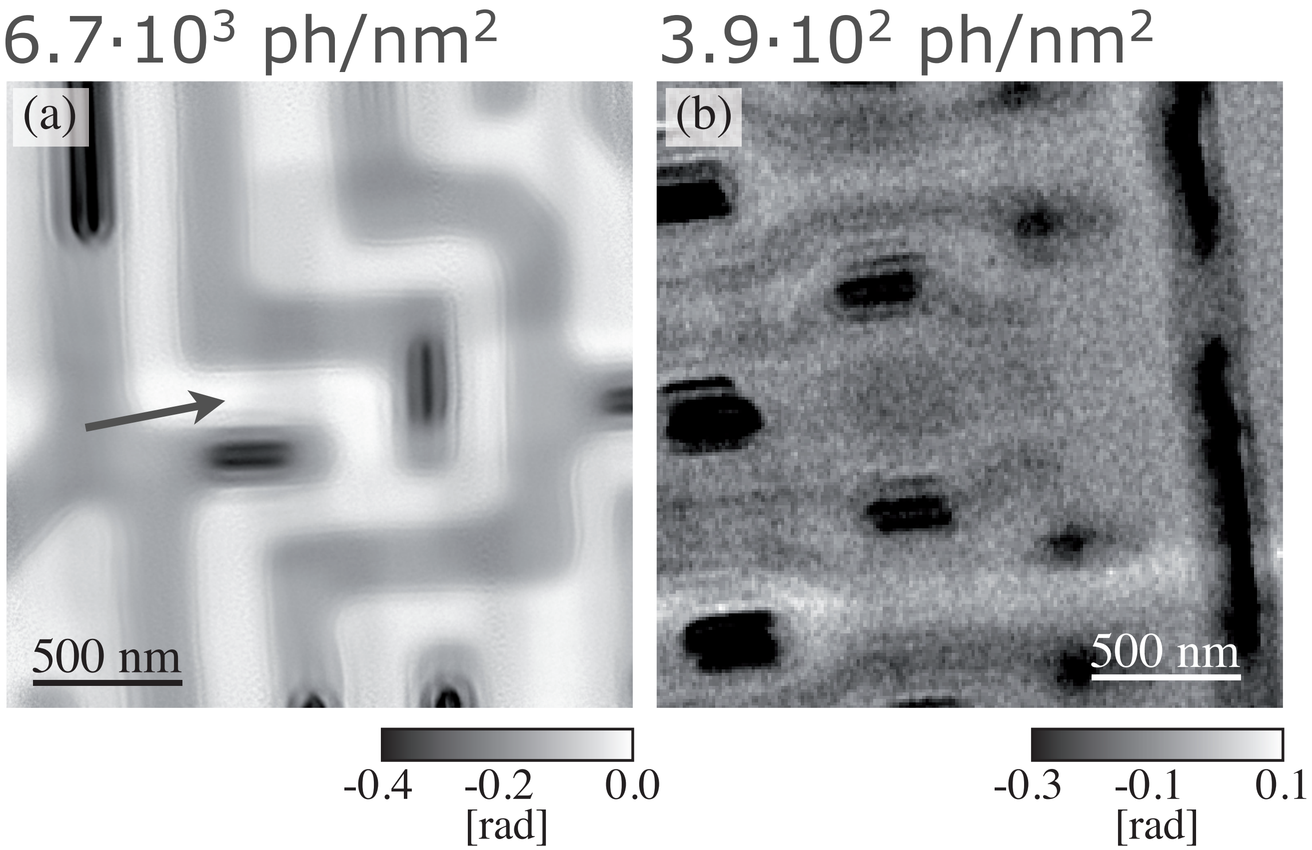
Schropp & Schroer, NJP **12**, 035016 (2010).

Resolution and Contrast in CXDI and Ptychography

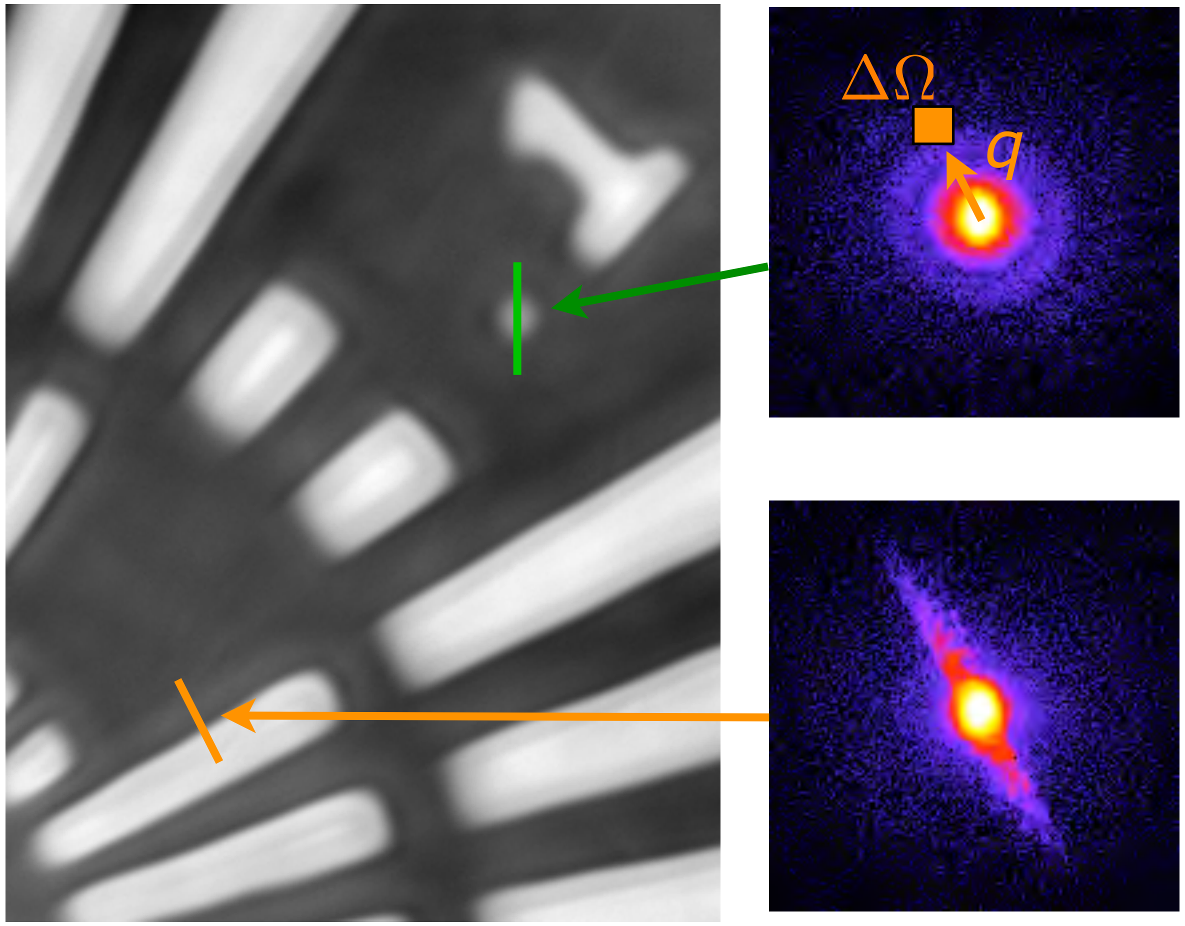
Signal for a given feature: $I_c \cdot t \cdot \left(\frac{d\sigma}{d\Omega}\right)_d \Delta\Omega_d$

Signal = fluence * scattering cross section * speckle size

coherent fluence on feature:



~ structure factor of feature:

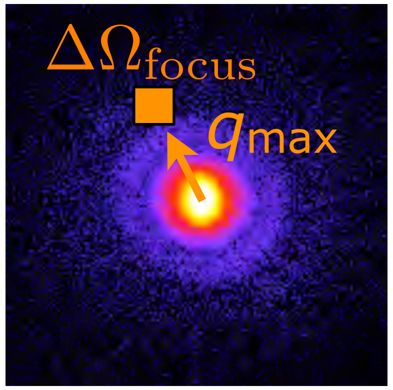


Schropp & Schroer, NJP **12**, 035016 (2010).

Locating a Feature at High Spatial Resolution

Signal from small feature in given speckle at high $q_{\max}$:

$$I_c \cdot t \cdot \frac{d\sigma}{d\Omega}(\vec{q}_{\mathrm{max}}) \cdot \Delta\Omega_{\mathrm{focus}} \geq \frac{\alpha^2}{4} \qquad \alpha = 5 \text{ Rose criterion}$$



- $I_c \cdot t$: coherent fluence on feature
- $\frac{d\sigma}{d\Omega}(\vec{q}_{\mathrm{max}})$: scattering cross section of feature at highest q
- $\Delta\Omega_{\mathrm{focus}}$: speckle size defining a piece of information in reciprocal space

Figure of merit of x-ray microscope:

$I_c \cdot t \cdot \Delta\Omega_{\mathrm{focus}}$ coherent fluence per information in diff. pattern

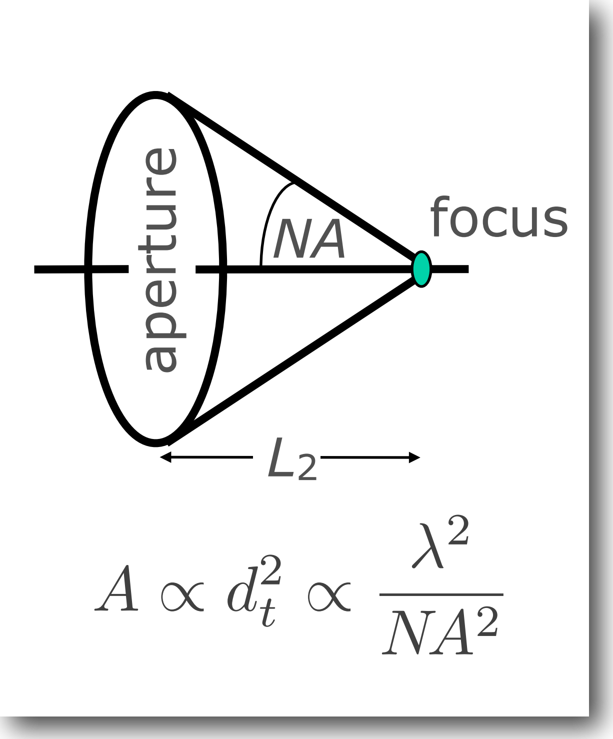
Locating a Feature at High Spatial Resolution

Coherent fluence:

$$I_c \cdot t = \frac{F_c}{A} \cdot T \cdot t \qquad F_c \propto Br \cdot \lambda^2 \cdot \frac{\Delta E}{E}$$ coherent flux

optic's transmission

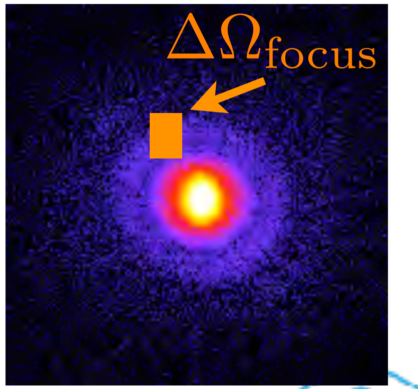
illuminated area



Diffraction limited focus:

$$I_c \cdot t \propto Br \cdot \frac{\Delta E}{E} \cdot \underbrace{NA^2 \cdot T}_{} \cdot t$$

source optic



Size of speckle in diffraction pattern:

$$\Delta\Omega_{\text{focus}} = \pi \frac{\lambda^2}{4d_t^2} = \pi NA^2$$

optic

Figure of Merit of X-Ray Microscope

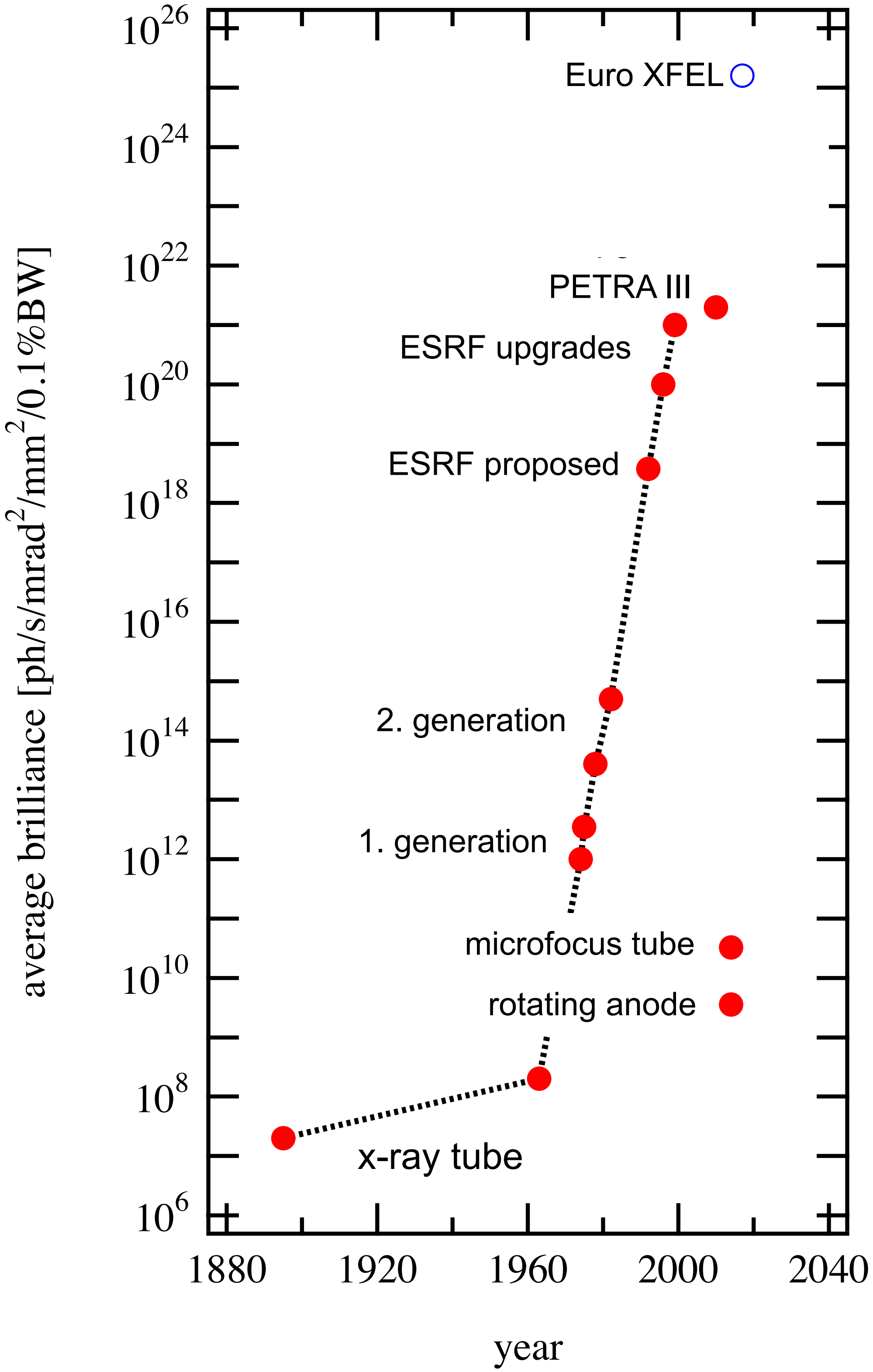
Coherent fluence per piece of information of microscopic data:

$$I_c \cdot t \cdot \Delta\Omega_{\text{focus}} \propto \underset{\substack{\uparrow \\ \text{source}}}{Br} \cdot \frac{\Delta E}{E} \cdot \underbrace{NA^4 \cdot T}_{\substack{\uparrow \\ \text{optic}}} \cdot t$$

Improve microscope for different imaging modes:

- Fixed beam size (for single-pulse CXDI or serial crystallography): $\propto Br$
  beam size determines *NA*
- Fixed field of view: $\propto Br \cdot NA^2$ (aberrations of optic not important)
- Image nano object (smaller than any achievable beam size): $\propto Br \cdot NA^4$

Brilliance / Spectral Brightness

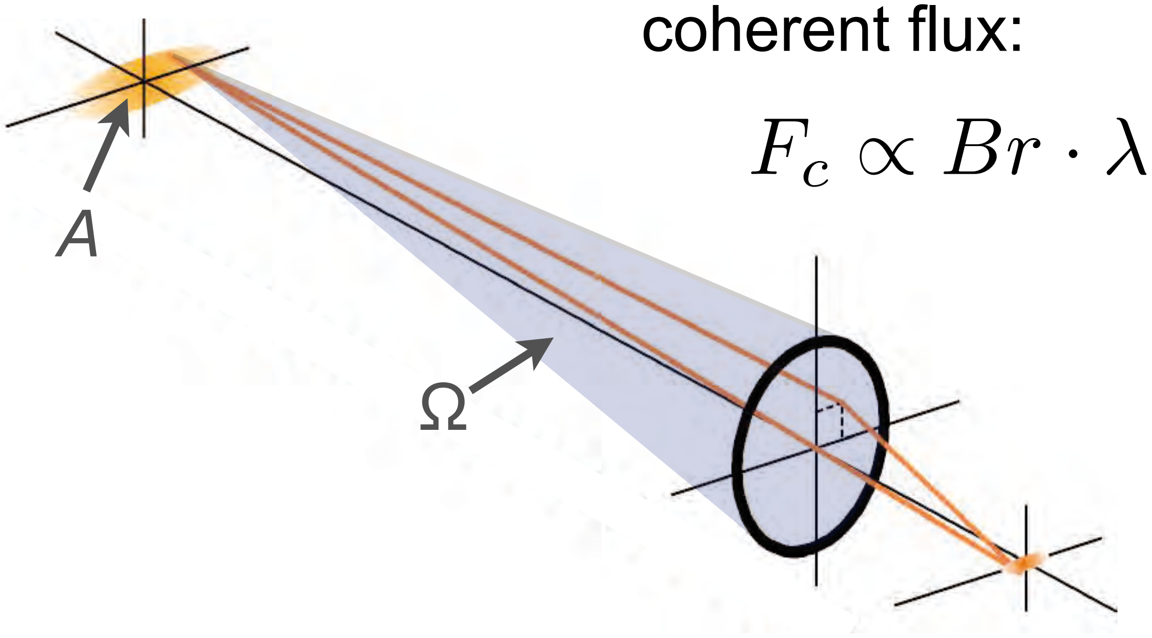


10000x more “light” per decade!!

Spectral brightness:

$$Br = \frac{F}{\Omega \cdot A \cdot \Delta E/E}$$

Flux per phase-space volume



coherent flux:

$$F_c \propto Br \cdot \lambda^2 \cdot \frac{\Delta E}{E}$$

Improvements in brightness:

- faster measurements (time resolution)
- nano-imaging (spatial resolution)
- spectroscopy (energy resolution)

PETRA IV

source size:
140 µm x 6 µm

source size:
6 µm x 6 µm

asymmetrical
x-ray beam

round
x-ray beam

New Multi-Bend-Achromat technology
MAX IV, SIRIUS, ESRF, APS

Gain factor
100

PETRA III

3rd generation SR source
1000 pm rad

Max. brilliance: ~10^{20}
coherence: ~0.1-1%

nanometer
focusing

PETRA IV

4th generation SR source
~10 pmrad

Max. Brilliance: >10^{22}
Coherence: > 25%

PETRA IV

- new multi-bend-achromat (MBA) technology +
- 2.3 km circumference (largest SR source)
  emittance scales as 1/(circumference)^3

→ diffraction limited down to a wavelength of 1 Å (ultimate storage ring)

Qualitative step in synchrotron analytics

In-situ 3D-microscopy on nanometer scale

Operando nanoimaging of

- structure, chemistry
- electronic and magnetic properties
- dynamics on the sub-nanosecond scale

Imaging the Chemistry of Light Elements in the Bulk

Inelastic x-ray scattering:

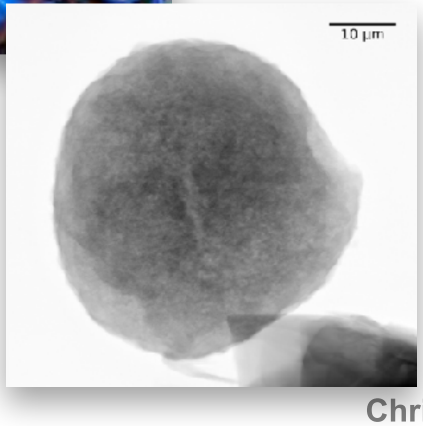
- spectroscopy of light elements (Li, C, N, O, …)
- probe with hard x-rays (penetrate sample and sample environment)

Combination with nanobeam:

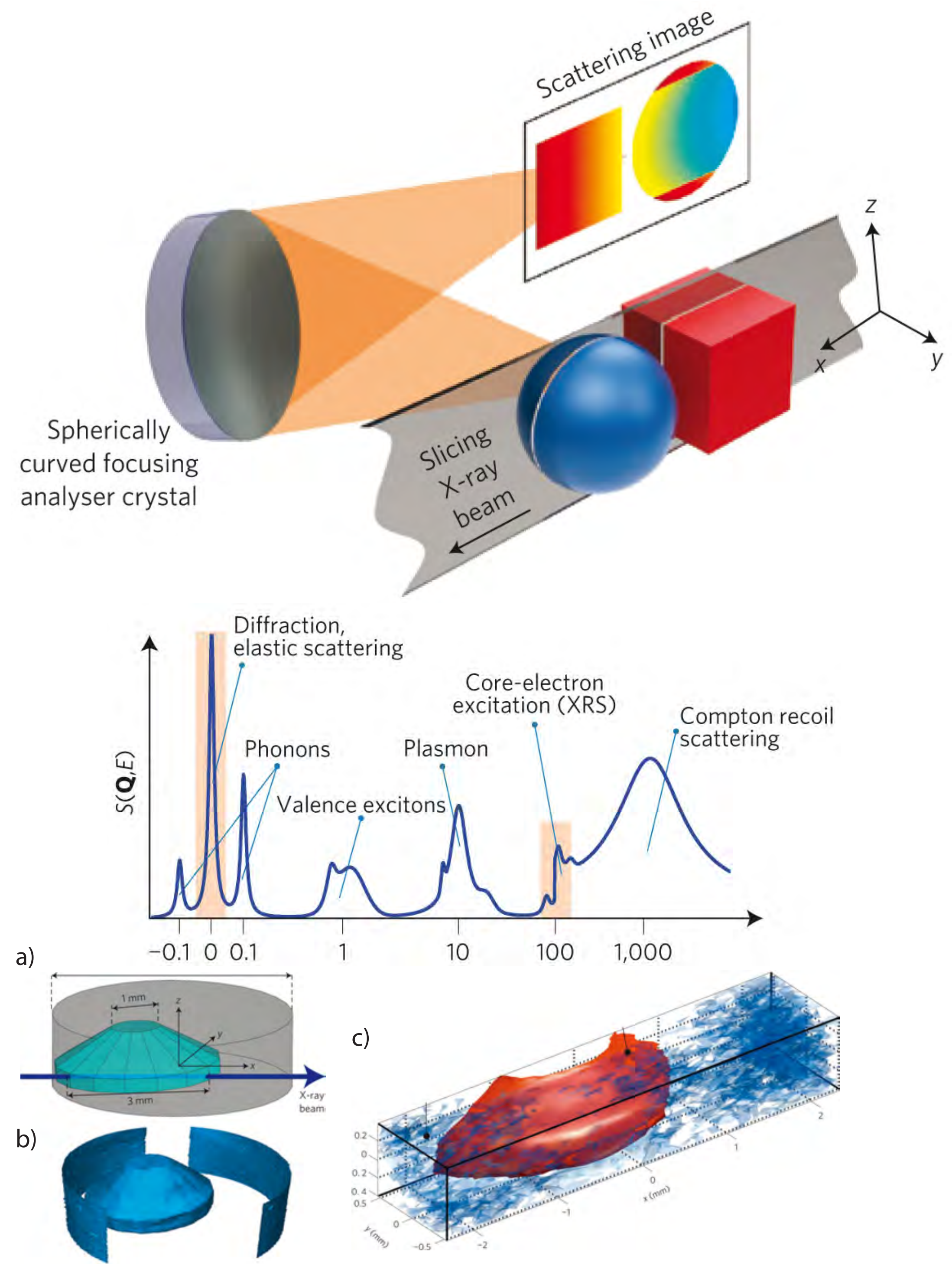
- scanning microscopy: scalable in spatial resolution
- tomography: 3D imaging

Applications:

- batteries
- fuel cells
- catalysts
- …

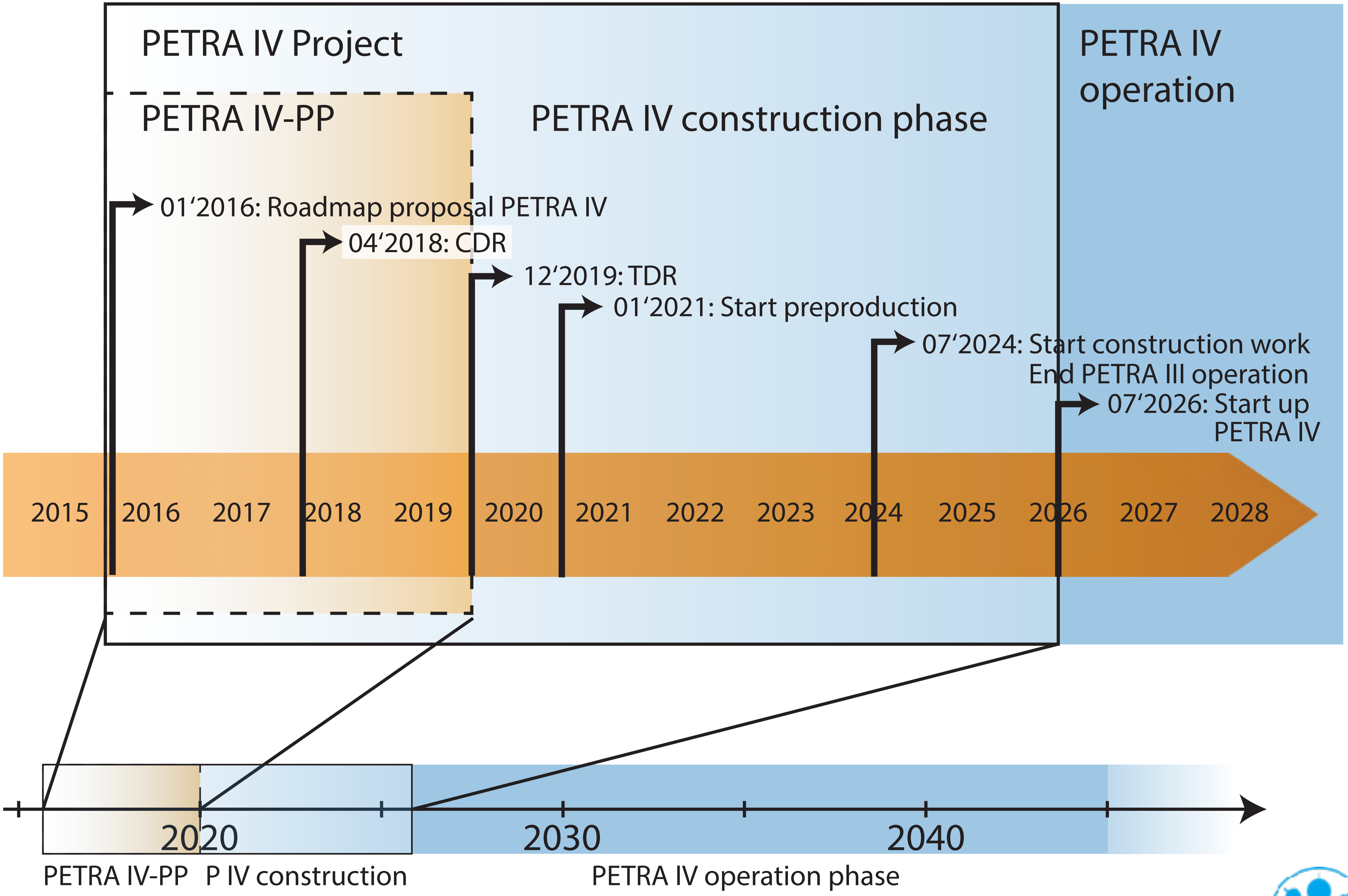


Direct tomography with chemical-bond contrast



S. Huotari, et al., Nature Mat. **10**, 489 (2011).

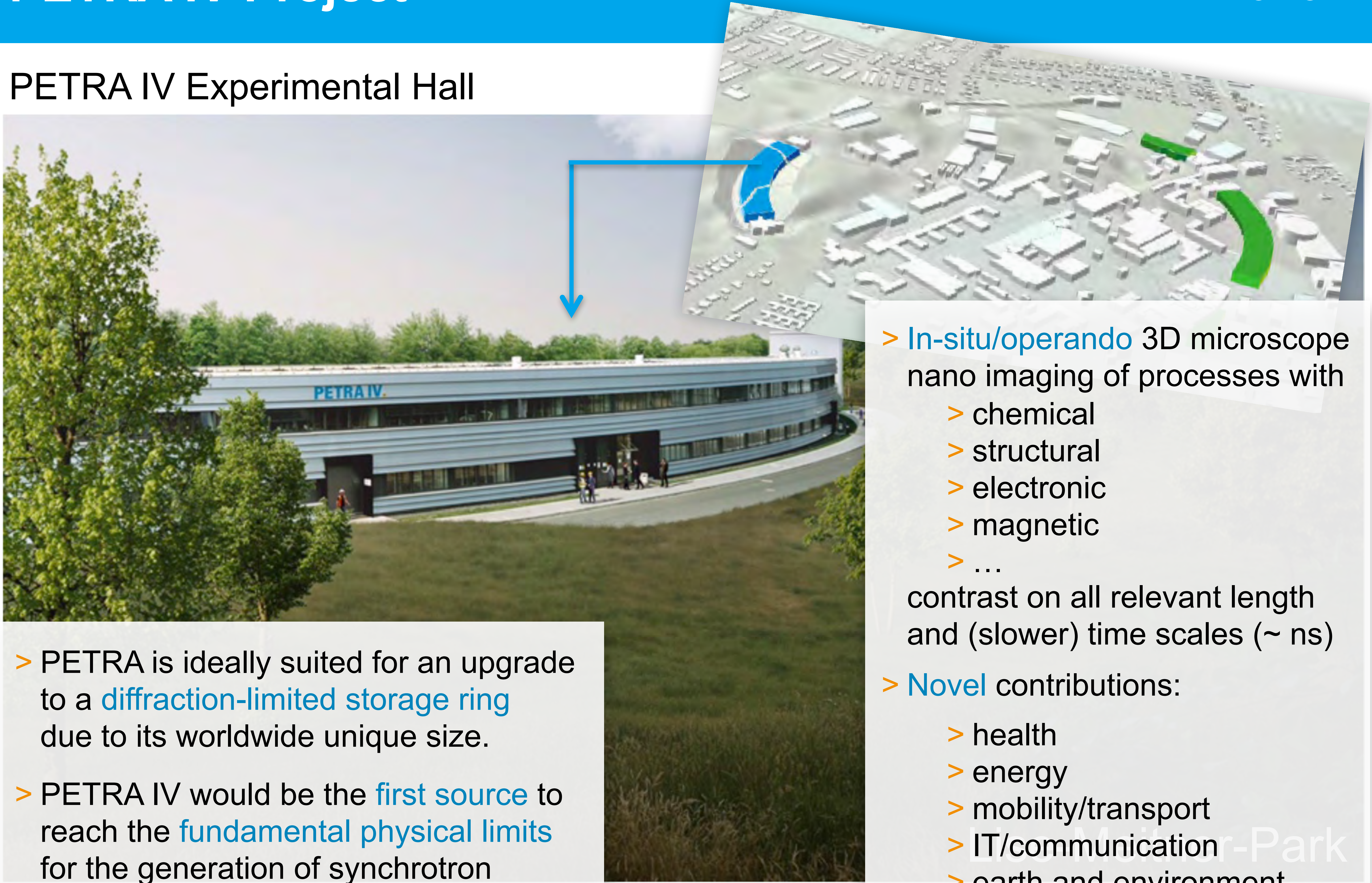
PETRA IV Project



PETRA IV Project

2026+

PETRA IV Experimental Hall



- PETRA is ideally suited for an upgrade to a diffraction-limited storage ring due to its worldwide unique size.
- PETRA IV would be the first source to reach the fundamental physical limits for the generation of synchrotron radiation at 1 Å wave length.

- In-situ/operando 3D microscope nano imaging of processes with
  - chemical
  - structural
  - electronic
  - magnetic
  - …

  contrast on all relevant length and (slower) time scales (~ ns)
- Novel contributions:
  - health
  - energy
  - mobility/transport
  - IT/communication
  - earth and environment
  - …

An X-Ray Microscopists Dream

Quantitive in-situ measurement of physical properties of matter

- on all relevant length scales
- on all relevant time scales

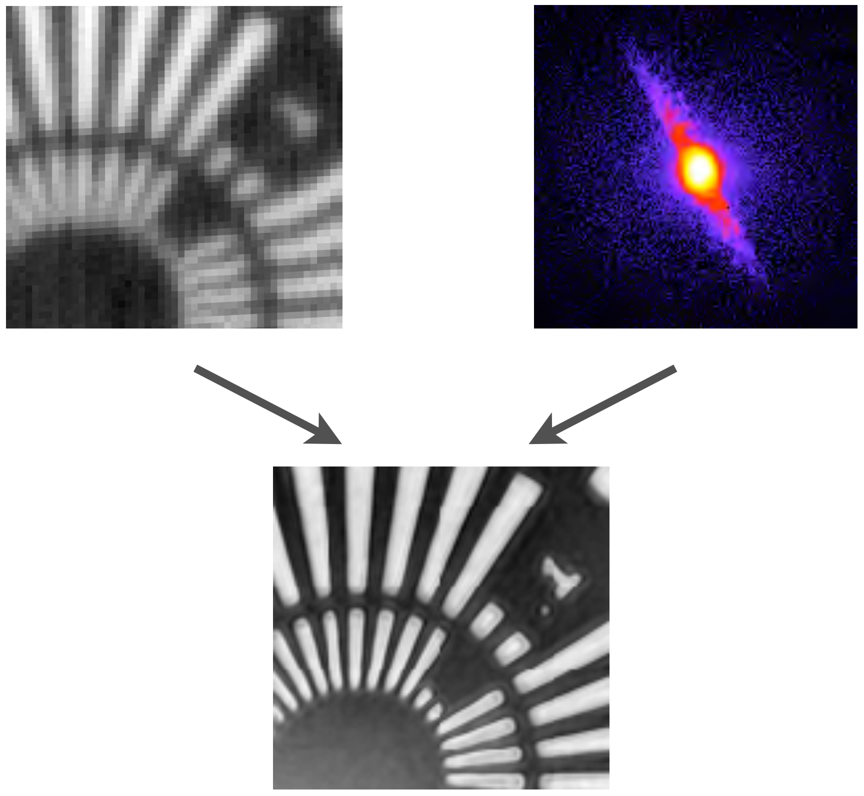
→ (in principle) from Å to millimeters

Key technology: brilliant, coherent x-rays with time structure

Requirements:

- high coherent flux
  - → x-ray free-electron lasers
  - → diffraction limited storage rings (e. g., PETRA IV)
- efficient nanofocusing
  - → optics
- stability on nanometer scale

Fusion of real and reciprocal space!



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