

**Christian Danvad
Damsgaard**

Associate Professor



DTU Fysik and DTU Nanolab

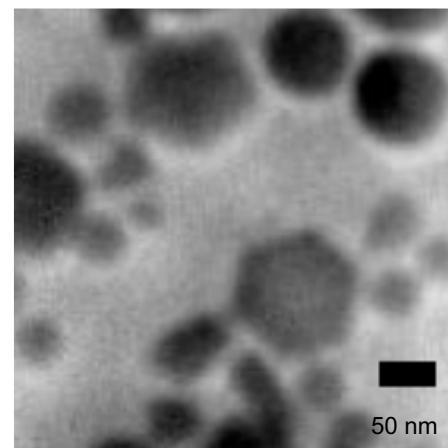
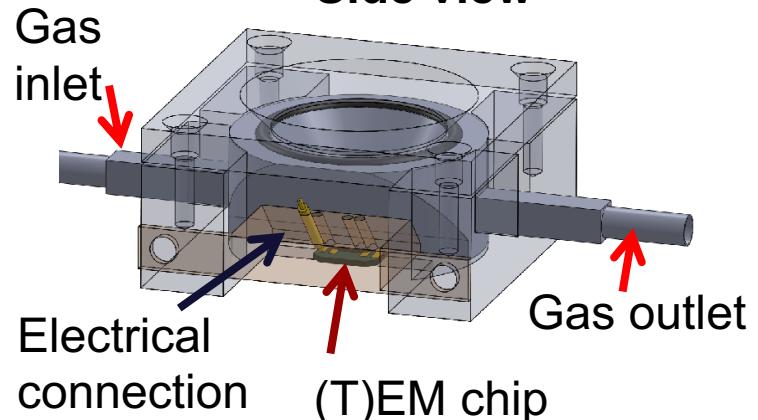
Building 307, room 116

2800 Kgs. Lyngby

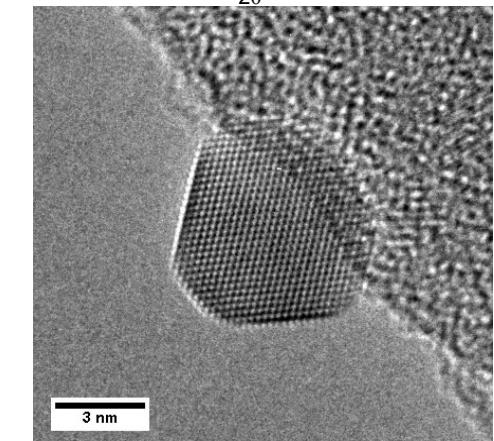
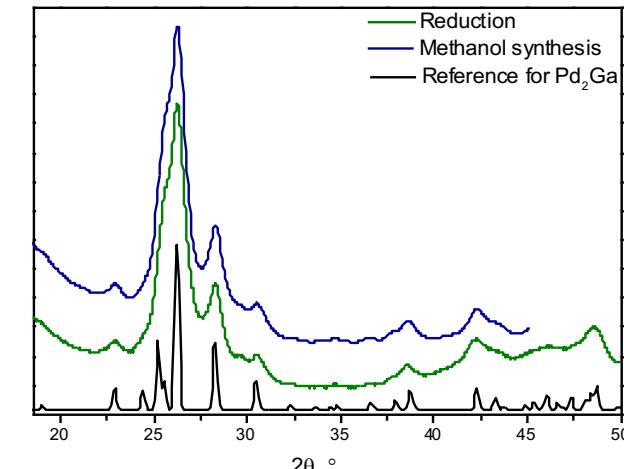
SURFCAT section

Works with *In situ* characterization of catalysts by use of EM and X-rays

Side view



Reinhardt, J., Hoppe, R., Hofmann, G., Damsgaard, C. D., Patommel, J., Baumbach, C., Baier, S., Rochet, A., Grunwaldt, J. D., Falkenberg, G. & Schroer, C. G. Beamstop-based low-background ptychography to image weakly scattering objects. *Ultramicroscopy* **173**, 52–57 (2017).



Fiordaliso, E. M., Sharafutdinov, I., Carvalho, H. W. P., Grunwaldt, J.-D., Hansen, T. W., Chorkendorff, I., Wagner, J. B. & Damsgaard, C.D. Intermetallic GaPd 2 nanoparticles on SiO₂ for low pressure CO₂ hydrogenation to methanol: catalytic performance and *in situ* characterization. *ACS Catal.* **5**, 5827–5836 (2015).

What material properties/parameters are important to know (characterize) when working with catalysts/energy materials?



Paste the link to the slide you want to display here:

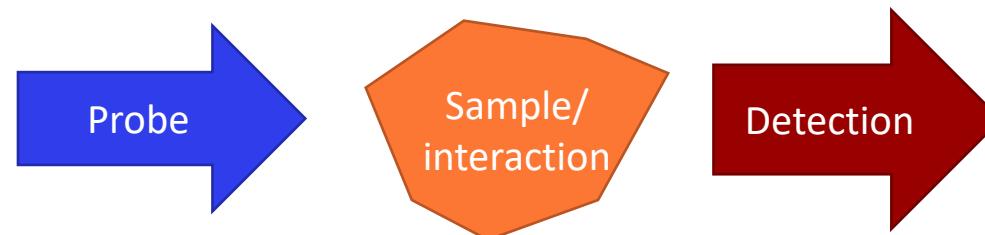
<https://www.mentimeter.com/app/presentation/asdfakn3290874y/dfvh873/>

Select

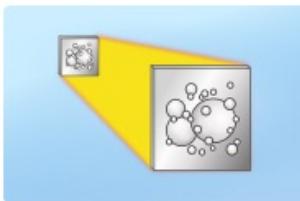
How does it work?

Log out

- Elemental composition
- Binding energies
- Porosity - surface area
- Adsorbed molecules
- Facets – crystal structure
- Particle size distribution
- Ionization energy
- Spatial distribution
- Defects
- Chemical states



Method	Acronym	Probe	Detection	Scattering
Scanning electron microscopy	SEM	Electrons	Electrons	Inelastic, elastic
Transmission electron microscopy	TEM	Electrons	Electrons	Inelastic, elastic
Scanning transmission electron microscopy	STEM	Electrons	Electrons	Inelastic, elastic
X-ray diffraction	XRD	Photons	Photons	Elastic
Energy dispersive x-ray spectroscopy	EDX, EDS	Electrons	Photons	Inelastic
X-ray photoemission spectroscopy	XPS	Photons	Electrons	Inelastic
X-ray absorption spectroscopy	XAS, XANES, EXAFS	Photons	Photons	Inelastic
Electron energy loss spectroscopy	EELS	Electrons	Electrons	Inelastic, elastic



Microscopy Concepts



Scanning Electron Microscopy



Transmission Electron Microscopy



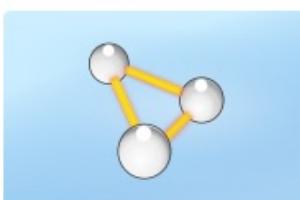
Light & Fluorescence Microscopy



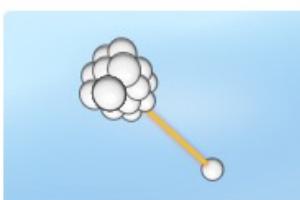
Cryo-Electron Microscopy



X-ray Diffraction



Energy Dispersive Spectroscopy



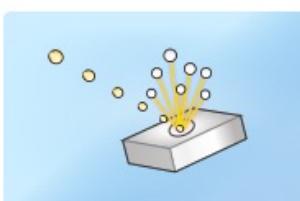
Atom Probe Tomography



Focused Ion Beam



Scanning Probe & Atomic Force Microscopy



Secondary Ion Mass Spectrometry



Research Data Management

<https://myscope.training/>

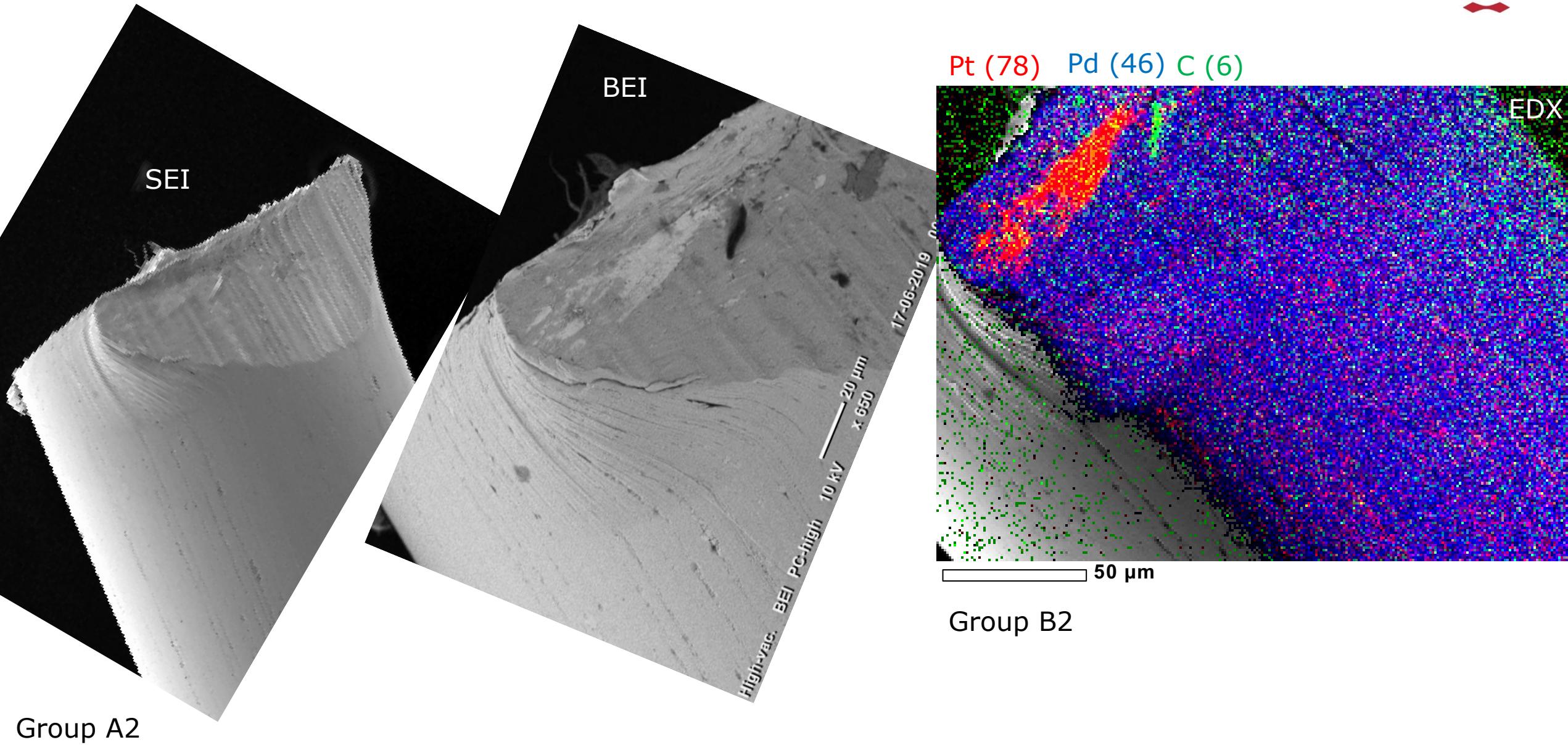
Characterization of catalysts by electron microscopy

Electron microscopy (EM) in general – Setup

Scanning electron microscopy (SEM) – Imaging

Energy dispersive x-ray spectroscopy (EDX) - Elemental analysis

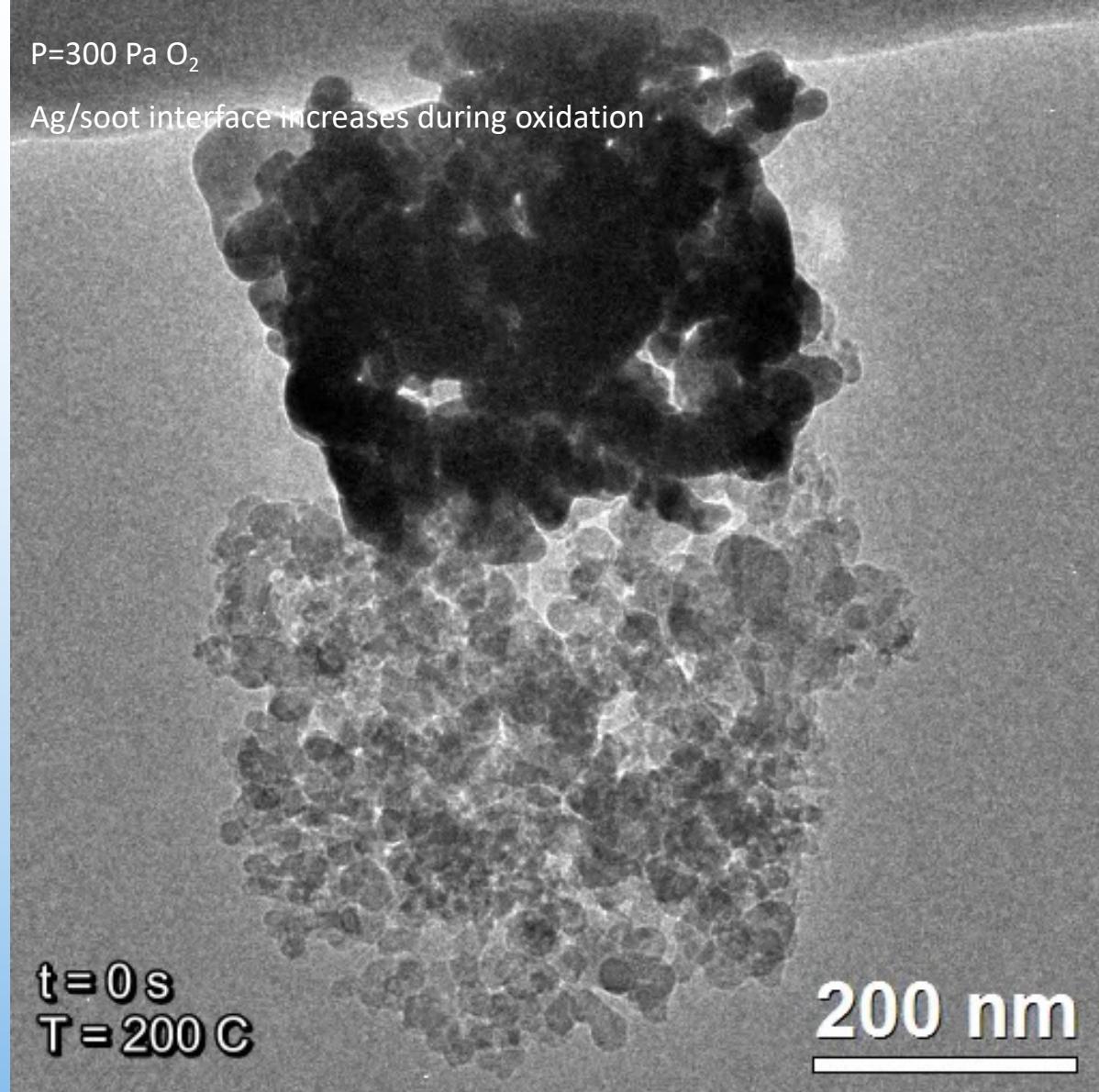
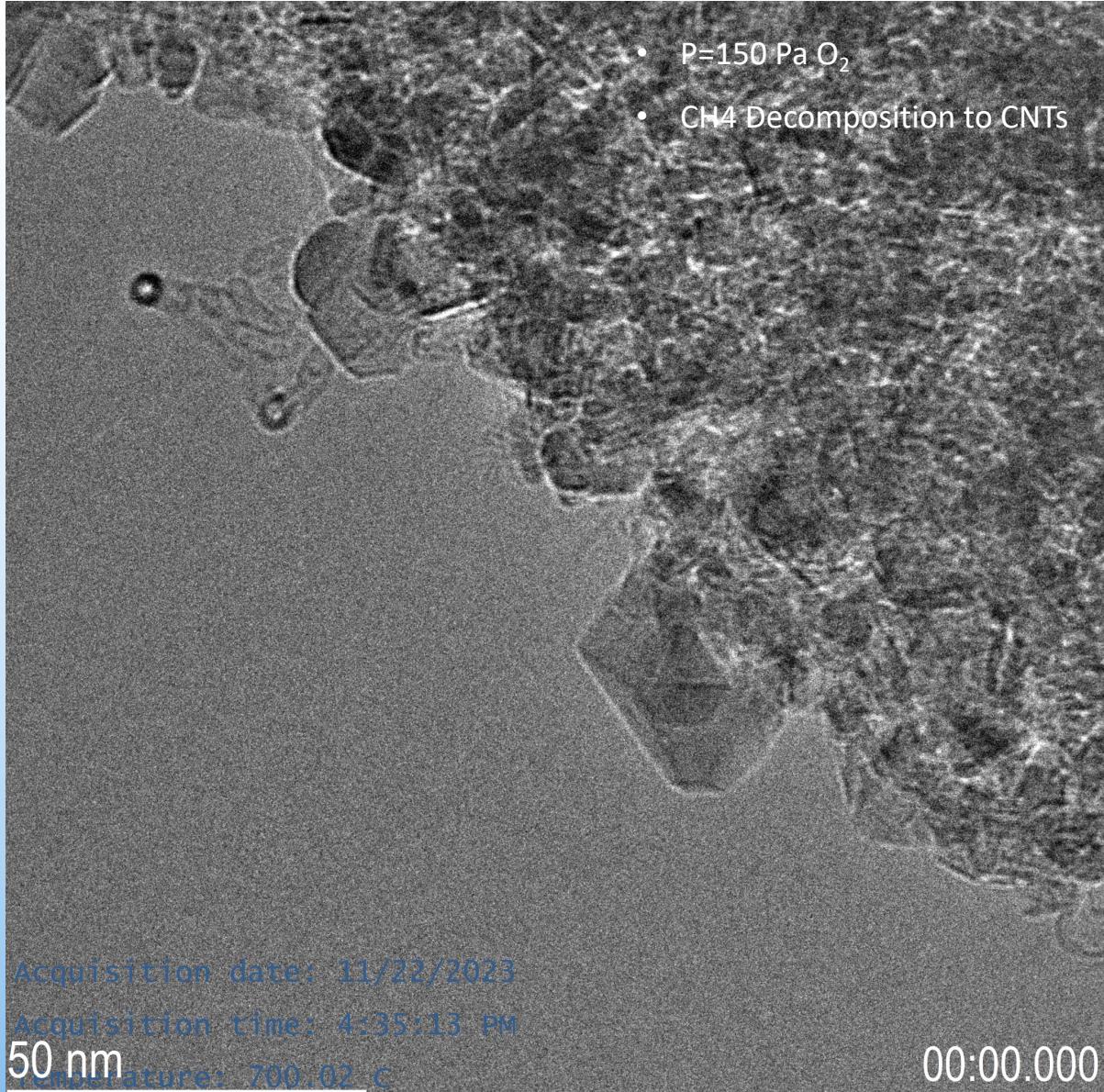
Scanning Electron Microscopy – MODES of operation: SEI, BEI, and EDX



Group A2

Group B2

Some examples of catalysts in action: CNT growth and soot oxidation



3 minutters buzz

- Electrons interacts strongly with matter -> high response
- Relatively easy to change electron energy -> flexible microscope
- short wave length -> high resolution
- You can make efficient lenses



Louis-Victor Pierre Raymond de
Broglie
(1892 - 1987)

Nobel prize: 1929

De Broglies doctoral thesis (1924):

Application of the idea of particle – wave dualism (only known for photons up to then) for any kind of matter.

Inspired by Bohr's theory of the hydrogen atom, in which the electron follows certain orbitals around the nucleus.

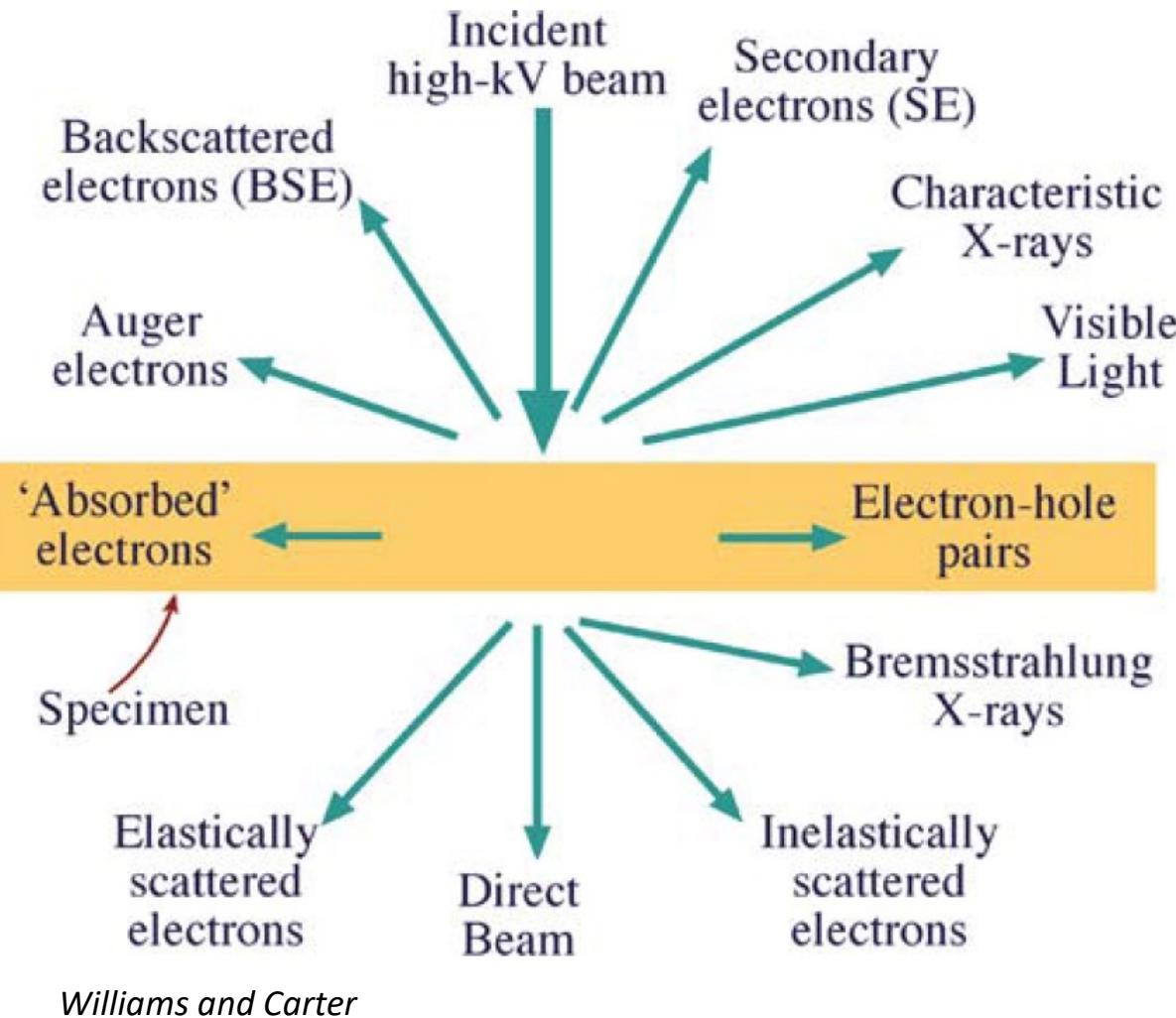
=> Matter Waves

$$\lambda = \frac{h}{p}$$

Electron-Specimen Interactions

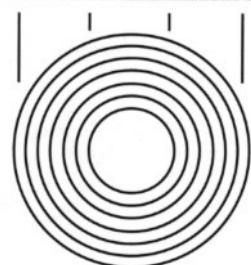
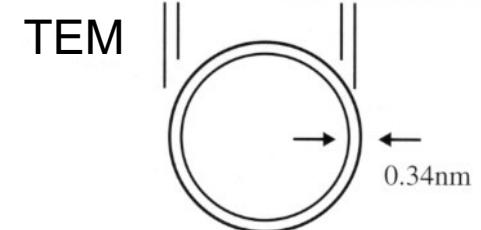
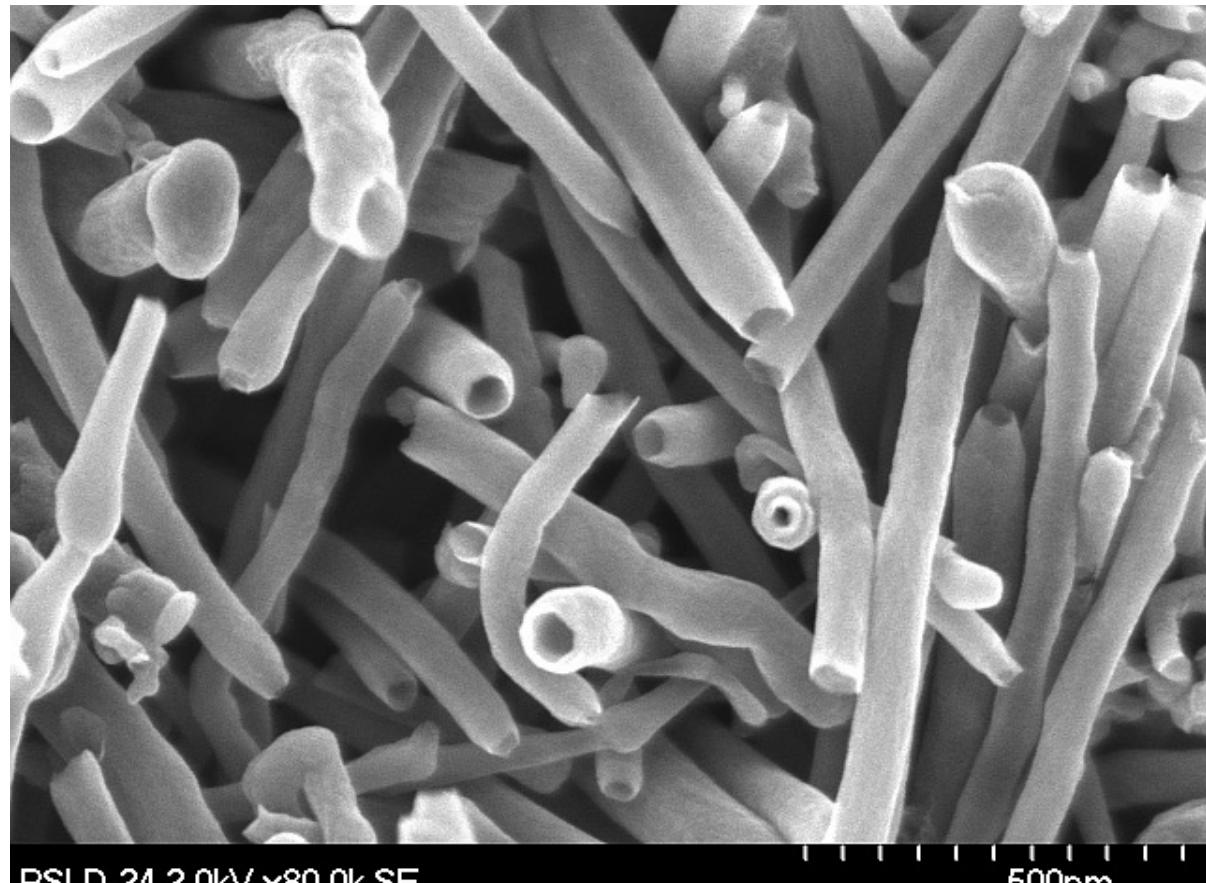
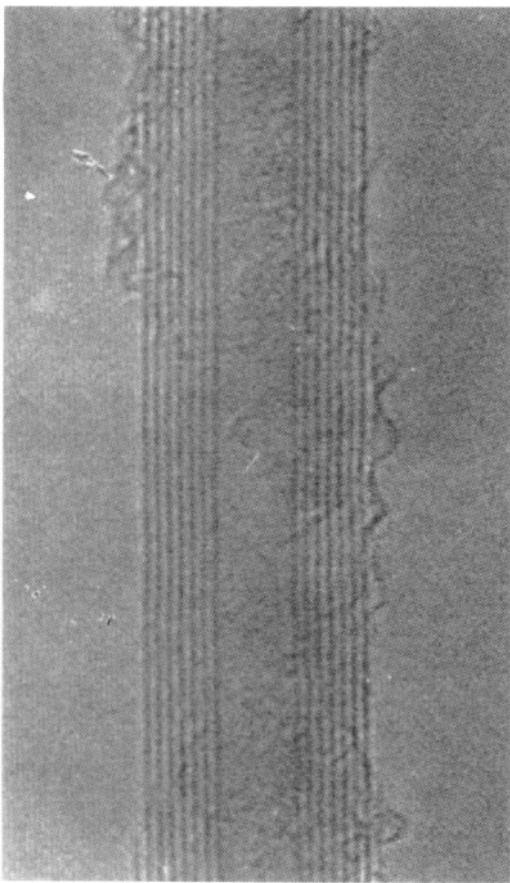
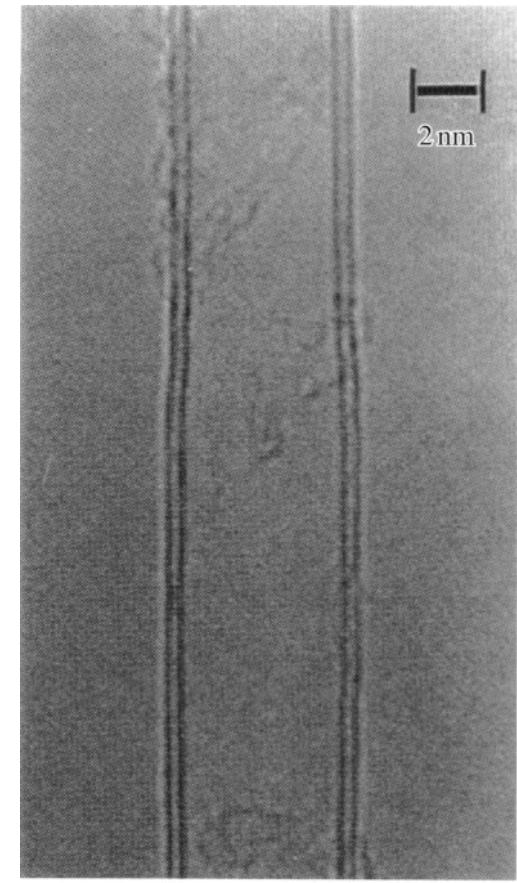


SEM



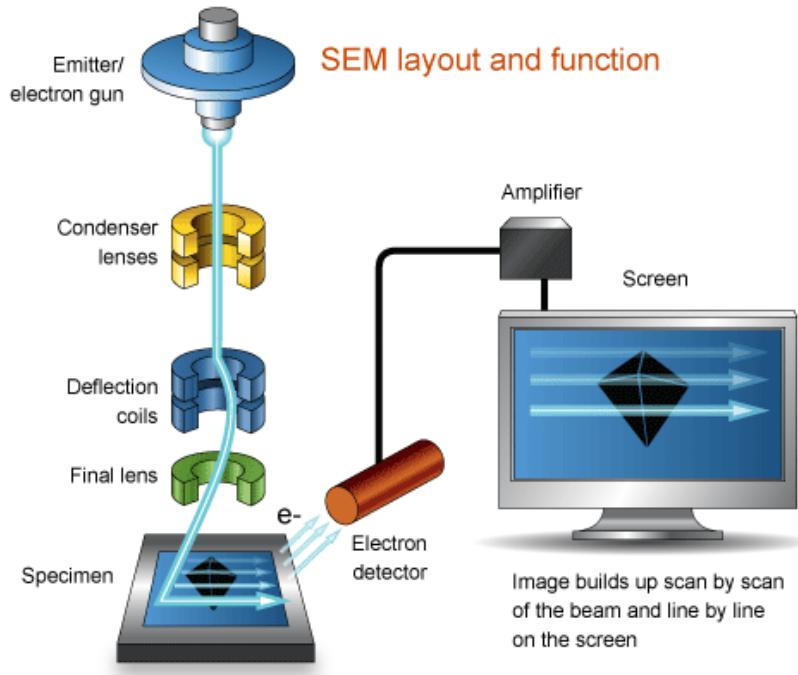
(S)TEM

Images in electron microscopy



Carbon nanotubes, S Iijima Nature 354 (1991) 56

How can we use electrons for visualization?

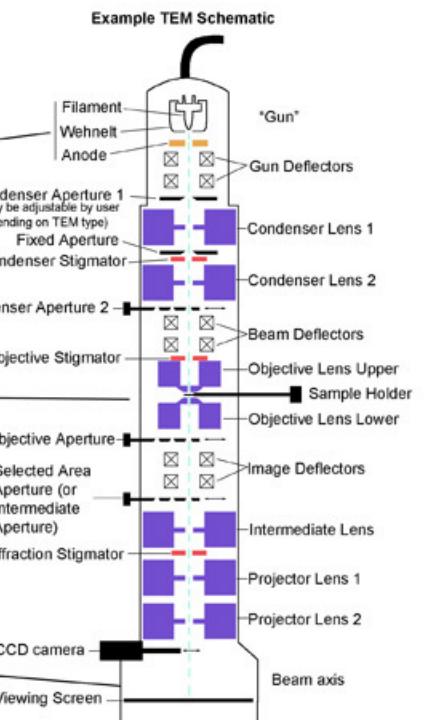


SEM



TEM

<http://www.ammrf.org.au/myscope/>



- Electron source
 - Creates monochromatic beam of fast electrons
 - $E_0=500\text{eV} - 1\text{MeV}$
- Electromagnetic lenses
 - Control and focus the electron beam
 - Probe forming (before sample interaction)
 - Image forming (after sample interaction)
 - Suffer from aberrations
- Detectors
 - Electron detectors
 - X-ray detectors
- Sample



Comparison of Electron Sources

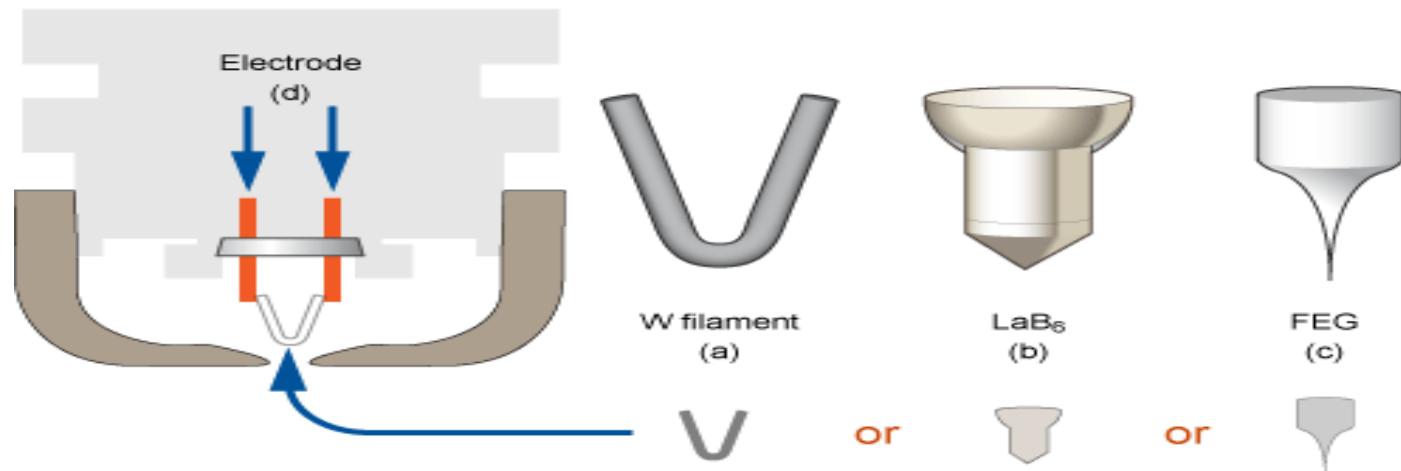


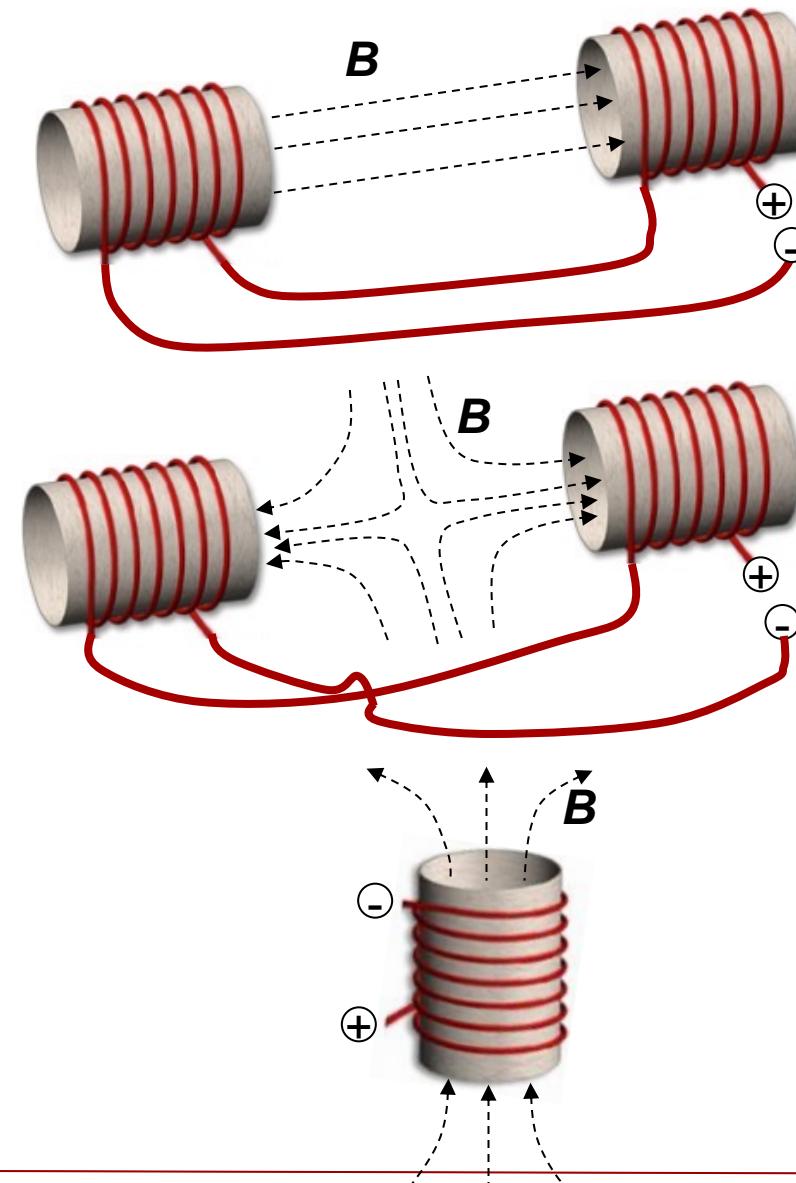
TABLE 5.1 Characteristics of the Principal Electron Sources

	Units	Tungsten	LaB ₆	Schottky FEG	Cold FEG
Work function, Φ	eV	4.5	2.4	3.0	4.5
Richardson's constant	A/m ² K ²	6×10^9	4×10^9		
Operating temperature	K	2700	1700	1700	300
Current density (at 100 kV)	A/m ²	5	10^2	10^5	10^6
Crossover size	nm	$> 10^5$	10^4	15	3
Brightness (at 100 kV)	A/m ² sr	10^{10}	5×10^{11}	5×10^{12}	10^{13}
Energy spread (at 100 kV)	eV	3	1.5	0.7	0.3
Emission current stability	%/hr	<1	<1	<1	5
Vacuum	Pa	10^{-2}	10^{-4}	10^{-8}	10^{-9}
Lifetime	hr	100	1000	>5000	>5000

Magnetic Electron Optical Elements in a TEM

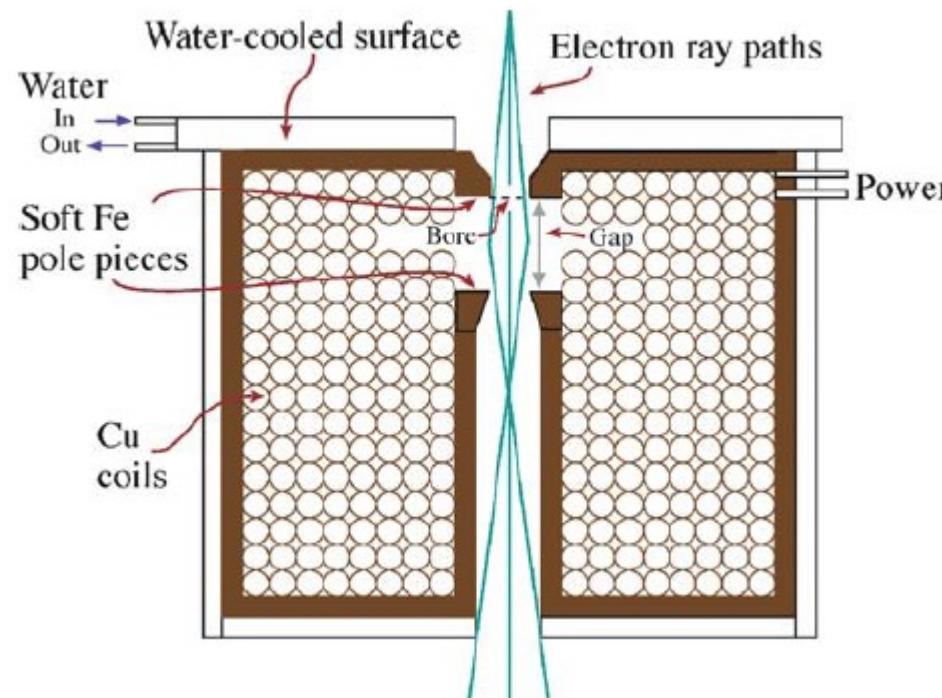
$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

- Dipole
 - Used for deflecting the beam
- Quadrupole
 - Used for compressing / stretching the beam in one direction
- Lens
- Modern electron optics also uses hexapoles, octupoles and higher order elements.

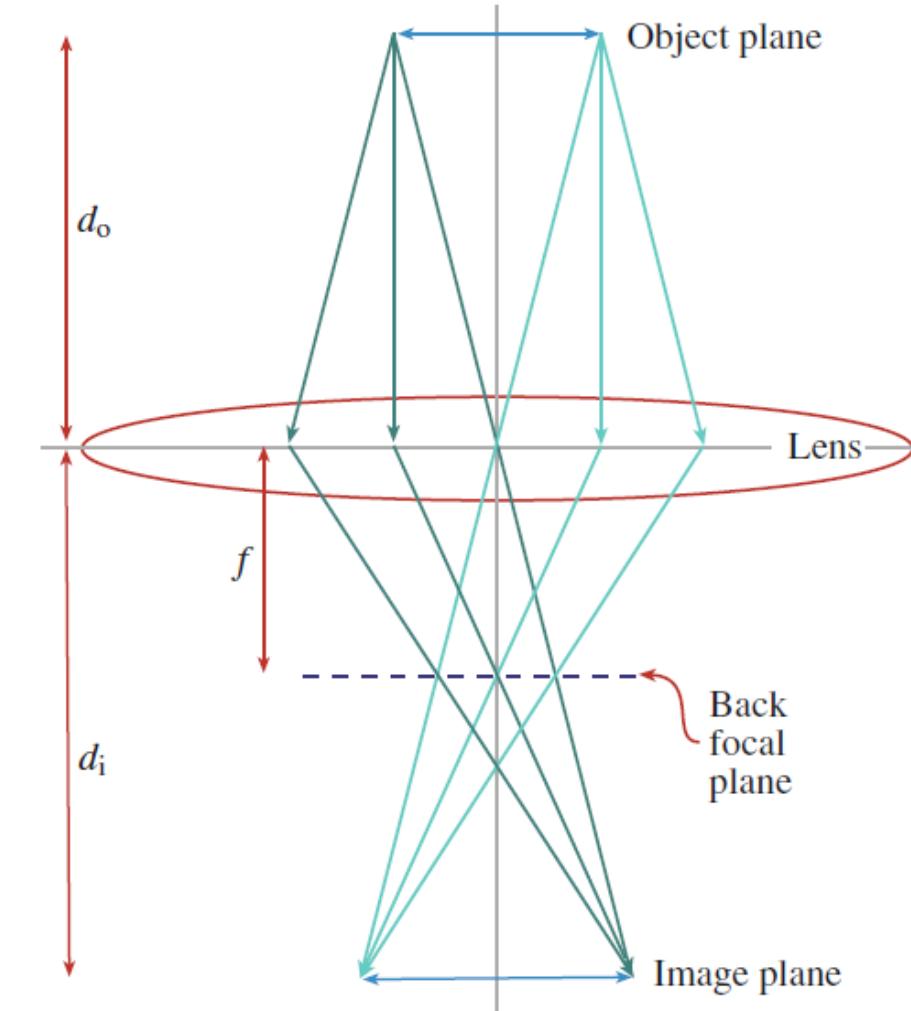


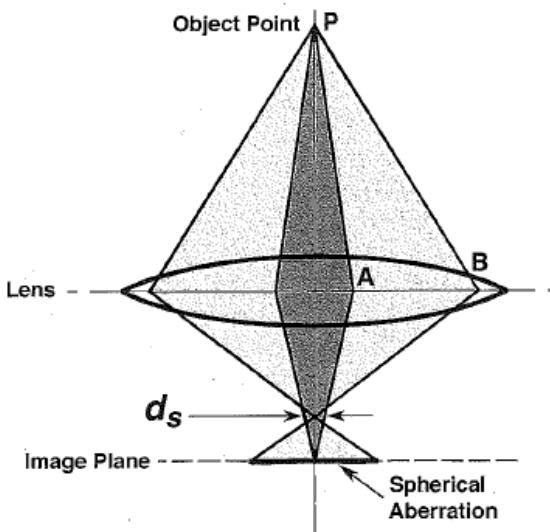
Electron Trajectories

Williams and Carter



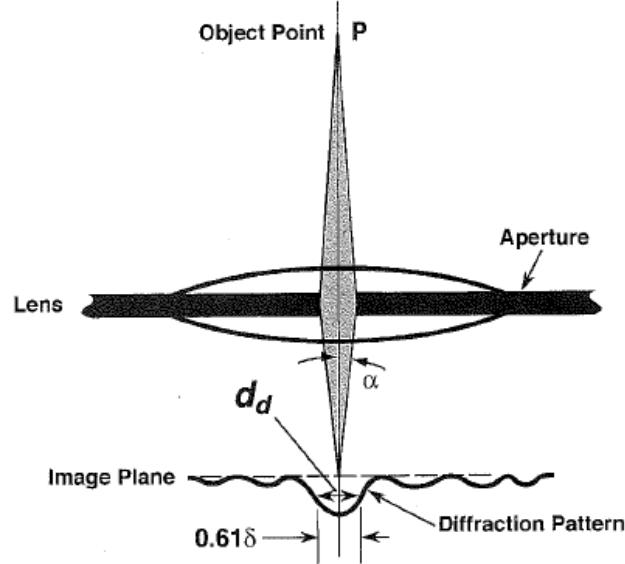
Field strength $|B| \approx 1$ Tesla
(typical value in a 200 kV TEM)





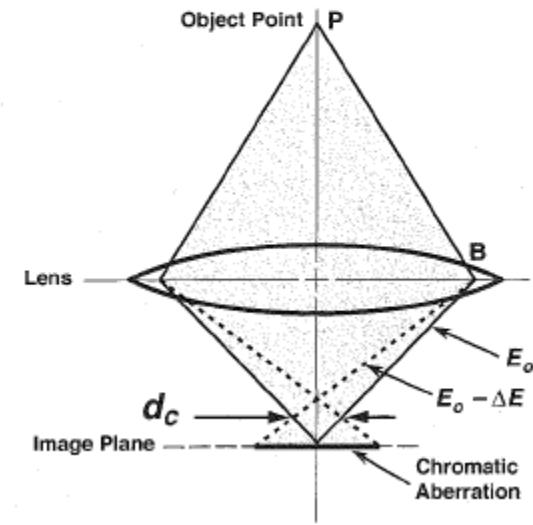
$$d_s = 0.5 C_s \alpha_p^3$$

Spherical aberrations



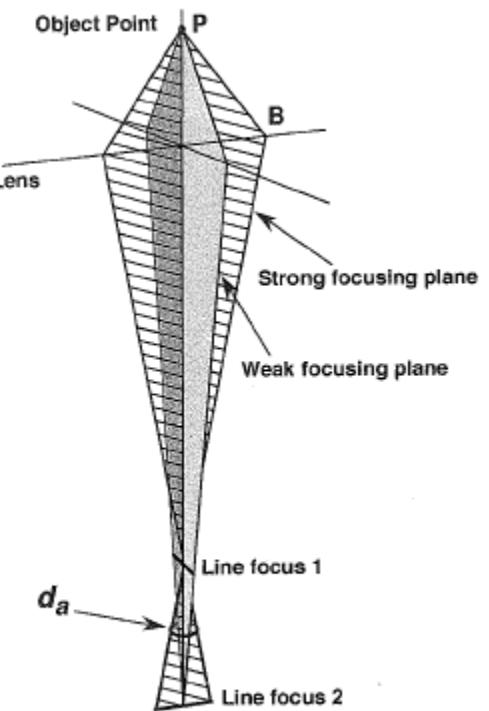
$$d_d = \frac{0.61\lambda}{\alpha}$$

Diffraction limit



$$d_c = C_c \frac{\Delta E}{E} \alpha$$

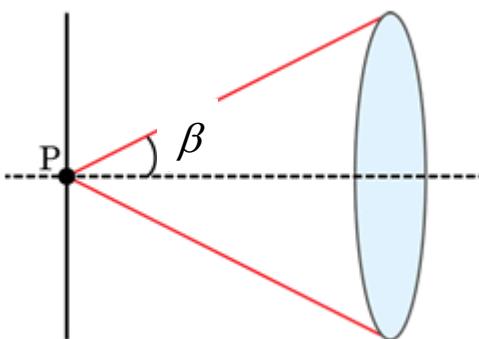
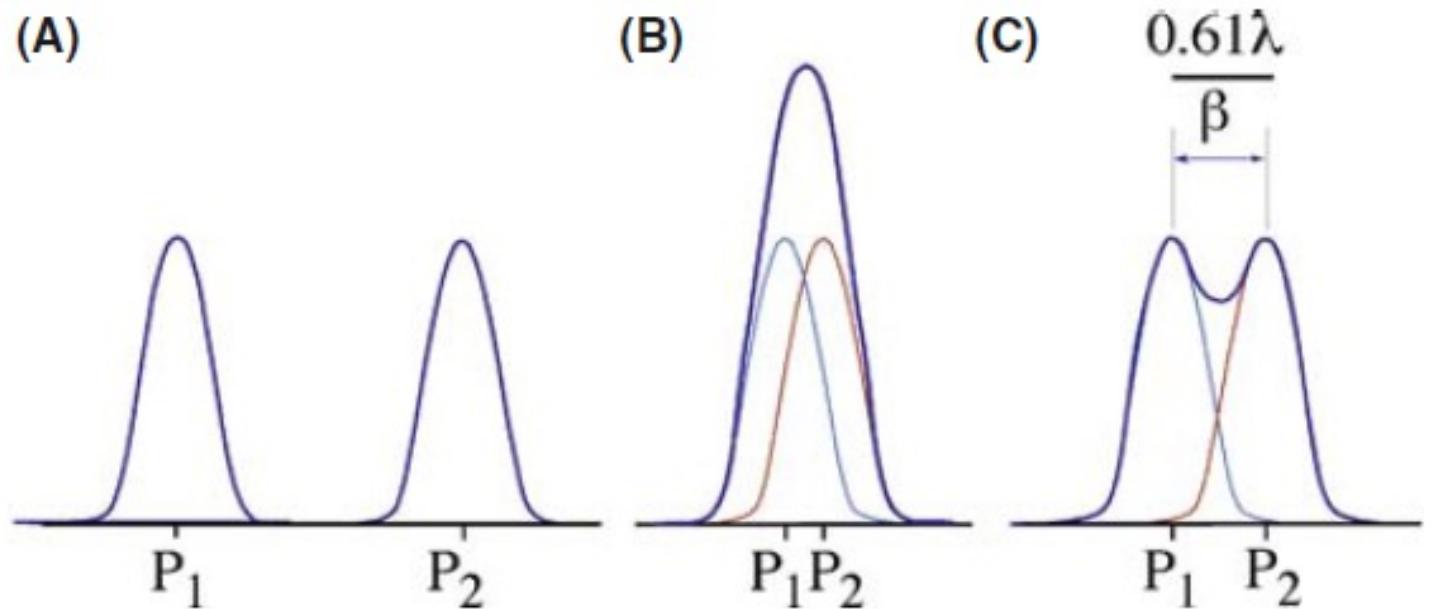
Chromatic aberrations



$d_a \sim 0$, when corrected

Astigmatism

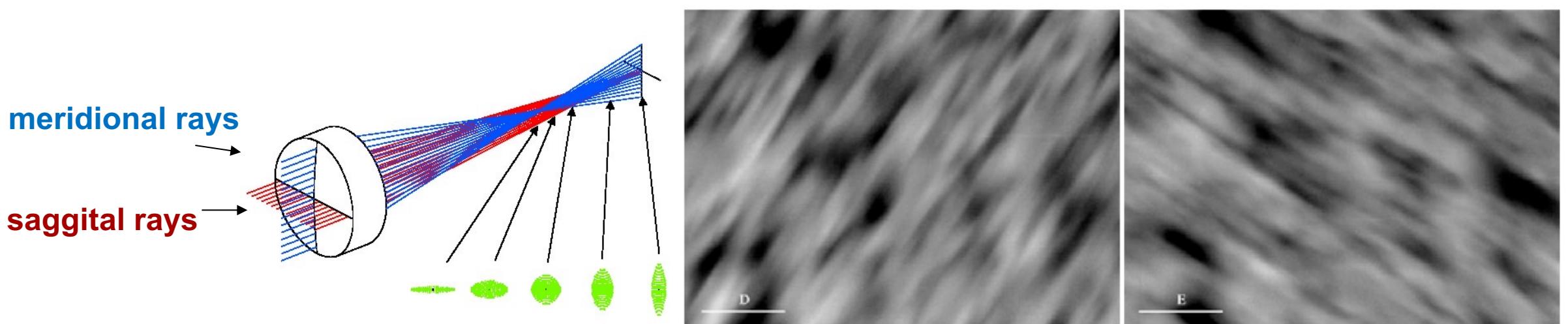
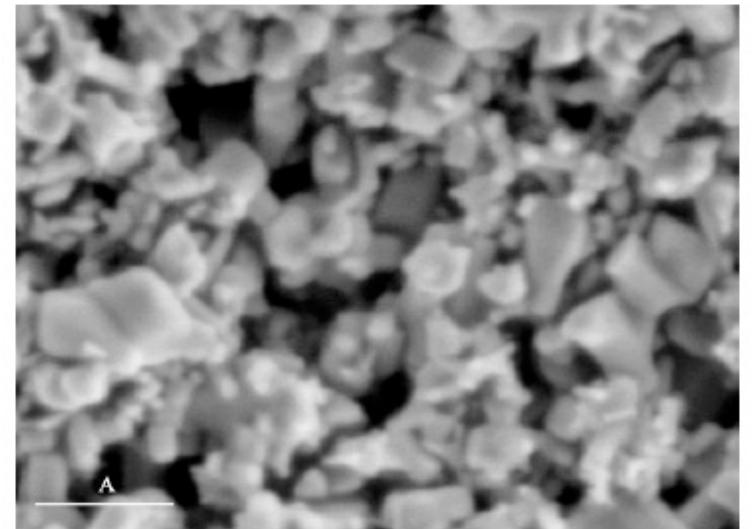
$$\delta = \frac{0.61\lambda}{\mu \sin \beta} \approx \frac{0.61\lambda}{\beta}$$

**Table 3.2** Correlation between Acceleration Voltage and Resolution

Acceleration voltage (kV)	Electron wavelength (nm)	TEM resolution (nm)
40	0.00601	0.56
60	0.00487	0.46
80	0.00418	0.39
100	0.00370	0.35
200	0.00251	0.24
500	0.00142	0.13

Astigmatism

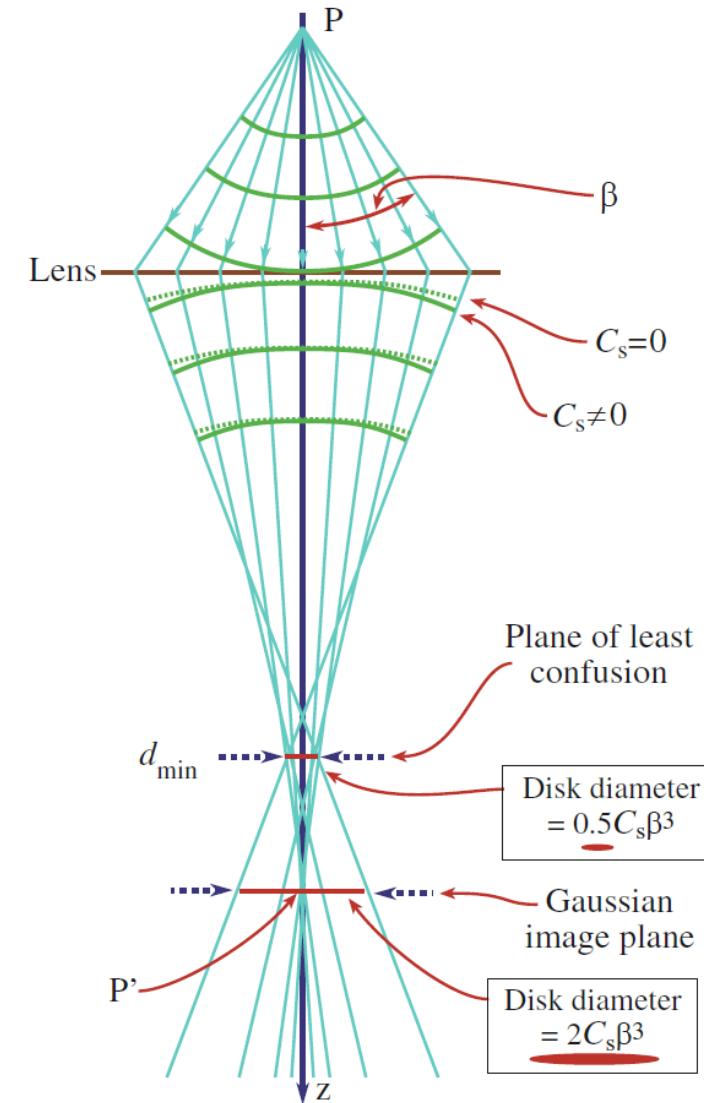
- Electrons passing at different directions away from the optical axis have different focal lengths.
- Defects arise because
 - the soft iron polepieces can't be machined perfectly cylindrical
 - Microstructural inhomogenities
 - Dirt on apertures
- Astigmatism is corrected using stigmators in the form of small octupoles introducing compensating fields



Spherical Aberration

- Caused by the lens field acting inhomogeneously on off-axis rays
- The further off axis the electron is, the more strongly it is bent back toward the axis
- As a result, a point object is imaged as a disc
- Ultimately the limiting factor of modern (non- C_s corrected) TEMs

$$r_{\text{sph}} = C_s \beta^3 \quad (C_s \sim 1-3 \text{ mm})$$





Wide Field Planetary Camera 1

Before service mission 1

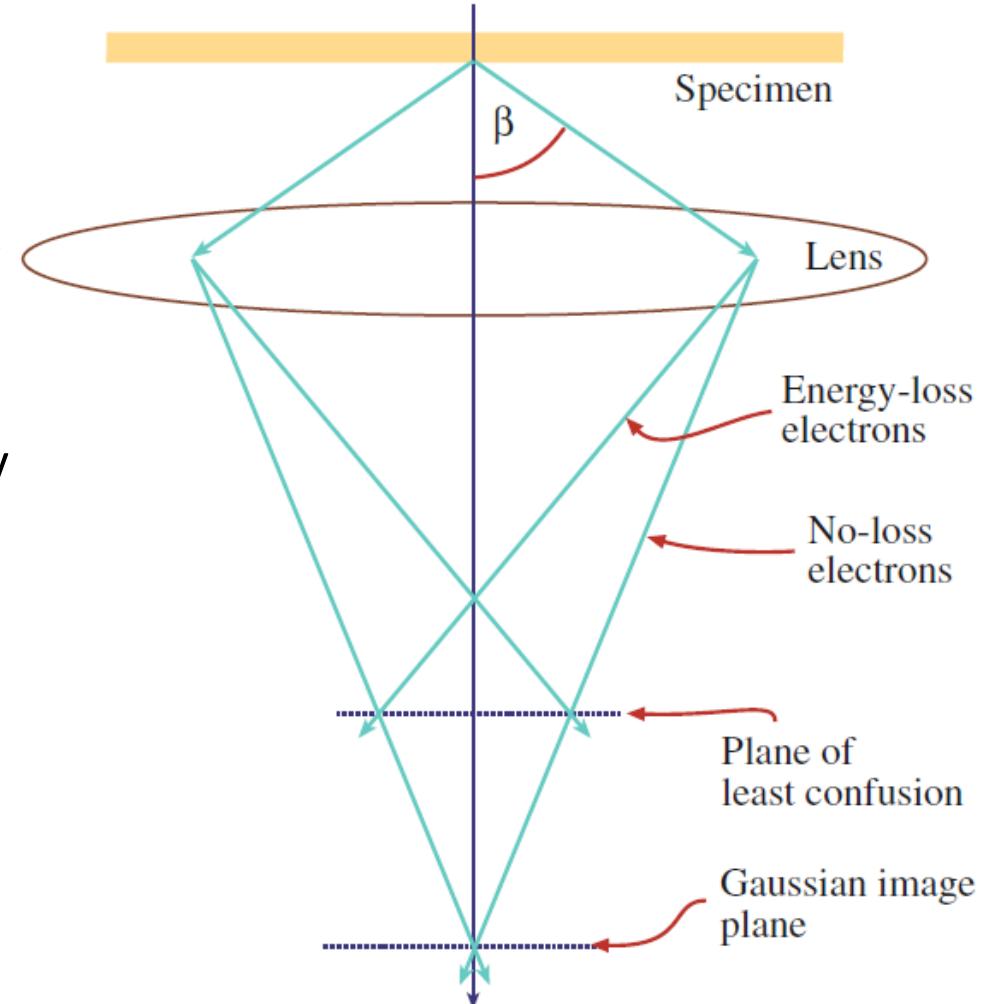
Wide Field Planetary Camera 2

After service mission 1

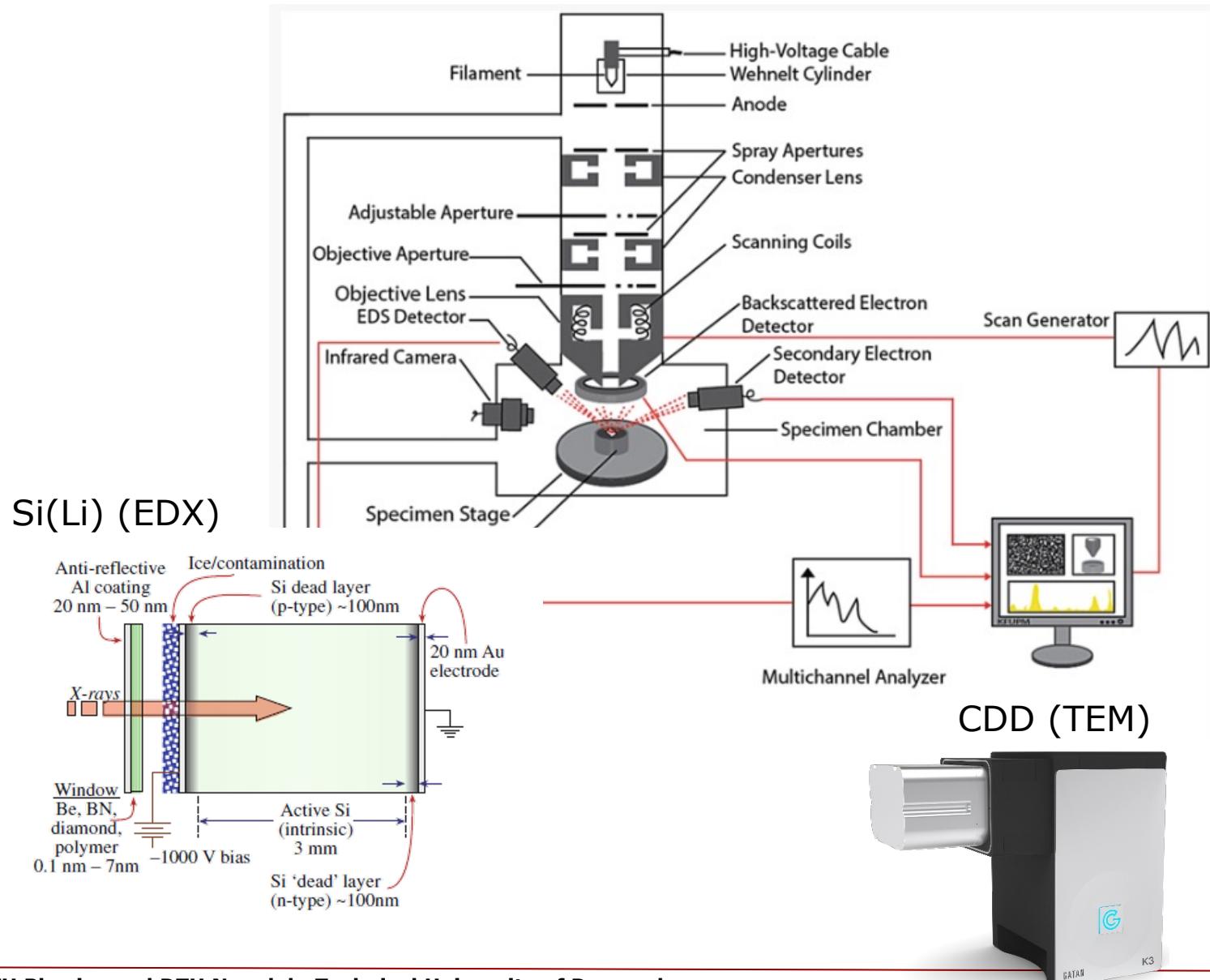
Chromatic aberration

- The focusing power of the lens depends on the energy of the electrons
- Electron travelling with higher energy are focused further away from the lens than slower electrons
- Electrons emerging from the source are not uniform in energy
- As the electron traverse the specimen, they loss energy

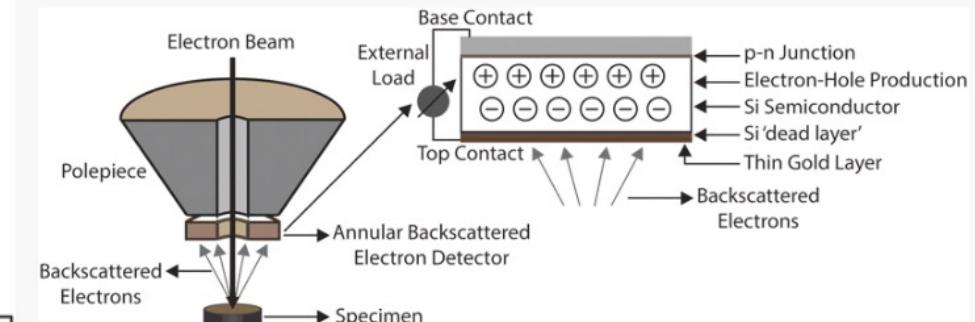
$$r_{\text{chr}} = C_c \Delta E / E \beta \quad (C_c \sim 1-2 \text{ mm})$$



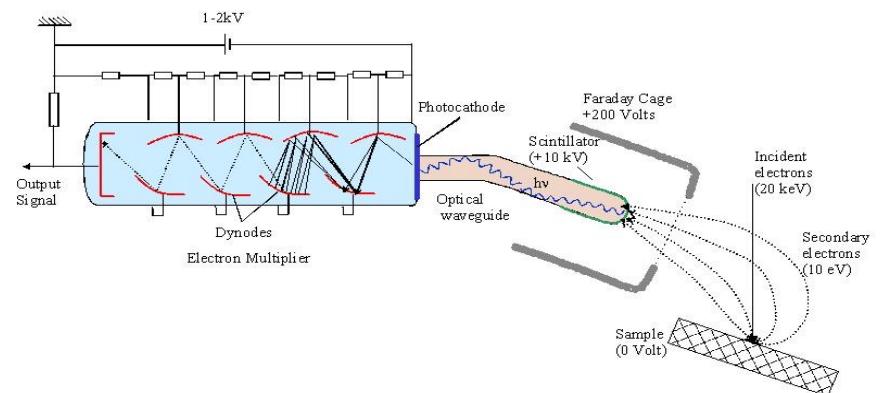
Ul-Hamid A. (2018) Components of the SEM. In: A Beginners' Guide to Scanning Electron Microscopy. Springer, Cham



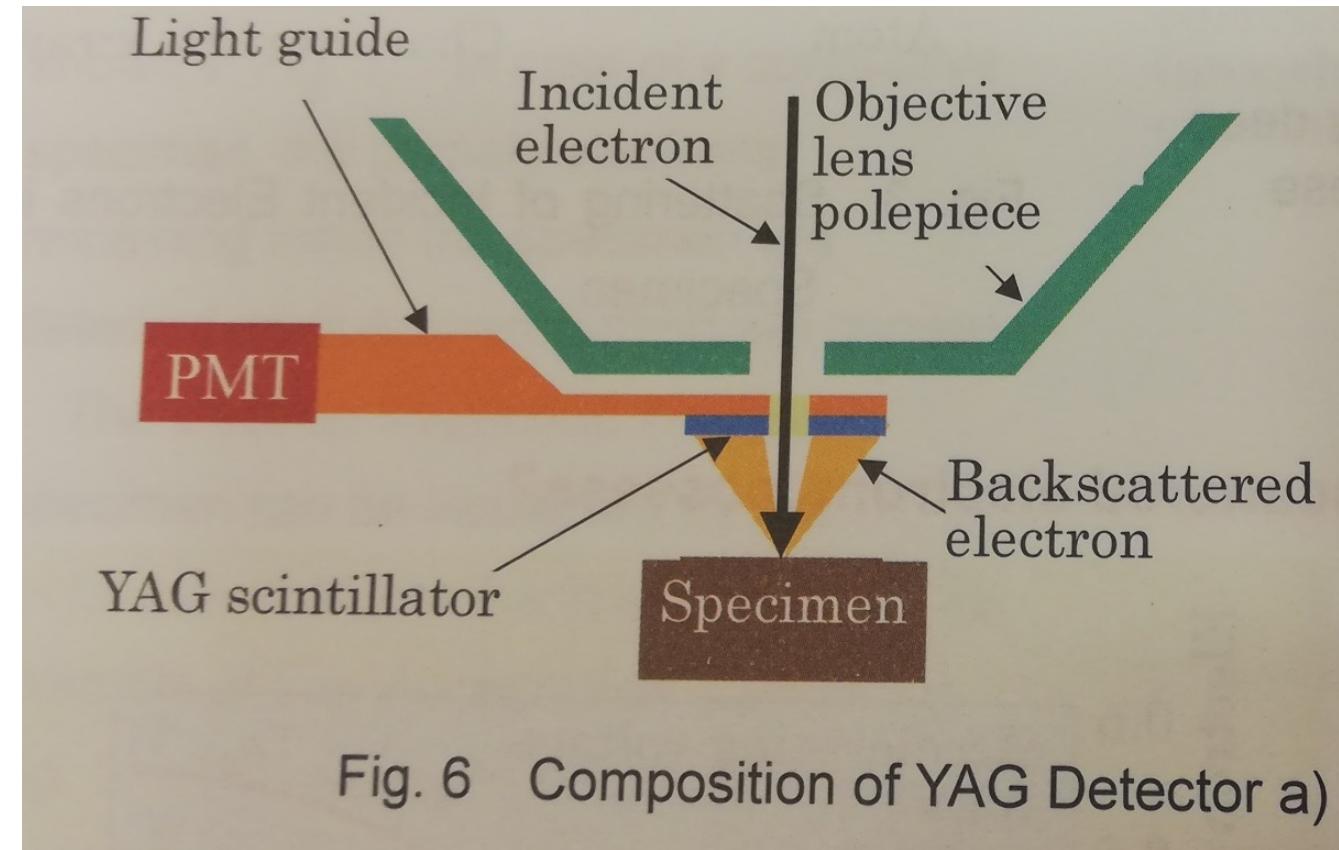
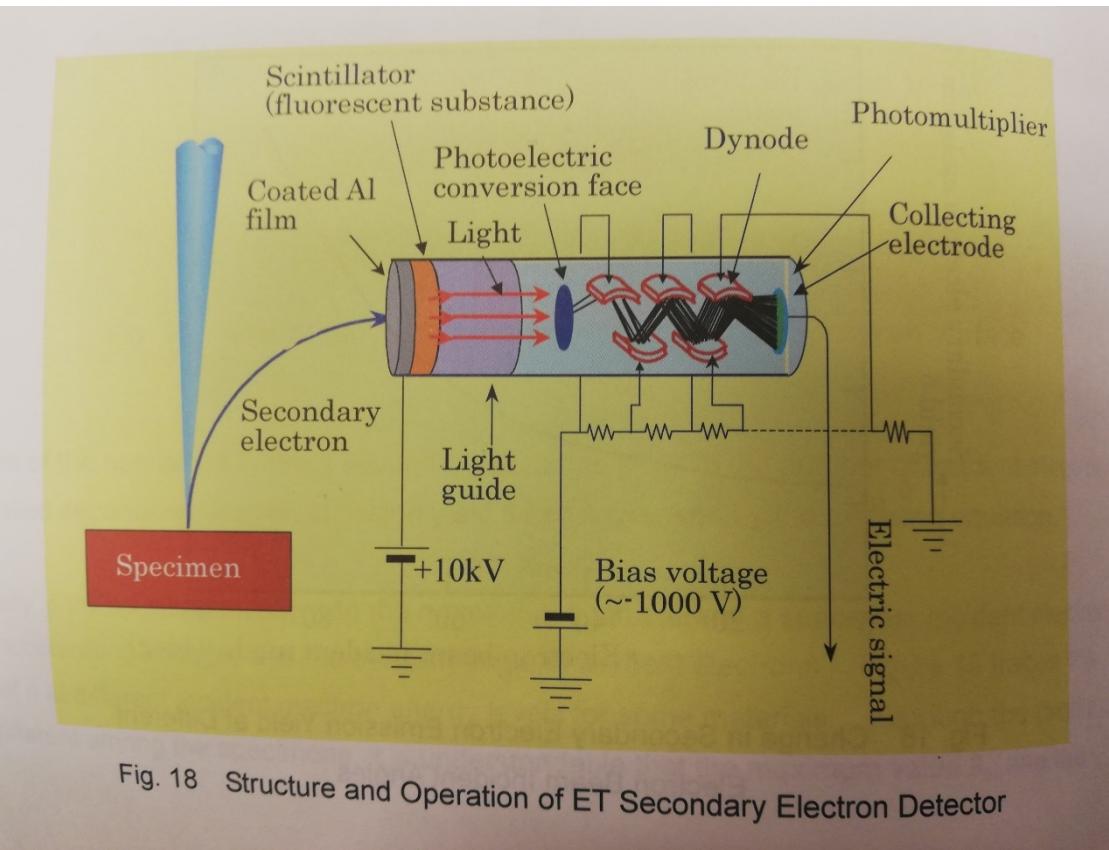
PN-junction (BSE)



ETD (SE and BSE)



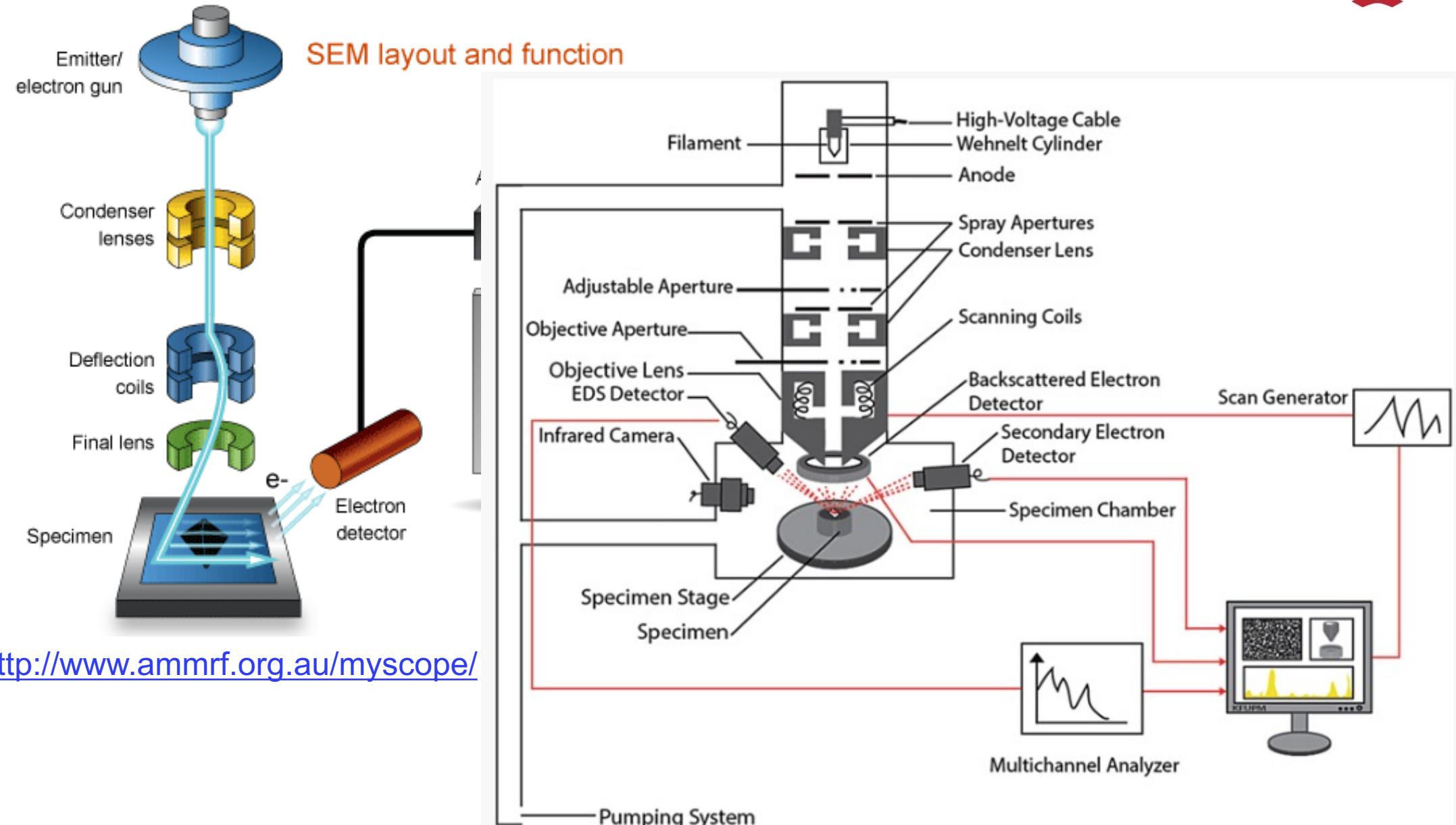
Detectors on the Nanoteket SEMs



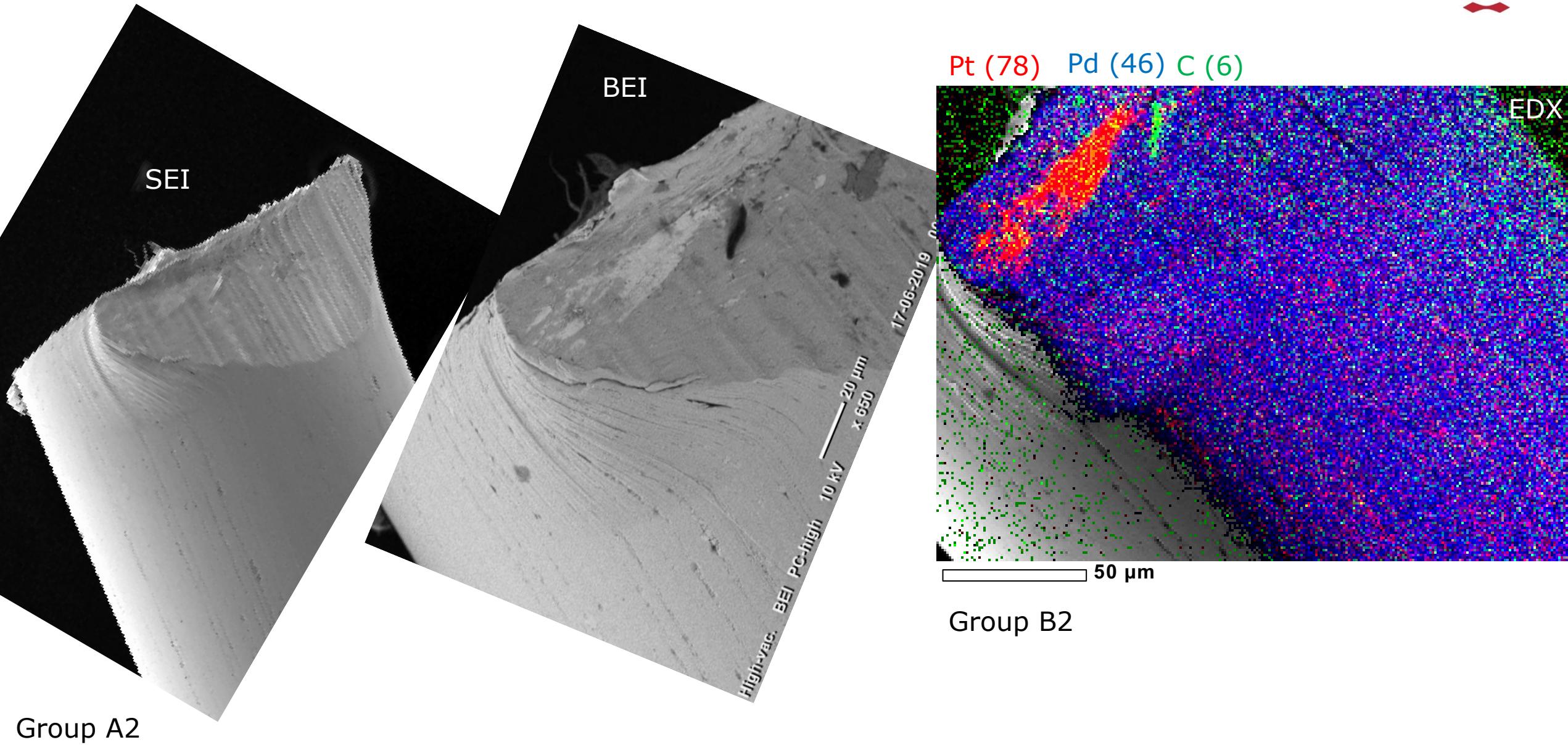
- Picometer wavelength λ
- Abberations limit our resolution
- TEM: approx. $0.5\text{\AA}=0.05\text{nm}$
- SEM: approx. 1nm
 - Nanotekets teaching SEMs: approx. 50nm

Scanning electron microscopy

Introduction to



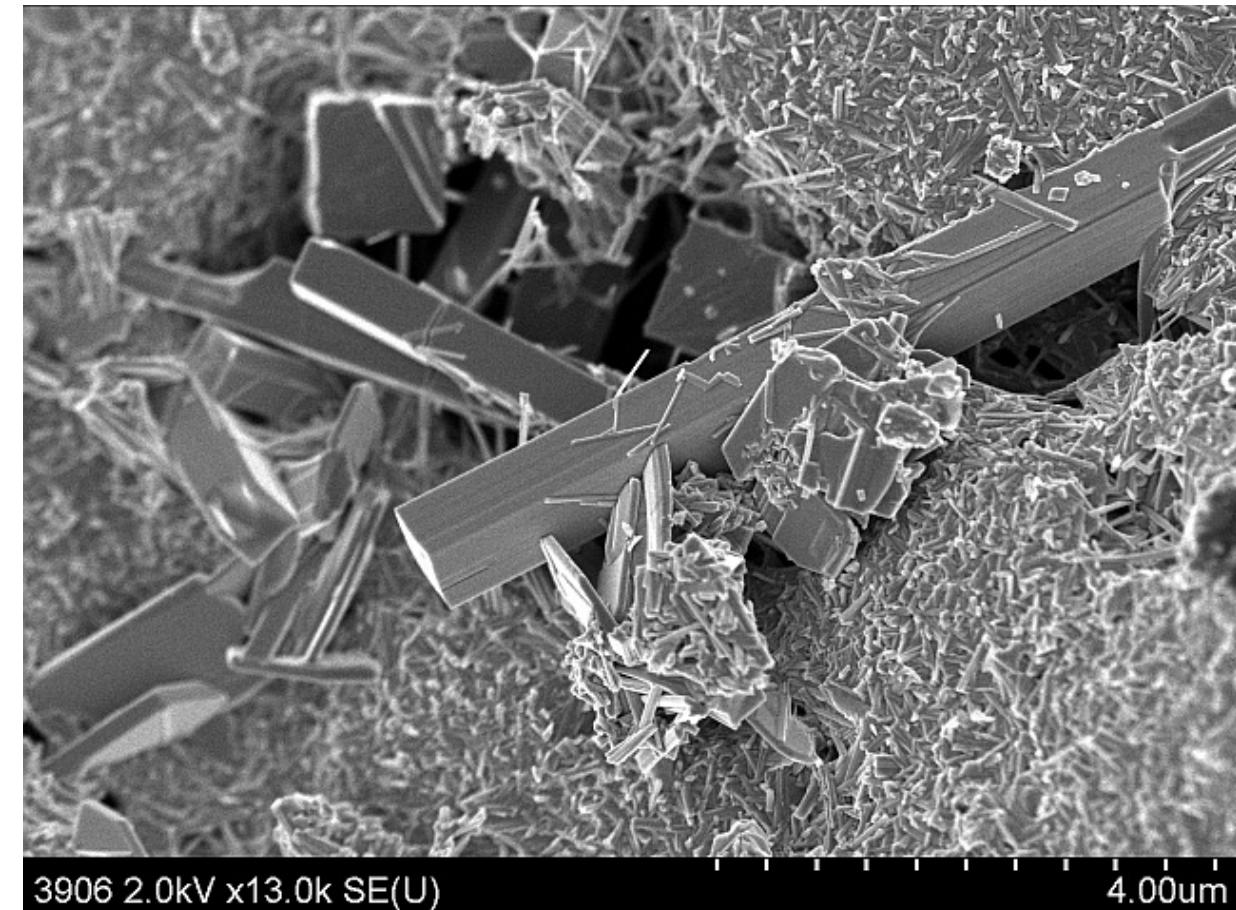
Scanning Electron Microscopy – MODES of operation: SEI, BEI, and EDX



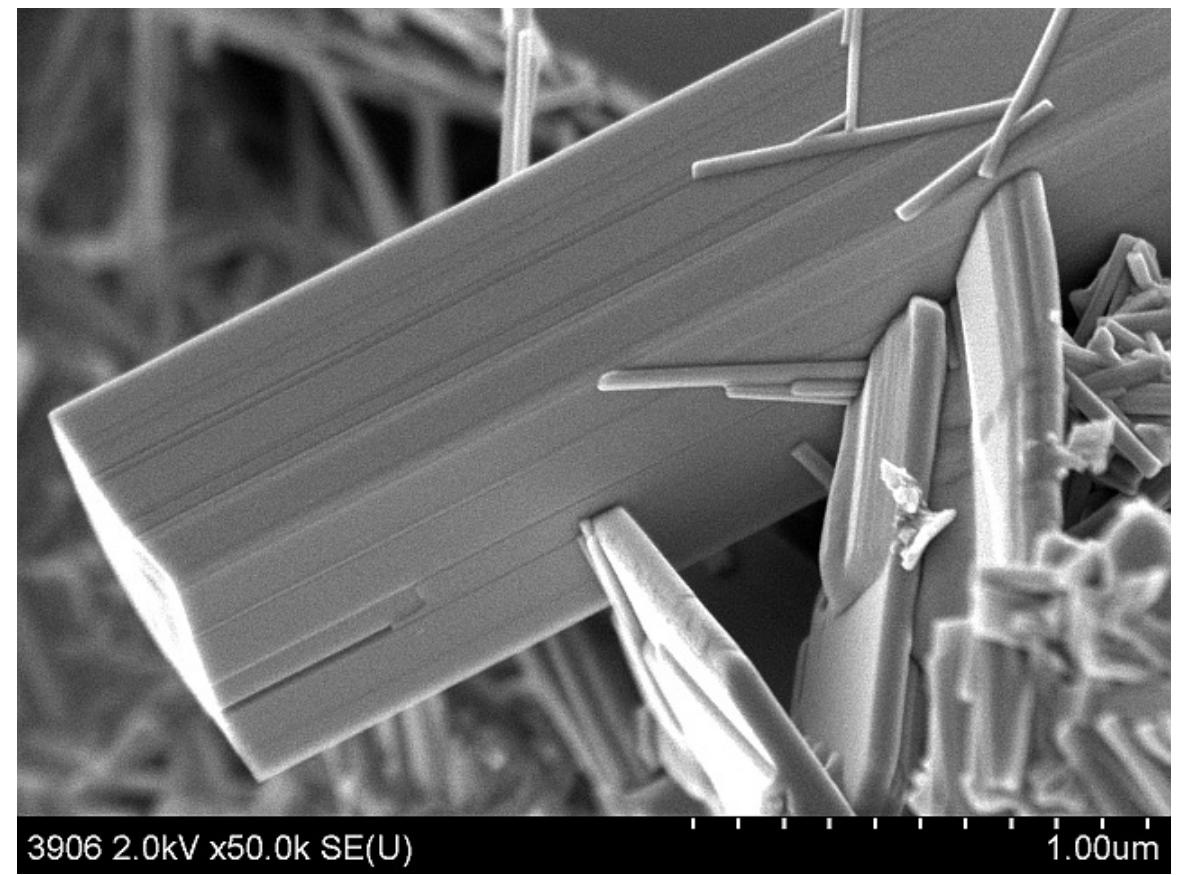
Group A2

Group B2

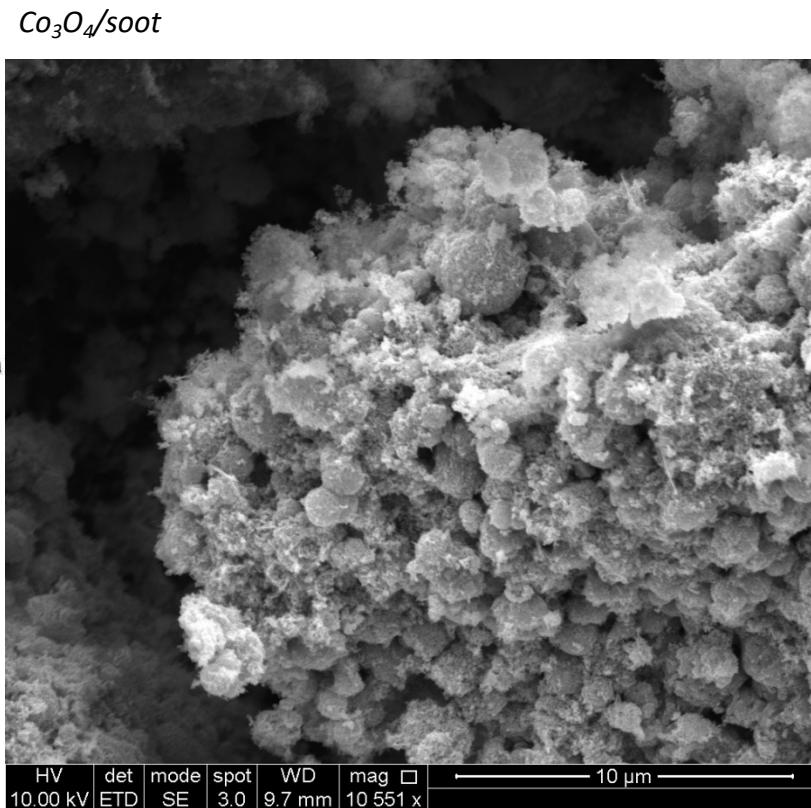
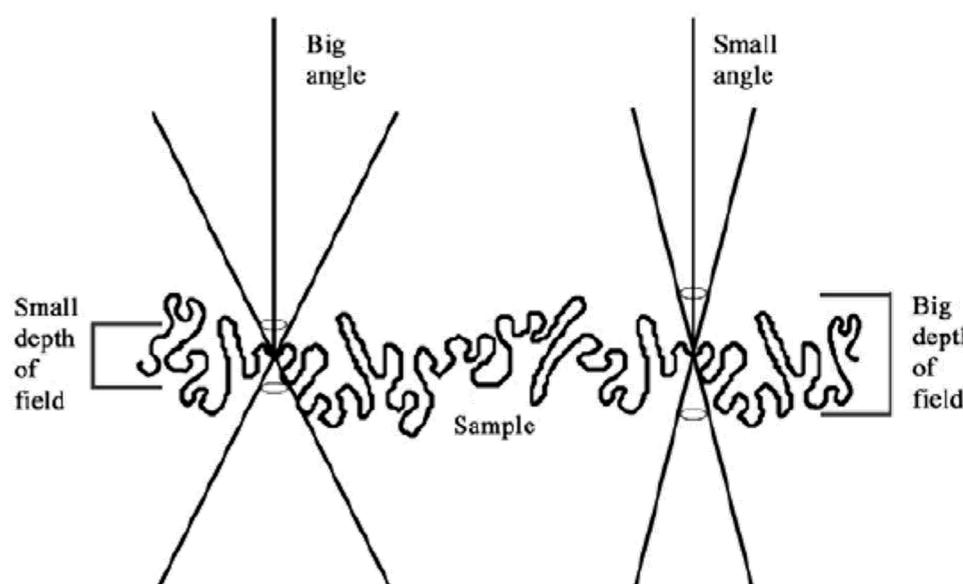
Images in electron microscopy



SEM



- Small convergence angle gives large depth of field (compared to the lateral dimensions) (10-20 mrad)

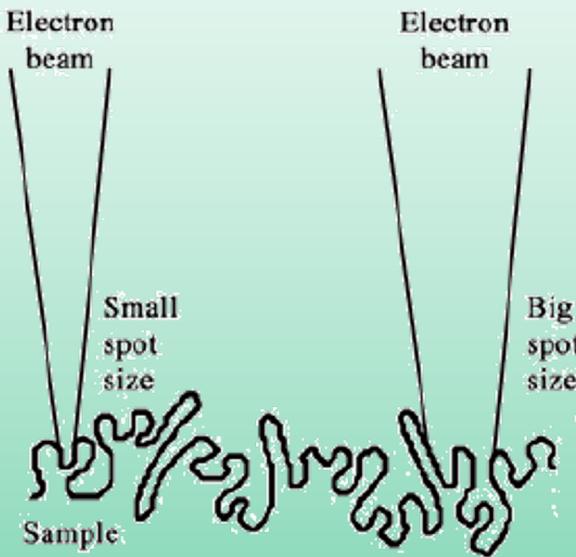


<http://131.229.88.77/microscopy/semvar.html>

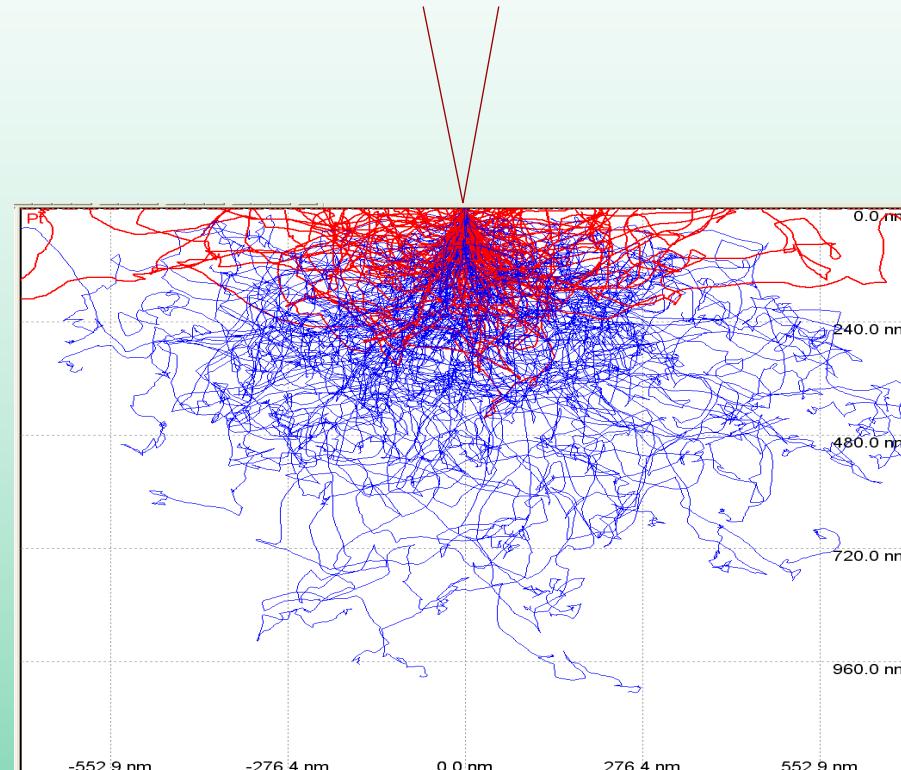
What determines the resolution of a Scanning electron microscope?



- The resolution in an SEM is dependent on the **probe size** and the **interaction volume**

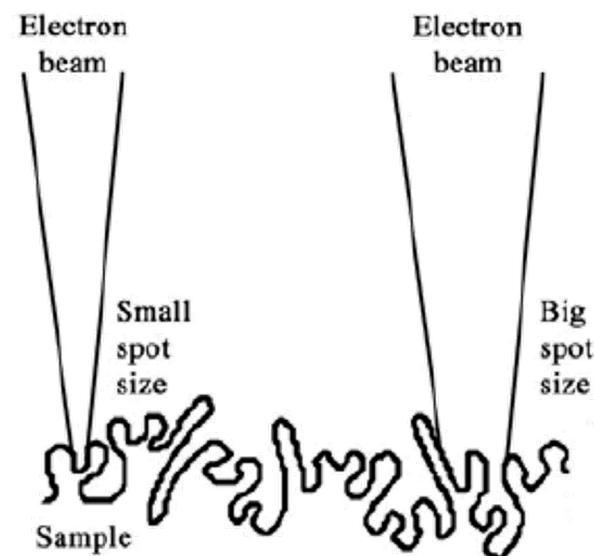


<http://131.229.88.77/microscopy/semvar.html>



Pt bulk
30keV electrons (10nm diameter)

- Spherical and Chromatic aberrations influence the minimum probe size
- Astigmatism influence the probe shape and size
- Working distance (convergence angle)



<http://131.229.88.77/microscopy/semvar.html>

Interaction volume –What happens to the incident electron beam

Science of microscopy
by Hawkes and Spence

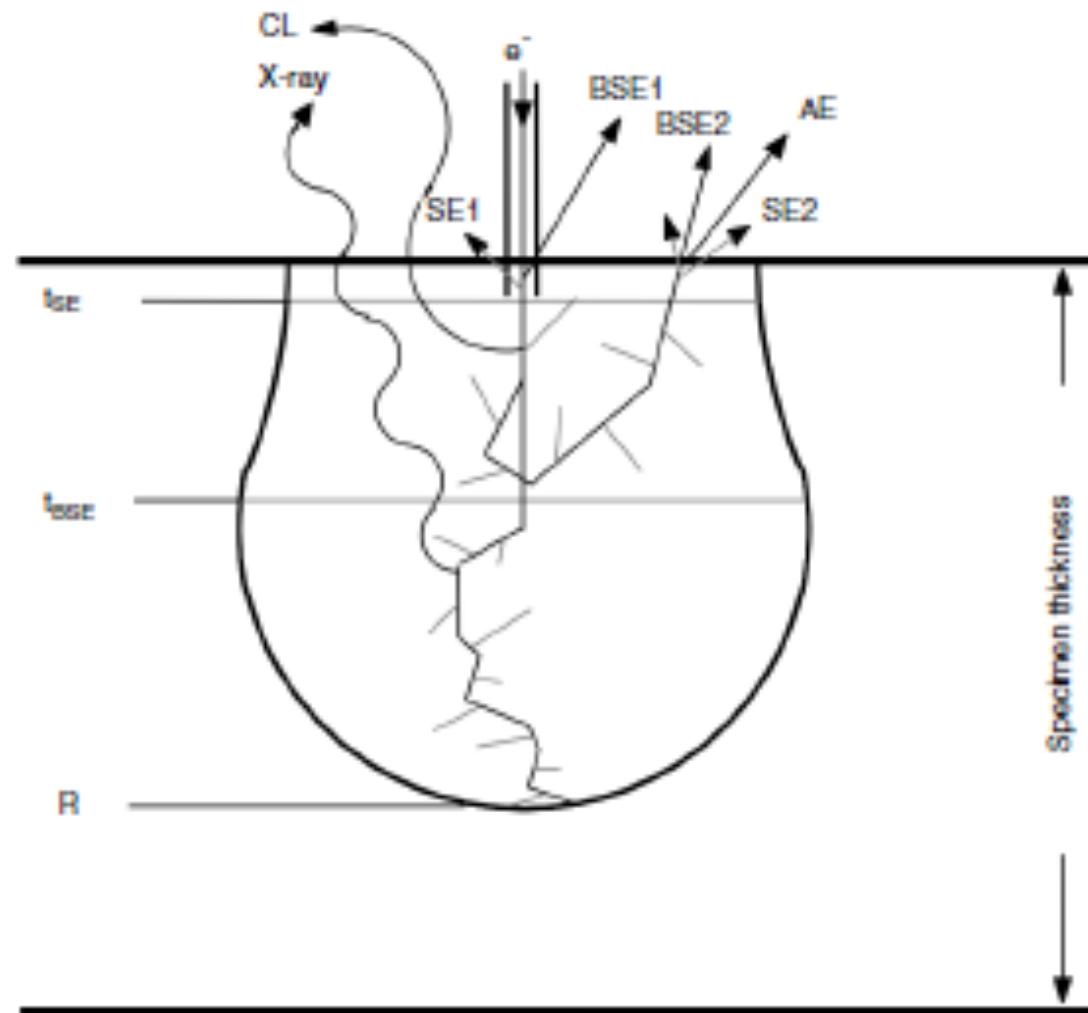
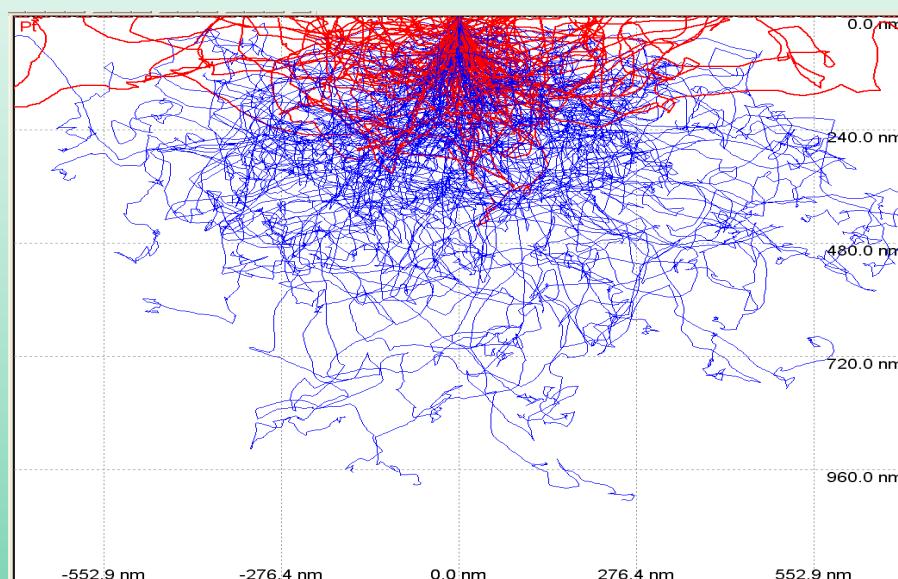


Figure 3–14. Schematic illustration of the generation of secondary electrons SE1 and SE2, backscattered electrons BSE1 and BSE2, Auger electrons AE, cathodoluminescence CL, and X-rays in a bulky specimen. t_{SE} and t_{BSE} indicate the escape depth for SE and BSE, respectively. R is the electron range.

Interaction volume –What happens to the incident electron beam

- Both elastic and inelastic scattering occurs, but in bulk sample mostly inelastic.
- The electrons scatter in all directions and several times.
- Some electrons escape the specimen again – those and secondary electrons are used as imaging signal



Pt bulk
30keV electrons (10nm diameter)

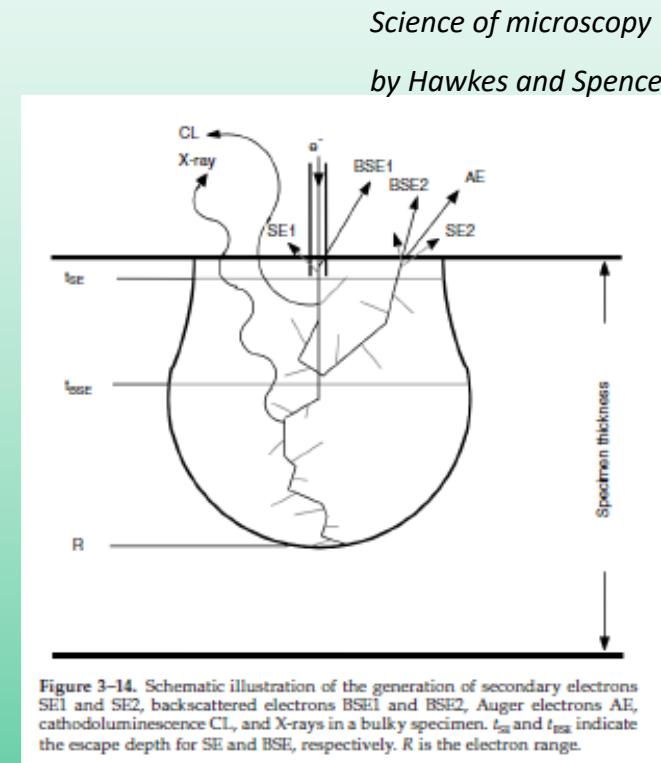
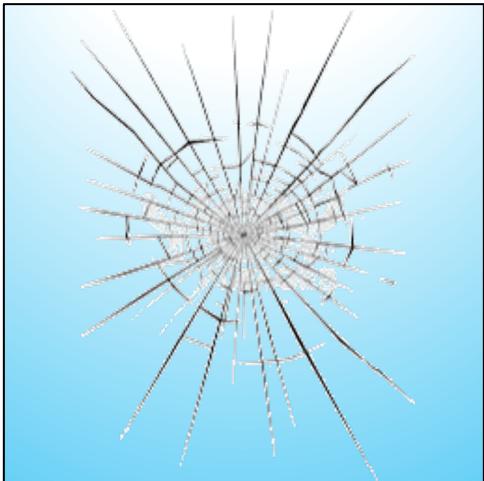


Figure 3-14. Schematic illustration of the generation of secondary electrons SE₁ and SE₂, backscattered electrons BSE₁ and BSE₂, Auger electrons AE, cathodoluminescence CL, and X-rays in a bulky specimen. t_{se} and t_{bse} indicate the escape depth for SE and BSE, respectively. R is the electron range.

What will happen to the interaction volume if I increase the primary electron energy?

What will happen to the interaction volume if I change specimen to a heavier element (e.g. C -> Au)?

Scattering cross section analog

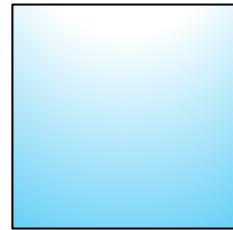


Window on $1 \times 1 \text{ m}^2$

Breaks 1 out of 4 times when hit with a small rock

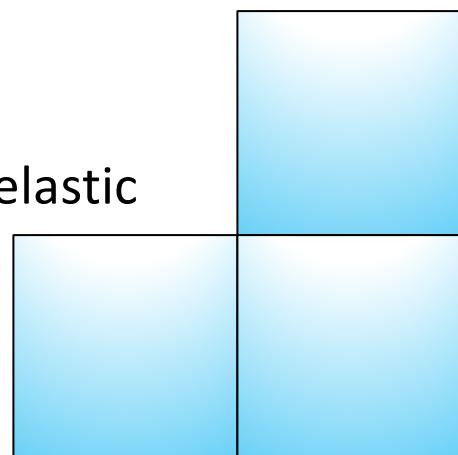


$\sigma_{\text{inelastic}}$



0.25 m^2

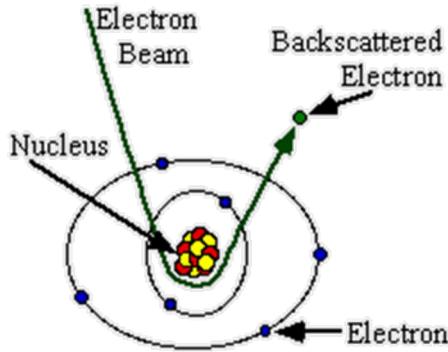
σ_{elastic}



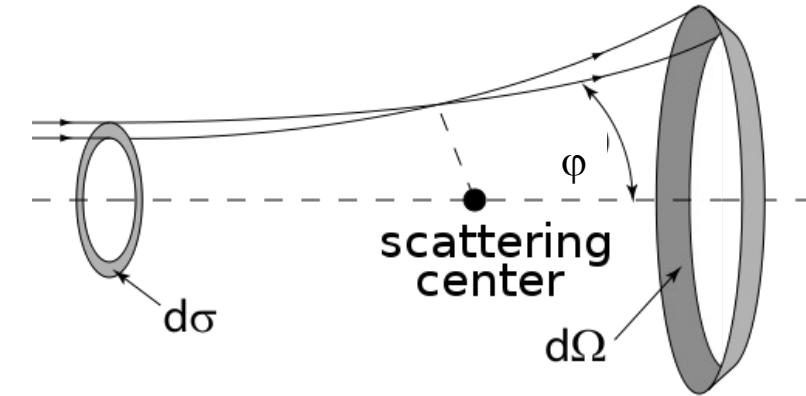
0.75 m^2

Scattering cross section

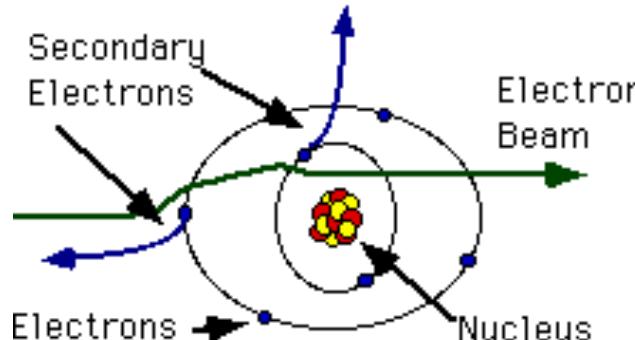
- Rutherford scattering (~BSE)



$$\frac{d\sigma}{d\Omega} = \frac{e^4 Z^2}{16(4\pi\epsilon_0 E)^2 \sin^4 \frac{\theta}{2}}$$



- Inelastic scattering (~SE and EDX)



$$\frac{d\sigma_{in}}{dE_L} = \frac{4\pi e^4}{(4\pi\epsilon_0)^2 E E_L^2}$$

Interaction volume

Science of microscopy
by Hawkes and Spence

Table 3–3. Characteristic values for R , σ_{el} , σ_{in} , Λ_{el} , and Λ_{in} .^a

Element	Parameter	$E_0 = 1\text{ keV}$	$E_0 = 5\text{ keV}$	$E_0 = 10\text{ keV}$	$E_0 = 30\text{ keV}$
Carbon $Z = 6$	$\sigma_{el} (\text{nm}^2) \times 10^2$	0.65	0.11	0.055	0.018
	$\sigma_{in} (\text{nm}^2) \times 10^2$	1.95	0.33	0.165	0.054
	$\Lambda_{el} (\text{nm})$	1.5	9.0	18	55
	$\Lambda_{in} (\text{nm})$	0.5	2.0	6	18
Copper $Z = 29$	$R (\mu\text{m})$	0.033	0.49	1.55	9.7
	$\sigma_{el} (\text{nm}^2) \times 10^{2s}$	1.84	0.64	0.37	0.15
	$\sigma_{in} (\text{nm}^2) \times 10^2$	1.10	0.38	0.22	0.09
	$\Lambda_{el} (\text{nm})$	0.64	1.8	3.2	7.8
	$\Lambda_{in} (\text{nm})$	1.07	3.0	5.3	13
Gold $Z = 79$	$R (\mu\text{m})$	0.007	0.11	0.35	2.16
	$\sigma_{el} (\text{nm}^2) \times 10^2$	3.93	1.6	1.05	0.52
	$\sigma_{in} (\text{nm}^2) \times 10^2$	0.79	0.32	0.21	0.10
	$\Lambda_{el} (\text{nm})$	0.43	1.0	1.6	3.3
	$\Lambda_{in} (\text{nm})$	2.15	5.0	8.0	16.5
	$R (\mu\text{m})$	0.003	0.05	0.17	1.0

^a Values are listed for four different electron energies between 1 and 30 keV and three elements having a low (C), medium (Cu), and high atomic number (Au), respectively. For calculation, the following densities were used: C, $\rho = 2\text{ g cm}^{-3}$; Cu, $\rho = 8.9\text{ g cm}^{-3}$; Au, $\rho = 19.3\text{ g cm}^{-3}$.

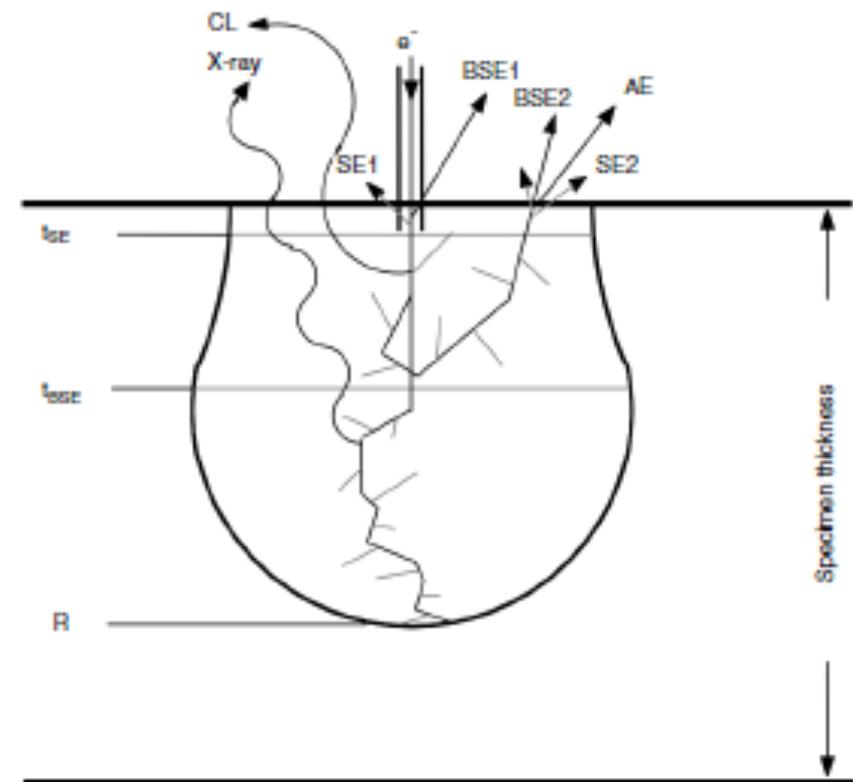


Figure 3–14. Schematic illustration of the generation of secondary electrons SE1 and SE2, backscattered electrons BSE1 and BSE2, Auger electrons AE, cathodoluminescence CL, and X-rays in a bulky specimen. t_{SE} and t_{BSE} indicate the escape depth for SE and BSE, respectively. R is the electron range.

What will happen to the interaction volume if I increase
the primary electron energy?

The interaction volume will increase

What will happen to the interaction volume if I change
specimen to a heavier element (e.g. C -> Au)?

The interaction volume will decrease

Electrons emitted from the probed sample

Science of Microscopy

by Hawkes and Spence

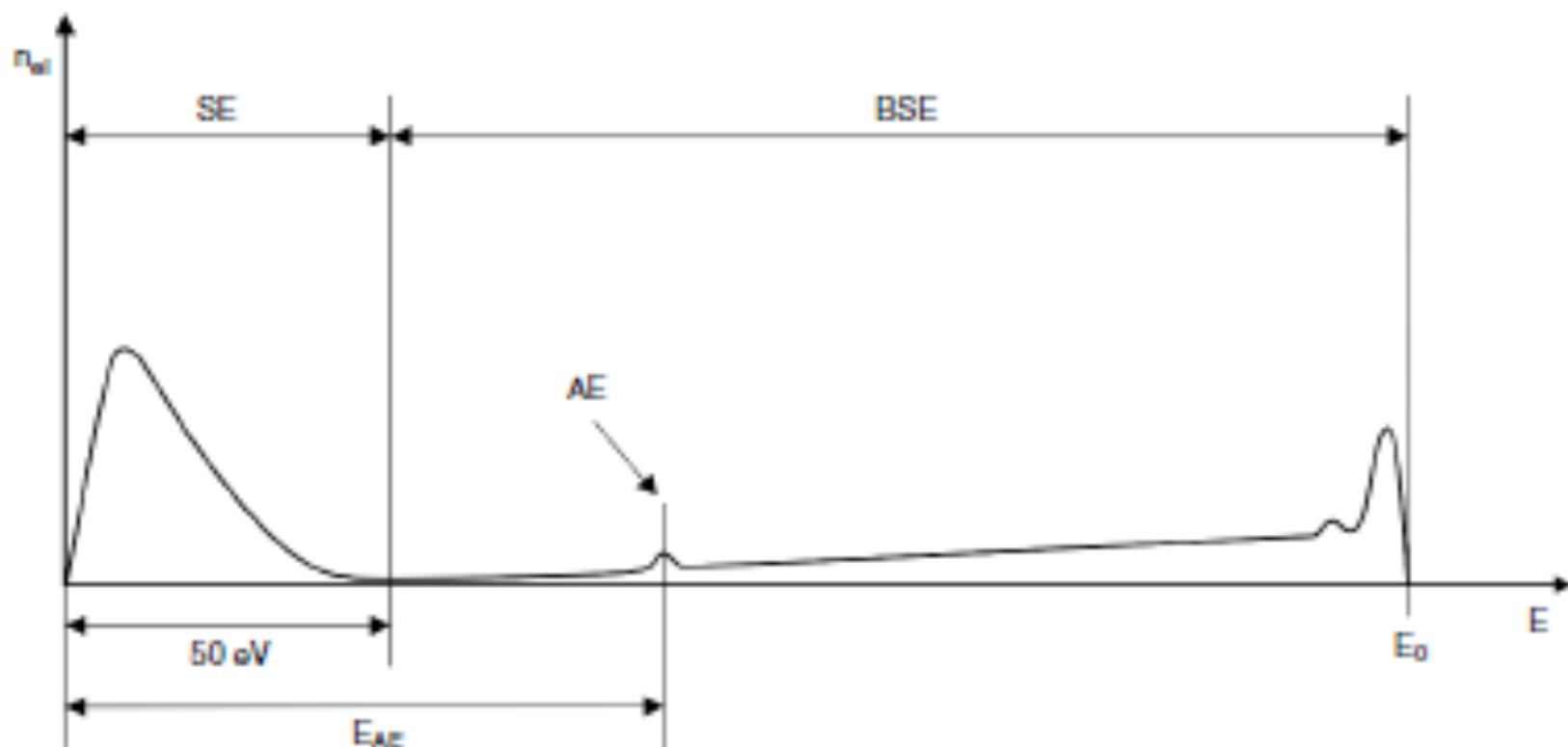


Figure 3-12. Schematic energy distribution of electrons emitted from a surface as a result of its bombardment with fast electrons with energy E_0 . AE, Auger electrons; BSE, backscattered electrons; SE, secondary electrons; E_{AE} , energy of AE; n_{el} , energy-dependent number of emitted electrons.

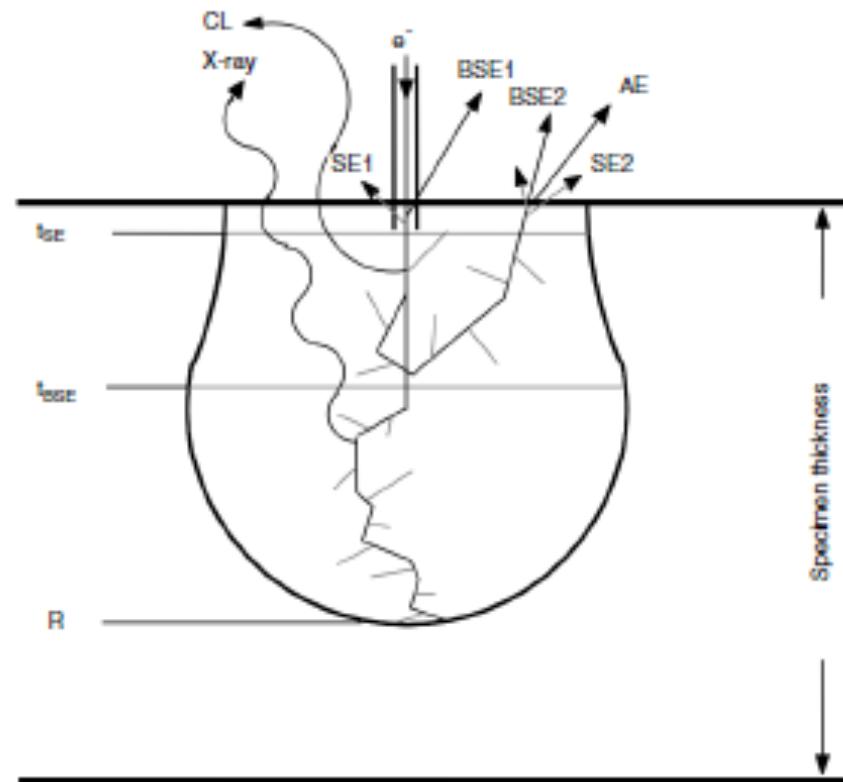
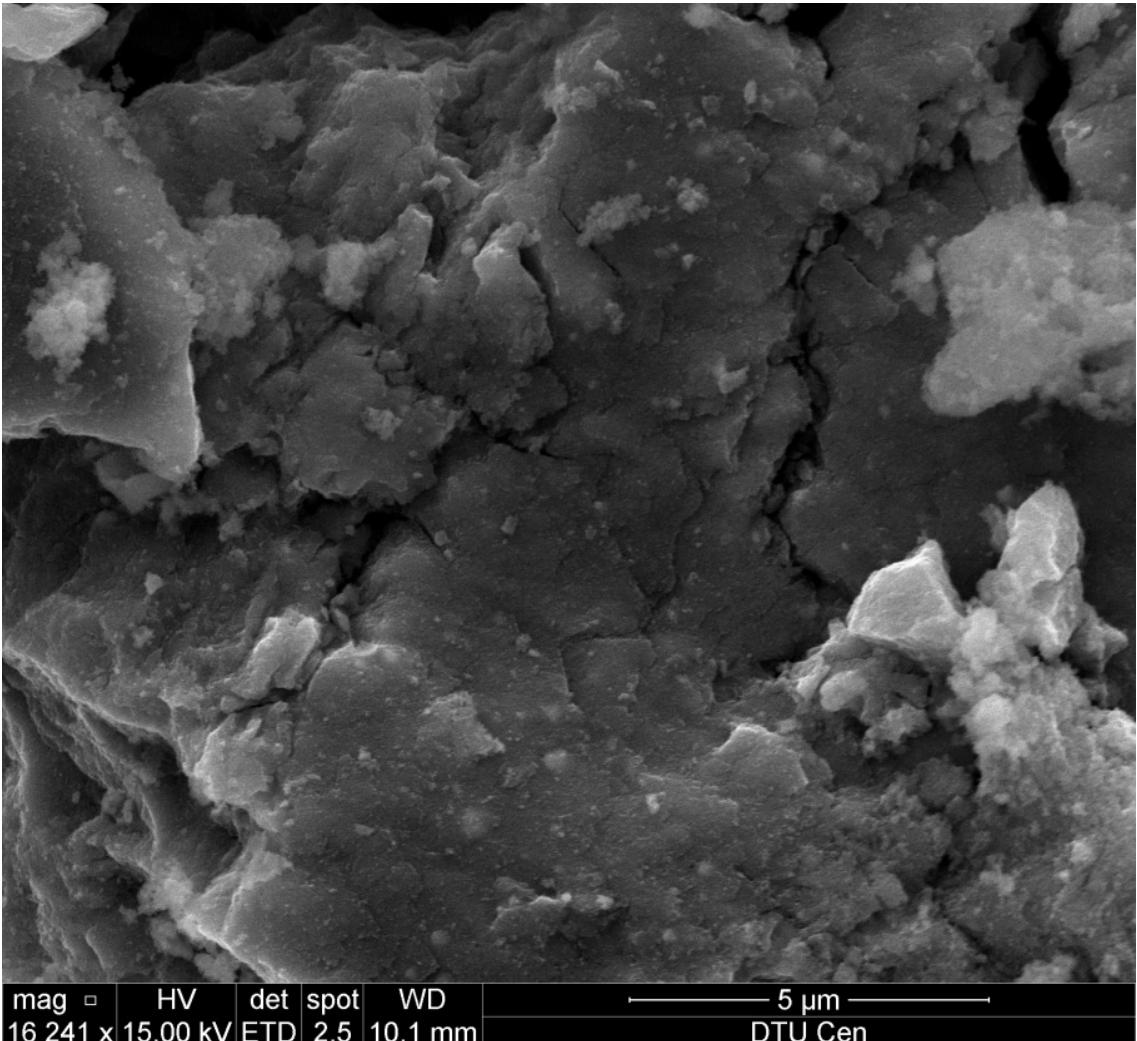
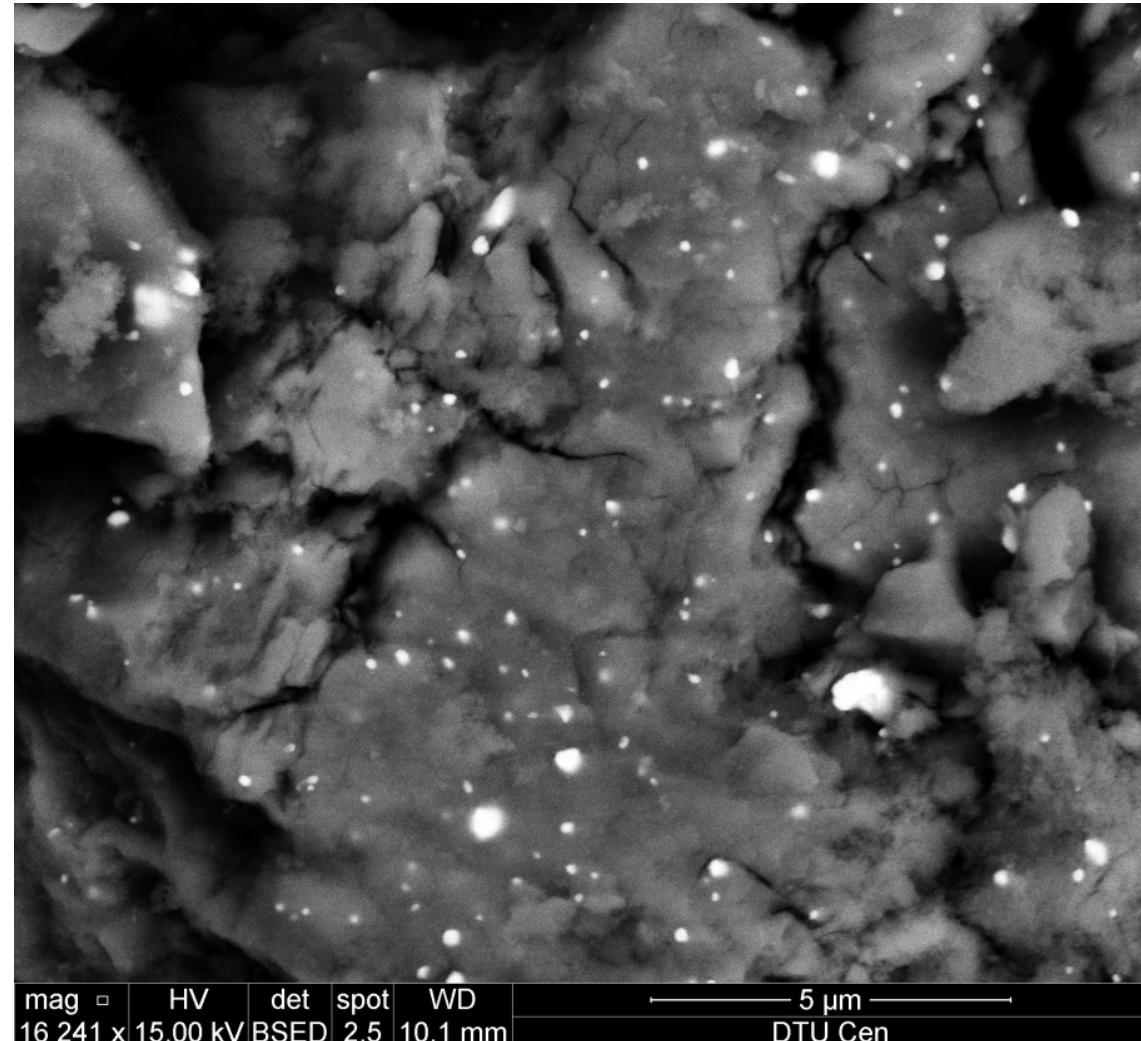


Figure 3-14. Schematic illustration of the generation of secondary electrons SE1 and SE2, backscattered electrons BSE1 and BSE2, Auger electrons AE, cathodoluminescence CL, and X-rays in a bulky specimen. t_{SE} and t_{BSE} indicate the escape depth for SE and BSE, respectively. R is the electron range.

Secondary Electrons (SE) vs. Back-scattered Electrons (BSE)

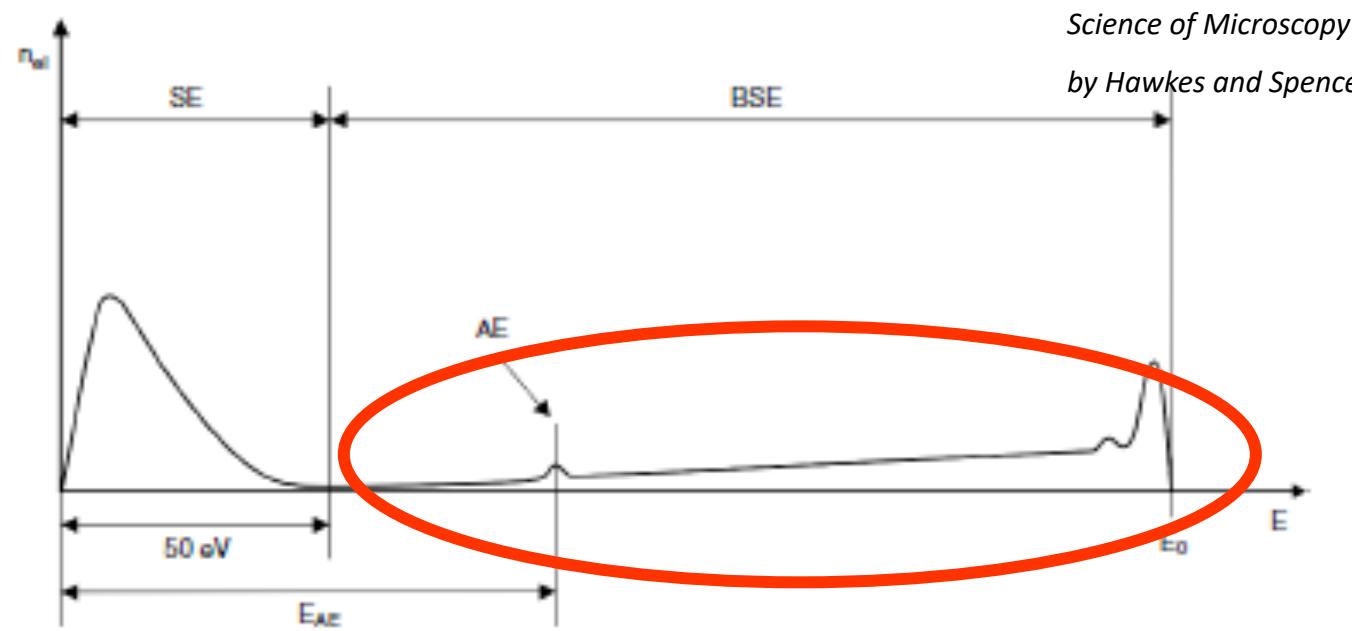


Ag/Co₃O₄



What signals to be used?

- **Backscattered electrons** (dominated by elastic scattering)
 - Electrons scattered by angles greater than π
 - Escaping from the surface
 - The fraction of backscattered electron depends strongly on the mass density due to Rutherford scattering



Backscattered electrons

$$\eta = n_{\text{BSE}} / n_p$$

Z contrast
Less dependent on
incident beam energy

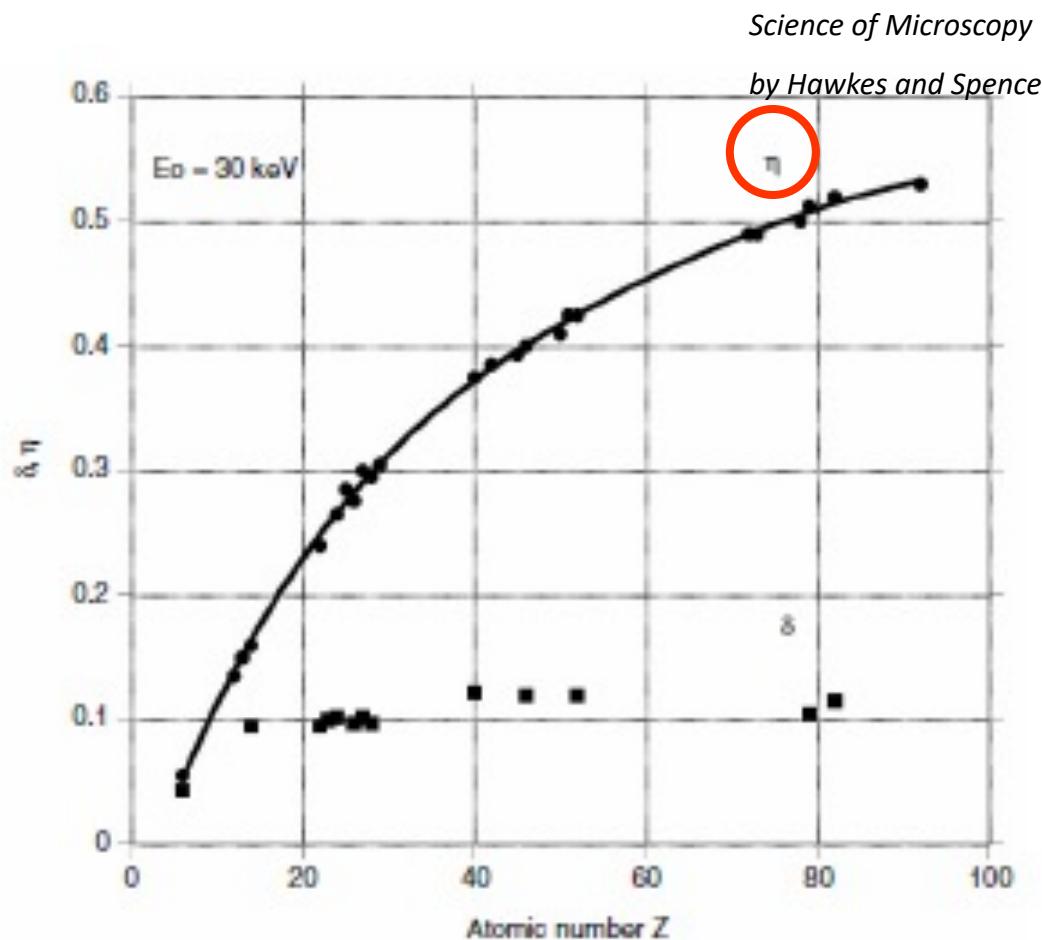
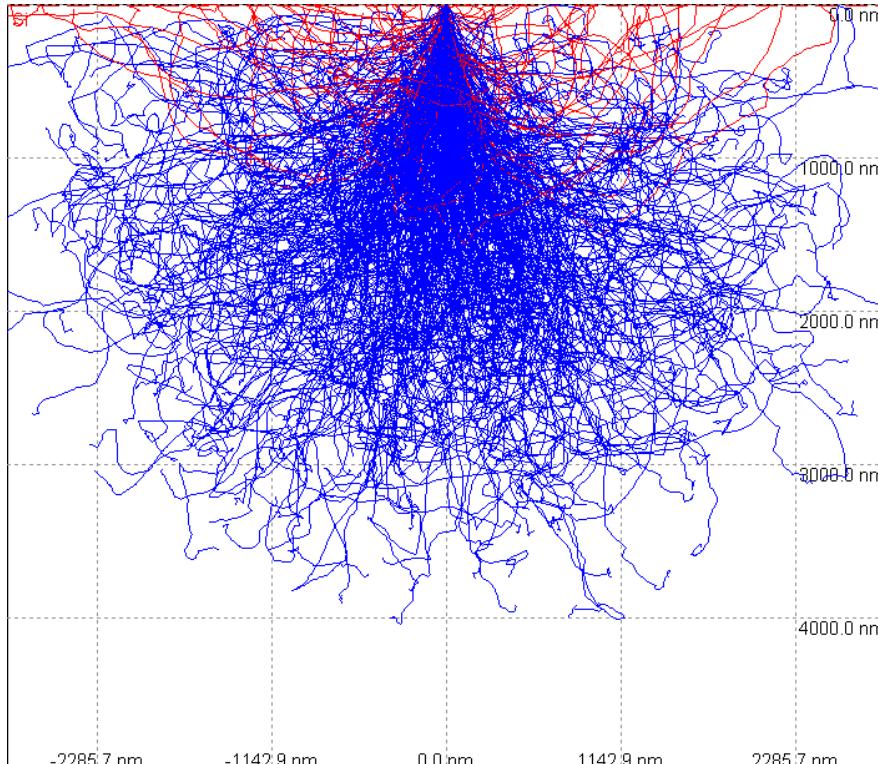


Figure 3-17. SE yield δ and BSE yield η versus atomic number Z at $E_0 = 30 \text{ keV}$ and $\theta = 0^\circ$. (Data from Heinrich, 1966; Wittry, 1966.)

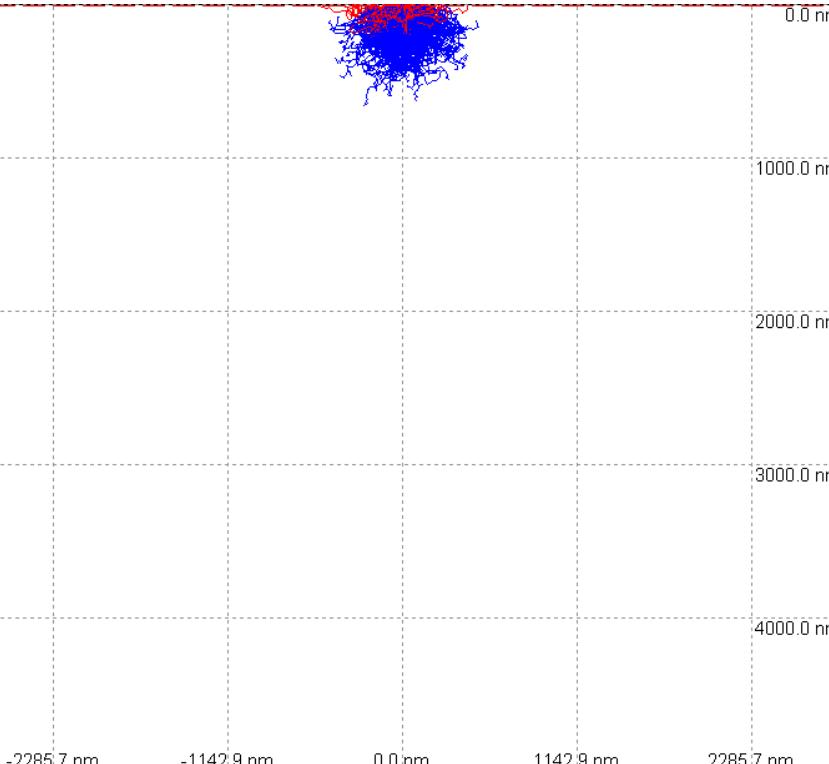
Backscattered coefficient

10nm beam

η BSC 0.162



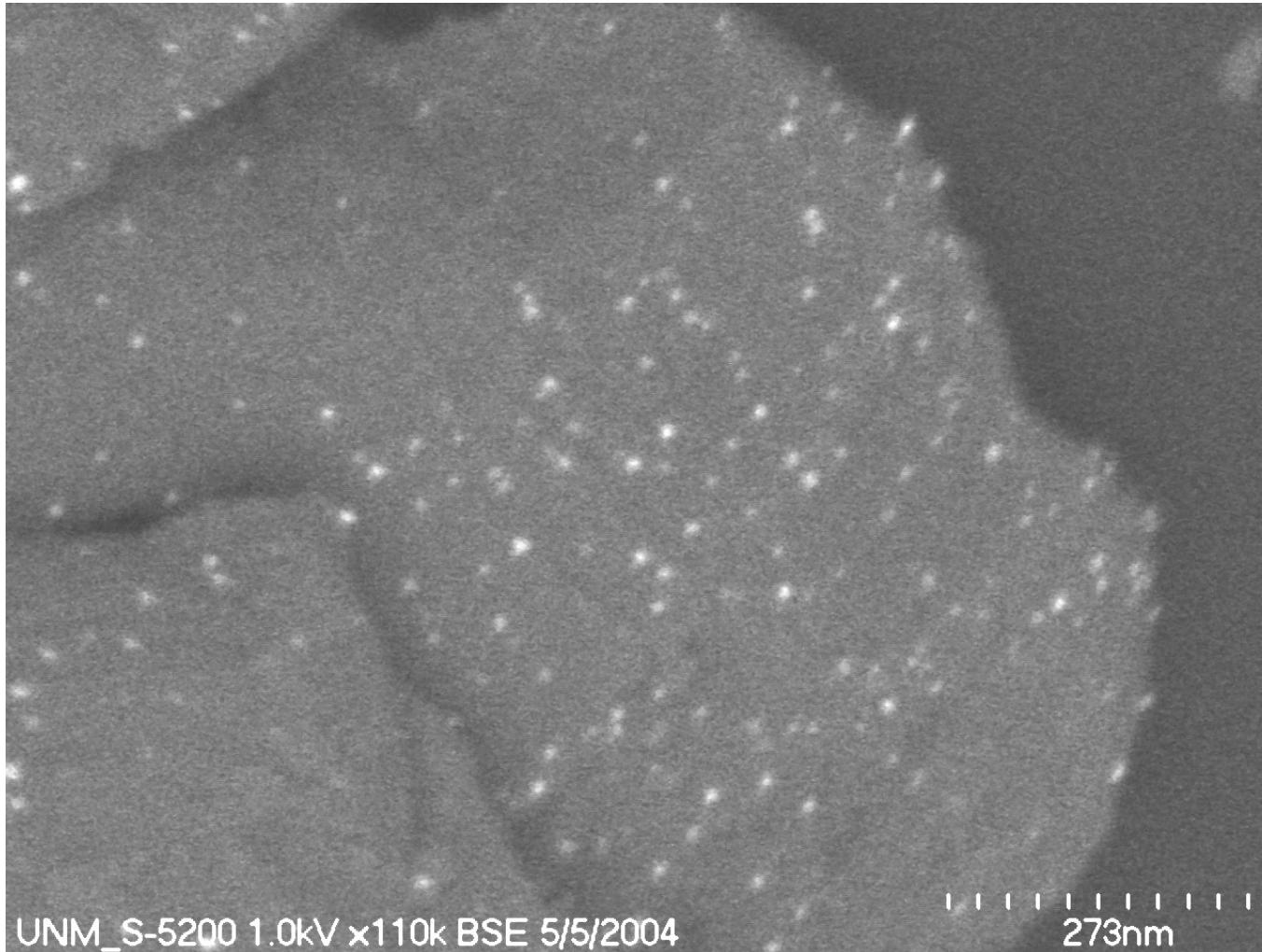
η BSC 0.442



Si 20keV

Au 20keV

Z contrast (Au on Zeolite)



Resolution (BSE)

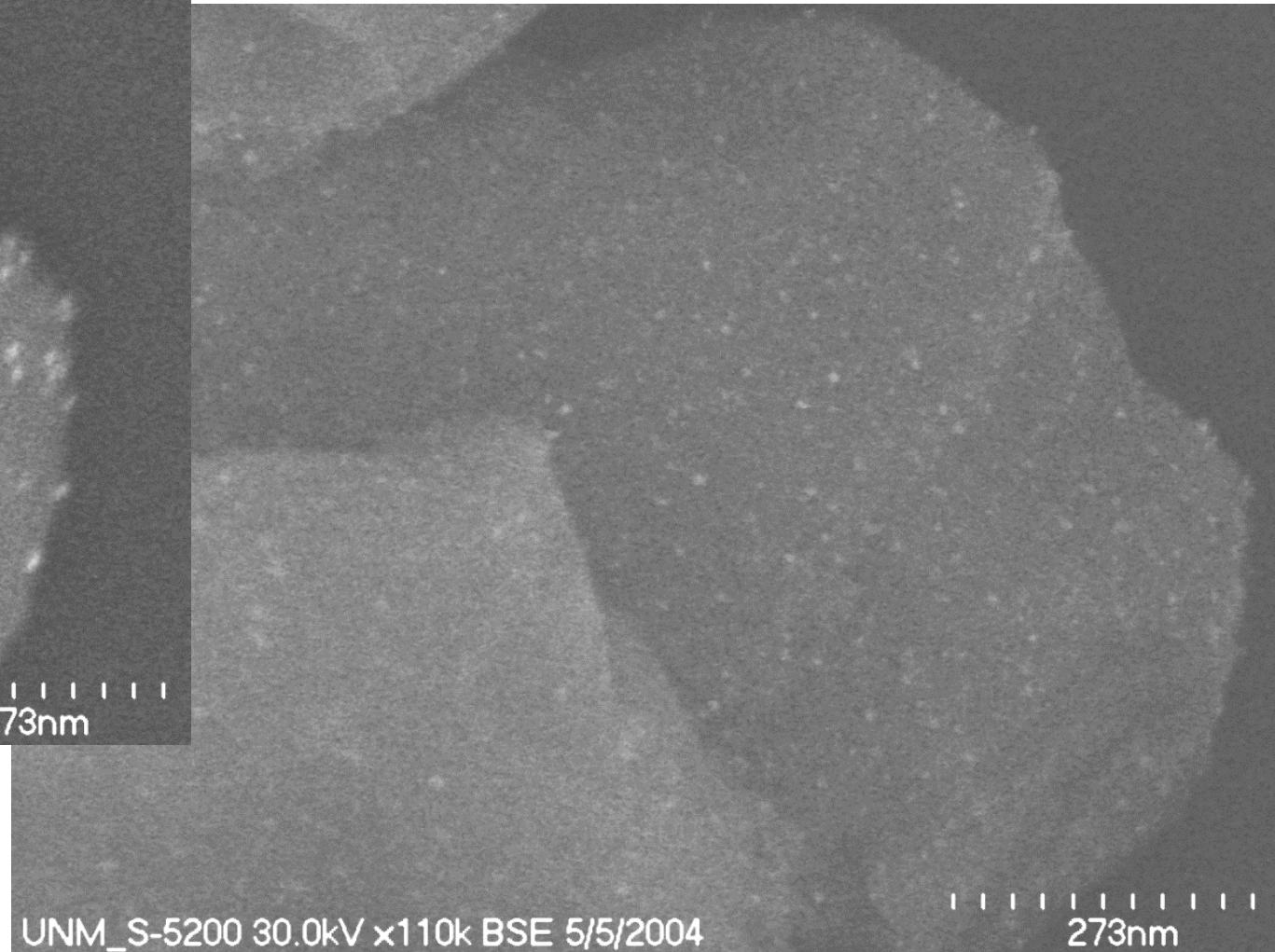
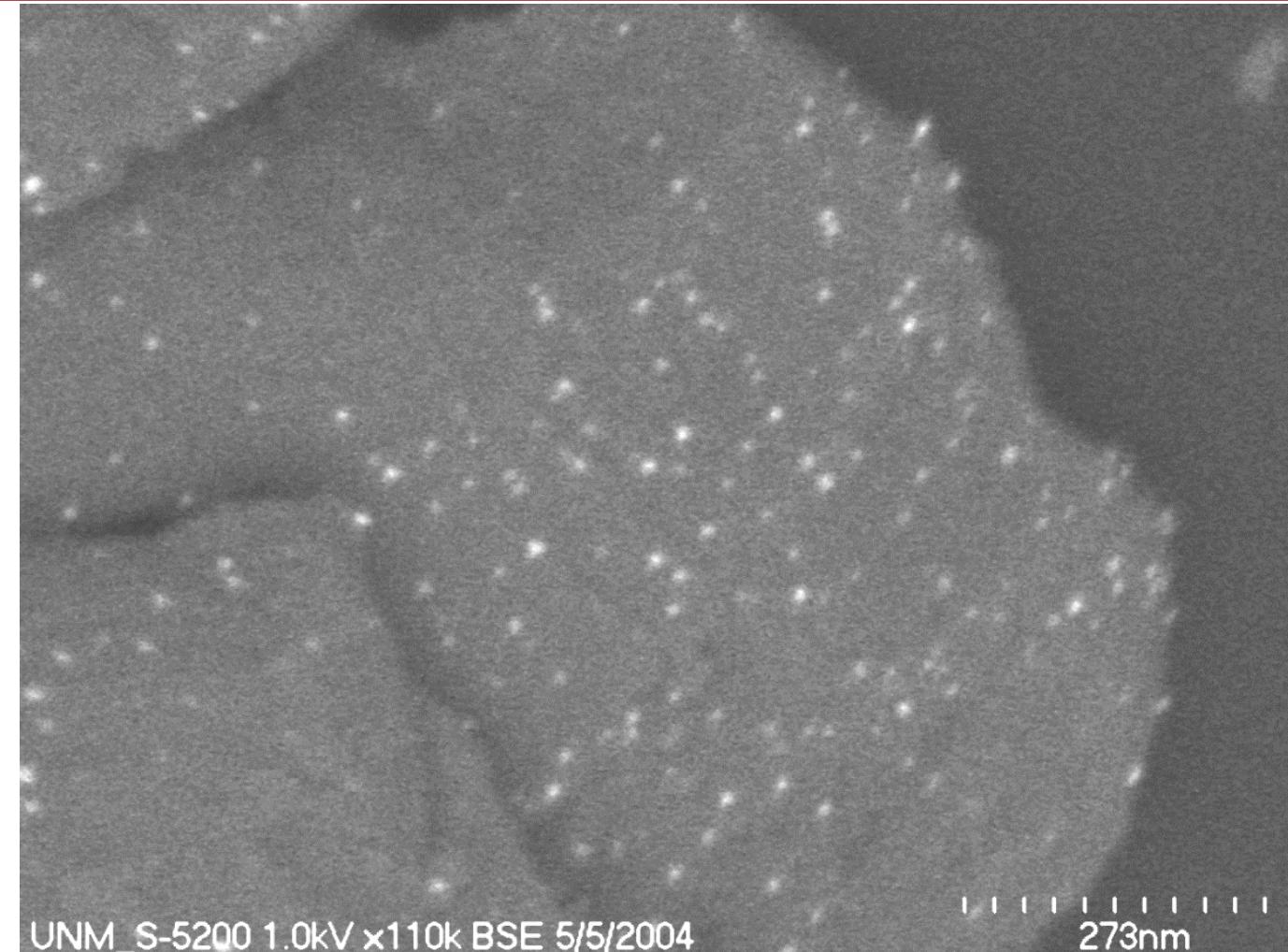
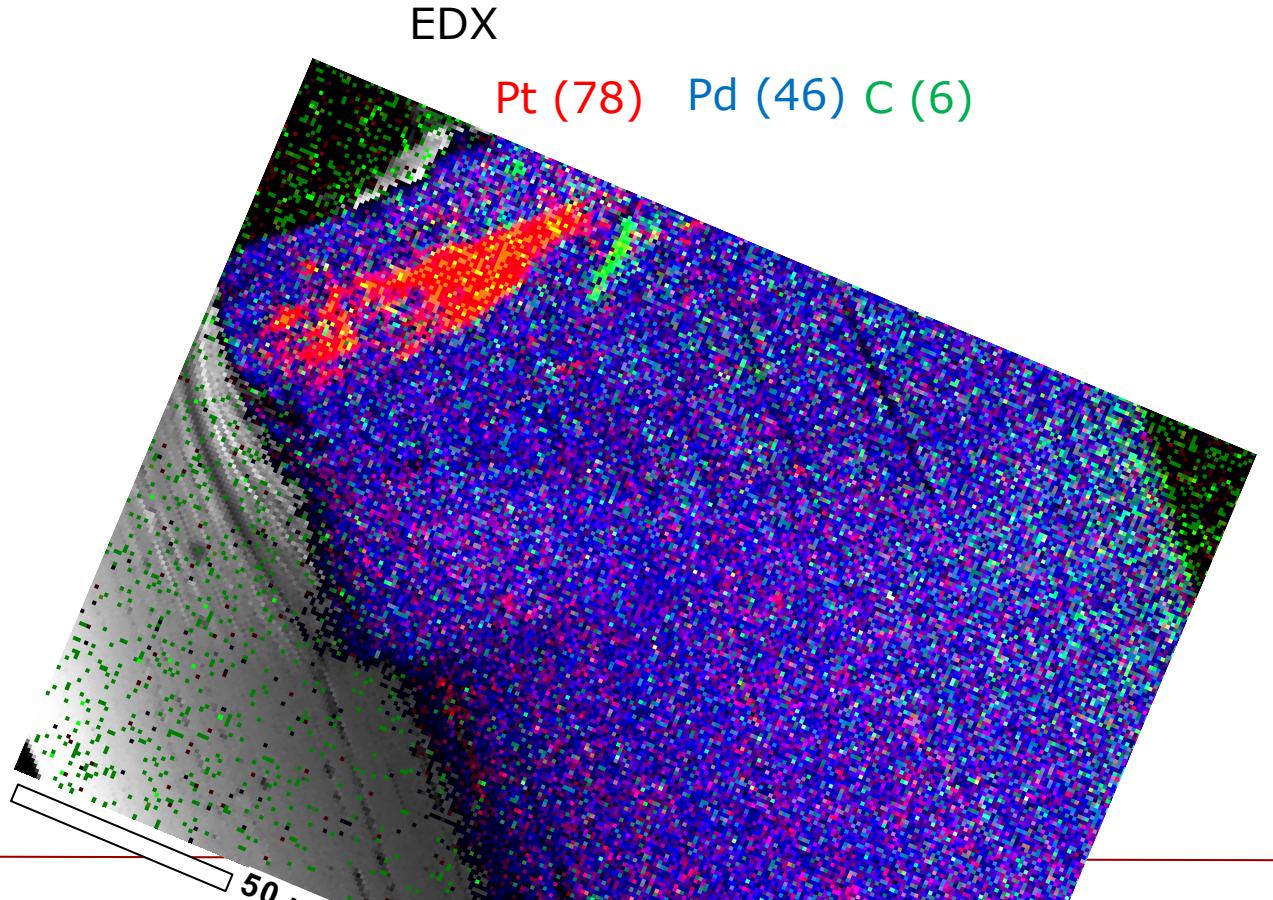
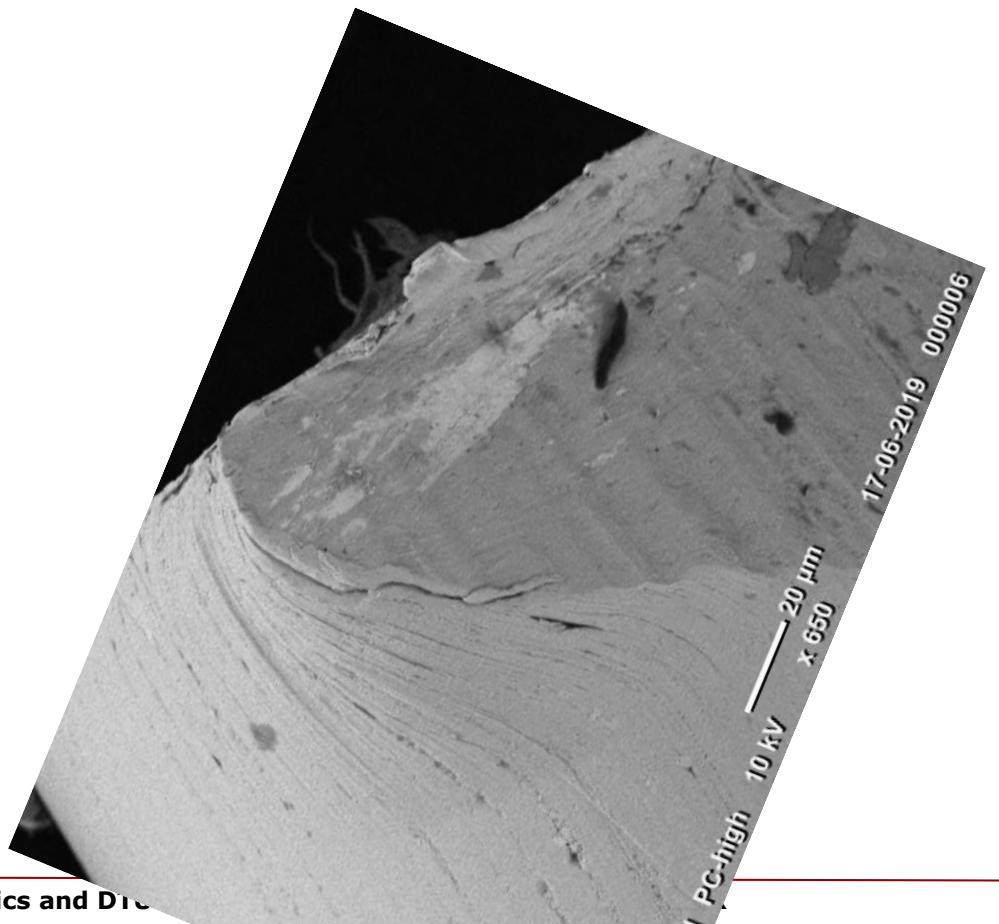


Image contrast / Resolution (BSE)

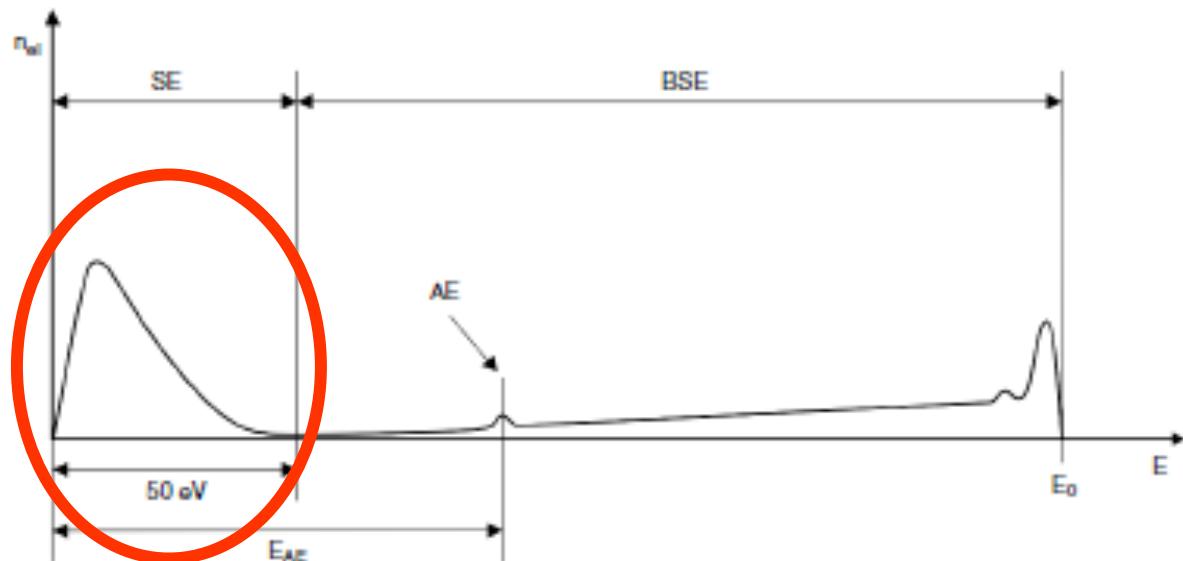
- Z contrast
- Ideally flat polished sample (pure Z-contrast)
- Resolution limited by interaction volume (diffusion length)



What signals to be used?

- **Secondary electrons (inelastic scattering)**

- Secondary electron emission coefficient can reach several hundreds
- Incident beam SE (limited by probe size)
- BSE @ surface – SE (emits from larger area)



Science of microscopy
by Hawkes and Spence

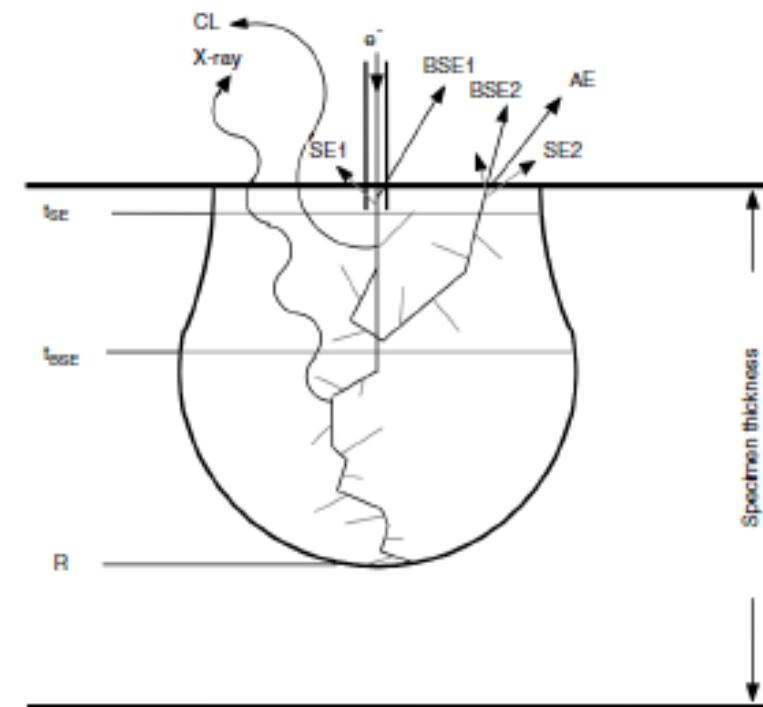
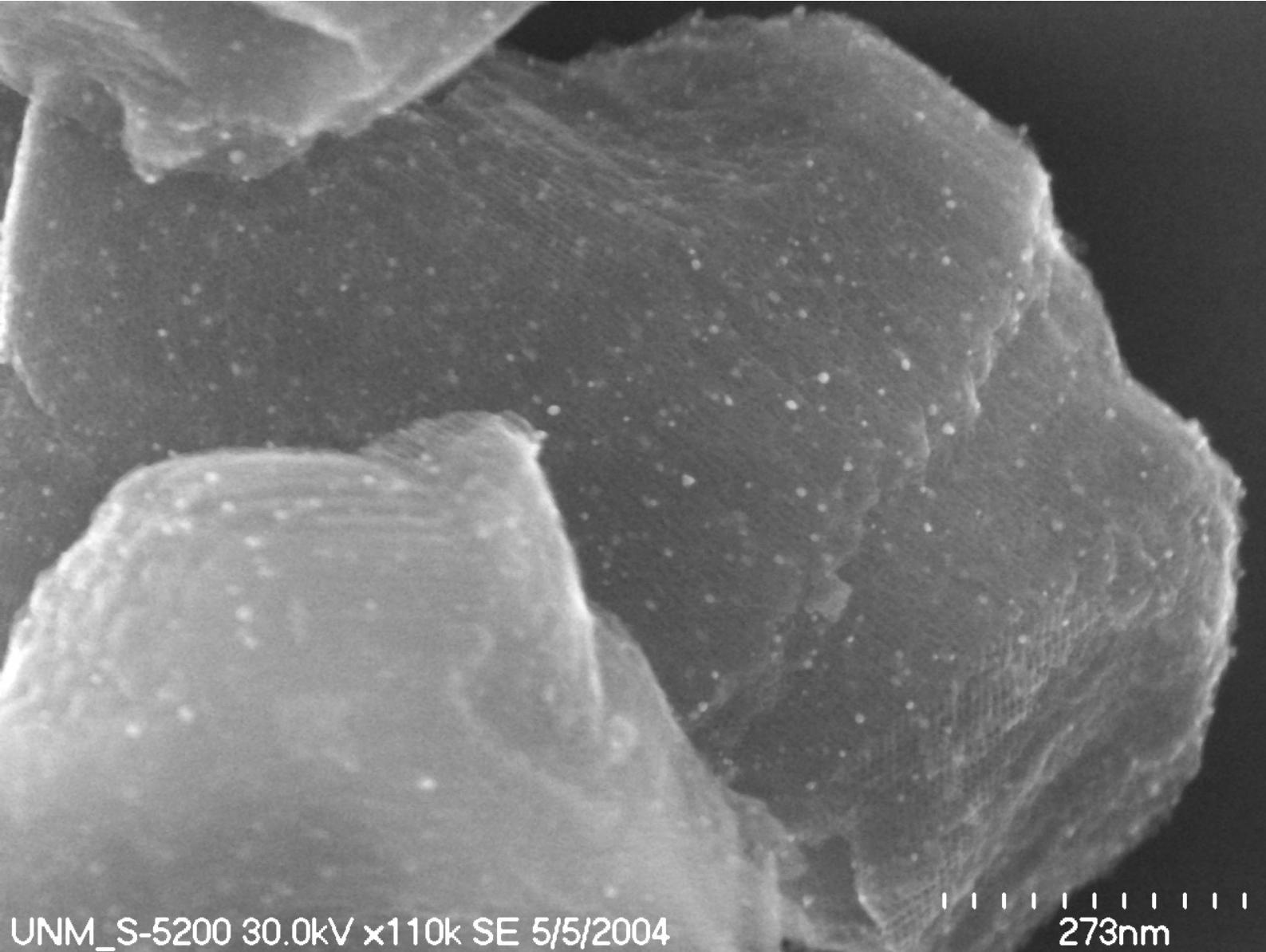
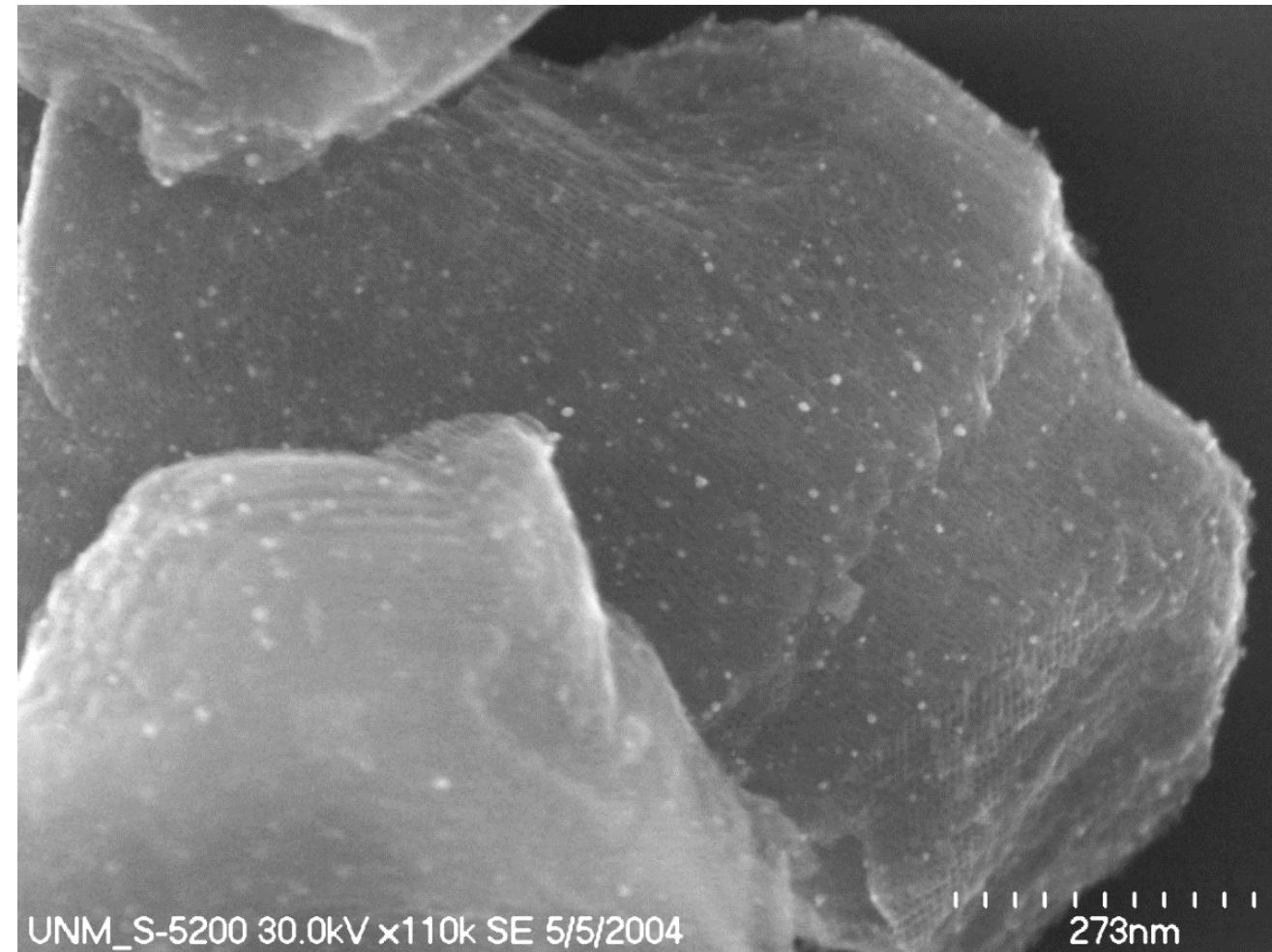


Figure 3-14. Schematic illustration of the generation of secondary electrons SE1 and SE2, backscattered electrons BSE1 and BSE2, Auger electrons AE, cathodoluminescence CL, and X-rays in a bulky specimen. t_{SE} and t_{BSE} indicate the escape depth for SE and BSE, respectively. R is the electron range.

Au on zeolite



BSE vs. SE



SE

UNM_S-5200 30.0kV x110k BSE 5/5/2004

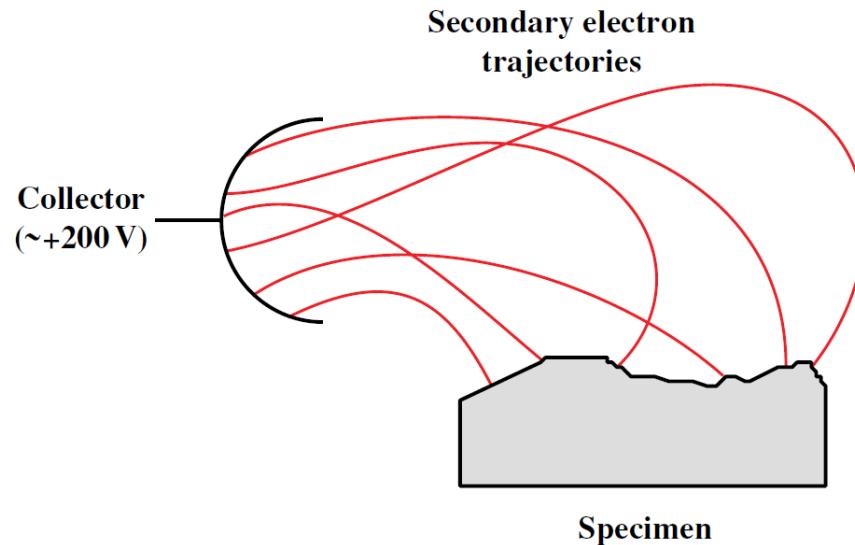
273nm

BSE

Secondary Electrons

- Low energy (10-50eV)
- High detection efficiency

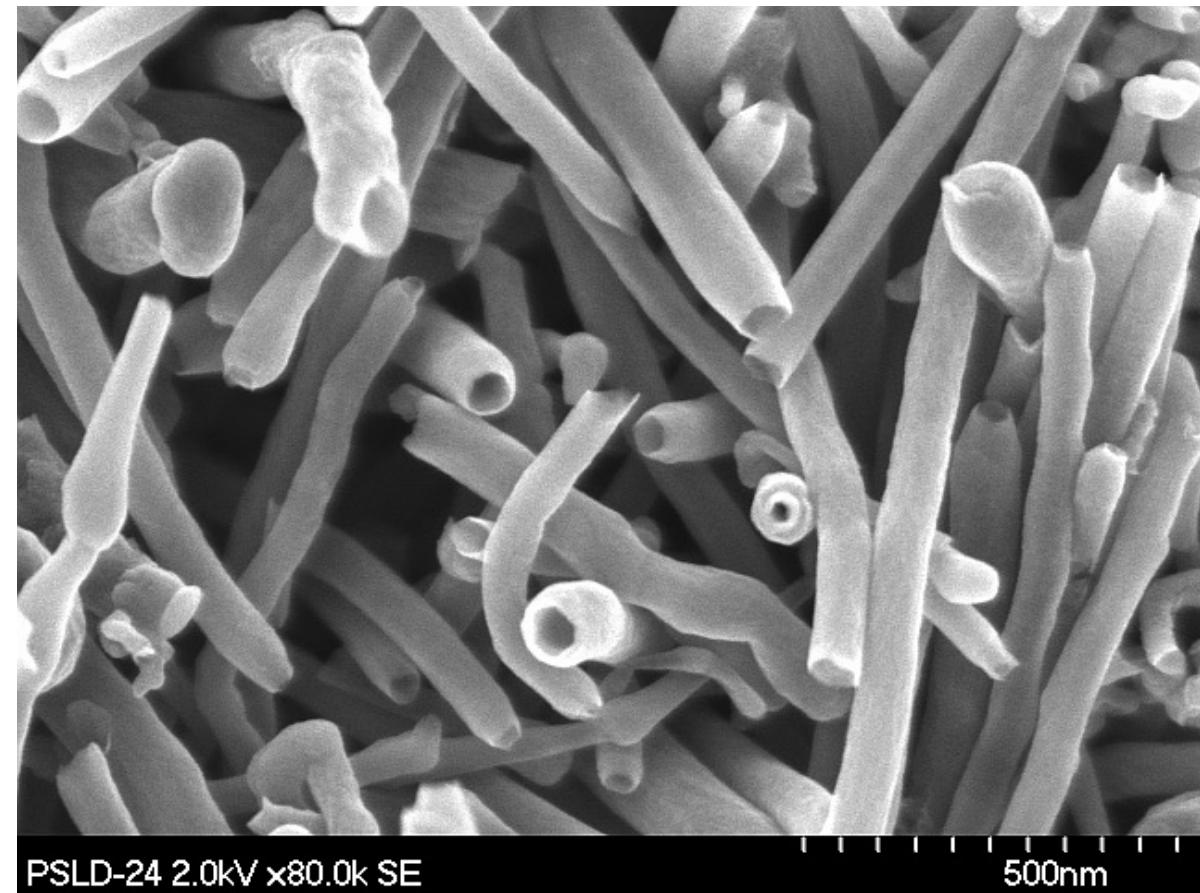
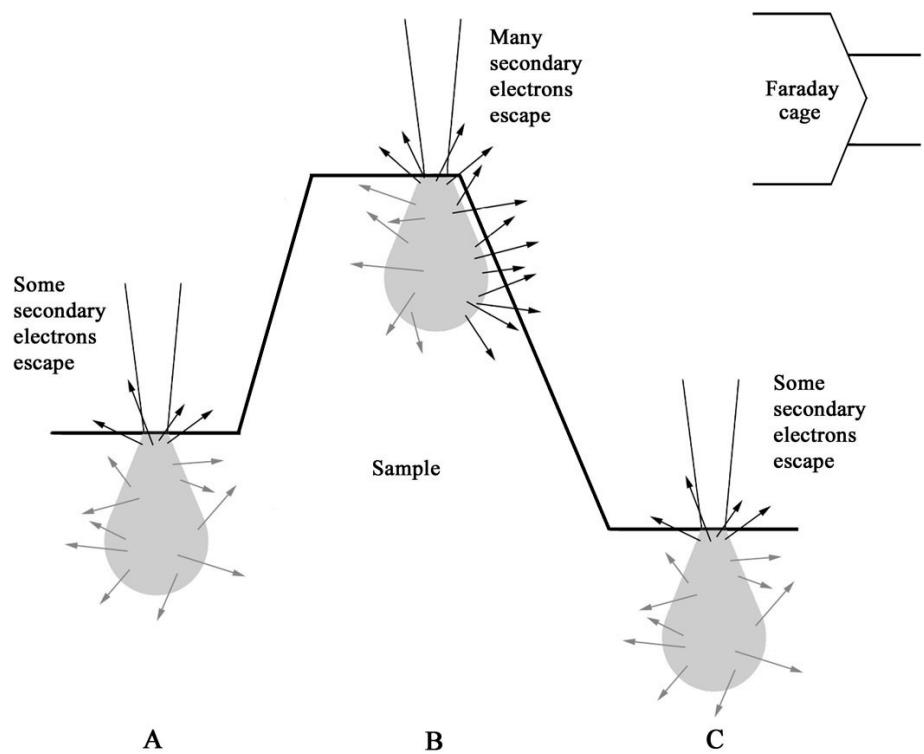
- Escape probability: $P_S = \exp(-r/L_S)$
 r : distance to escape
 L_S : mean free path (~ 2 for Pt, ~ 23 for MgO)



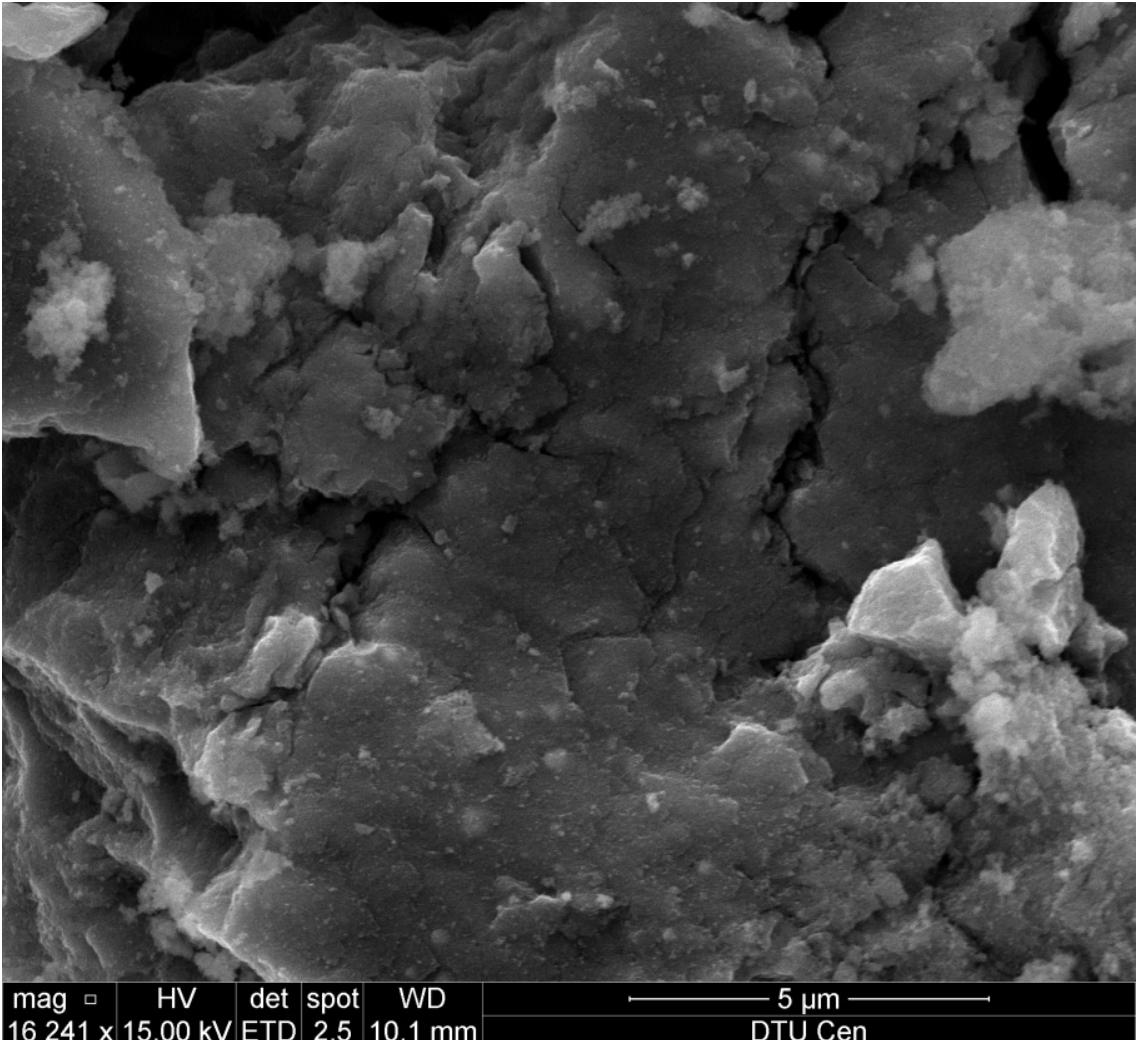
Microstructural Characterization of Materials by Brandon and Kaplan

Topography –Why edges appear brigther?

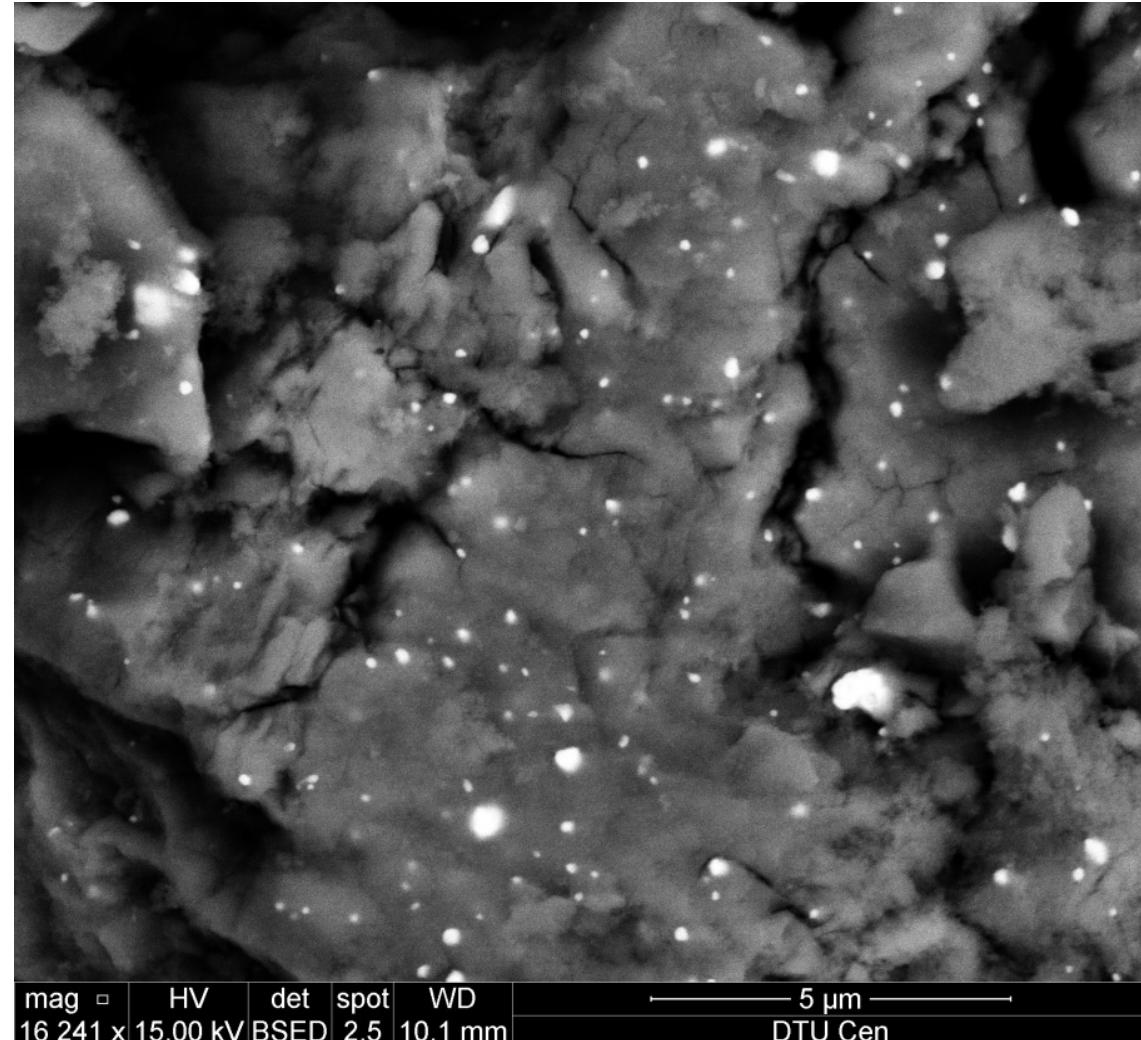
<http://131.229.88.77/microscopy/semvar.html>



Secondary Electrons (SE) vs. Back-scattered Electrons (BSE)



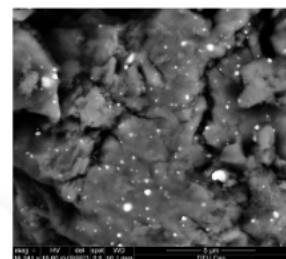
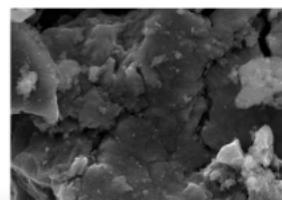
Ag/Co₃O₄



Join at menti.com | use code 7541 6948

 Mentimeter

Which micrograph is taken with BSE and SE detector, respectively?



Left: SE, Right:
BSE

Left: BSE, Right:
SE

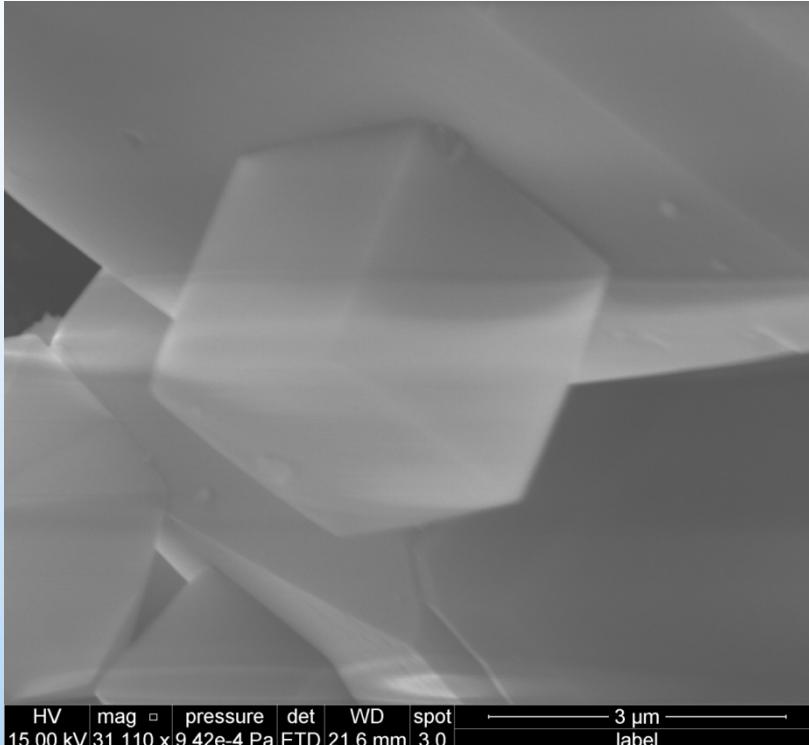
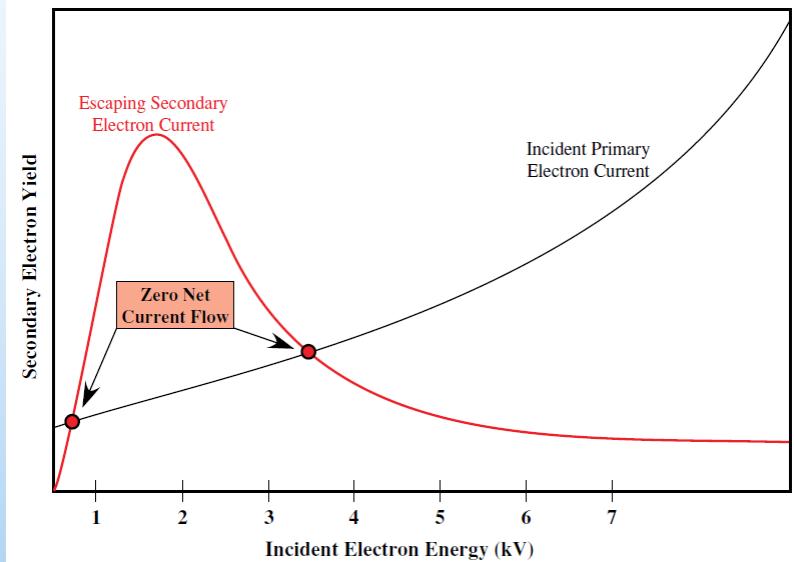
Press **ENTER** to show correct answer



Charging of insulating sample

- Positive or negative charging?

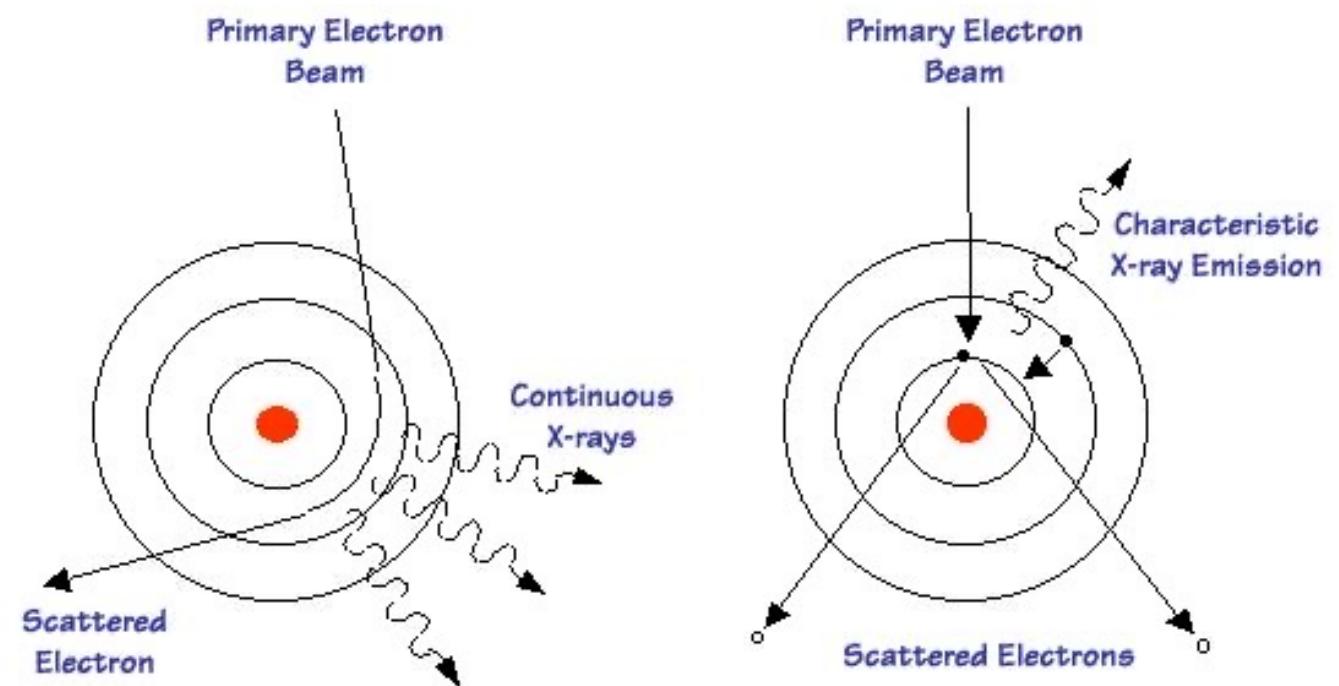
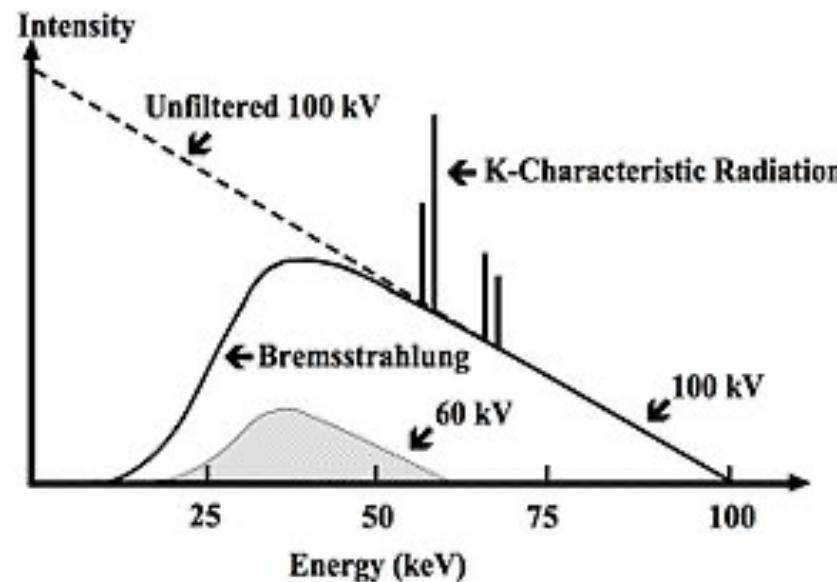
Microstructural Characterization of Materials by Brandon and Kaplan



- Can be compensated by using the optimal acceleration voltage
- Coating with conducting material (C/Pt/Au)

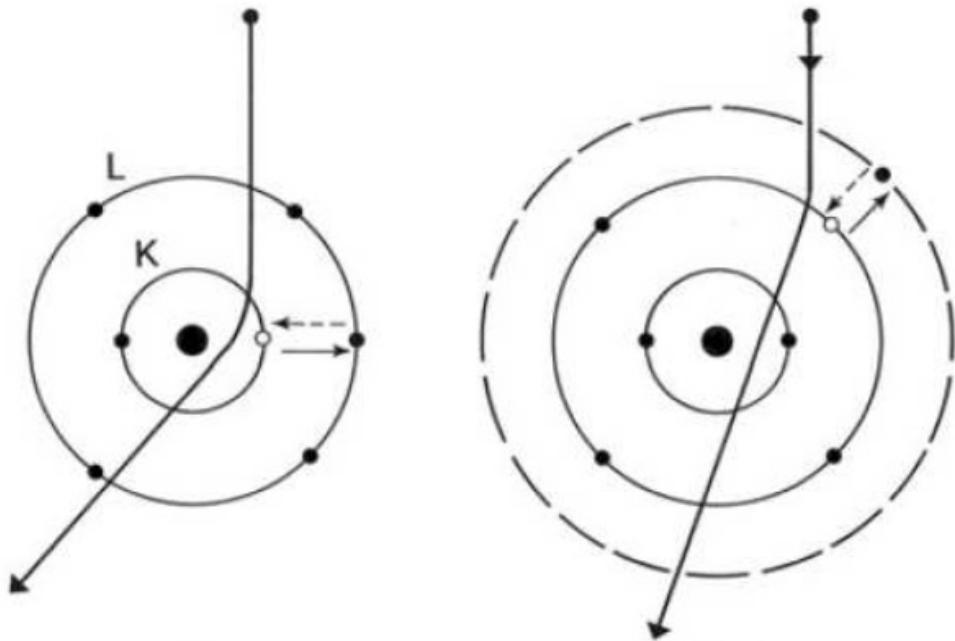
Energy dispersive x-ray spectroscopy (EDS): Electrons in - Photons out

- https://myscope.training/EDS_Bremsstrahlung_X_ray_generation
- https://myscope.training/EDS_Characteristic_X_ray_generation

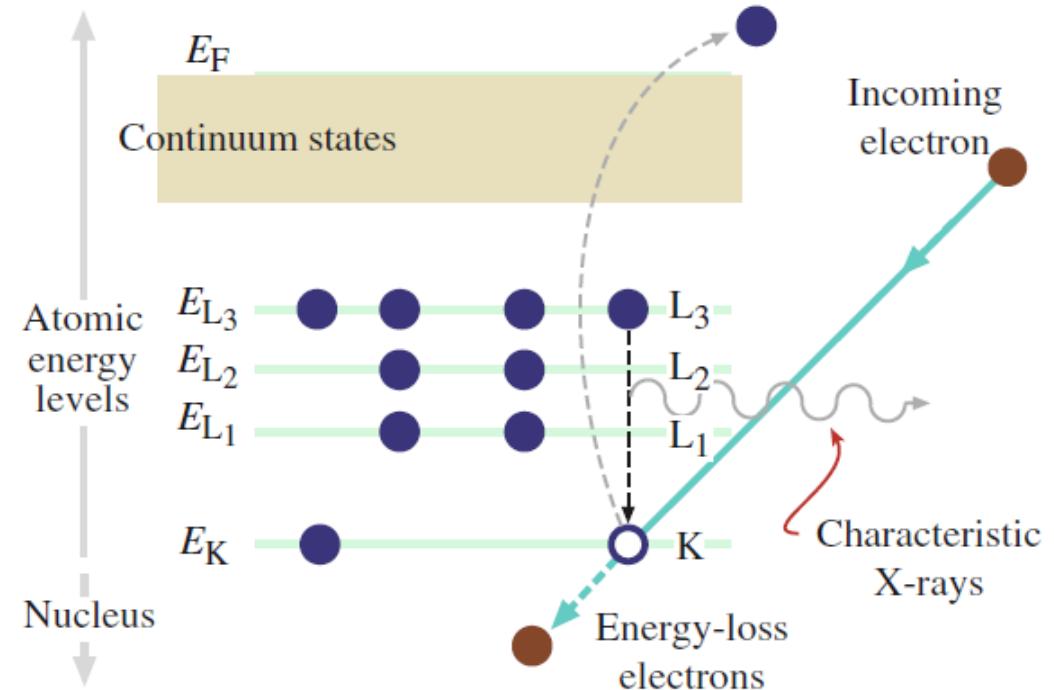


www2.rgu.ac.uk/life_semweb/xrayfig1.gif

Inelastic scattering - Spectroscopy

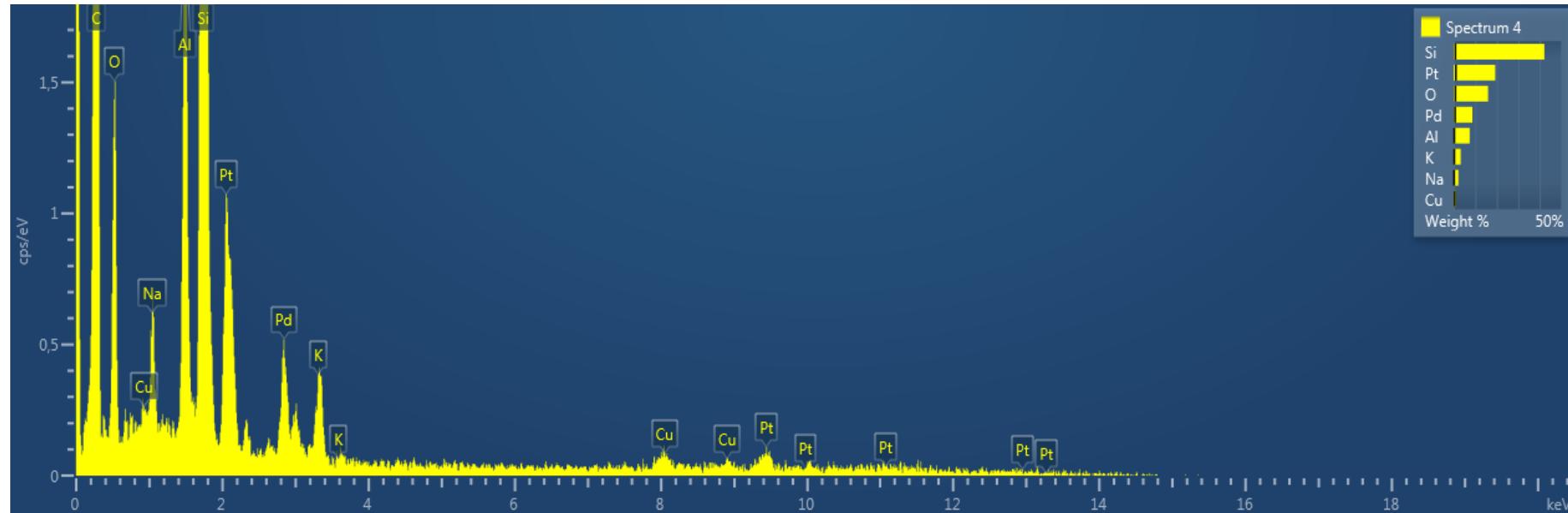


Inner and outer electron excitation by the primary electrons.



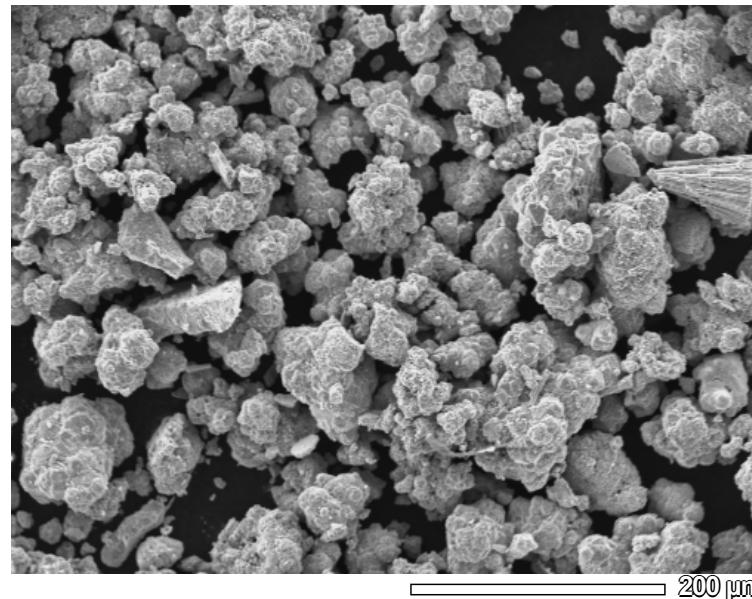
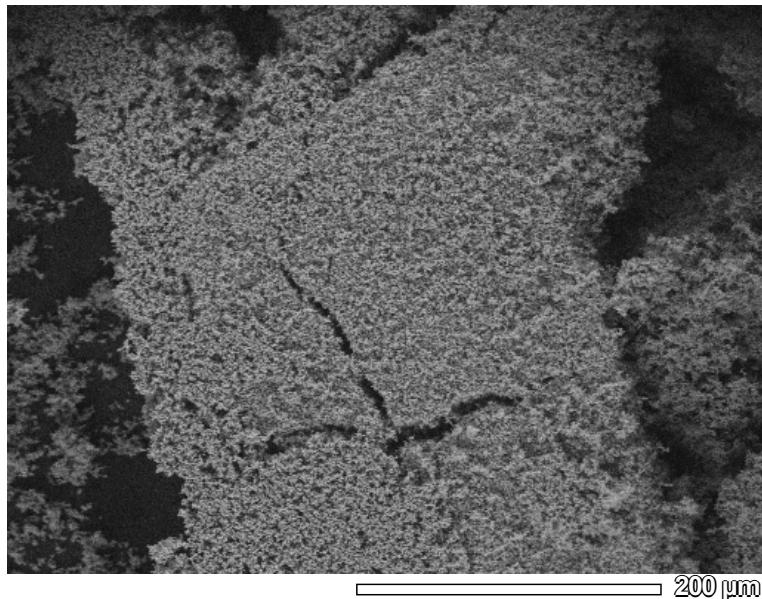
- Primary electrons can scatter with inner or outer electrons of an atom of the sample and loose energy.
- If inner electrons receive enough energy to escape the attraction of the nucleus they leave an hole in the atom's inner shell.
- Electrons belonging to outer shells can fill the hole. This transition is accompanied by the emision of either an X-Ray or an Auger electron.

The EDX spectrum

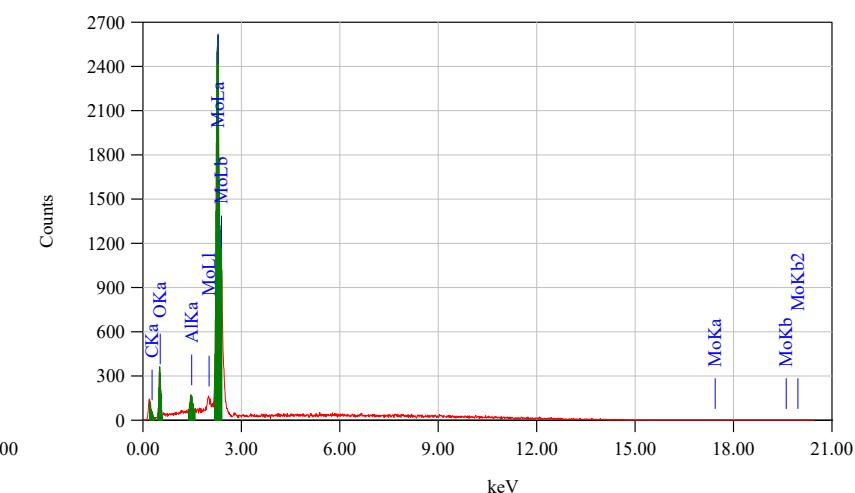
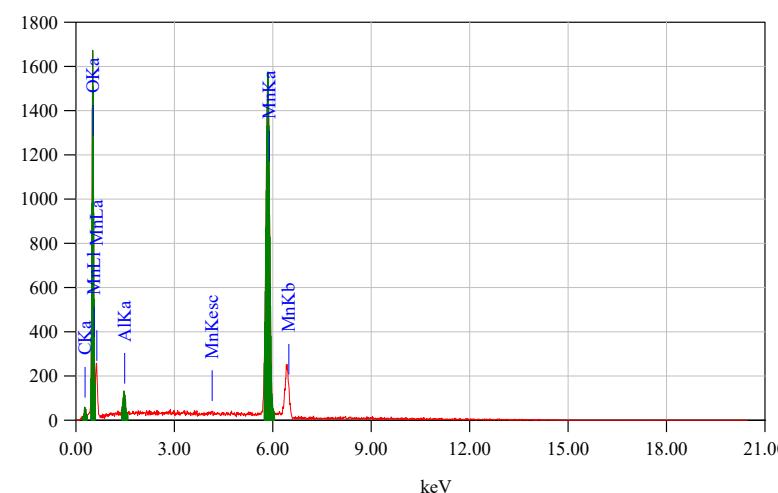
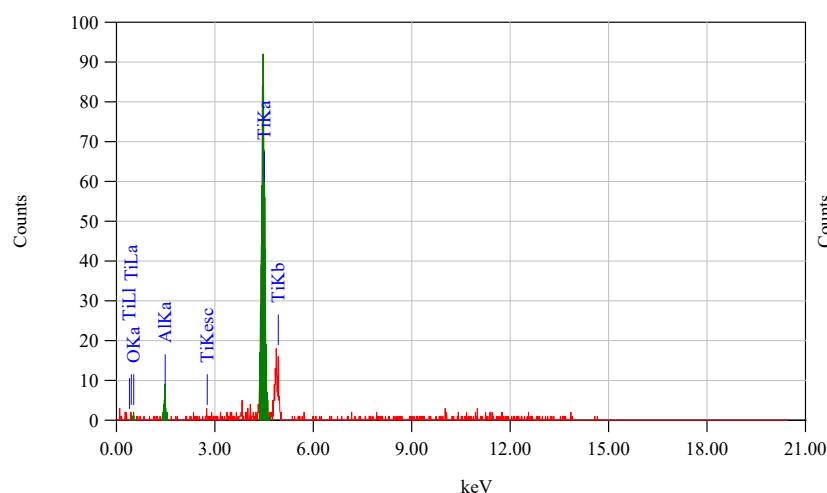


- Background: Bremsstrahlung radiation (primary electrons slow down due to attraction with nuclei, emitting X-Rays).
- Characteristic transition peaks! Si and Au are from the detector itself. Fe and Cu are from the microscope.

SEM and EDX of powders in H₂O₂ exercise

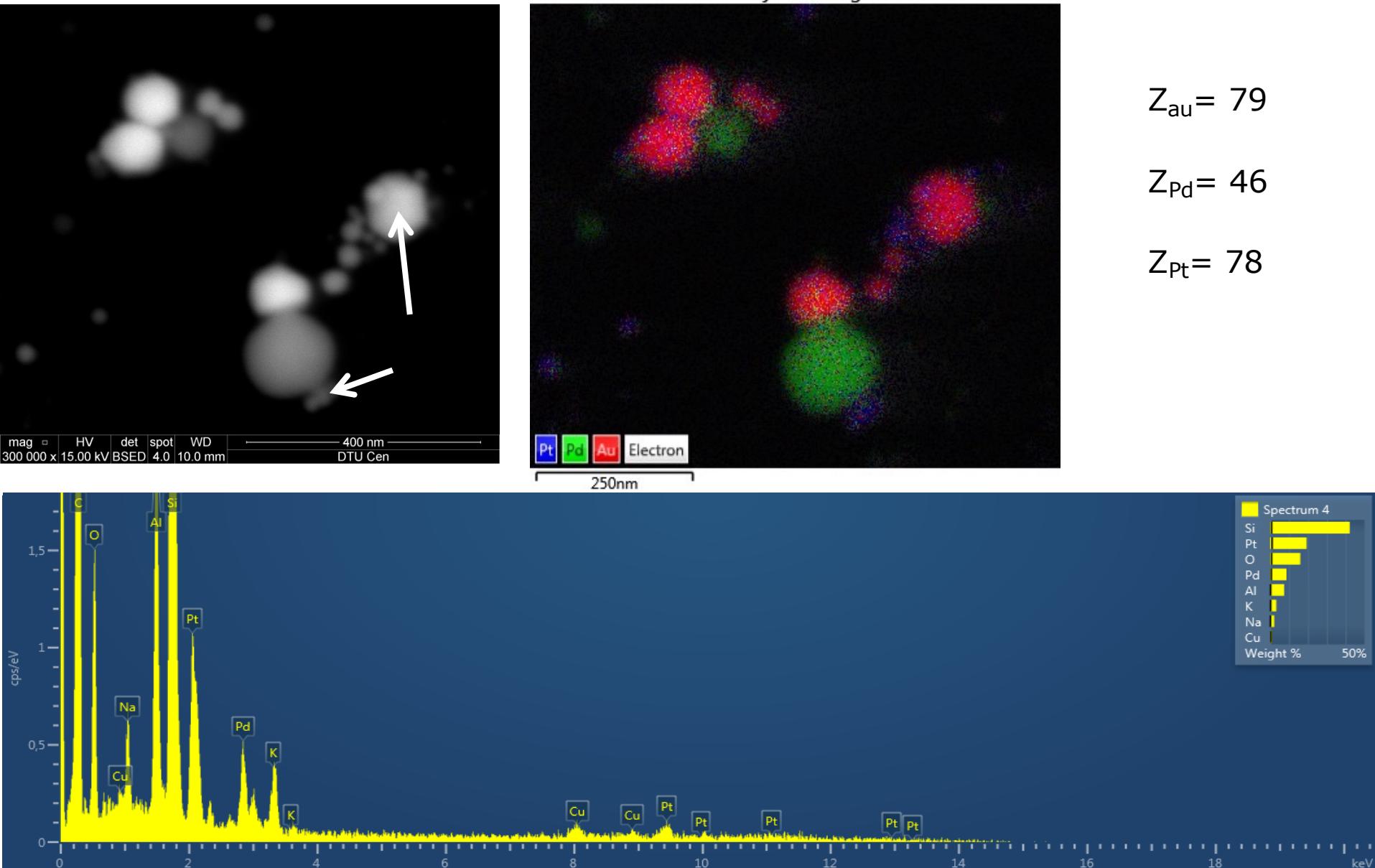


30 μm



Energy dispersive x-ray spectroscopy

Georg Hofmann and Juliane Reinhardt

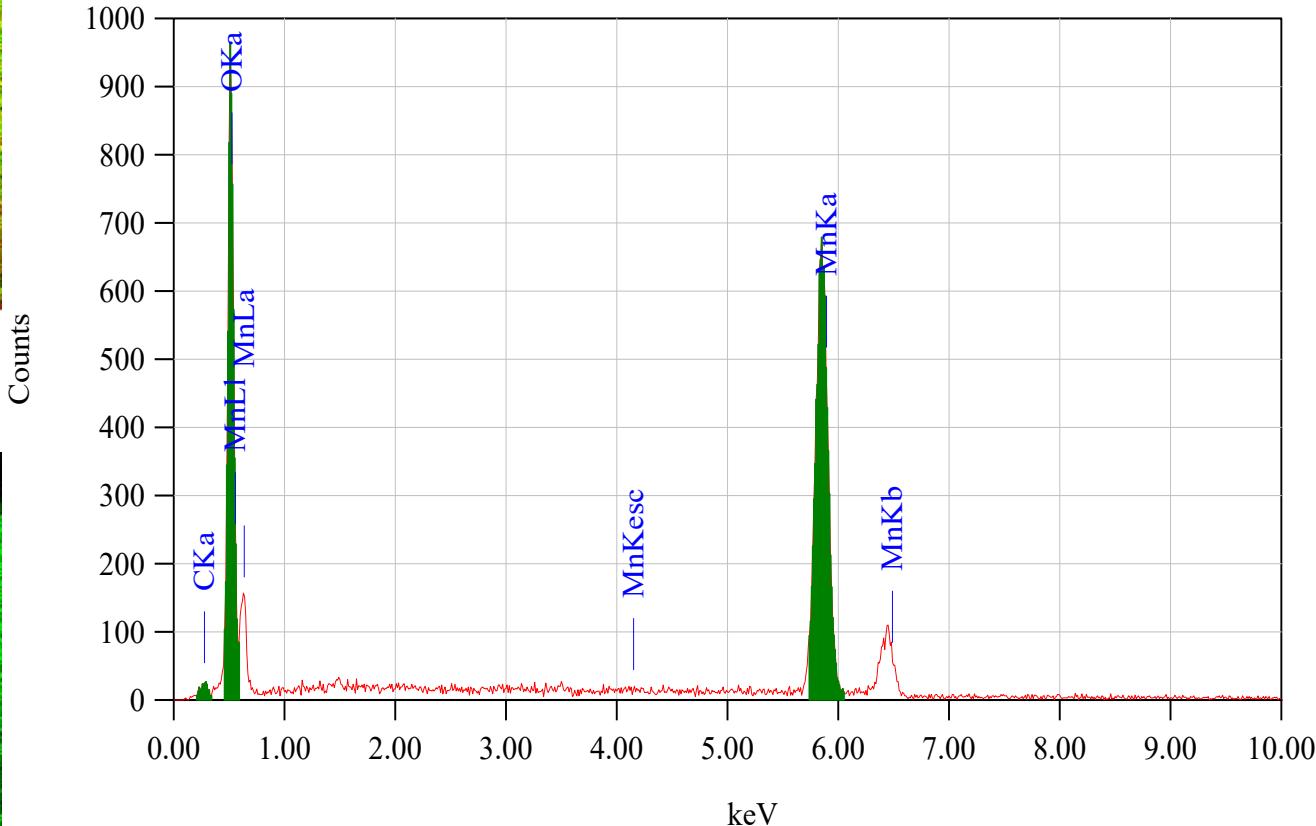
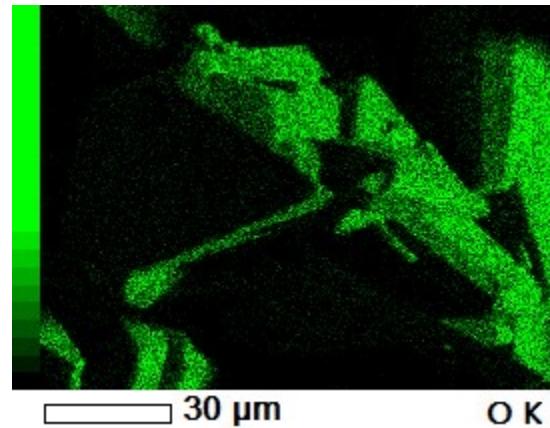
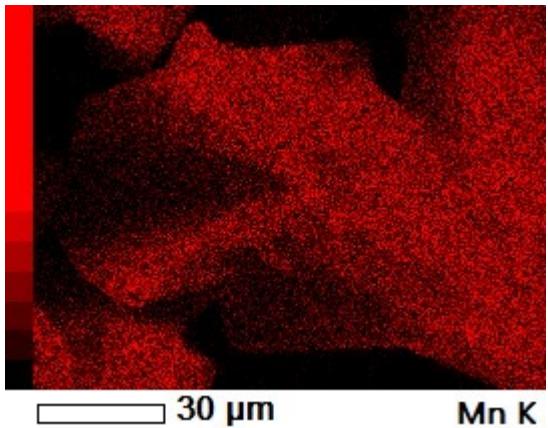
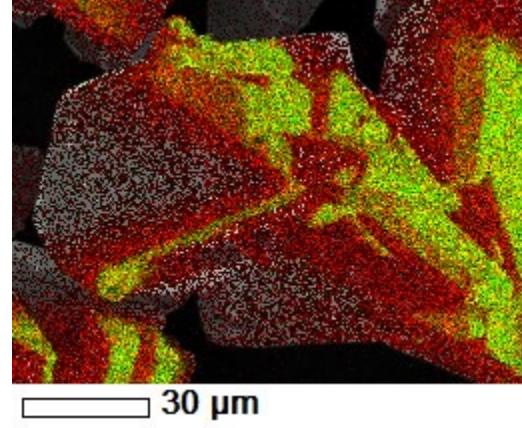
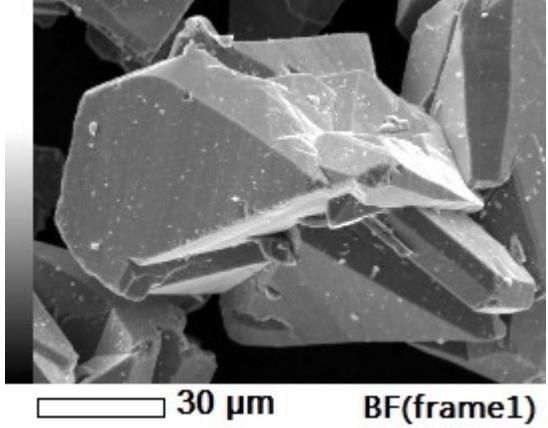


$$Z_{\text{Au}} = 79$$

$$Z_{\text{Pd}} = 46$$

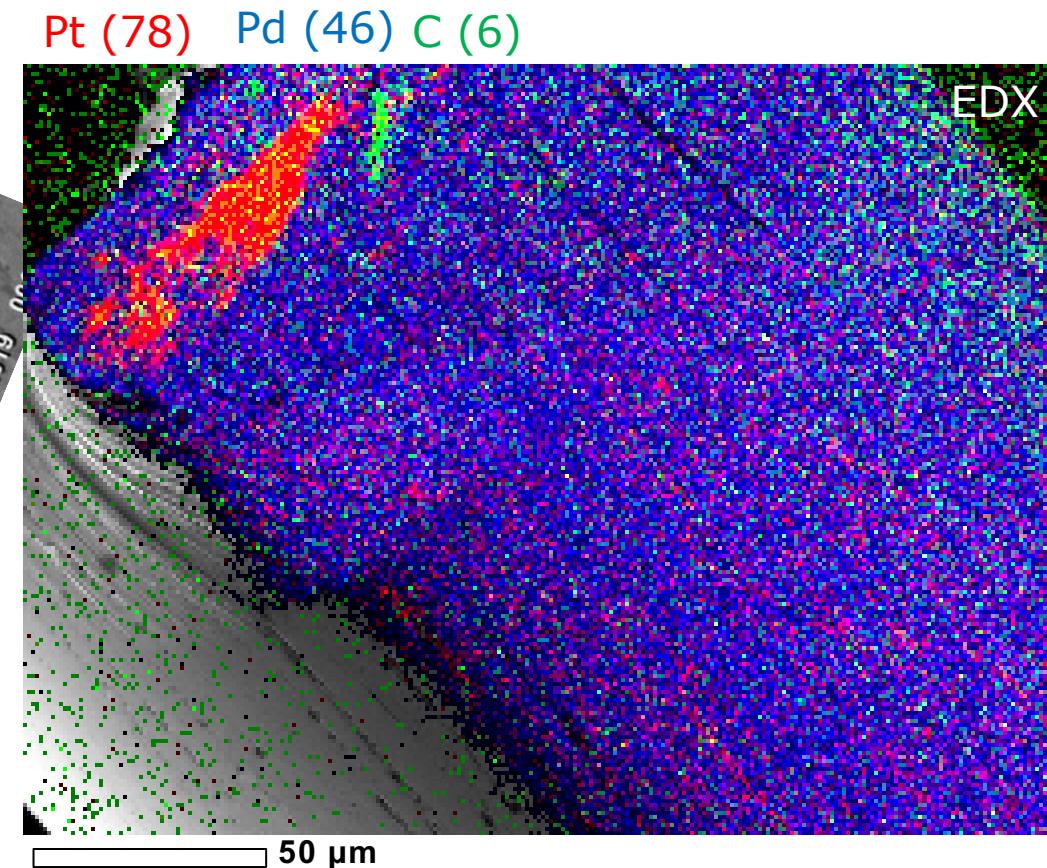
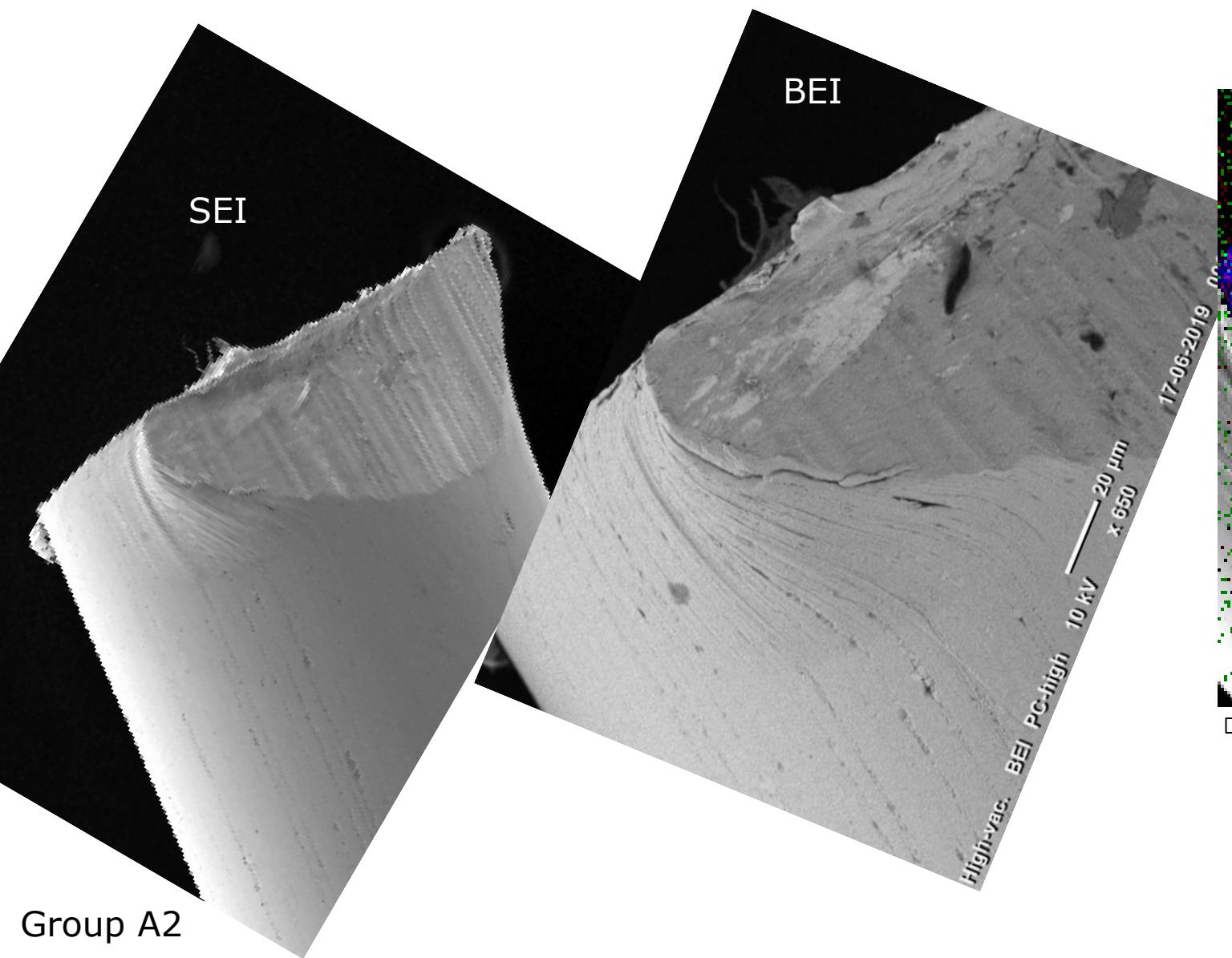
$$Z_{\text{Pt}} = 78$$

Problems with light elements...



Group C1

Scanning Electron Microscopy – exercise



Group B2

Characterization of catalysts by x-rays

- X-ray sources
- X-ray interaction with Matter
- X-ray diffraction
- X-ray absorption spectroscopy

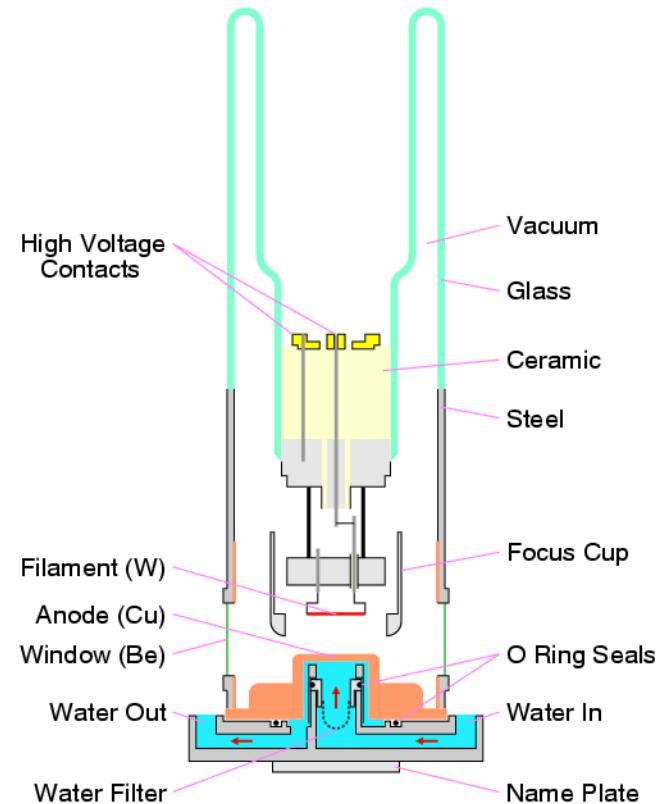
3 minutters buzz

- Wavelengths of the order of interatomic distances in solids
- Diffraction can resolve distances and structure
- Spectroscopy by interacting inelastically with the sample (ionizing)

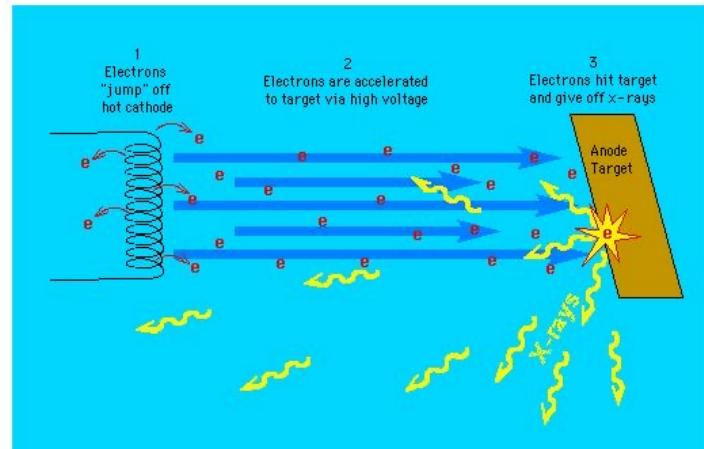
Acceleration of electrical charge produces electromagnetic radiation

X-rays have a high energy
-> require a strong acceleration

Easiest way: Accelerate an electron by a voltage drop and then brake ... *fast!*



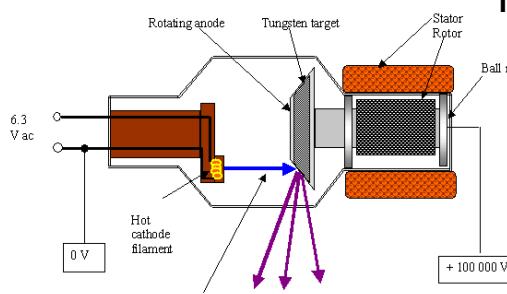
X-ray tube



High Voltage $U = 10,000 - 200,000$ volt

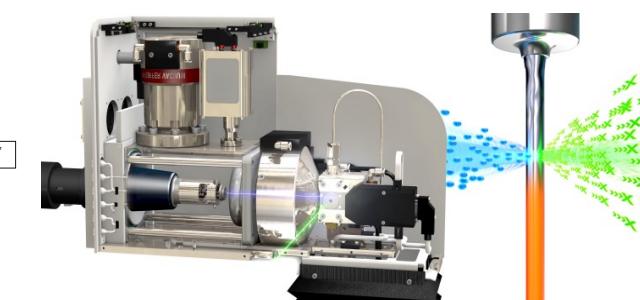


Anode tube, ca. 1900



Rotating anode, ca. 1960

"Liquid Metal target", ca. 2010



-A particle with charge q in a point x in an electric field E has a potential energy in the electric field $E_{pot, el.} = Uq$, where U is the electric potential in the point x .

By acceleration over the potential U the particle obtains the kinetic energy $E_{kin} = Uq$

$$\text{Electron: } E_{kin} = Uq = Ue$$

It is a small fraction of this mechanical energy that converts to radiation in an X-ray tube

But what is the physics and what are the properties of this radiation?

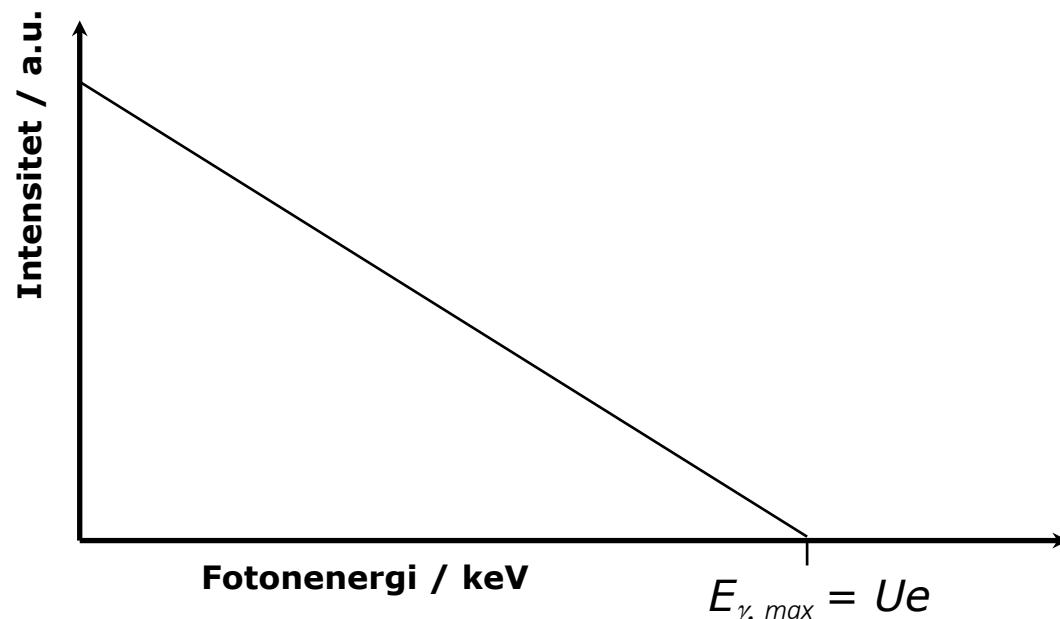
An electron can be slowed down either in one collision and emit all its kinetic energy as one photon:

$$E_{\gamma, \max} = Ue$$

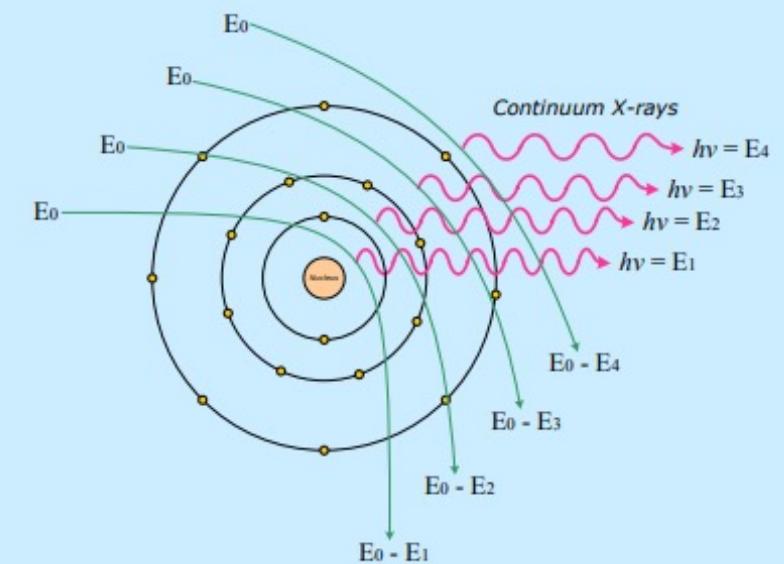
-or it can be slowed down/emit energy through many smaller collisions

$$Ue = \sum_i p(E_i) * E_i$$

Expected Bremsstrahlung-spectrum?



Continuum X-rays



https://myscope.training/EDS_Bremsstrahlung_X_ray_generation

Intensity distribution (Energy flux) (number of photons times their energy)

$$I(E) = C \cdot i \cdot Z \cdot (E_{\max} - E)$$

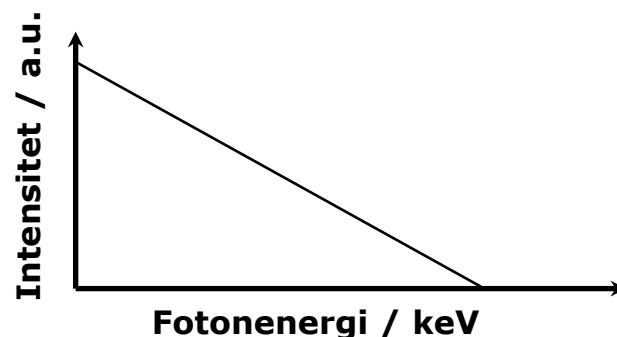
An electron can be slowed down either in one collision and emit all its kinetic energy as one photon:

$$E_{\gamma, \text{max}} = Ue$$

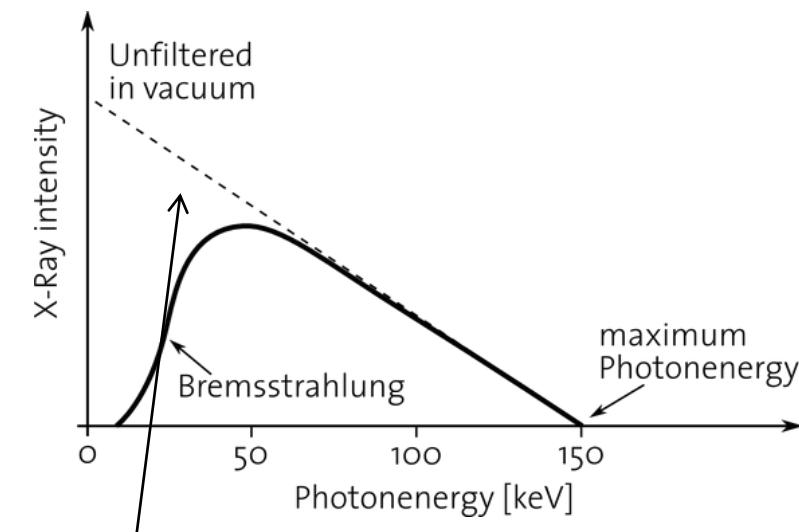
-or it can be slowed down/emit energy through many smaller collisions

$$Ue = \sum_i p(E_i) * E_i$$

Expected Bremstrahlung-spectrum :



Actual Bremstrahlung-spectrum



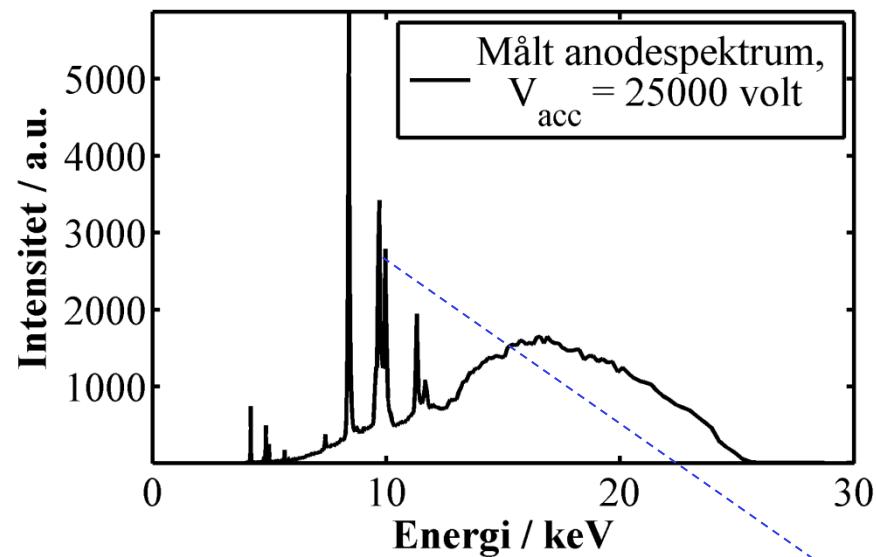
"Missing" photons, because the material in the anode absorbs some of the emitted radiation and most for lower energies

- This is called self-absorption

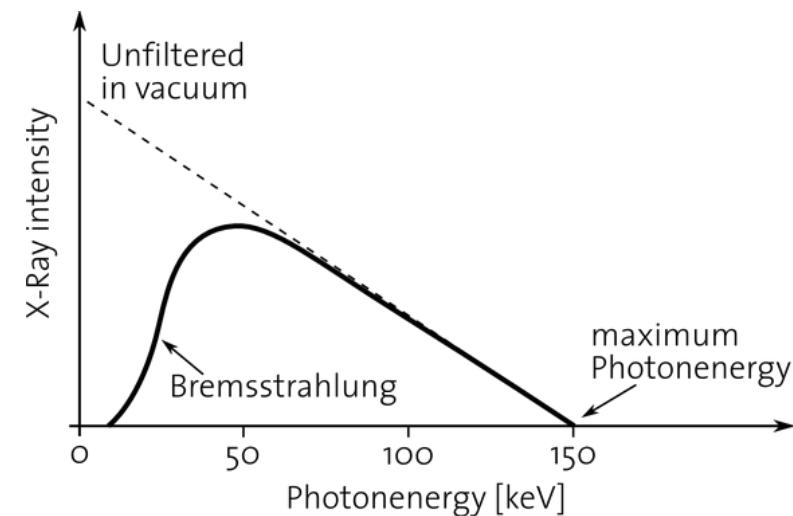
$$\mu \propto \sigma_a = f(Z^4, E_\gamma^{-3})$$

(Spectrum: Intensity as a function of wavelength/frequence/energy)

Measurement of the x-ray tube spectrum
in our own x-ray setups in Nanoteket

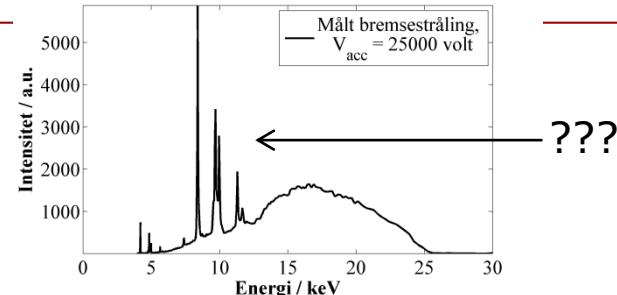


Actual Bremsstrahlung-spectrum



???

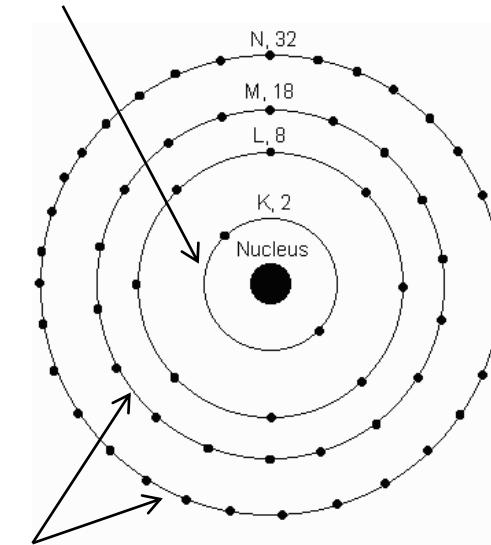
X-ray tube – Characteristic x-rays



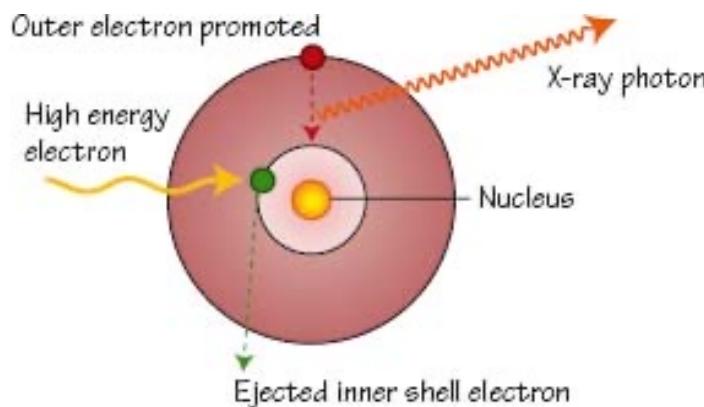
Electrons in the inner shell ("K"-shell) is bound strongest (highest binding energy, 1-100 keV)

The peaks in the spectrum is caused by electrons in the atom are distributed in "shells" with different binding energies

If an electron from an inner shell is ejected an electron from an outer shell will take its place



Electrons in the outer shells are bound more loosely (lower binding energy, ~10 eV)

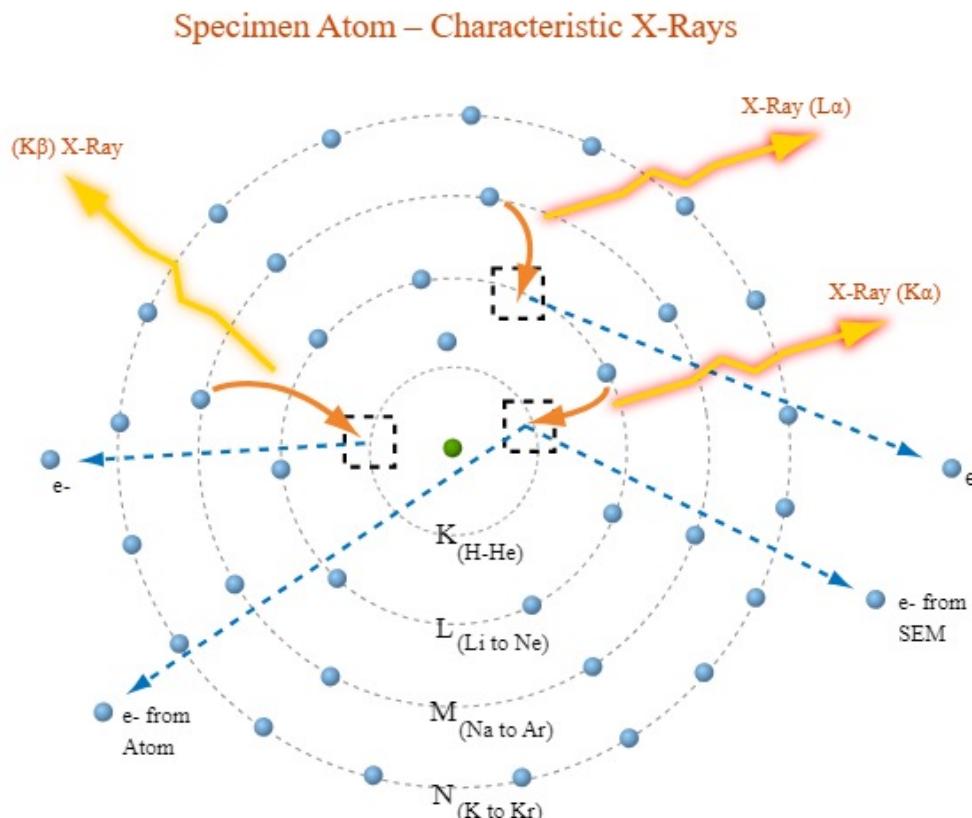


This "relaxation" causes a photon to be emitted with the characteristic energy determined by the energy difference between the "shells" – typically 1-100 keV

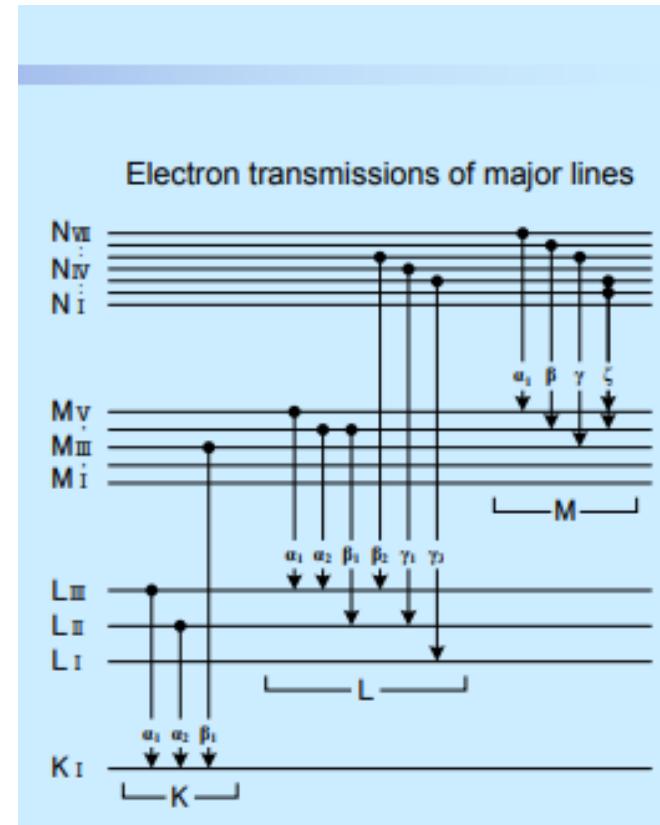
You will measure at this in the x-ray exercise

- Animations

https://myscope.training/EDS_Characteristic_X_ray_generation



The electron transitions involved in generating the $K\alpha$ $K\beta$ and La X-ray photons.



<http://www.ammrf.org.au/myscope/>

Siegbahn notation

- The first component of the name is the element involved, e.g. Si.
- The second component is the electron shell that was ionized to produce the X-ray, e.g. K, L or M.
- The third component reflects the relative intensity of the line within each shell, e.g. α is the most intense line, followed by β and γ .

The lines within each shell make up a family, or series, of lines for that shell, e.g., the K family comprises the $K\alpha$ and $K\beta$ X-ray lines.

e.g. Si $K\alpha$

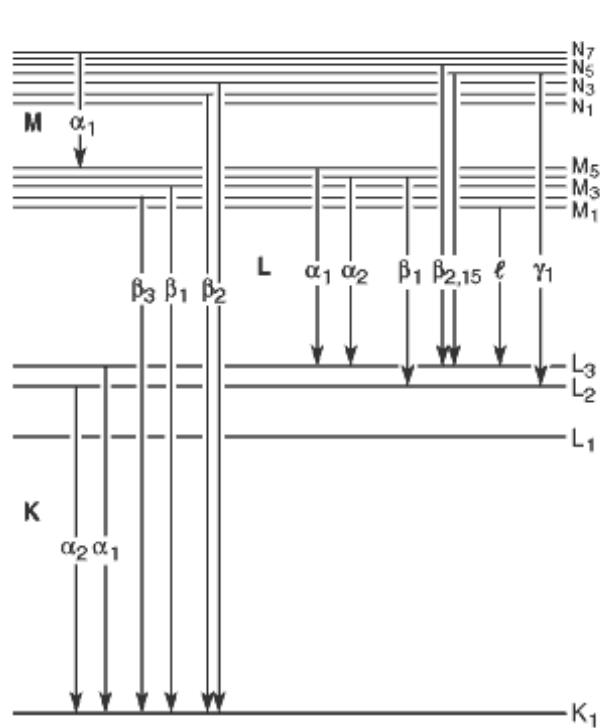
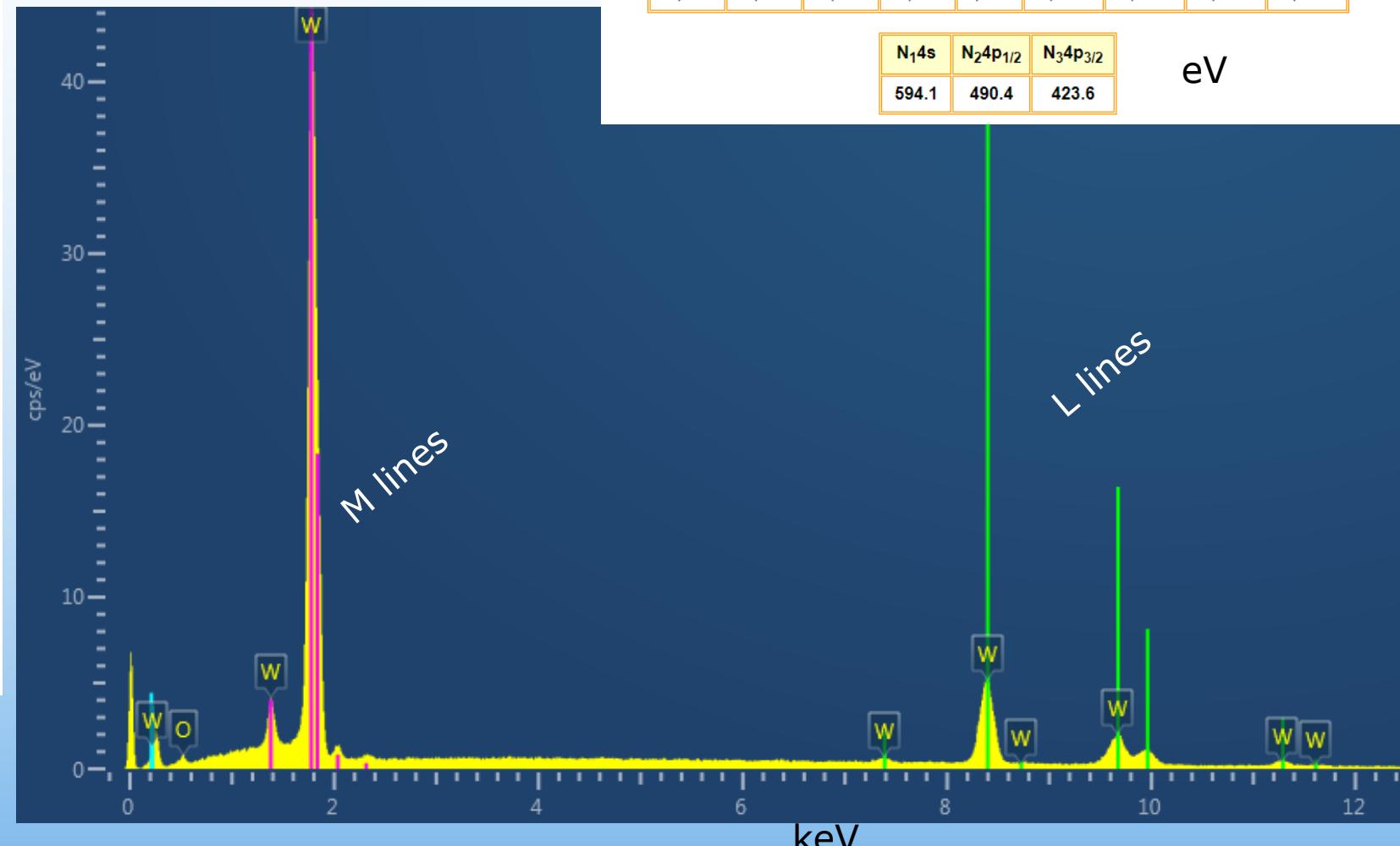
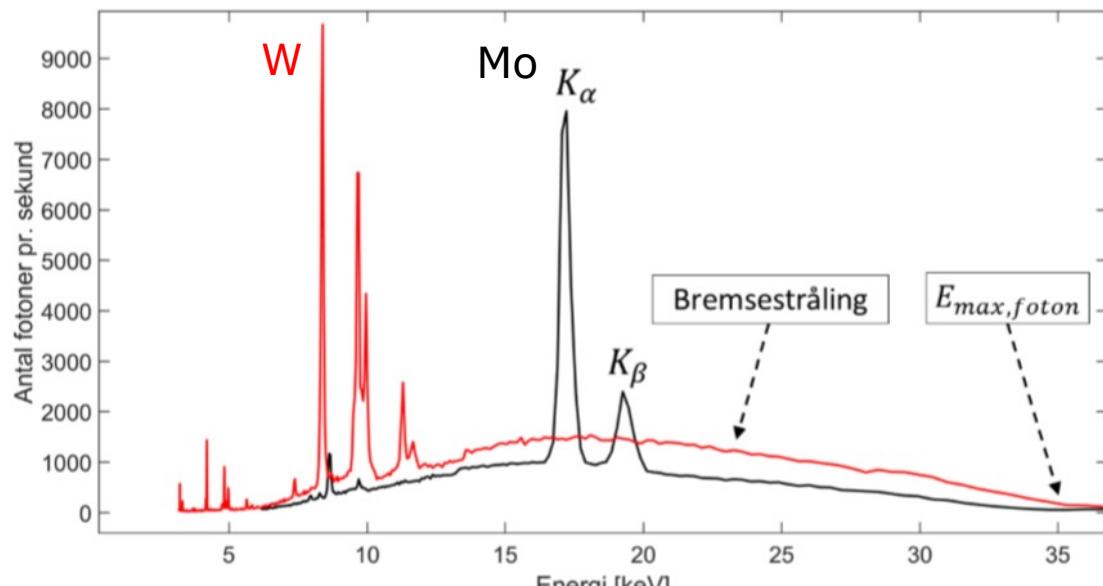


Fig 1-1. Transistions that give rise to the various emission lines.

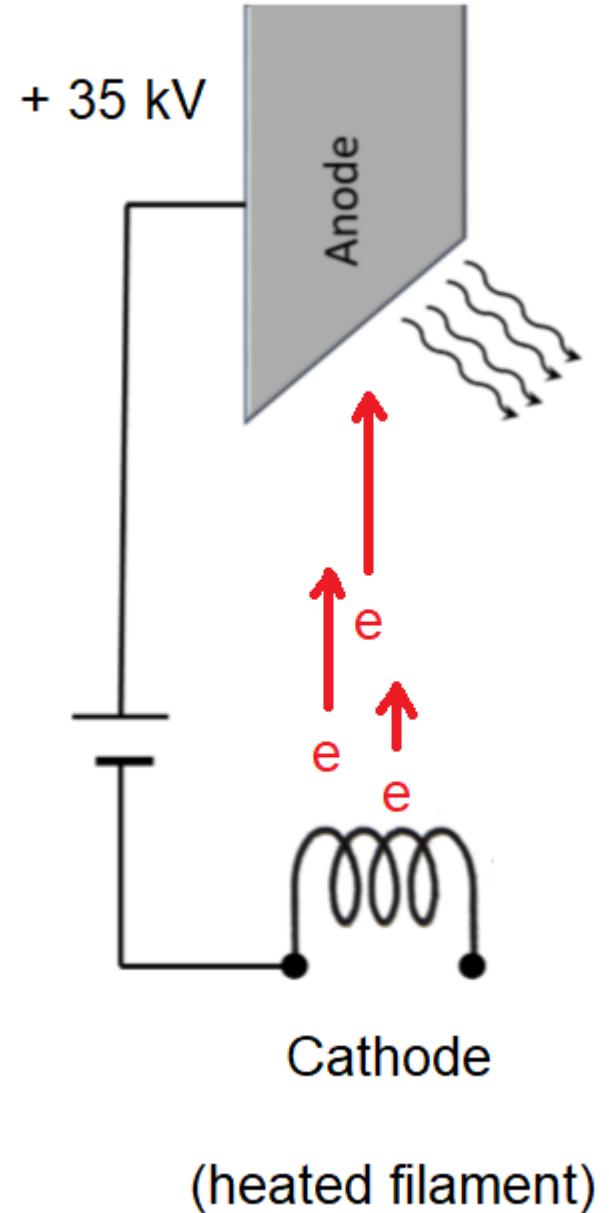


X-rays – how are they produced?

- Acceleration of electrons
- $\Delta E_{kin} = -\Delta E_{pot} = eU_{acc}$
- Deceleration in anode \rightarrow Bremsstrahlung

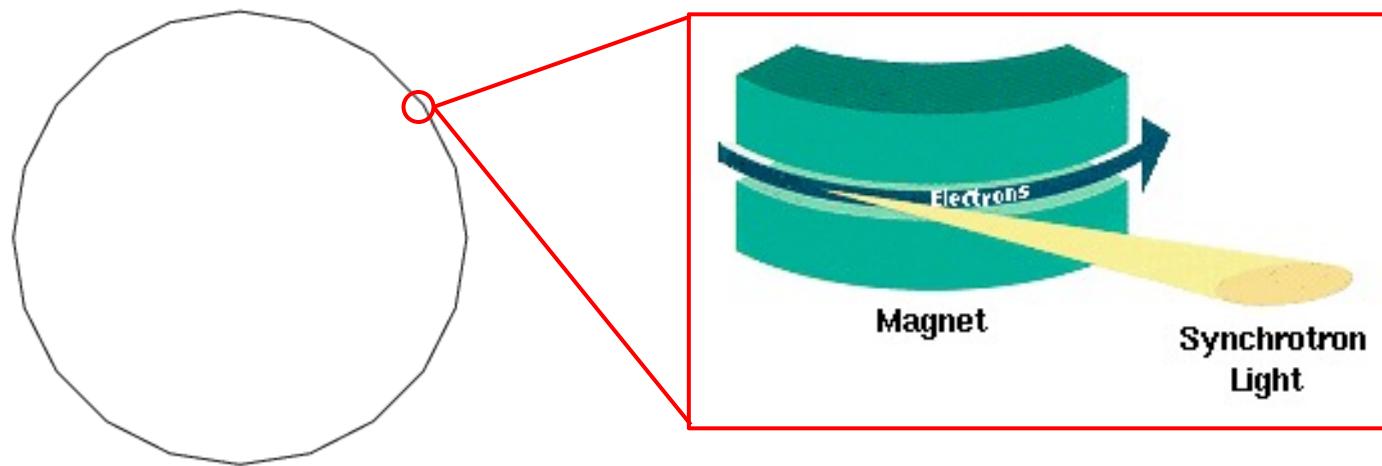
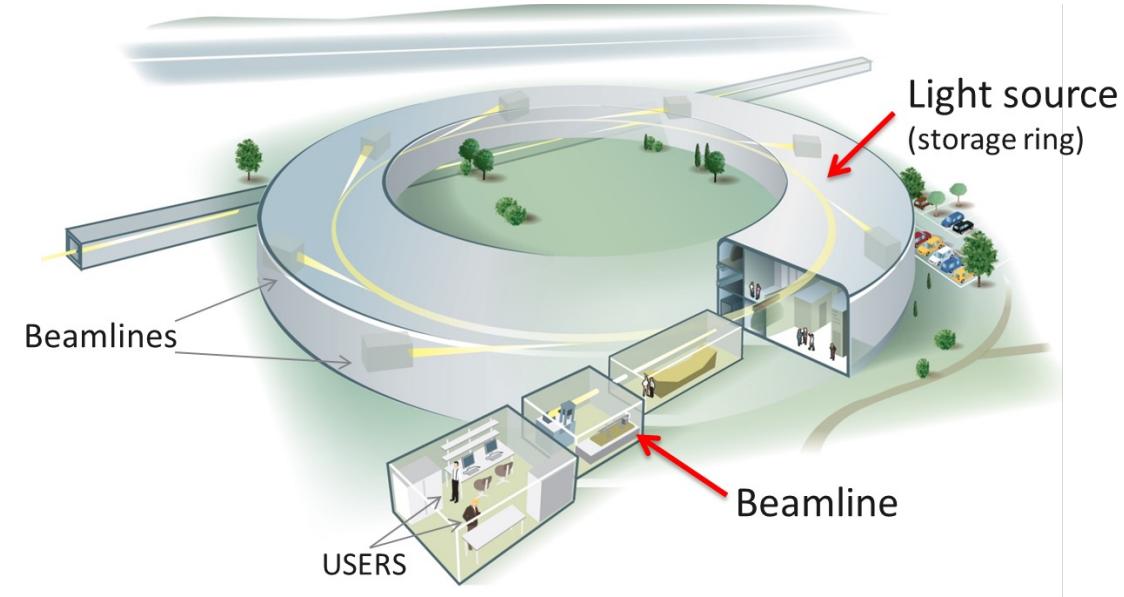


Images adapted from Elisabeth Ulrikkeholt



(heated filament)

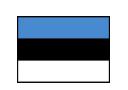
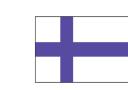
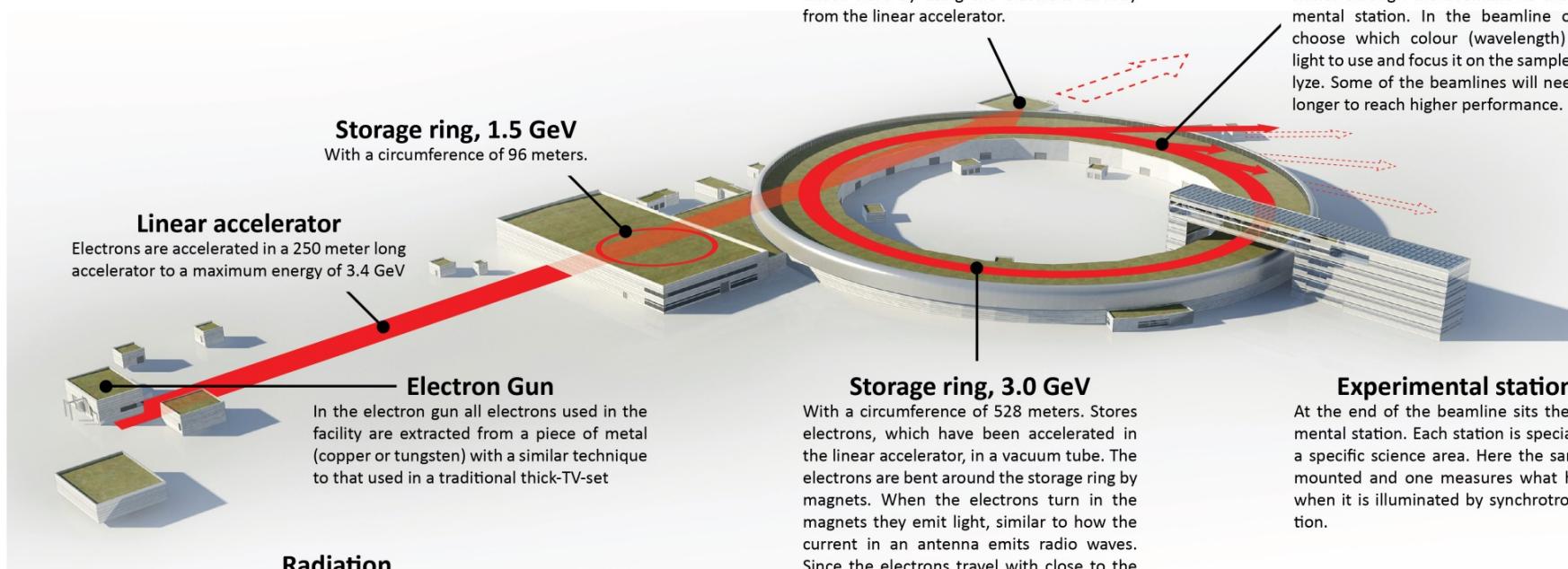
-electron energy ~ GeV



Accelerated electrical charge
↓
Emission of EM radiation

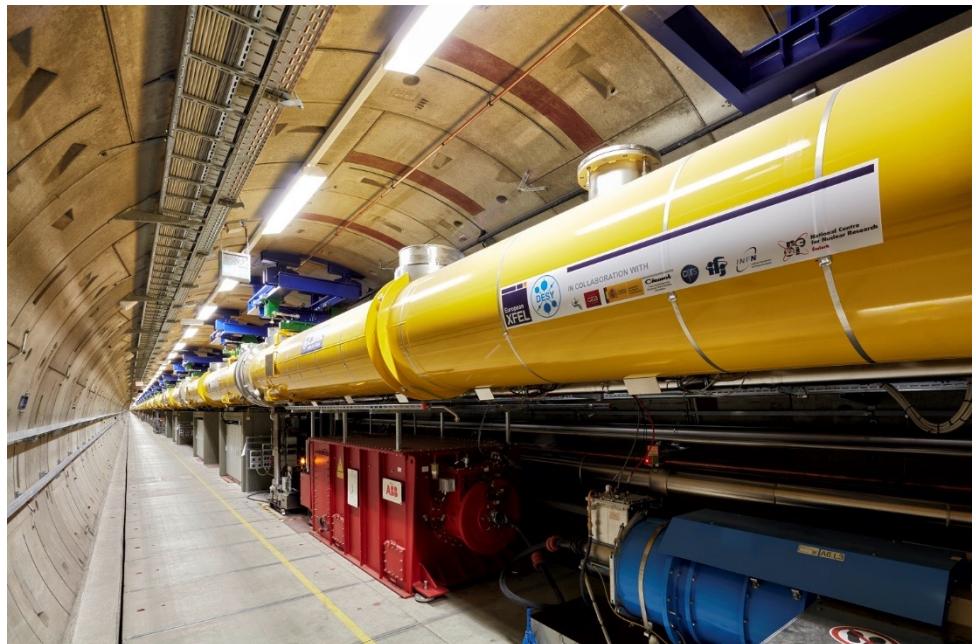
A problem for high energy physics, but great for x-ray science.

MAX IV



Region Skåne

- European XFEL
- (free electron laser)
- note scale bar in photo

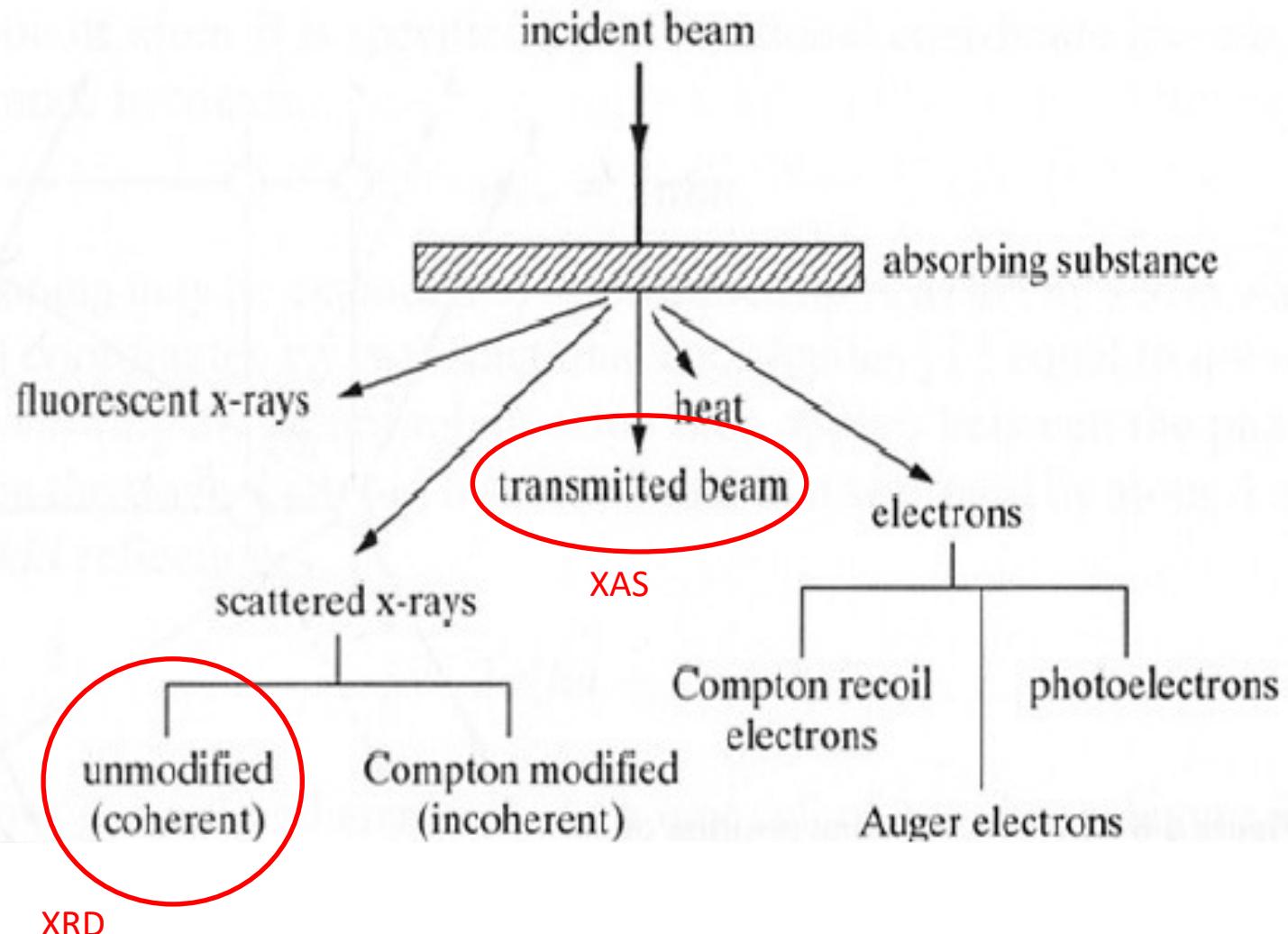


Copyright: European XFEL

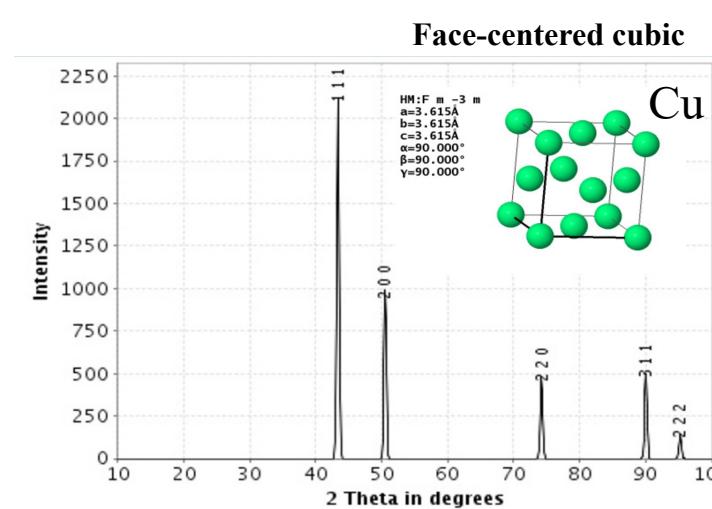
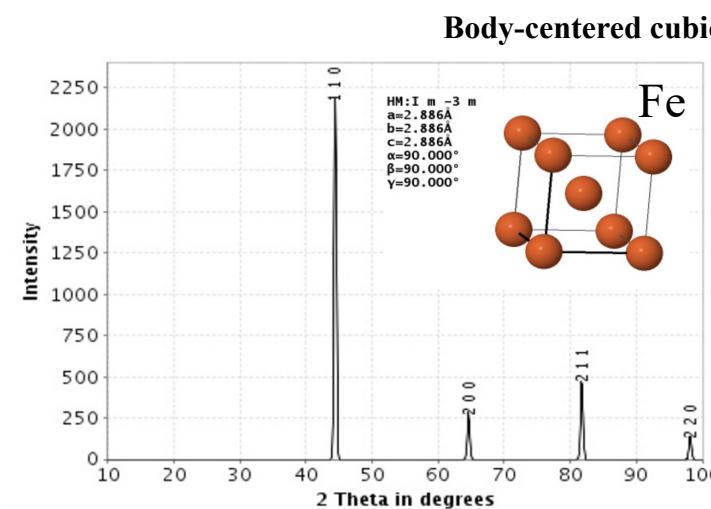
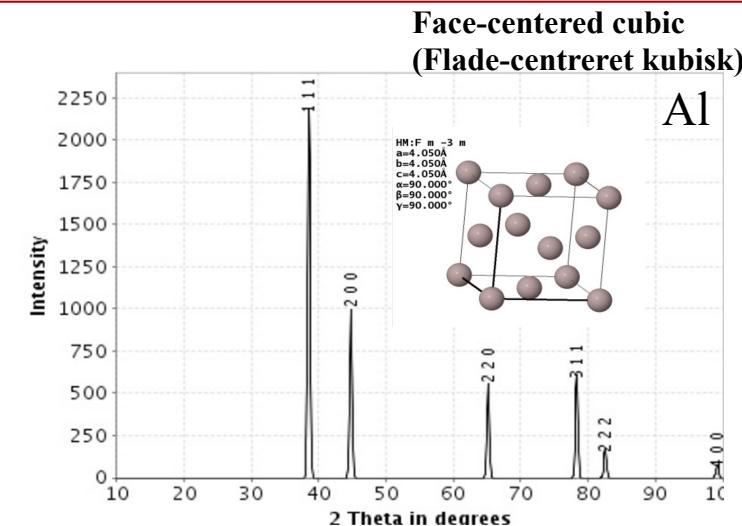
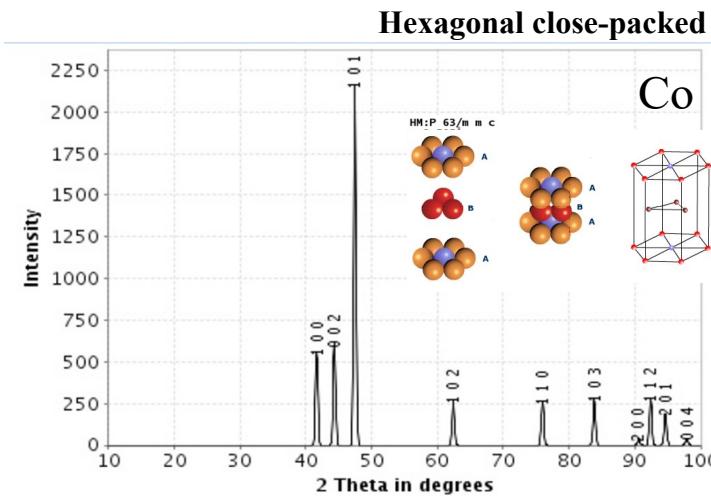


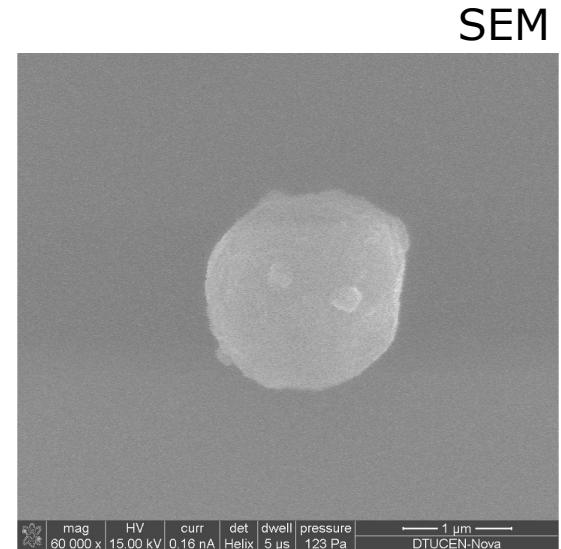
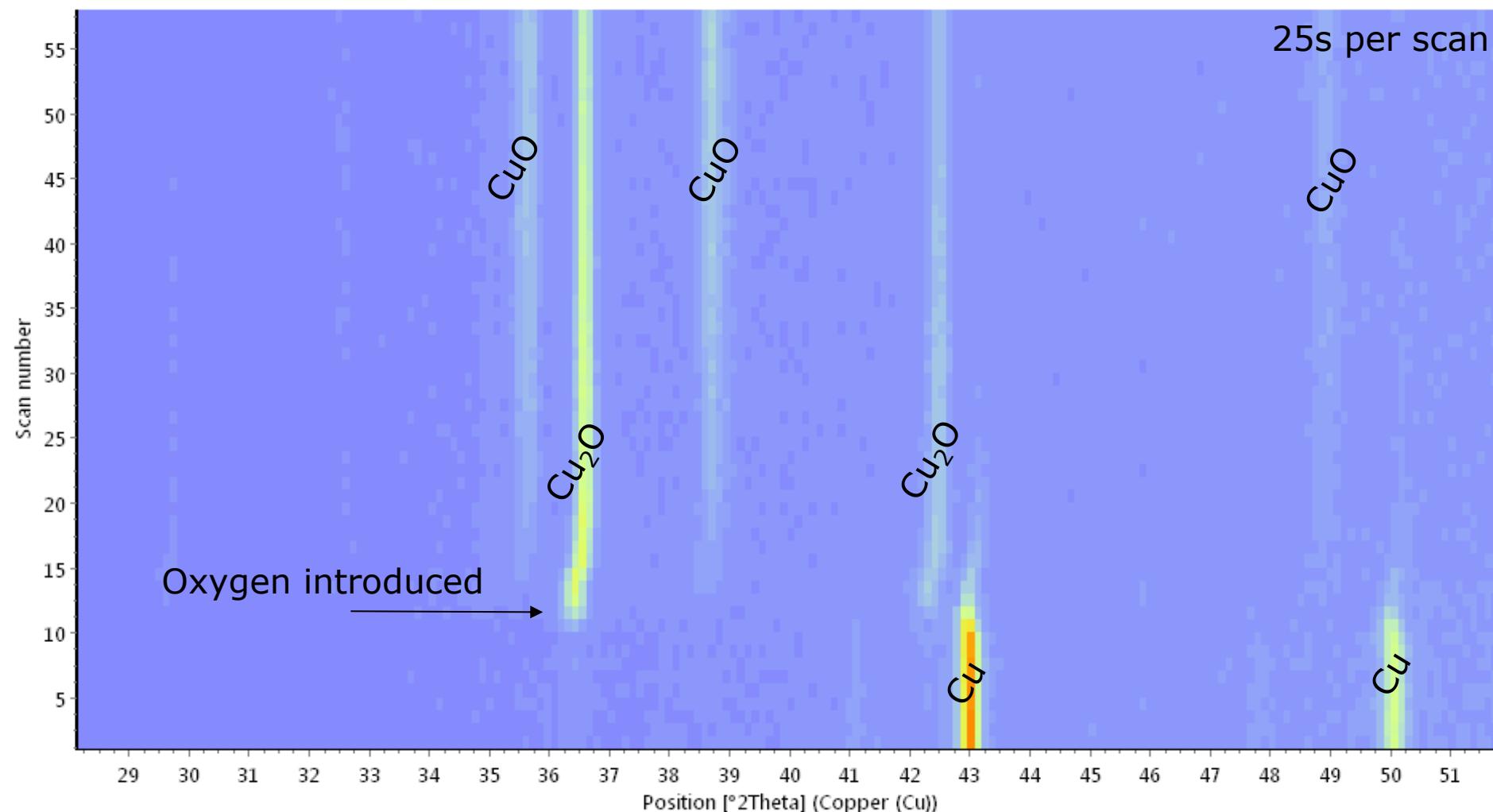
Copyright: European XFEL

Interaction between x-rays and matter

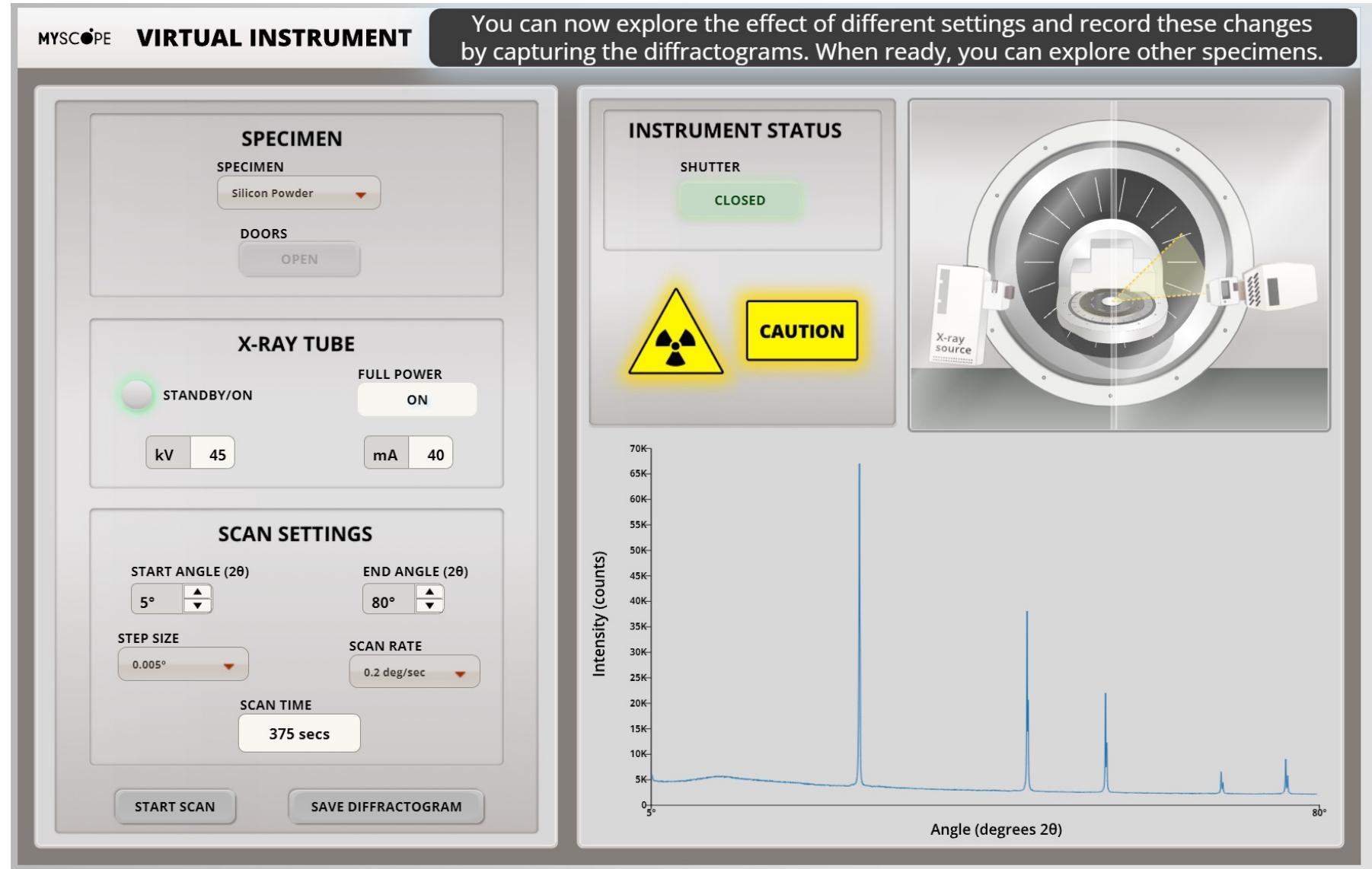


Examples XRD powder patterns

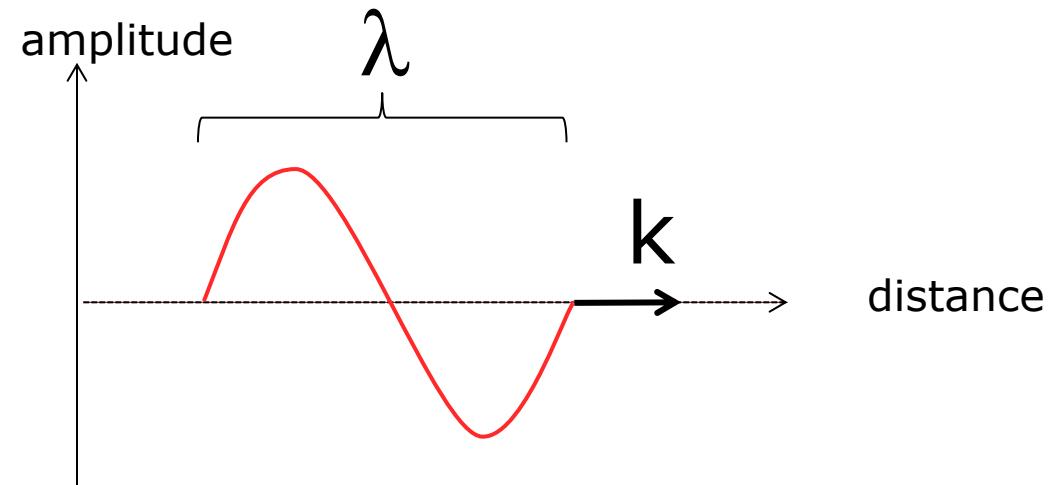




X-ray diffraction (XRD)



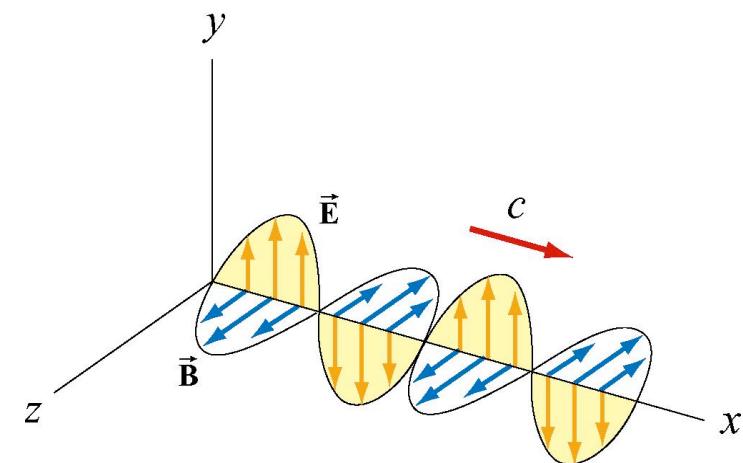
https://myscope.training/XRD_simulator.html

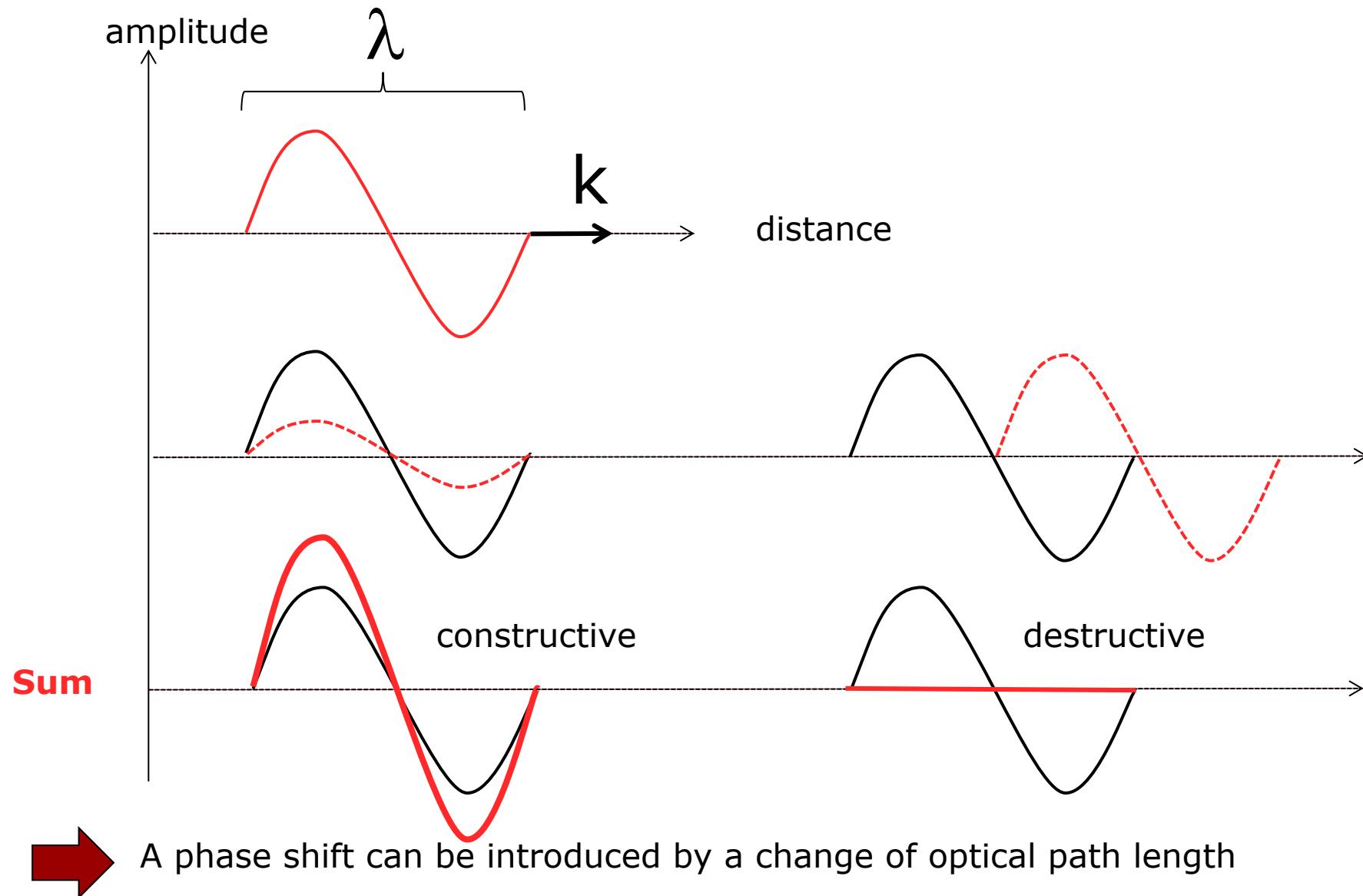


→ Light can be described as a plane wave (electromagnetism)

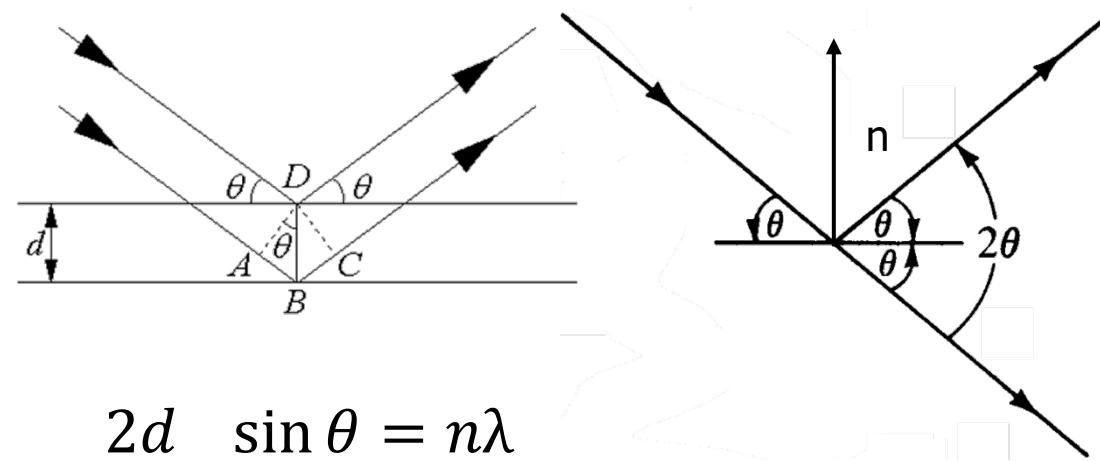
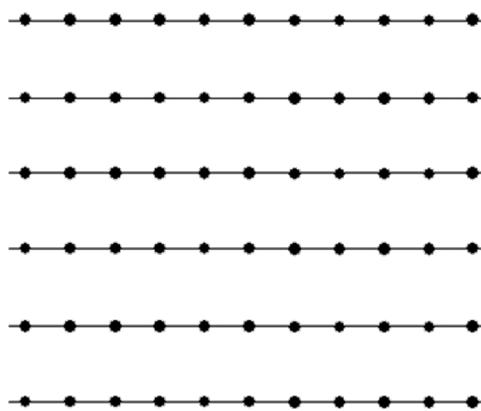
$$\vec{E} = E_y(x, t) \hat{j} = E_0 \sin(kx - \omega t) \hat{j}$$

$$\vec{B} = B_z(x, t) \hat{k} = B_0 \sin(kx - \omega t) \hat{k}$$

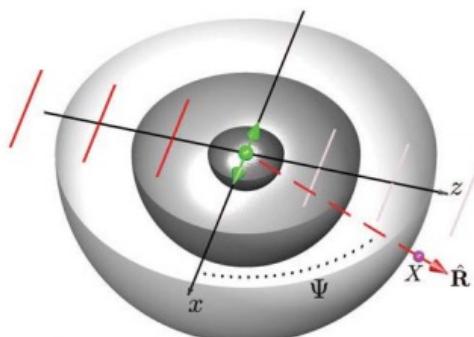




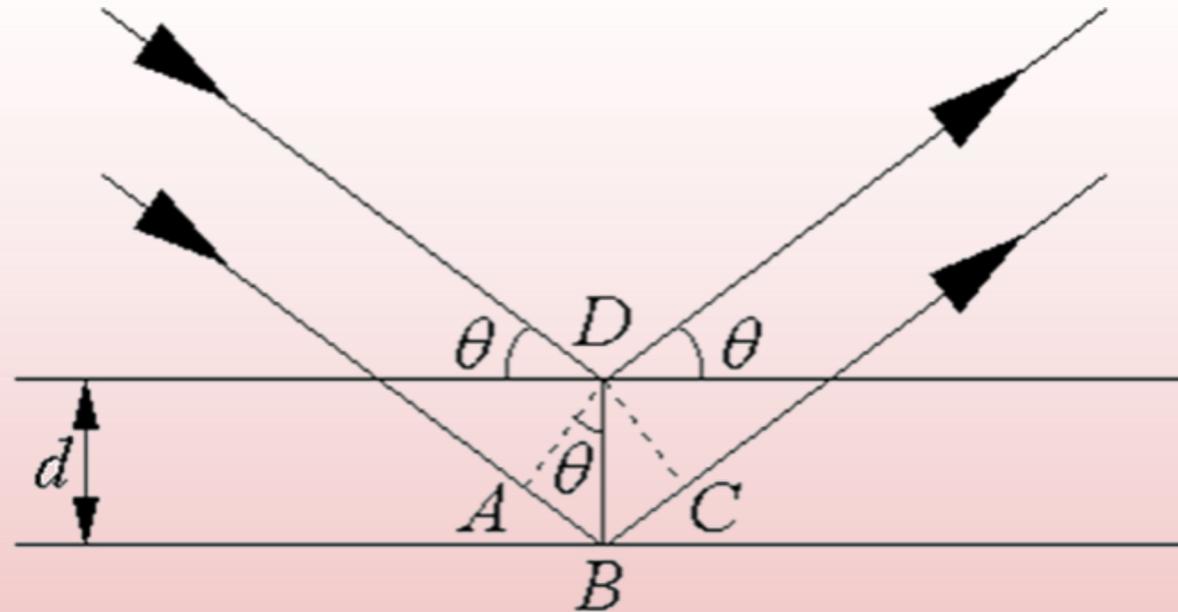
If the path $AB + BC$ is a multiple of the x-ray wavelength λ , then two waves will give a constructive interference:



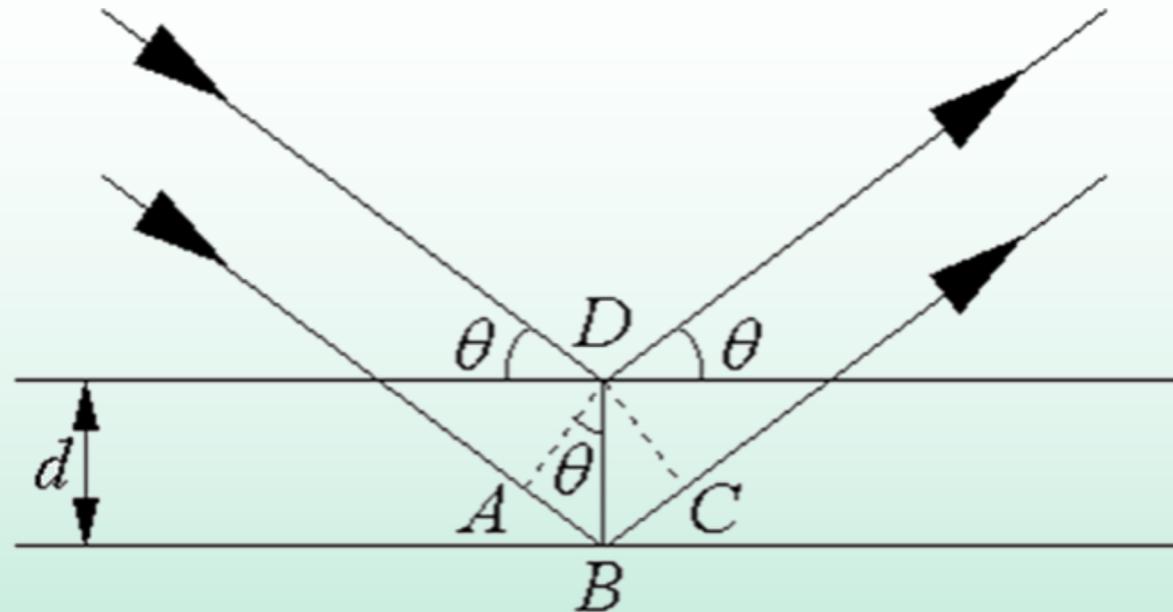
$$2d \sin \theta = n\lambda$$



Derive Braggs law



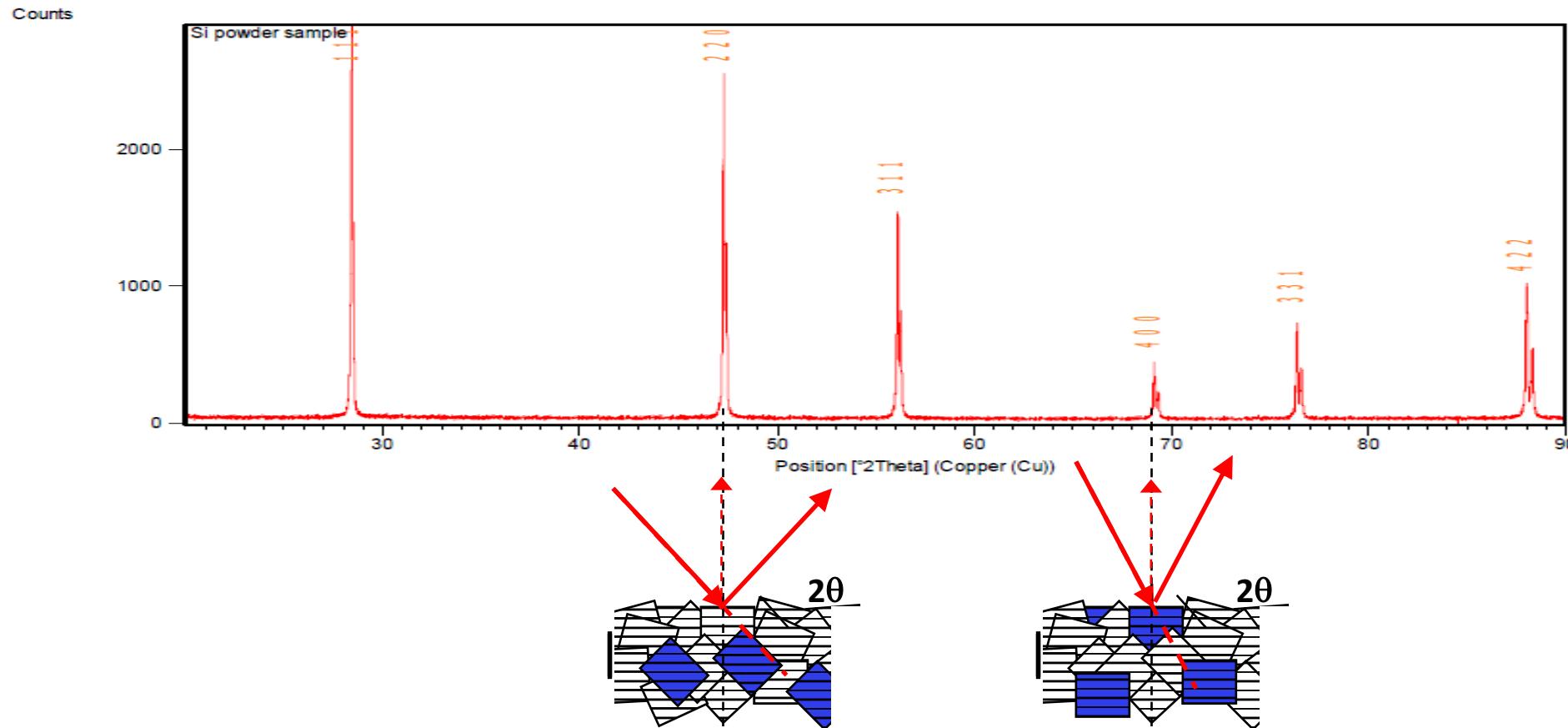
Derive Braggs law – what is required if the two rays should be in phase when exiting the surface?



$$n\lambda = AB + BC = 2d \sin \theta$$

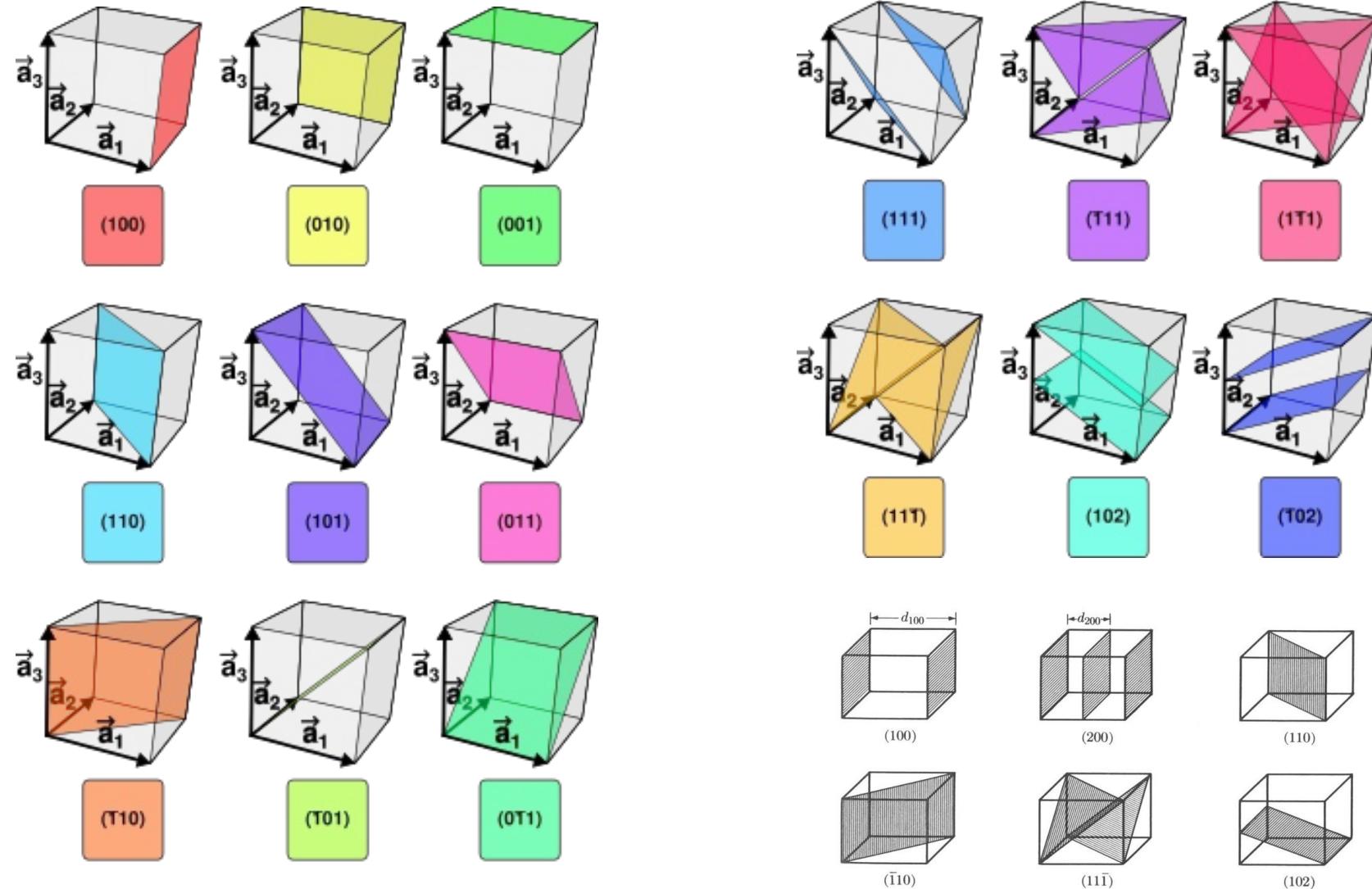
$$2d \sin \theta = n\lambda$$

A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



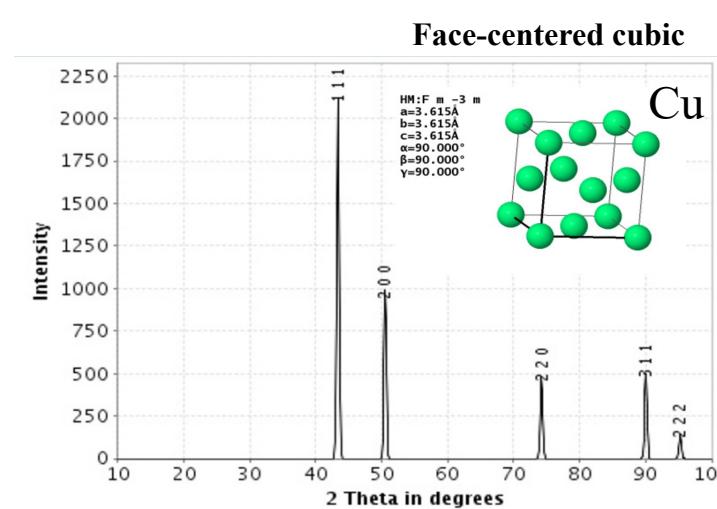
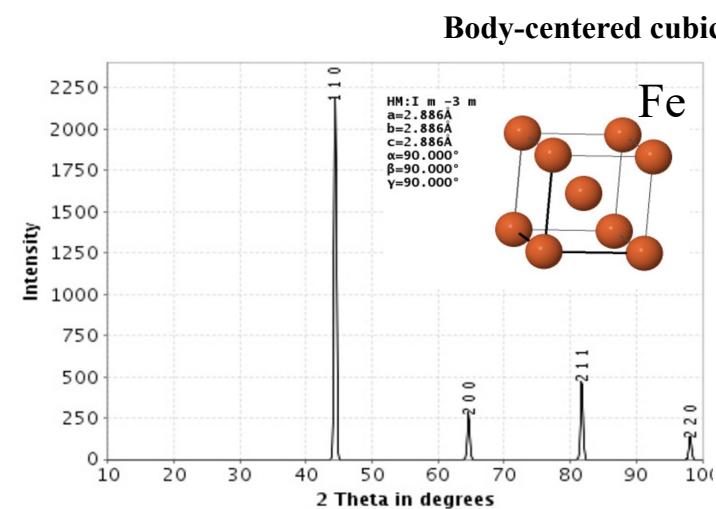
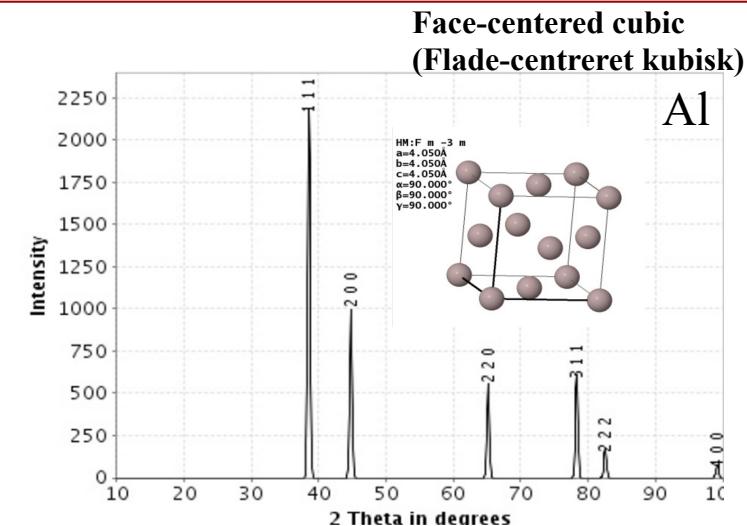
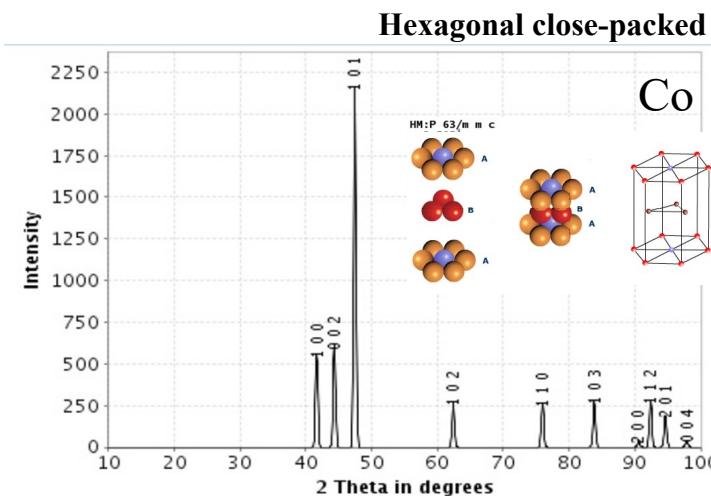
- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Crystal planes (Miller index)



https://en.wikipedia.org/wiki/Miller_index

Examples XRD powder patterns

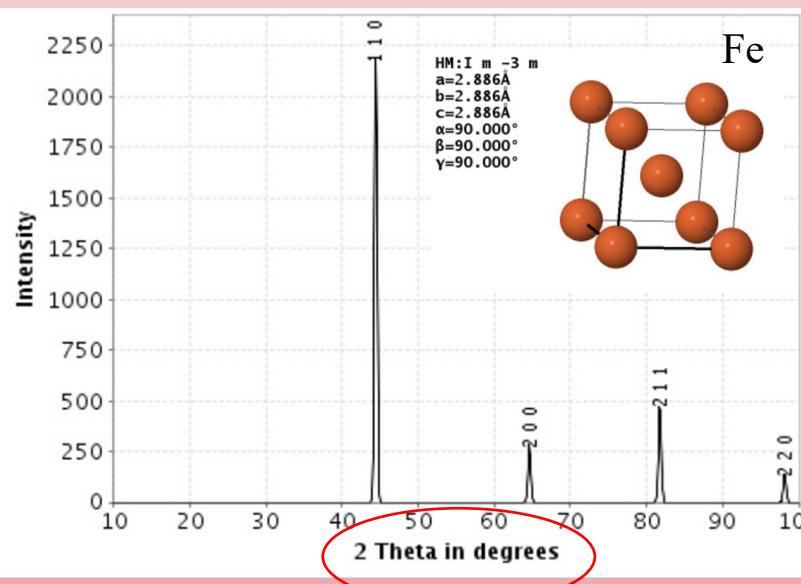
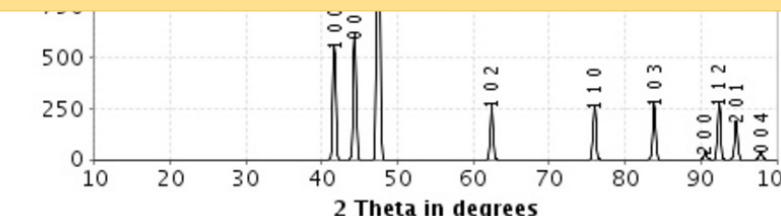


Examples XRD powder patterns

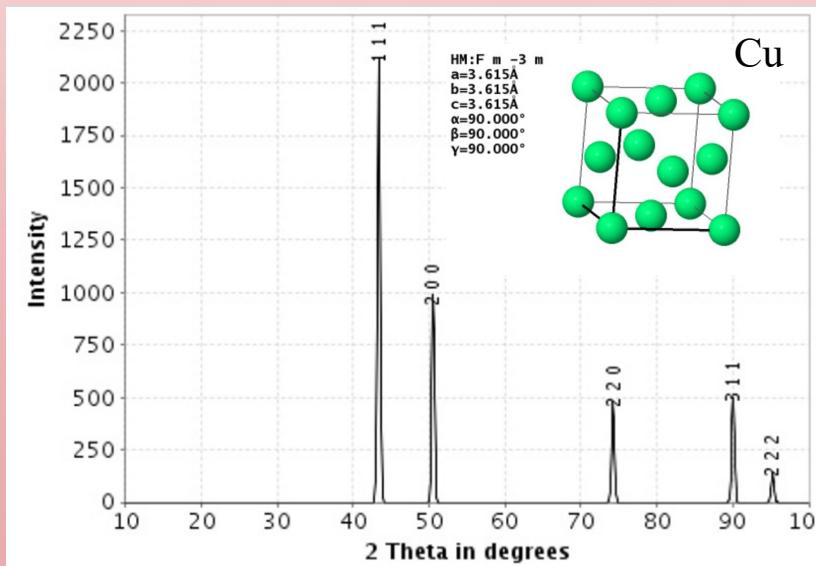
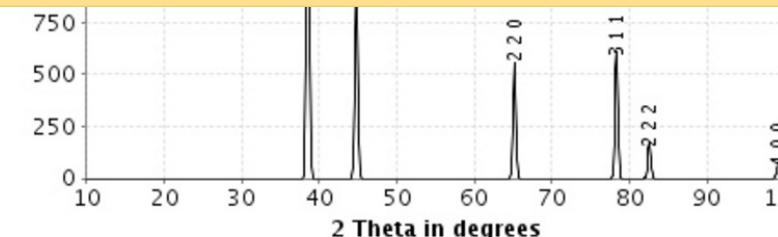
Which wavelength have been used to make these patterns?

$$d_{\text{Fe},110} = 2.04 \text{ \AA}$$

$$2d_{hkl} \sin \theta = \lambda$$



What is the interplanar distance of the {111}-planes in FCC Cu?



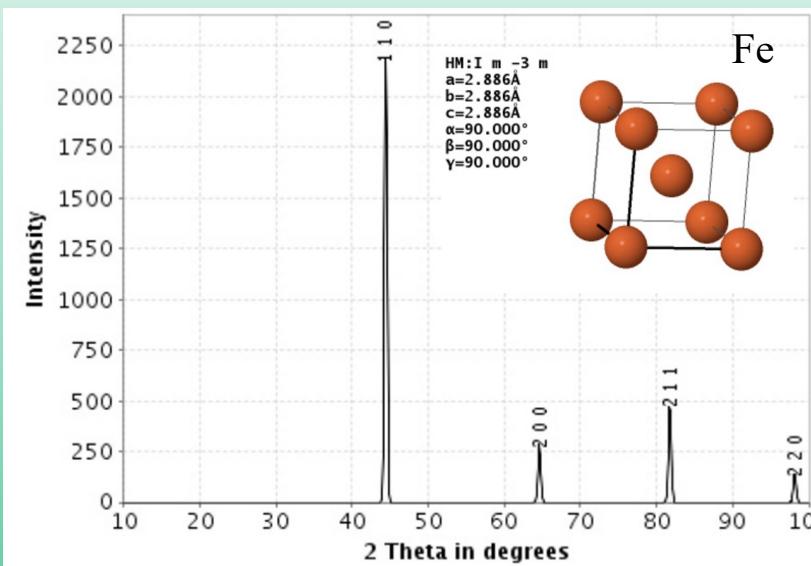
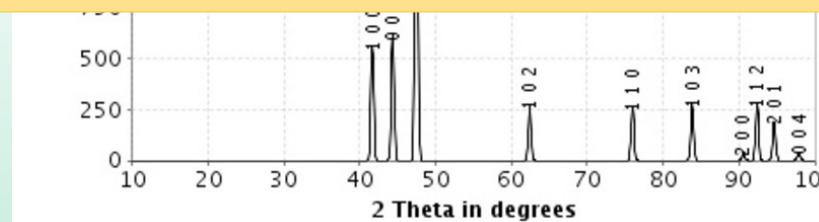
Examples XRD powder patterns

Which wave lenght have been used to make these patterns?

$$d_{\text{Fe},110} = 2.04 \text{ \AA}$$

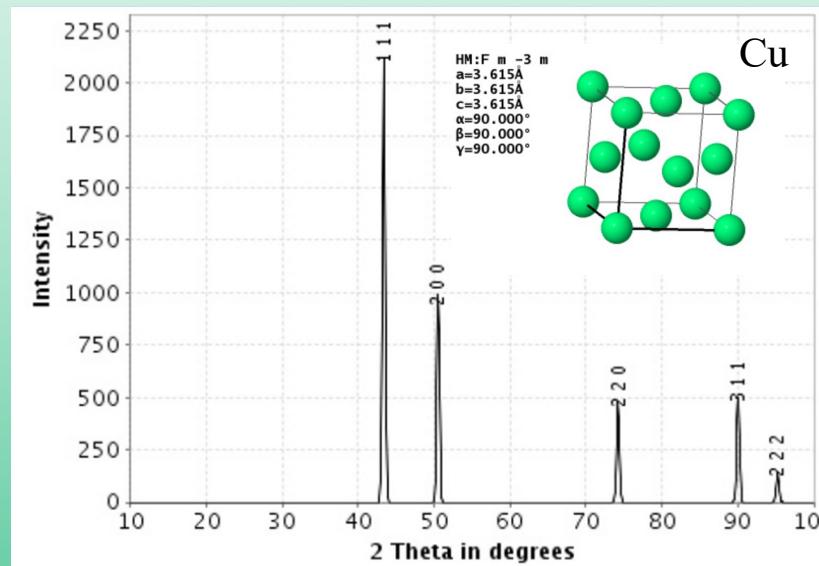
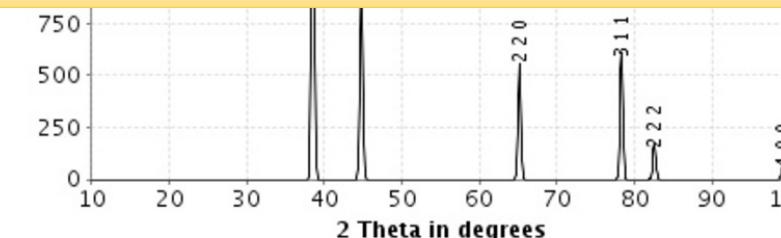
$$1.54 \text{ \AA} \sim \text{Cu}_{\text{k}\alpha}$$

$$2d_{hkl} \sin \theta = \lambda$$



What is the interplanar distance of the {111}-planes in FCC Cu?

$$d_{\text{Cu},111} = 2.08 \text{ \AA}$$



X-ray absorption spectroscopy XAS – element specific

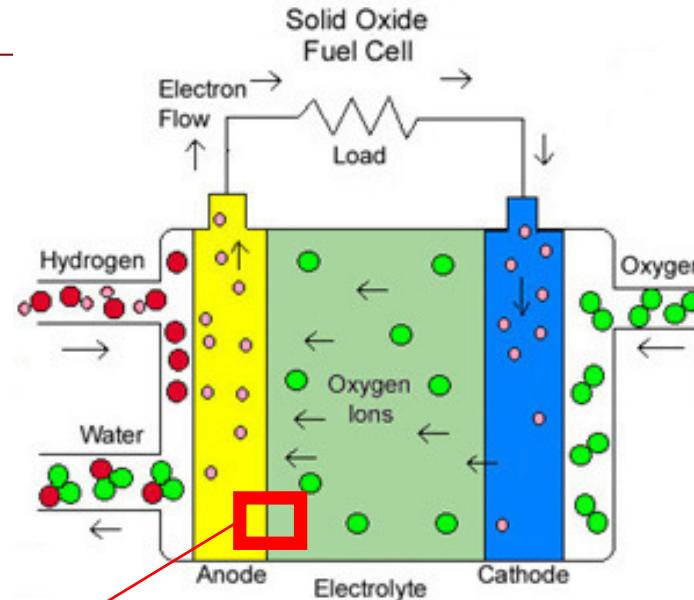
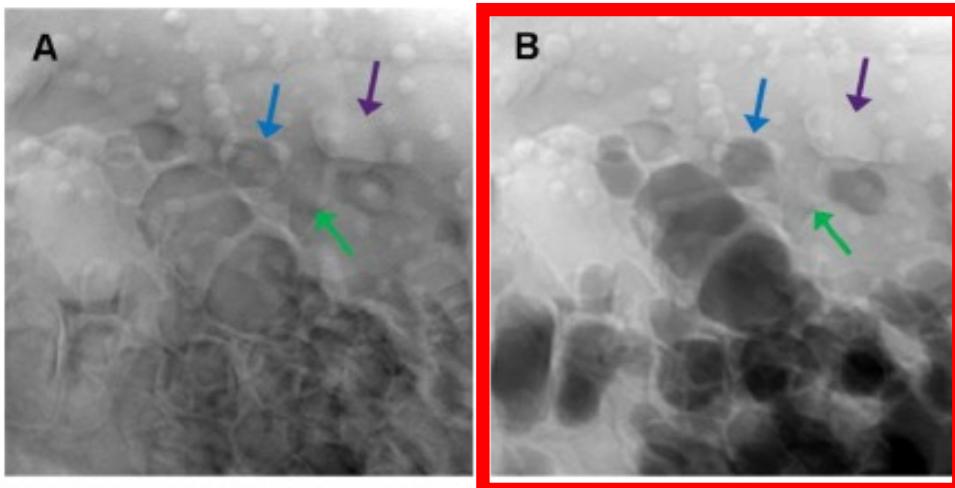
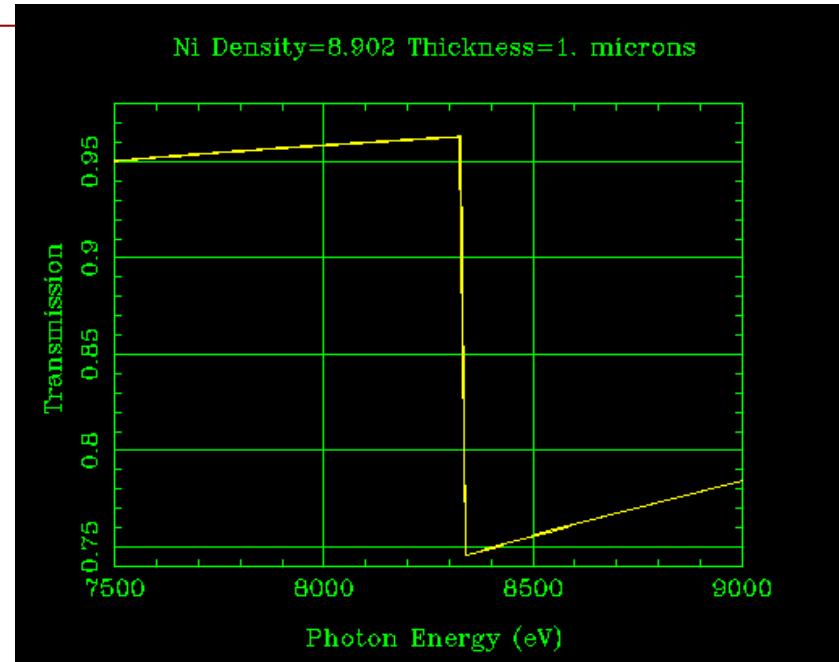
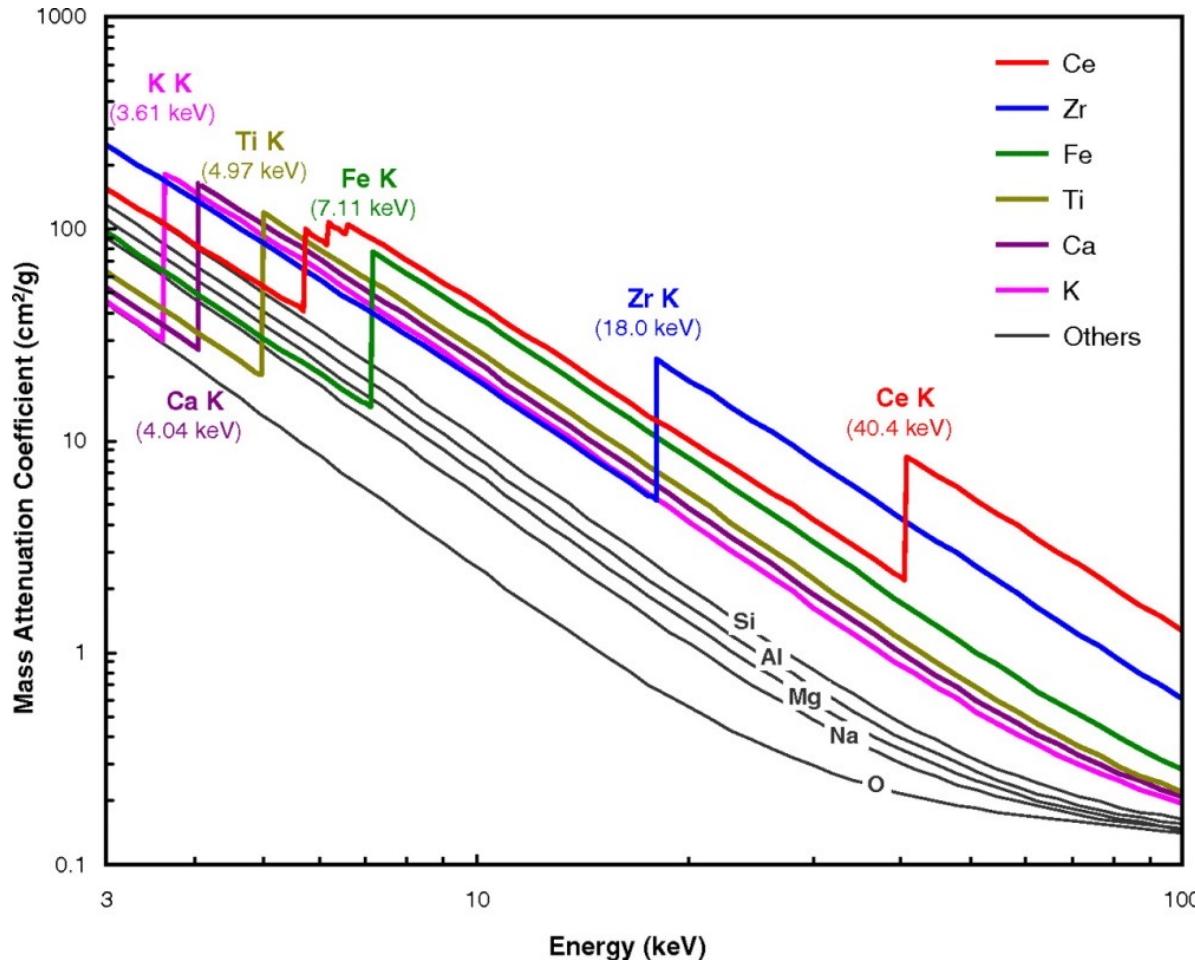


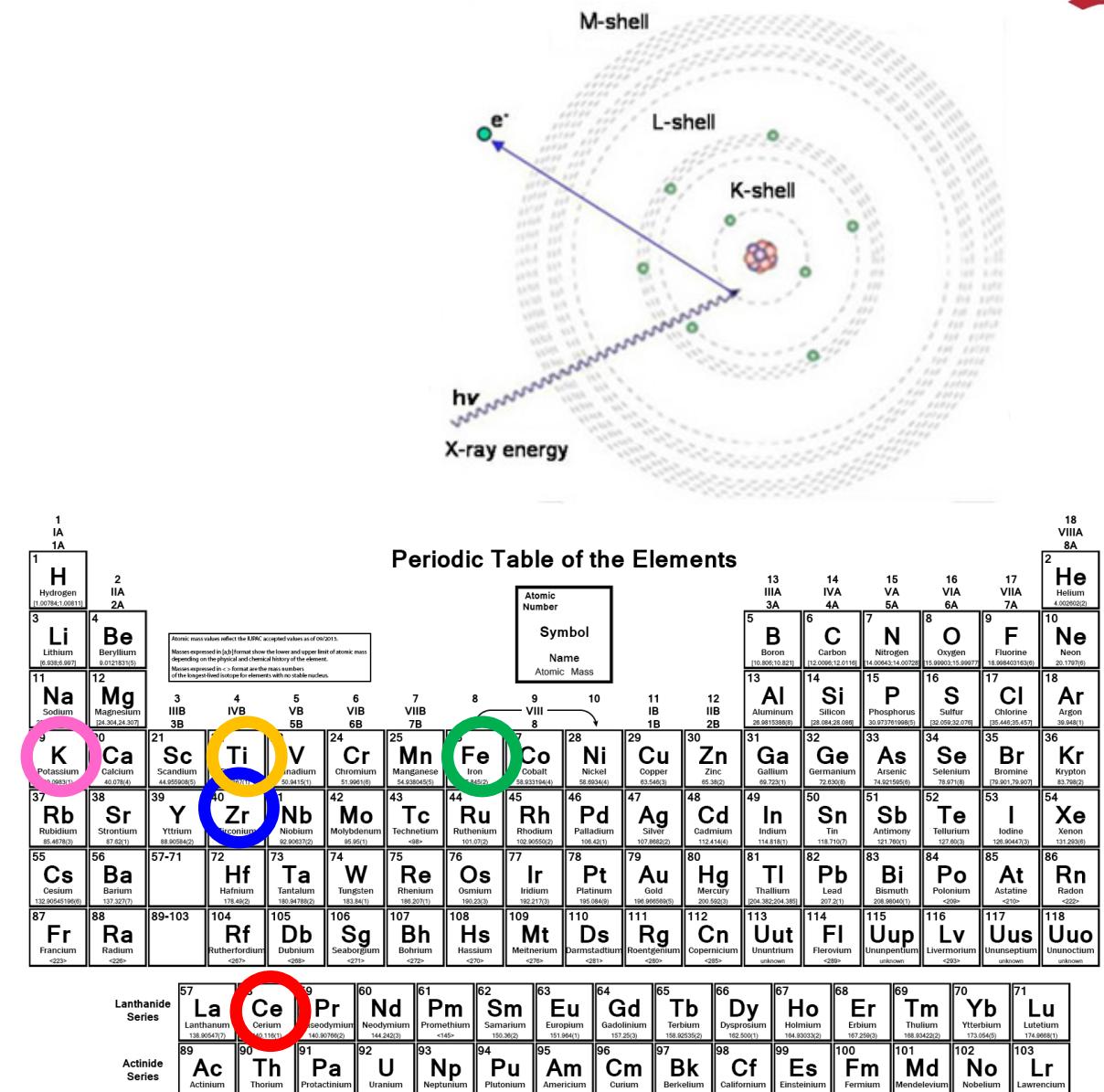
Figure 2. 'Color online' X-ray micrographs of the porous Ni-YSZ sample taken 'a' 16 eV below and 'b' 24 eV above the Ni K-edge of 8.333 keV with a spatial resolution of 38.5 nm. Darker tone indicates higher absorption. A projection of the reconstructed 3D

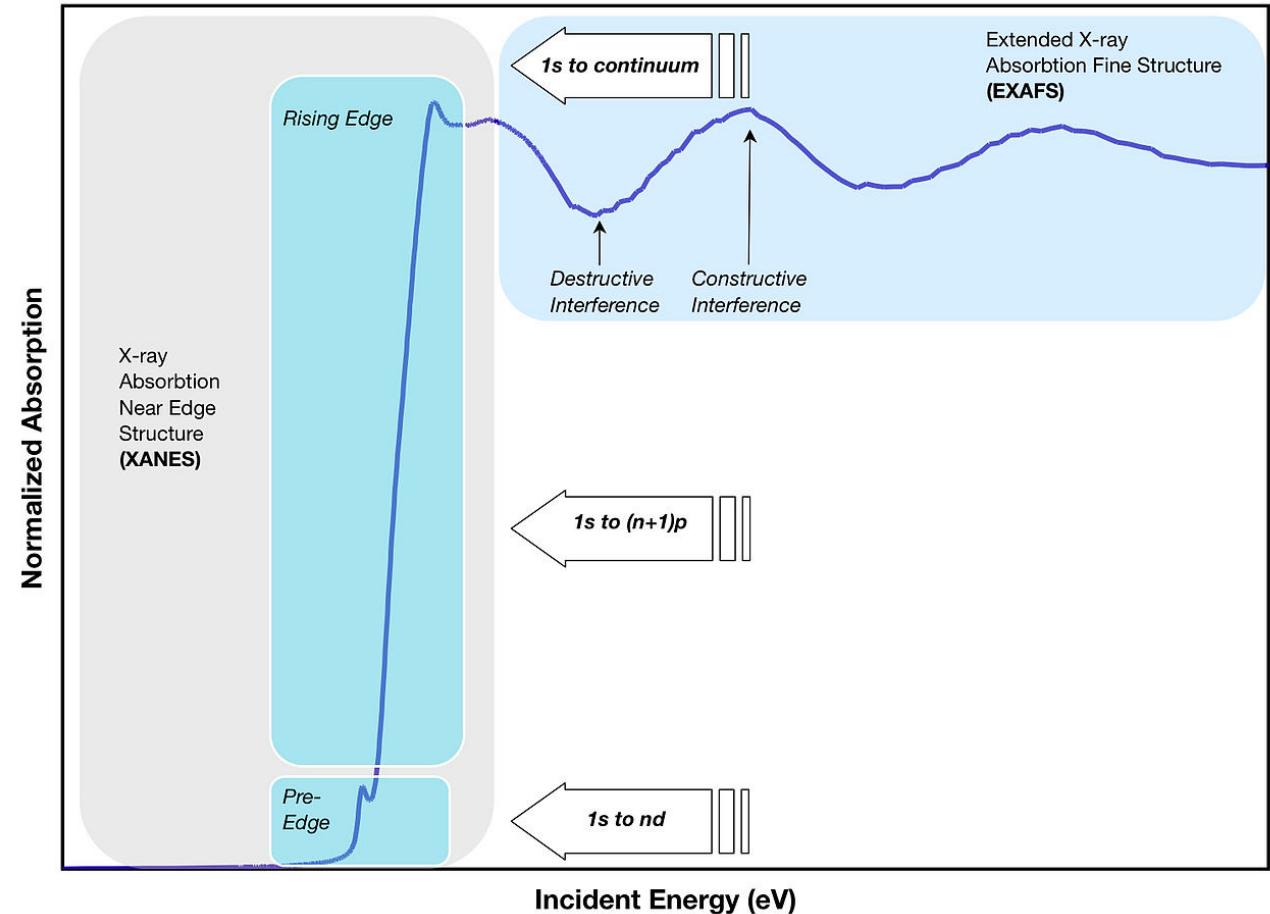
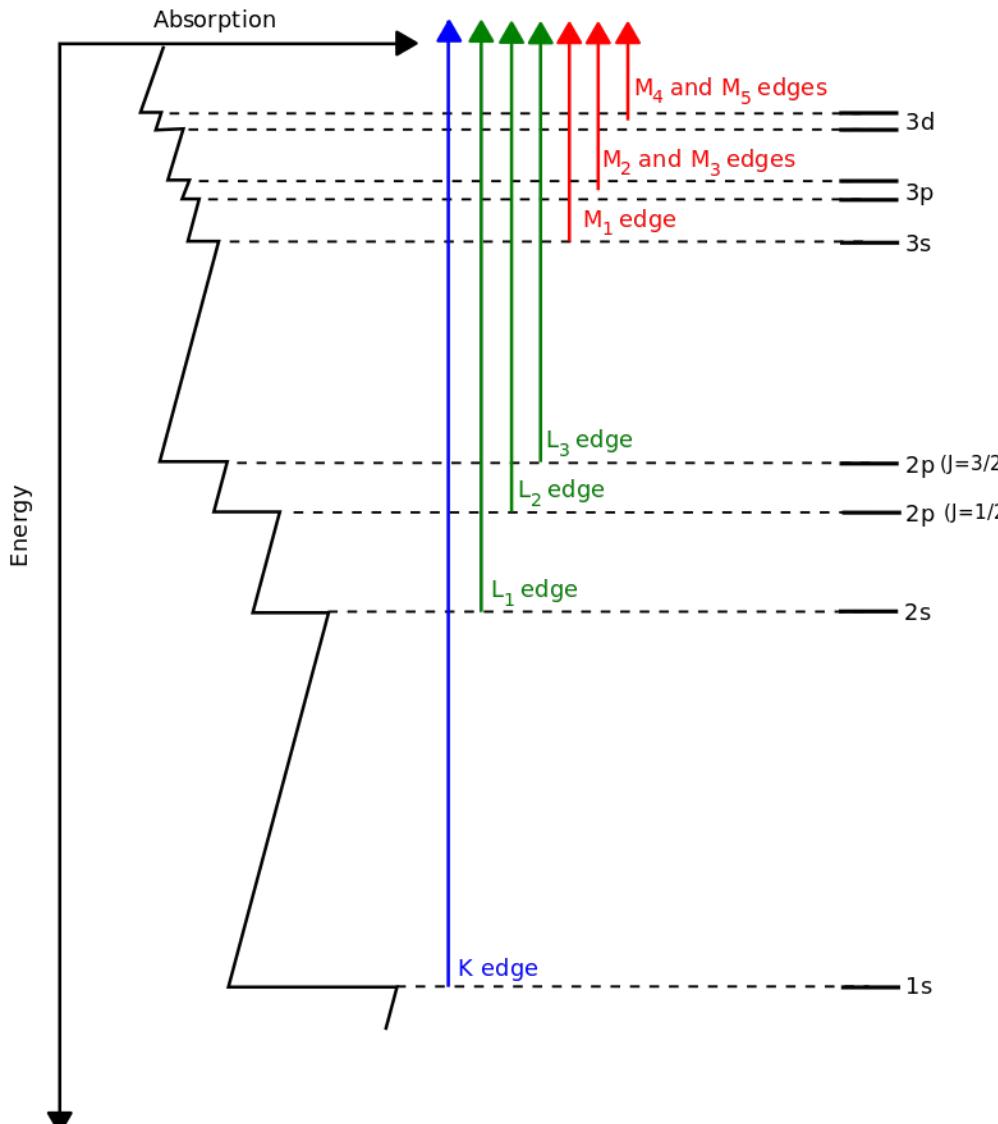
Nondestructive Nanoscale 3D Elemental Mapping and Analysis of a Solid Oxide Fuel Cell Anode, Grew et al., 2010

X-ray absorption



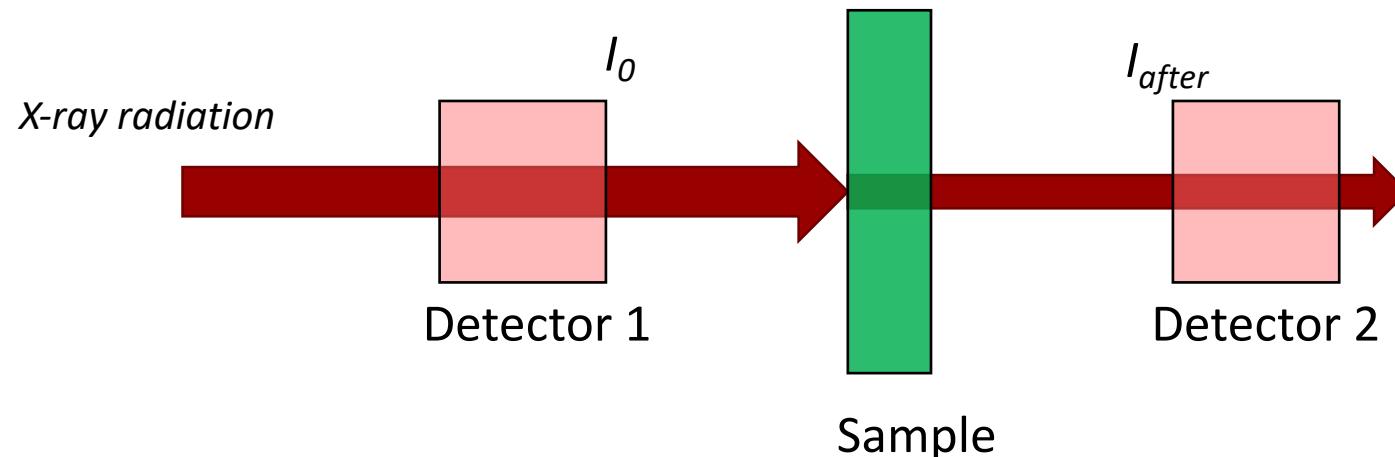
$$\mu \propto \sigma_a = f(Z^4, E_\gamma^{-3})$$





https://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy#/media/File:XASEdges.svg

https://en.wikipedia.org/wiki/X-ray_absorption_spectroscopy#/media/File:XASFig.jpg

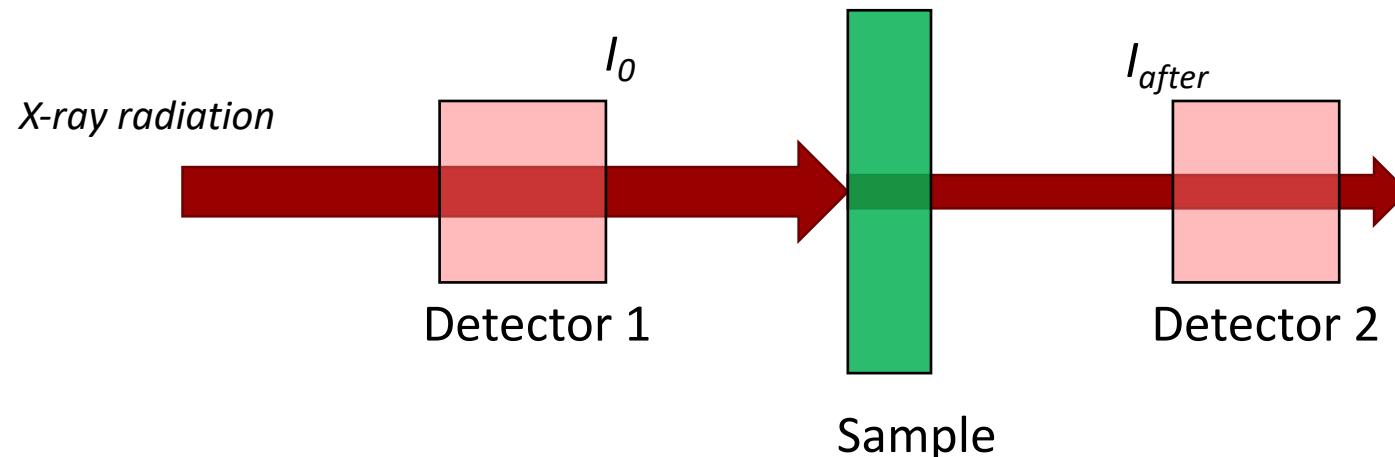


- Incident x-ray radiation with "varying" energy (wavelength) is measured with detector 1 and hits the sample
- The transmitted signal is measured with detector 2

$$\text{Transmission } T = I_{after} / I_0$$

$$\mu = -\ln \frac{I(z)}{I_0} / z$$

X-ray spectroscopy – XAS with only one detector?

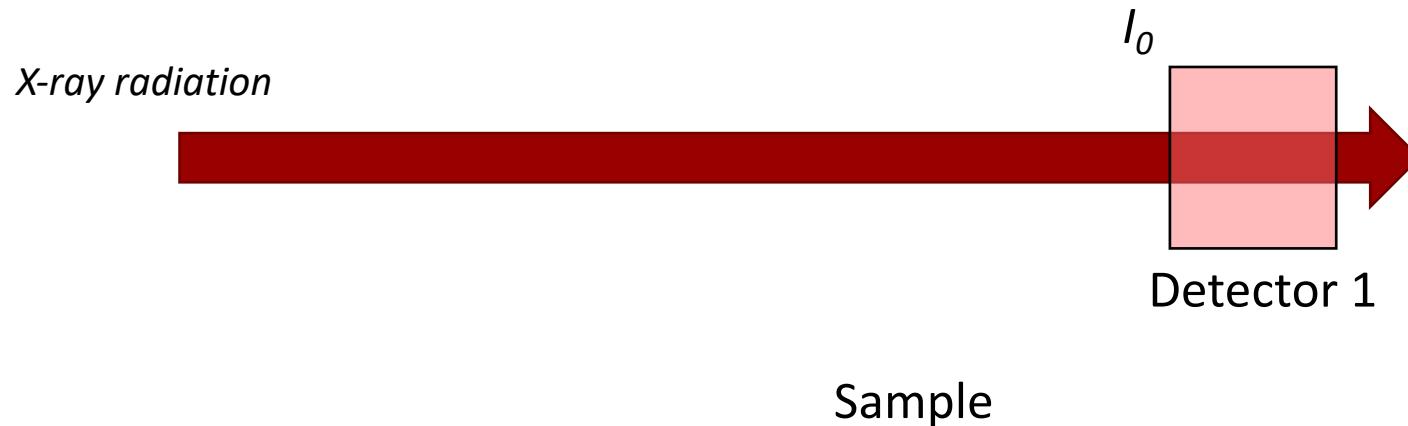


- Incident x-ray radiation with "varying" energy (wavelength) is measured with detector 1 and hits the sample
- The transmitted signal is measured with detector 2

$$\text{Transmission } T = I_{\text{after}} / I_0$$

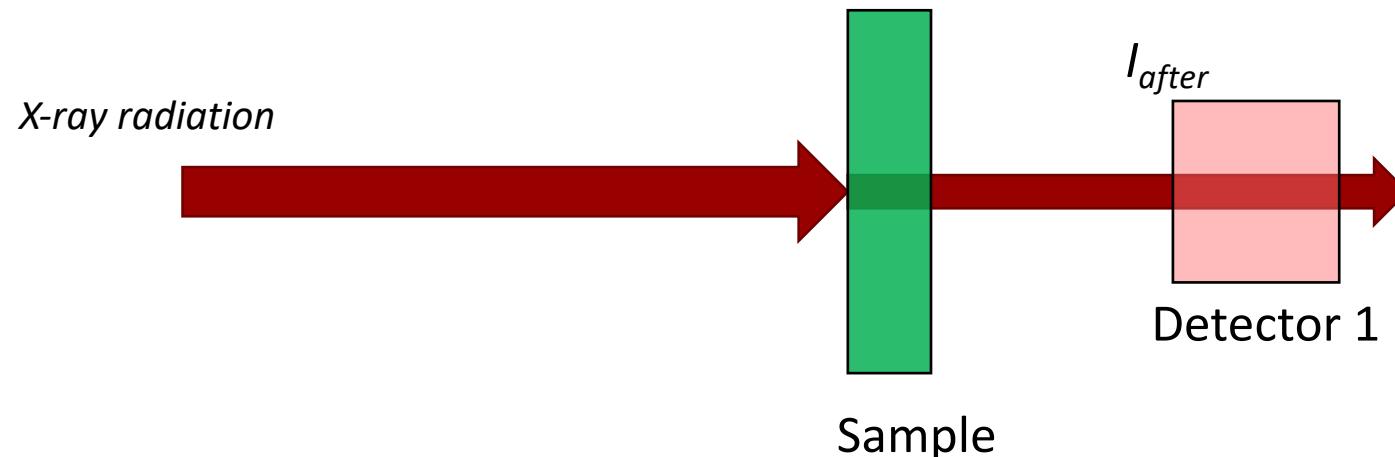
$$\mu = -\ln \frac{I(z)}{I_0} / z$$

X-ray spectroscopy – XAS with only one detector?



- Incident x-ray radiation with "varying" energy (wavelength) is measured with detector 1 without sample

X-ray spectroscopy – XAS with only one detector?

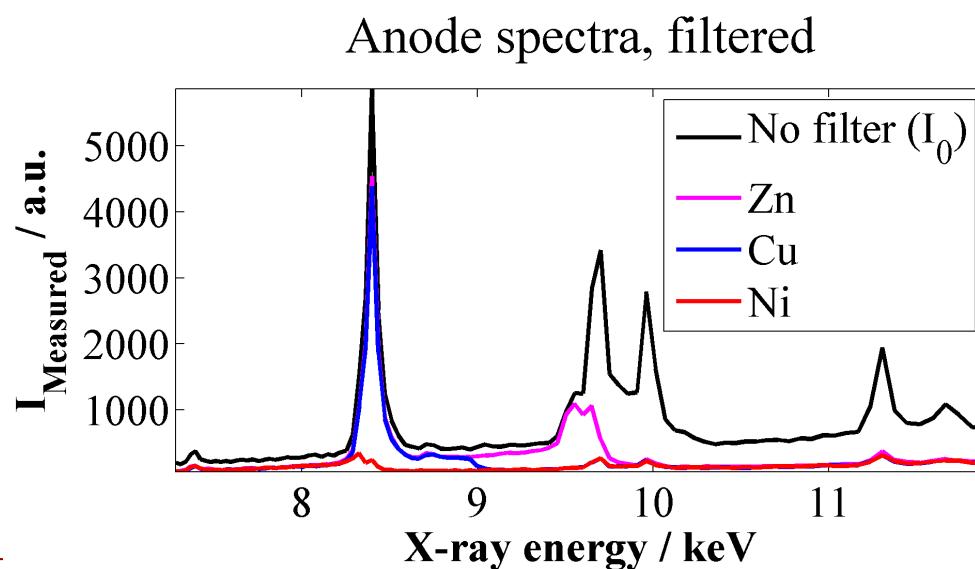
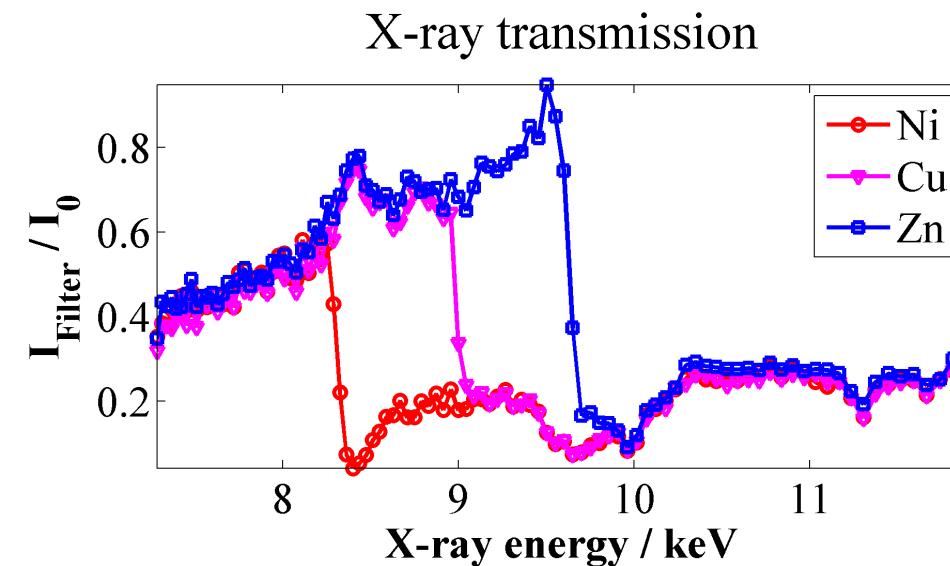
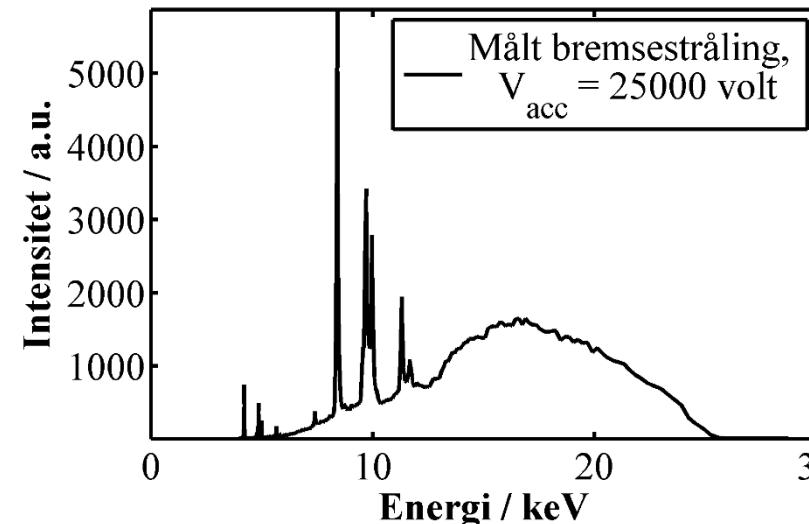


- Incident x-ray radiation with "varying" energy (wavelength) is measured with detector 1 without sample
- Sample is inserted and the transmitted signal is measured with detector 1

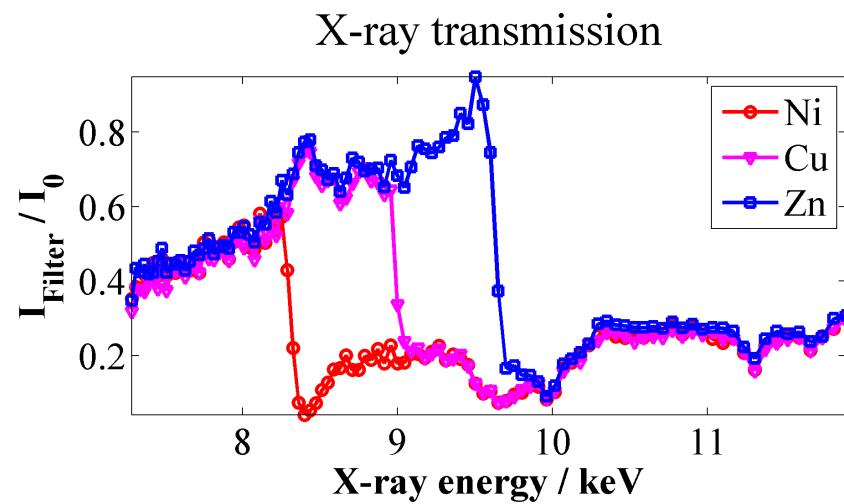
$$\text{Transmission } T = I_{\text{after}} / I_0$$

$$\mu = -\ln \frac{I(z)}{I_0} / z$$

X-ray spectroscopy - XAS



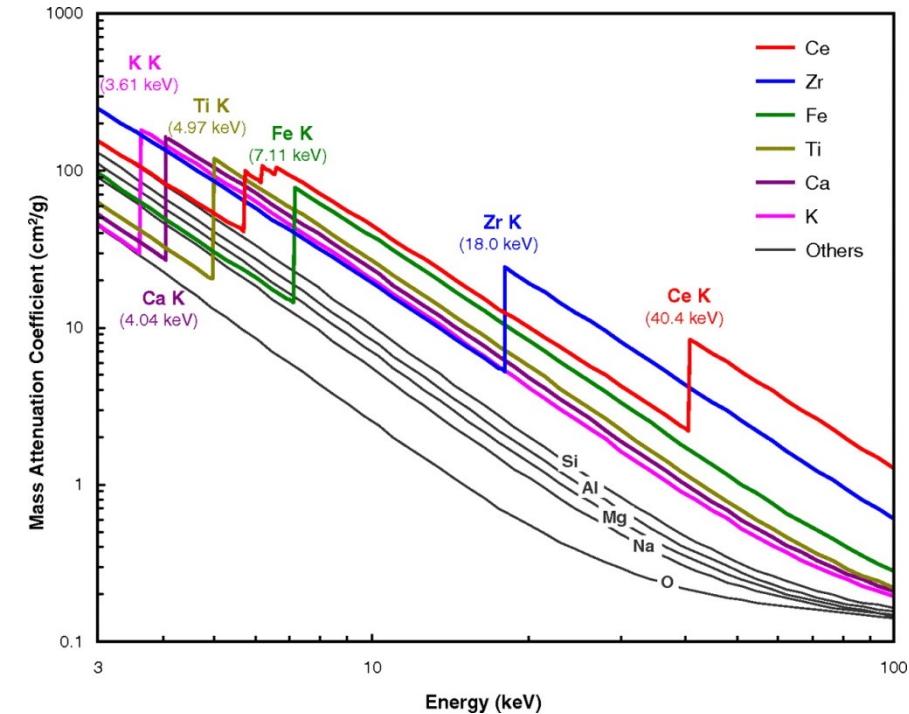
X-ray spectroscopy - XAS



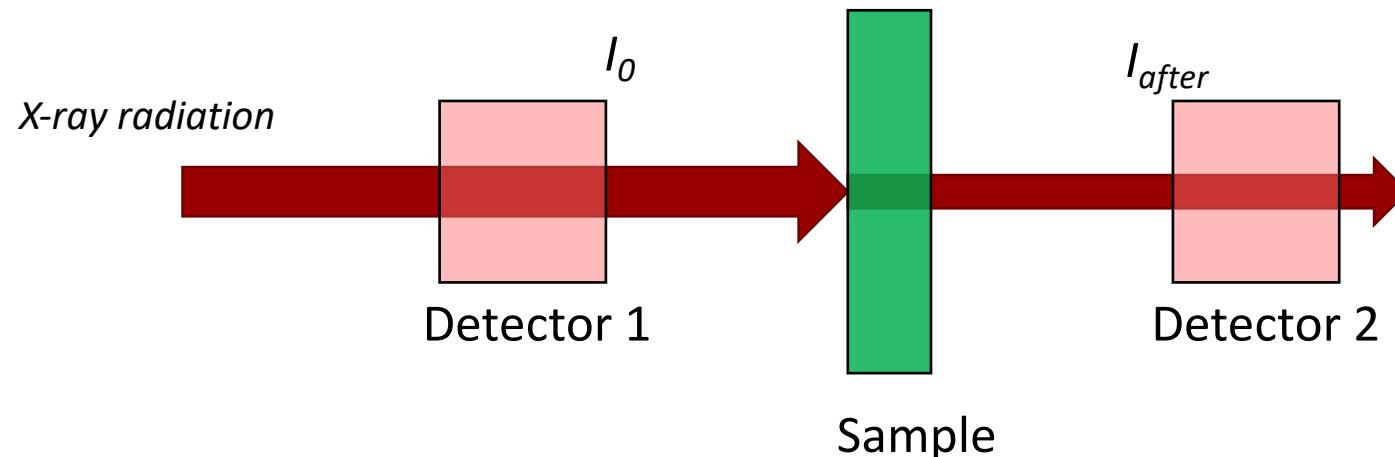
$$I(z) = I_0 e^{-\mu z} \Leftrightarrow$$

$$\frac{I(z)}{I_0} = e^{-\mu z} \Leftrightarrow$$

$$\mu = -\ln \frac{I(z)}{I_0} / z$$



masse-attenueringskoefficienten: μ/ρ



BUT we need a detector! What should it be able to do? What is its specifications?

A good spectrometer can cost several 100kkr.

By the use of Braggs law, we are going to build our own “cheaper” spectrometer!

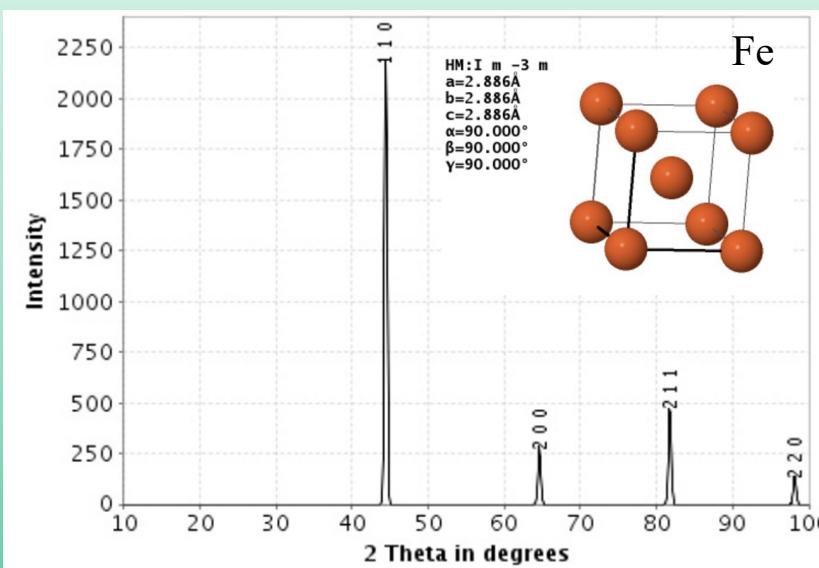
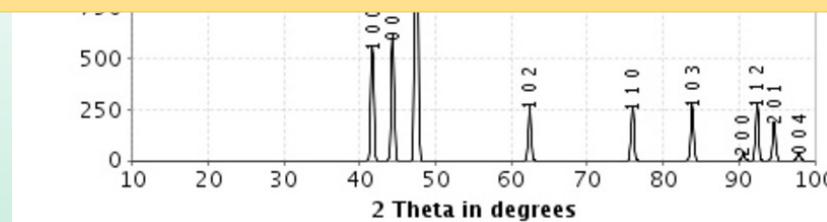
How can we measure the wavelength?

Which wave lenght have been used to make these patterns?

$$d_{\text{Fe},110} = 2.04 \text{ \AA}$$

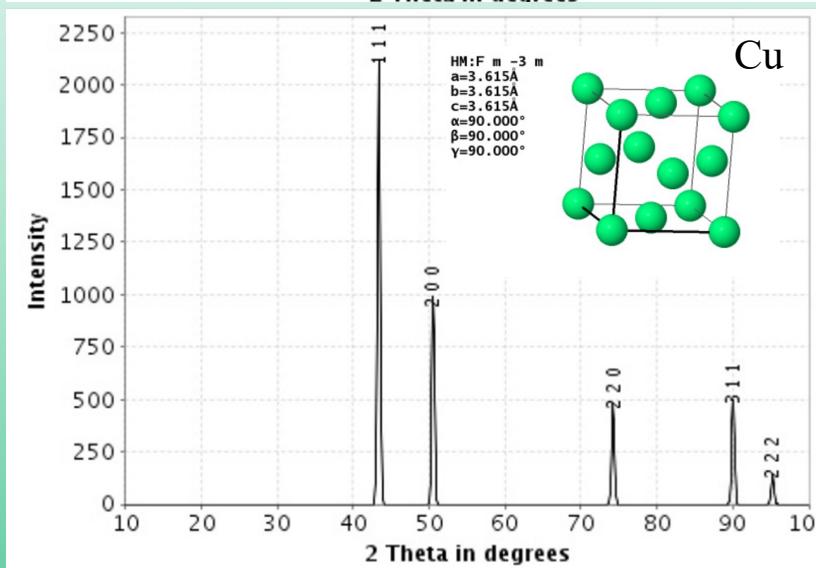
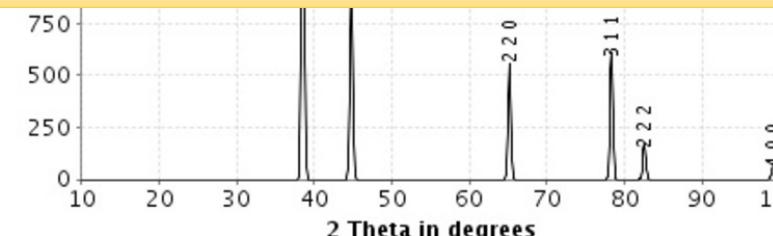
$$1.54 \text{ \AA} \sim \text{Cu}_{\text{k}\alpha}$$

$$2d_{hkl} \sin \theta = \lambda$$

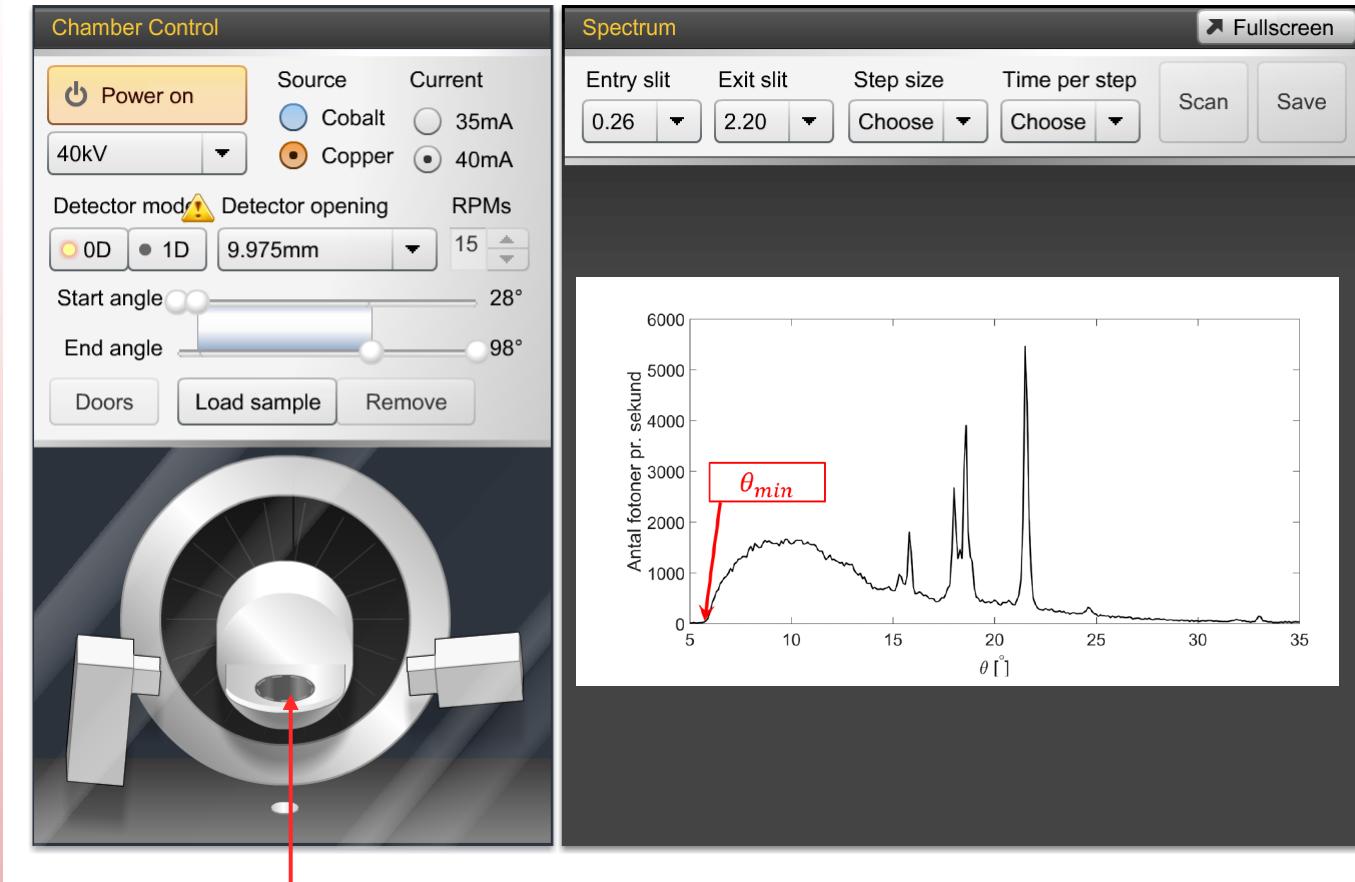


What is the interplanar distance of the {111}-planes in FCC Cu?

$$d_{\text{Cu},111} = 2.08 \text{ \AA}$$



Lets make our own spectrometer (a setup that can measure the intensity vs. energy/wavelength)



Sample with **known** lattice parameter d



Calculate the function $E(\theta)$

$$E = \frac{n \cdot h \cdot c}{2 \cdot d \cdot \sin \theta}$$

Photon energy:

$$E = h \cdot f = \frac{h \cdot c}{\lambda}$$

Braggs law:

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

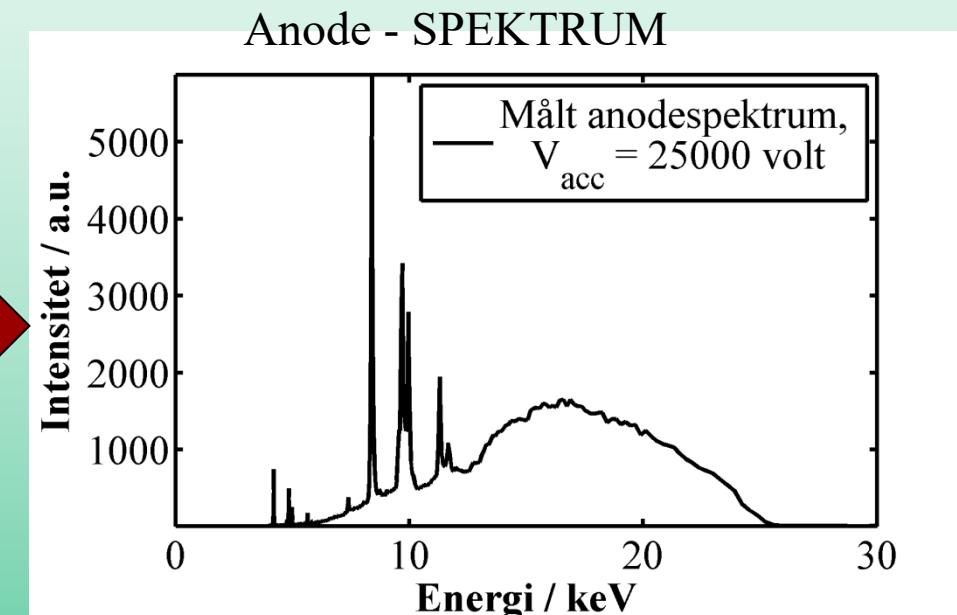
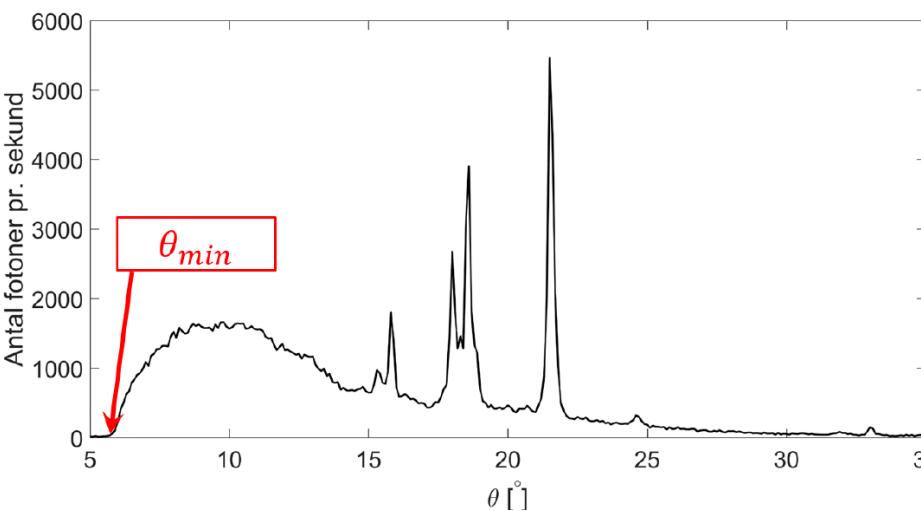
Lets make our own spectrometer (a setup that can measure the intensity vs. energy/wavelength)

constant measure unknown

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

$$E = h \cdot f = \frac{h \cdot c}{\lambda}$$

$$E = \frac{n \cdot h \cdot c}{2 \cdot d \cdot \sin \theta}$$



By applying Braggs law we have made our own cheap spectrometer



Image: Phywe.de

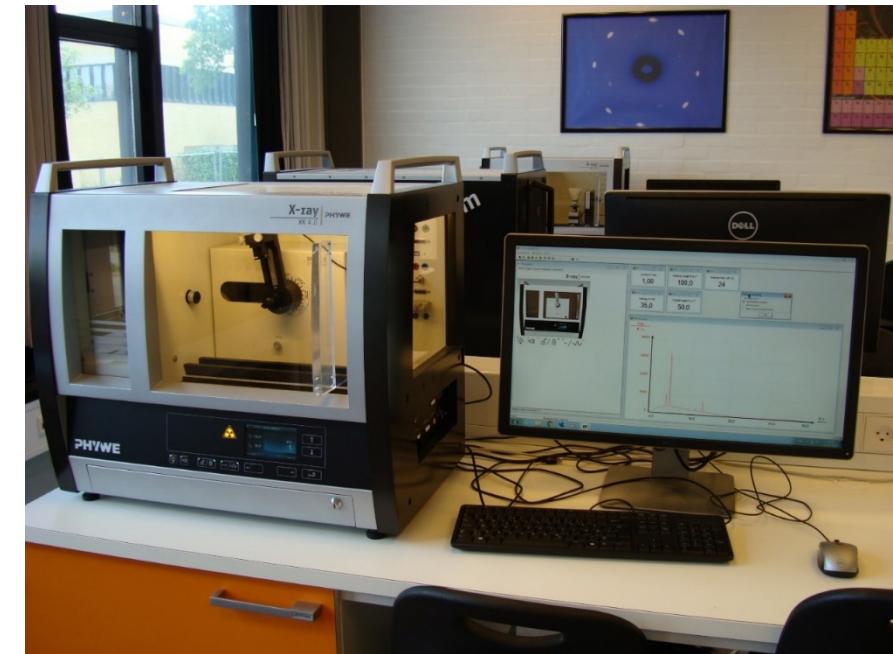
26.7 cm

Analyzer crystal
Top view



Image: Phywe.de

↔
1 cm



$\theta: 2\theta$ - coupling

Image credit: Nanoteket, DTU Physics

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

In the first part of the exercise the anode spectrum is measured by use of an analyser crystal. The acquired scattering data is converted to a spectrum $I(E)$ and discussed.

In the second part the absorption of different metal foils are measured.

The acquired data are treated to show the transmission $T=I_{\text{foils}}/I_0$ and the results are discussed

