Multidisciplinary approach to NPs characterization

Doctoral School, MSE-674

1st Edition

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PSI-Villigen, 7th-9thJanuary 2025

Agenda

1 Why Electron Microscopy

2 Intro

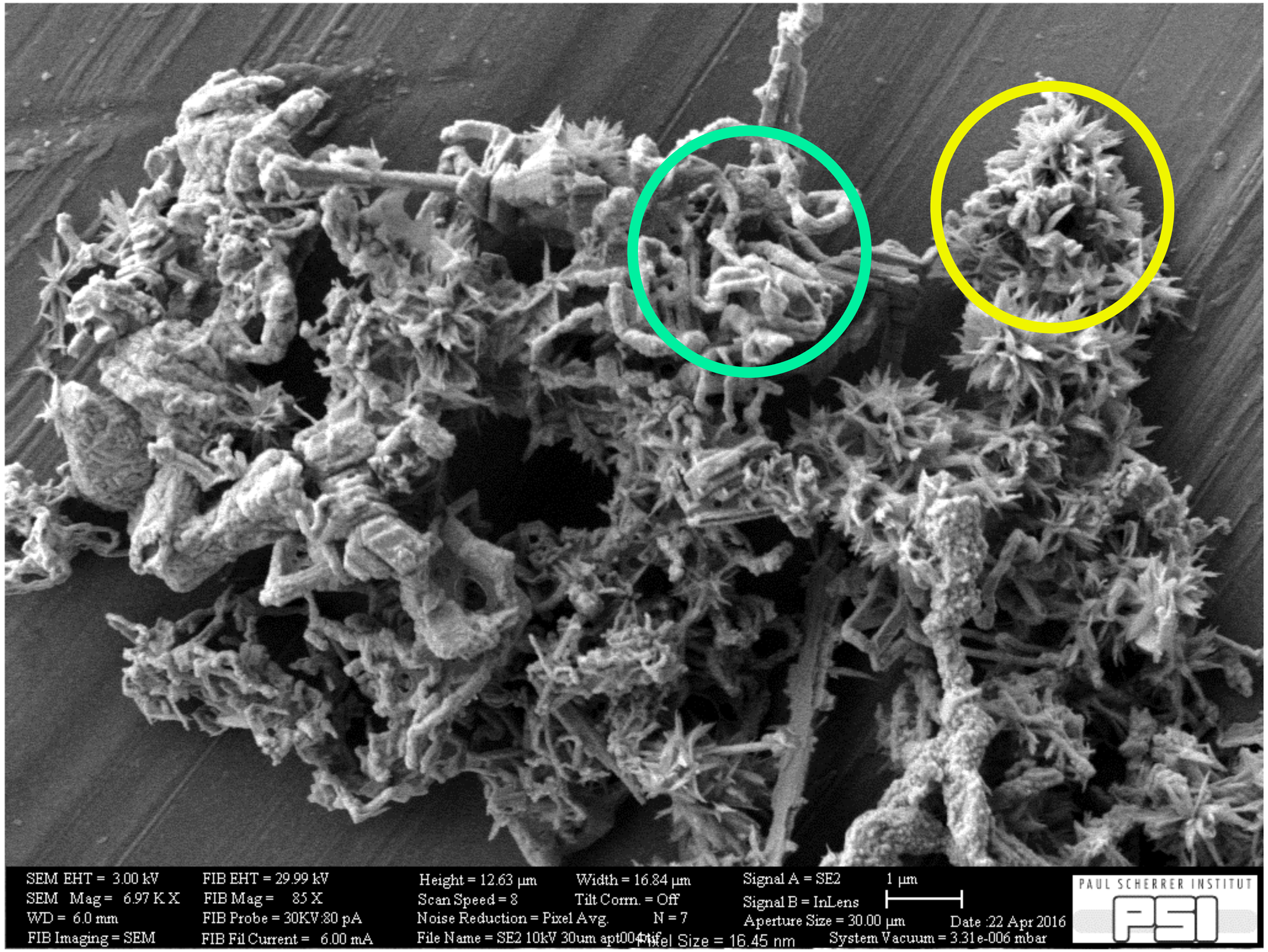
3 SEM Basics

4 (S)TEM Basics

5 Analytics

6 Special Examples

Zn crystals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SEM Mag = 6.97 K X
WD = 6.0 mm
FIB Imaging = SEM
FIB EHT = 29.99 kV
FIB Mag = 85 X
FIB Probe = 30KV:80 pA
FIB Fil Current = 6.00 mA
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Noise Reduction = Pixel Avg.
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Signal A = SE2
Signal B = InLens
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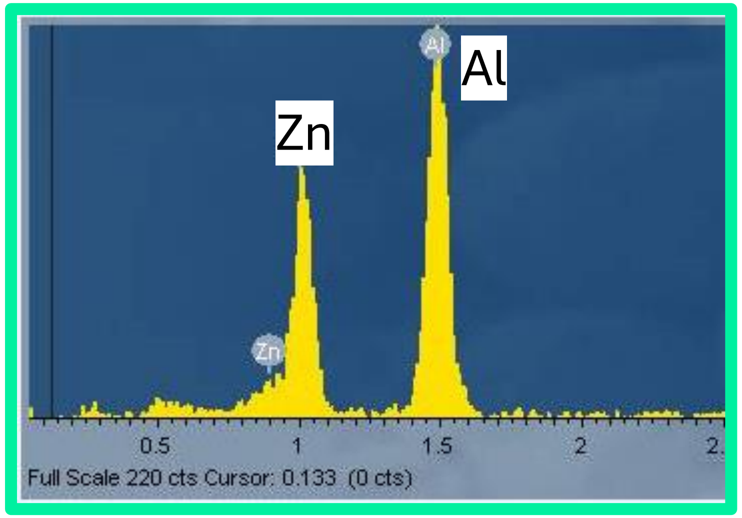
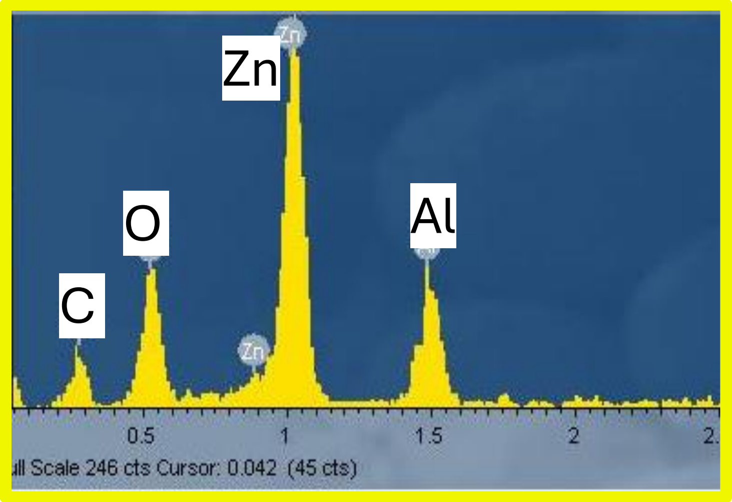
System Vacuum = 3.31e-006 mbar
1 µm
Date :22 Apr 2016
Pixel Size = 16.45 nm
PAUL SCHERRER INSTITUT
PSI


Zn
Al
0.5
1
1.5
2
Full Scale 220 cts Cursor: 0.133 (0 cts)


Zn
C
O
Al
0.5
1
1.5
2
ll Scale 246 cts Cursor: 0.042 (45 cts)

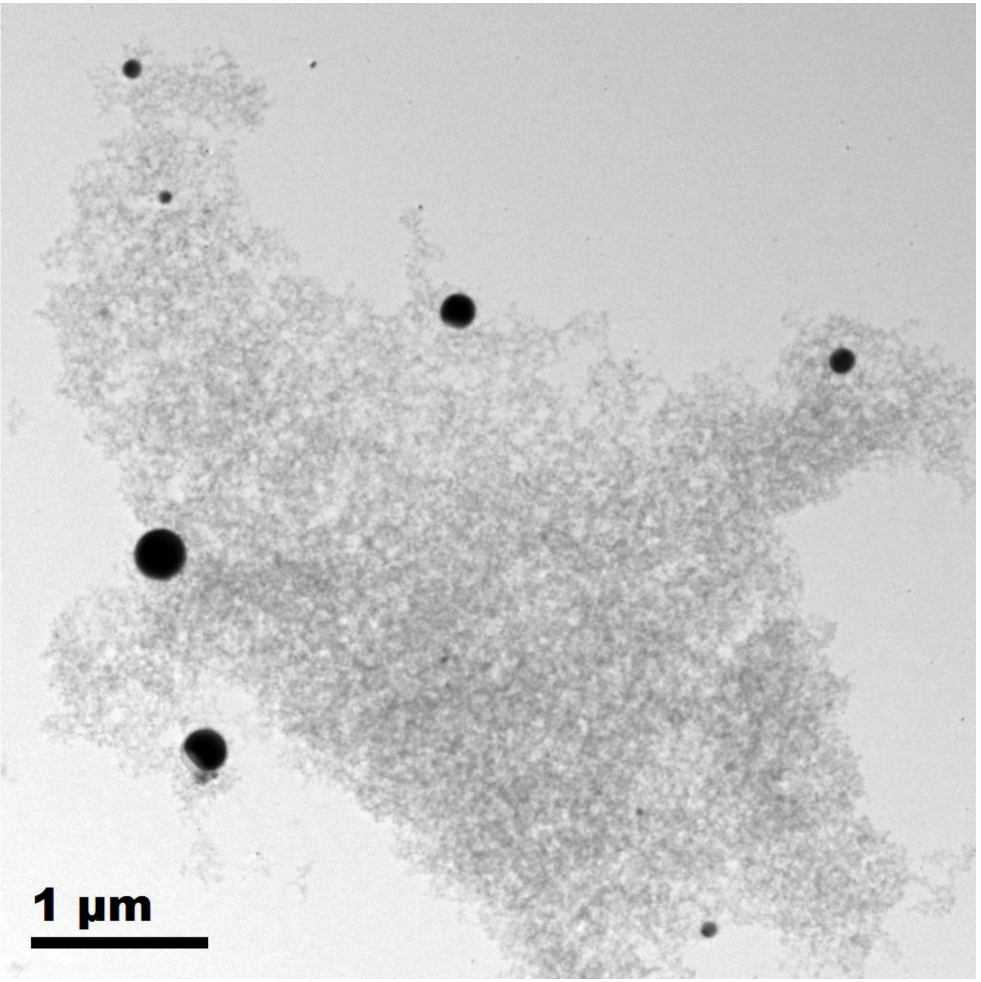
Ag nPs

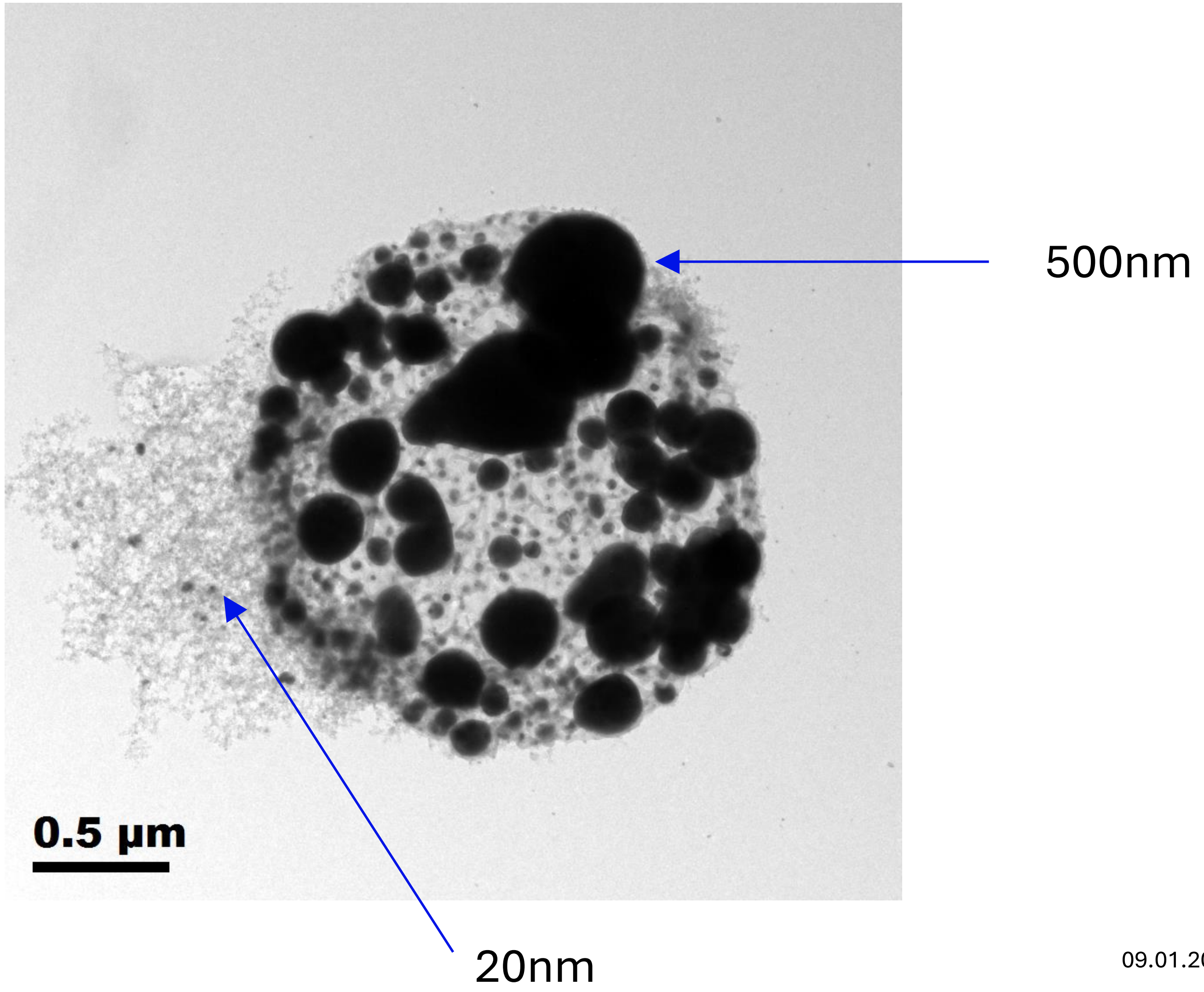
Ag-nanoparticles as anti-bacteriocides
In sports and medical cloths

Information from provider:
Size of Ag-nanoparticles from XRD: 20-40nm

Ag nPs

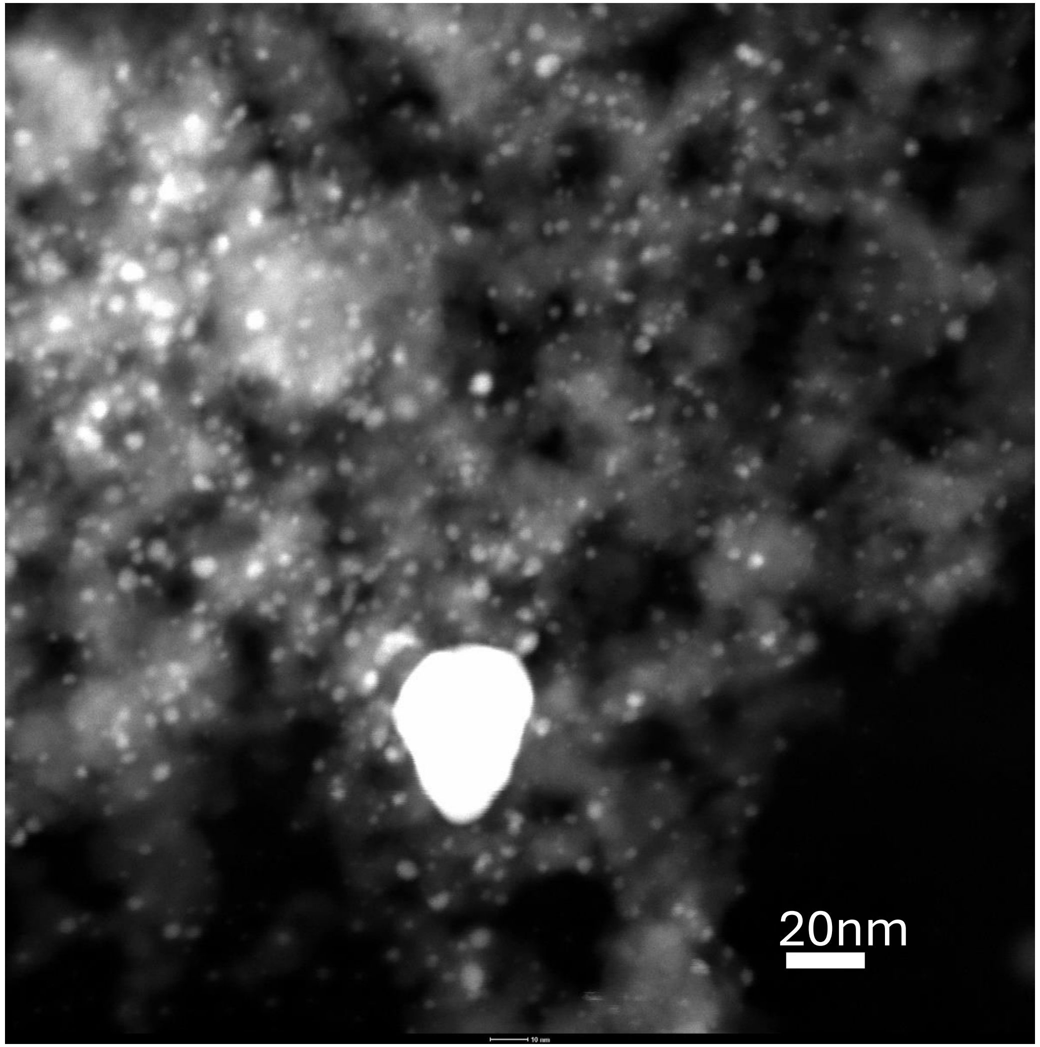
From normal TEM images: few particles 200-1000nm, some 20-50nm

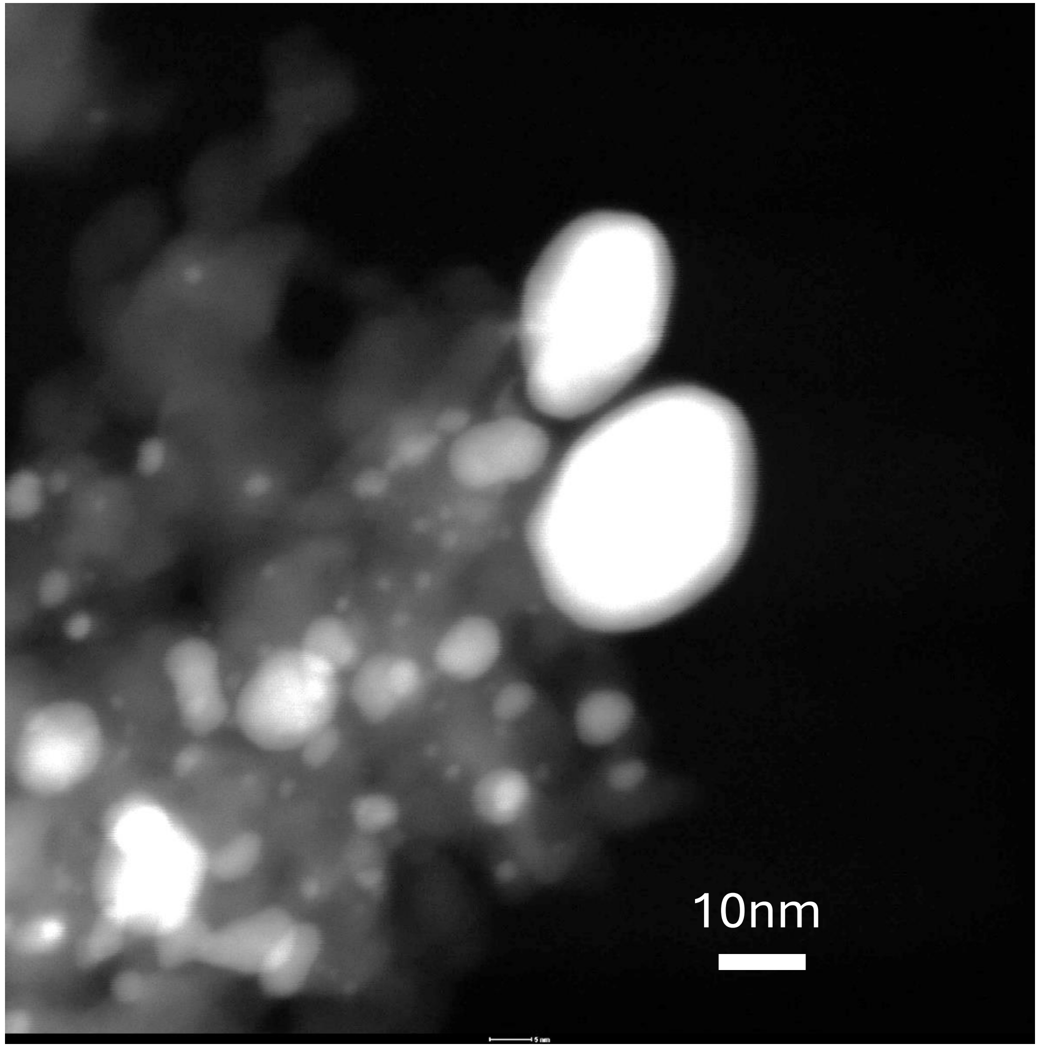




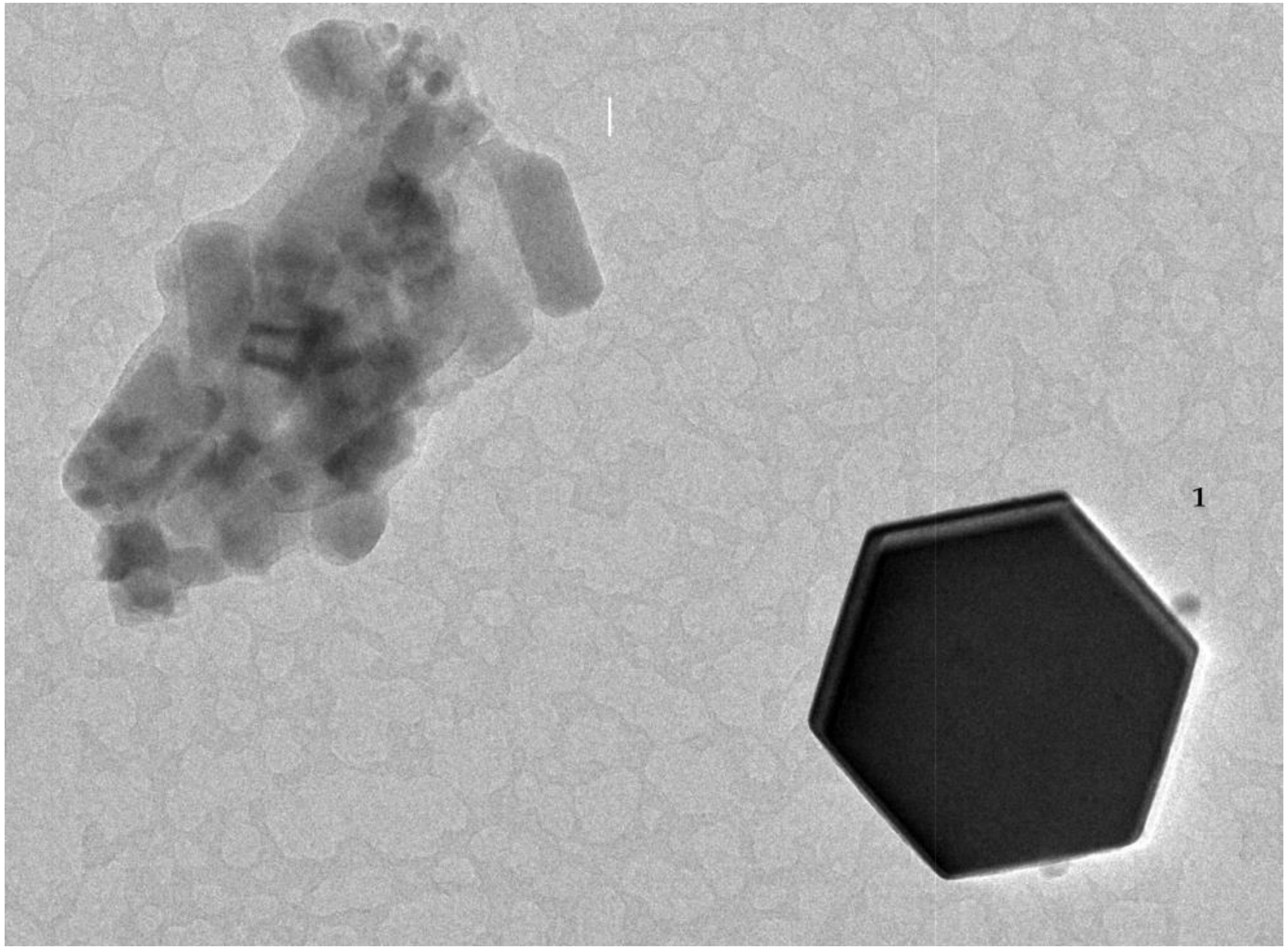
Ag nPs

From HAADF STEM images: few particles 200-1000nm, some 20-50nm, most <5nm





Nanoparticles: crystallites of different shapes/habit



These particles may have the same size, but is the crystal structure the same?

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2 **Intro**

3 SEM Basics

4 (S)TEM Basics

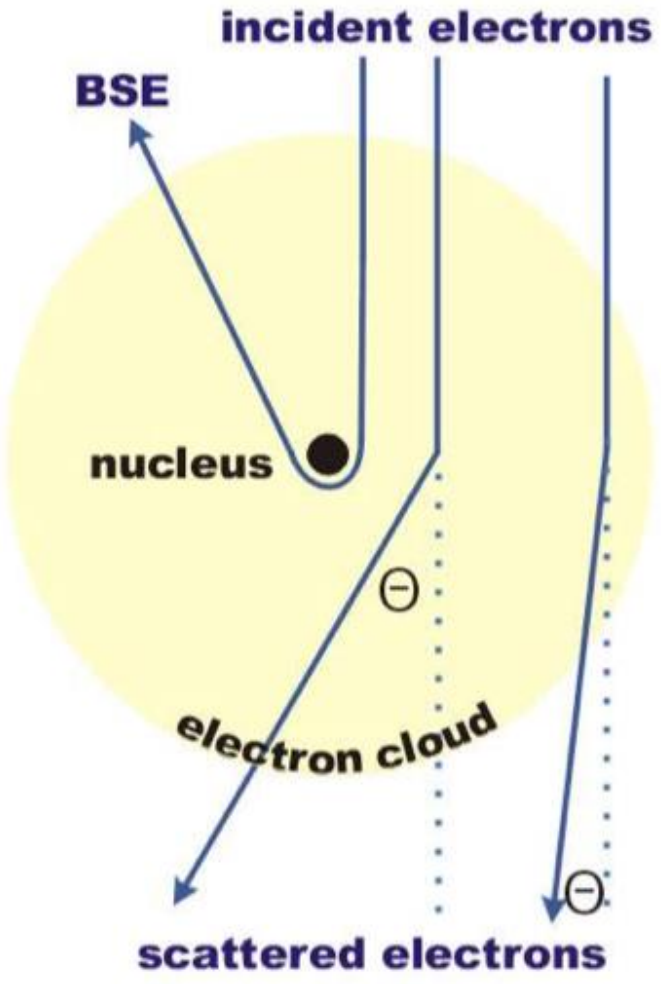
5 Analytics

6 Special Examples

Interaction of the beam with the specimen

Scattering of an electron

- Electrons scatter elastically at the positive charge of the atom core
- Electron scatter inelastically at the electron shell of an atom within the sample

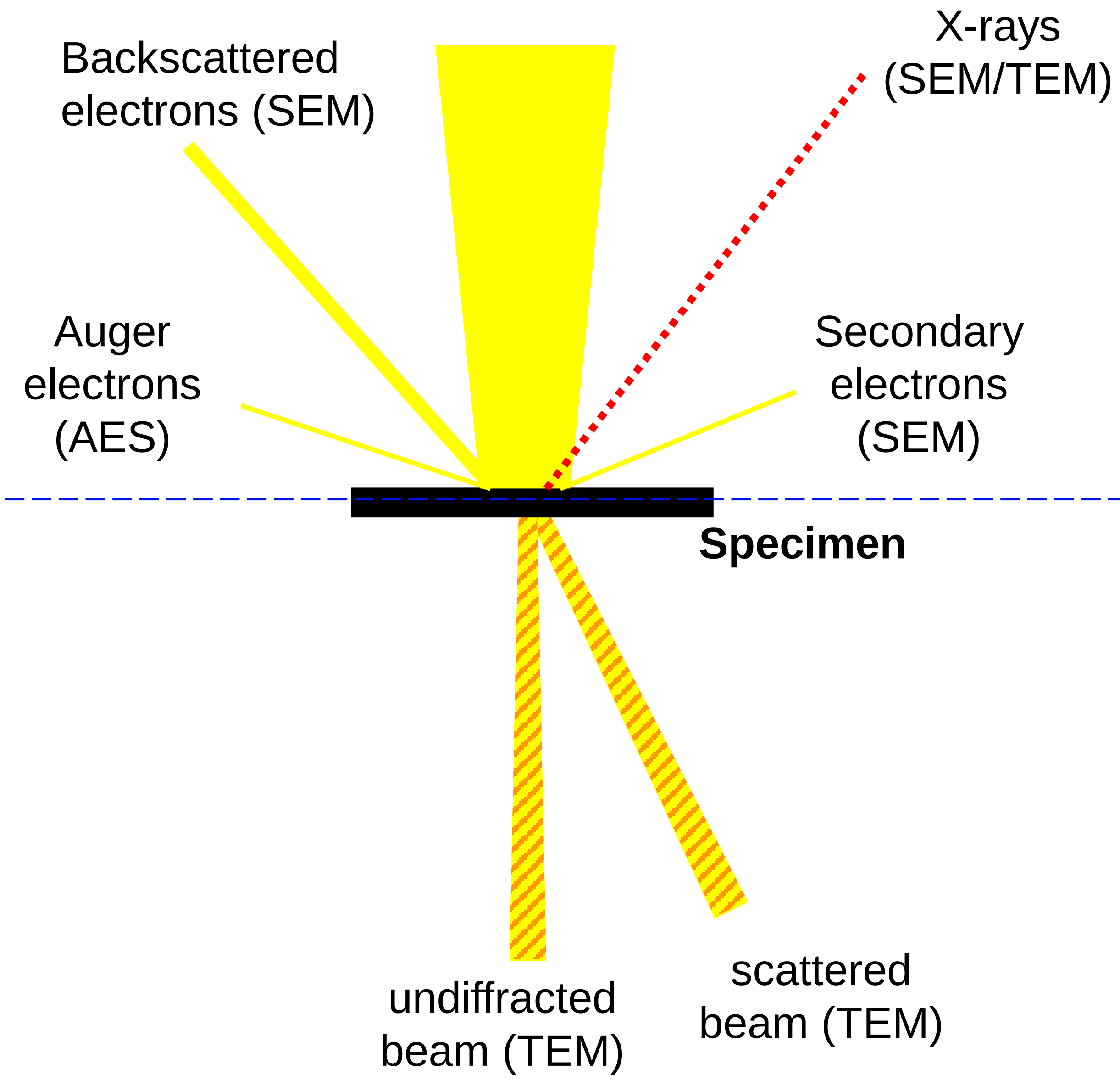


Interaction of Electrons with Matter

SEM:

imaging

X-rays:
XEDS (EDX, EDS), WDS, EPMA



TEM:

elastic scattering:
TEM, HRTEM, STEM, SAED, CBED

inelastic scattering:
EELS, ESI

X-rays:
XEDS (EDX, EDS)

Light Microscope

Electron Microscope

Opaque specimen:
reflected-light microscope
- illumination from above
- surface = ?

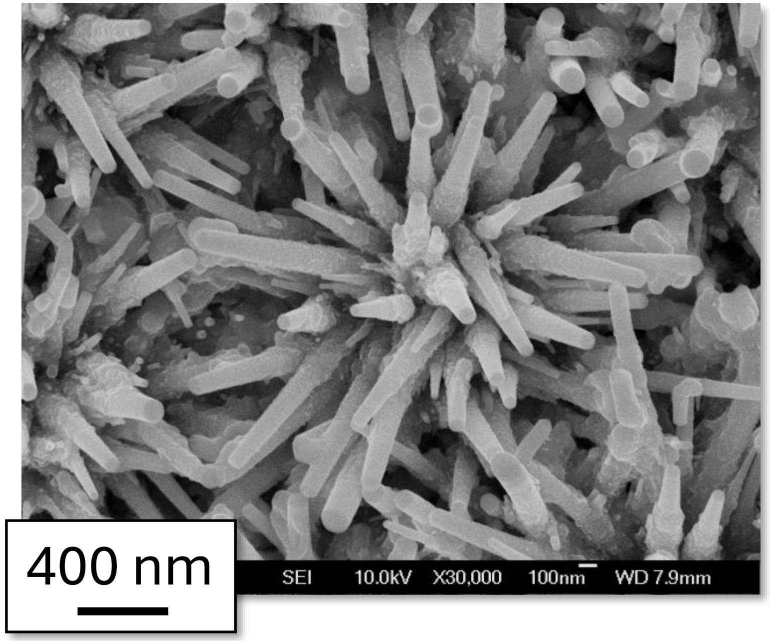
Scanning Electron Microscope

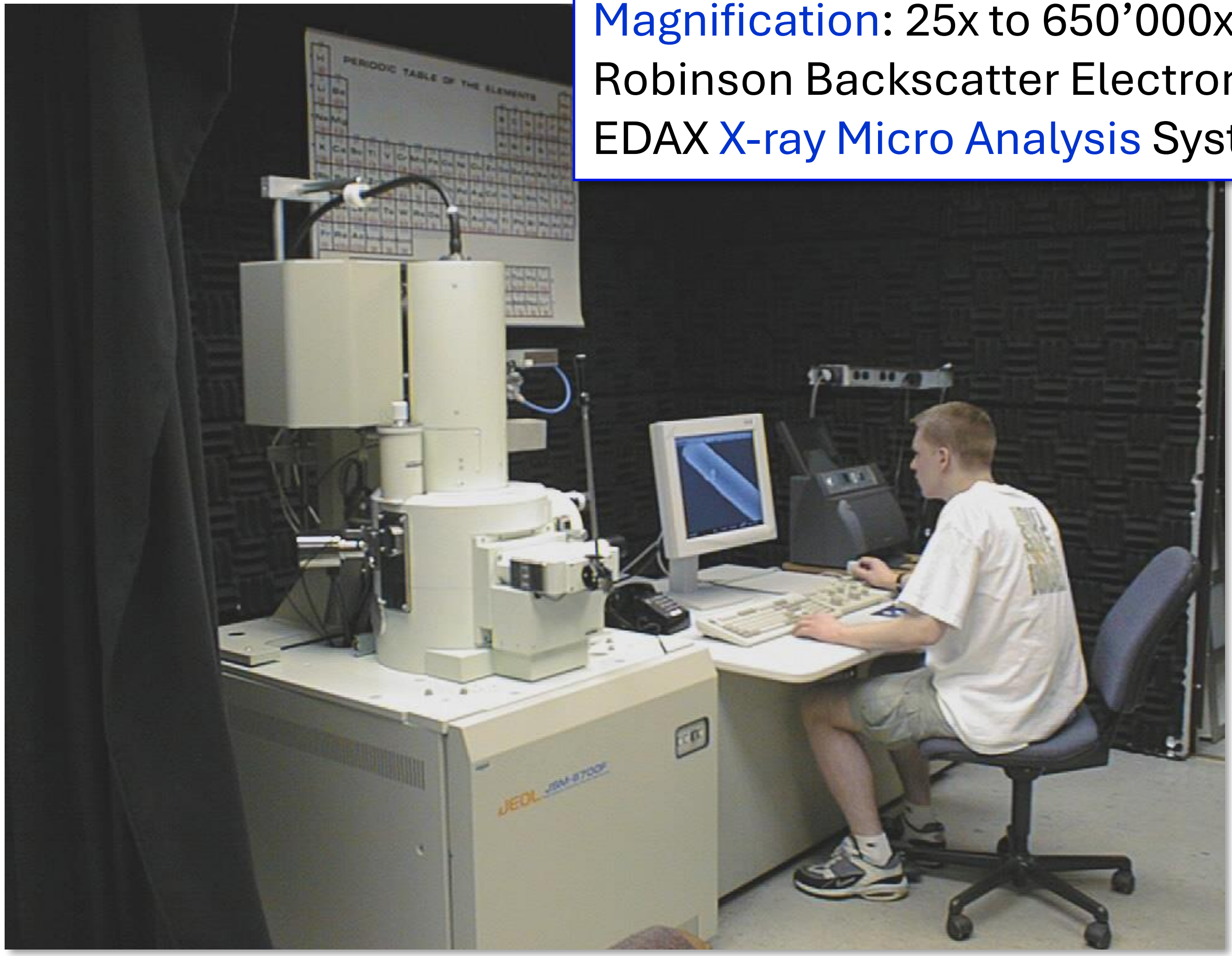
Transparent specimen:
transmitted-light microscope
- illumination from below
- bulk structure = ?

Transmission Electron Microscope

Scanning Electron Microscope

Focused beam scanned over the sample ; detection in reflection (serial acquisition)



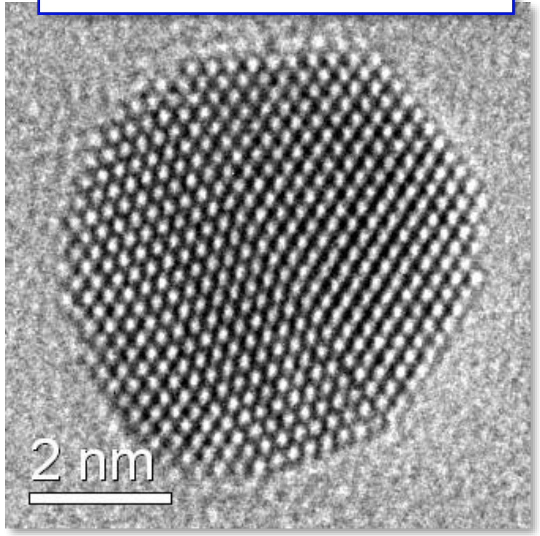


JEOL 6700F Scanning Electron Microscope
1.0 nm resolution @ 15 kV
2.2 nm resolution @ 1 kV
Magnification: 25x to 650’000x
Robinson Backscatter Electron Detector
EDAX X-ray Micro Analysis System

Transmission Electron Microscope

Parallel or scanning beam illumination; detection in transmission (parallel/serial acquisition)

Gold Nanoparticle



FEI Tecnai F-30
Field emission gun
Acceleration voltage: 300 kV
Point resolution: 0.18 nm
Information limit: 0.12 nm
Magnification: 50x to 10’000’000x
Imaging filter (GIF), EDX system
2 slow-scan CCD cameras (1k x 1k)
1 TV-rate CCD camera
Stages: heating, cooling, tomography, in situ etc.

Wave Lengths of Electrons

Accelerating voltages:

SEM 0.1 – 40 kV

TEM 30 – 1‘000kV

Atomic distances:

~ 0.1 nm

V_{acc} / kV	Nonrelativistic wavelength [nm]	Relativistic wavelength [nm]	Effective resolution [nm]
1	0.0388	0.0388	~ 1.2
30	0.00706	0.00697	~ 0.6
100	0.00386	0.00370	~ 0.3 / 0.11
300	0.00223	0.00197	~ 0.18 / 0.05
1000	0.00124	0.00087	~ 0.1

SEM (1, 30 kV)

TEM (100, 300, 1000 kV)

(With spherical aberration corrector)

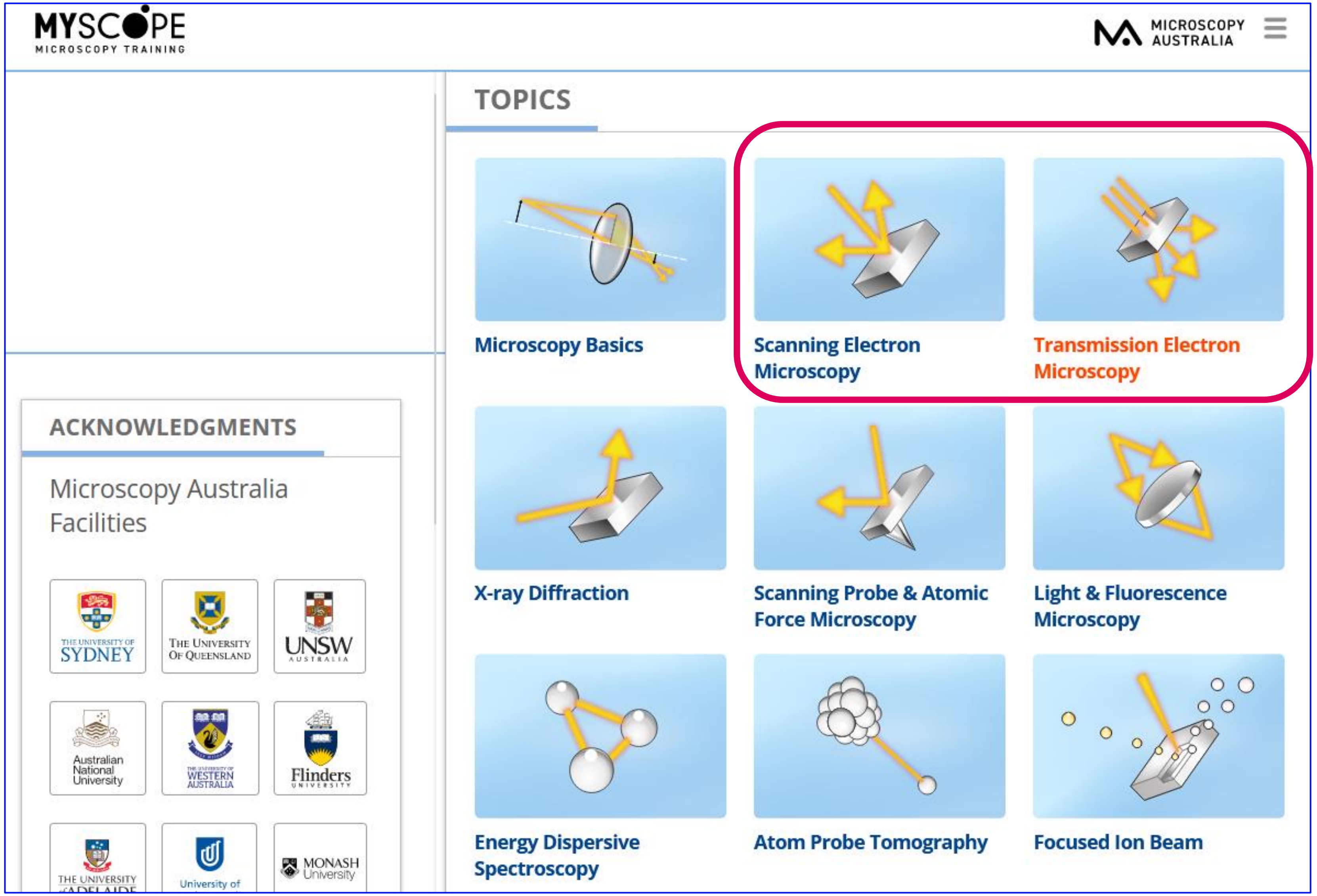
Compare with:

1 keV Soft X-rays → $\lambda \sim 10$ Å

100 keV Hard X-rays → $\lambda \sim 0.1$ Å

34 meV Neutrons → $\lambda \sim 1.5$ Å

Good intro to many techniques: https://myscope.training



Agenda

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1 Why Electron Microscopy

2 Intro

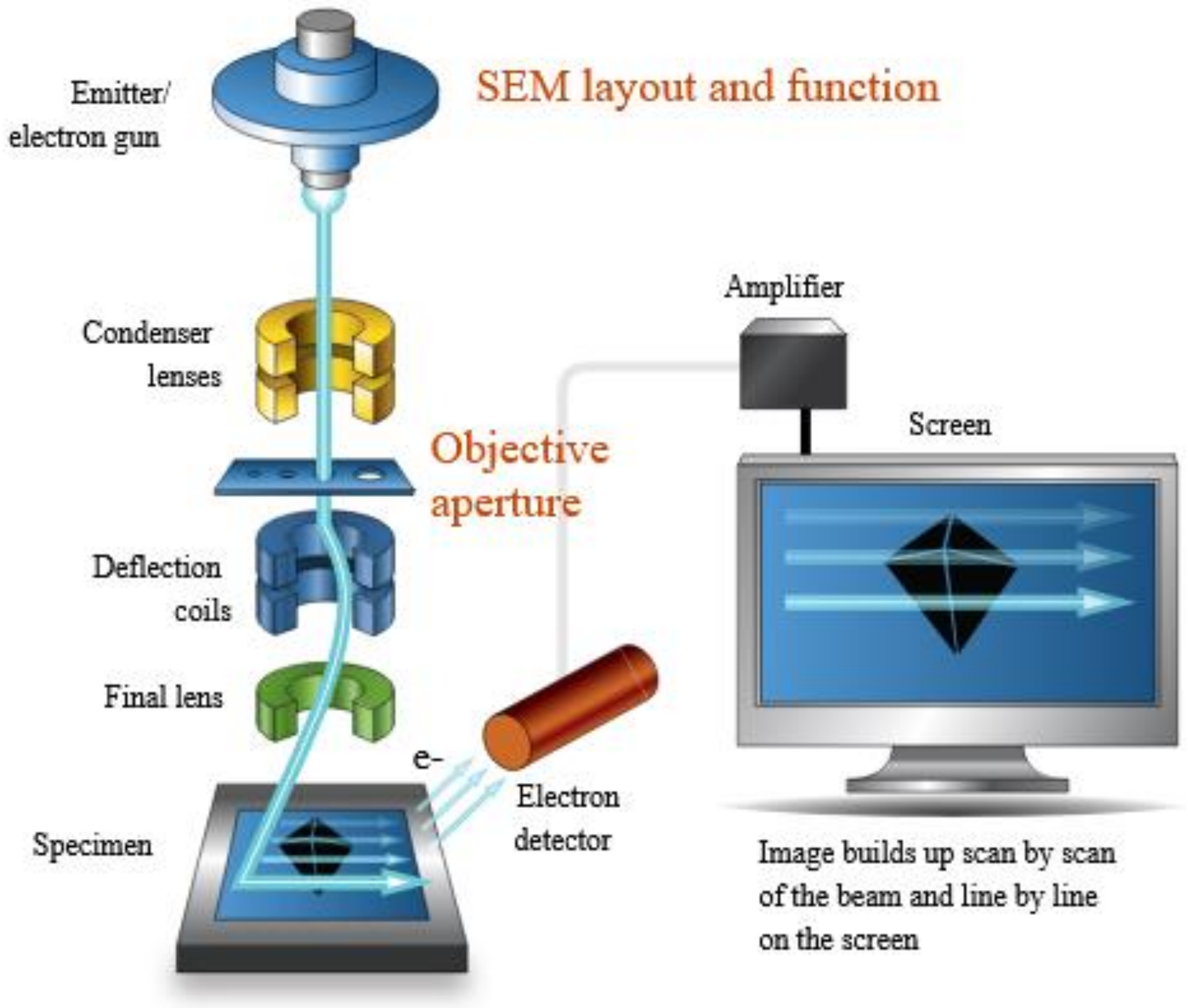
3 SEM Basics
- principles
- main signals
- effect of beam energy and sample material
- detection

4 (S)TEM Basics

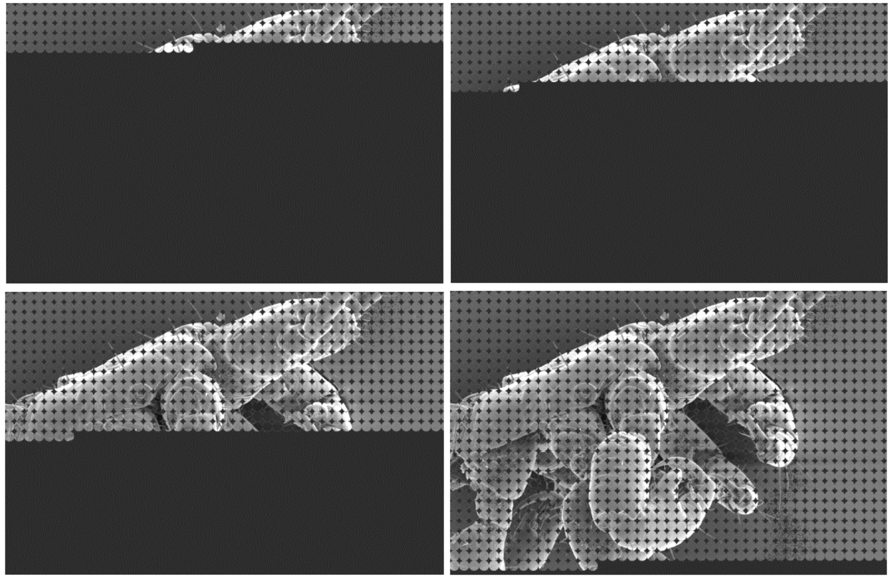
5 Analytics

6 Special Examples

SEM (scanning electron microscope)

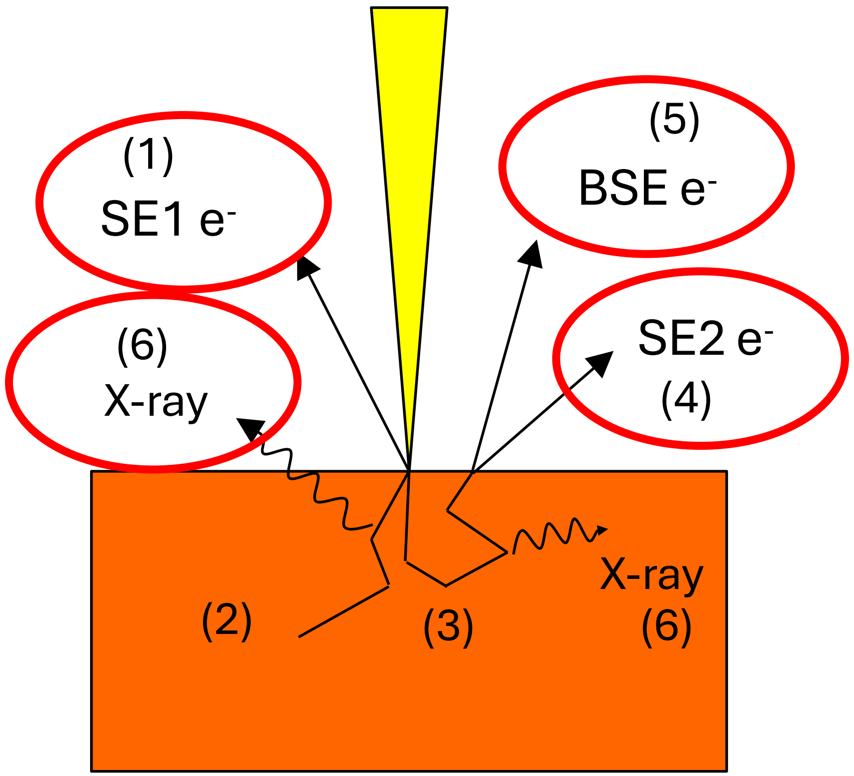


- Vacuum system
- Electron source demagnified by electro-magnetic lenses and focused onto specimen
- Beam scanned over specimen area
- Signal detected per scan position (serial acquisition)
- Magnification defined by size of scanned area



Electron Beam Interactions & Imaging

Main signals



Typical interactions with the sample and signals emitted from the specimen:

1. secondary electrons emitted due to incident electron (SE1)
2. (absorbed electrons)
3. elastically and inelastically scattered electrons
4. secondary electrons emitted due to BSE (SE2)
5. backscatter electrons (BSE)
6. X-rays due to (in)elastic scattering of the beam electron

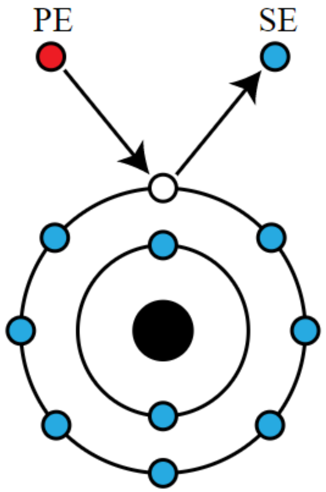
additional signals:

1. heat
2. sound
3. Auger electrons
4. cathodoluminescence
5. fluorenscence X-rays

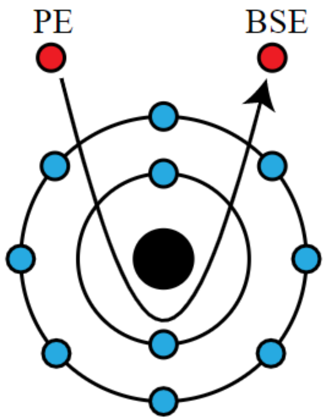
Typical usage of an SEM

- Acceleration voltage: 0.2-30 kV
- Magnification 30x - 500’000x
- Field Emission Electron Source Microscope: point resolution ~ 1 nm

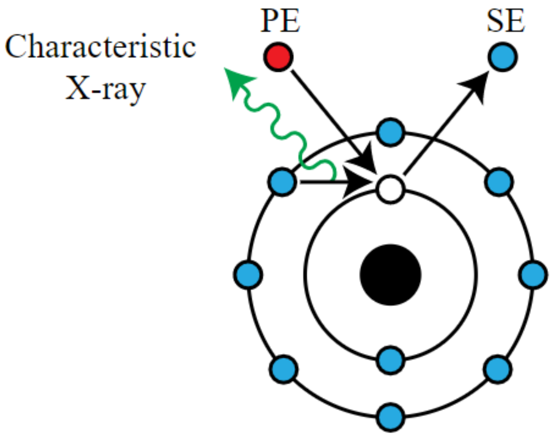
- **Frequently measured signals:**



Secondary electrons

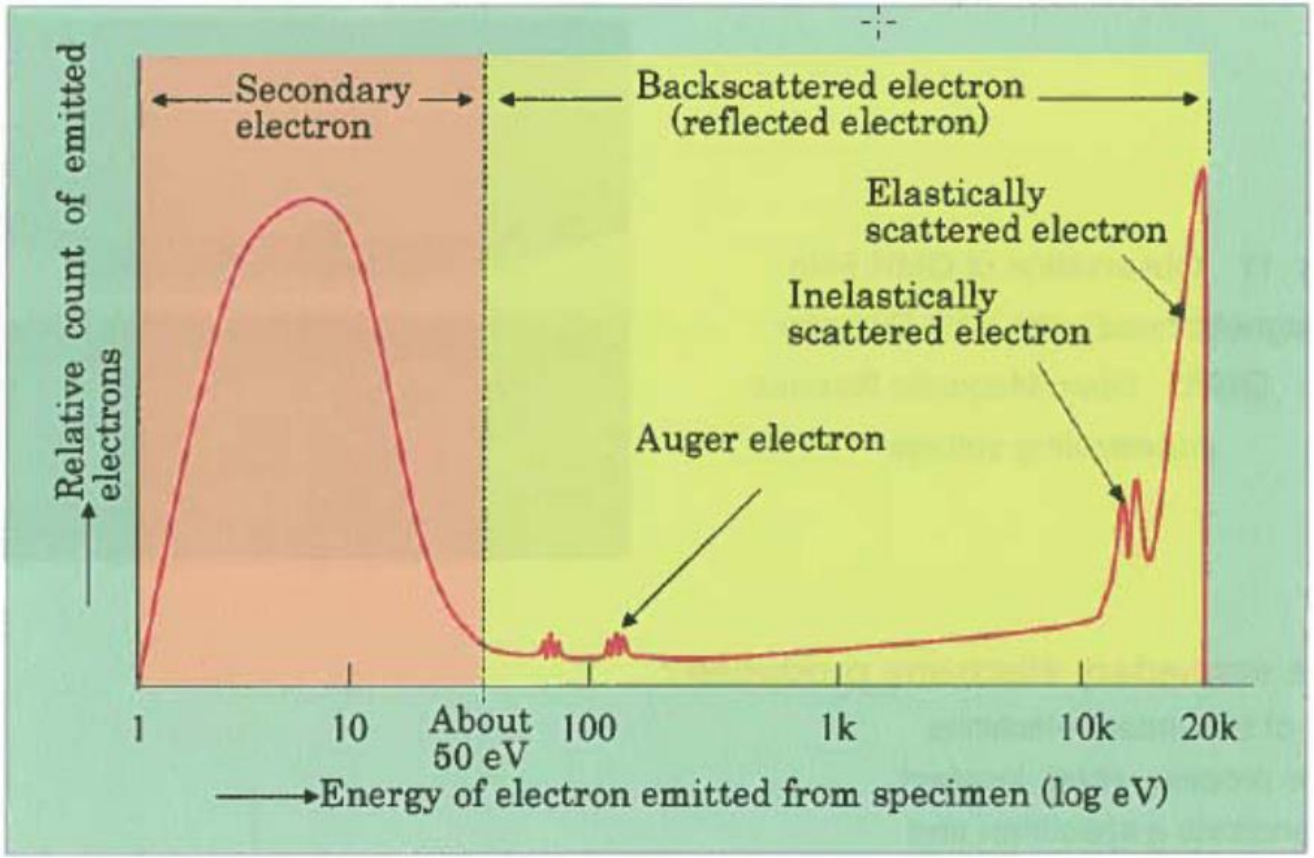


Back scattered electrons



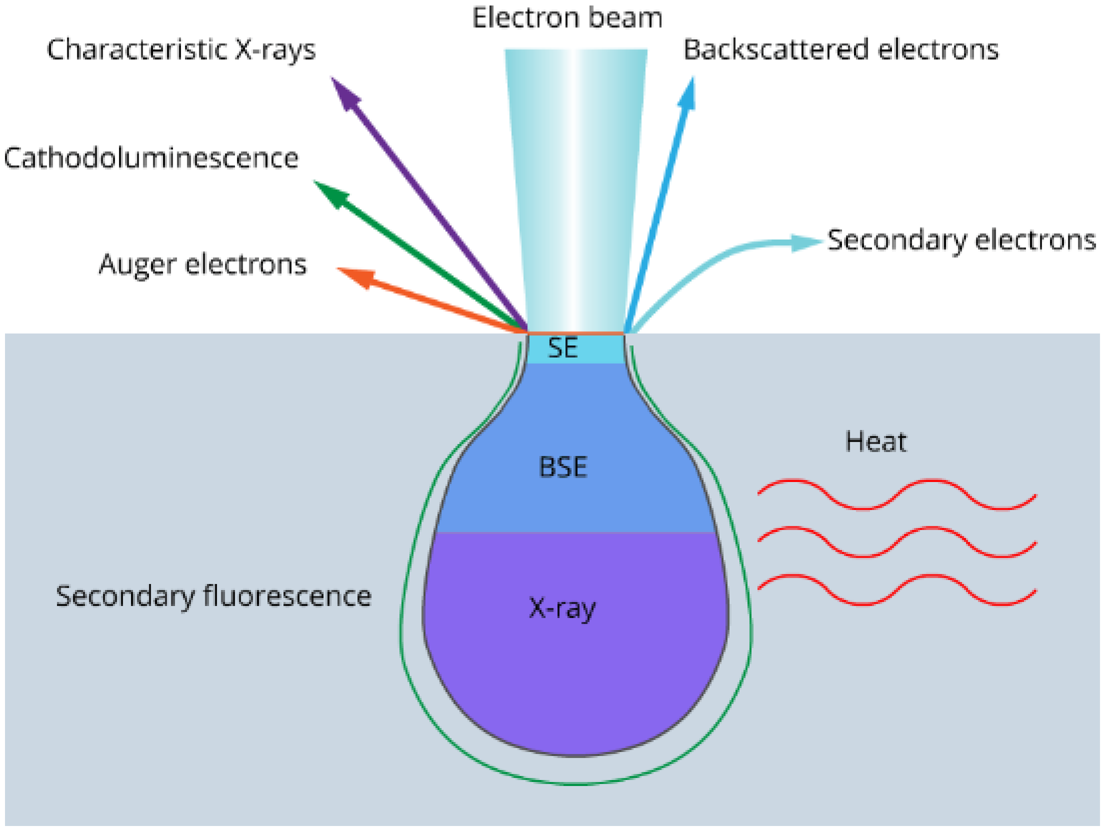
Characteristic X-rays

Energy and intensity of emitted electrons



electron yield as a function of the energy of the emitted electron

http://www.engr.uvic.ca/~mech580/electron-microscopy/Introduction%20SEM.pdf



SE: from few nm depth
BSE: up to few μm, f(Z)
X-rays: several μm

https://www.epfl.ch/research/facilities/cime/wp-content/uploads/2019/11/SEM_Fall2019.pdf

Characteristics of BSE and SE

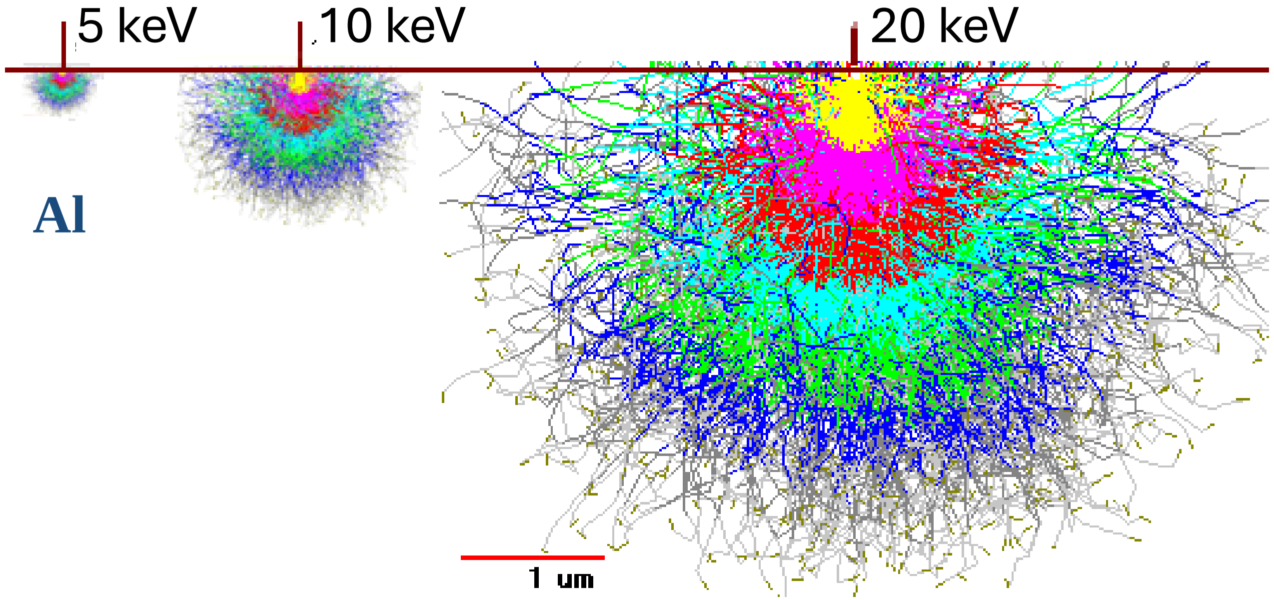
Backscattered electons

- Energy of backscattered electrons up to energy of the incident electrons
- 20-40% of electrons backscattered with 50-60% of the energy
- Originate from a large sample volume → low spatial resolution

Secondary electrons

- From inelastic scattering processes
- Transfer of energy to weakly bound electrons in outer atomic shells
- Low energy electrons (≤50 eV) independent of excitation voltage
- Can only pass through a few nm's
  → come from surface region referred to as escape region
- SE1 electrons: high spatial resolution; SE2 electrons not: watermark of BSE!

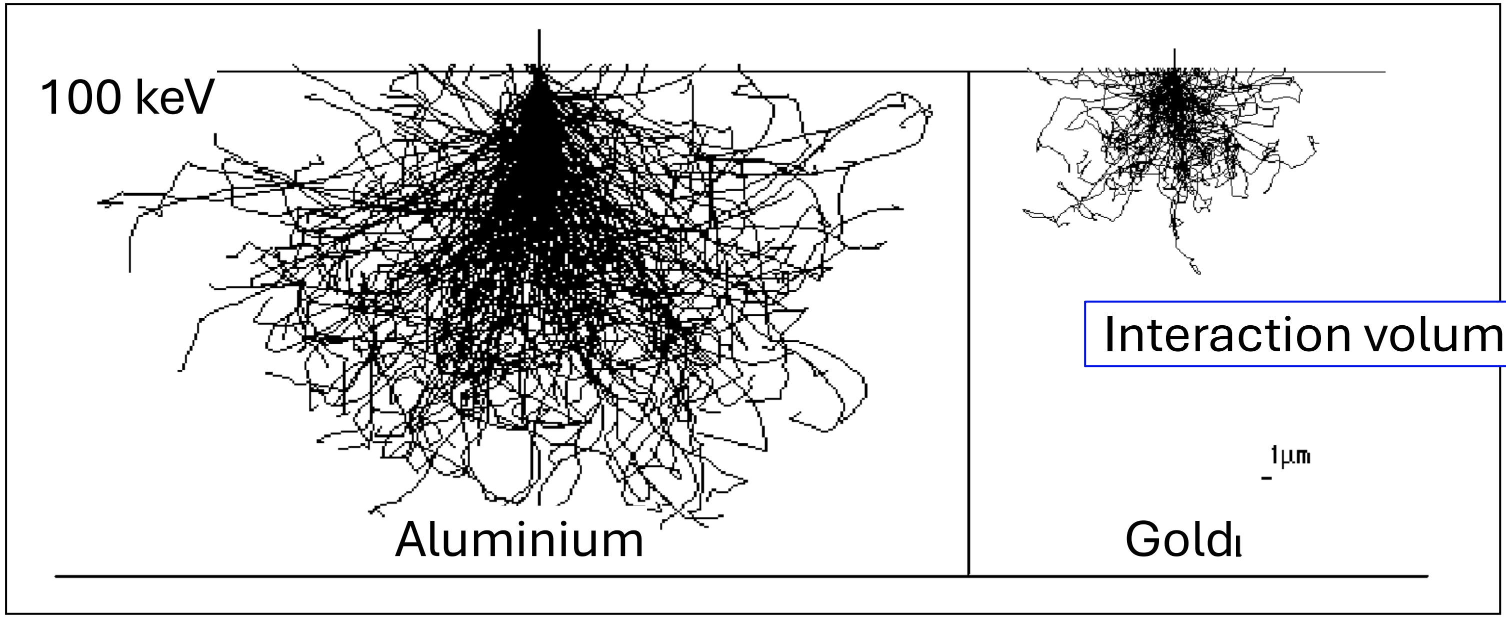
Interaction volume as a function of voltage and atomic species



Slide by N. Zaluzec

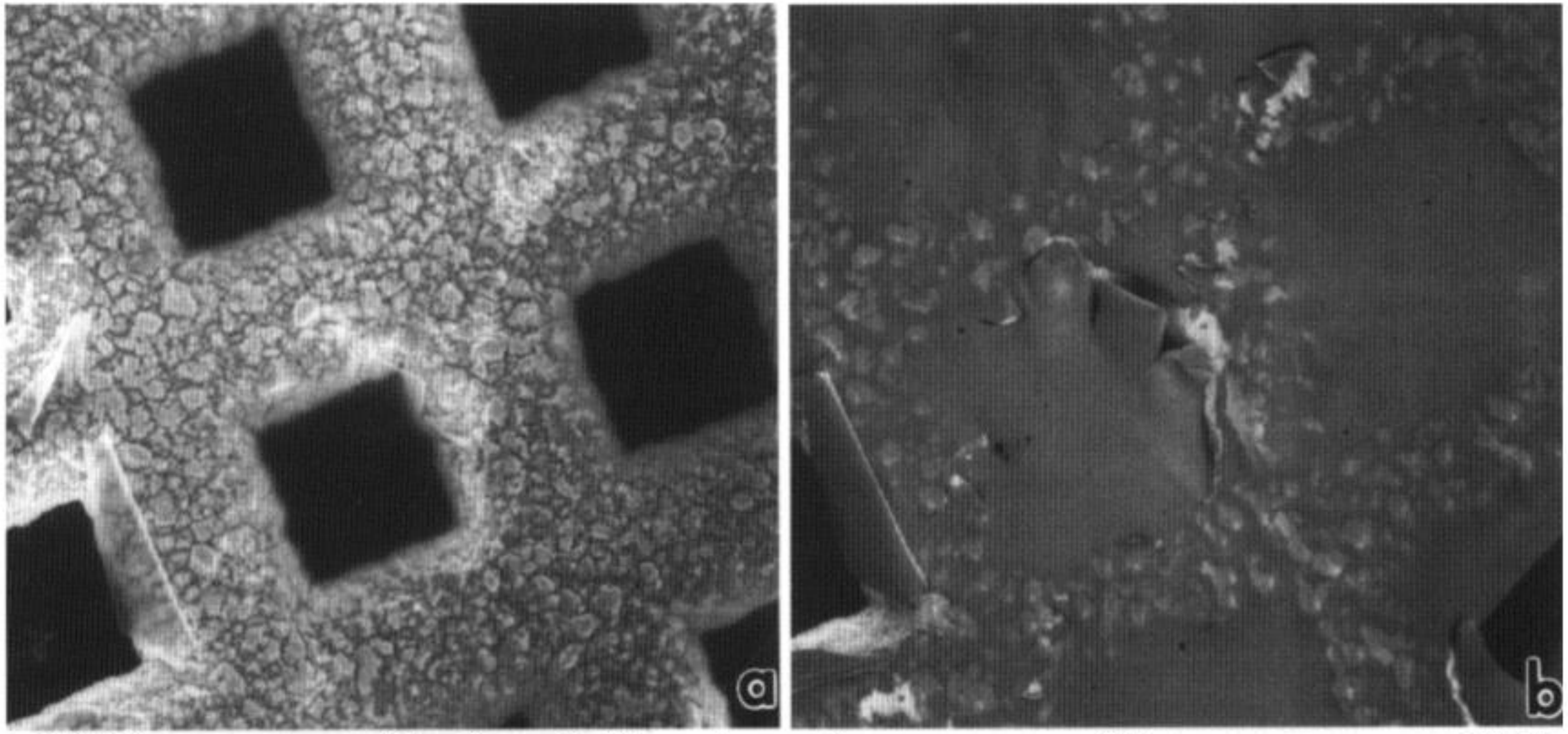
DC Joy's Monte Carlo Simulation Program

Interaction volume = f(E_0)



Interaction volume = f(Z)

Effect of accelerating voltage on penetration depth and signal



20kV Carbon foil on top of a copper grid 2kV

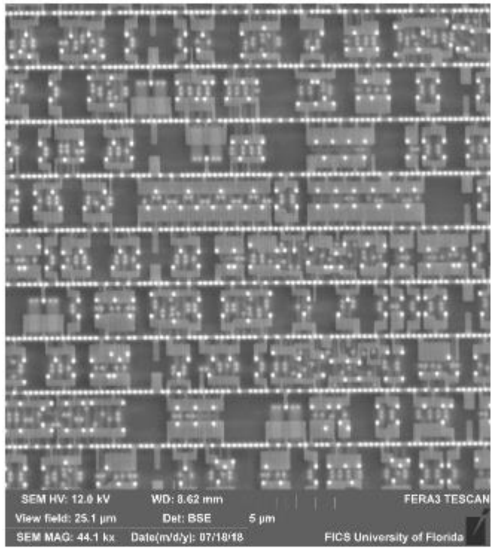
SE image of thin C-film on Cu-grid

- Strong penetration
- Cu grid under C-film visible through electron backscattering, structure of C-film hidden

- Low penetration through C-grid, most signal produced in the C-film.
- C-film and its defects become visible

Effect of Beam Energy on SE Imaging

5keV



12keV

20keV

30keV

https://faculty.eng.ufl.edu/navid-asadi/wp-content/uploads/sites/84/2021/09/lecture-3-SEM-Principle.pdf

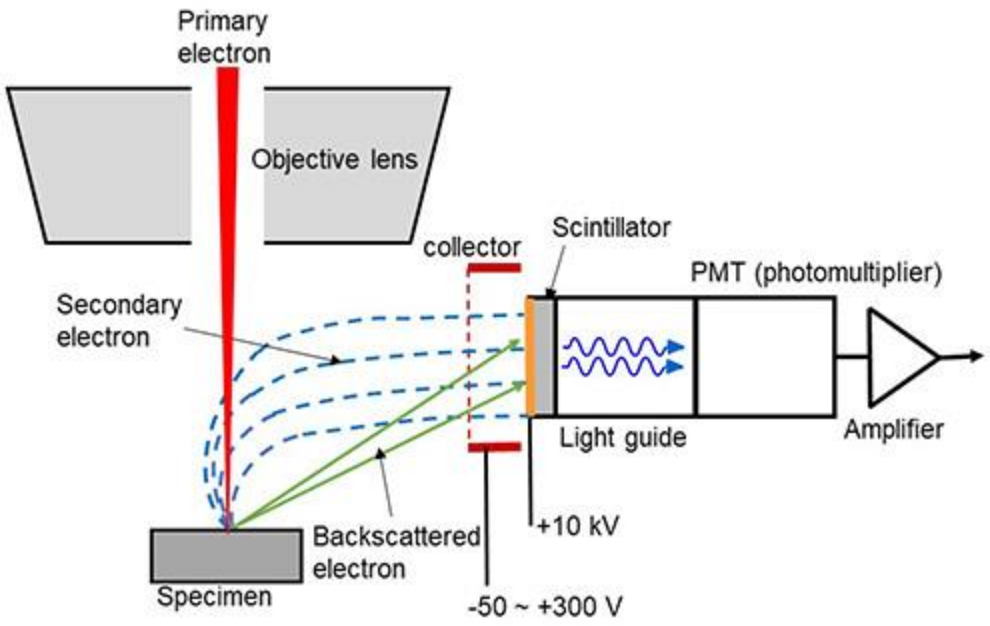
Higher voltage;

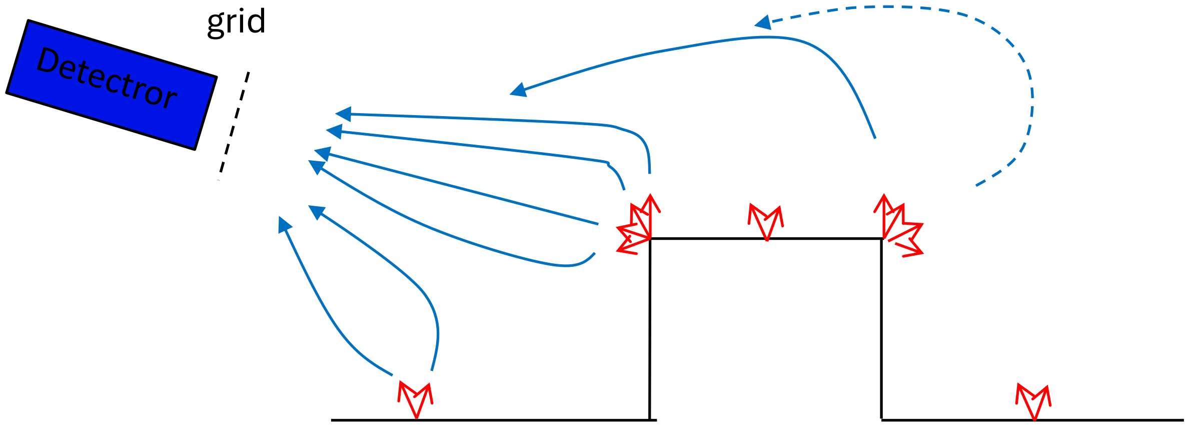
- Less SE1
- More SE2 carrying the watermark from BSE caused by high Z species

Detection: off-axis detectors

Principle of Everhart-Thornley detector

- Positioned at the side
- Secondary electrons attracted by positive voltage
- Further accelerated for interaction with scintillator
- Enhanced by a photomultiplier



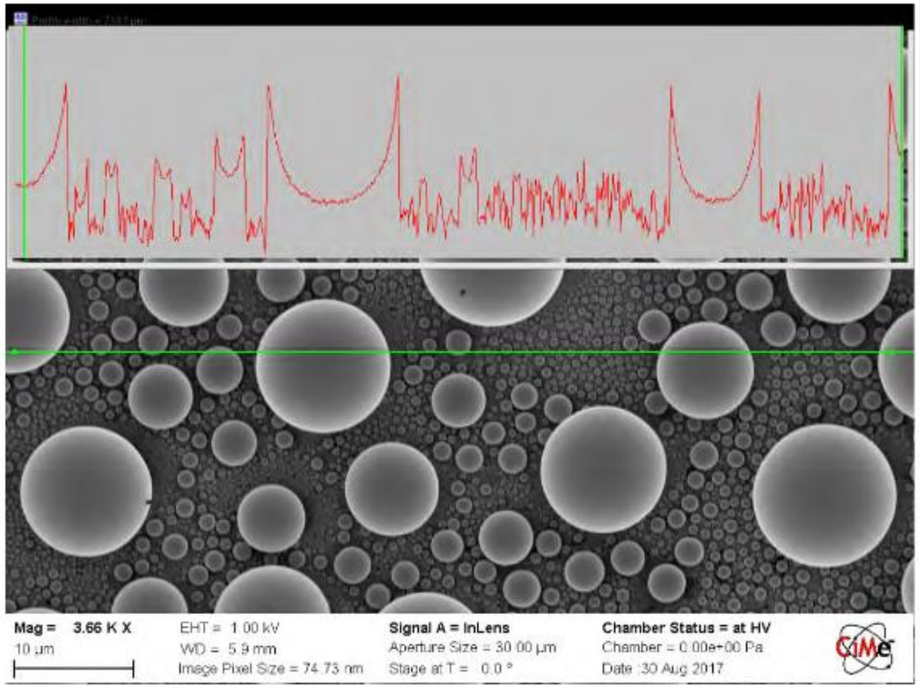


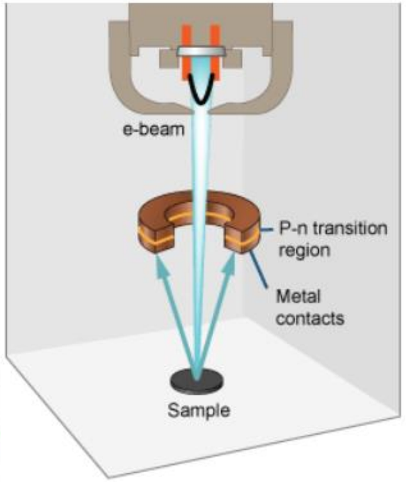
3d effect:

- Edge-effect: at edge, more electrons can escape
- Shadow-effect: higher probability for electrons to reach the detector from sample side facing towards the detector

Detection: on-axis detectors

In-lens SE detector

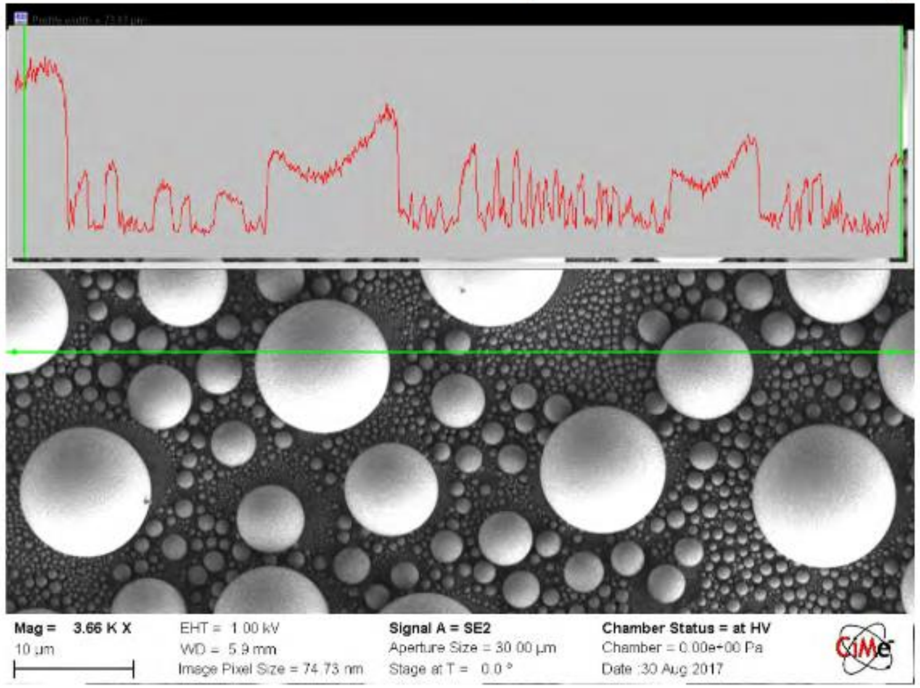




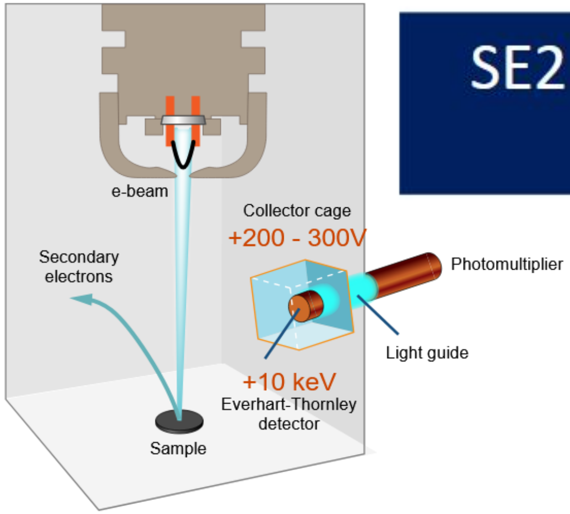
In-lens SE Detector located directly above and centered

(In-lens BSE detector is analogous)

Everhart Thornley detector



SE2 Detector located on the lower right



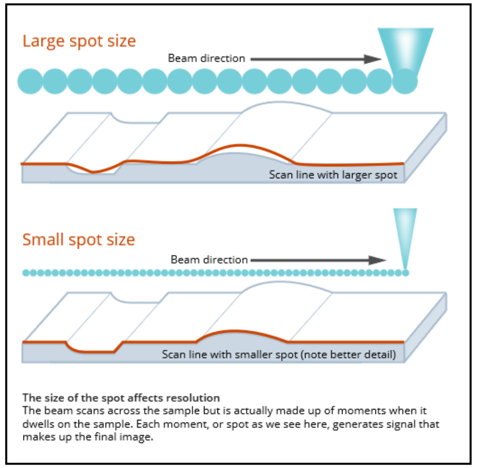
Critical aspects for nanoparticles

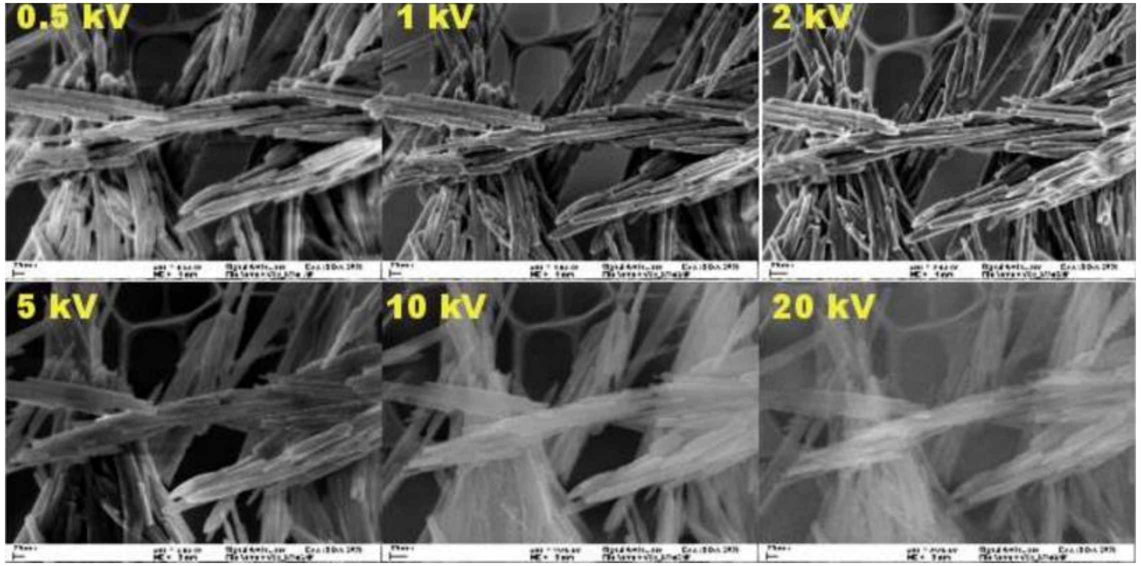
The spatial resolution of the SEM depends on:

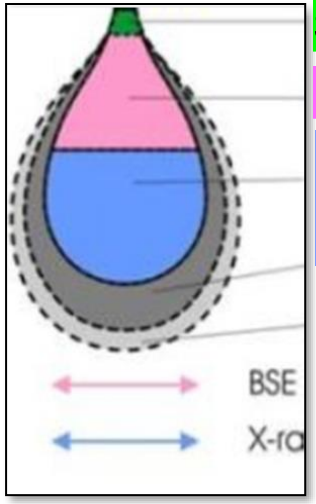
- Size of the electron spot = function of wavelength of the electrons and the electron-optical system.
- more importantly: size of the interaction volume.
- spot size and the interaction volume are large compared to the distances between atoms!

→ Resolution of SEM not high enough to image individual atoms.

Spot size:







Interaction volume:

SE1

BSE

Characteristic X-rays

Requirements for sample material

Clean!
(contamination…)

Electrically conducting
Coat insulating samples with thin (3-10 nm) conducting layer e.g. C or Au and connect to ground

Suitable for high vacuum
Porous samples need long pumping times

Beam tolerance:
Beam sensitive materials can benefit from low voltage, or from cryogenic temperatures

Environmental SEM (ESEM) for humid samples:
Low vacuum possible due to a differential pumping system.
Humidity is also useful for conducting away surface charges in insulating samples.

Etc.

X-ray spectroscopy

See TEM-lecture

Agenda

1 Why Electron Microscopy

2 Intro

3 SEM Basics

4 (S)TEM Basics
- components/principles
- parallel beam illumination imaging and diffraction
- specimen preparation

5 Analytics

6 Special Examples

All TEMs based on same principals

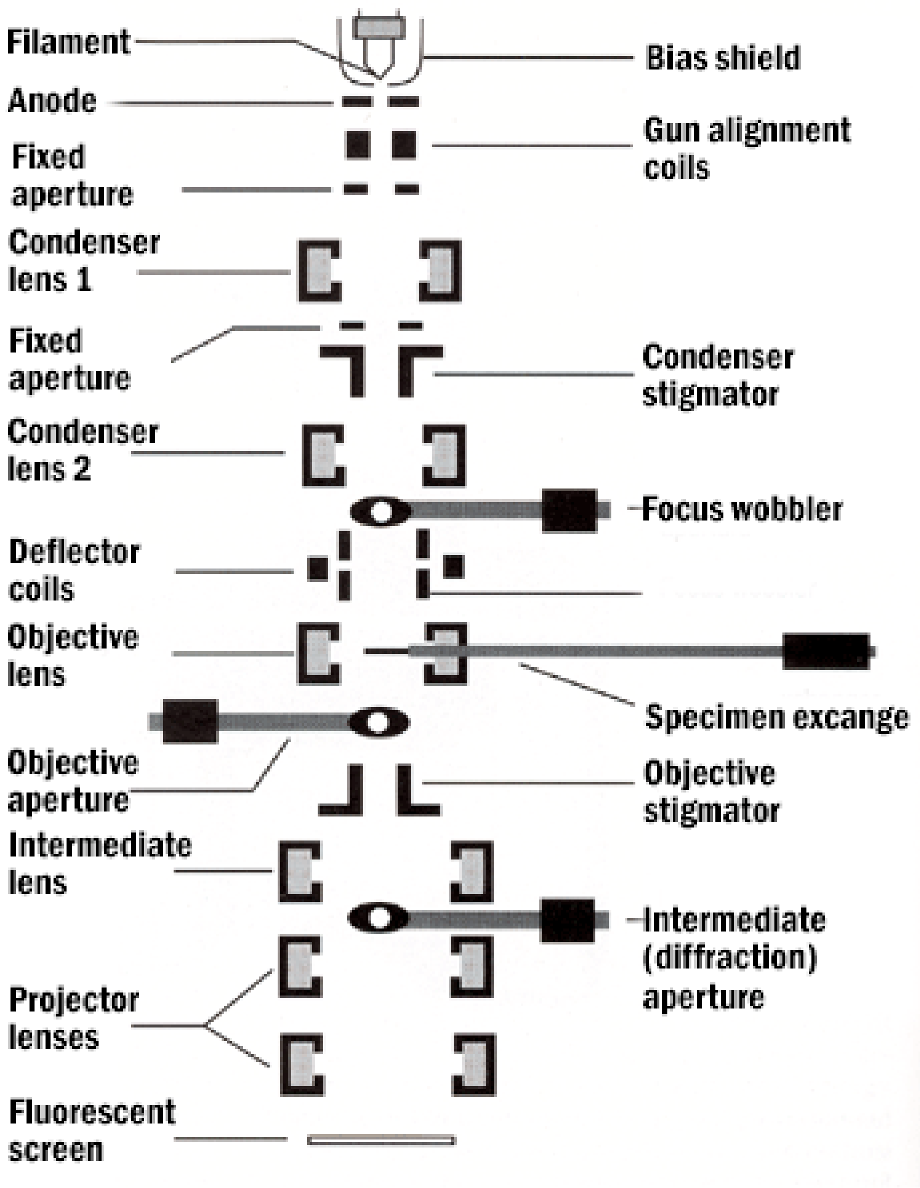
First Electron Microscope constructed by Ernst Ruska with Resolving Power greater than a Light Microscope (1931; Ernst Ruska Archiv))

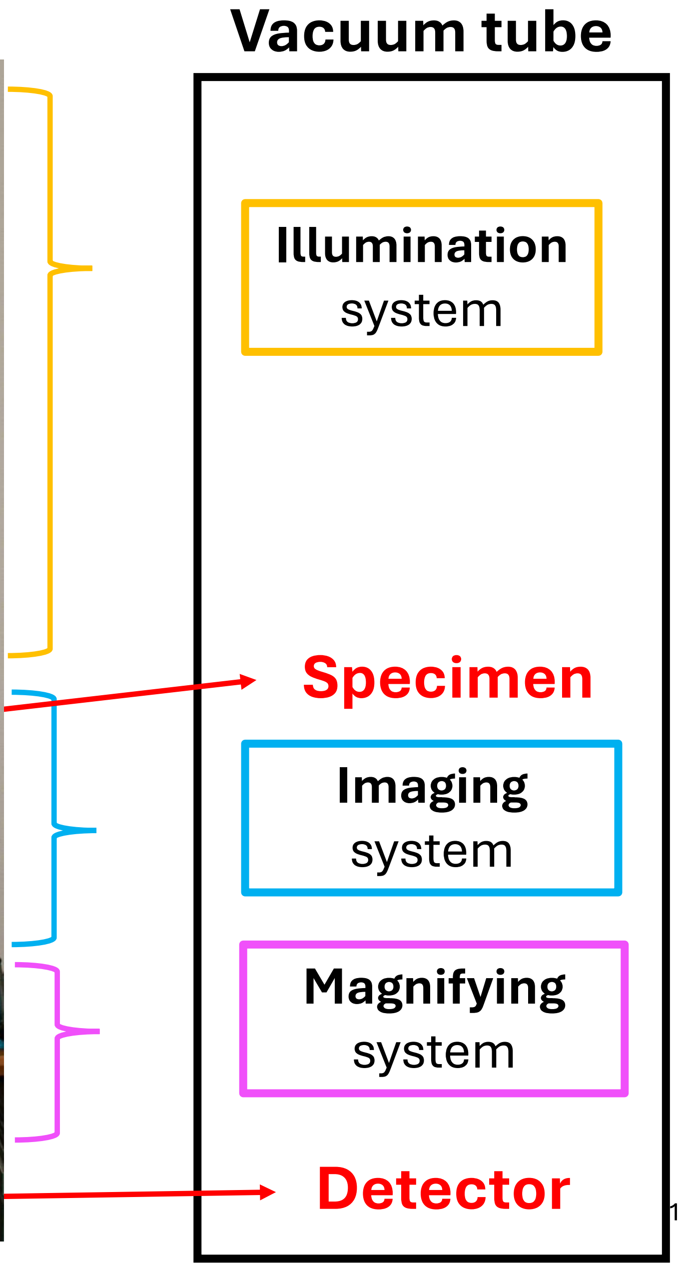
Modern „boxed“ TEM (Thermo Scientific, 300kV)

Highvoltage TEM (JEOL, 1MeV)

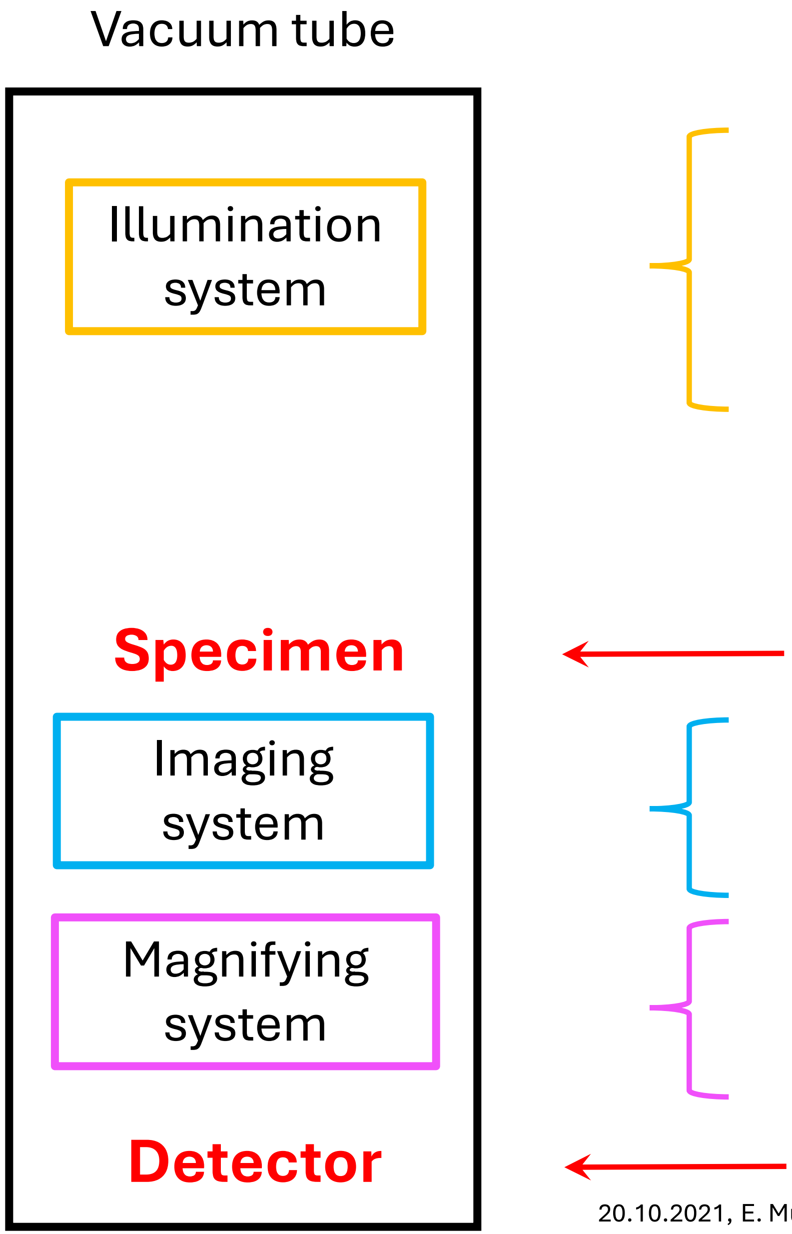
Table top TEM (Delong, 5kV)

Main components of a TEM





Function of the different parts



Prepare an electron beam and position it in the correct intensity, convergence angle and tilt at the right place on the sample

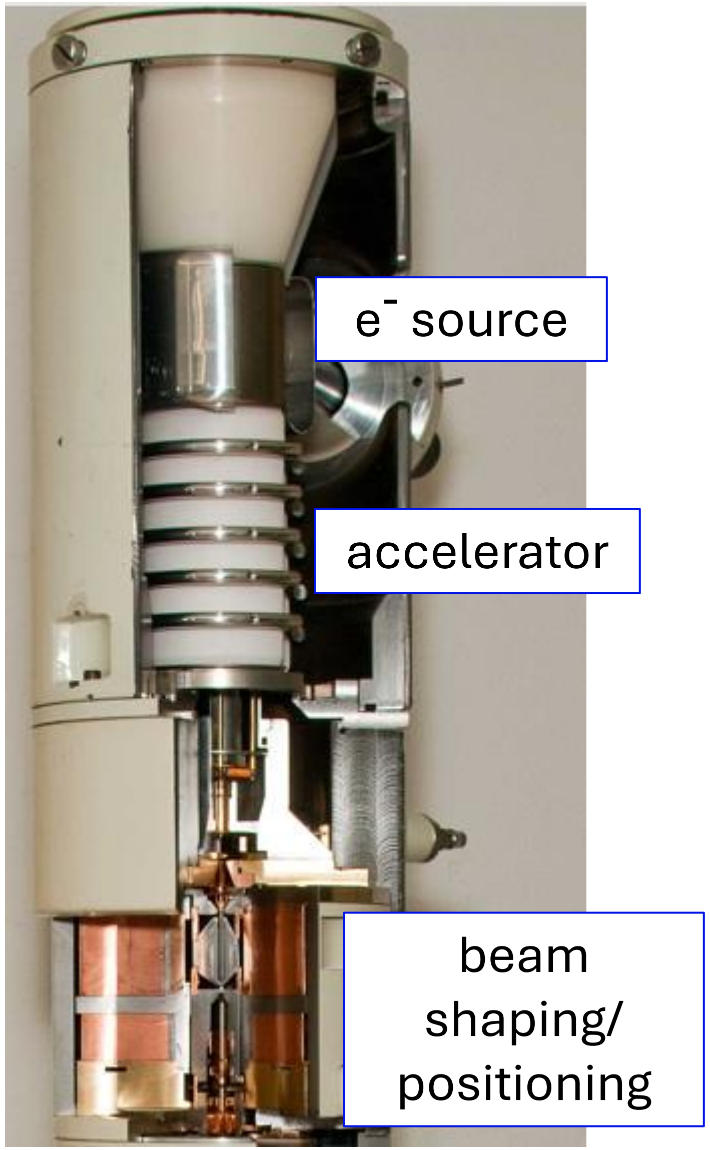
Expose the sample in the right way to the beam

Produce an image or diffraction pattern of a specific area of your specimen

Magnify this image or diffraction pattern as required

Record the data

Illumination system



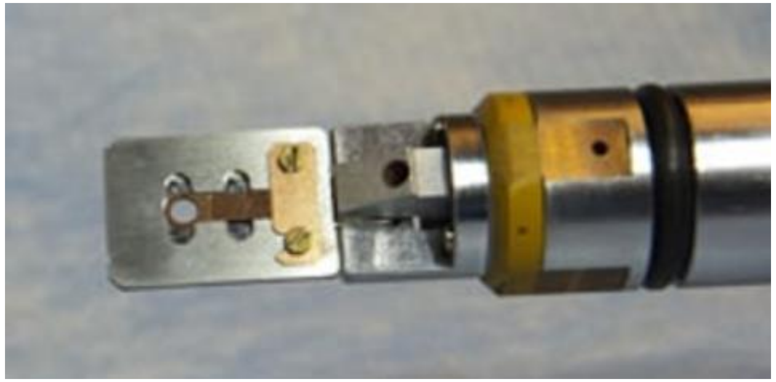
Function of the components

- Source: provide electrons (different source types)
- Acceleration: voltage applied to produce electrons with specific wavelength λ
  Possible voltages: 5keV - 3MeV
  Typical voltages: 60, 80, 100, 120, 200, 300keV
- Lens set: provide a convergent or parallel beam of a specific intensity and diameter

Important

- All in vacuum
- Electro-magnetic lenses
- Wave lengths few picometers <-> Resolution 0.5 – 3 Å

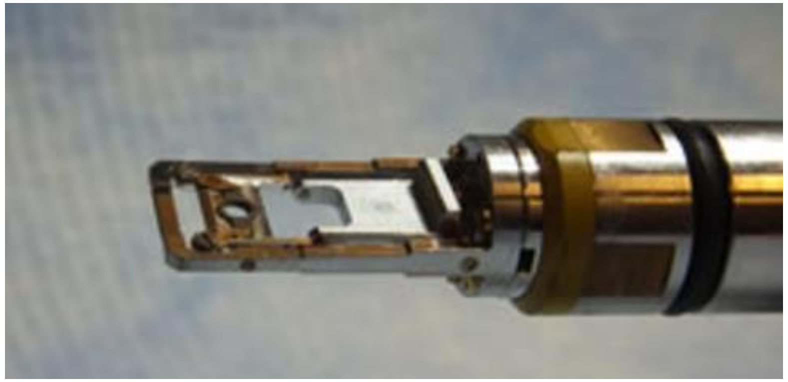
Holders: examples for room temperature/cryo holders



Single tilt holder

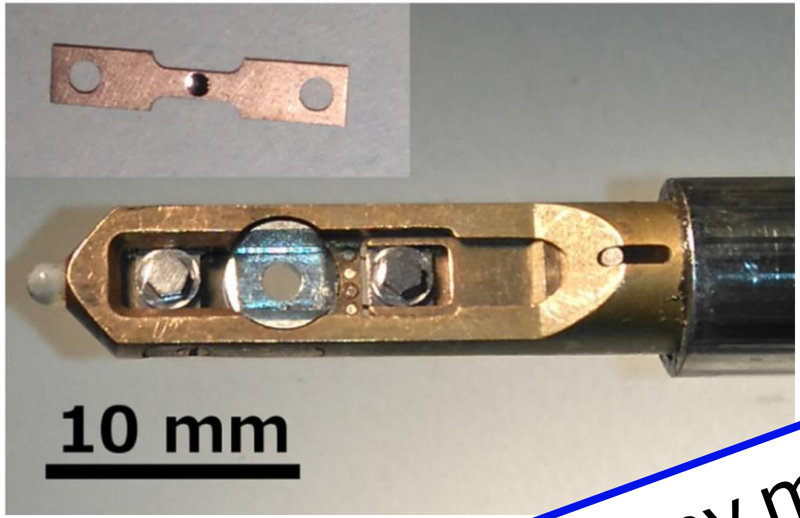
Single tilt holder tomography holder

Cryo transfer holder



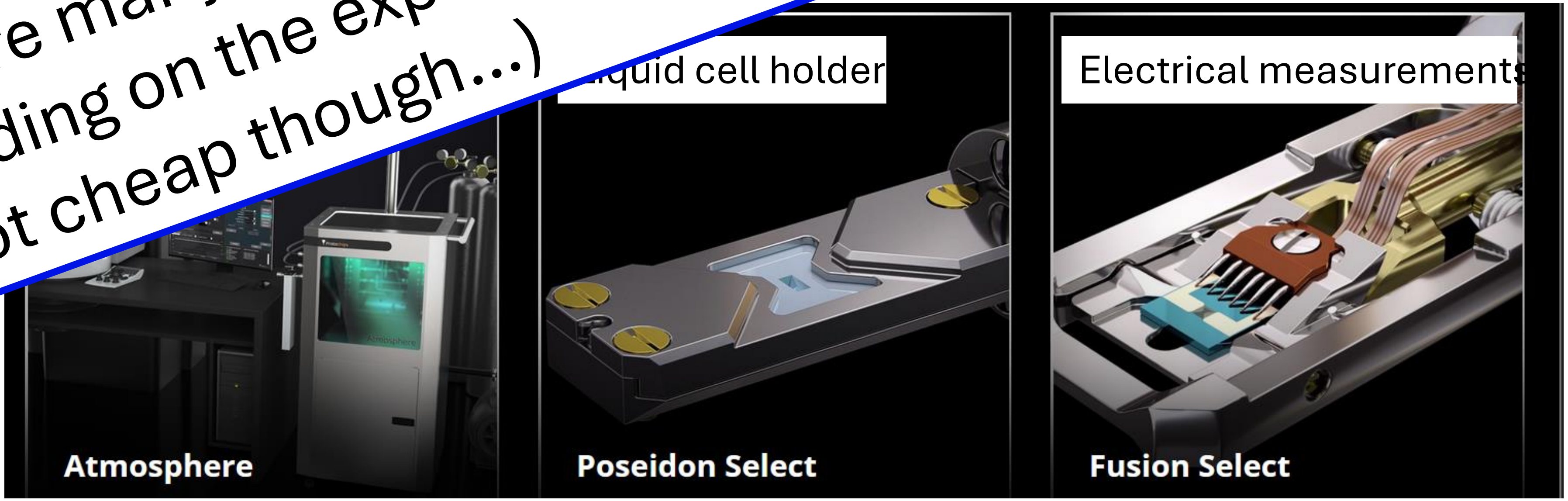
Double tilt holder

In situ holders



Tensile straining holder

There are many more holder types available – just depending on the experiments you need to do (they are not cheap though…)



Gas atmosphe… holder

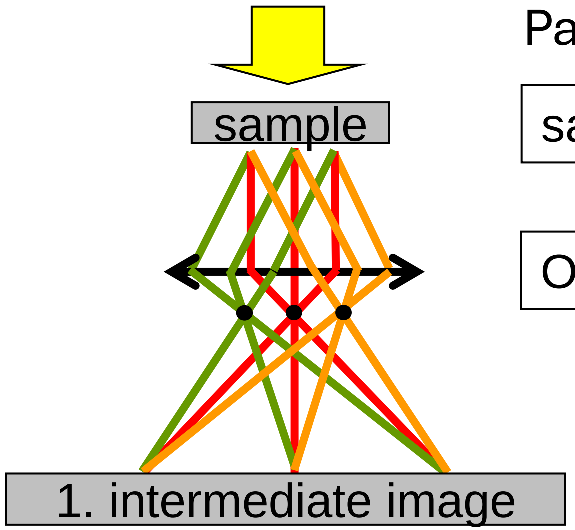
Specimen and imaging system: specimen position

Specimen

Imaging system

Text books

Parallel beam illumination



sample

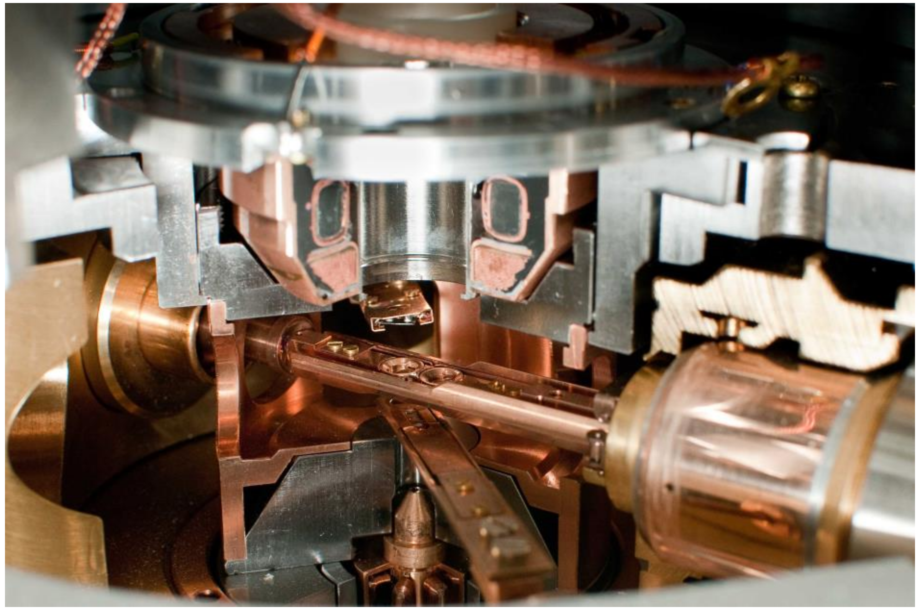
Objective lens

diffraction pattern

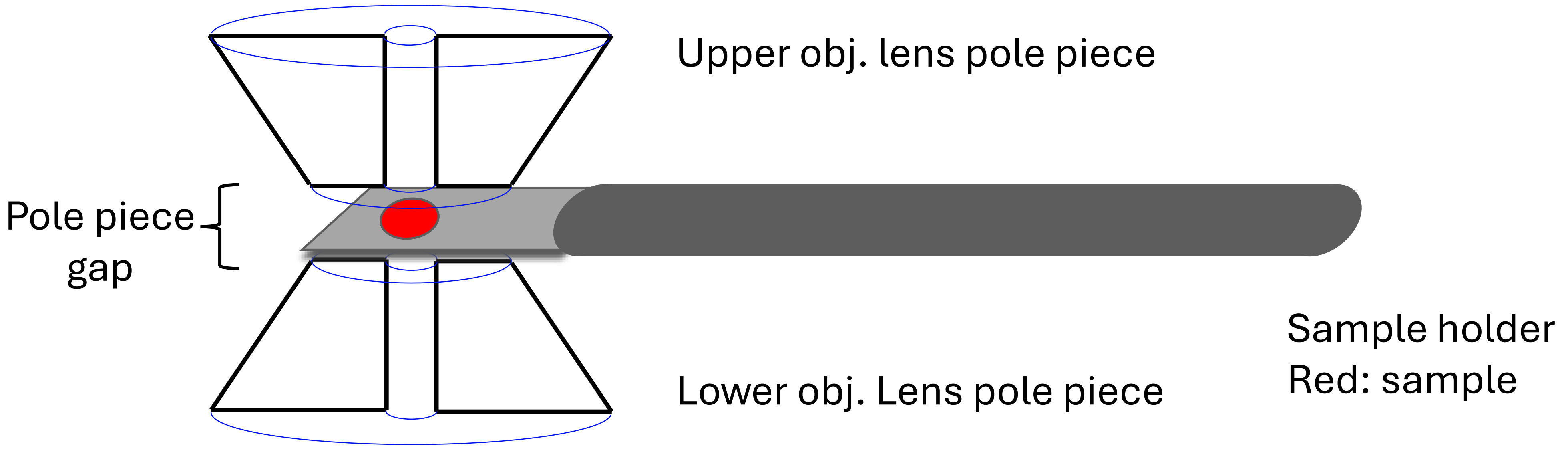
magnified image

Reality

Specimen sits in the pole piece gap



Specimen and imaging system: objective lens

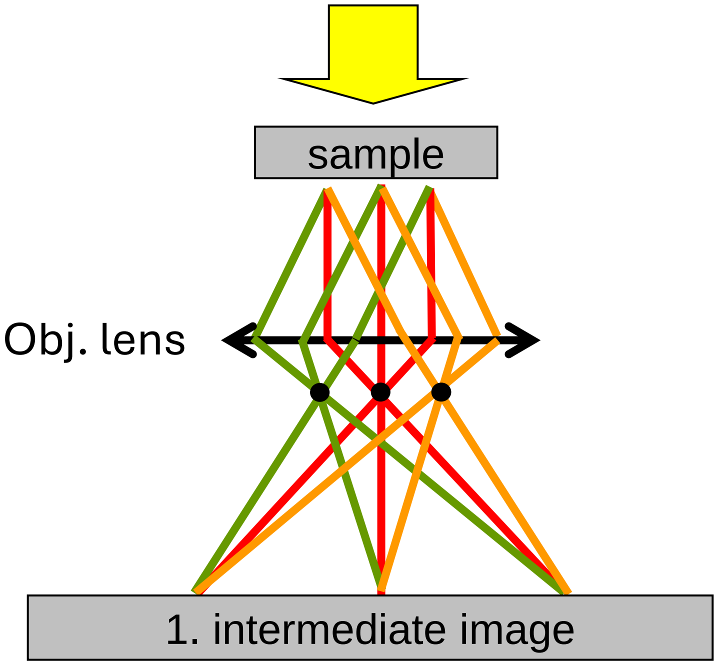


- The function of the objective lens is to produce a diffraction pattern and an image
- Large gap = high tilt capability, but lower resolution; small gap = low tilt, but higher resolution
  High tilt capability and high resolution are contradictory requests
- Typical pole piece gaps: 2-10mm <-> resolution at 200kV: 2.3A – 2.7A <-> λ = 2.5pm
- Typical tilt angles for standard holders (not tomography): 5-35°
- The specimen is in a high magnetic field (> 2T !!!!)

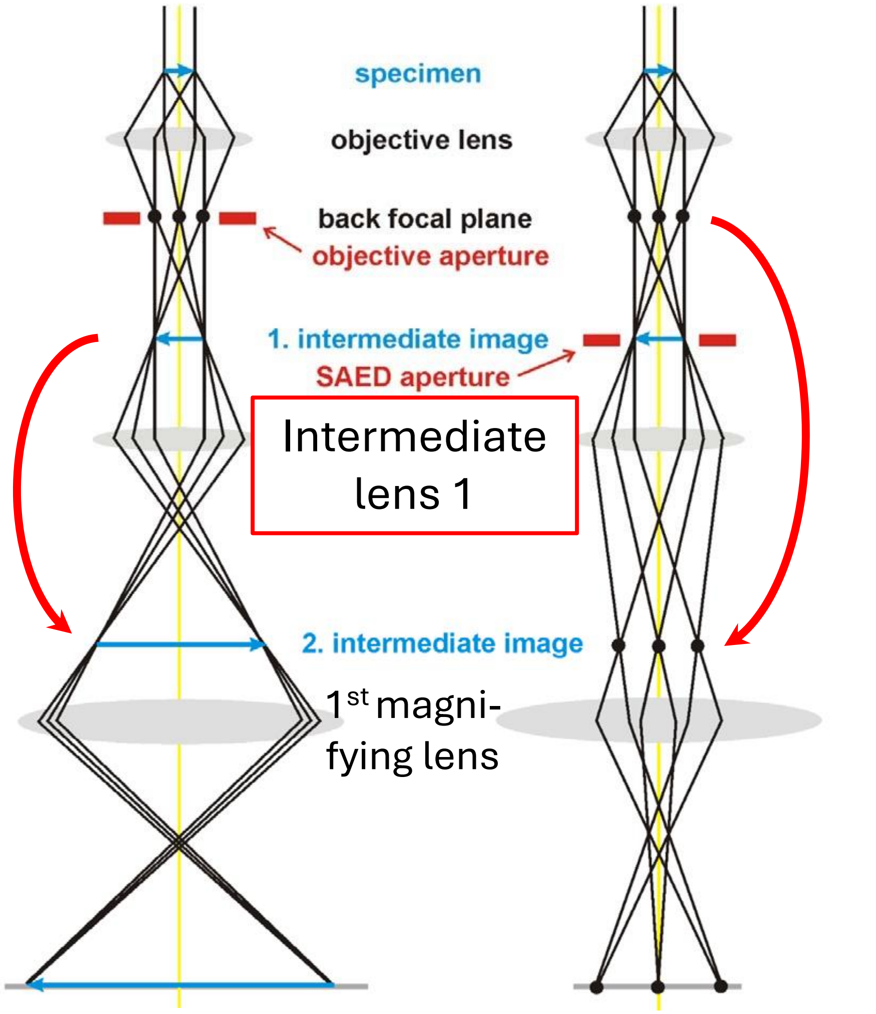
Specimen and imaging system

Specimen

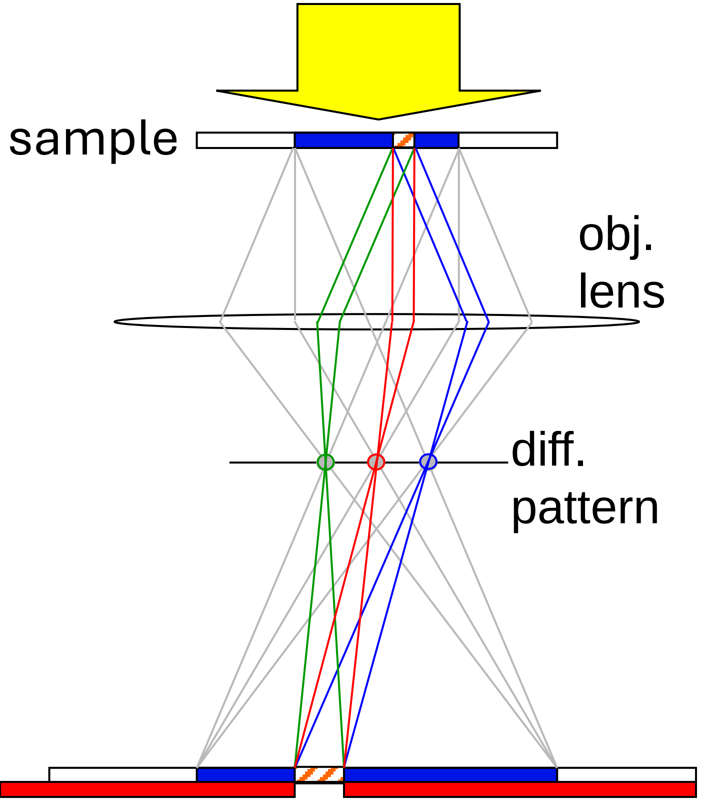
Imaging system



TEM provides direct and reciprocal space information from the same specimen area



Selected Area Electron Diffraction

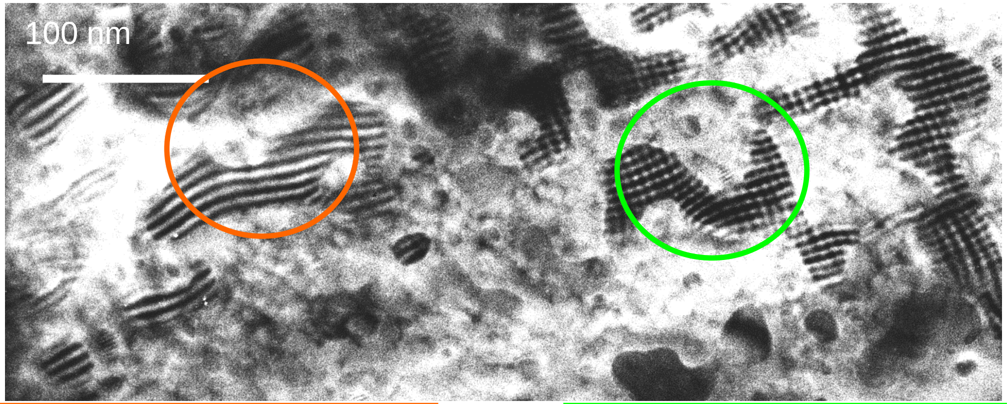


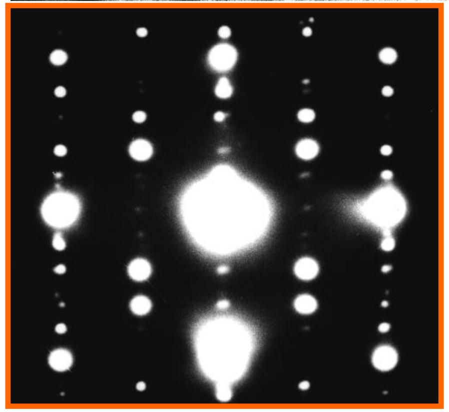
1st intemediate image:
SAED aperture

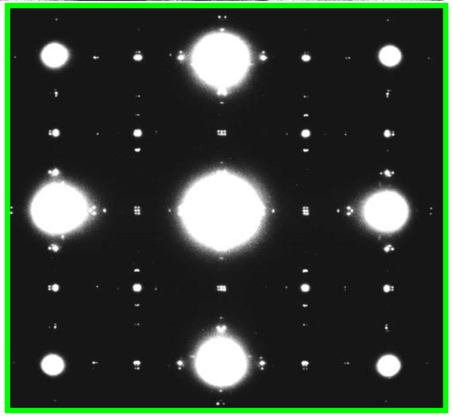
a part of the illuminated area is selected by SAED aperture in first image plane (principle of reciprocity; only fully true for a perfect lens!)

⇩

diffraction pattern stems from the selected specimen area (e.g. from a precipitate on nP).

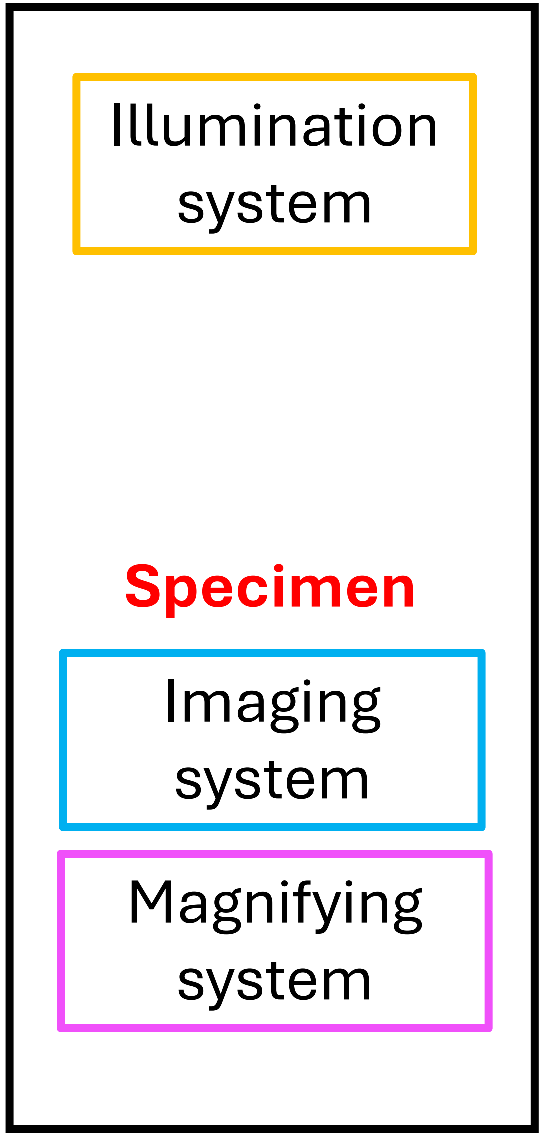






SAED aperture: selects the sample area (in first intermediat image) from with a diffraction pattern is formed (shown in last lecture)

Magnifying system: intermediate lenses + projective lenses



Magnifying lenses:

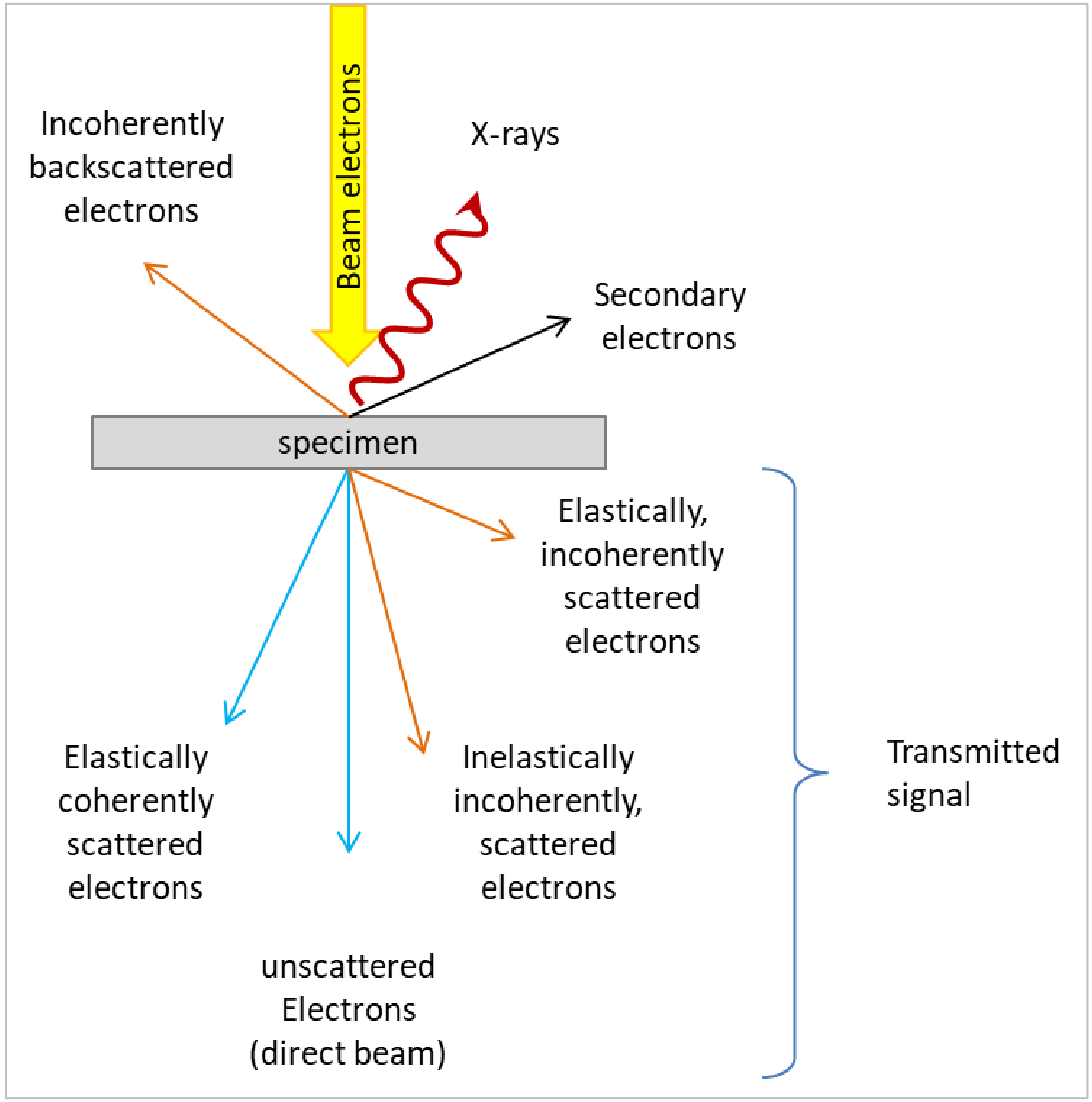
- all lenses after the 1st intermediate lens are magnifying lenses
- There are 2-4 magnifying lenses (they are called intermediate lenses or projective lenses, depending on the manufacturer)
- In imaging the magnification of the image is called „magnification“
- In diffraction the magnification is called „camera lenth“
- The strength of each lens the the combination of the lenses give a set of magnifications choosable (typically 50x – 5‘000‘000x)

After the magnifying system, an image or a diffraction pattern is ready to be recorded

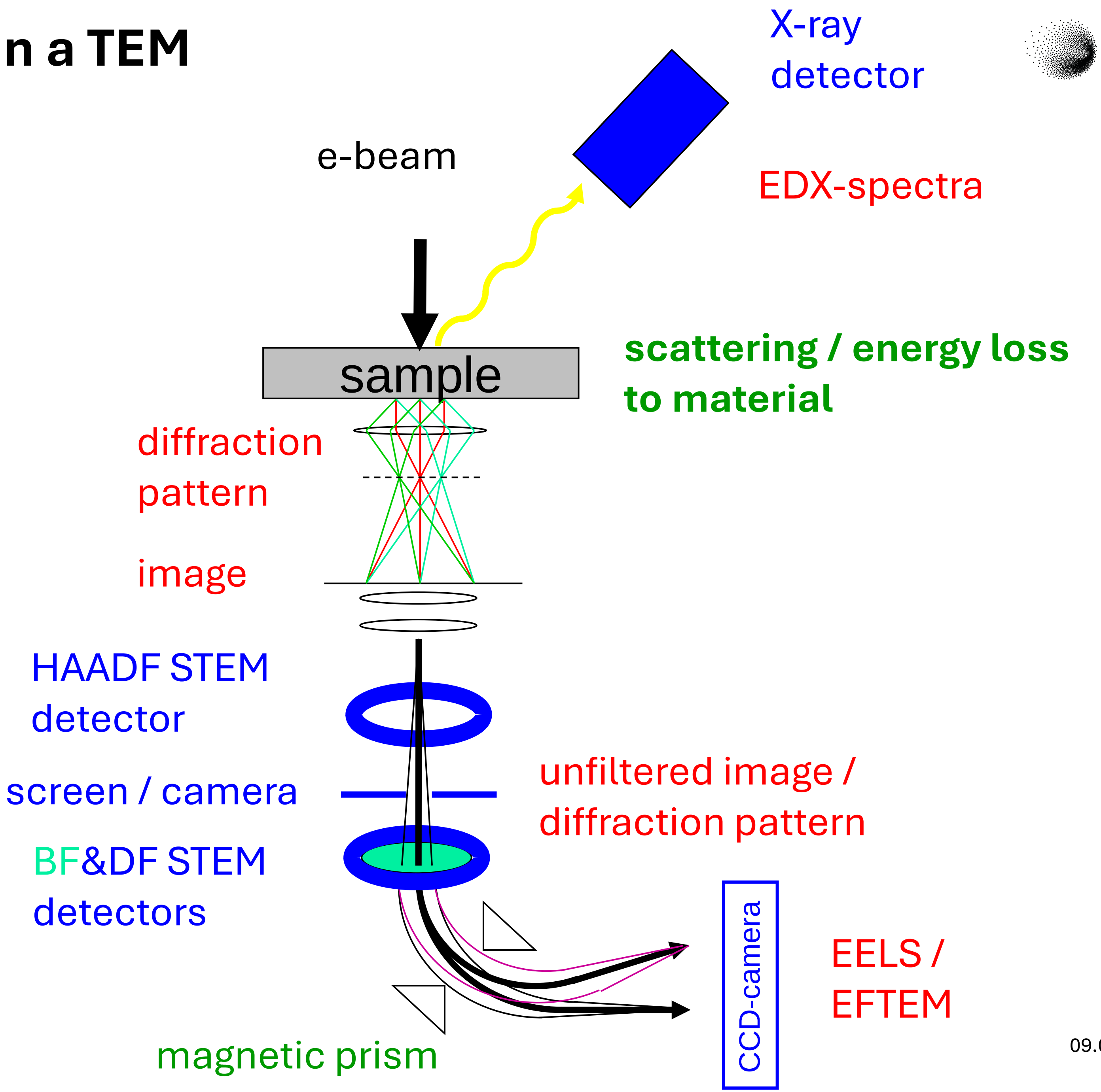
Interaction of electrons with matter: chemical composition

Types of scattering

- **forward or backward**. For TEM, usually forward scatter is used.
- **coherent or incoherent**. For *coherent* scattering, phase relationship between electrons is maintained, amplitudes are summed up, giving interference phenomena. For incoherent interactions, phase relationship is lost and their intensities are summed up to form the signal.
- **elastic** ($E_{el} = E_0$) **or inelastic** ($E_{el} < E_0$). At *in*elastic interactions, beam electrons lose energy to an electron of the respective atom and is mostly scattered under a small angle. If undergoing an elastic interaction, the electron does not lose energy, but in a crystal, it can be scattered under larger angles (Bragg scattering).



Typical signals detected in a TEM



red: signal type

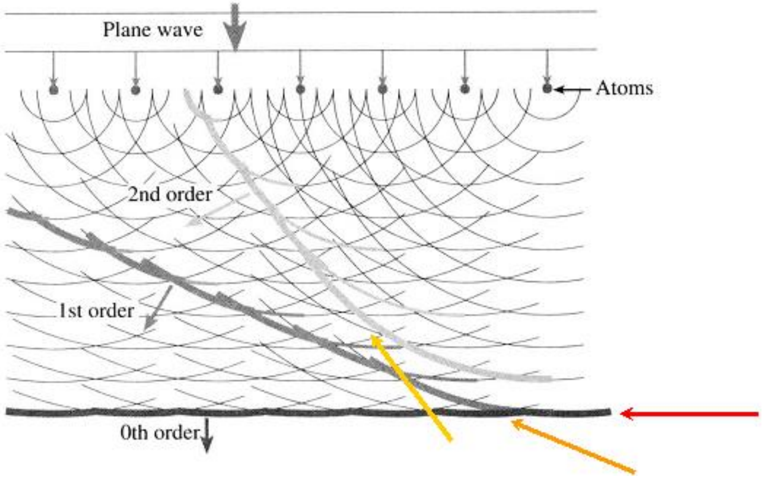
blue: detector type

Elastically scattered electrons: TEM imaging and diffraction

I assume you are familiar with the following concepts:

- Collective scattering on a periodic arrangement = diffraction
- In the far field, the electrons propagate along specific directions, where they interfere constructively
- The relation between scattering angle and real space distance is described by the Bragg equation (= constructive interference)

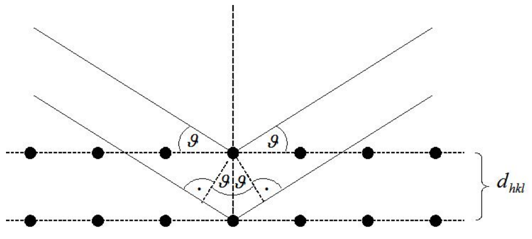
$$2d_{hkl} \sin \vartheta = n\lambda$$



- The direct space lattice is connected with the so called reciprocal space lattice which is defined by basic reciprocal lattice vectors:

$$\underline{a}^* = \frac{\underline{b} \times \underline{c}}{V}; \quad \underline{b}^* = \frac{\underline{c} \times \underline{a}}{V}; \quad \underline{c}^* = \frac{\underline{a} \times \underline{b}}{V}$$

$V = a(b \times c)$ = volume of the direct lattice unit cell



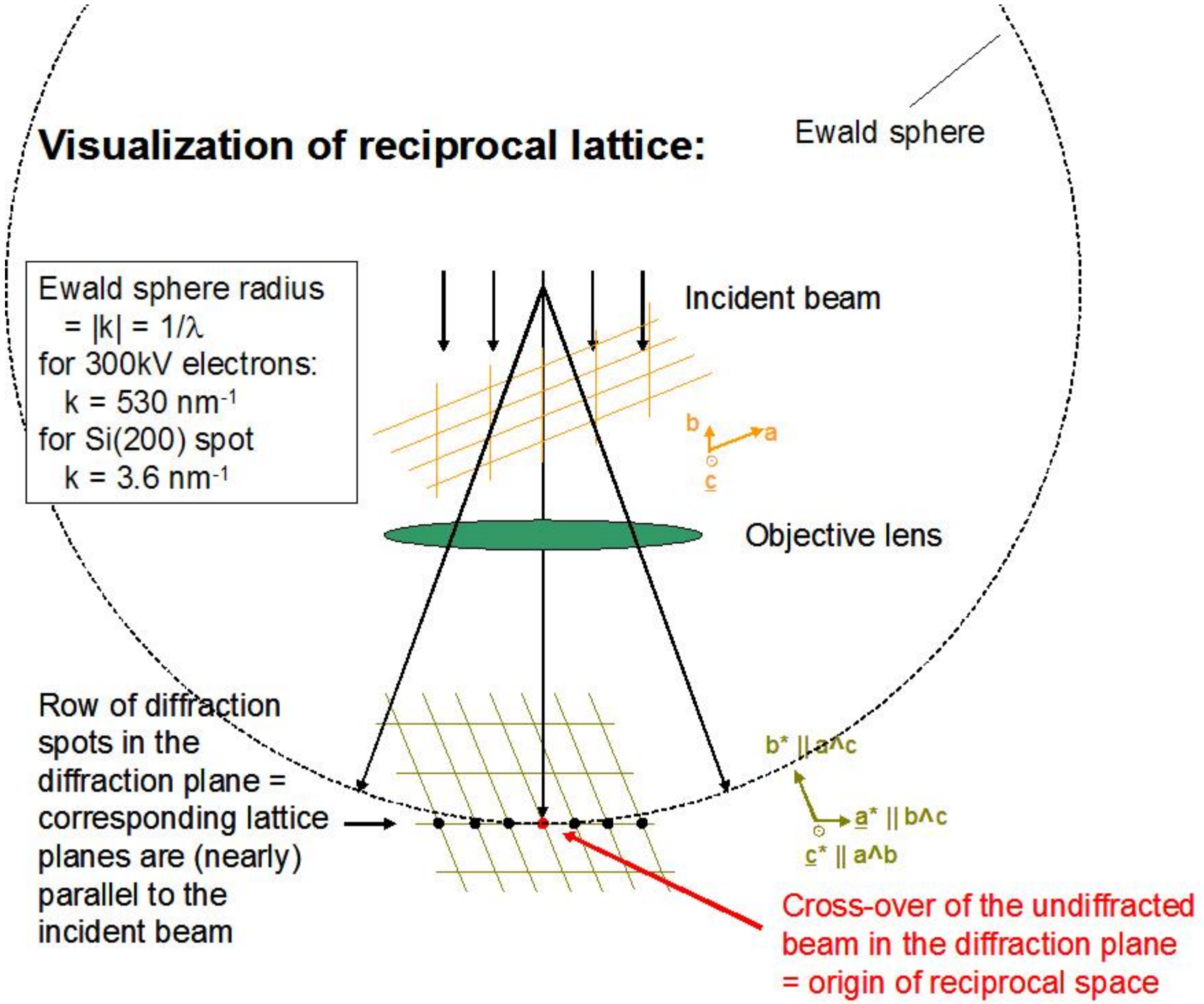
Bragg condition

Elastically scattered electrons: parallel beam TEM imaging and diffraction

PSI

I assume you are familiar with the following concepts:

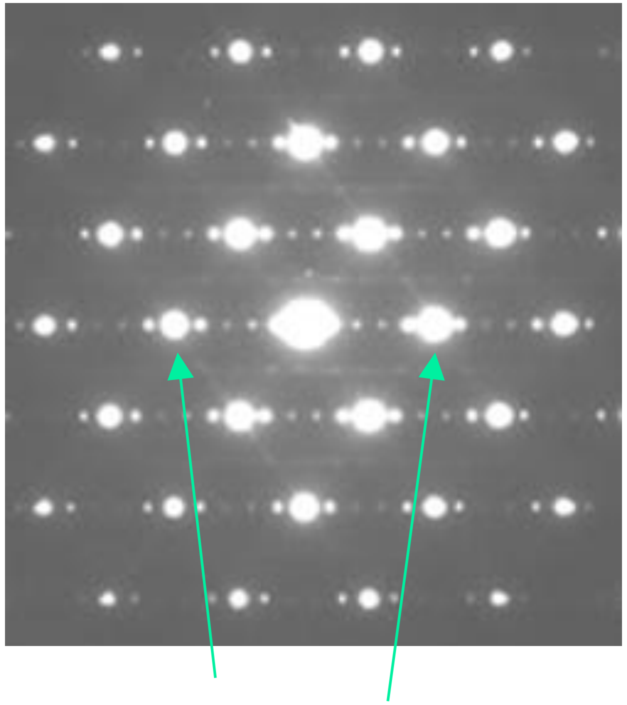
- In Ewald sphere construction: reciprocal lattice points are excited (= show an intensity peak), if it lies on the Ewald sphere (= the scattered vector has the same length as the unscattered one = no energy loss or gain)



Electron diffraction: differences to X-rays

	X-rays	electrons	effect
Wave length	0.1-1A	1-3pm	
Ewald sphere diameter	~ a_{hkl}	~ 100* a_{hkl}	Many spots visible
Interaction	Weak -> single scattering	Strong -> Multiple scattering	Forbidden spots may be visible
Required crystal size for structure solution	µm	few 10nm	Structure of small crystals solvable
precision	high	low	

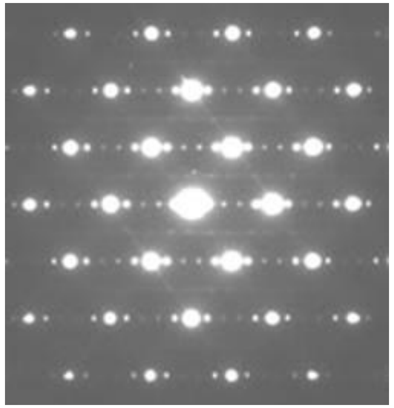
Diffraction pattern of a single crystalline SiGe superlattice



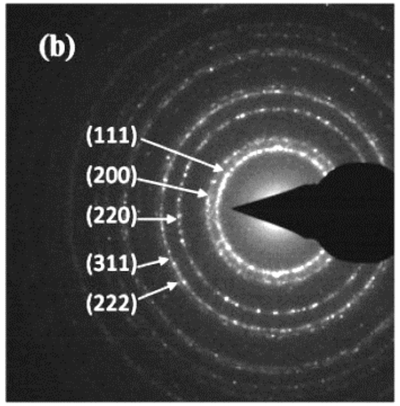
Forbidden (200) type reflections

Electron diffraction

Phase determination



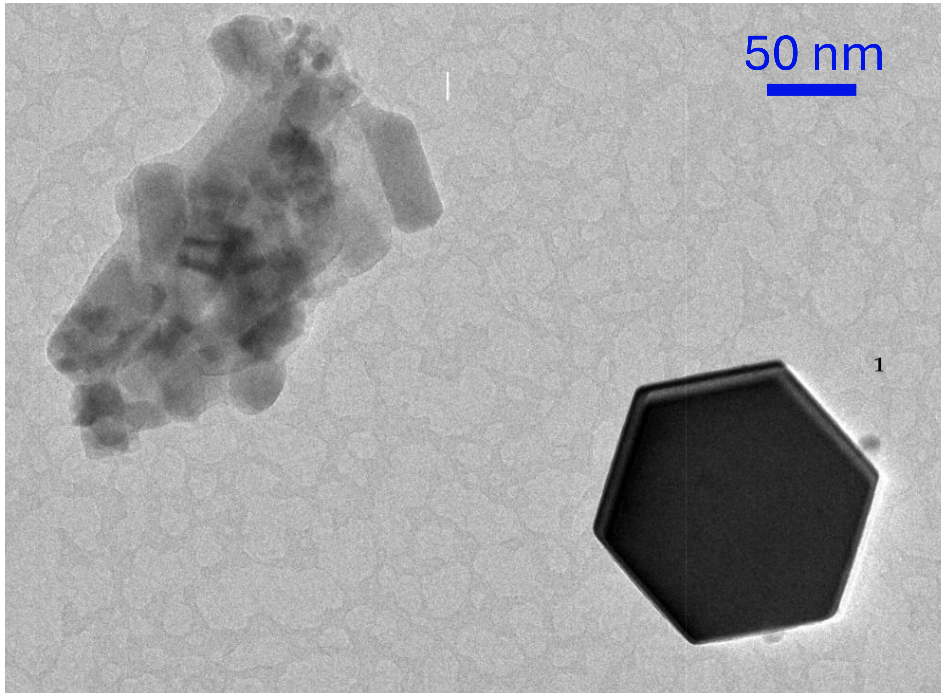
Single crystaline

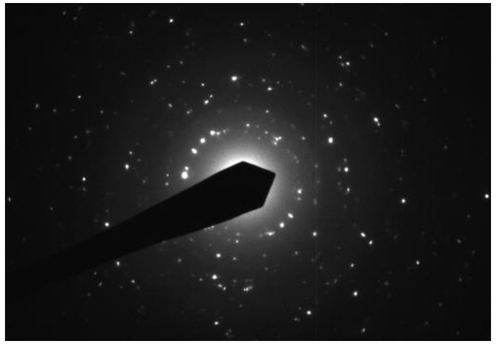


Poly crystaline

Amorphous

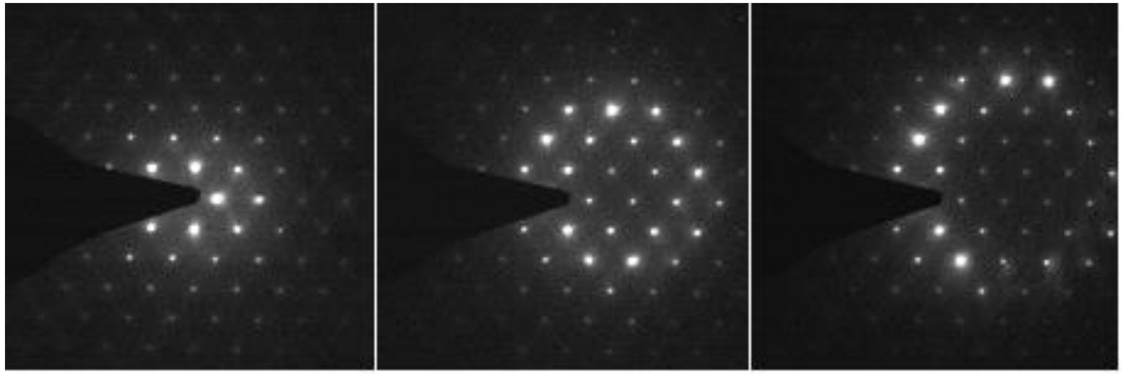
Zn-nanoparticles:
Are they metallic or oxydized?



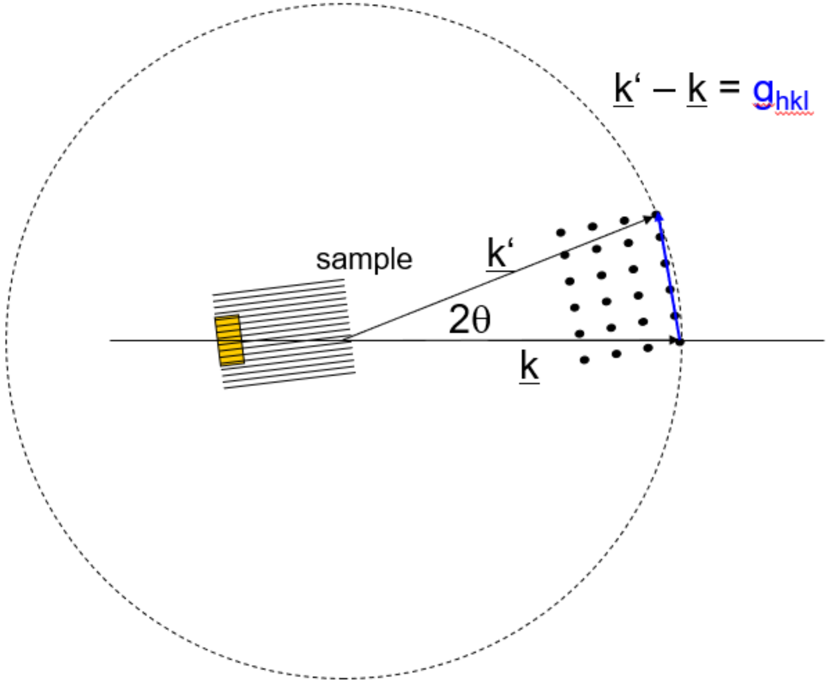


Electron diffraction

Crystal tilt and structure solution



For a tilted specimen, the intersection with the Ewald sphere is a circle.



Known from XRD:

Reciprocal space = Fourier transform of crystal

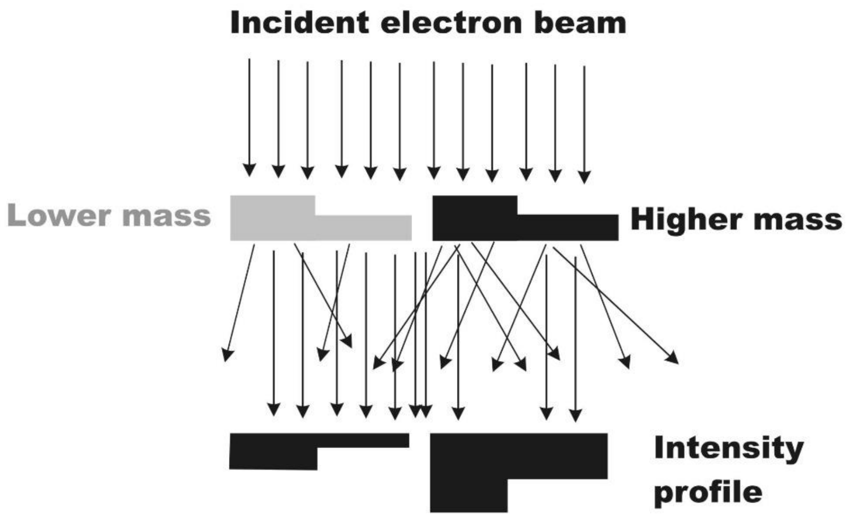
-> Mapping reciprocal space should allow to solve the structure in **kinematical situation**.

Principle problem: electron diffraction = multiple scattering (especially in low index zone axis)

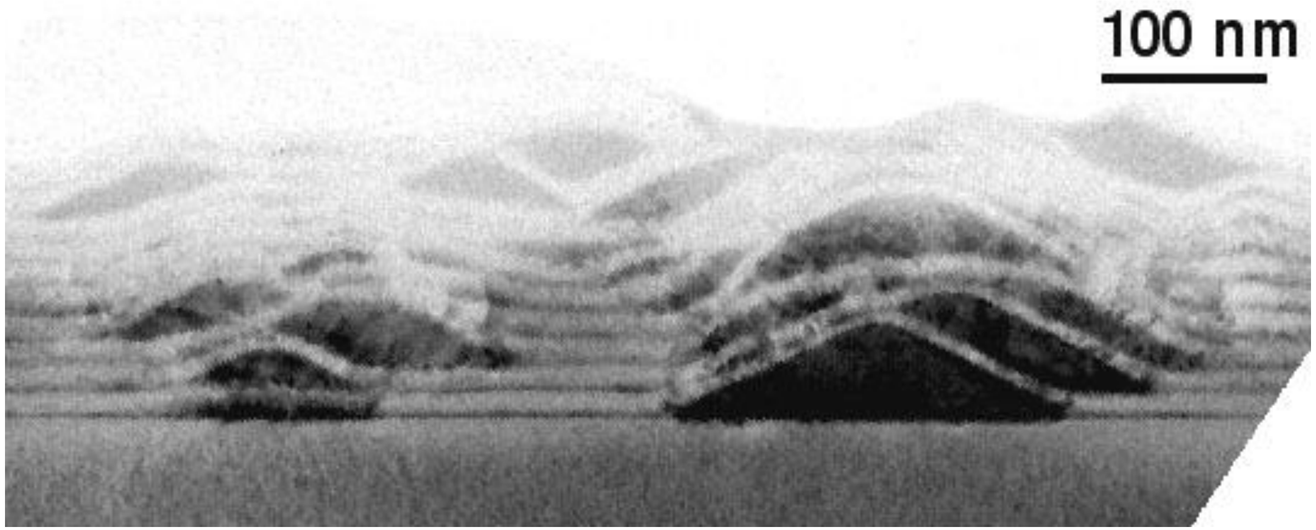
Practical aspects:

- Crystallite far enough away from other crystals
- Mapping of reciprocal space by sample rotation in steps of 0.5° - 1°, tilt range at least ±50°-60°
- Data evaluation with XRD software or software developed for electron microscopy

Imaging: How to get contrast? Mass/thickness contrast



Absorption increases with thickness of the specimen and with mass of the atomic species.
Selecting the undiffracted beam only, adds artificial absorption.



objective aperture
in diffraction plane

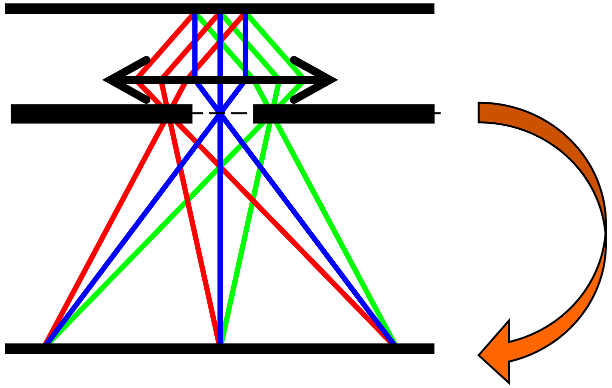
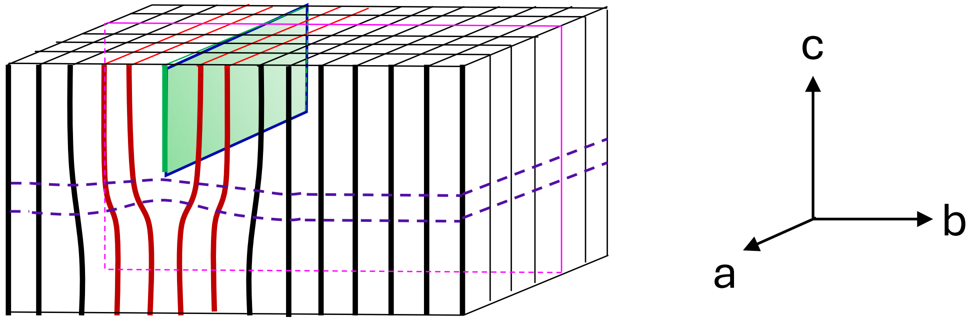


Image plane

Selective information

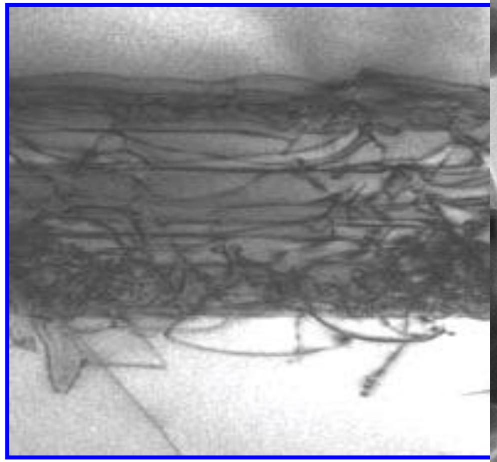
Mass/thickness contrast is **most often not sufficient**.

Imaging: How to get contrast? Diffraction contrast

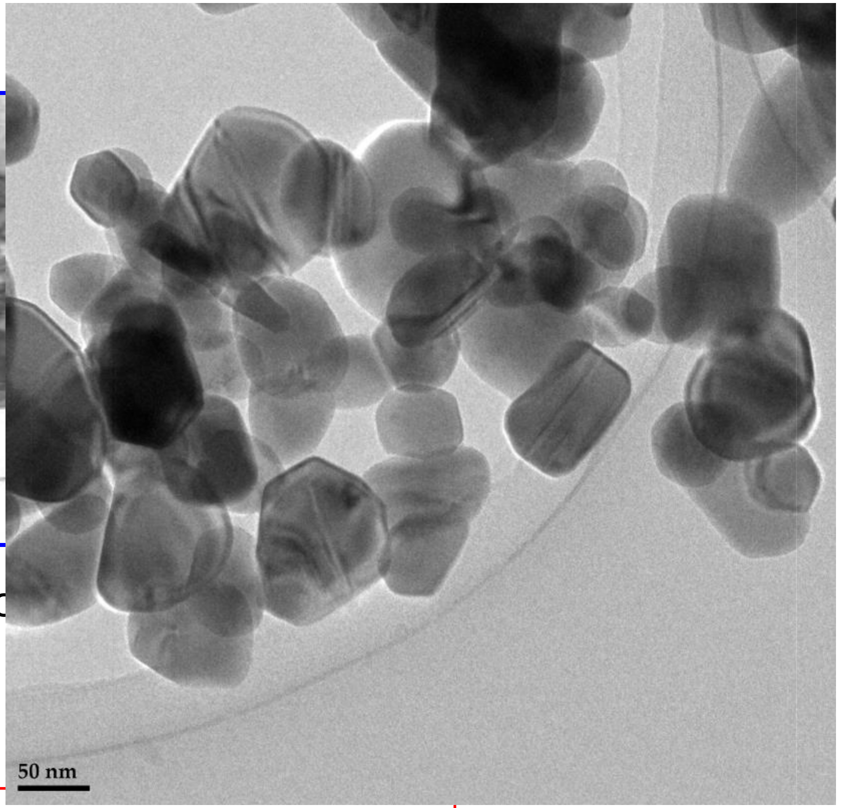


Example of an edge dislocation:

- Strong bending of the read planes (a-c)
- Weaker bending of brownish planes (a-b)
- No bending of the pink planes (b-c)



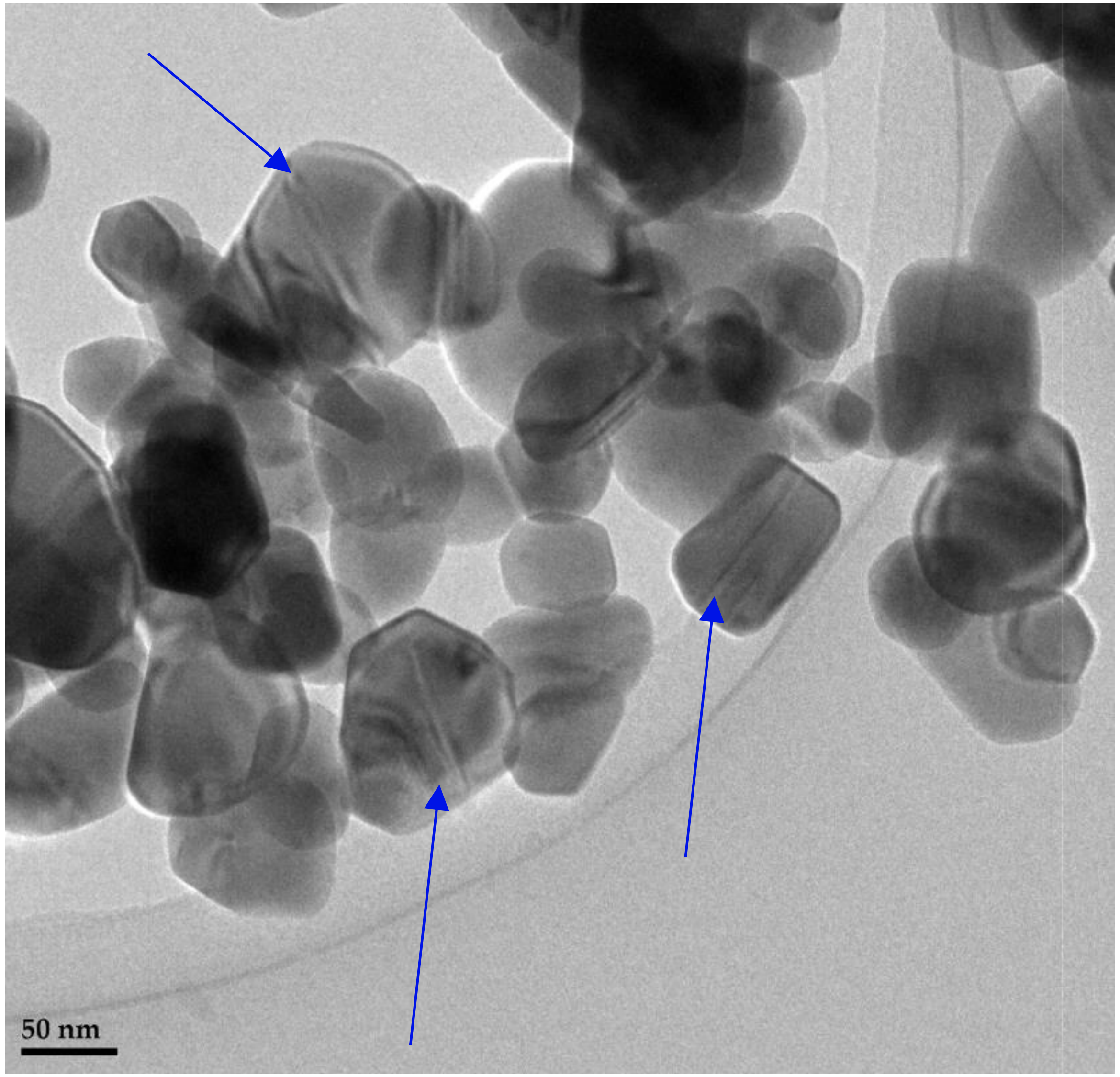
Crystalline SiGe layer c

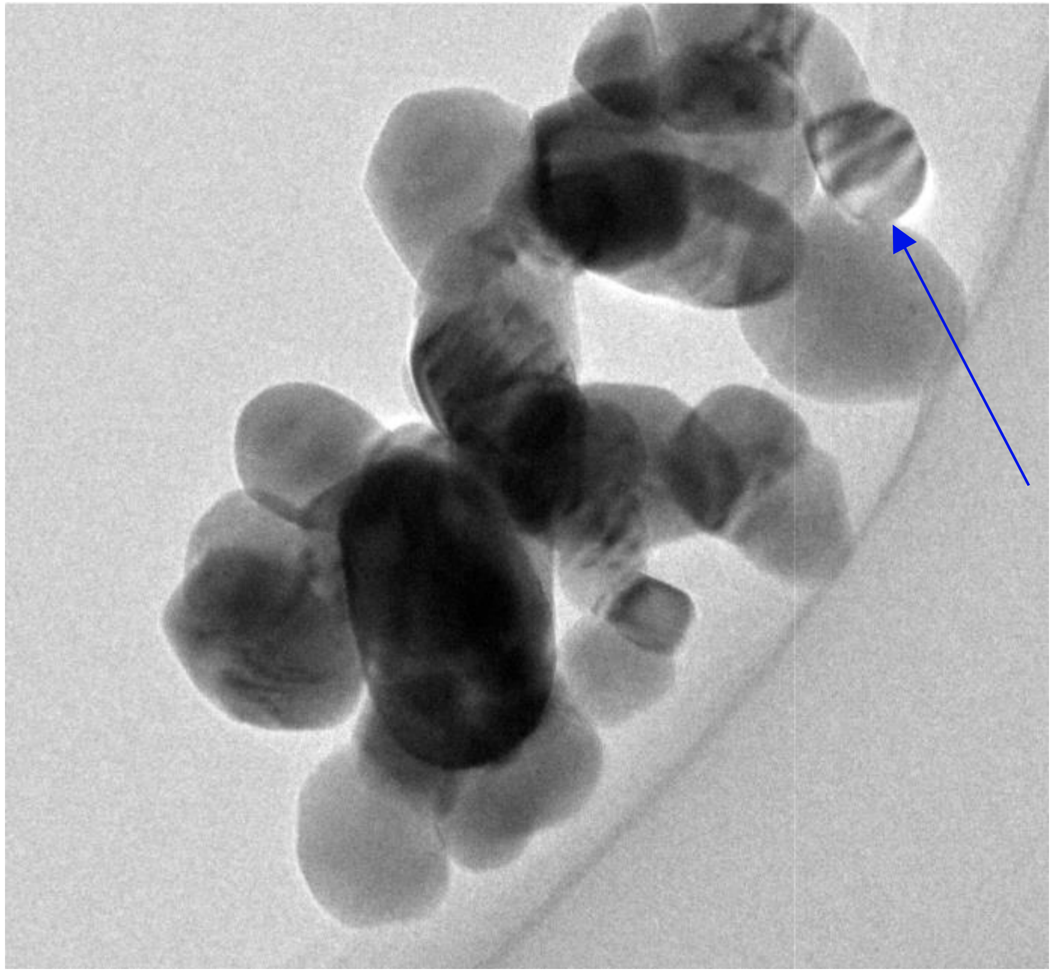


The electron beam gets selectively deflected close to the dislocation core:

- Strong contrast from the (a-c) plane
- Weak contrast from the (a-b) plane
- No contrast at all from scattering at the b-c) plane

How to get contrast? Diffraction contrast

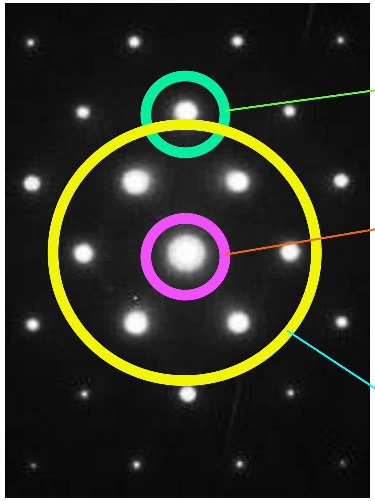




With nanoparticles, internal structure or (parts of) particles being unexpectedly dark or bright are typically a consequence of diffraction contrast

Objective aperture for enhancing image contrast:

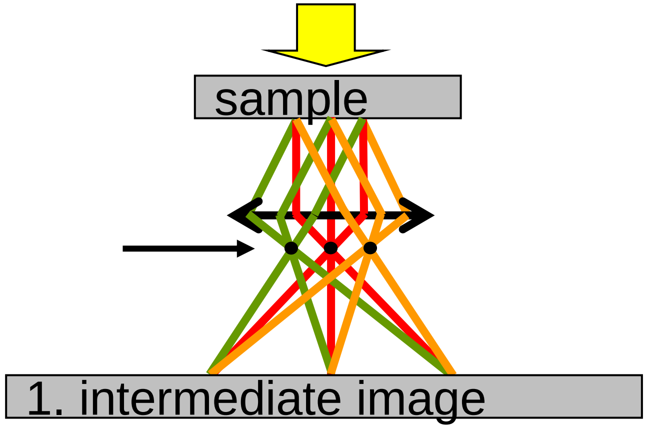
Selection of electrons with specific angle highlights specific phenomena.



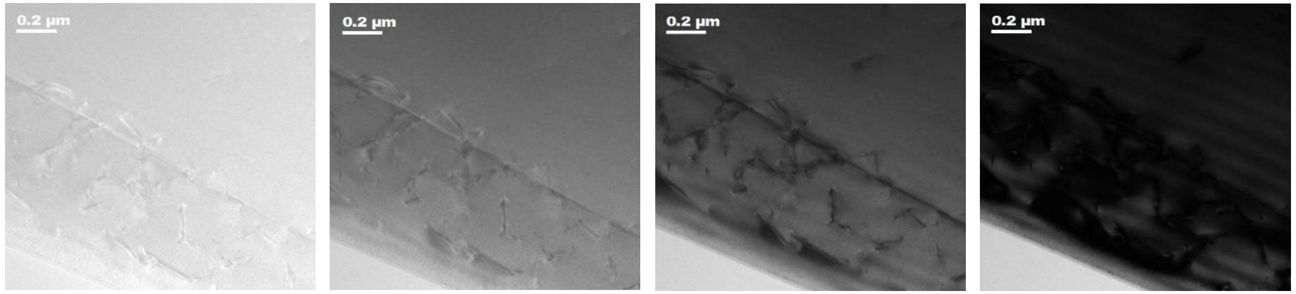
Dark field image (DF)

Bright field image (BF)

Multi-beam image

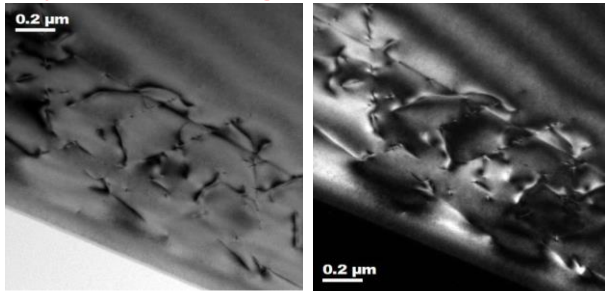


contrast



without aperture	aperture incl. Si(400)	aperture incl. Si(200)	BF

Specific things visible



BF (220)	DF (220)

DF highlights

- High-Z atoms
- High-diff areas

Smaller aperture = more contrast, but lower resolution

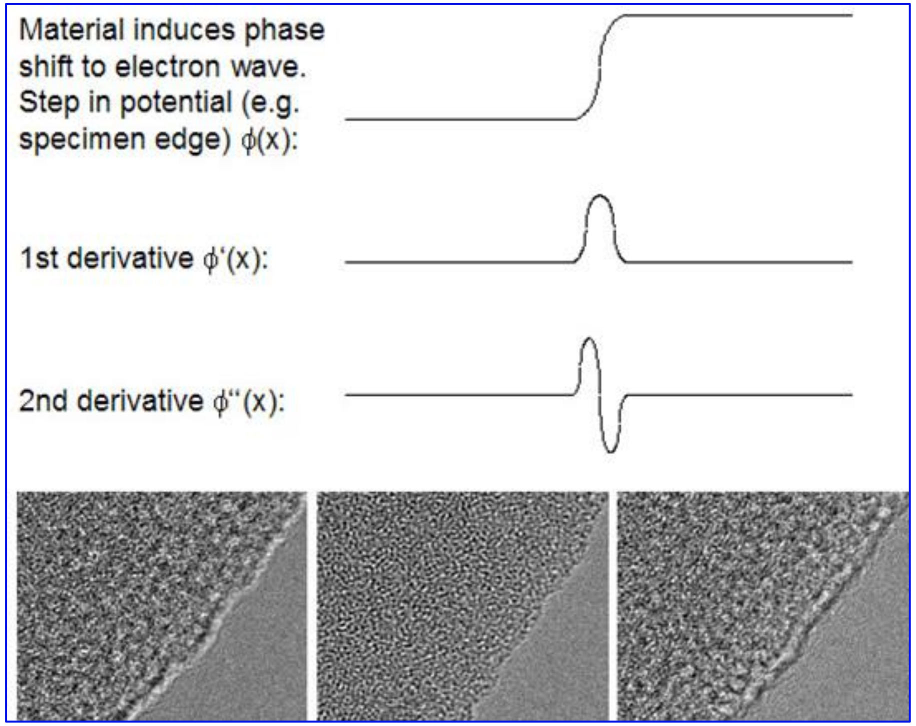
Imaging: How to get contrast? Phase contrast

Phase contrast: most important contrast mechanism in high-resolution TEM (HRTEM) imaging:

- Differences in intensity due to interference effects between scattered and unscattered electrons are known as phase contrast.
- Applicable to highly magnified images of thin crystalline or non-crystalline specimens.
- proportional to the (positive or negative) defocus *D* and to the second derivative of the phase shift function:

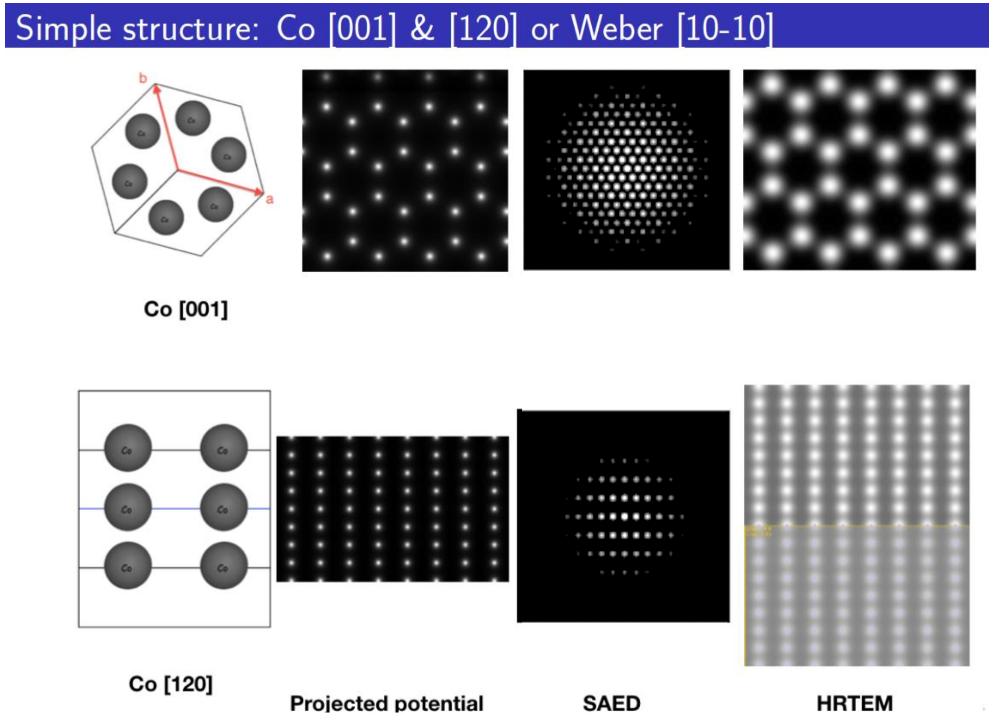
$$I(x) = 1 + \frac{\Delta\lambda}{2\pi}\phi''(x)$$

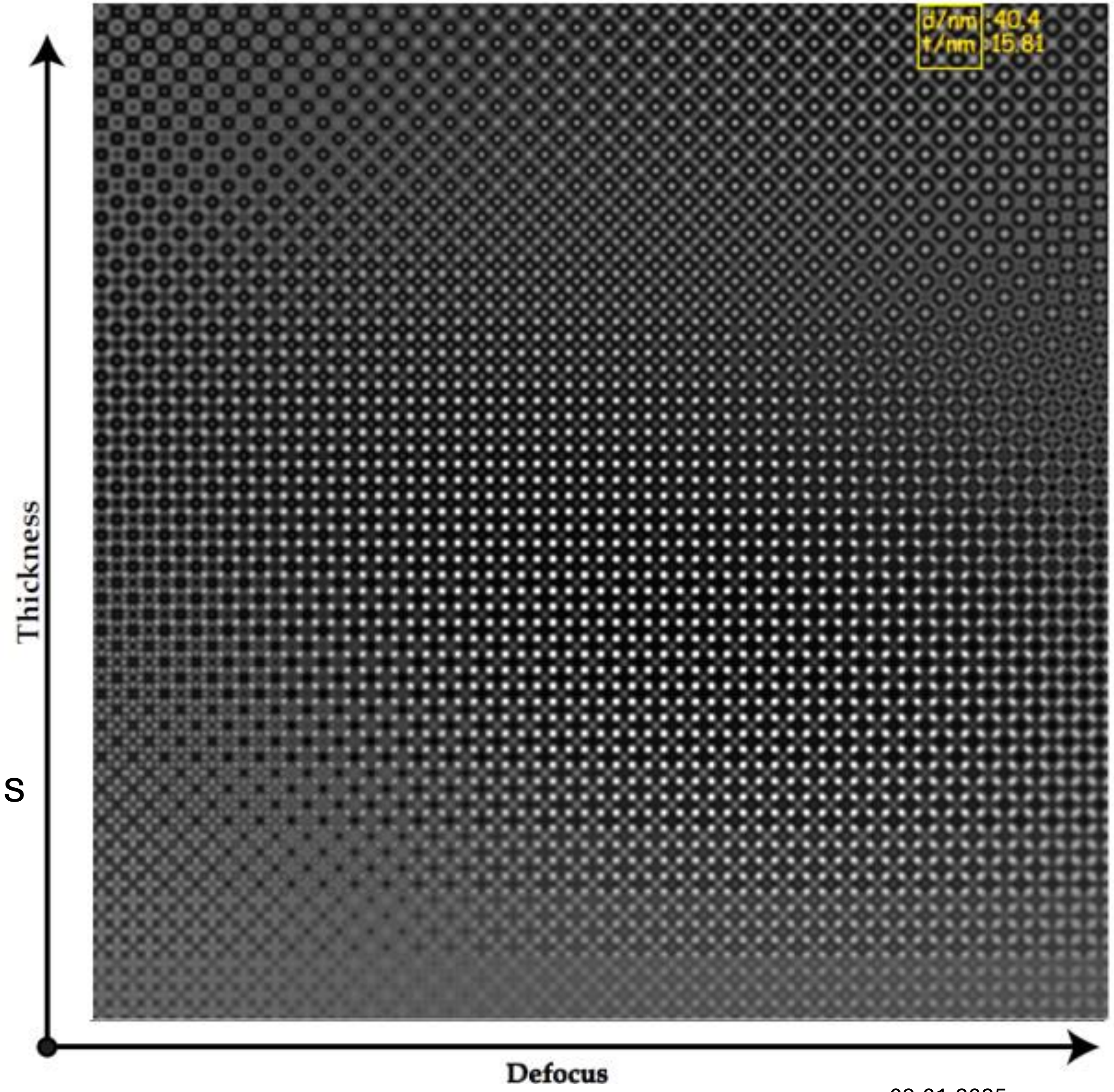
- Defocus increases contrast, but reduces resolution.



Edge of amorphous C-layer at underfocus (left), close to focus (center) and overfocus (right)

High-resolution TEM (HRTEM)





- **HRTEM = interference pattern** of diffracted beams with the undiffracted beam, function of atom positions
- Aberrations limit the resolution
- Perfectly along low-indexed zone axes
- Pattern = function of defocus and sample thickness
- Only interpretable for very thin specimens

Quality of electromagnetic lenses: poor lenses!

Electro-magnetic lenses suffer from **aberrations**, the most „famous“ ones are:
Defocus (variable), **astigmatism** (correctable), **spherical aberration** (main aberration), **chromatic aberration** (critical mainly at low voltages)

Core of the M100 galaxy seen through Hubble (source: NASA)

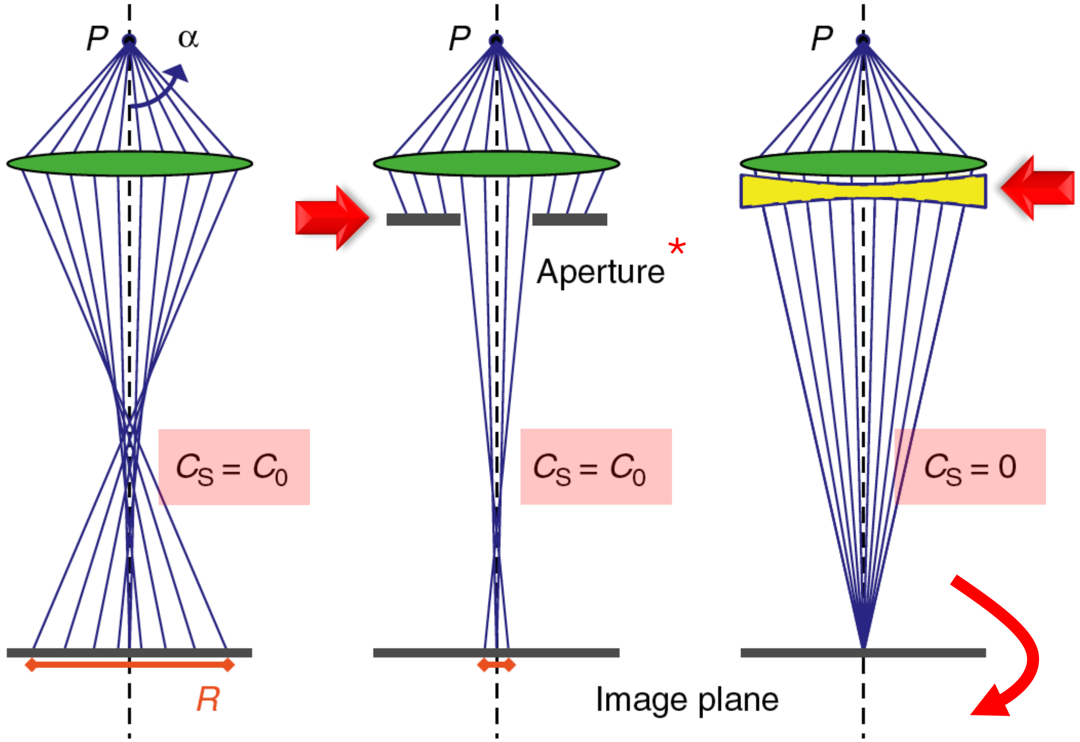
Graph by Quentin Ramasse
SuperSTEM course 2012

<u>Glass lenses:</u>
combination of convex and concave lenses allows correction of aberrations

<u>Electro-magnetic lenses:</u>
Physics laws make rotationally symmetric concave electro-magnetic lenses impossible

Spherical aberration correctors based on non-rotational symmetric lenses only exist since 1998. Resolution improvement ~ 3x

Spherical-aberration correction: improved resolution (~3x)

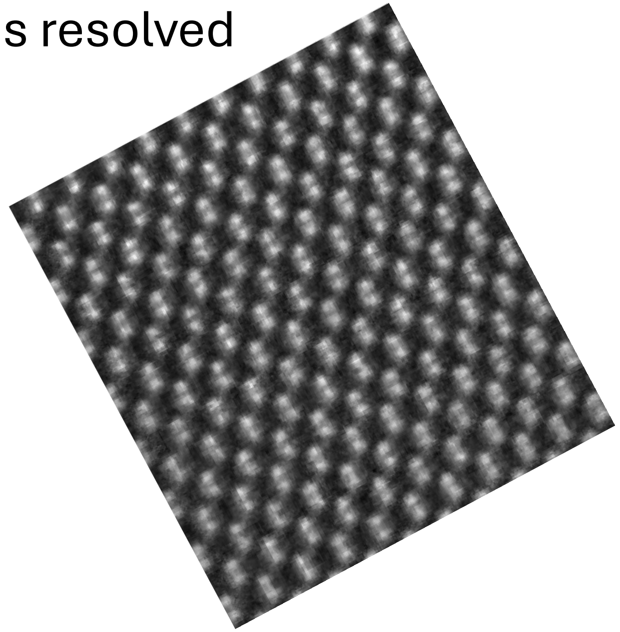


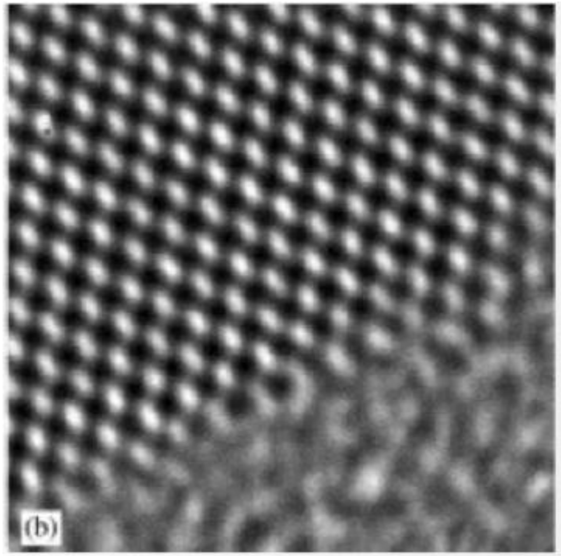
delocalisation

Aperture reduces influence of aberrations

eliminate dispersion of scattering angle

With Cs-correction
-> individual atomic columns resolved



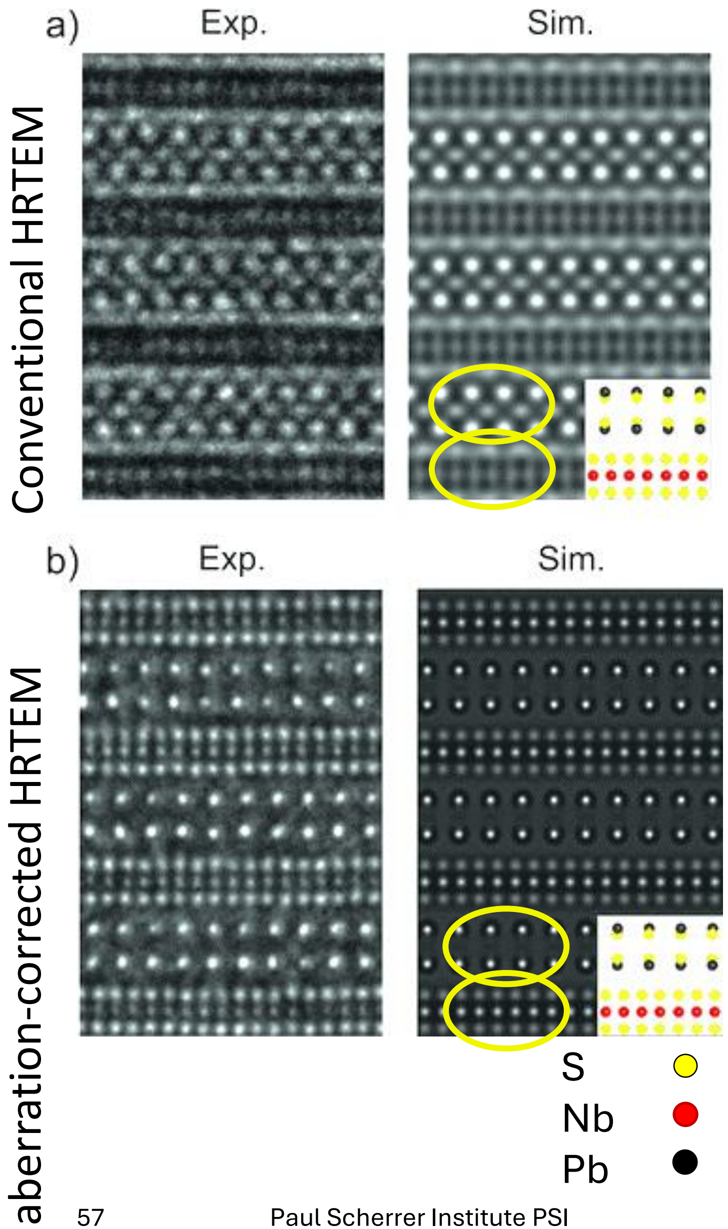


Without Cs-correction
-> only periodicity resolved

Silicon crystal in (110) projecton

Achievable resolution with Cs-correction:
@ 200keV: < 0.8A (instead of 2.5A)
@ 300keV: ≈ 0.5A (instead of 1.8A)

Advantages of aberration correction: see the atoms



perfect $(PbS)_{1.14}NbS_2$ layer compound

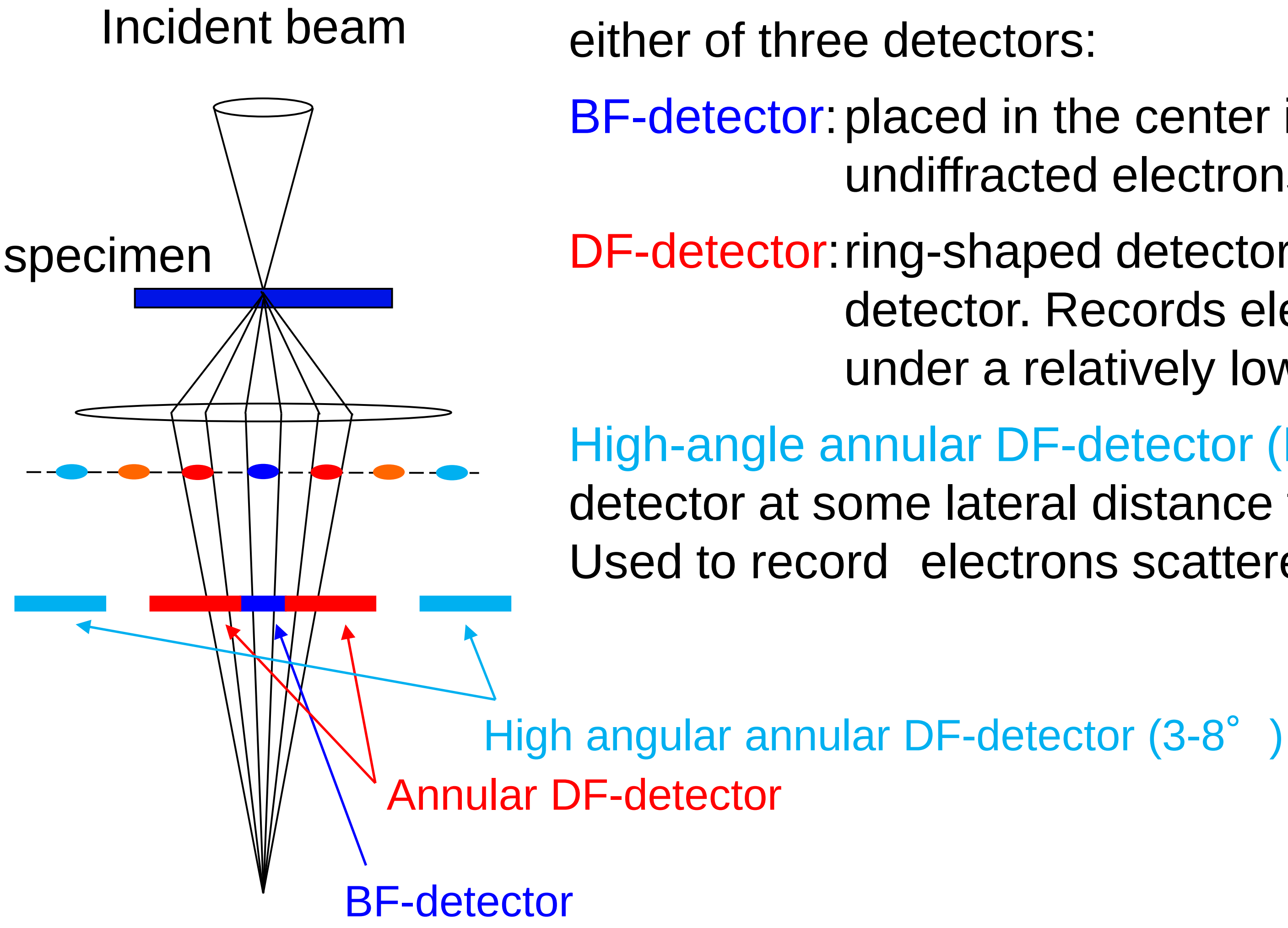
Comparison of experimental and simulated HRTEM images along the commensurate interface direction.

(a) Conventional HRTEM imaging (simulation parameters: U= 300 kV, C_s= 0.7 mm, Δf=−60 nm, t= 3.2 nm) and

(b) aberration-corrected HRTEM imaging under optimized conditions (U= 300 kV, C_s=−13 µm, Δf=+5.8 nm, t= 3.2 nm). Only in the latter case there is a direct relationship between the image contrast and the projected crystal structure (insets).

E. Spieker et al.; Journal of Microscopy, Volume: 237, Issue: 3, Pages: 341-346, First published: 15 February 2010, DOI: (10.1111/j.1365-2818.2009.03257.x)

Scanning transmission electron microscopy (STEM)



In STEM, a **focussed beam is scanned** over the sample. The transmitted electrons are measured pixel by pixel with either of three detectors:

BF-detector: placed in the center in order to record the undiffracted electrons

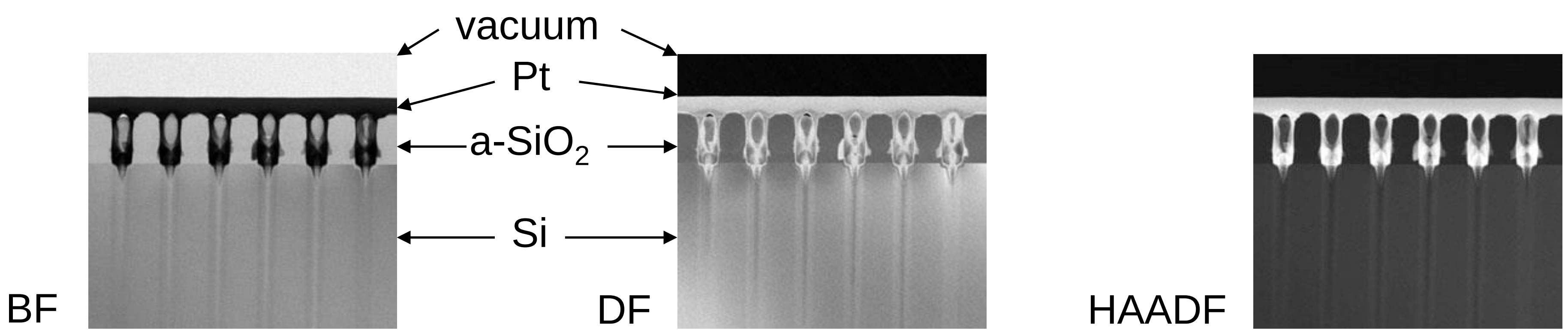
DF-detector: ring-shaped detector adjacent to the BF-detector. Records electrons scattered under a relatively low angle (Bragg-region)

High-angle annular DF-detector (HAADF): ring-shaped detector at some lateral distance from the DF-detector. Used to record electrons scattered under a high angle

Jeol News 2001

Imaging modes in STEM

- **BF and DF STEM** provide information comparable to BF and DF TEM
- **HAADF STEM = Z-contrast imaging**: nearly incoherent imaging, strong dependence on atomic number Z (chemical contrast!, corresponds to Rutherford scattering with electrons)



- **Very important application of STEM: Micro-probe analysis!!** With the very small beam diameter a correspondingly high spatial resolution can be reached for EELS (and EDX)

Especially interesting for nPs: HAADF STEM

- **HRTEM** makes use of coherent elastically scattered electron beams to image phase contrast.

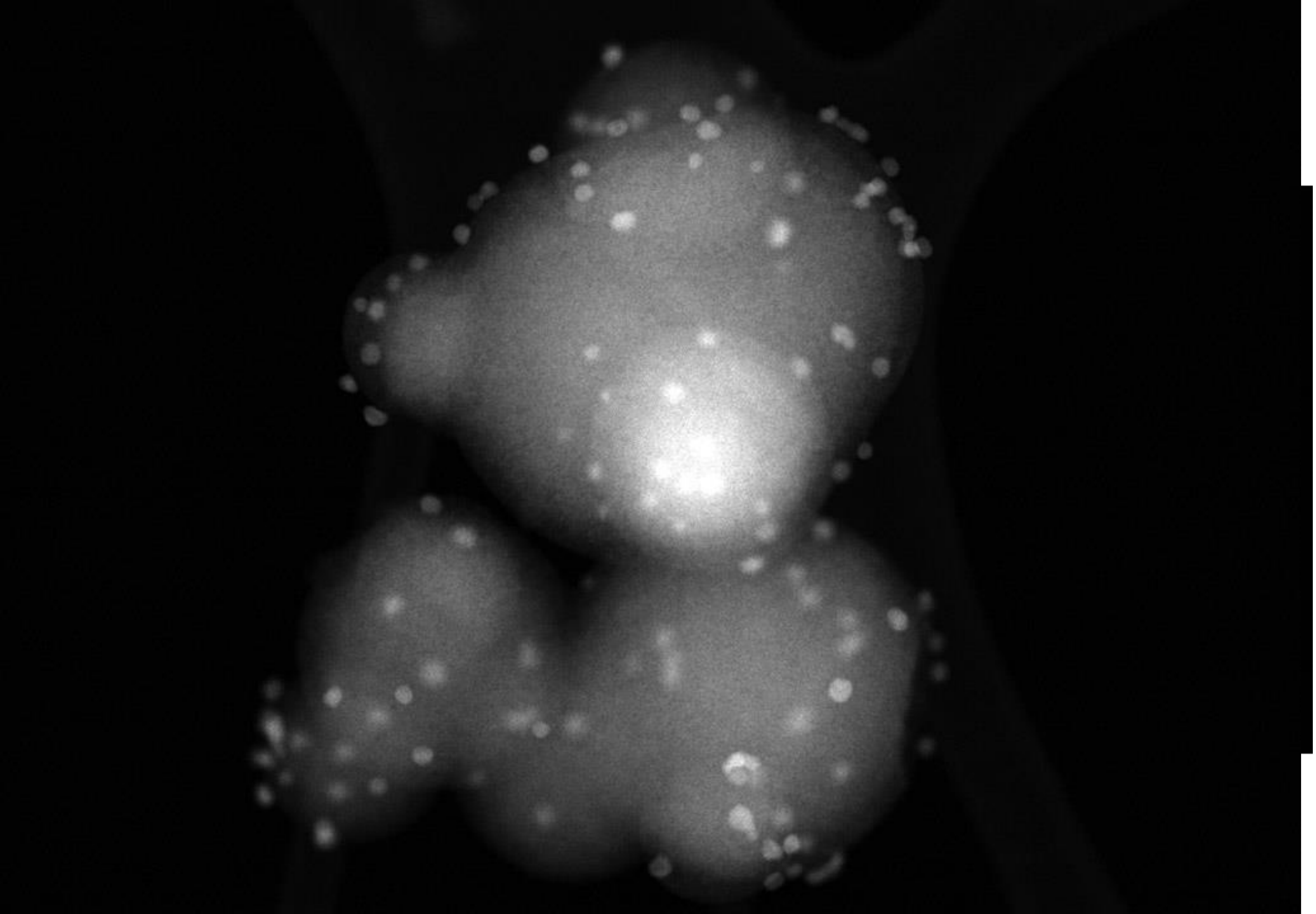
- **HAADF** (high-angle annular dark-field) **STEM** makes use of incoherent elastically scattered electrons

  - Scattering intensity → incoherent superposition of scattering contributions from individual atoms $\propto Z^2$ → «Z-contrast imaging»

  - Atom columns always appear bright and channels dark

  - Dark field mode: use STEM with ring detector to detect electrons elastically scattered at large angles (4 to 9°)

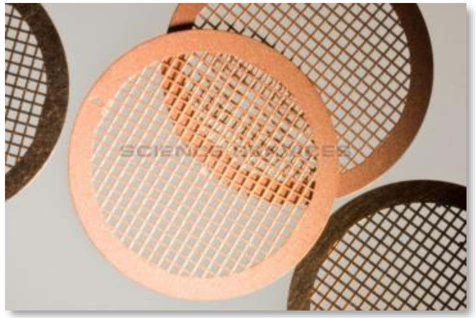
  - Spatial resolution defined by beam size



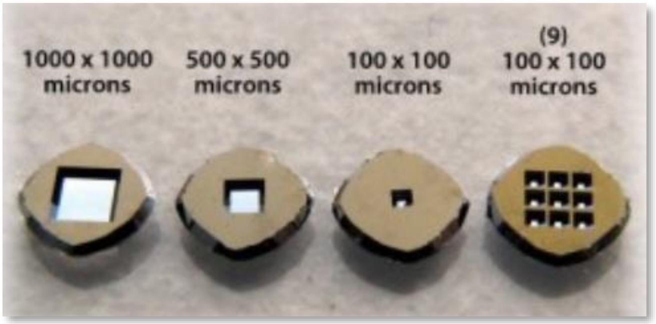
Specimen preparation

C-coated Copper Grids

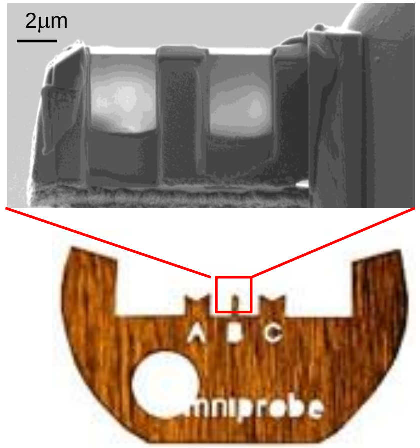
SiN Membranes

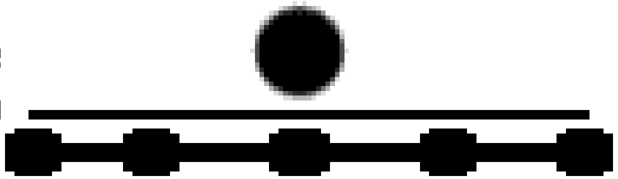


https://scienceservices.de



http://www.octalab.com





Sample must be

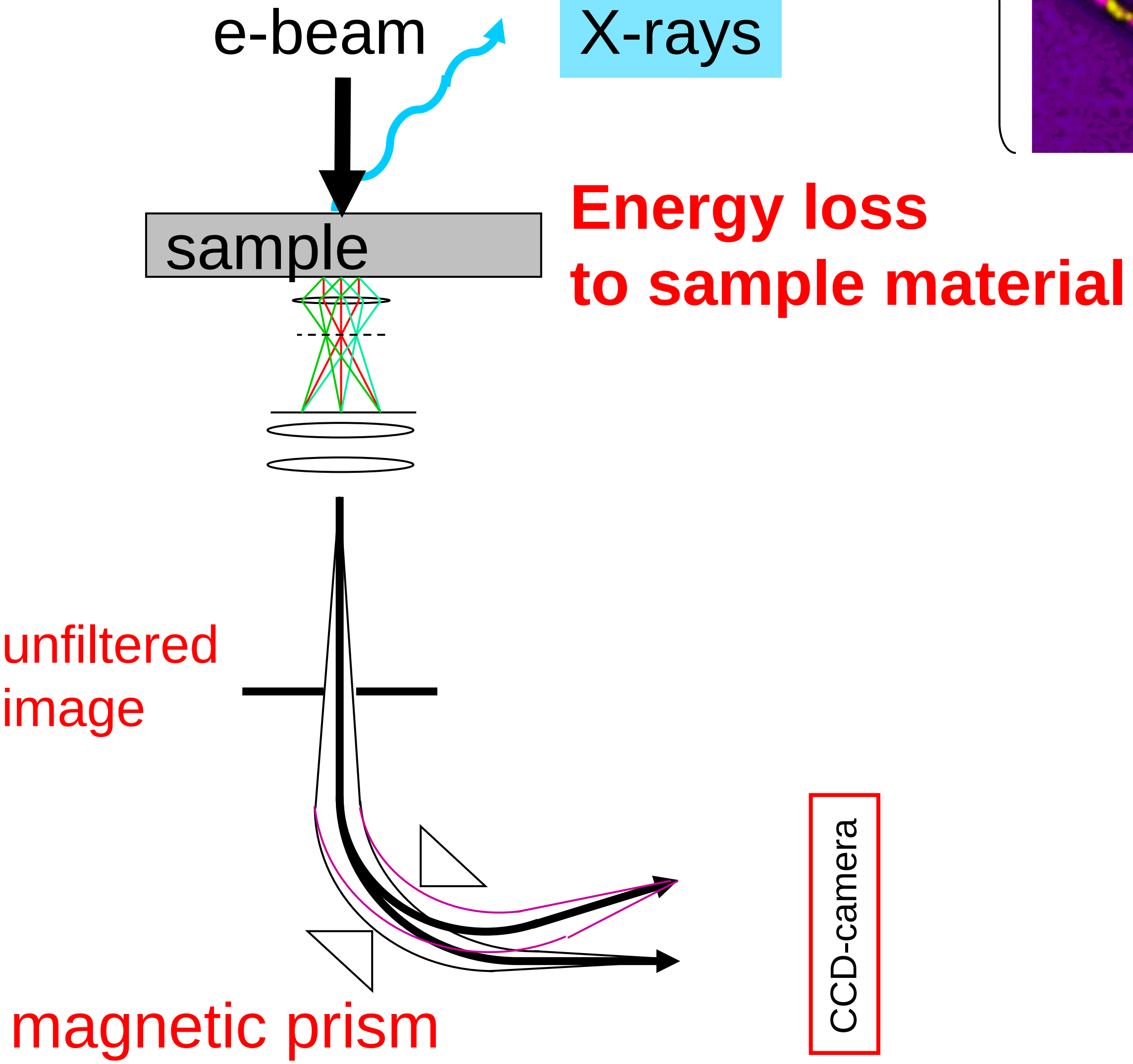
- transparent to electrons, so for most applications < 100 nm thick!
- Vacuum compatible (usually dry)
- Clean (contamination!)
- Beam resistant (-> cryo for beam sensitive specimens)

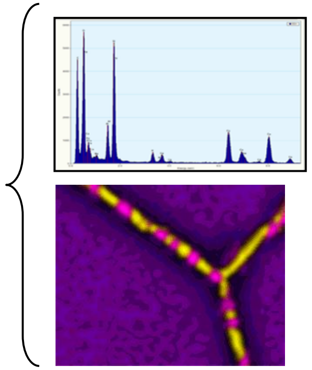
Specimen preparation

But why a Carbon or SiN support?

- Transparent to electrons
- Low Background
- Heat resistant
- Excellent chemical stability
- Does not electrically charge

Analytical TEM



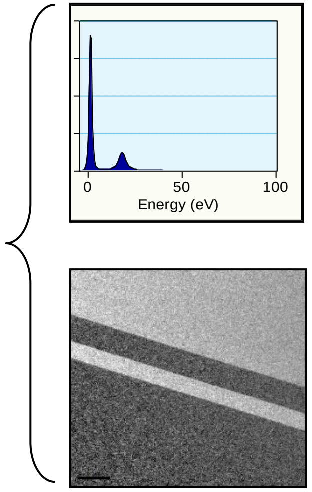


EDX-
spectrum

EDX-map

Primary signal:
- EELS
- ESI/EFTEM

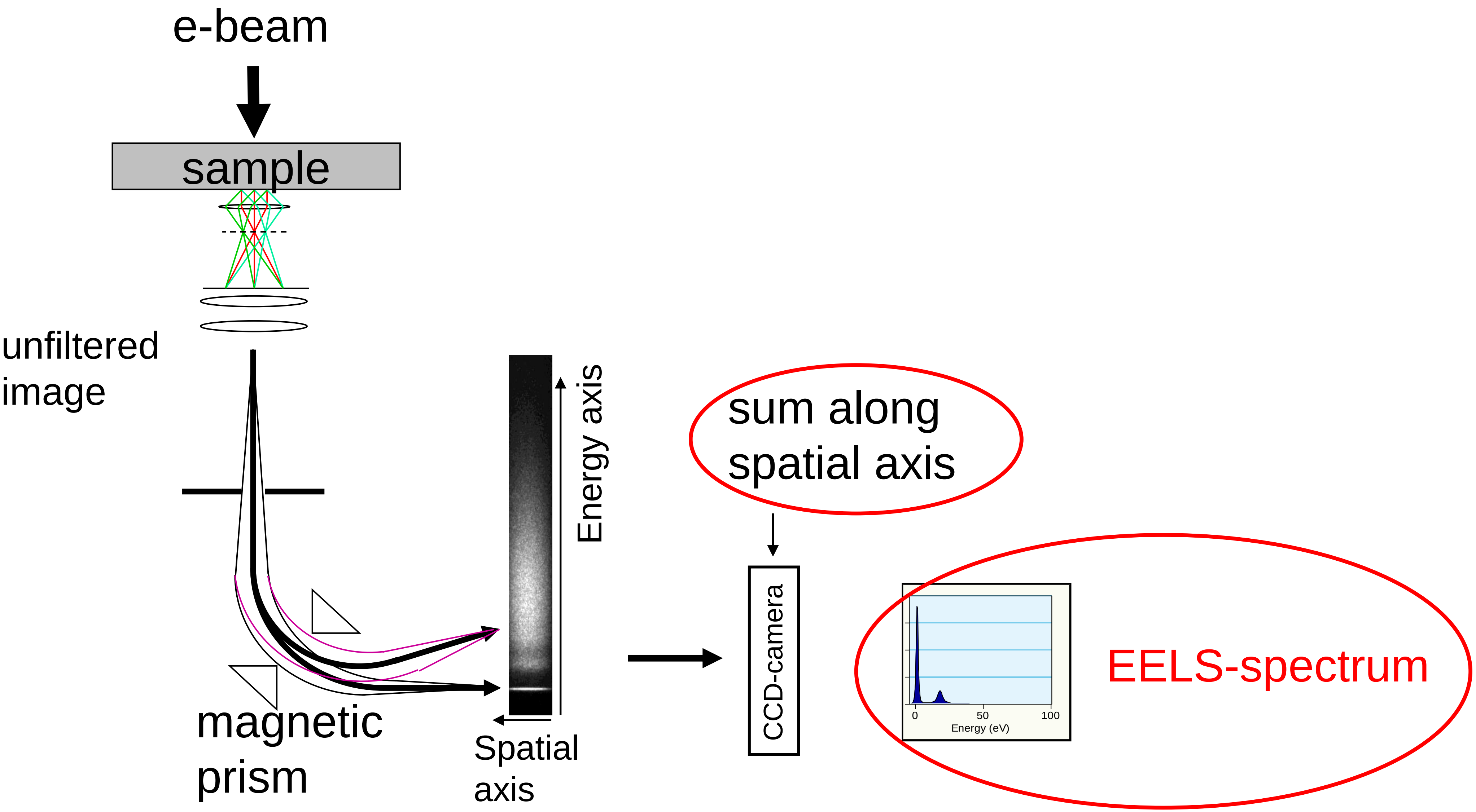
Secondary signal:
- EDX
- EDX-mapping



EELS-spectrum

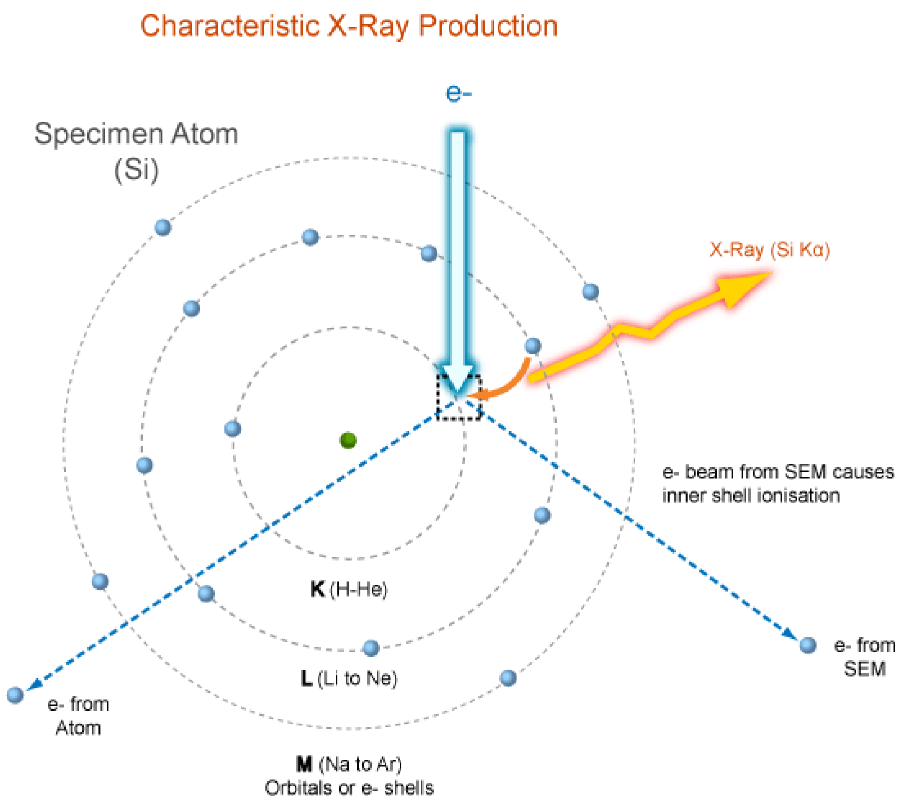
Loss image

Electron Energy Loss Spectroscopy (EELS)



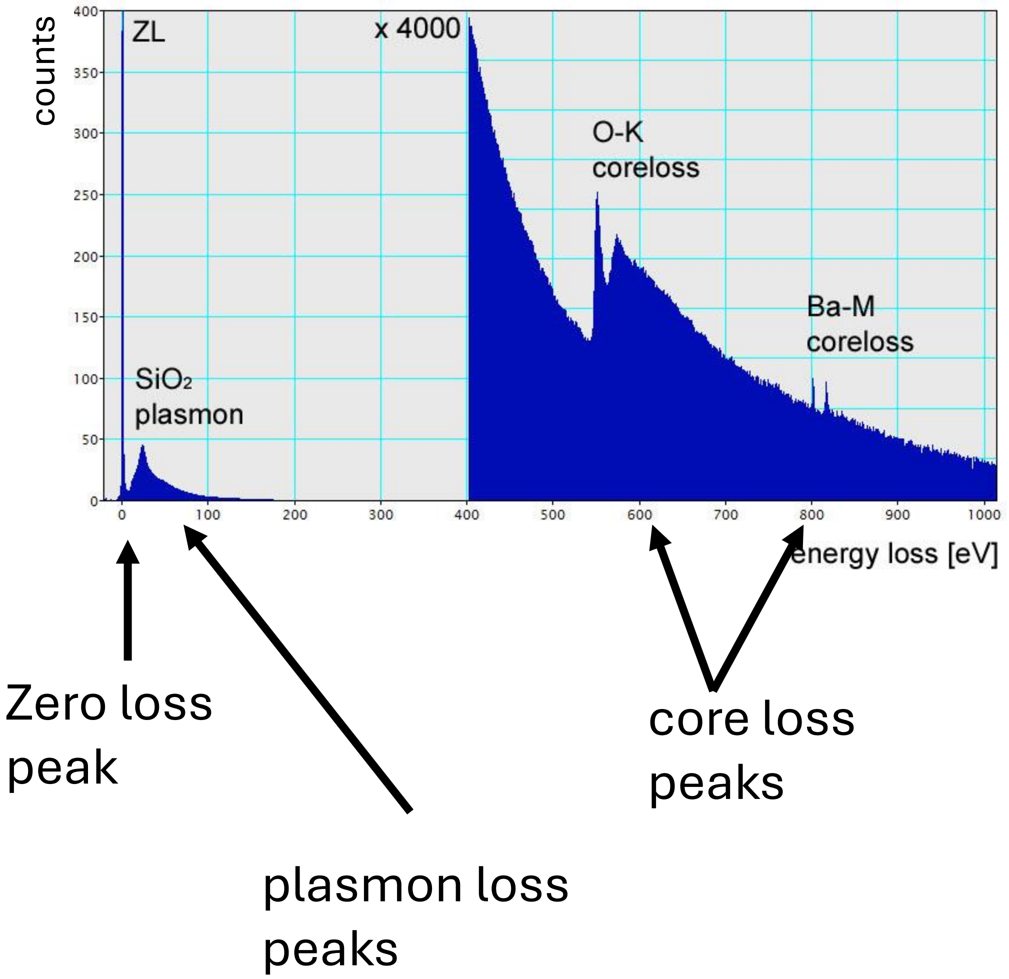
EELS

- The beam electron can transfer energy to an electron of an atom of the specimen:
  - excitation to an unoccupied state or
  - shooting an electron out
- The unoccupied state can be filled by an electron of an outer shell under the emission of an X-ray.
- The energy of the X-ray is specific for the respective atomic species



Electron Energy Loss Spectroscopy

Electron of a sample atom is excited to an empty state



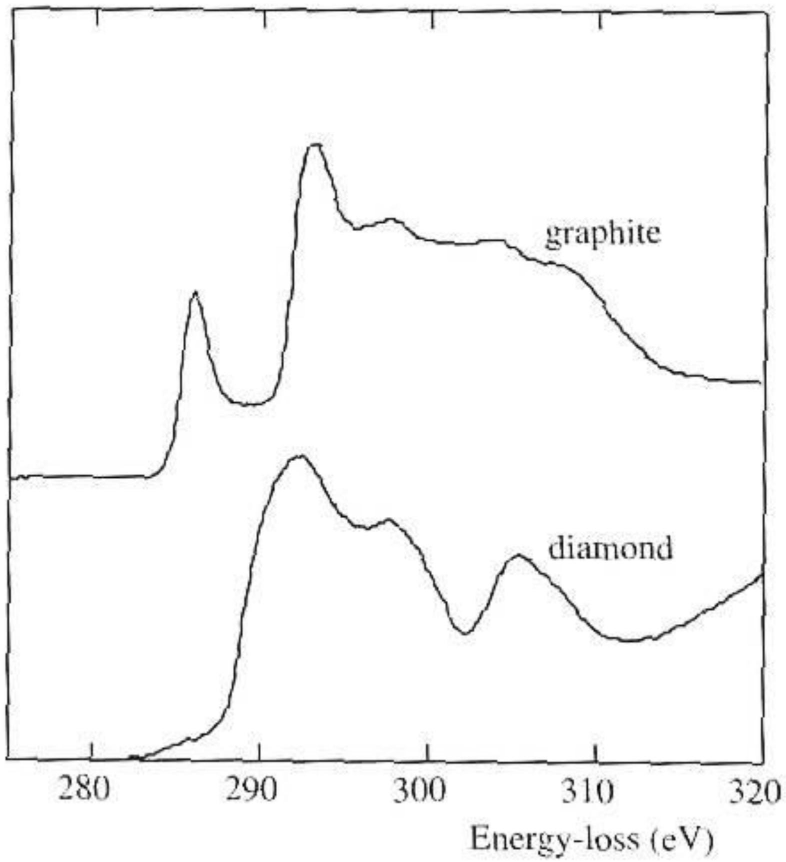
EELS characteristics

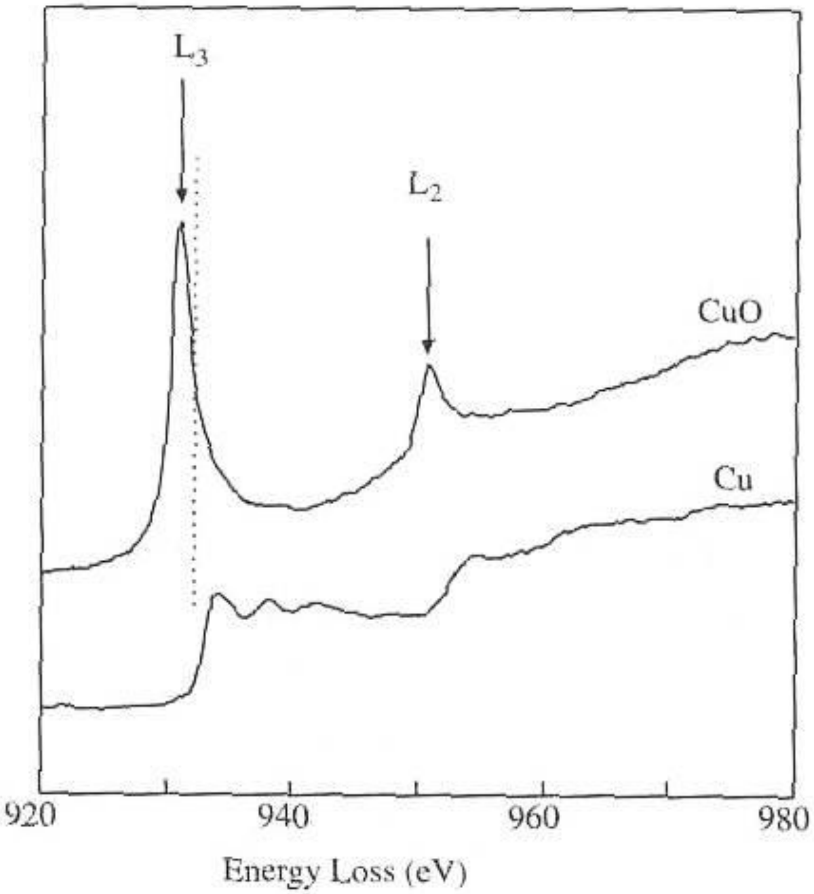
- intensity decrease
- large background
- high sensitivity for light elements!
- Usable energy range: $\leq$ 2000eV

Information on

- sample thickness
- sample composition (quantitative)
- local bonding configuration

Fine structures in EELS: bonding information

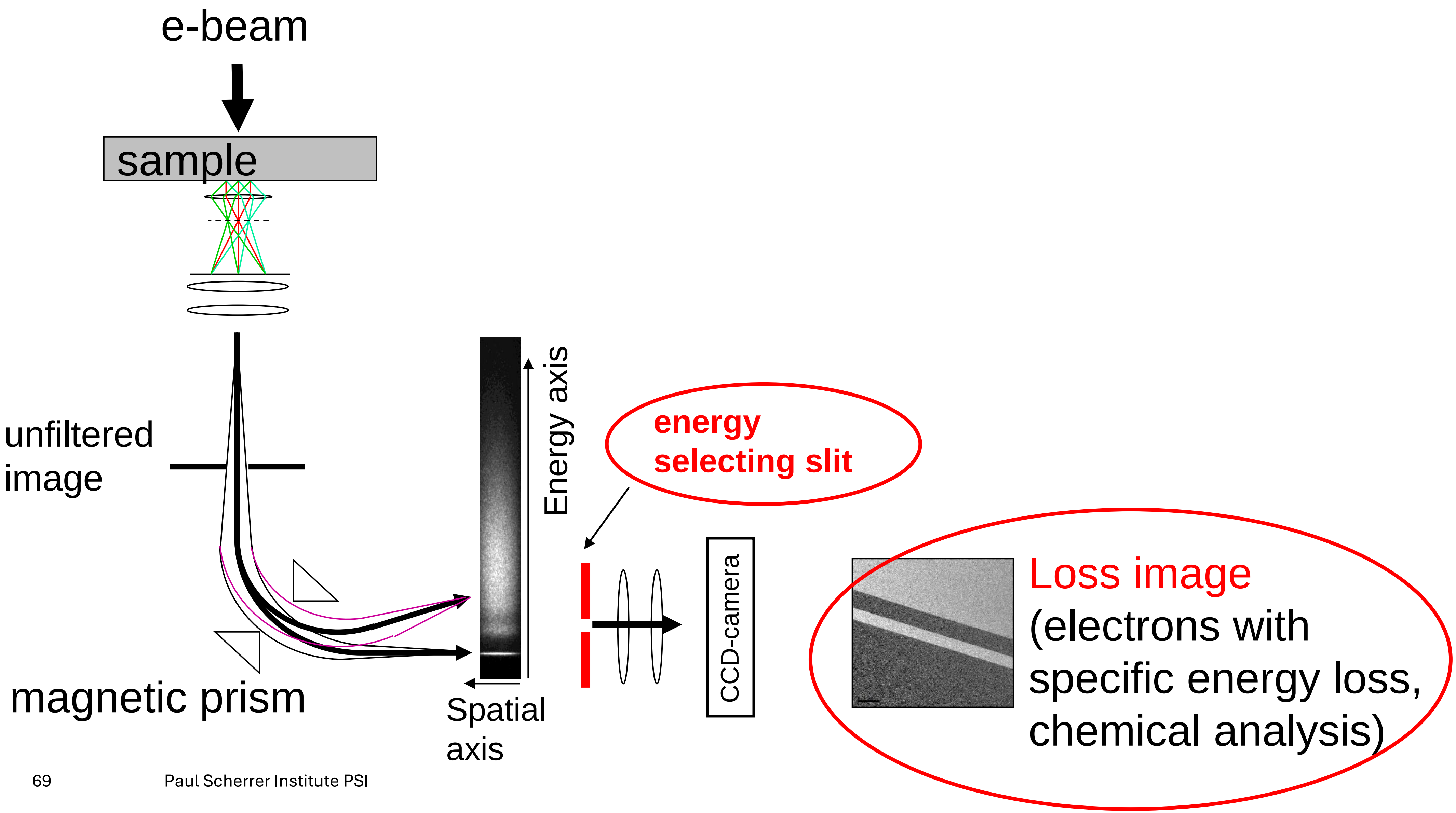




Characteristics of the C_K edge depending on hybridization

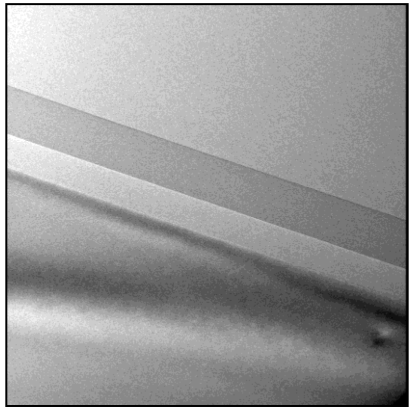
Characteristics of the $Cu\_L_{2,3}$ edges depending on oxidation state of Cu

Electron Spectroscopic Imaging (ESI) = Energy Filtered TEM (EFTEM)

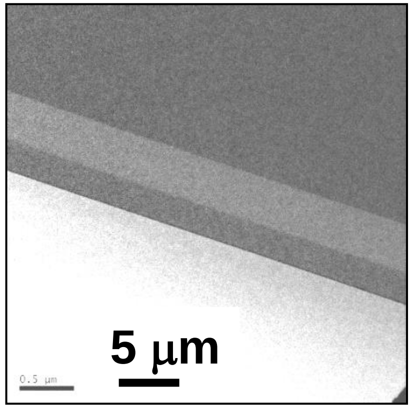


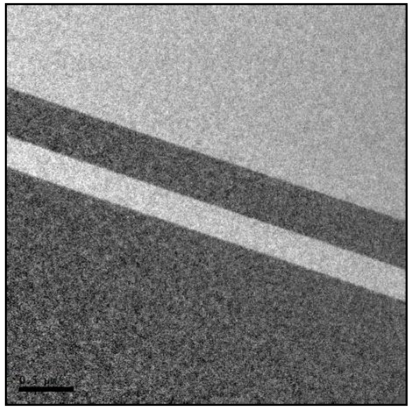
Energy filtered TEM (EFTEM)

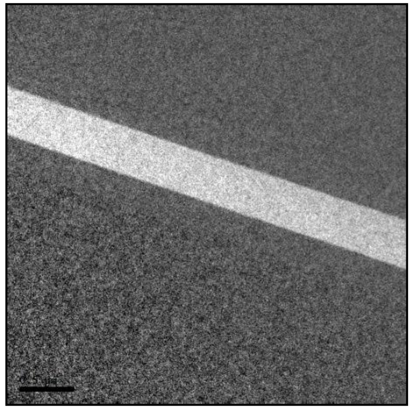
Images are acquired with electrons of a specific energy loss



Si-O
Si-N
Si-O
Si-substrate







Unfiltered　Si-map　O-map　N-map

Elemental maps:

- areas containing the specific element are bright
- only relative intensities

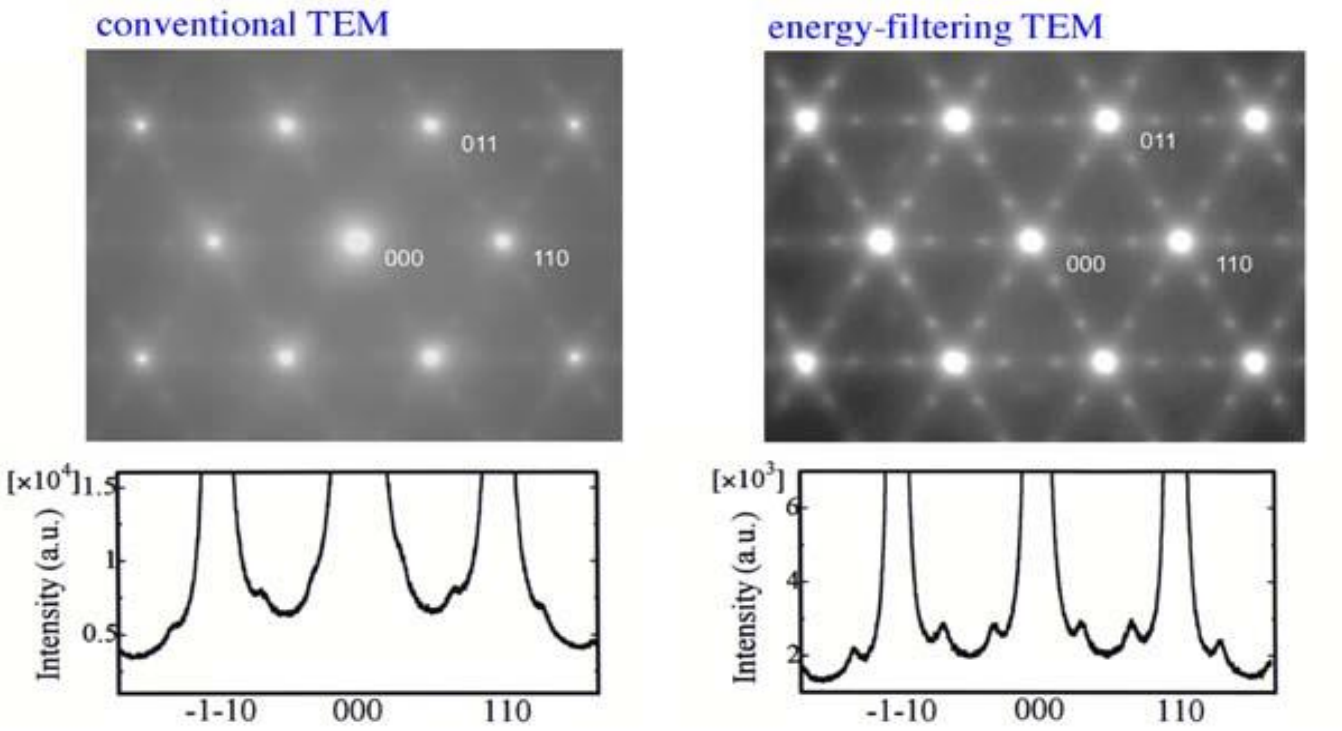
Restrictions:

- Thin specimen areas required
- Signal to noise ratio is poor (especially at high energy losses!)
- No overlaping edges
- No maps without EEL spectrum!

Special application of EFTEM/ESI: Zero-loss filtering

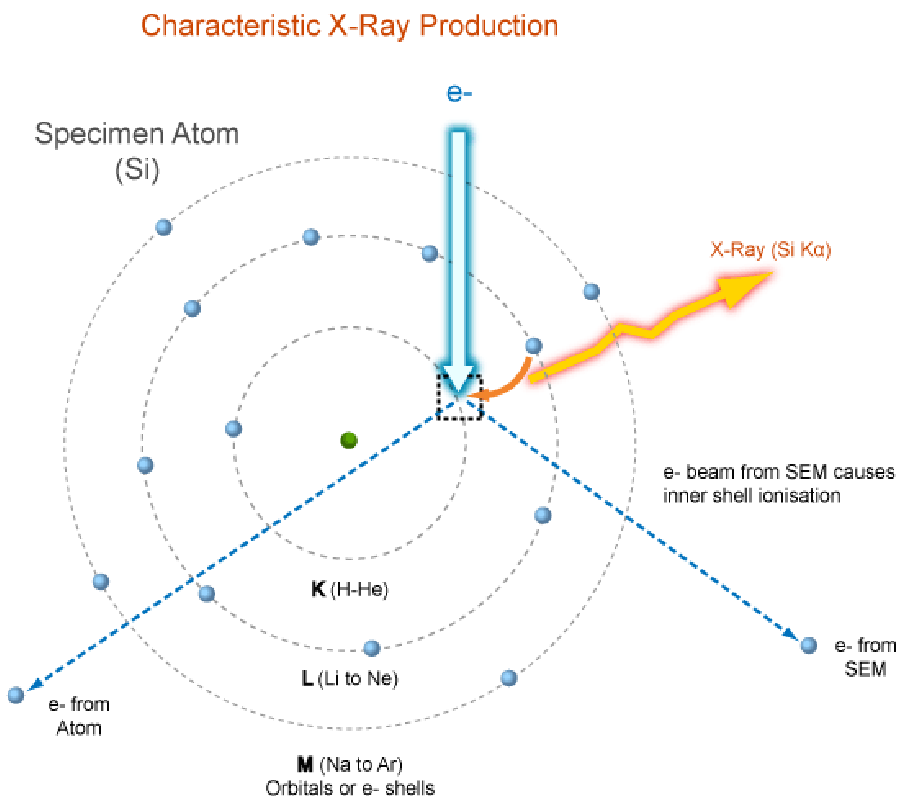
ZL-filtering: All inelastically scattered electrons are removed

- blurring due to inelastic scattering is removed
- no chemical information



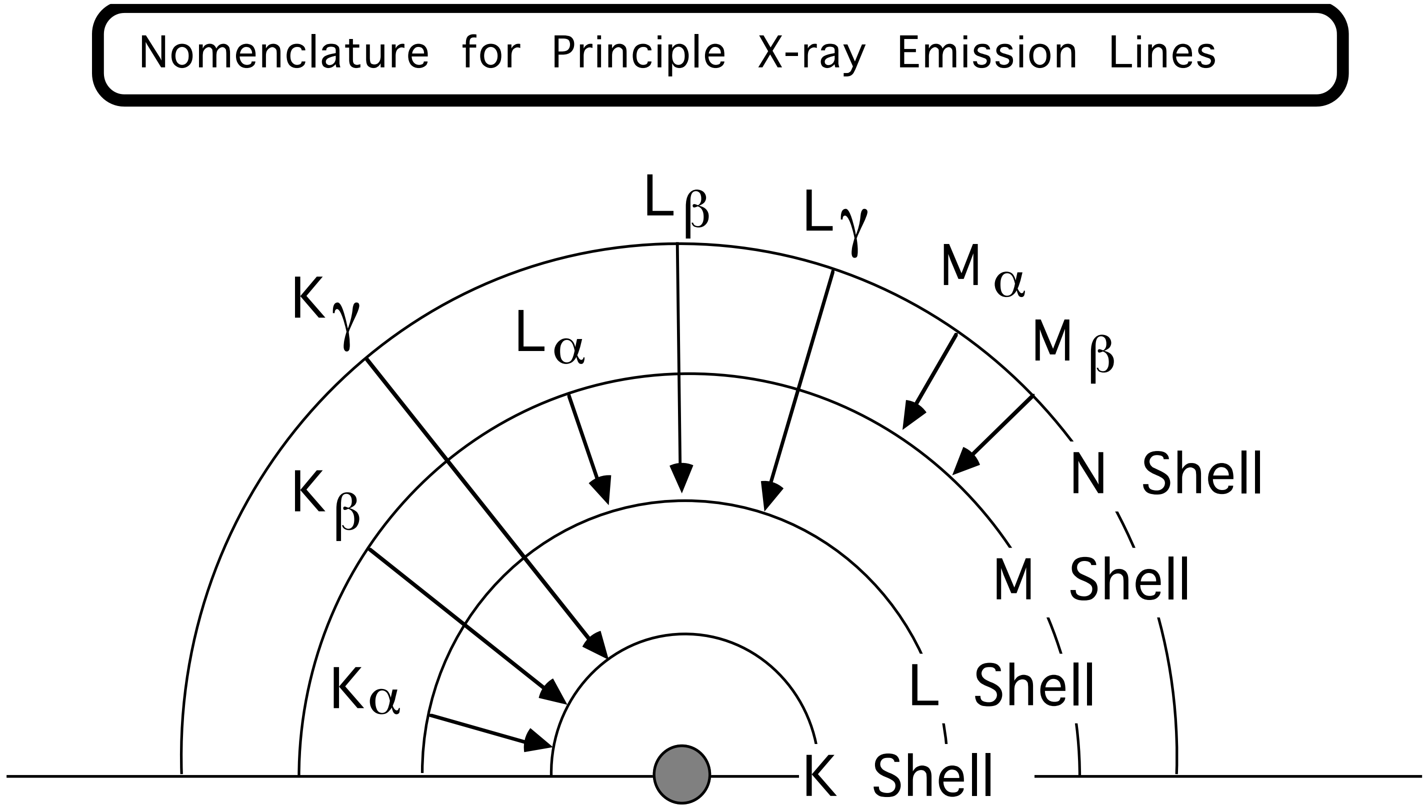
EDX

- The beam electron can transfer energy to an electron of an atom of the specimen:
  - excitation to an unoccupied state or
  - shooting an electron out
- The unoccupied state can be filled by an electron of an outer shell under the emission of an X-ray.
- The energy of the X-ray is specific for the respective atomic species



- The ionisation energy for a removel of an atom from the K-shell requires highest energy as it is more strongly bound to the atom core than an outer shell electron.
- Characteristic X-rays are due to electron transitions between different shells
- The energy of each sub shell is characteristic for the respective atomic species.
- The characteristic X-rays give rise to comparably narrow peaks in the spectrum on top of the Bremsstrahlung (electromagnetic radiation produced by the acceleration or especially the deceleration of a charged particle after passing through the electric and magnetic fields of a nucleus).

Characteristic X-ray lines



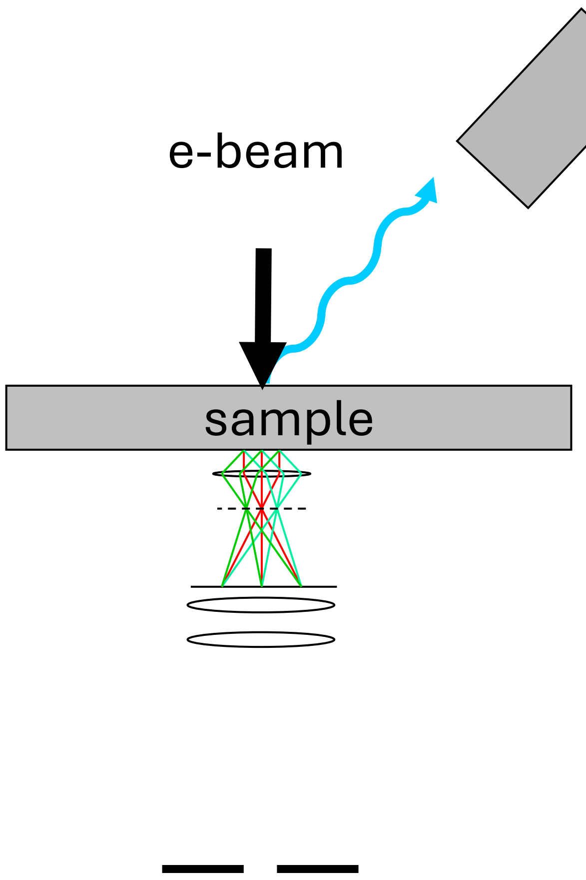
Characteristic X-ray Line Energy = $E_{final} - E_{initial}$

Recall that for each atom every shell has a unique energy level determined by the atomic configuration for that element.

Slide from N. Zaluzec

∴ X-ray line energies are unique.

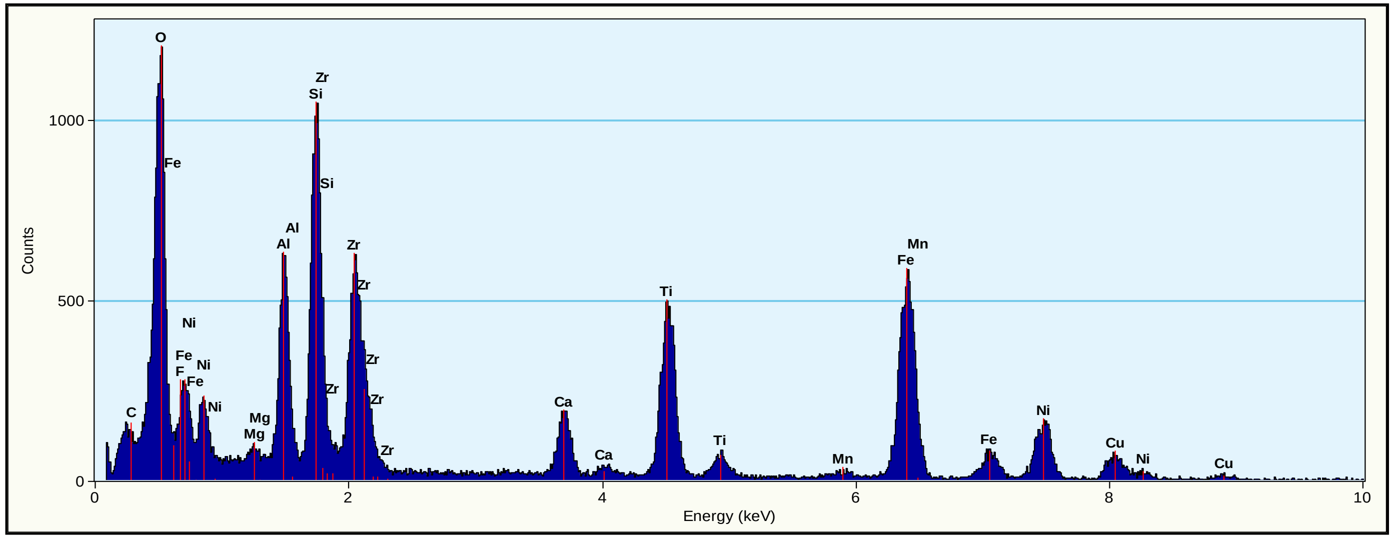
Energy dispersive X-ray spectroscopy (EDX)



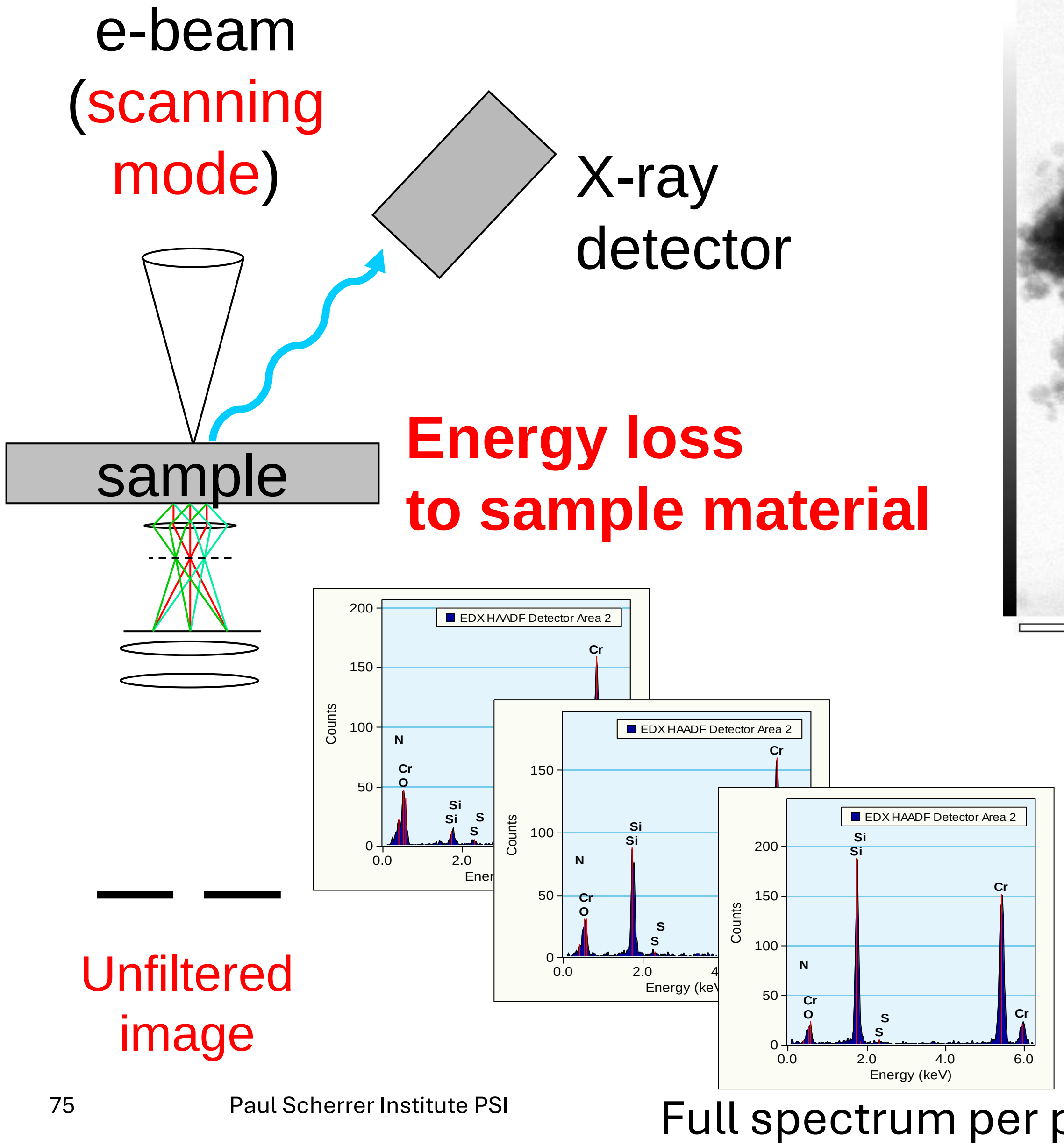
Energy loss
to sample material

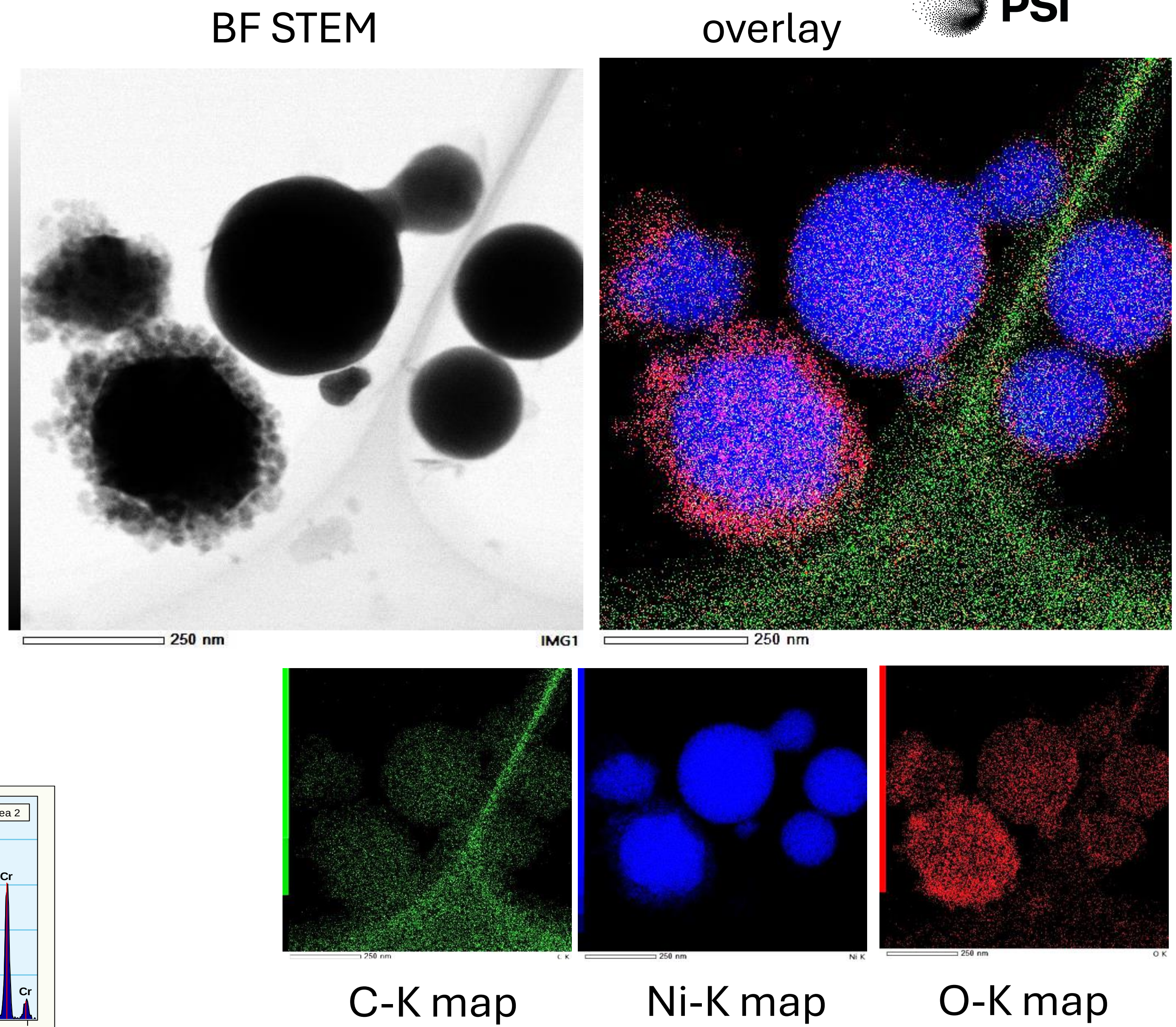
unfiltered
image

Quantification reliable for a specimen
- Homogeneous
- Thin
- with atomically flat surfaces
- if compared to standard material of defined composition....



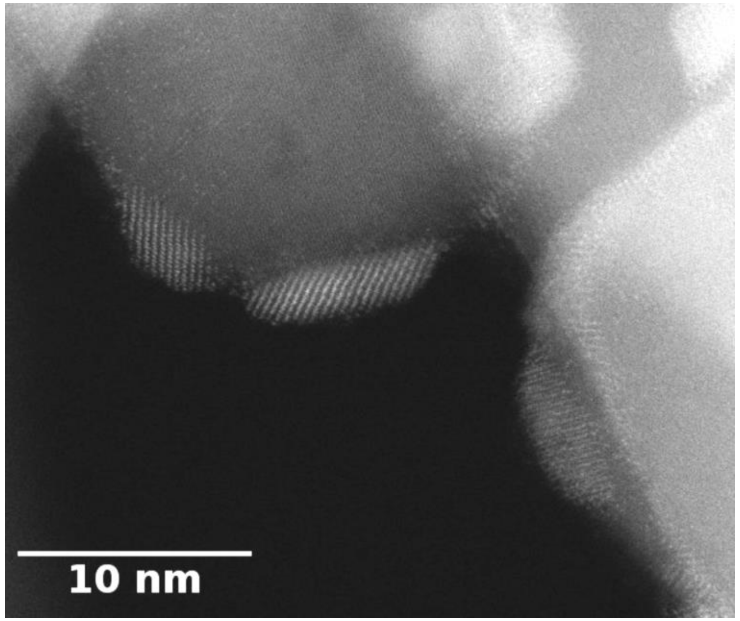
EDX-mapping

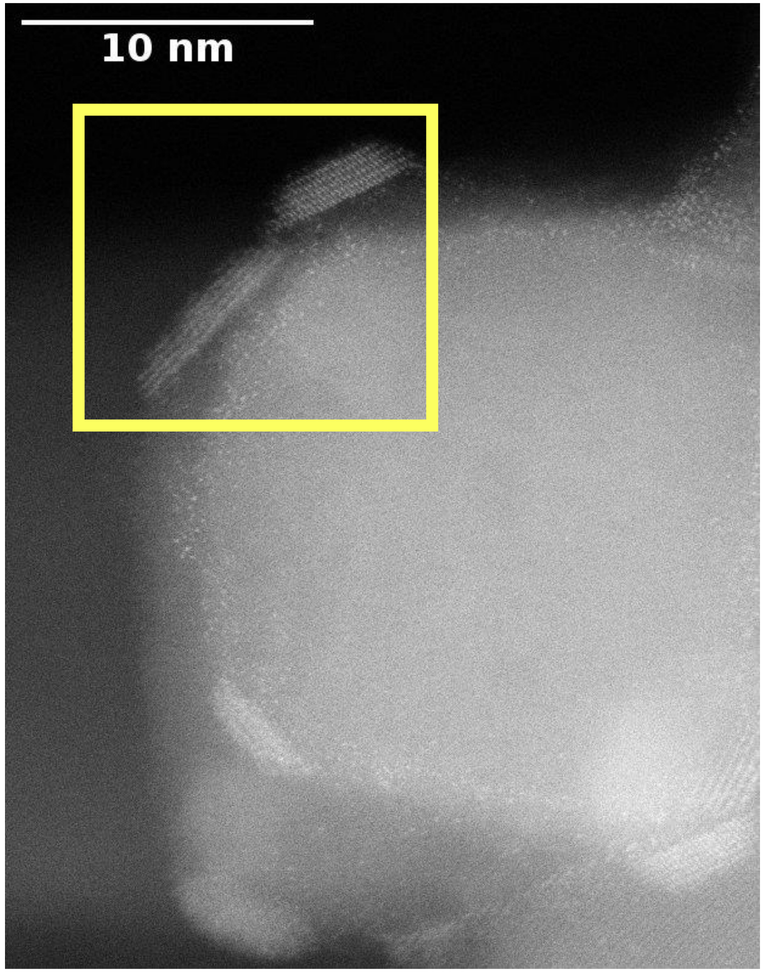

e-beam
(scanning mode)
X-ray detector
sample
Energy loss to sample material
Unfiltered image
EDX HAADF Detector Area 2
Counts
Energy (keV)
Full spectrum per pixel

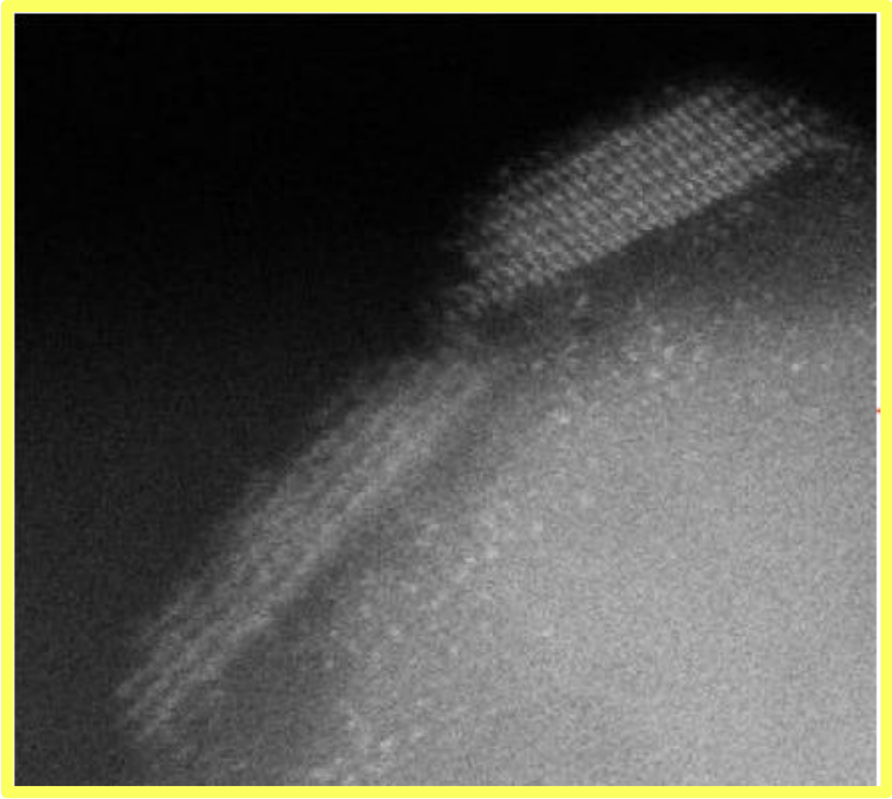

BF STEM
250 nm
IMG1
overlay
250 nm
C-K map
Ni-K map
O-K map

StatSTEM

CeO_2 / TiO_2



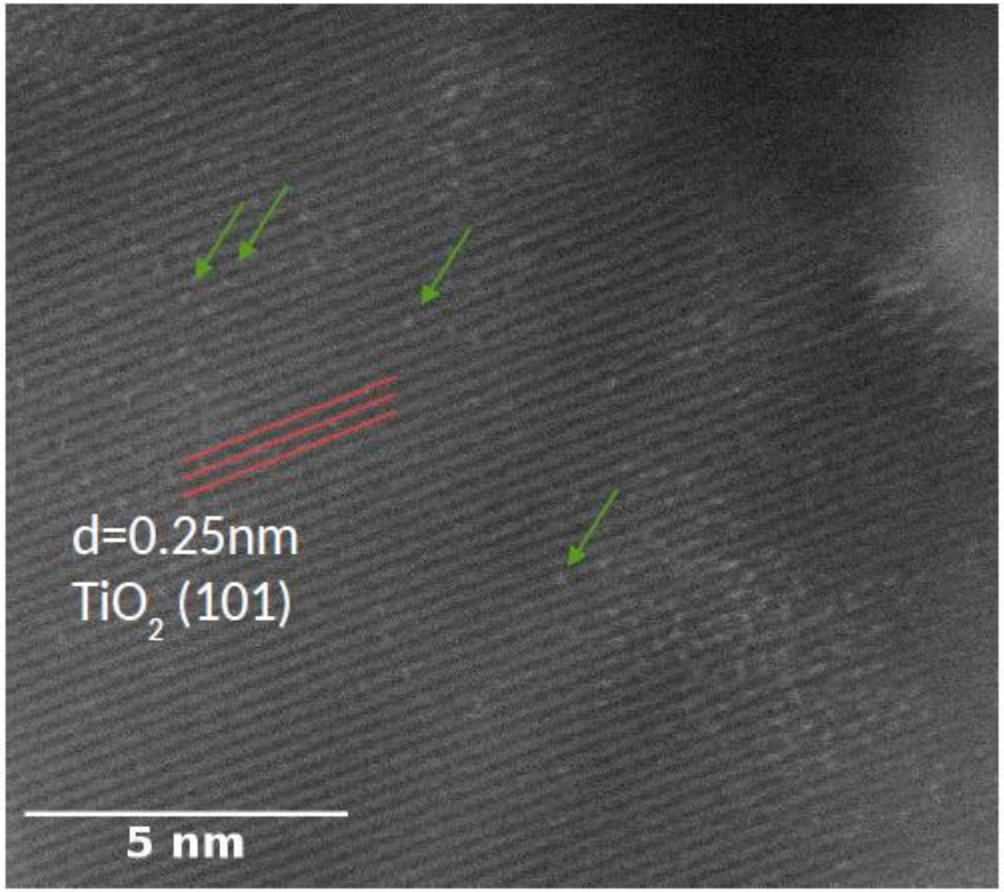




Courtesy Dr. Ivo Alxneit, PSI

StatSTEM

CeO_2 / TiO_2 Ce atoms (ordered)



Ce atoms are located exclusively on the bright lines

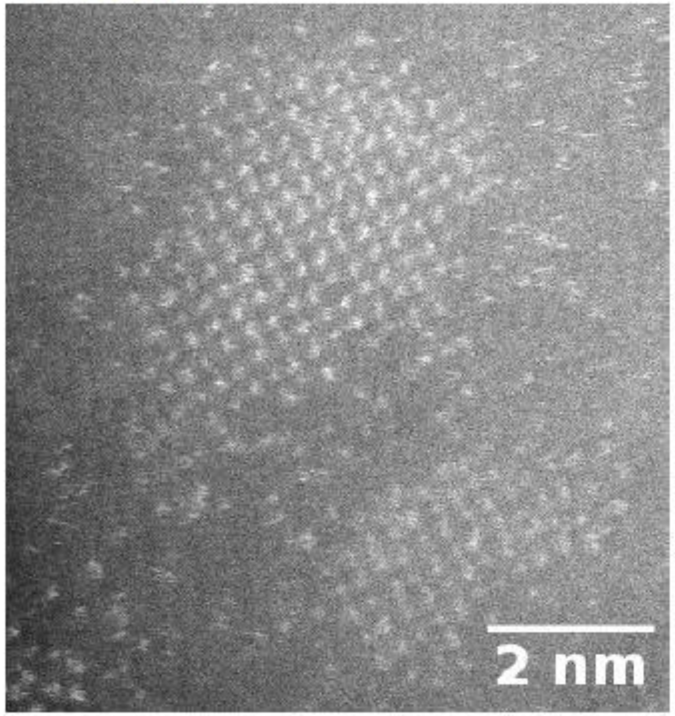
Ce atoms bind to specific surface sites

Courtesy Dr. Ivo Alxneit, PSI

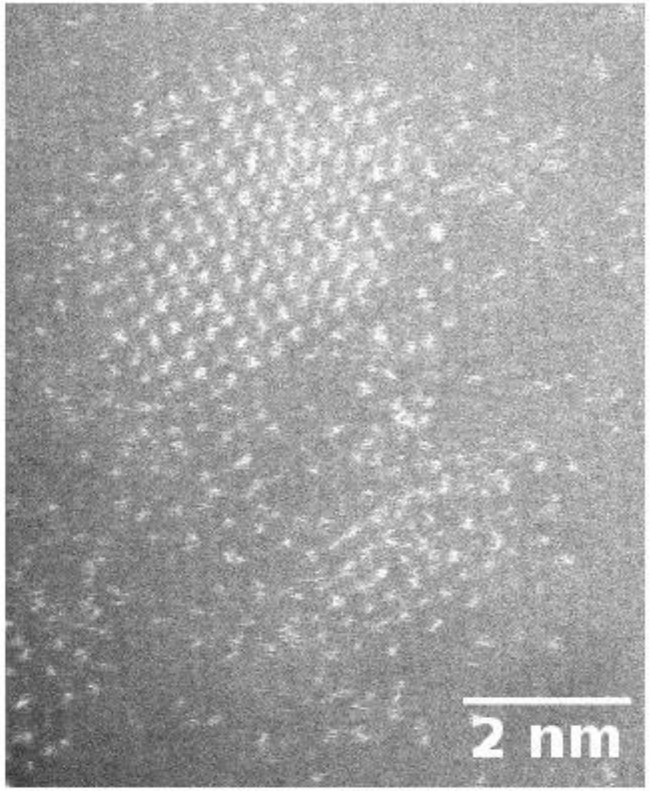
StatSTEM

CeO_2 / TiO_2 Ce atoms (ordered monolayer)

1. scan



2. scan

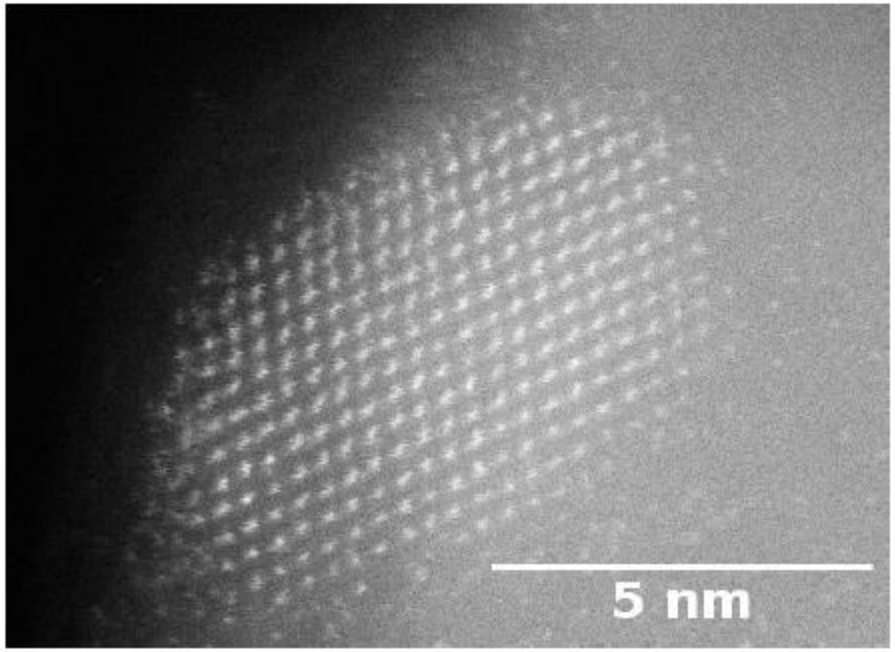


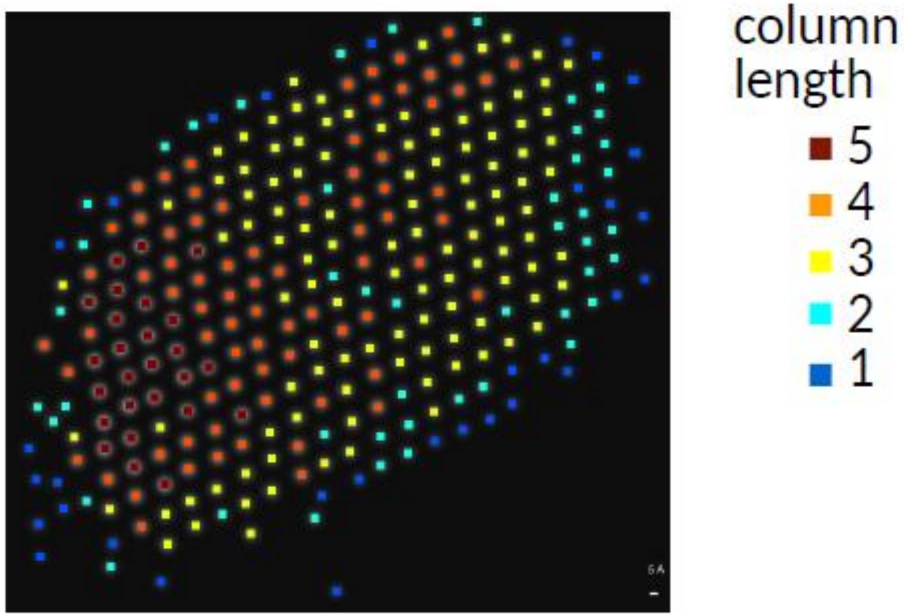
- CeO_2 islands seem to form layer by layer not from lateral grows of particles
- Initial layer is not very stable (Ce atoms are mobile)

Courtesy Dr. Ivo Alxneit, PSI

StatSTEM

CeO_2 / TiO_2 top view of CeO_2 island



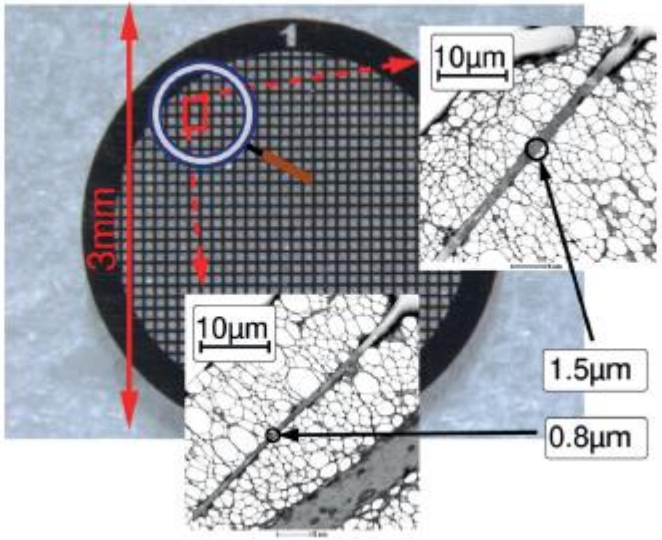


statistical analysis of brightness values (StatSTEM)

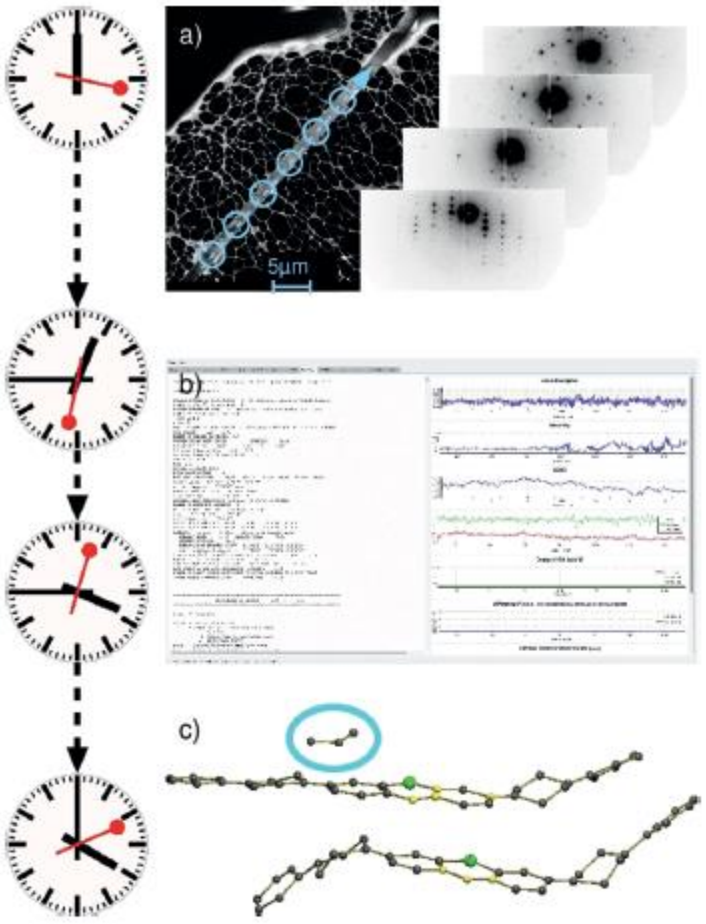
- consistent with side view (5 layers)
- indirectly also confirms monolayer

Courtesy Dr. Ivo Alxneit, PSI

Structure solution from crystaline needle: el. diff. works!



A thin crystalline needle out of the active pharmaceutical ingredient of the drug Grippostad® could be identified as methylene blue derivative, $MBBF_4$

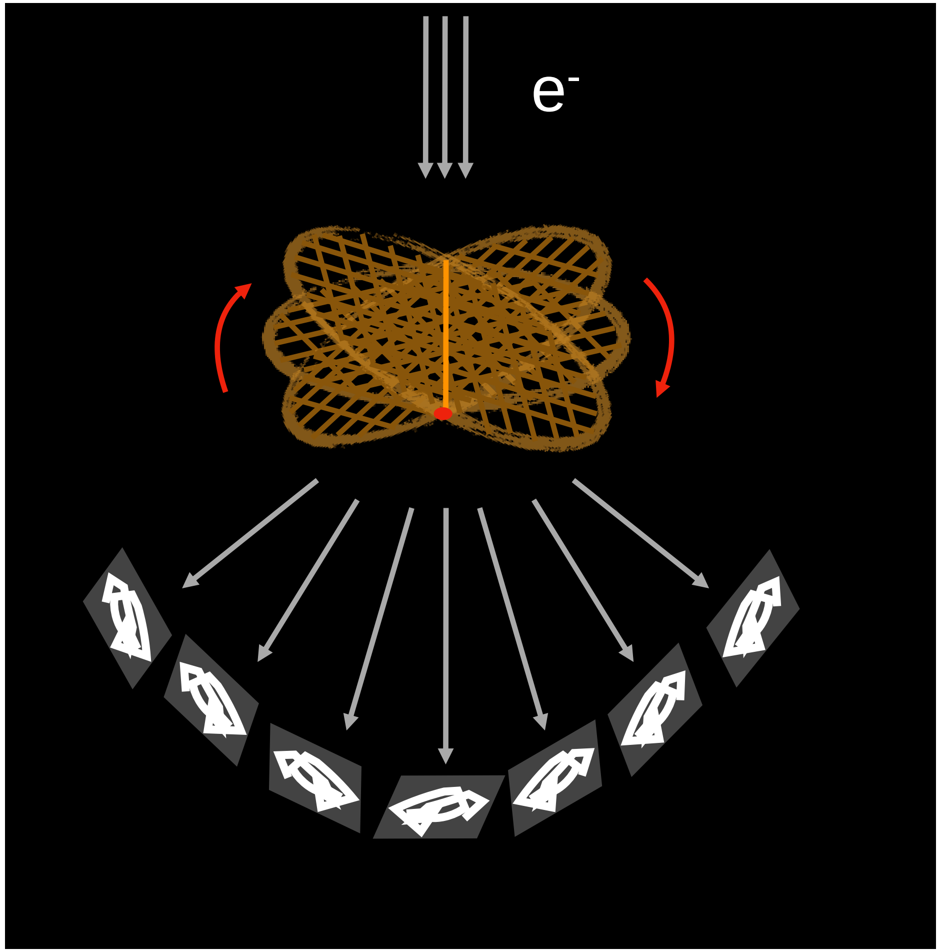


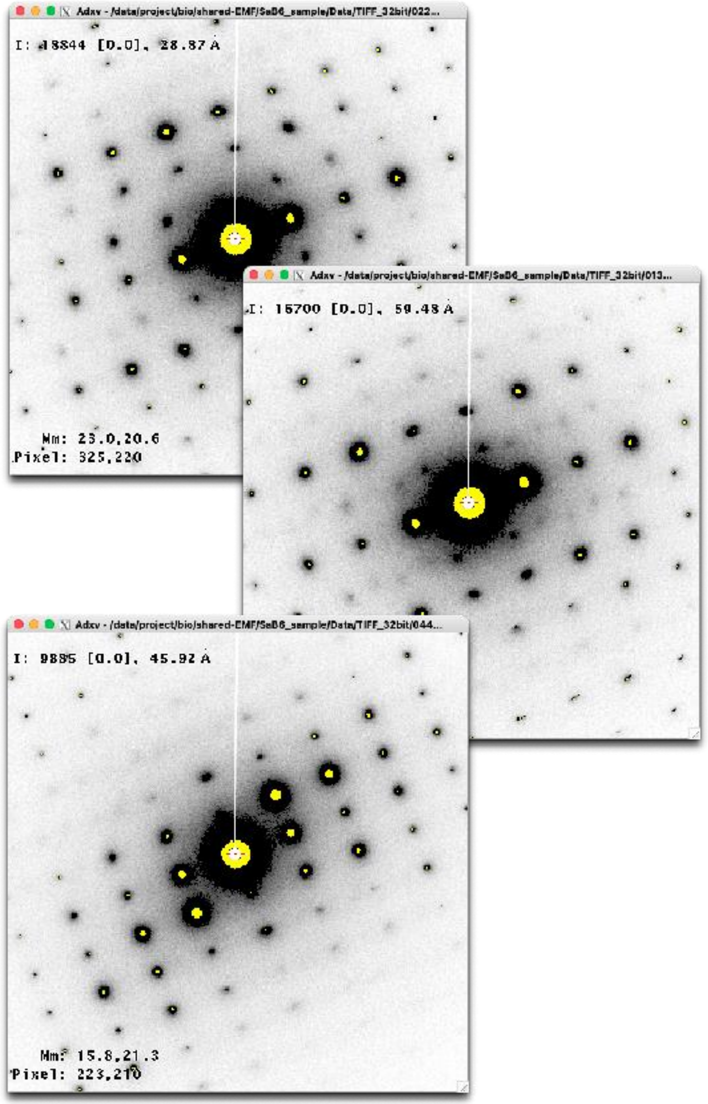
a) **Rotation diffraction = diff. tomography**
Data from 15 segments collected in 45 min.

b) **Data processing**
data format, alignment of diffraction patterns, determination of rotation axis, determination of space group. Data of the first nine segments were processed in 3 h and were sufficient for

c) **structure solution**
using XRD software or software for electron diffraction. Done in 15 min.

Structure solution from crystaline needle: el. diff. works!





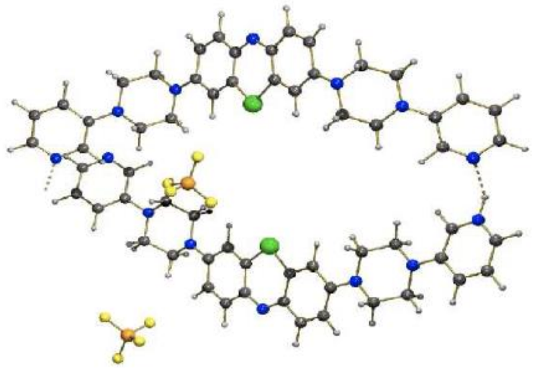
Structure solution from crystaline needle: el. diff. works!

PSI

- Indexing diffraction patterns -> PETS (developed for processing diffraction data), XDS
- Integrating, scaling and merging
  - rotation axis refinement
  - peak analysis and clustering
  - unit cell determination
  - frame processing and peak integration
  - creating reflection files
- Phasing and refinement -> JANA, ShelX, Refmac5
  - space group determination
  - electron scattering factors (ShelxL)
  - structure solution (Shelxt, Syperflip)
  - kinematic and dynamic refinement (Dyngo)

- Merge intensities to reflections
- Determin cell parameters

- Determine unit cell



MBBF4 structure

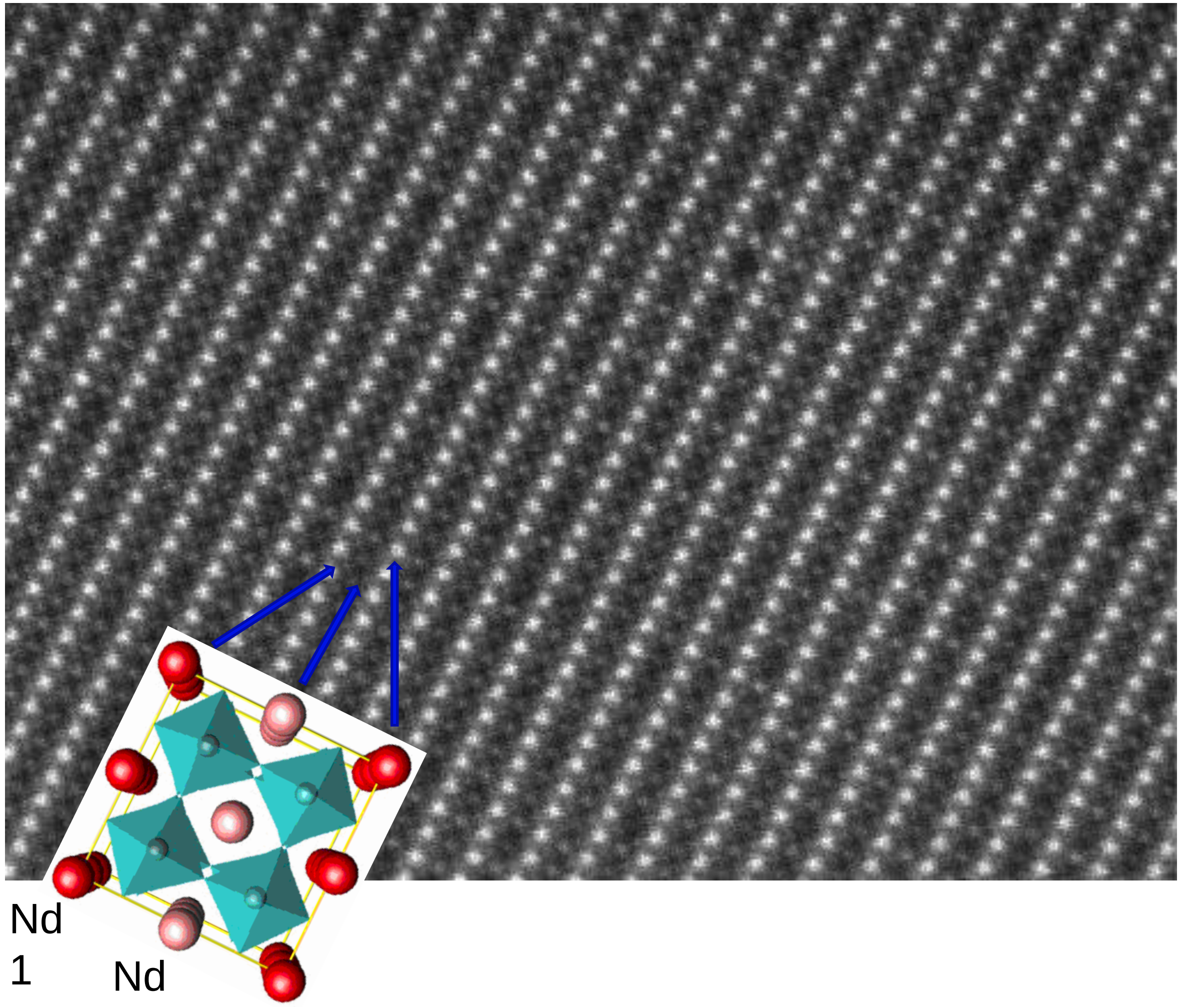
Breakthrough of the year 2018 according to Science magazine!

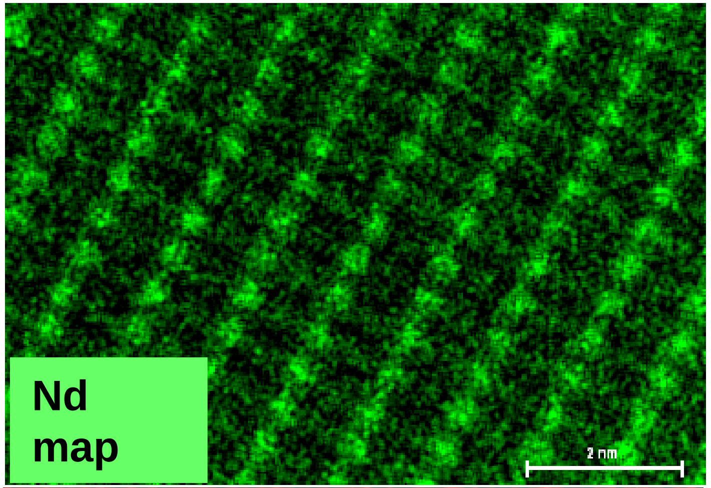
https://vis.sciencemag.org/breakthrough2018/finalists/#rapid-structure

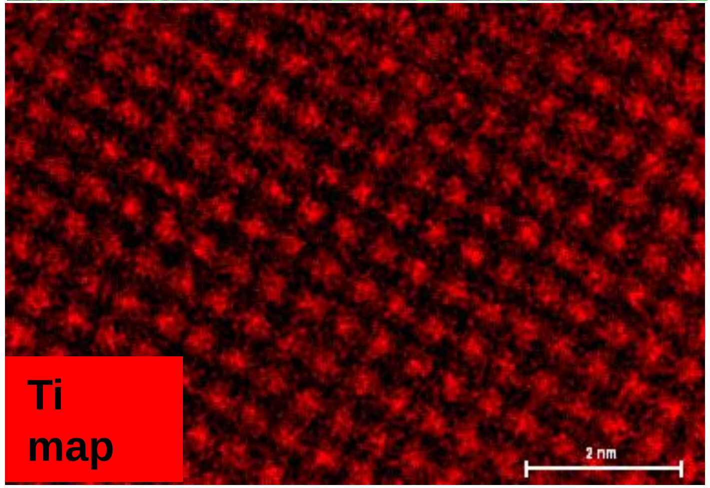
Angew. Chem. Int. Ed. 2018, 57, 16313 –16317

Atomically resolved EDX

HAADF-EDS study of $Nd_{2/3}TiO_3$ perovskite

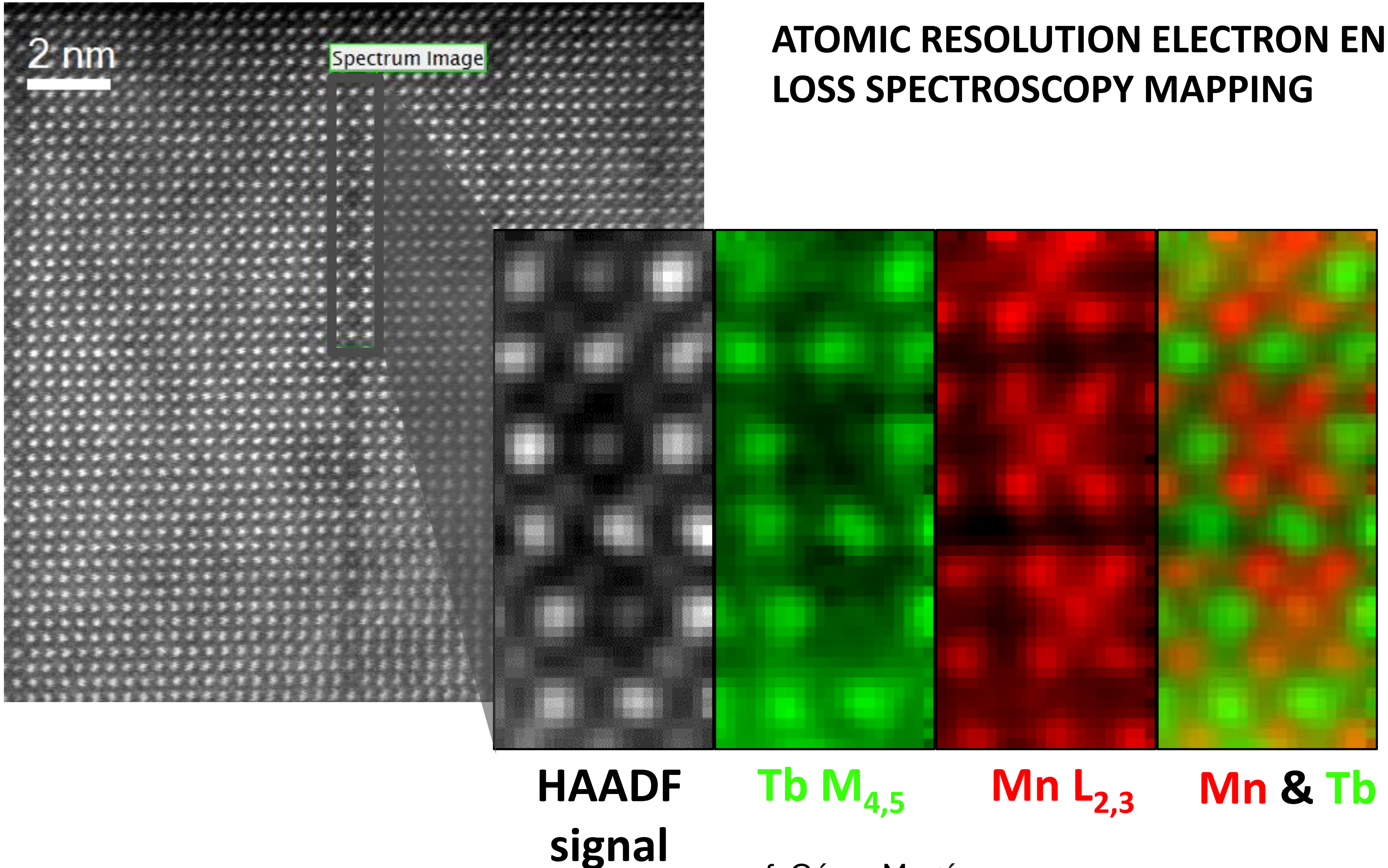






F Azough, R Freer, S.J Haigh
University of Manchester, UK

Strained $TbMnO_3$ Films



ATOMIC RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY MAPPING

cf. César Magén
http://ina.unizar.es/es/cesar-magen-dominguez/