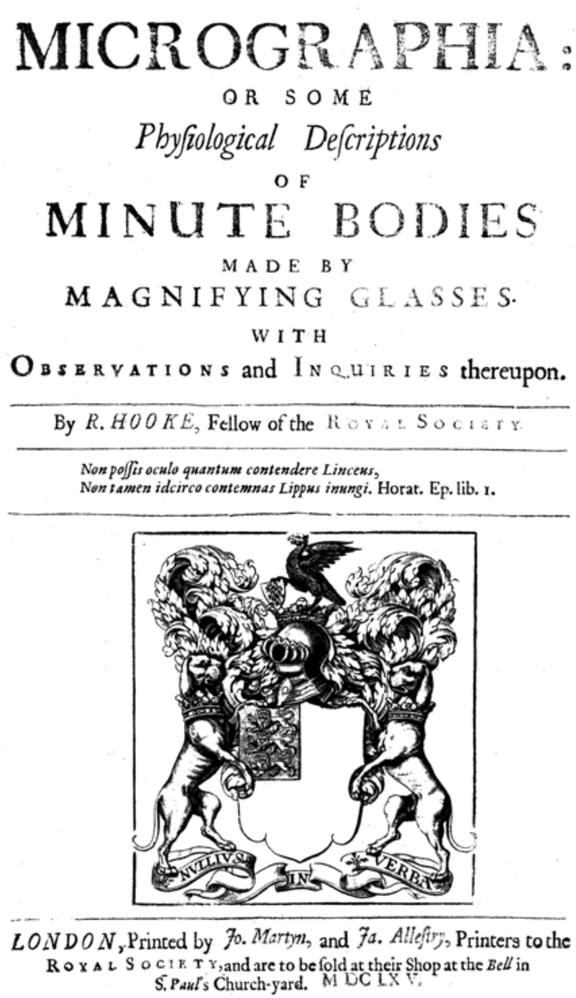
Chemical Analysis in **SEM/TEM**

Marc Willinger

Outline

- SEM:
  - components of the SEM
  - signals and their information content
  - Focused Ion Beam/SEM
- TEM
- Examples

Robert Hooke (1665)



MICROGRAPHIA:
OR SOME
Physiological Descriptions
OF
MINUTE BODIES
MADE BY
MAGNIFYING GLASSES.
WITH
OBSERVATIONS and INQUIRIES thereupon.

By *R. HOOKE*, Fellow of the ROYAL SOCIETY.

Non possis oculo quantum contendere Linceus,
Non tamen idcirco contemnas Lippus inungi. Horat. Ep. lib. 1.

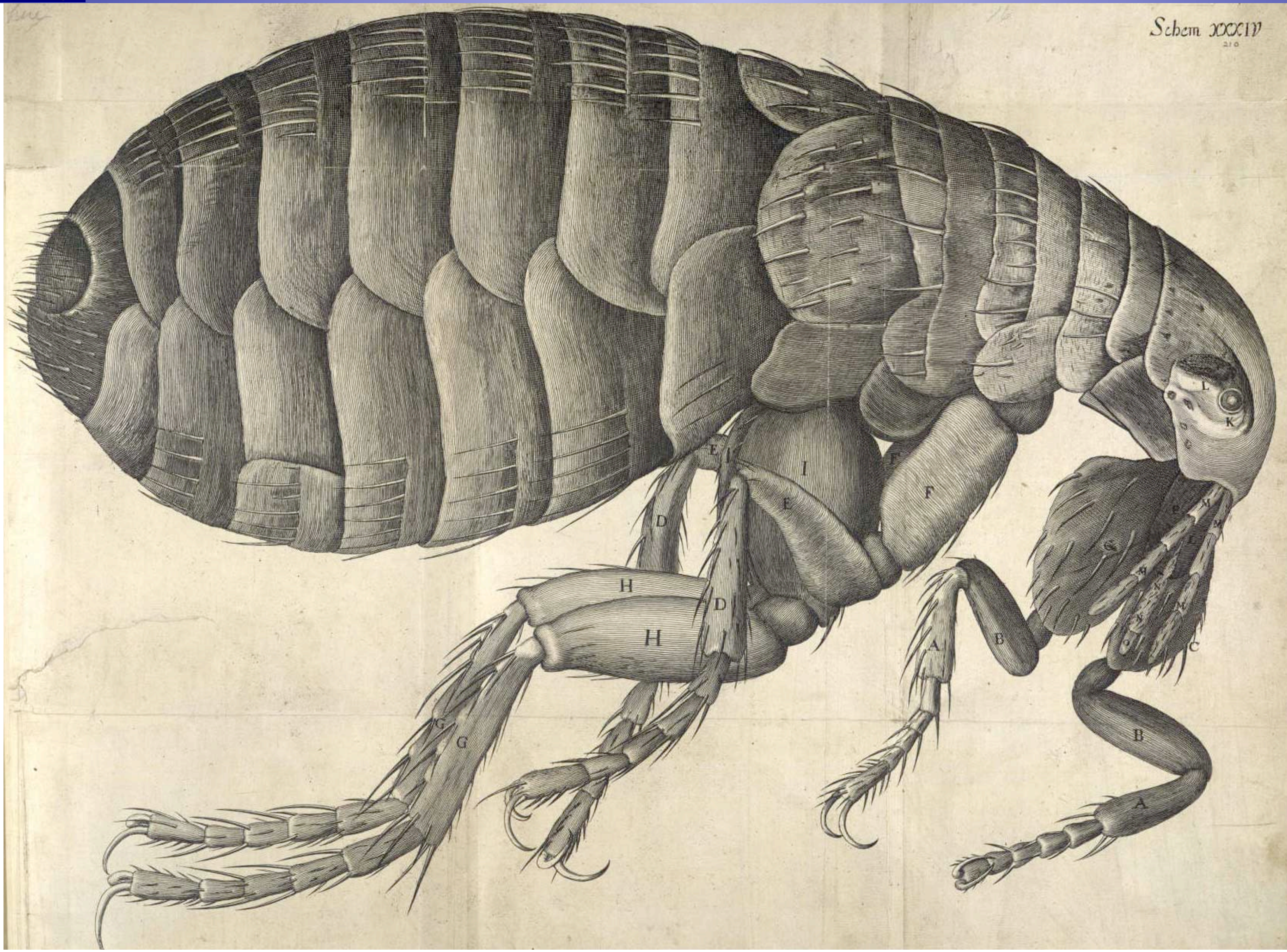
LONDON, Printed by *Jo. Martyn*, and *Ja. Allestry*, Printers to the ROYAL SOCIETY, and are to be sold at their Shop at the *Bell* in *S. Paul's* Church-yard. M DC LX V.

V. Title-page of *Micrographia*, 1665

Merely because one says something might be so, it does not follow that it has been proved that it is.

(Newton in conversation with Hooke, concerning Hooke's claim to have discovered the inverse square law of gravitation before him)

Robert Hooke (1665)

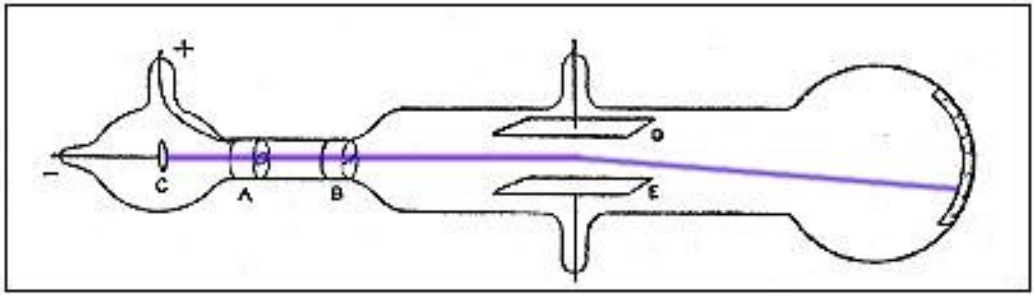


Observations in a Microscope can be Unpleasant

Abb. 1. »Thames Water«, Stich von William Heath um 1828.

Entdeckung des Elektrons

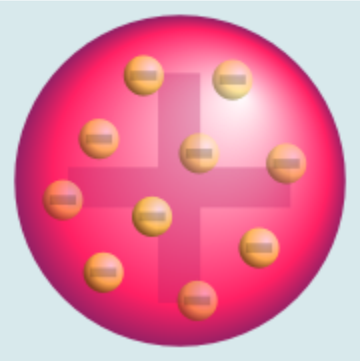
Sir Joseph John Thomson
(1856 – 1940)
Nobelpreis 1906



J.J. Thomson's 2nd Cathode ray experiment

1897: discovered "corpuscles", small particles with a charge/mass ratio more than 1000 times greater than that of protons, swarming in a see of positive charge ("plum pudding model").

=> Discovery of the ELECTRON



Plum pudding model (1904)

Elektron: Welle-Teilchen Dualismus

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.

=> Matter Waves

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

Nachweis: Elektron = Welle

Sir George Paget Thomson
(1892 – 1975)
Nobel Prize: 1937
(shared with C.J. Davison)

Entdeckte 1927 in Aberdeen unabhängig vom Amerikaner Clinton Joseph Davisson die Elektronenbeugung am Kristallgitter, ein Beweis für die Materiewellen-Theorie de Broglies. Hierfür erhielten beide den Nobelpreis für Physik 1937.

Why electrons?

Smallest visible objects…

-with eye : 0.1 mm = 10^{-4} m
(size of one eye «"stick"»)

- with light microscope ~ 300nm
(magnification max ~ 2000x)

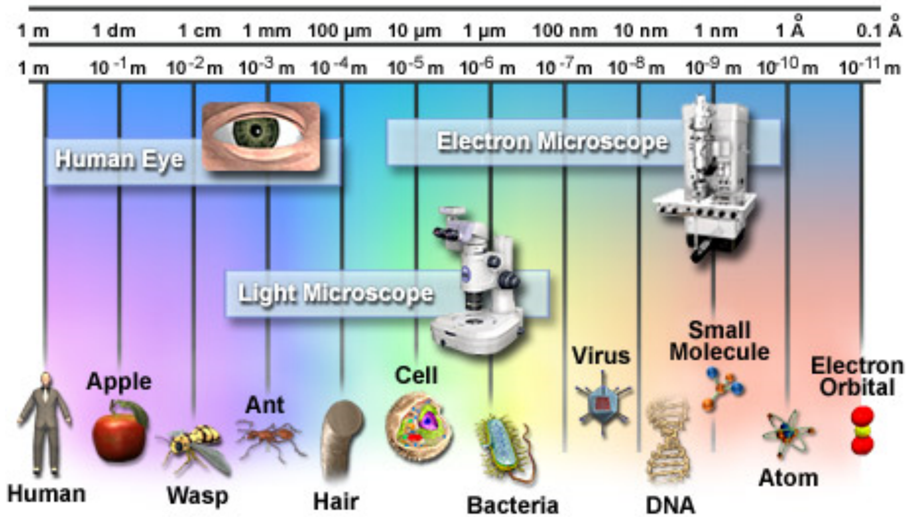
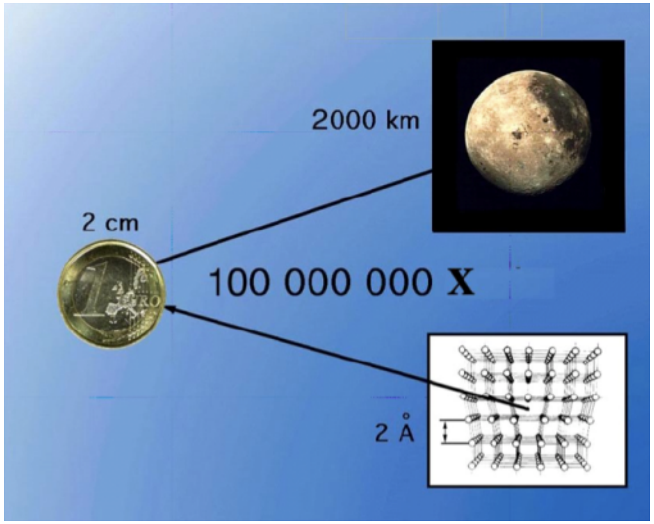


Figure 1

Can we simply magnify the image of an object to observe every detail ?



Rayleigh criterion (1869):

$$\delta = \frac{0.61\lambda}{n\sin\beta}$$

λ: wavelength of the radiation,
n: refractive index of the viewing medium
β: semi-angle of collection of the magnifying lens.

M. Willinger, FHI

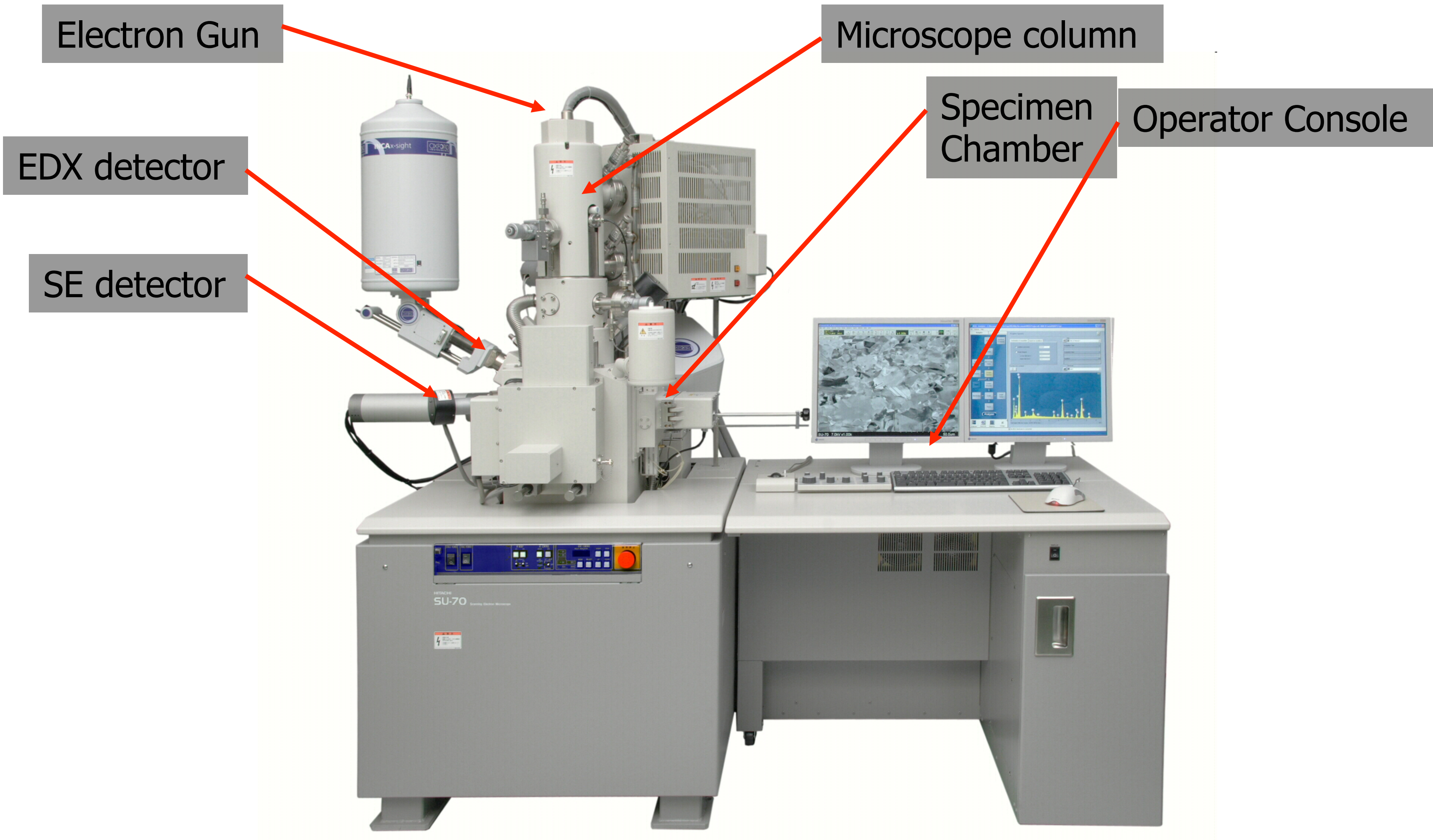
Why electrons?

The interaction of waves with an obstacle:

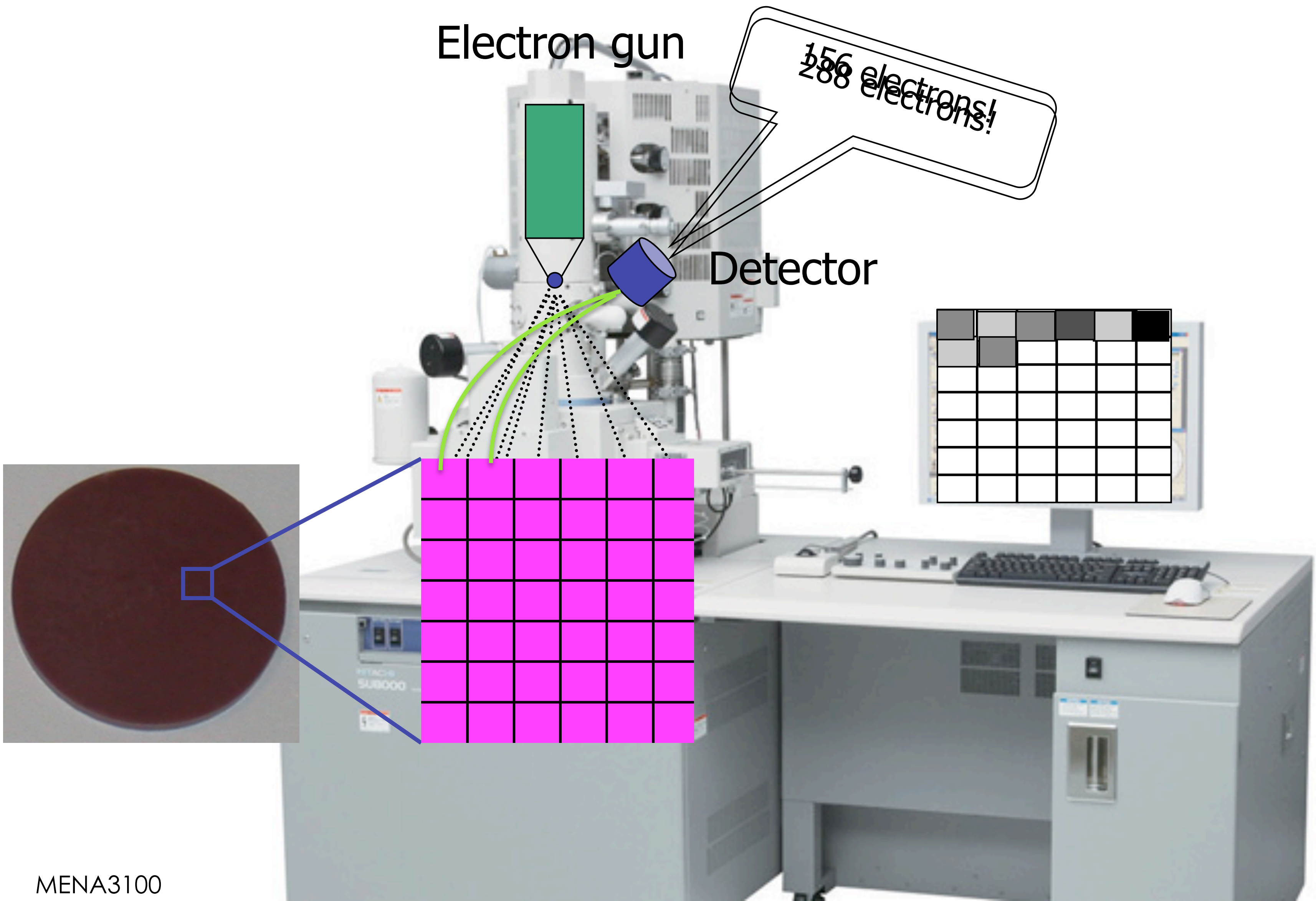
The boat rides the long wavelength ocean wave, but reflects the small wavelength surface ripple. An observer who wishes to detect the presence of the boat can do so only by observing waves which have wavelengths smaller than, or comparable to, the length of the boat. (From Sherwood, p.19)

Waves on water surface

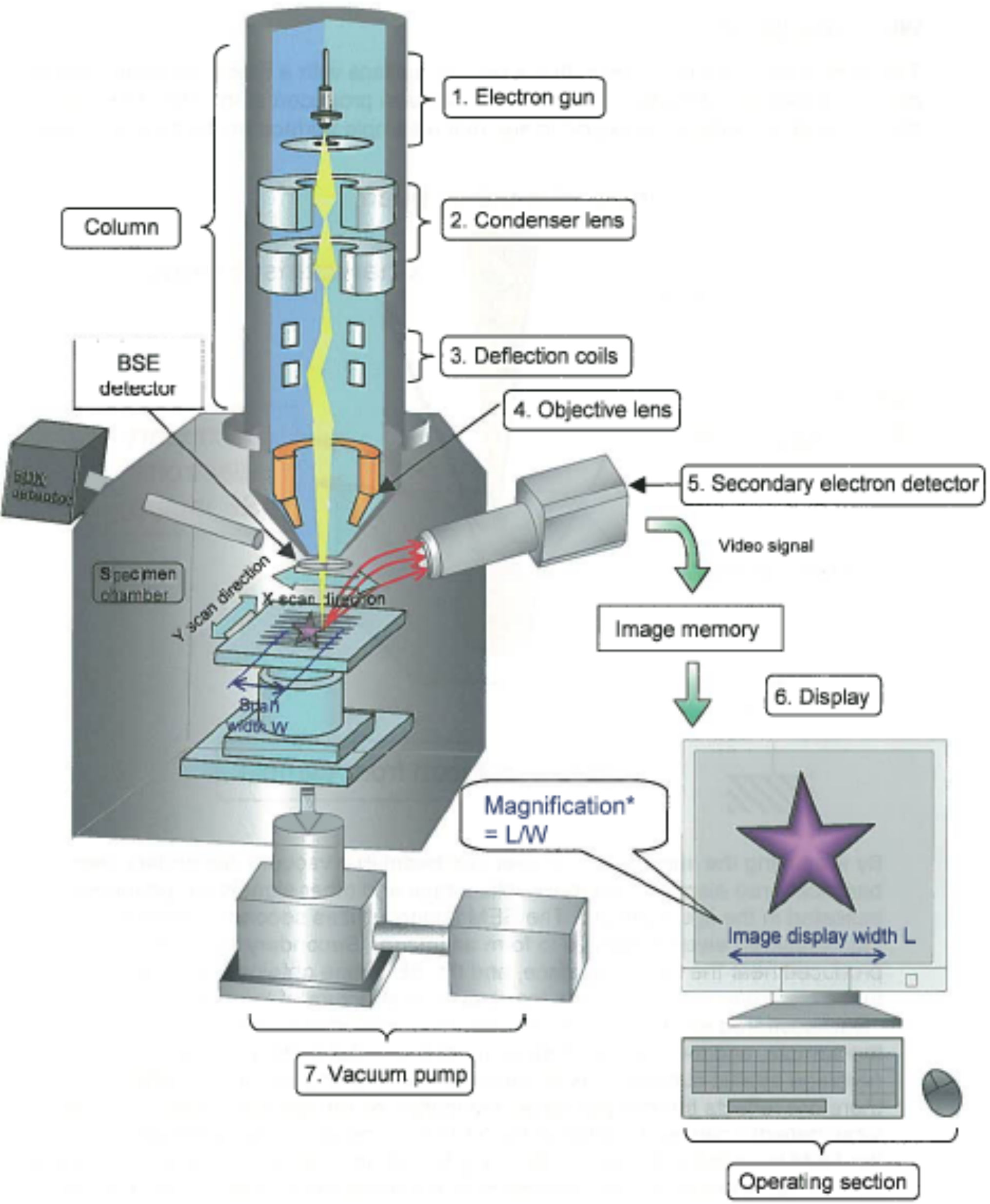
Components of the SEM



Principle

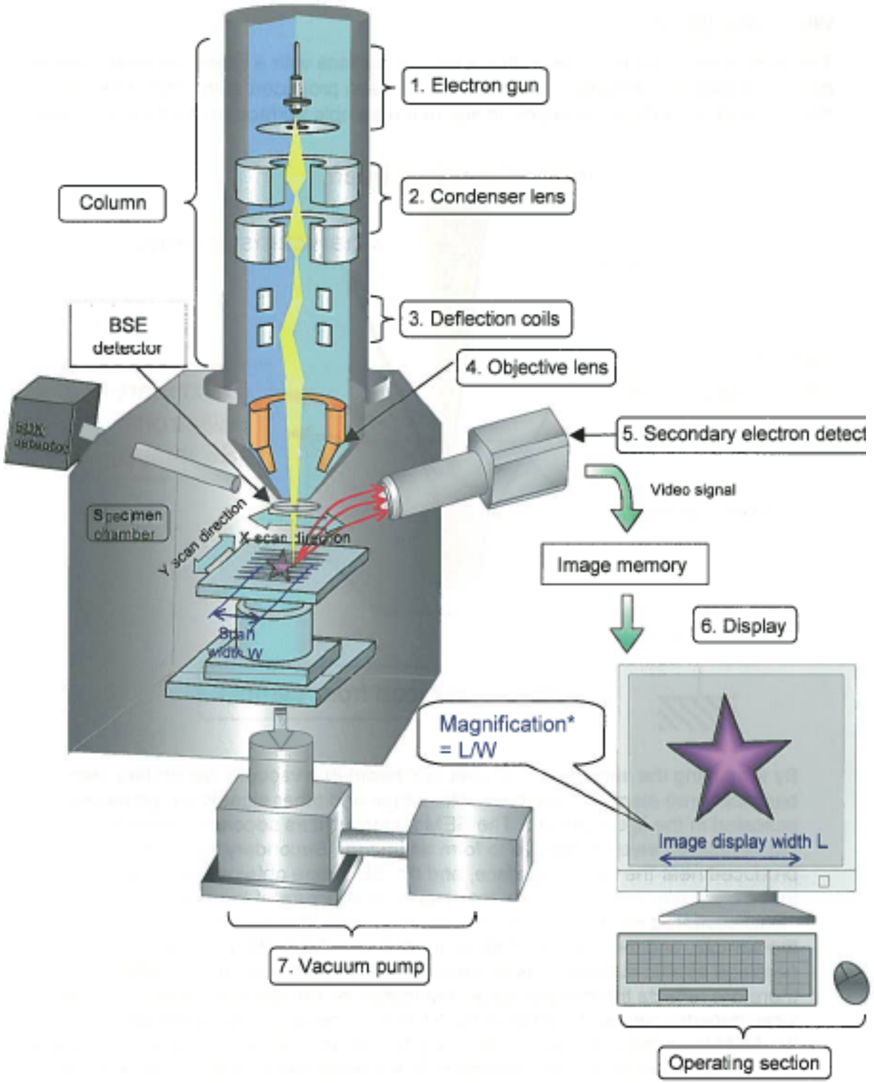


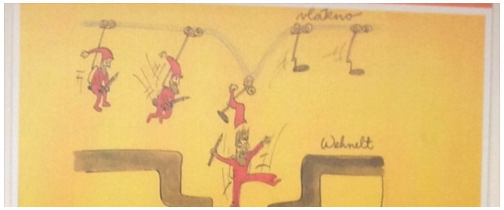
Components of the SEM



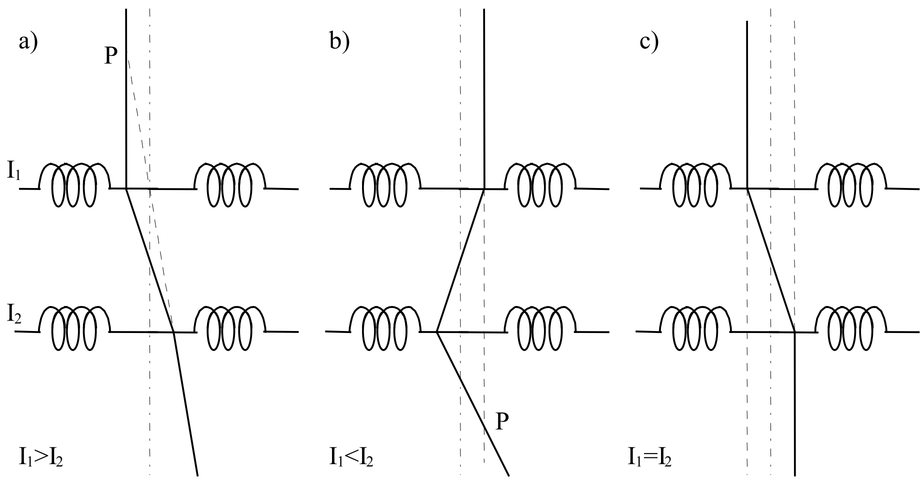
http://www.ammrf.org.au/myscope/sem/practice/virtualsem/sparkler.php

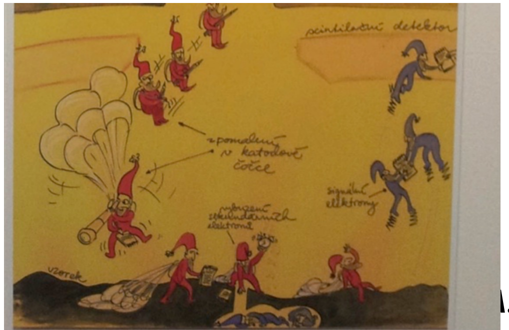
Components of the SEM



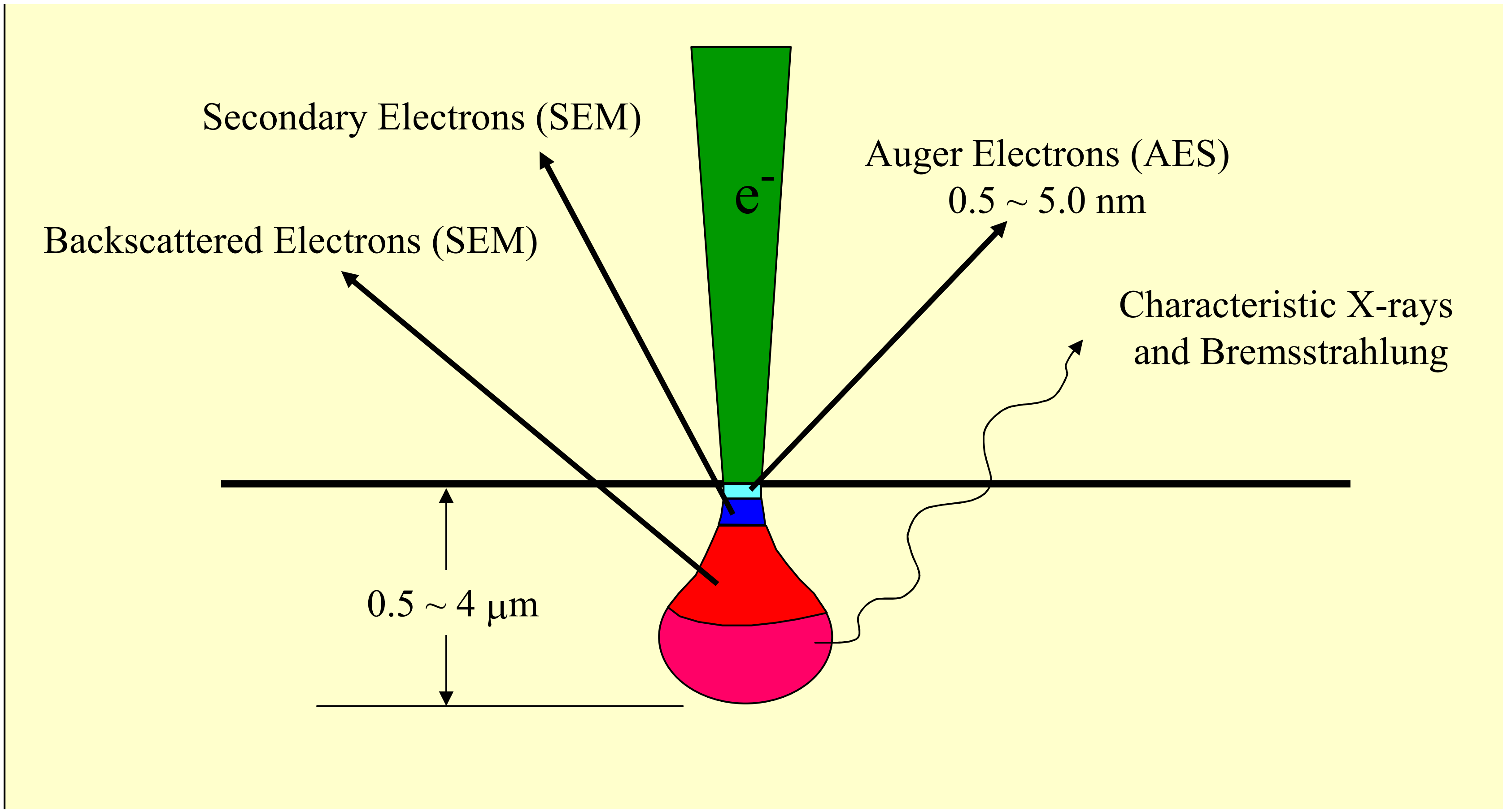


Deflection Coils





Signals and their Information Content



Signals and their Information Content

- SE1- at point of primary interaction
- SE2- away from initial interaction point
- SE3- by BSE outside of sample
- BSE1- at point of primary interaction
- BSE2- away from initial interaction point

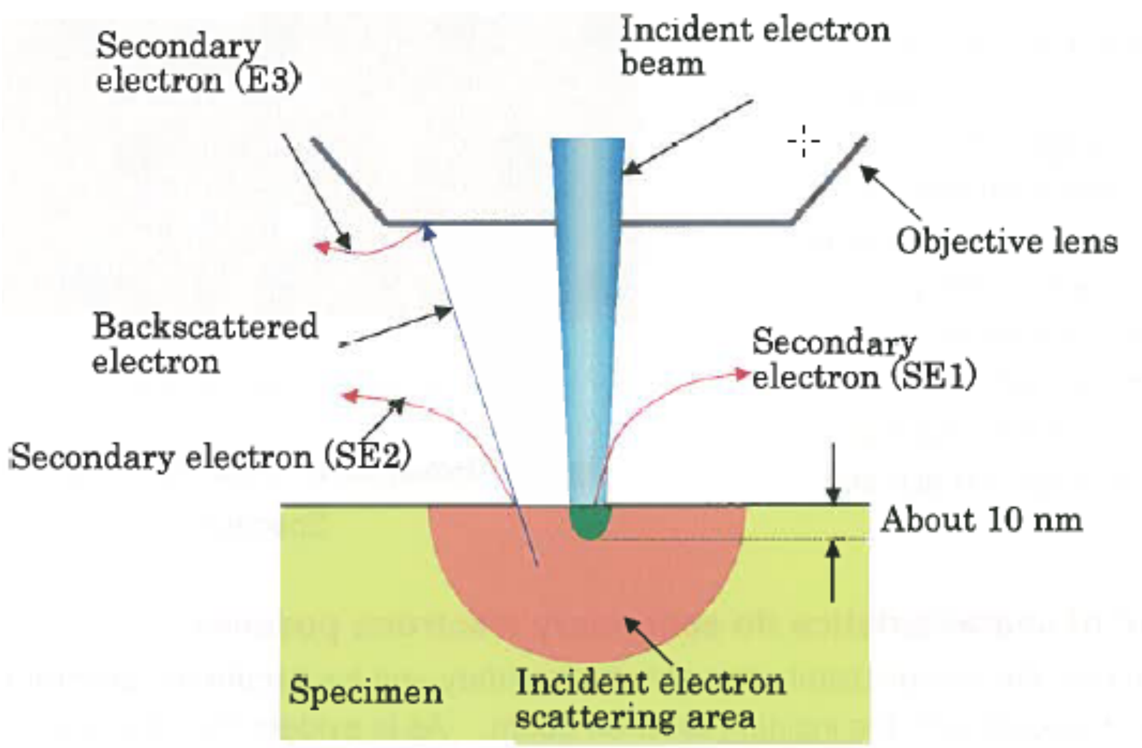
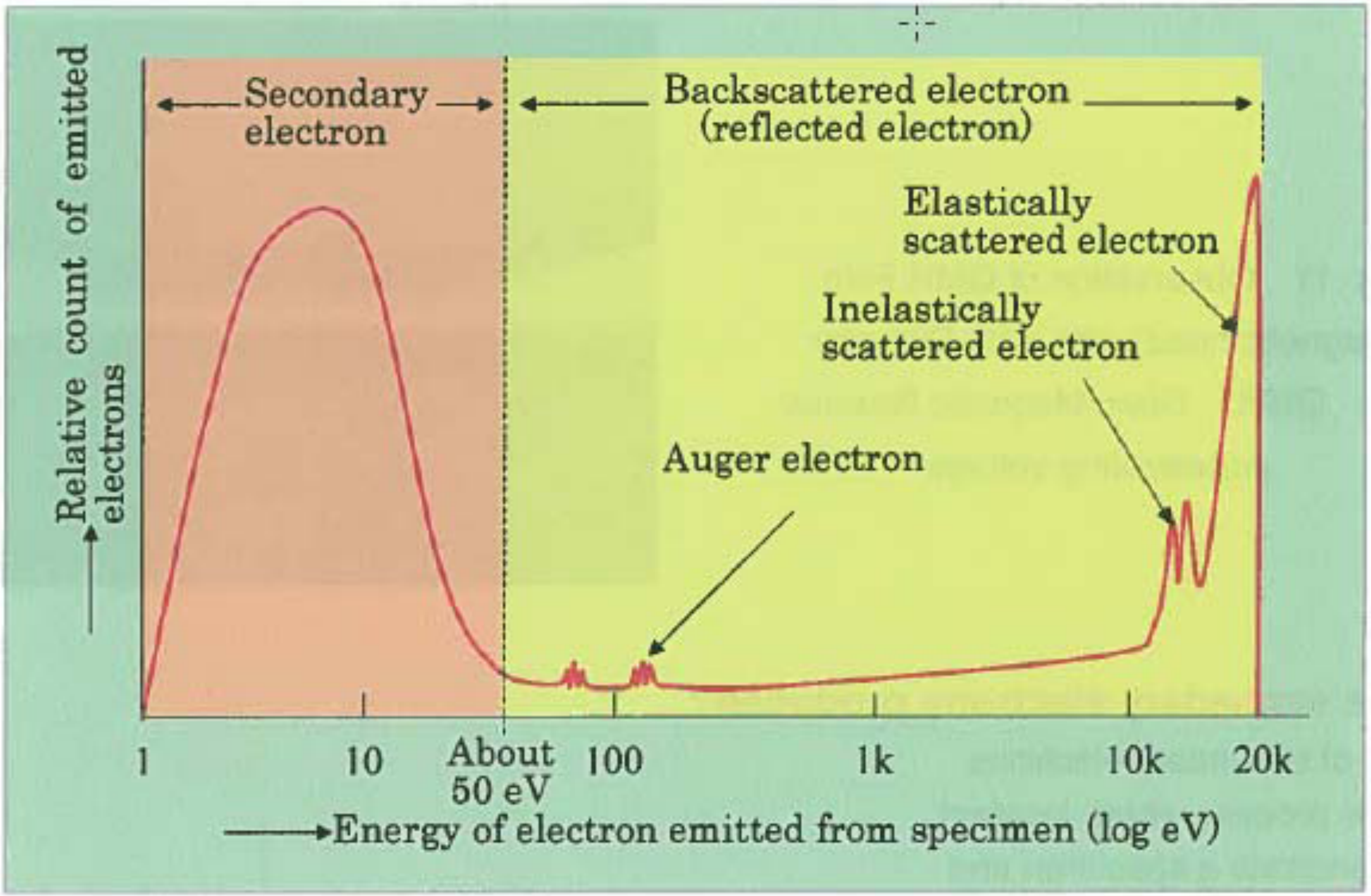


Fig. 14 Area of Secondary Electron Emission from Specimen Surface

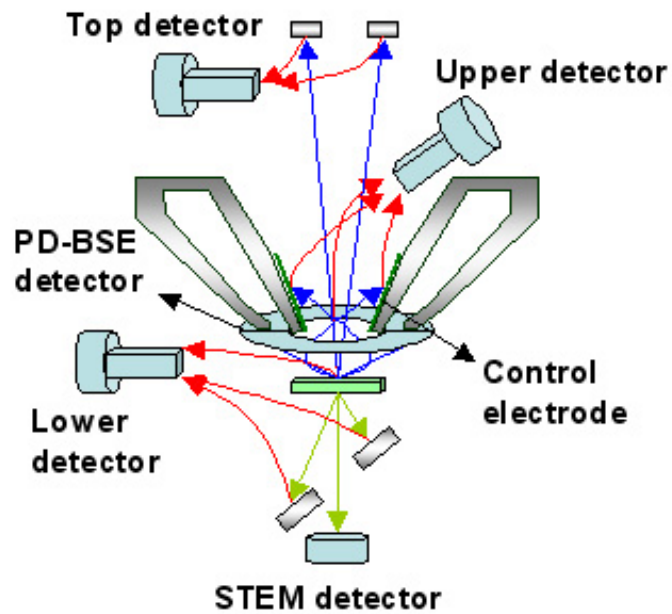
http://www.engr.uvic.ca/~mech580/electron-microscopy/Introduction%20SEM.pdf



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

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

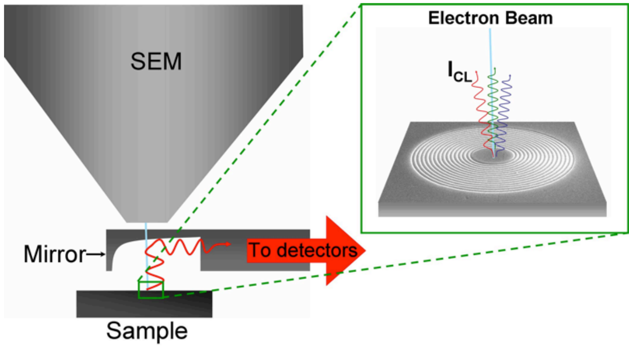
Signals and their Information Content



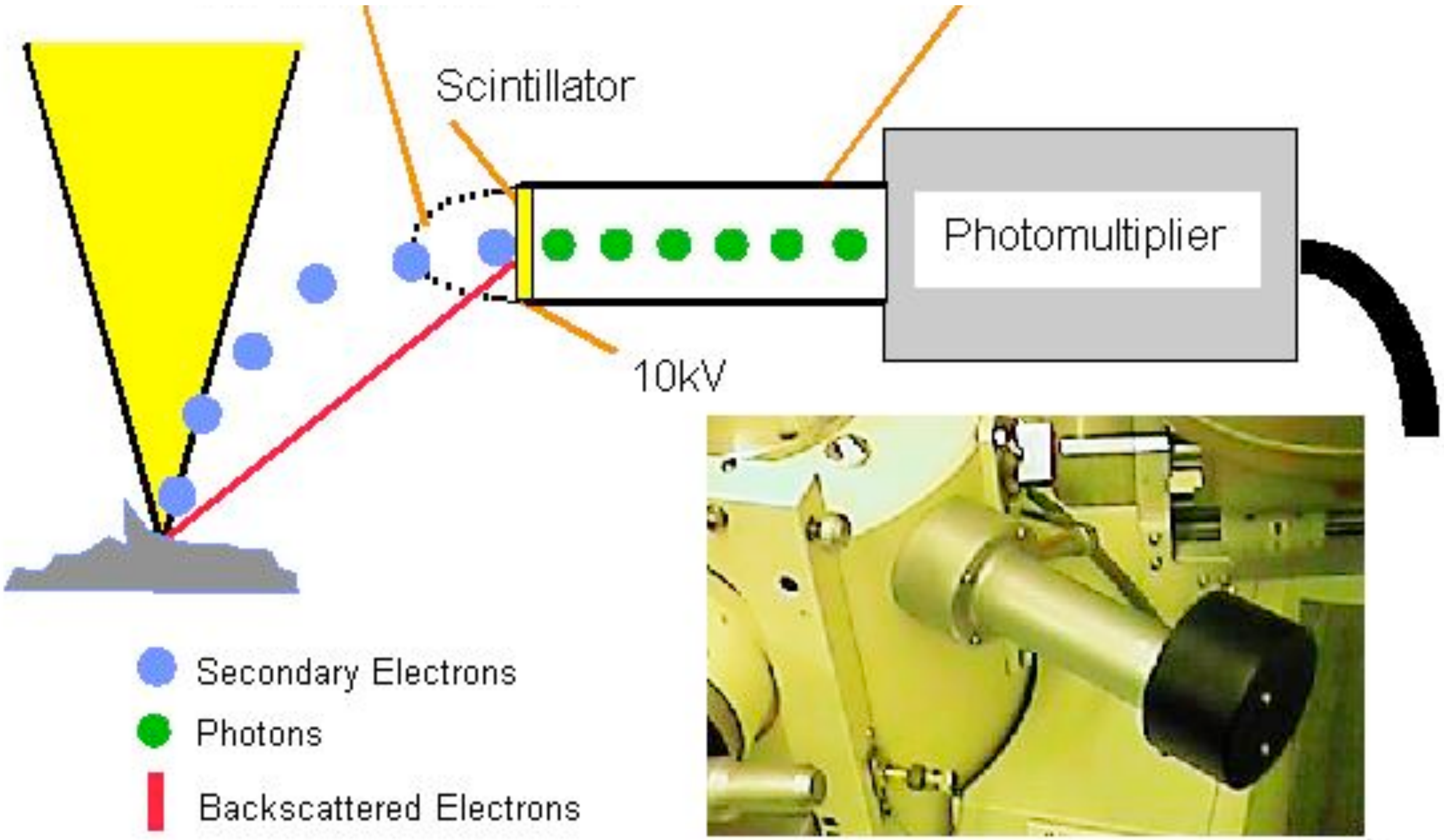
- SE: less than 50 eV of kinetic energy originate from a very shallow region at the sample surface
  → good for high resolution
  → topographic information

- BSE: back scattered primary electrons (from the beam) due to elastic collis with nuclei of sample atoms
  → high energy
  → larger interaction volume
  → contrast related to average atomic number

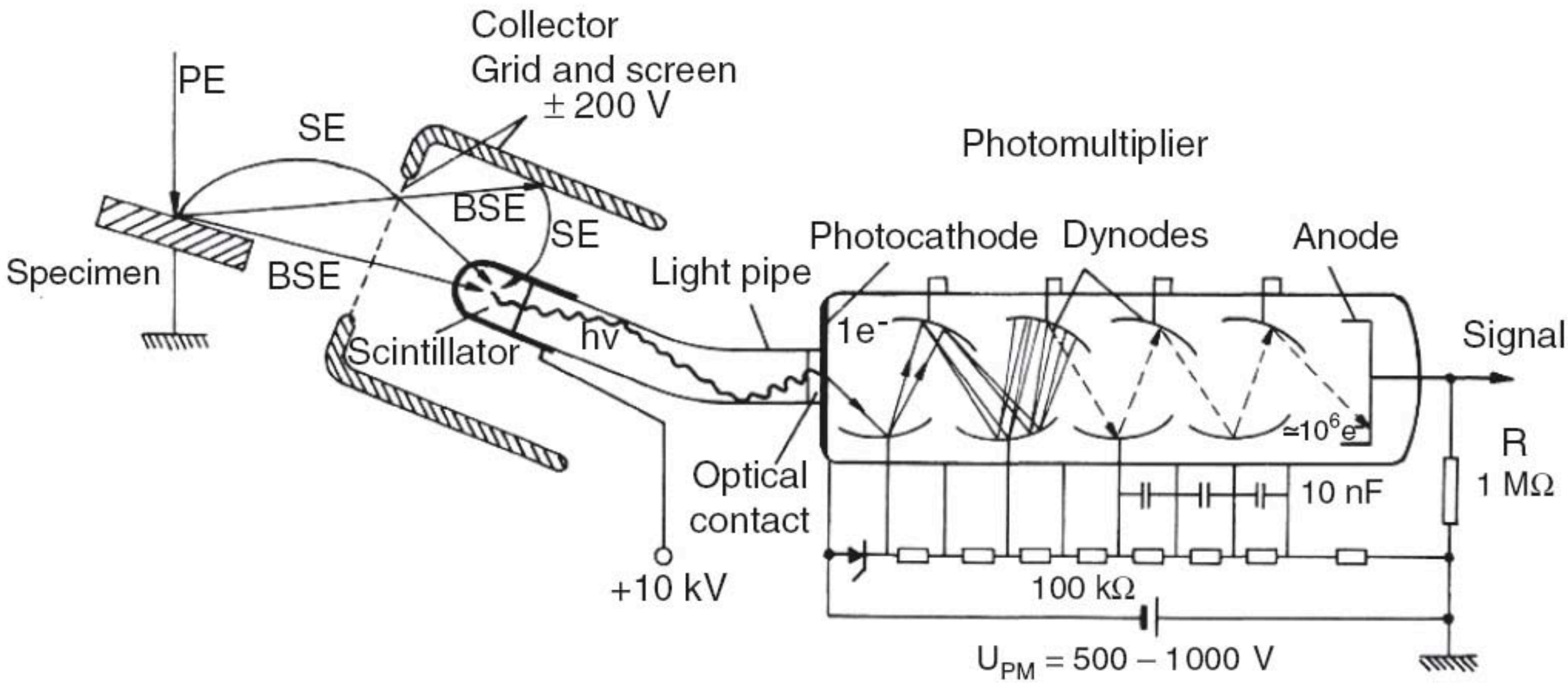
- EDX, Cathodoluminescence, EBSD, …



Everhart-Thornley SE detector



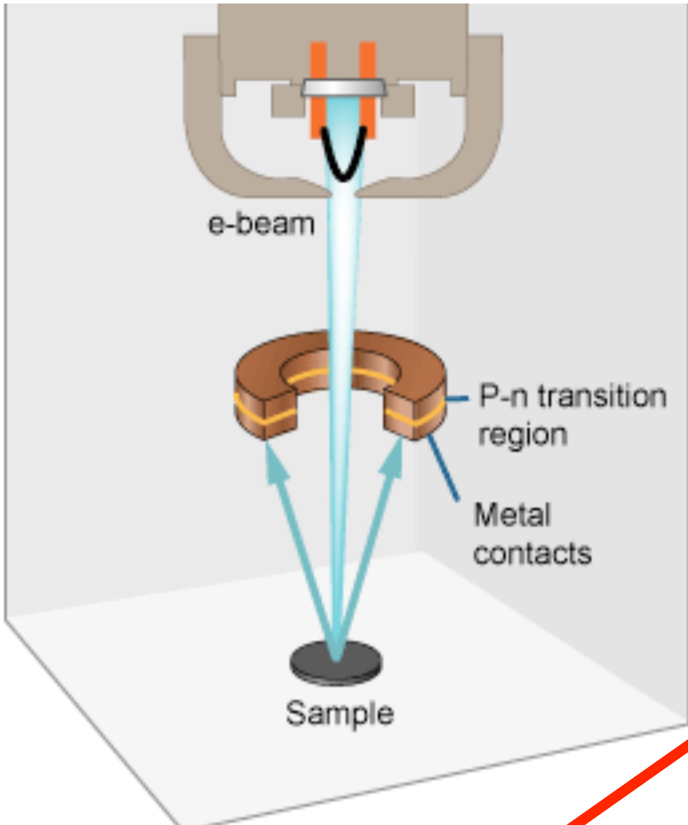
Combined SE/BSE Detector

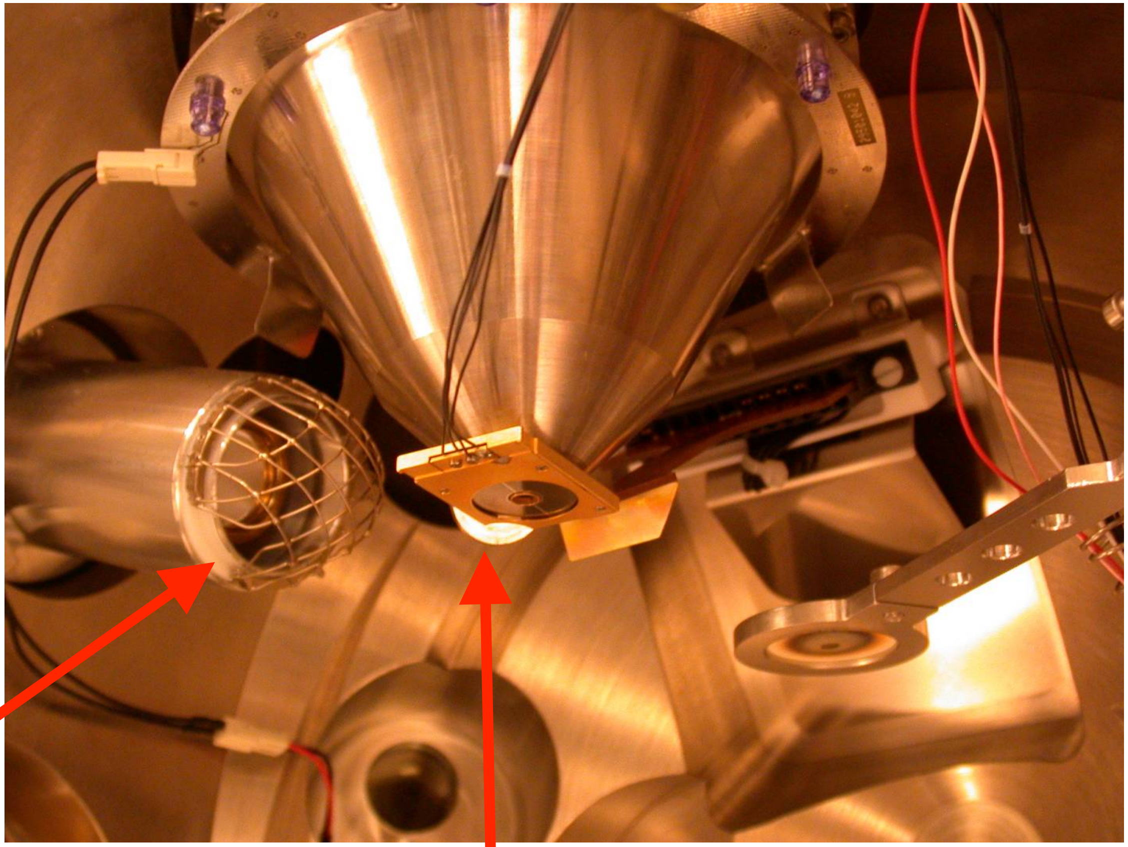


SE: a positive collector voltage (ca. +200 to +400V) attracts SE toward the detector, where a 10kV post acceleration gives them enough energy to create a bunch of photons for each SE.

BSE: a negative collector polarisation (ca. -100V) repels SE and the only (fast) BSE emitted in the narrow cone to the scintillator are detected

BSE Detector

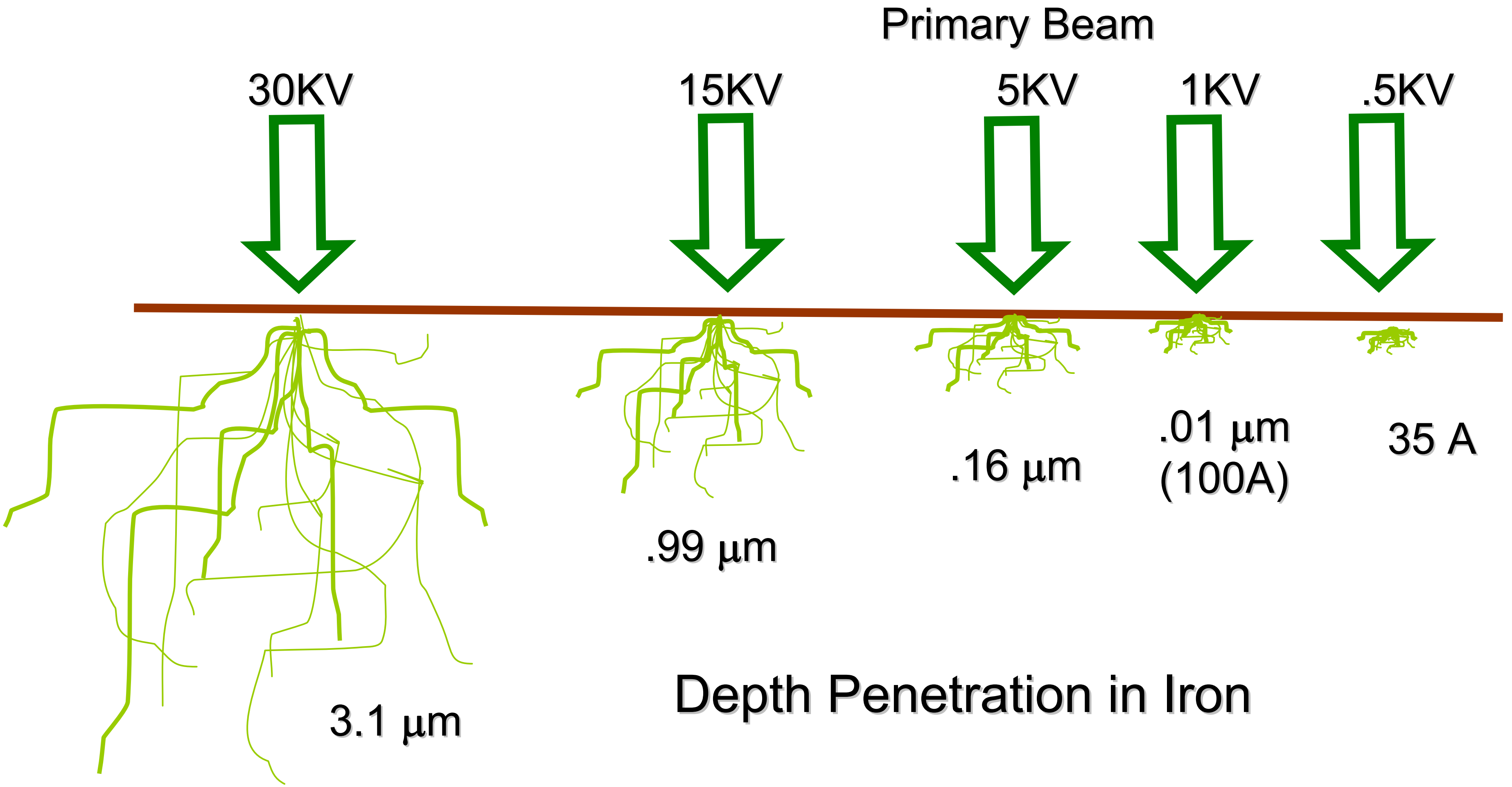




Secondary electron detector:
(Everhart-Thornley)

Backscattered electron detector:
(Solid-State Detector)

- *Kanaya-Okayama Depth Penetration*



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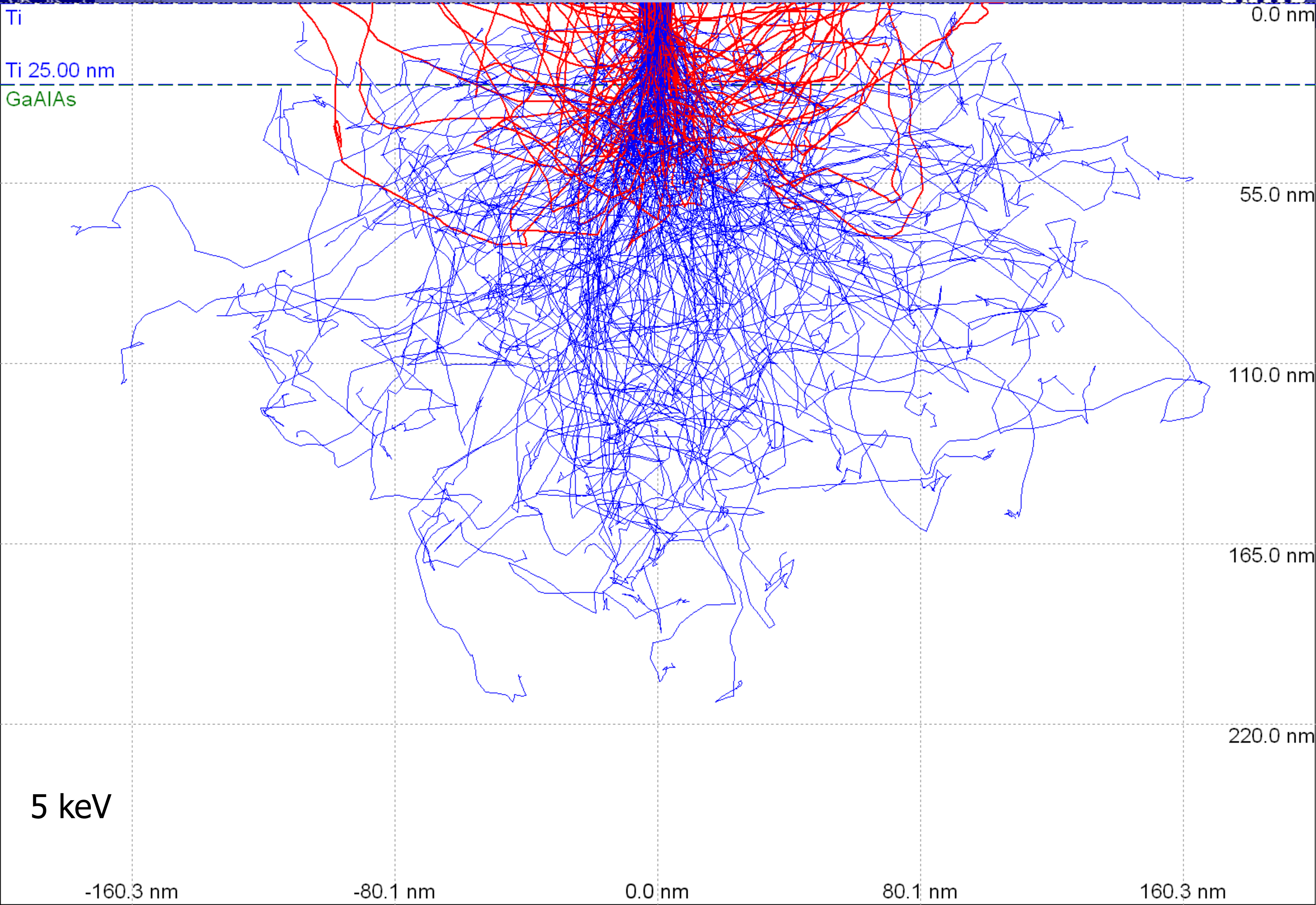
Signals and their Information Content

Simulate the electron trajectories in a solid constituted of 25 nm thick Ti film on a GaAlAs substrate

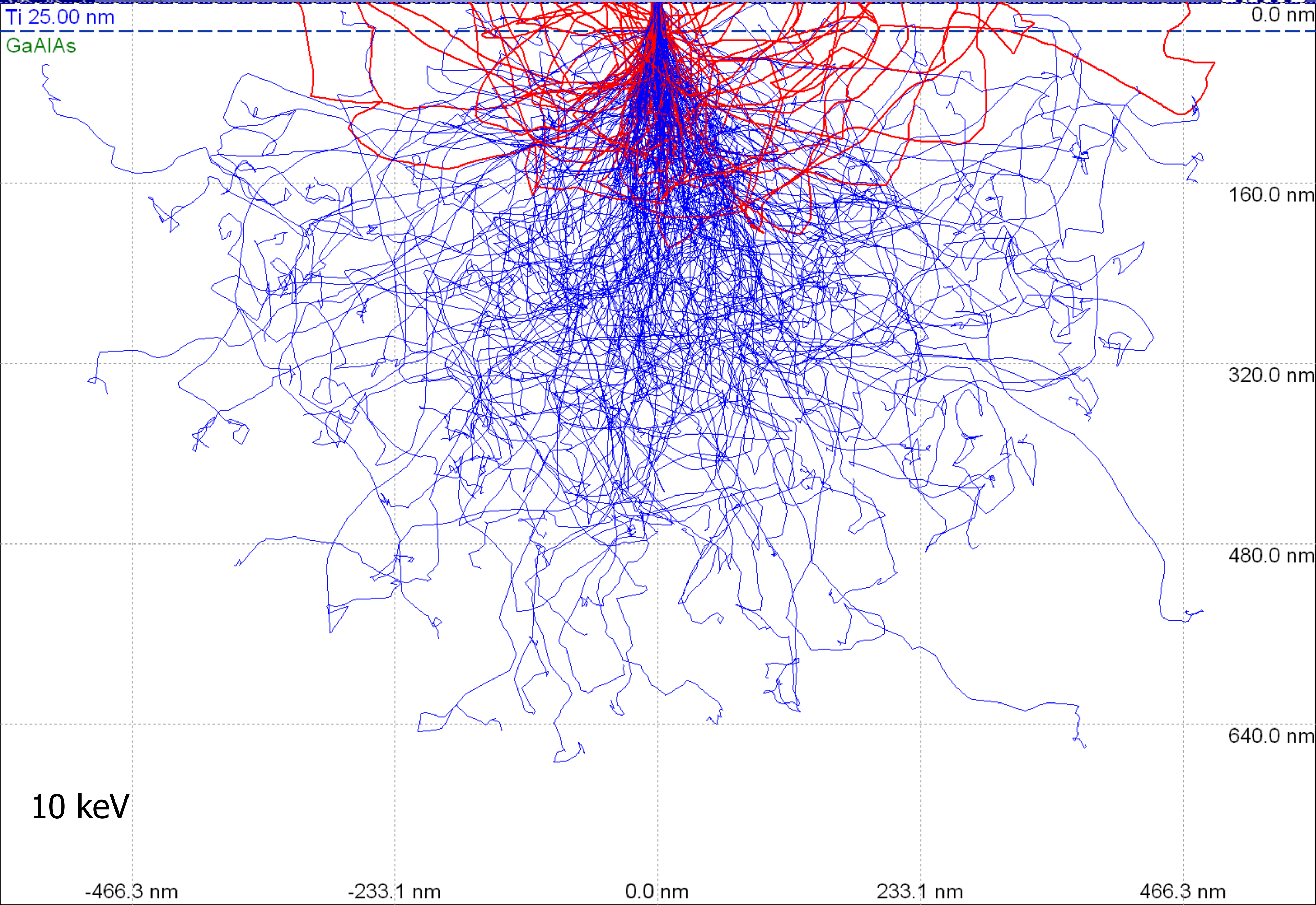
- 200 electron trajectories are displayed
- Incident energy varies from 5 to 30 keV
- Red trajectories represent electrons that are backscattered
- Blue trajectories represent electrons that are absorbed

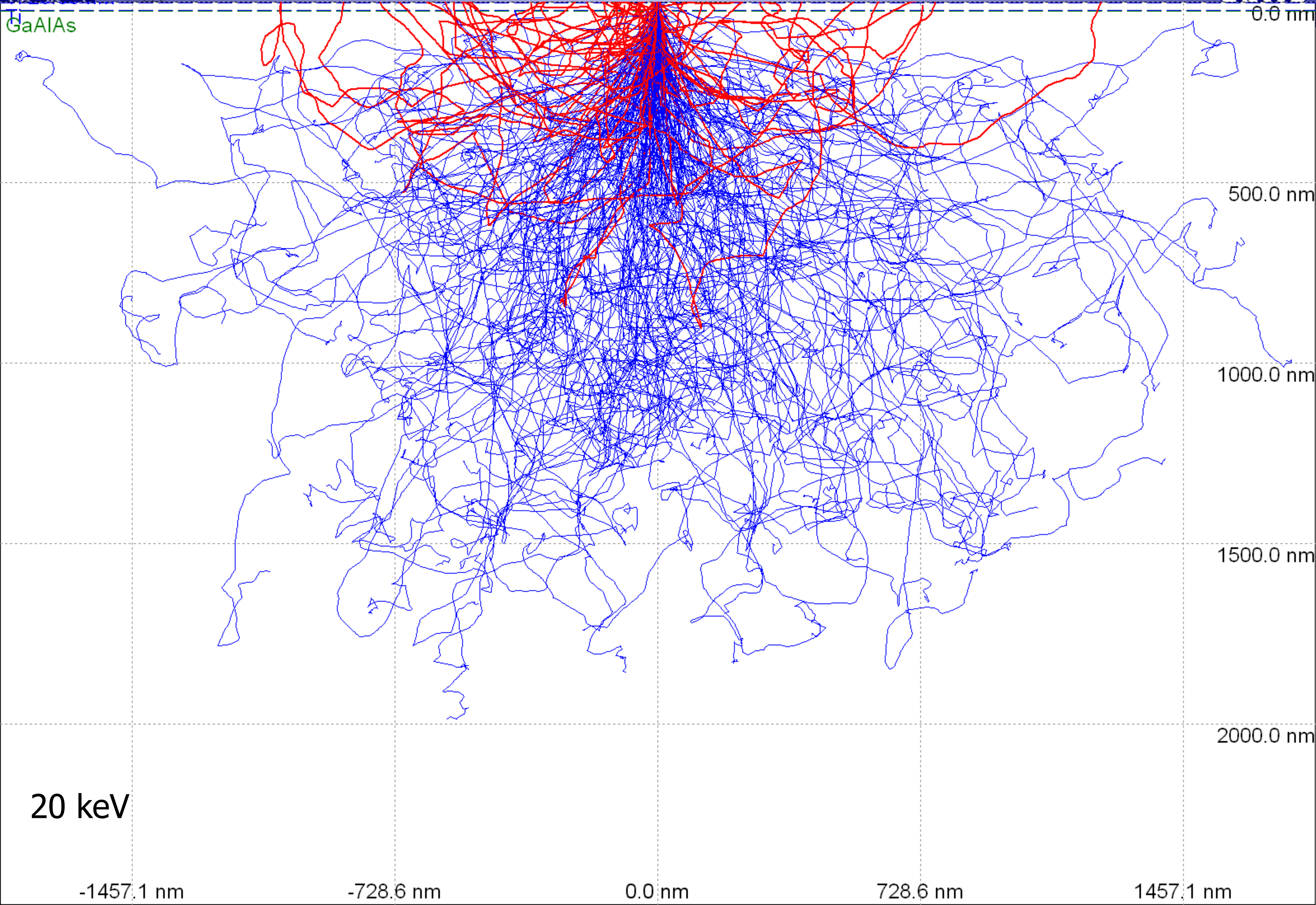
The generation of secondary electrons is not taken into account !

http://www.gel.usherbrooke.ca/casino/download2.html
CASINO : "monte CArlo SImulation of electroN trajectory in sOlids"

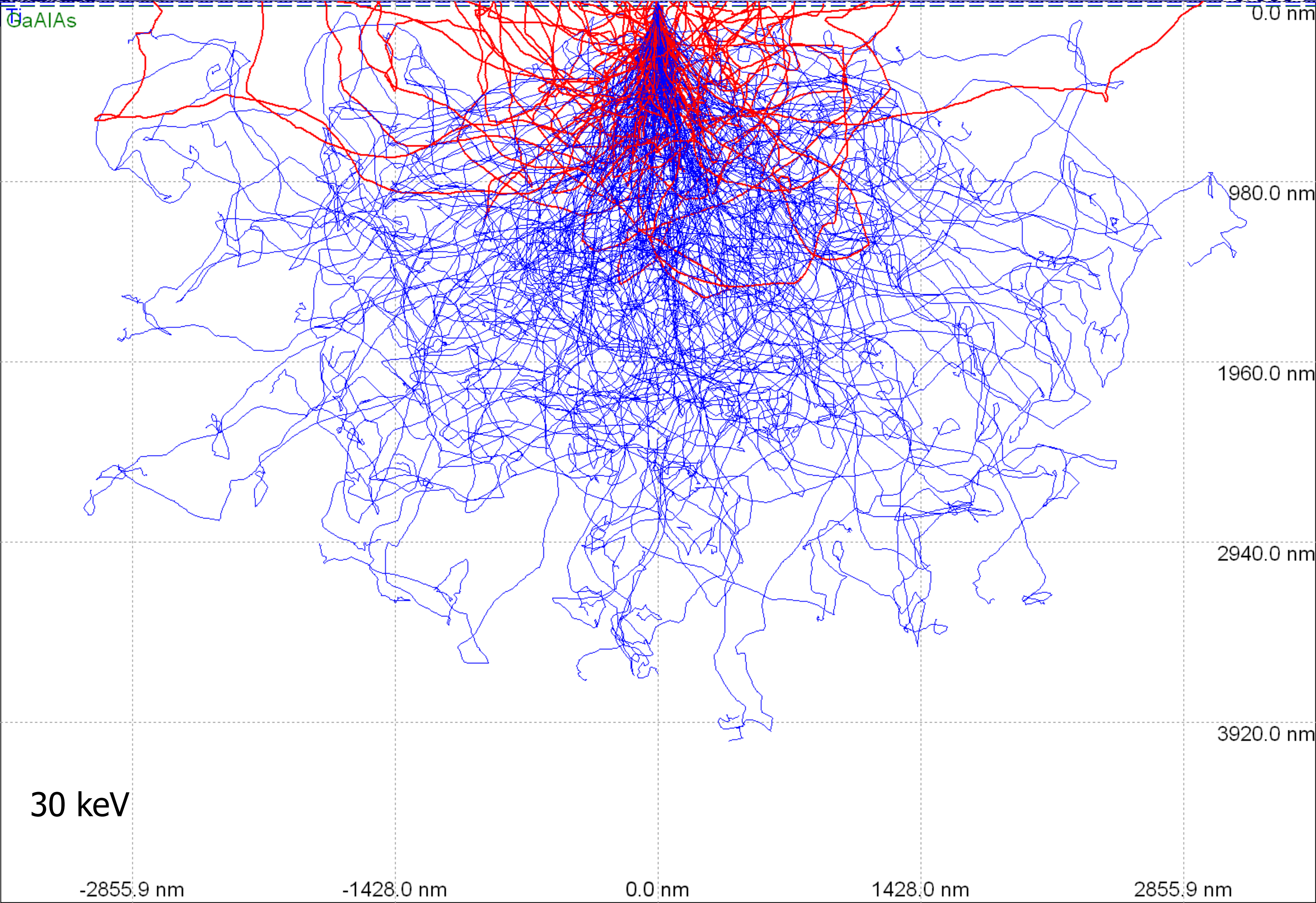


Ti
Ti 25.00 nm
GaAlAs
0.0 nm
55.0 nm
110.0 nm
165.0 nm
220.0 nm
-160.3 nm
-80.1 nm
0.0 nm
80.1 nm
160.3 nm
5 keV


Ti 25.00 nm
GaAlAs
0.0 nm
160.0 nm
320.0 nm
480.0 nm
640.0 nm
10 keV
-466.3 nm
-233.1 nm
0.0 nm
233.1 nm
466.3 nm

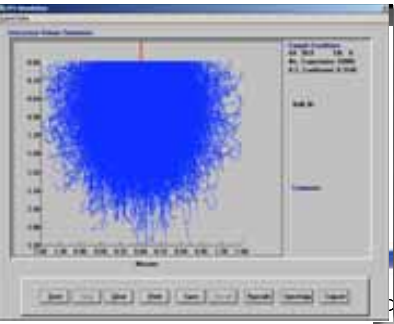


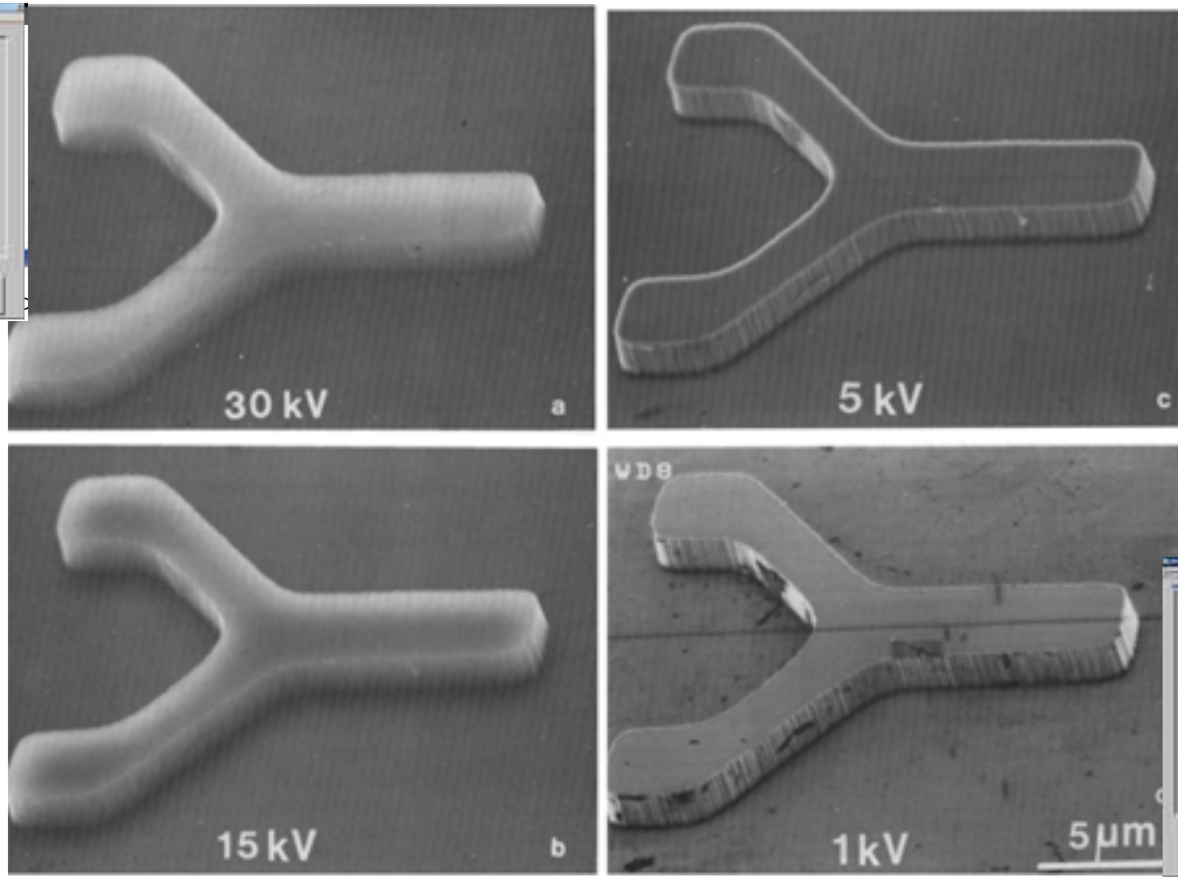
Ti
GaAlAs
0.0 nm
500.0 nm
1000.0 nm
1500.0 nm
2000.0 nm
20 keV
-1457.1 nm
-728.6 nm
0.0 nm
728.6 nm
1457.1 nm

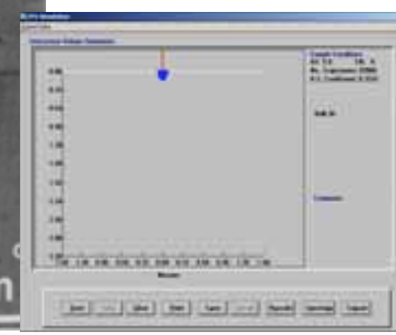

Ti
GaAlAs
0.0 nm
980.0 nm
1960.0 nm
2940.0 nm
3920.0 nm
30 keV
-2855.9 nm
-1428.0 nm
0.0 nm
1428.0 nm
2855.9 nm

Interaction volume / Information Depth

Change in SE contrast with the voltage

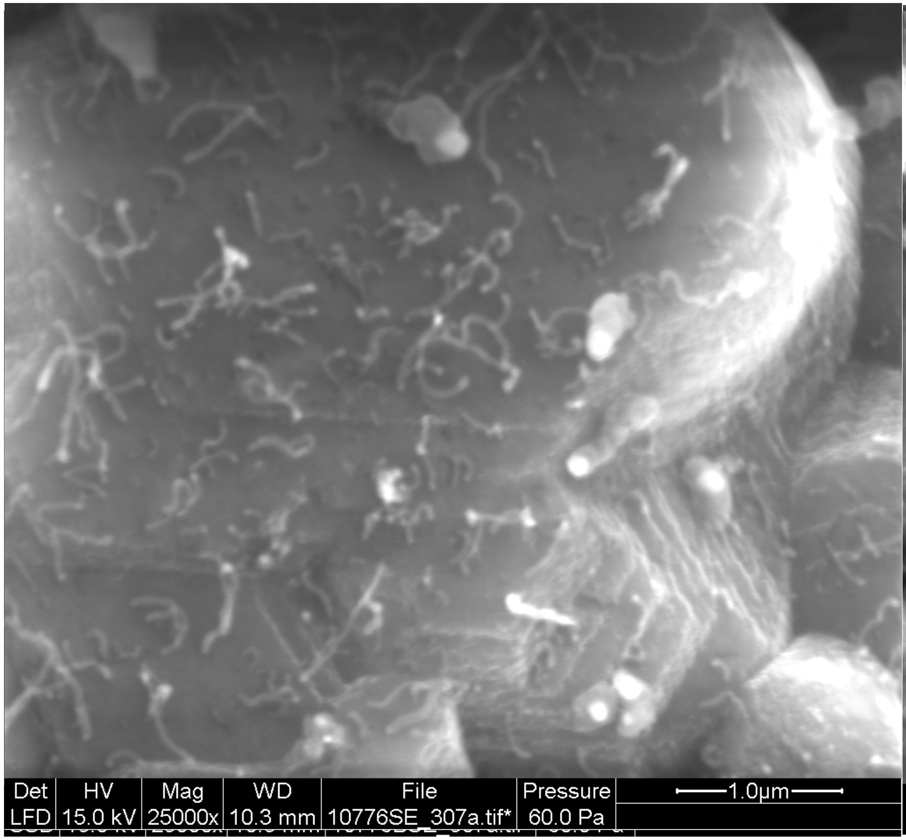


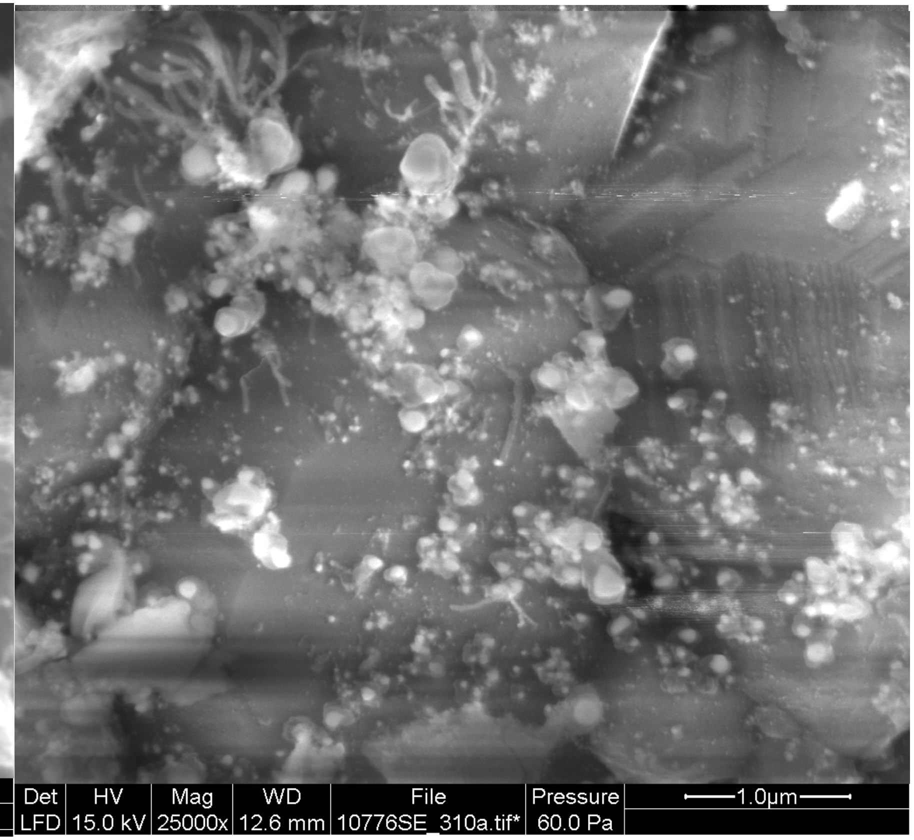




(from L.Reimer, Image formation in the low-voltage SEM)

SE versus BSE



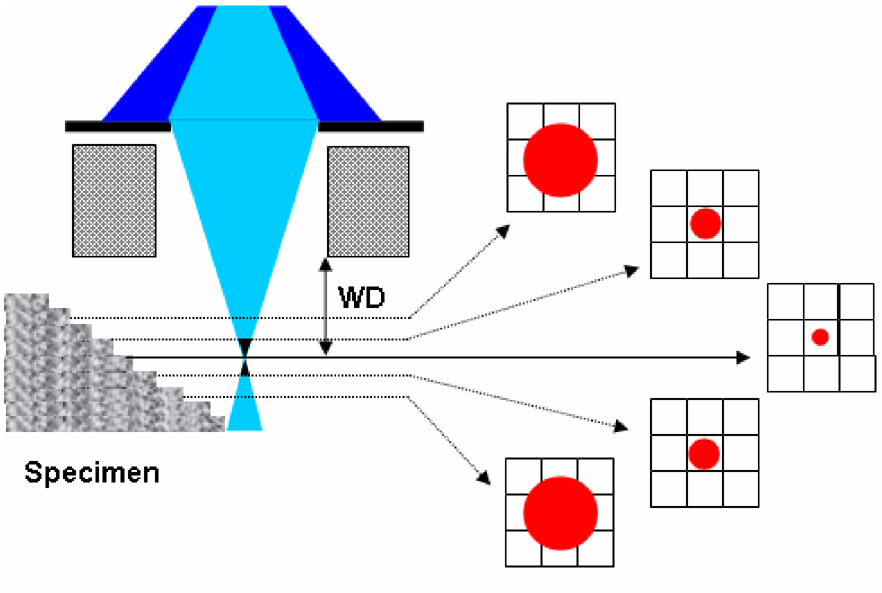


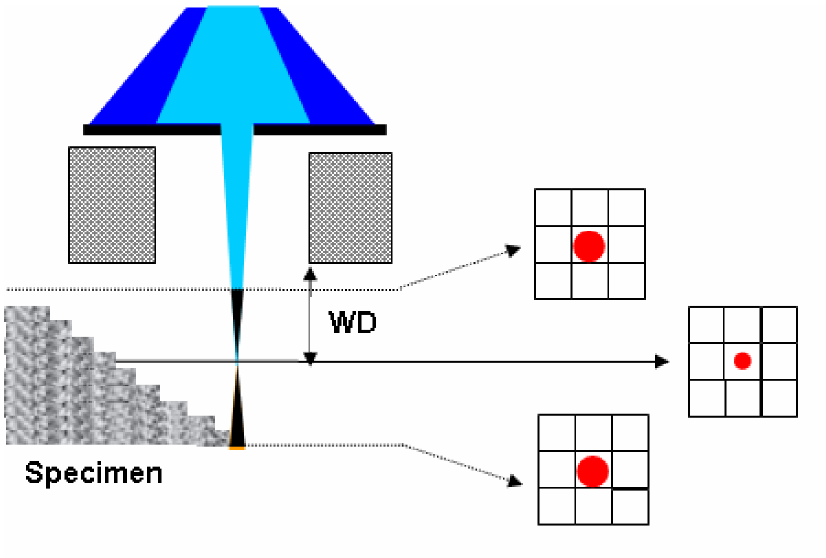
SEM analysis of a catalyst for the partial oxidation of methane on Pt

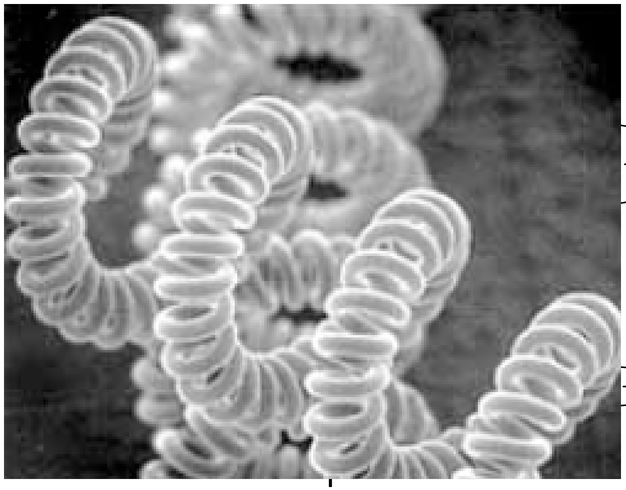
To consider in a SEM session:

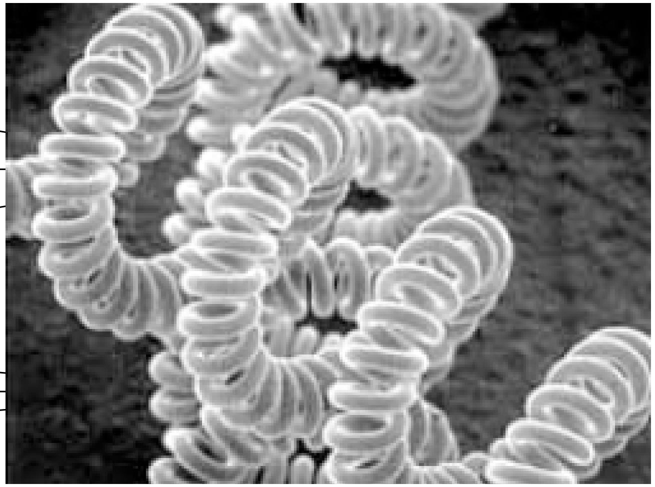
- Which signals can I use for my sample?
  - characteristic X-rays,
  - backscattered electrons,
  - secondary electrons,
  - cathodoluminescence,…
- Which acceleration voltage should I use?
  - information depth
- Which working distance is best?
  - resolution

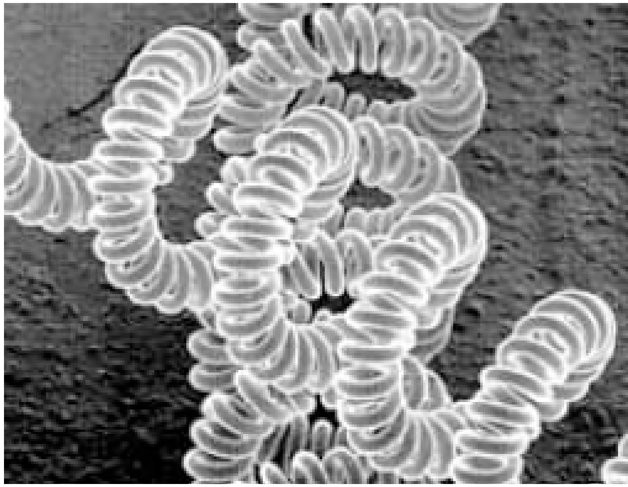
Depth of Field











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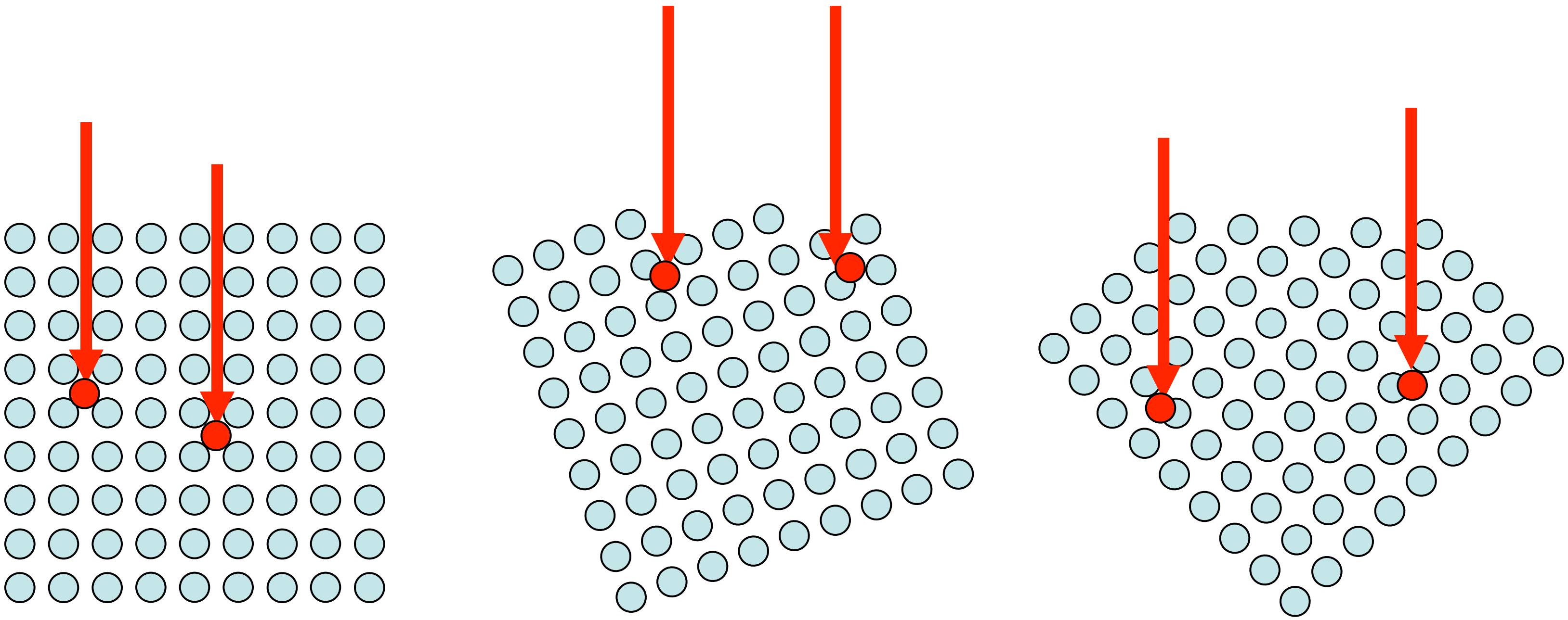
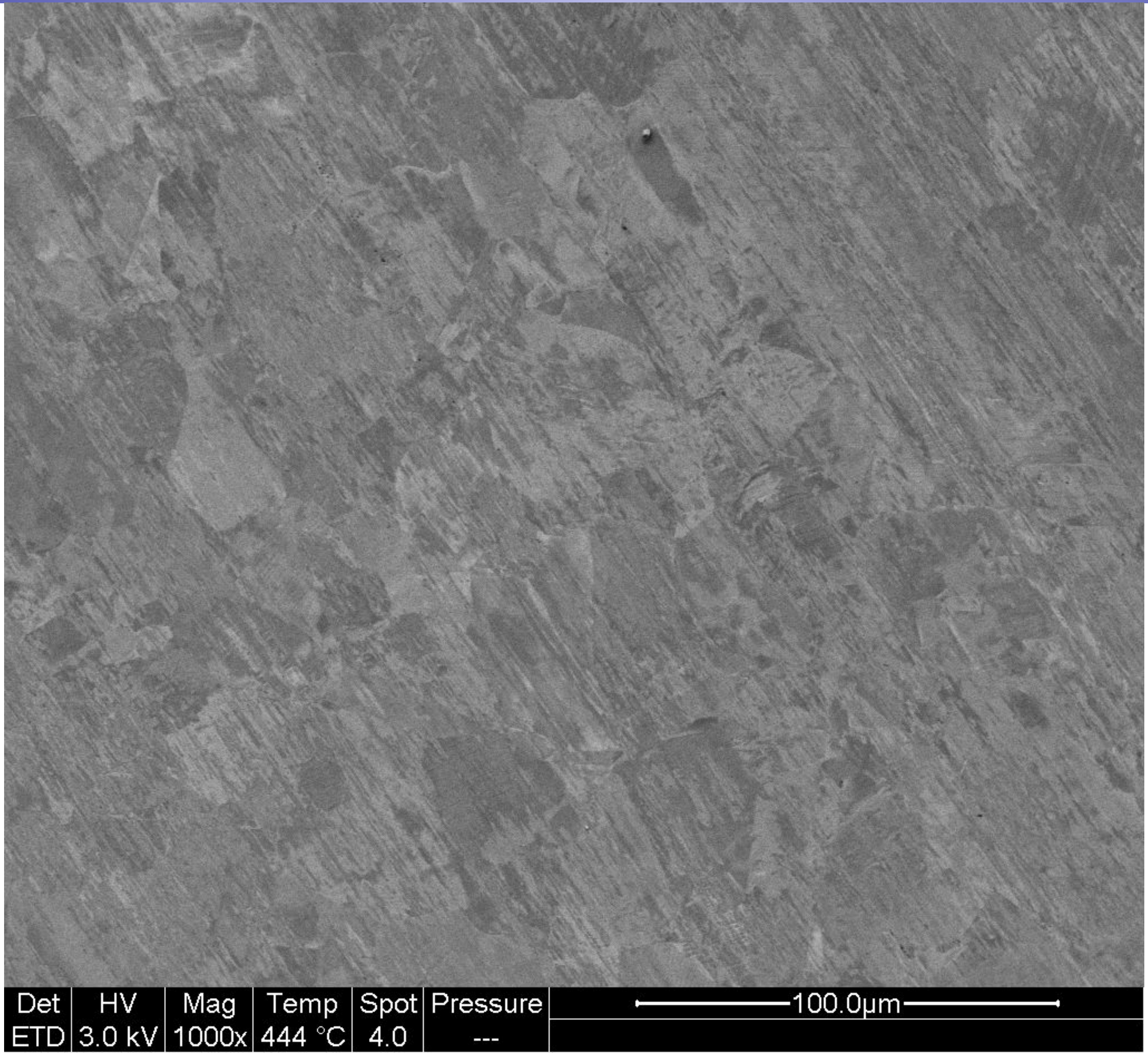
Electron Channelling Contrast

Atom columns align with the ion trajectory = higher penetration
-> less SE electrons



Electron Channelling Contrast



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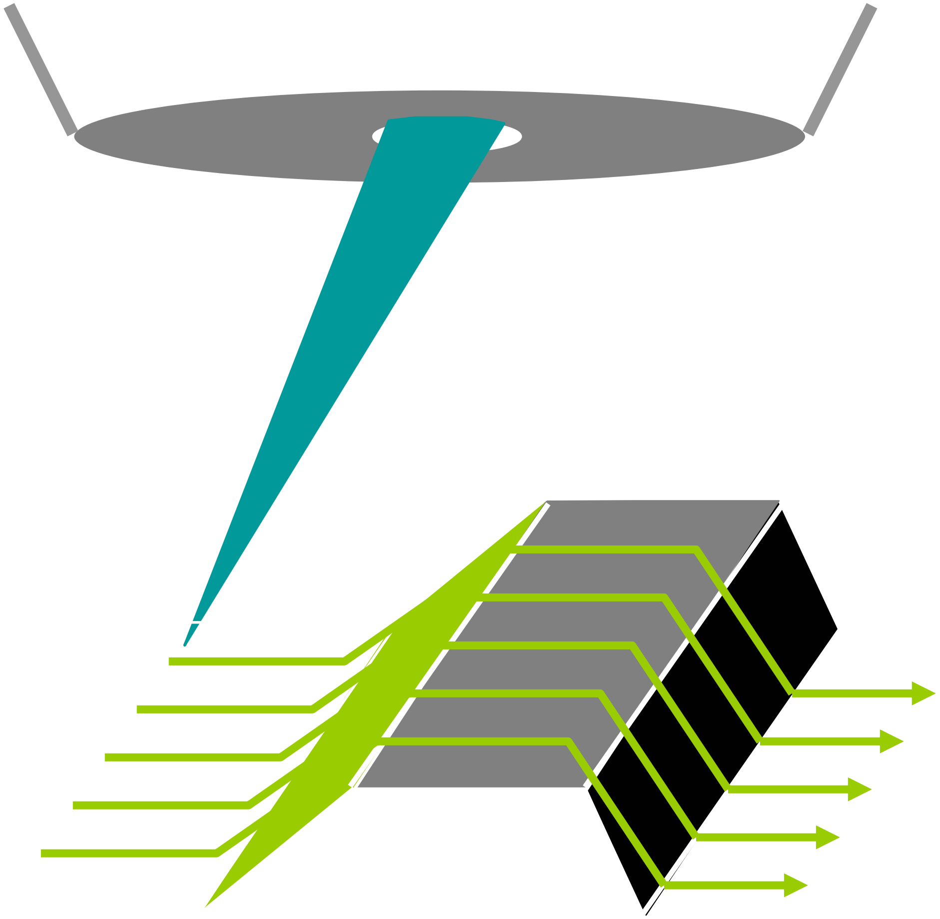
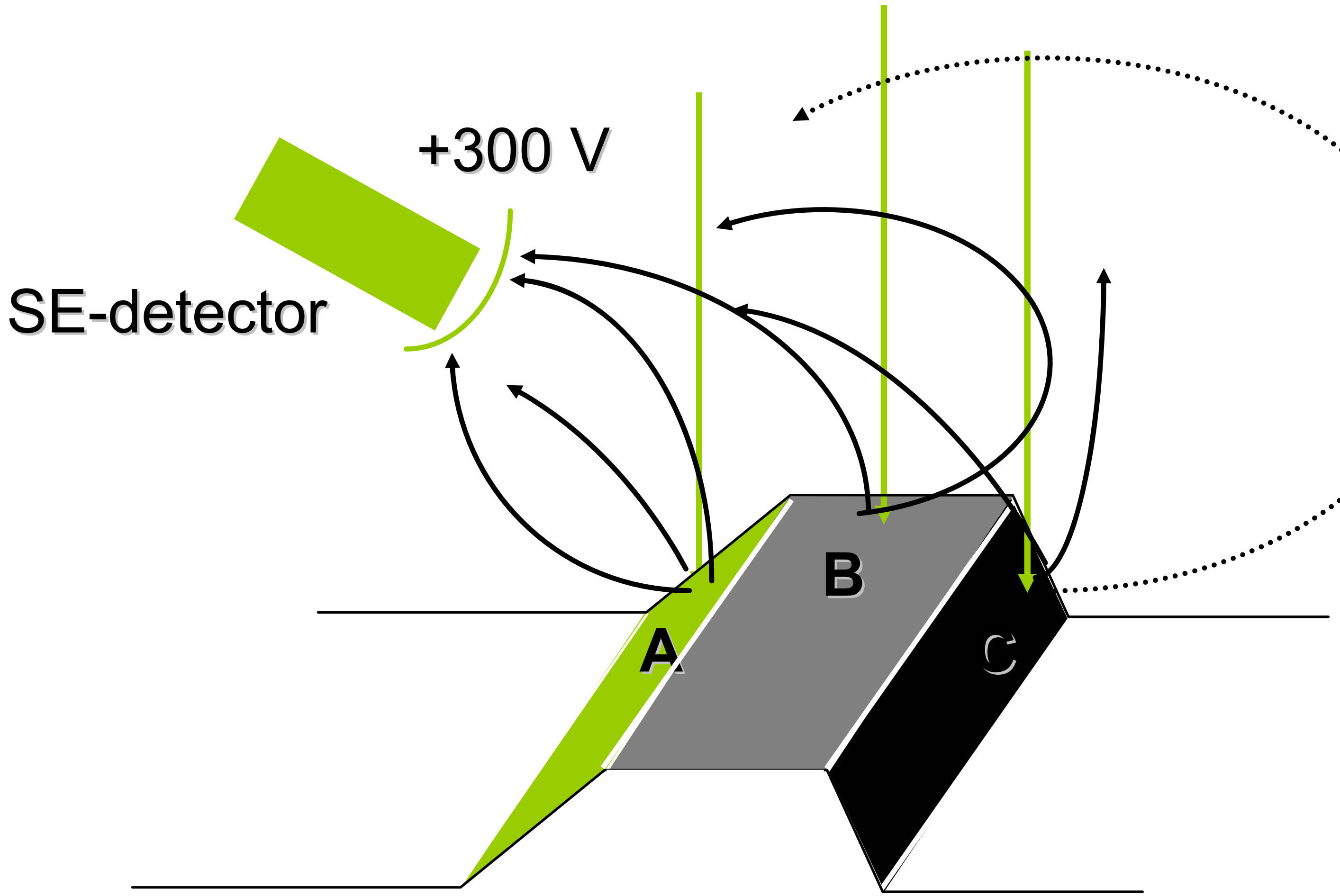
Effects of Morphology



David Muller 2008

Effects of Morphology



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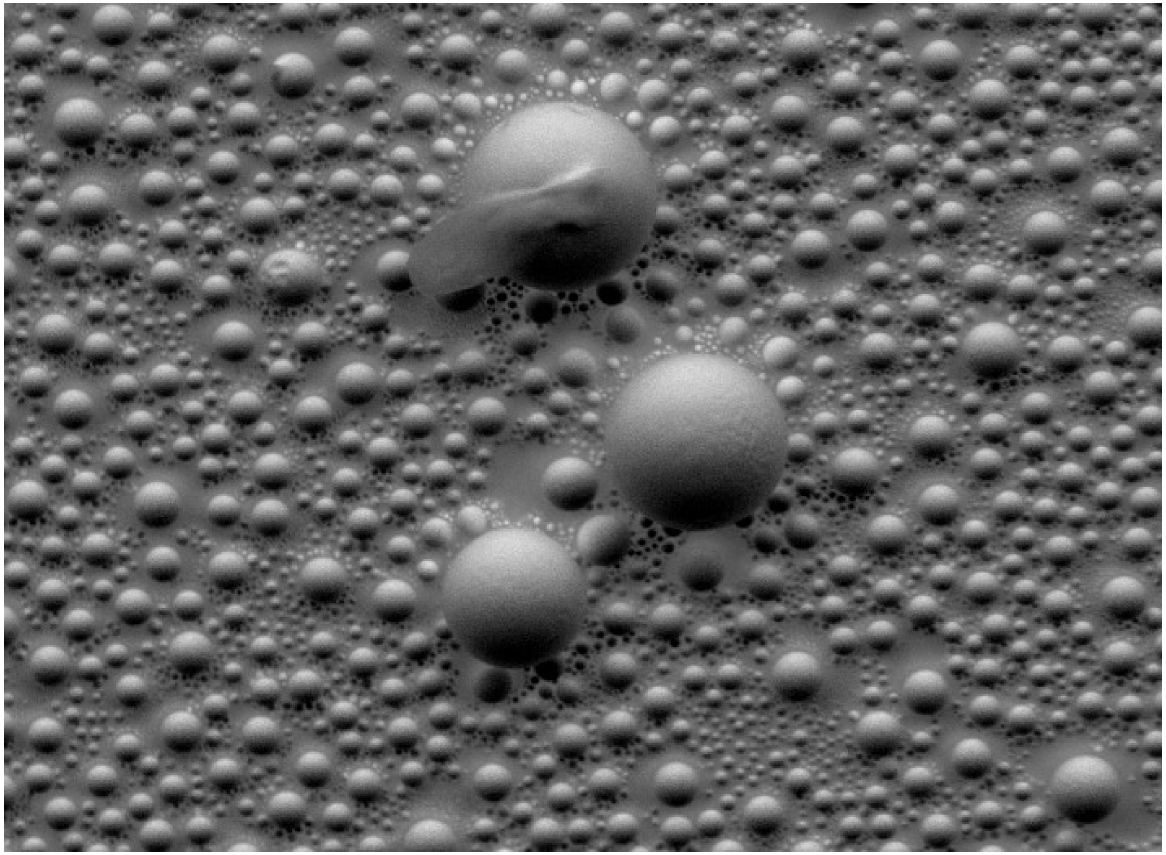
Effects of Morphology



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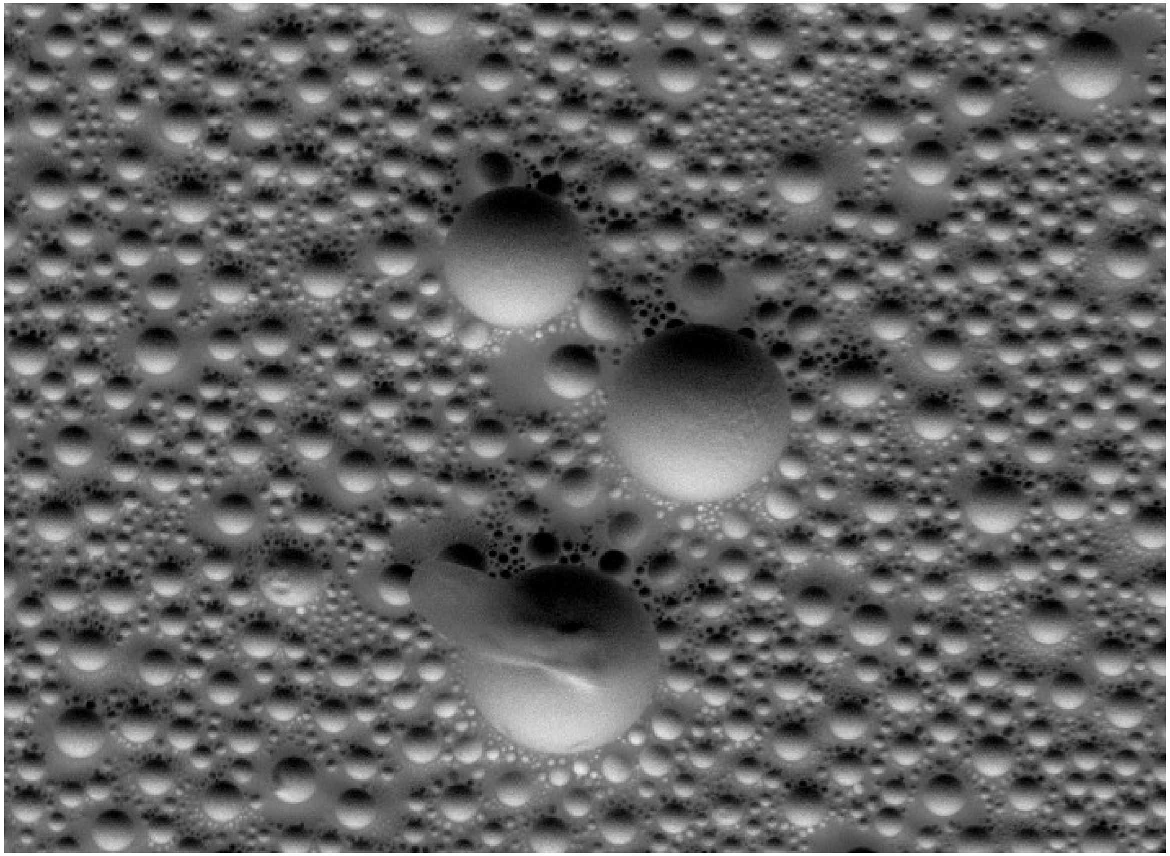
Effects of Morphology

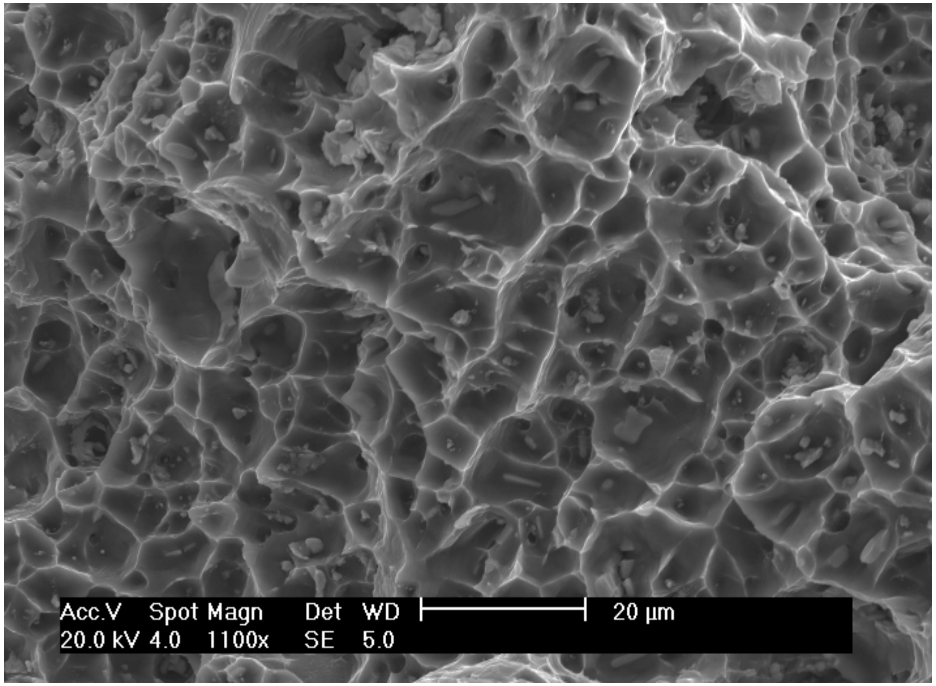


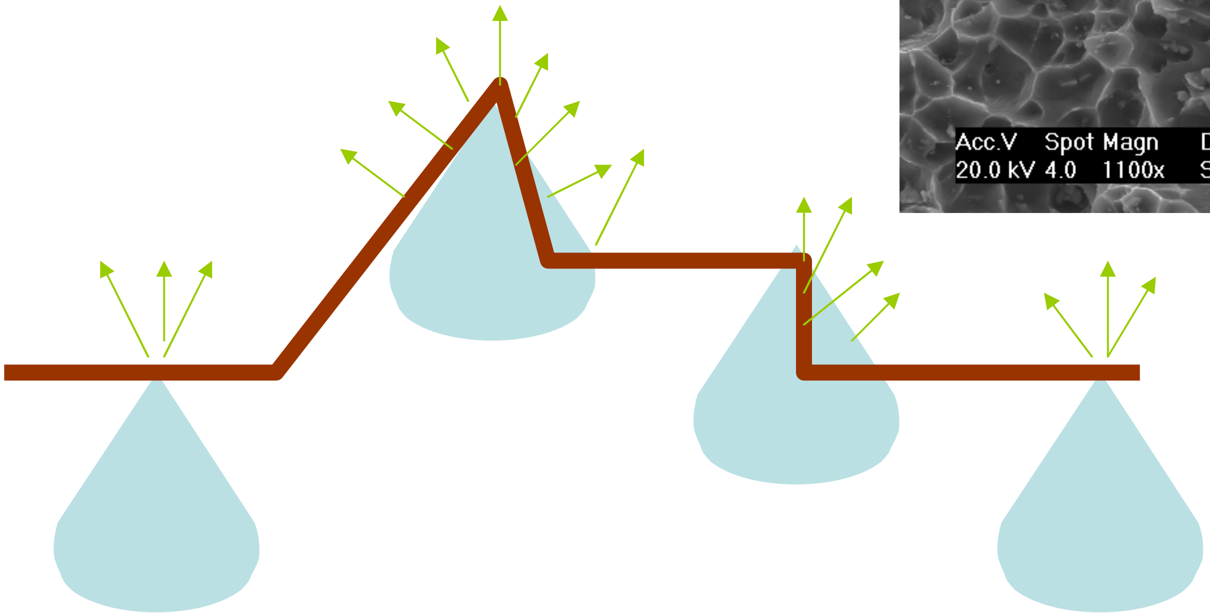
Previous image turned upside down.
We need to know where the detector is to tell bumps from pits!

David Muller 2008

Effects of Morphology

Why Edges appear brighter





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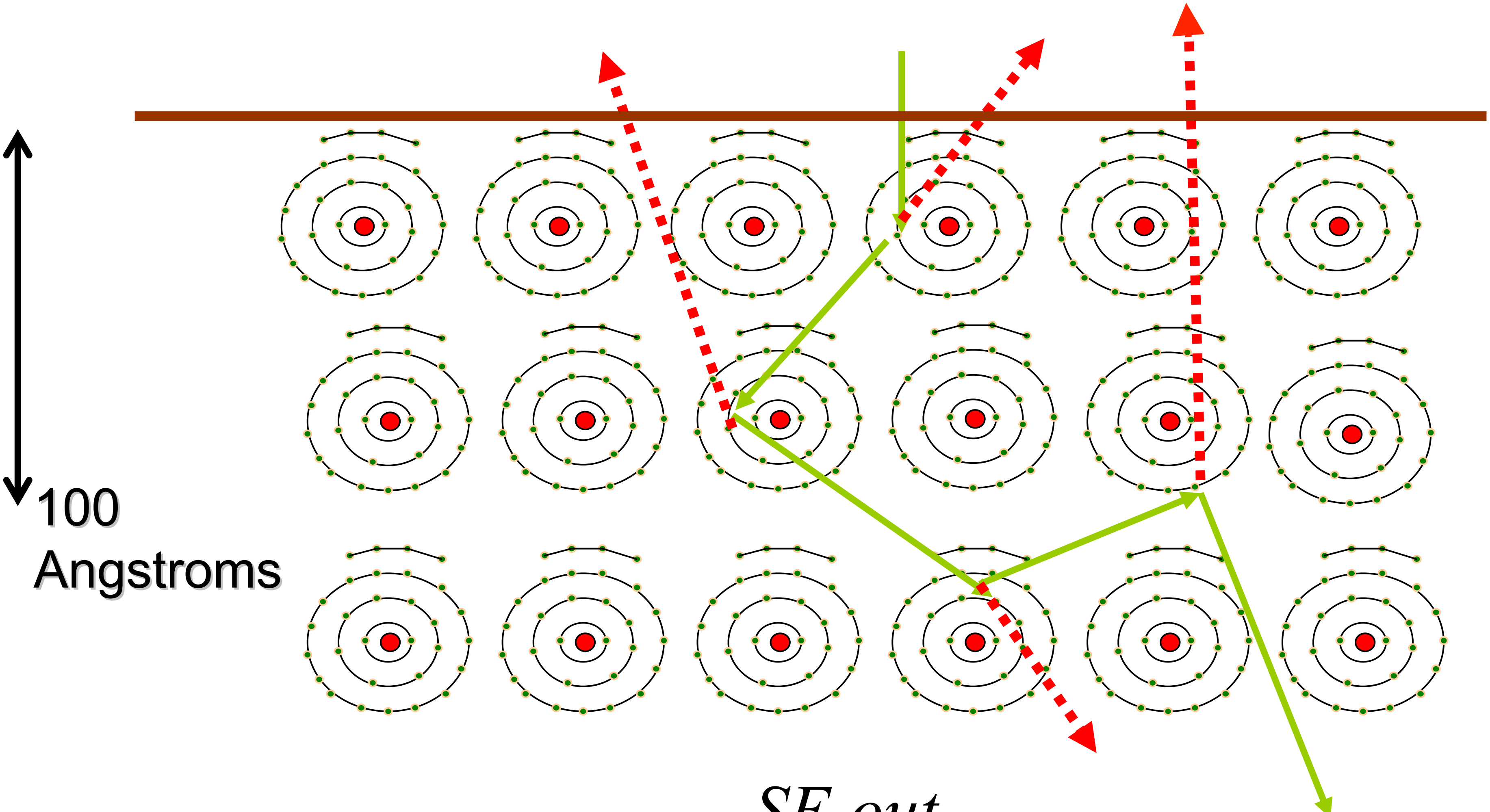
Secondary Electron Yield



Secondary Electron
Yield Coefficient

$$\delta = \frac{SE\ out}{PE\ in}$$

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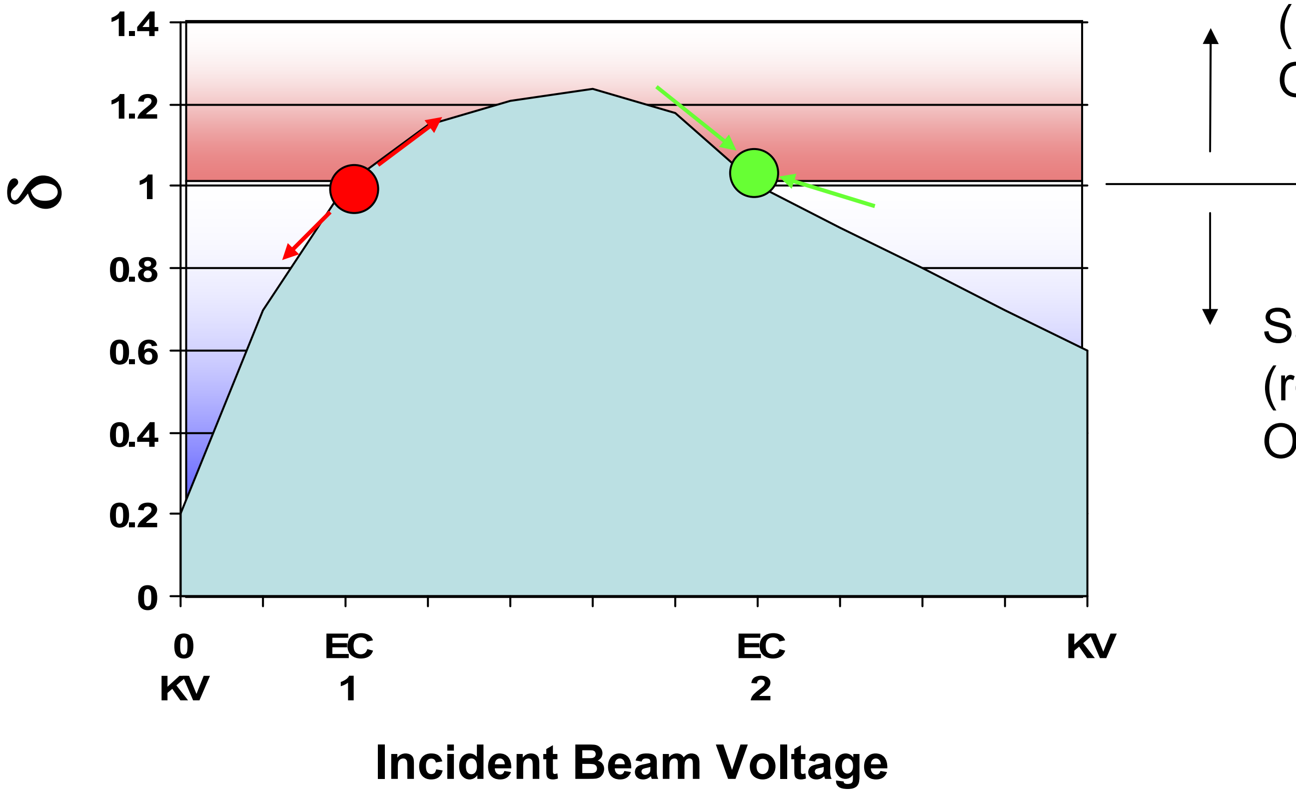
Charging and Charge Neutralization

Electron Yield δ = # SE out / # e- in



Sample charges +ve
(increases landing energy
Of incident electrons)

Sample charges –ve
(reduces landing energy
Of incident electrons)

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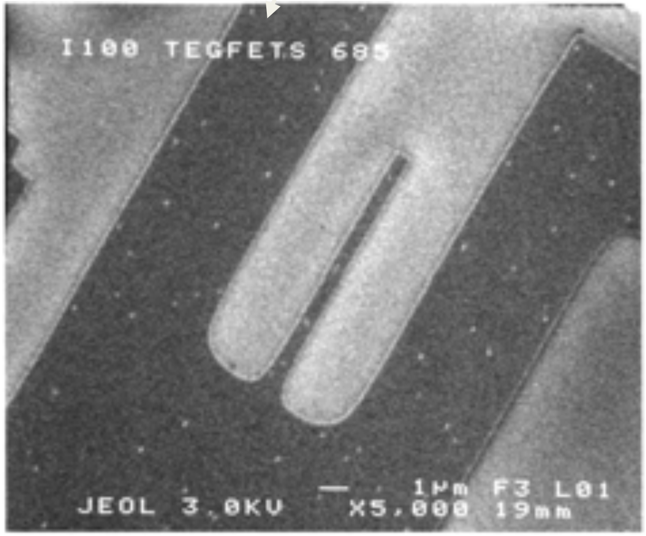
Contrast reversal in SE mode close to the neutrality point

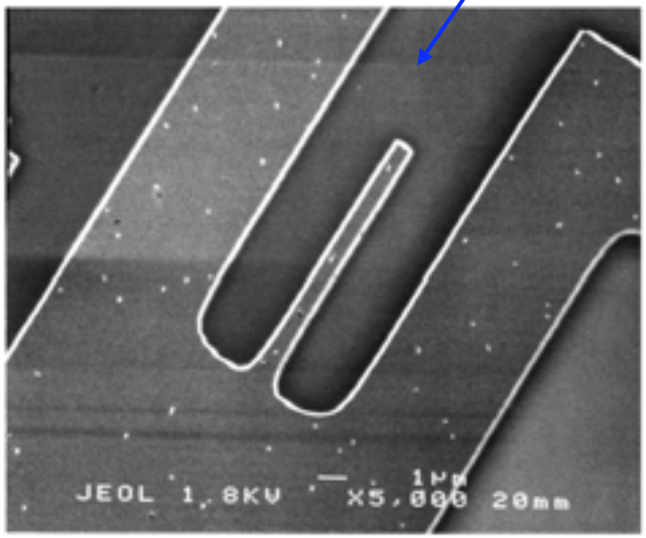
SiO_2-Cr mask for TEG-FET transistors production

SiO_2 (E_2~3.0keV)

Cr (E_2~1.8keV)



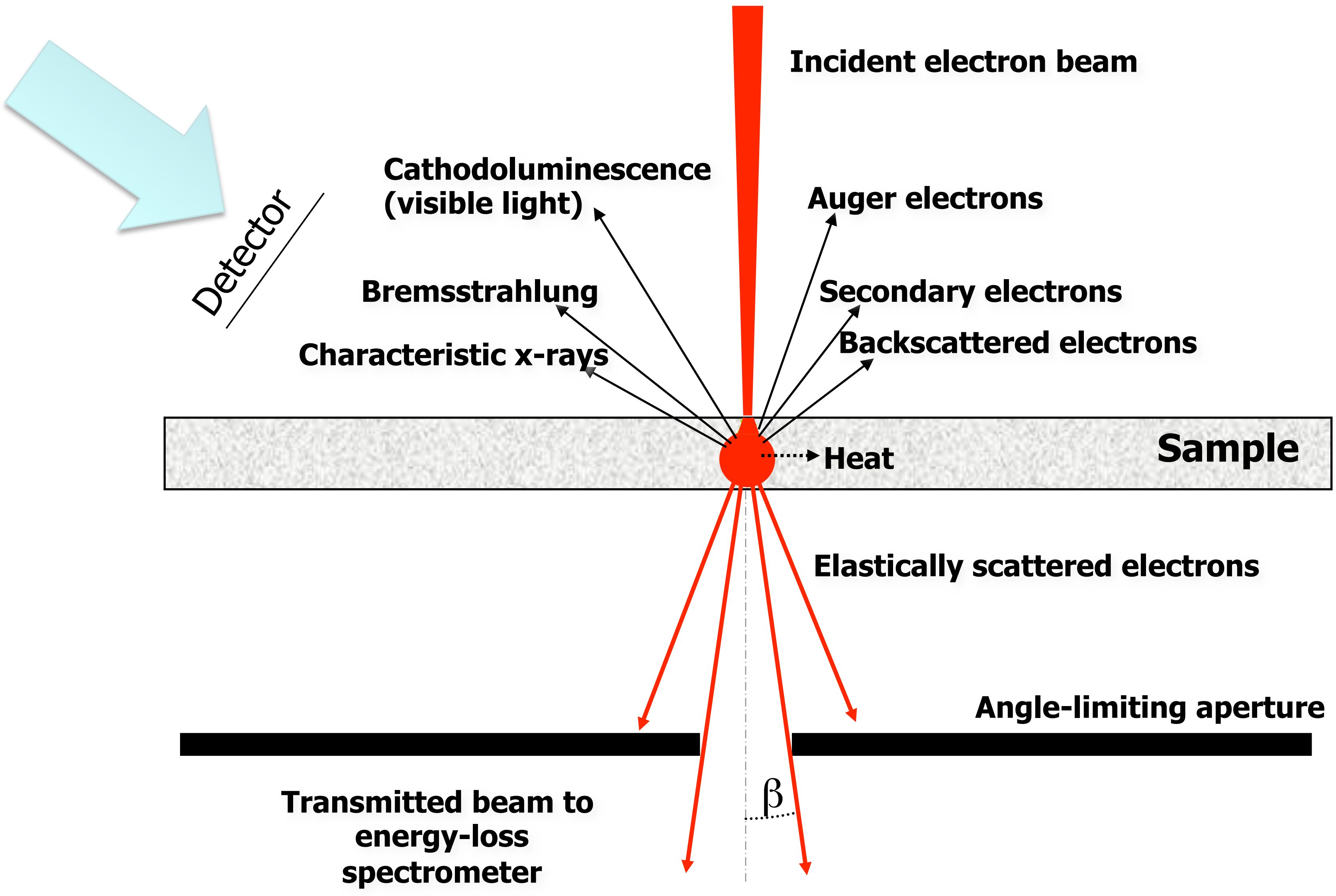
3.0 kV



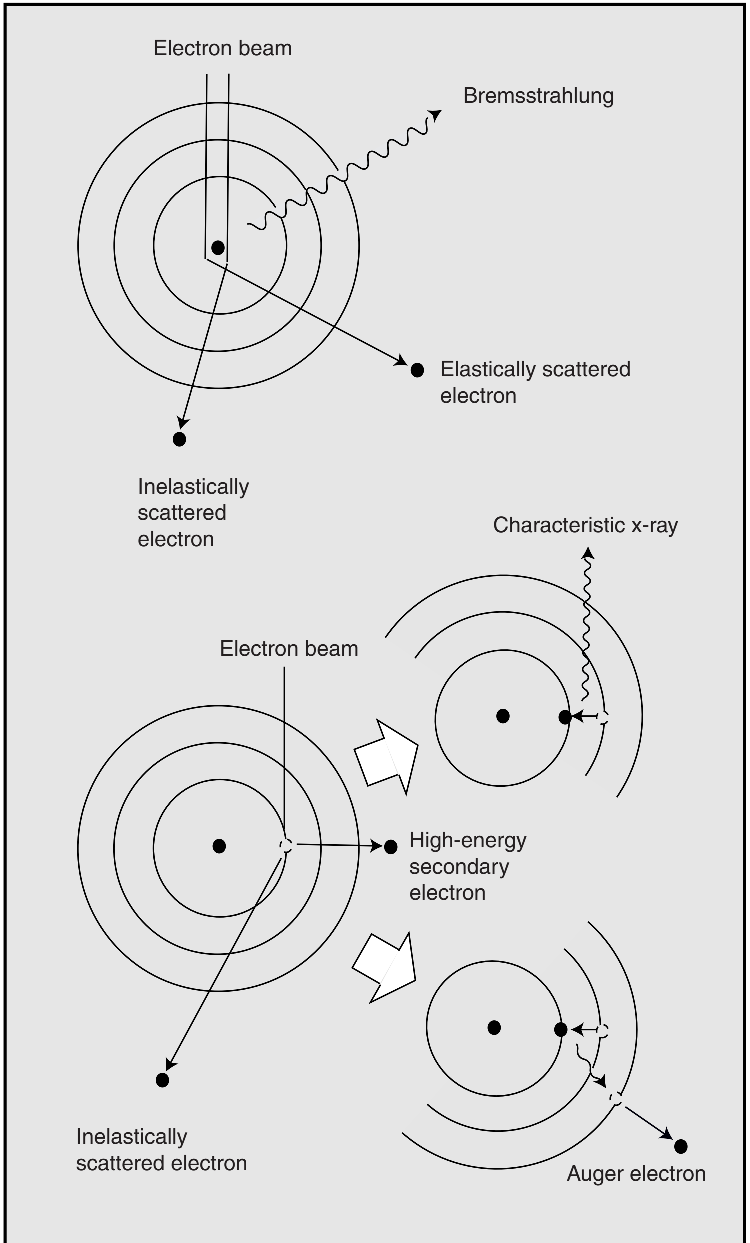
1.8 kV

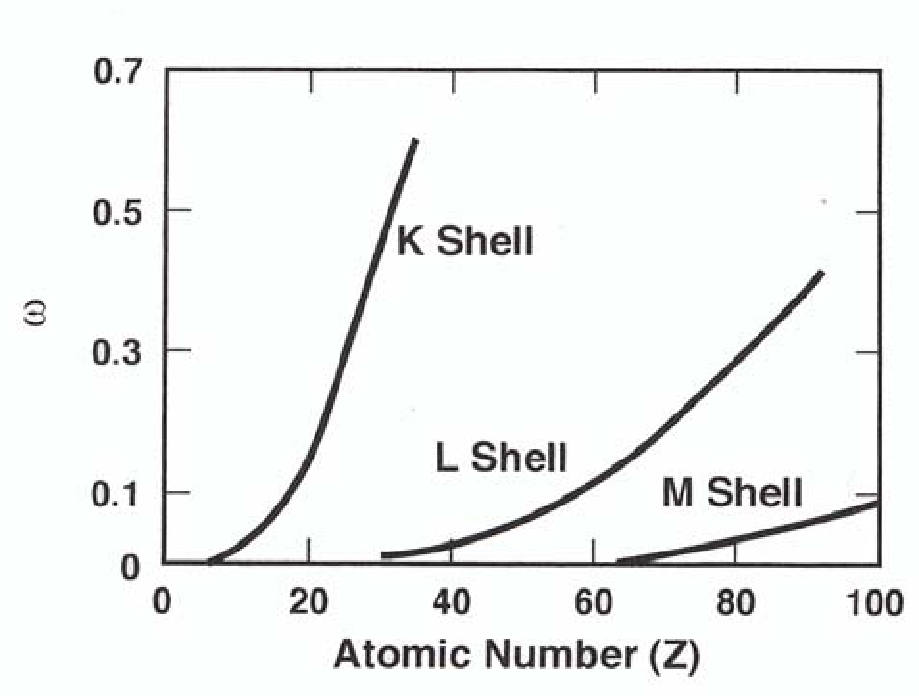
Cliché Kontron (Kuschek)pour CIME

Electron - Sample Interactions



Energy Dispersive X-Ray Spectroscopy (EDX)





Fluorescence Yield (ω):
ω = # X-ray photons produced / # shell ionizations

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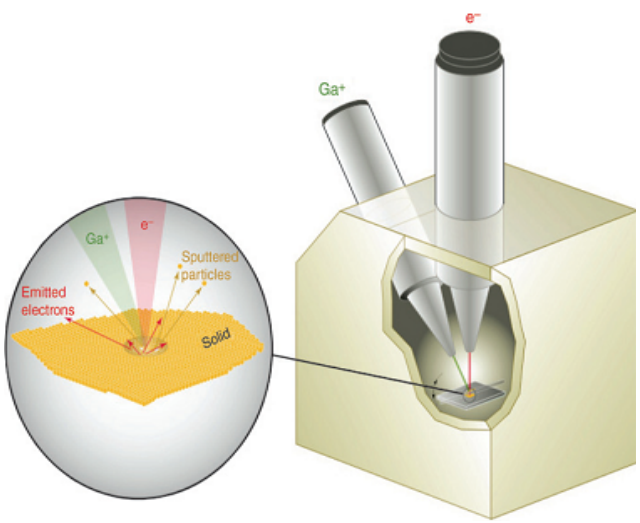
Outline

- SEM:
  - components of the SEM
  - signals and their information content
  - Focused Ion Beam/SEM
- TEM
- Examples

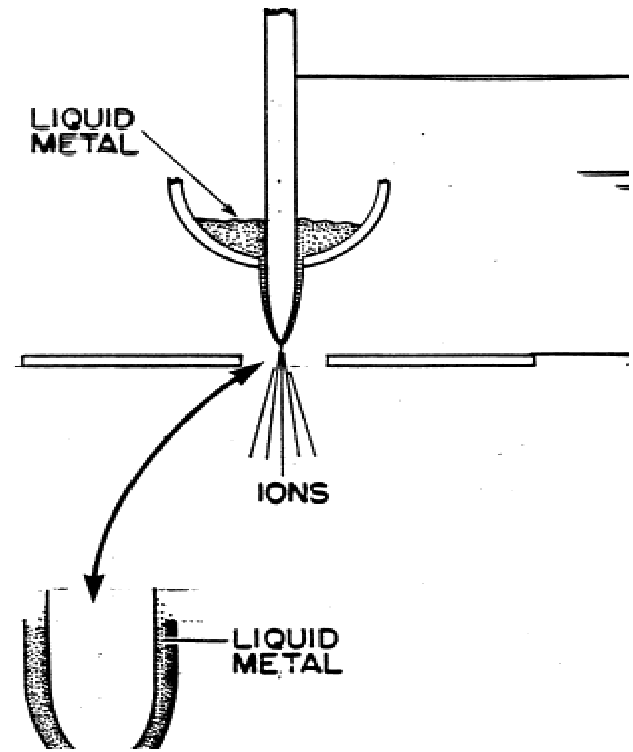
FIB: Focused Ion Beam

- *a complete state of the art (high -performance) SEM equipped with*
  a) focused ion column
  b) Gas injector system
  c) micromanipulators

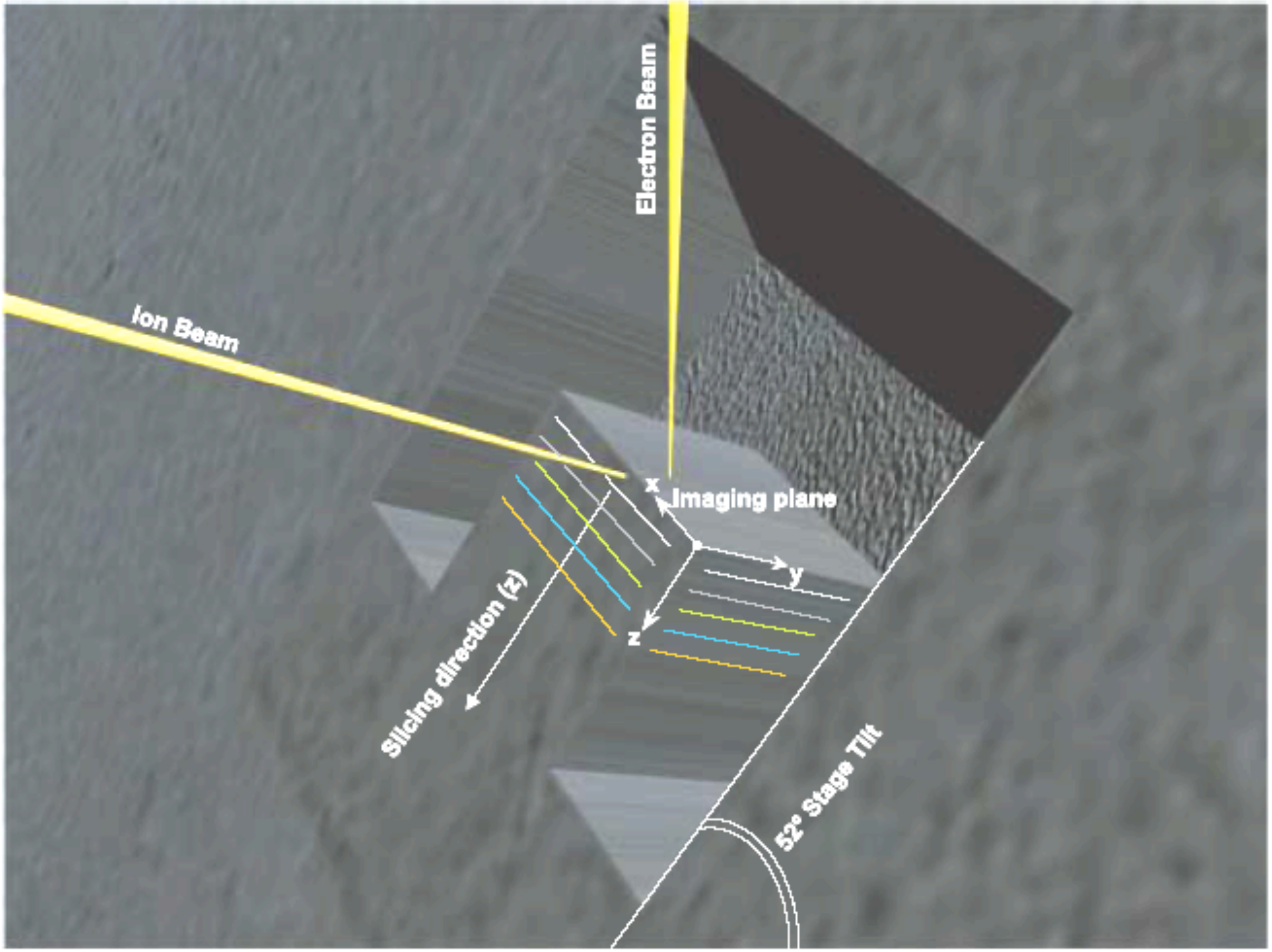


Dual beam ®, crossbeam ®

Liquid Metal Source

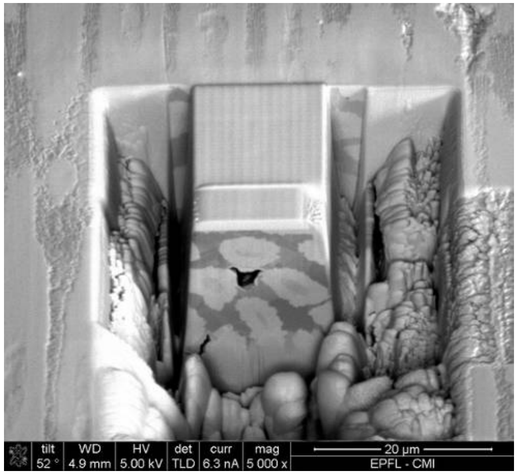


FIB Nanotomography

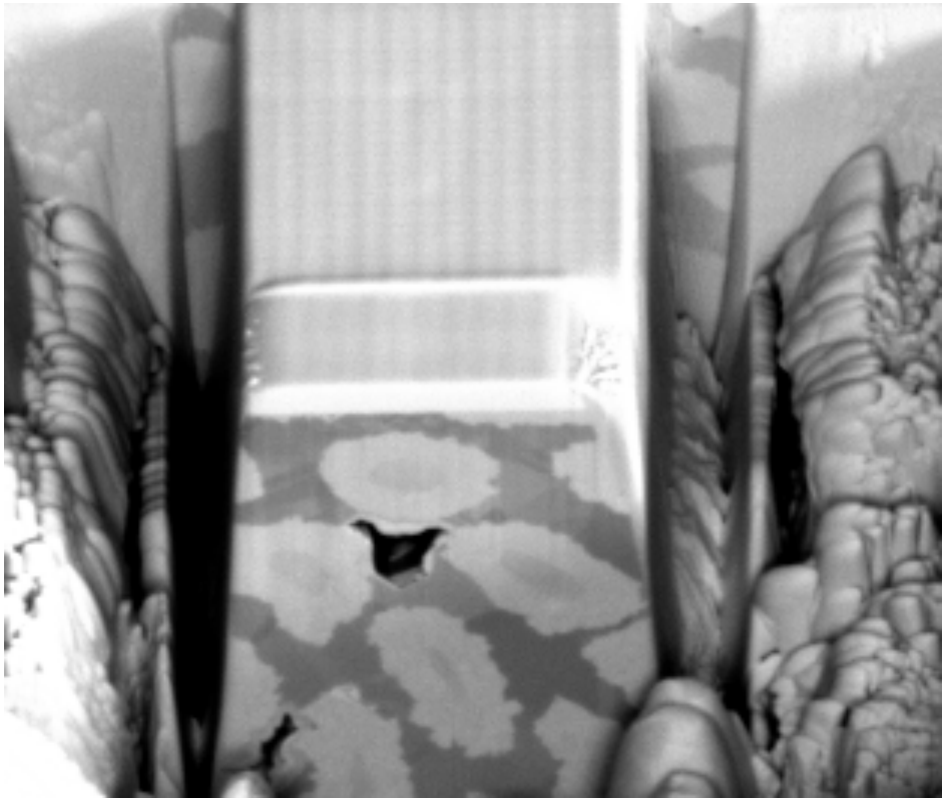


3D Microscopy

FIB Nanotomography

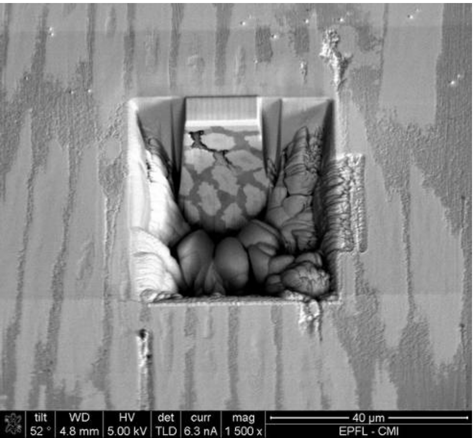


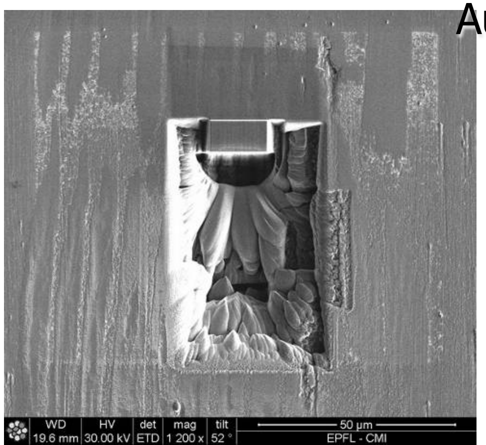
Preparing for slicing



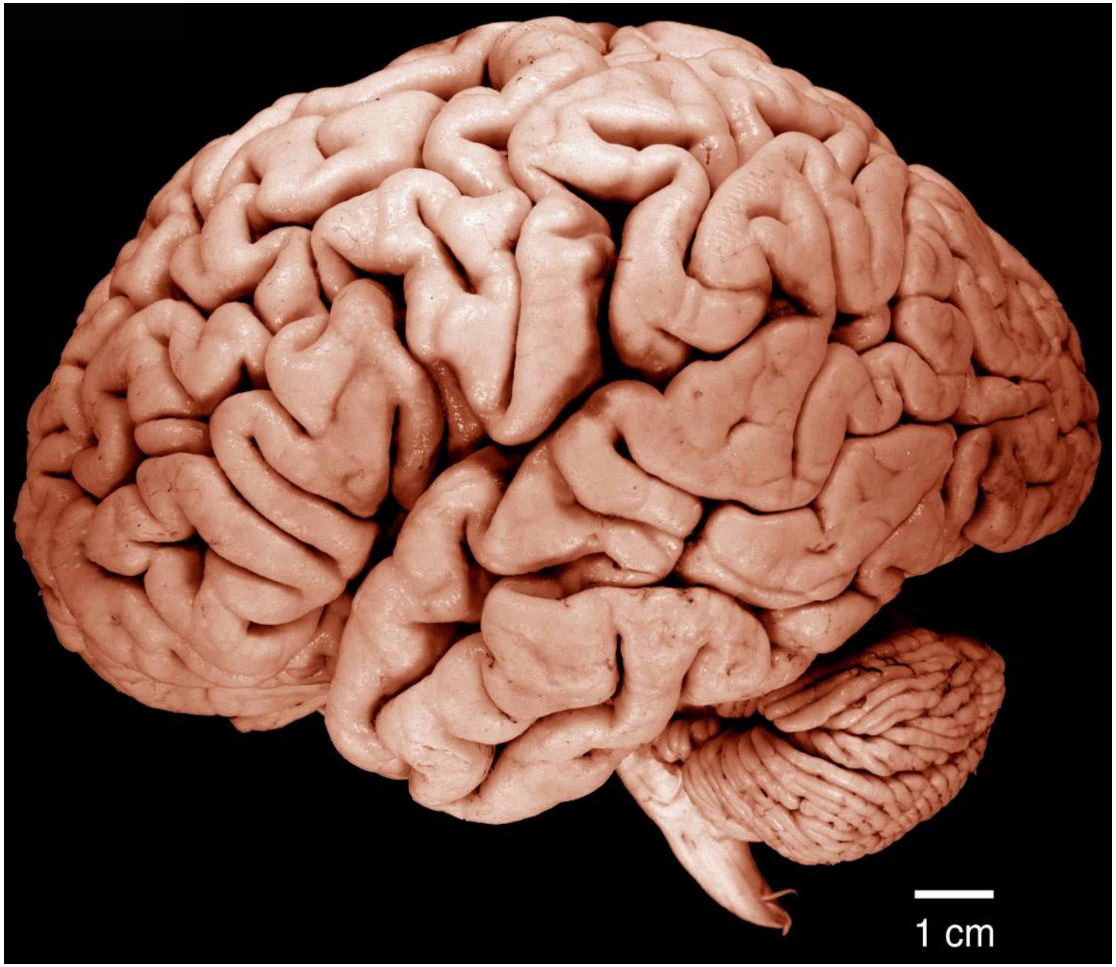
Automated milling and imaging of 170 slices (10h)

the end





One of the biggest challenge in Life Science

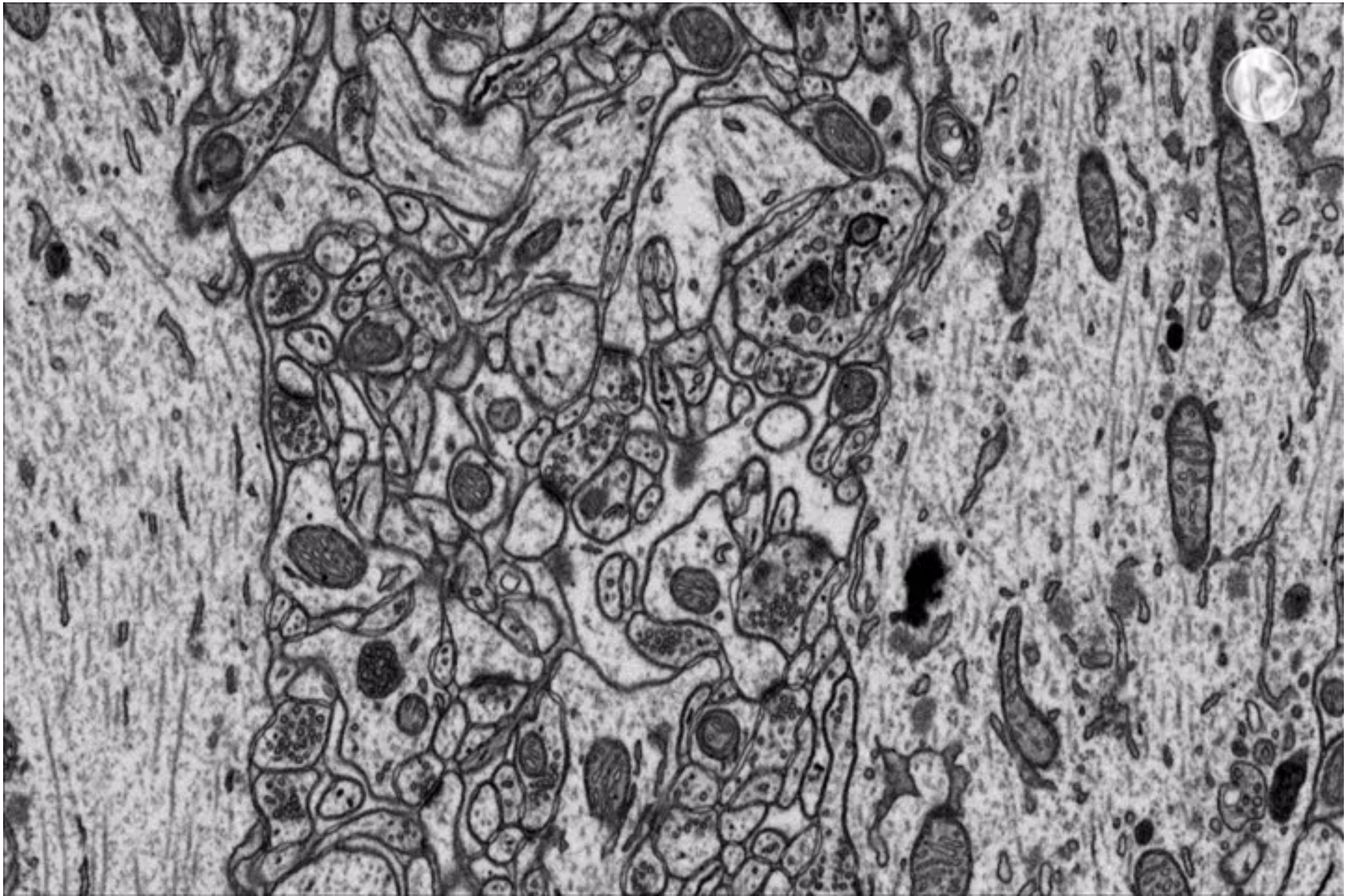


~1’ 000’ 000’ 000 neurons
~10’ 000’ 000’ 000 connections

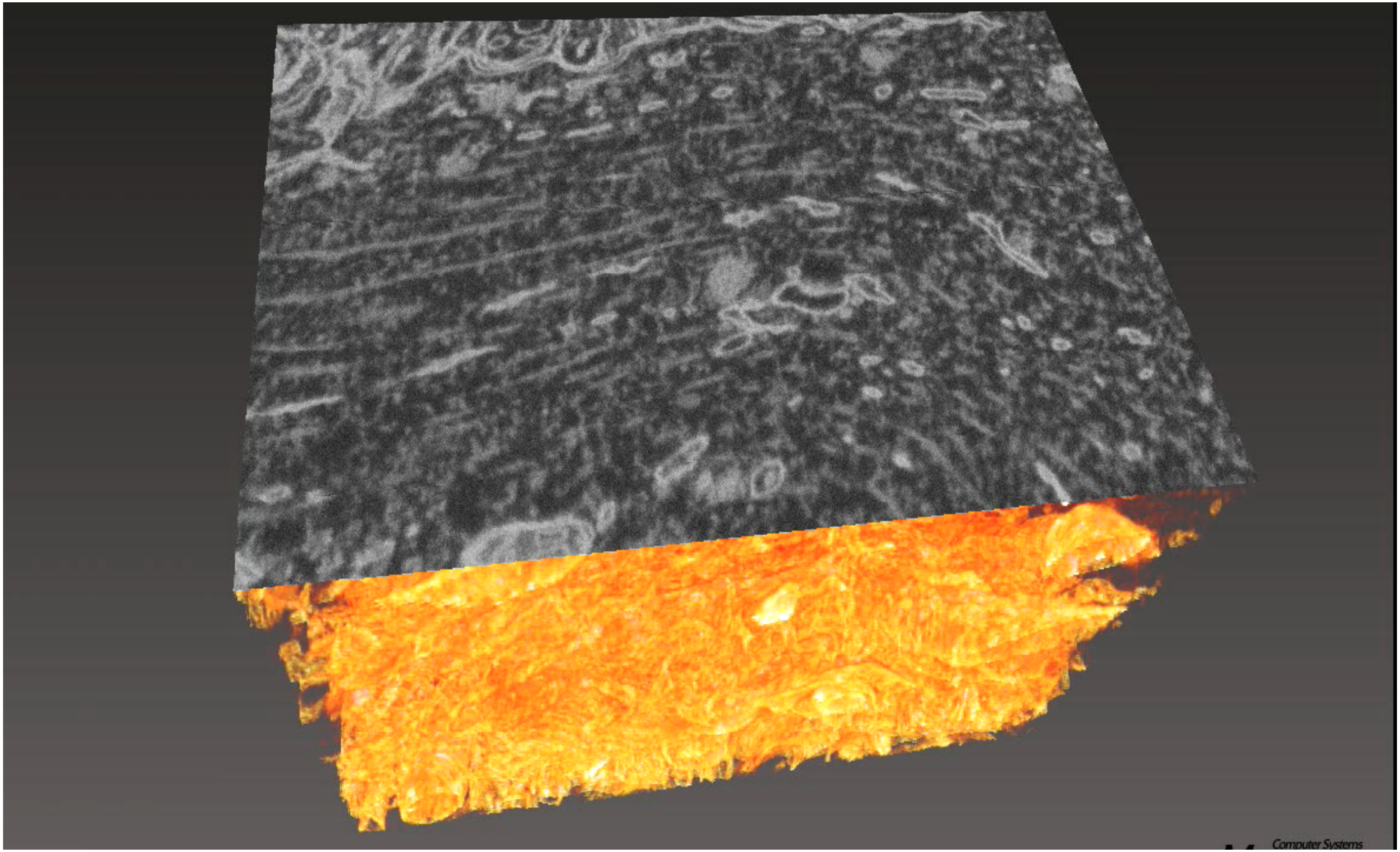
THE STACK

2048 x 1536 x 1600   8 x 6 x 8 um   voxel: 5x5x6nm

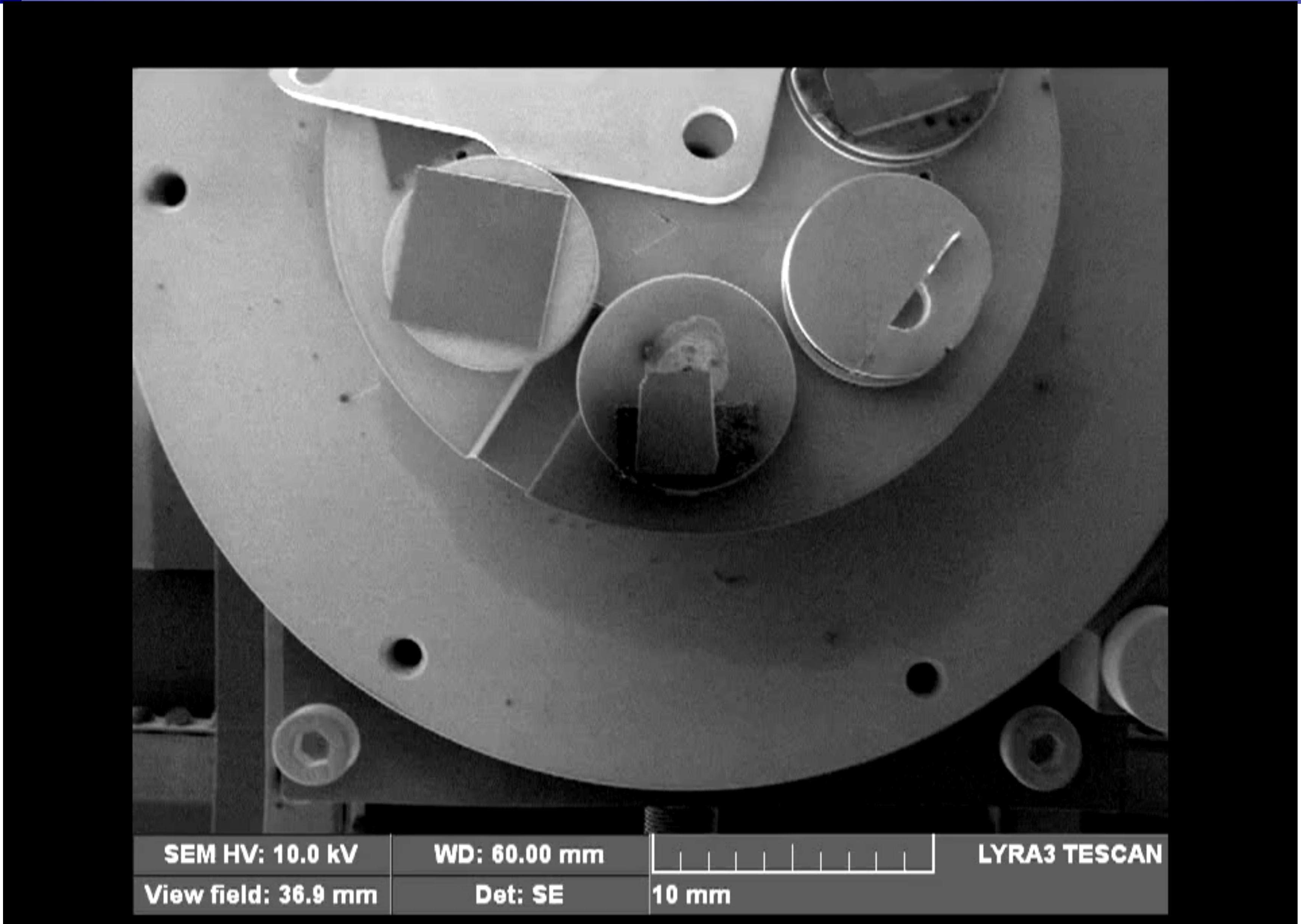
2 days of fully automated acqusition



Reconstruction…

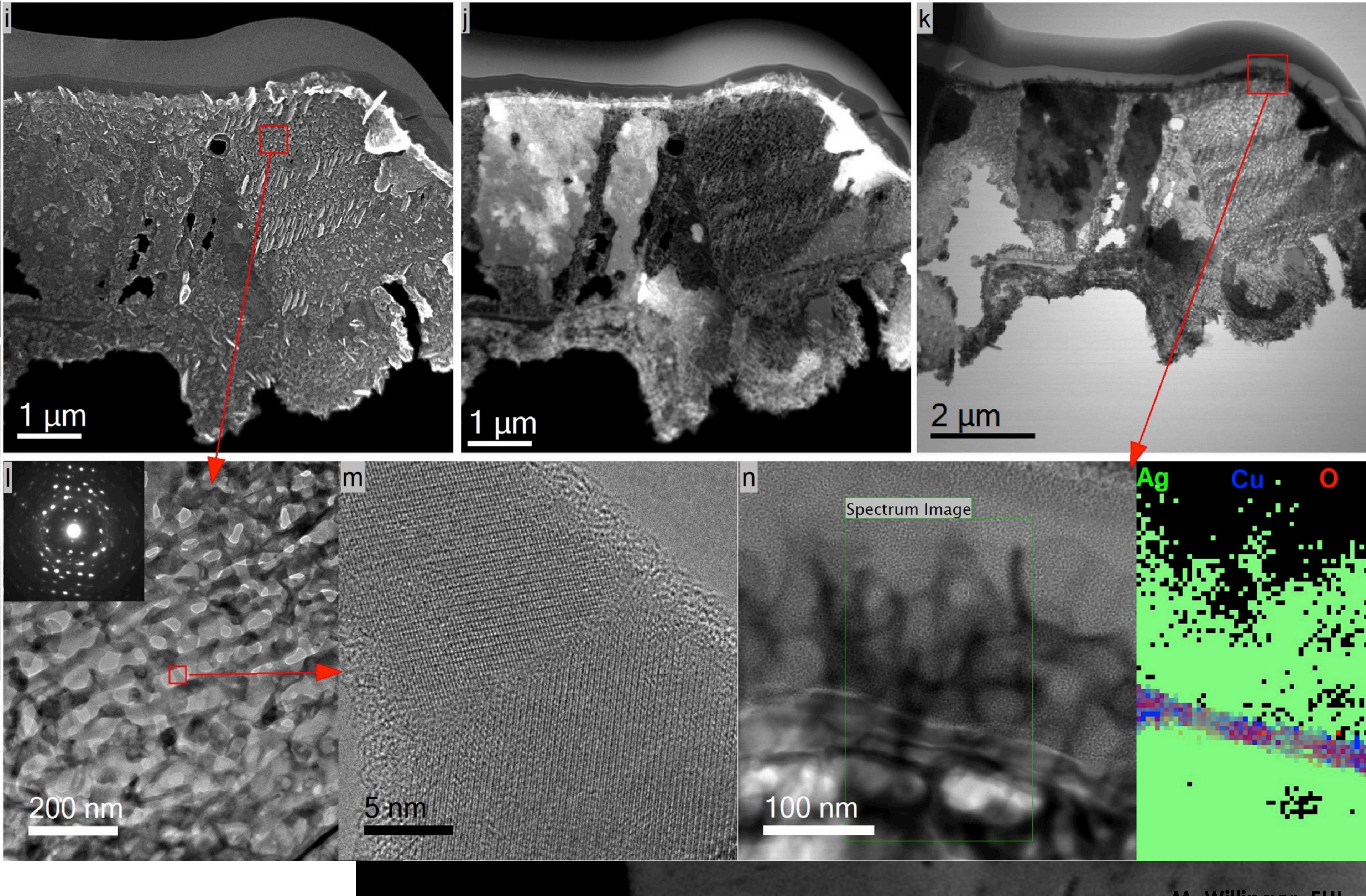


Preparation of TEM Lamella



tp://www.youtube.com/watch?v=MadIrIGMhDw

future FIB @ FHI

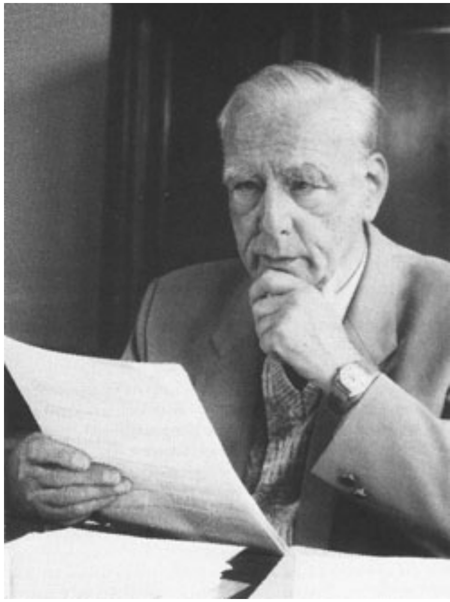


M. Willinger, FHI

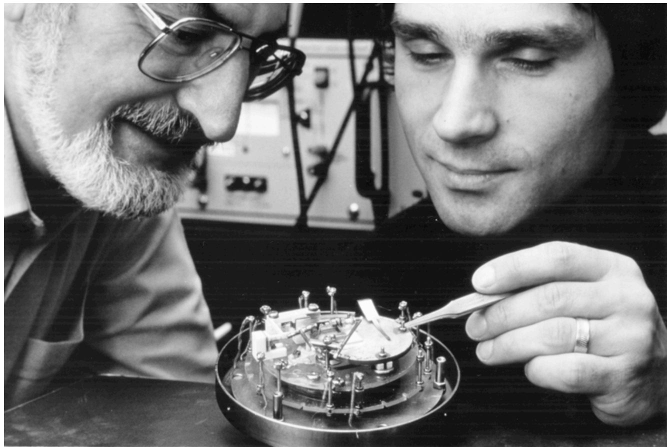
TEM

- Set-up of a TEM
  - Electron Gun, Coherency, Lenses
- Basic Interactions
  - Elastic: imaging
    - Demo: Interference, Lattice Fringes, FFT
  - Inelastic: EDX and EELS
- Chemical Information

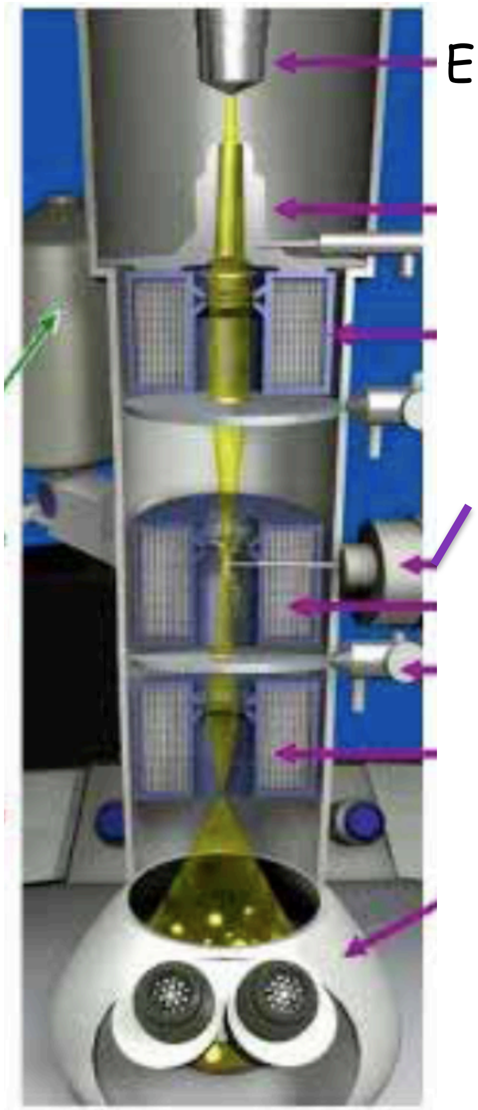
Ernst Ruska



Nobel Prize in Physics in 1986
Ernst Ruska, Gerd Binnig, Heinrich Rohrer

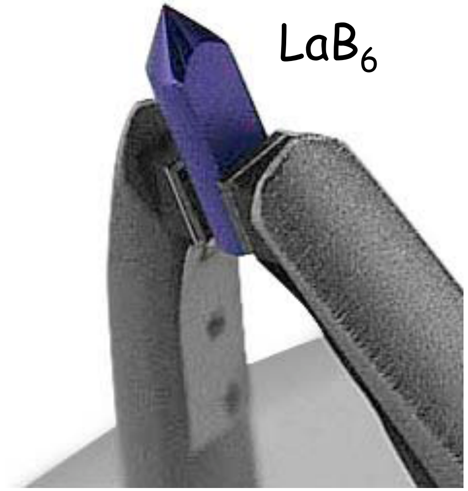


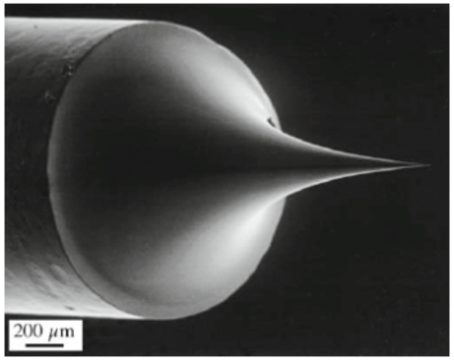
Basic set-up of the TEM



Electron gun

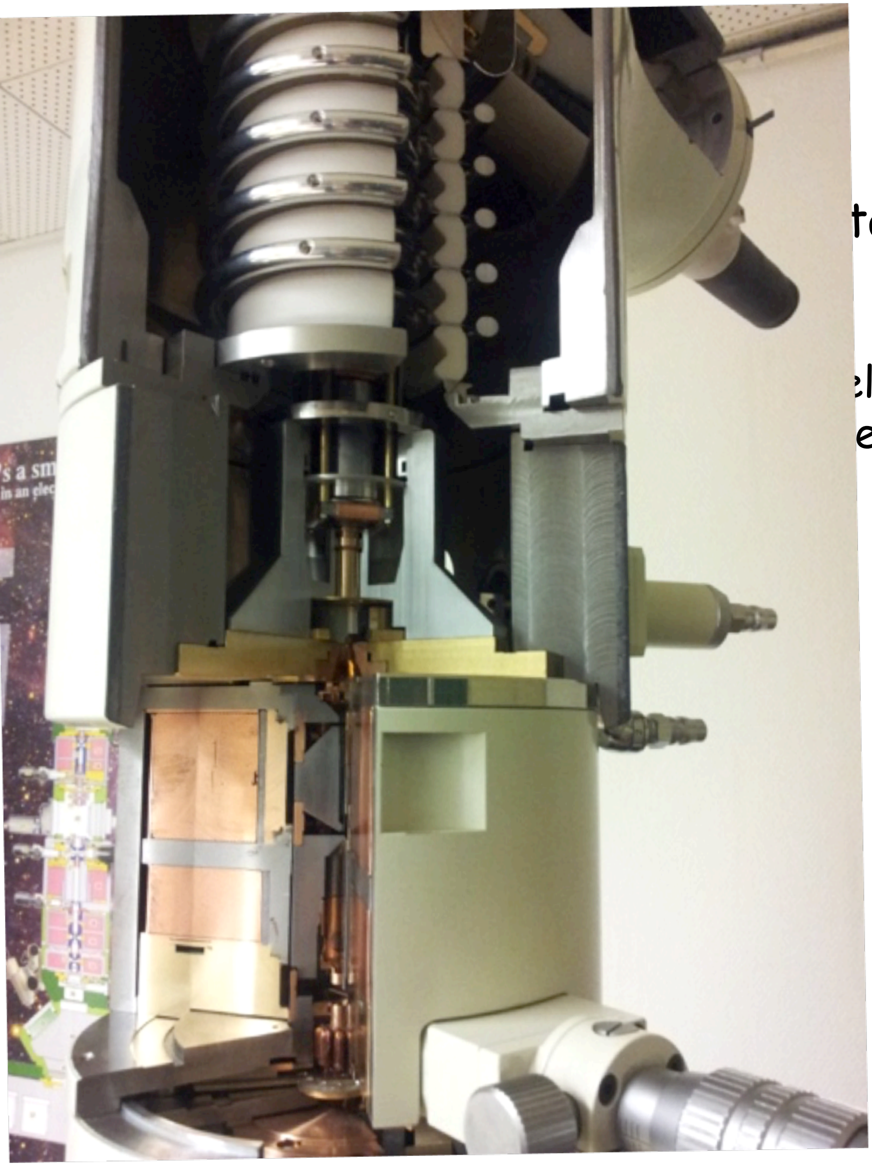
The electron gun produces a beam of monochromatic (coherent) electrons!!





a field-emission source: extraordinarily fine W needle

Basic set-up of the TEM



tage

High voltage accelerates the electrons to high kinetic energy.

elength of

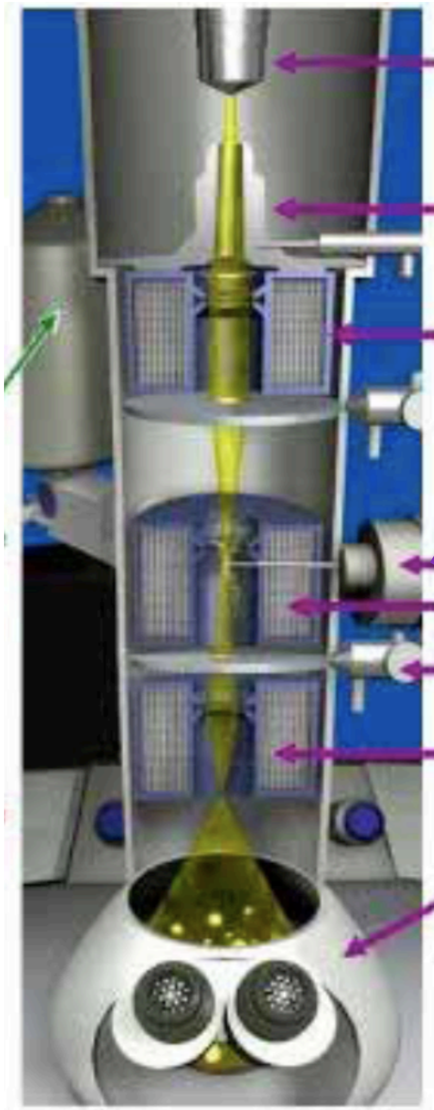
energy electrons:

E kV	γ	λ pm	$\frac{v}{c}$
50	1.098	5.362	0.412
100	1.119	3.706	0.548
200	1.391	2.511	0.695
500	1.978	1.423	0.862
1000	2.957	0.873	0.941

$$\delta = \frac{0.61\lambda}{n \sin \beta}$$

Rayleigh criterion!

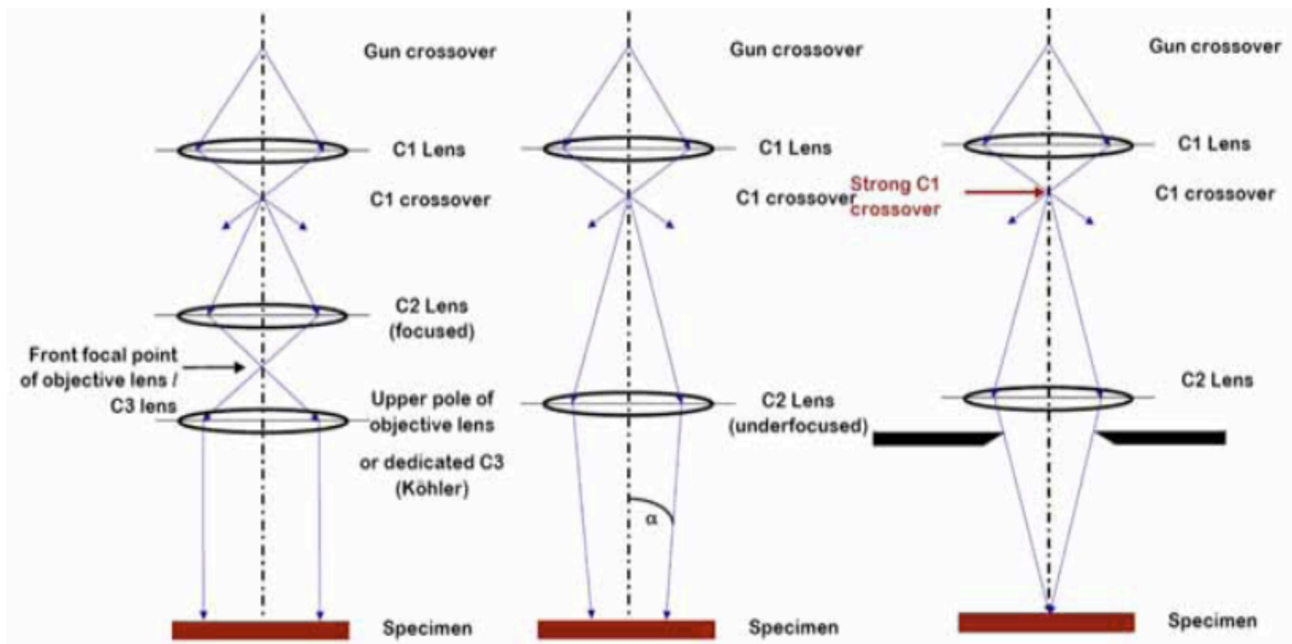
Basic set-up of the TEM



Electron gun

Acceleration stage

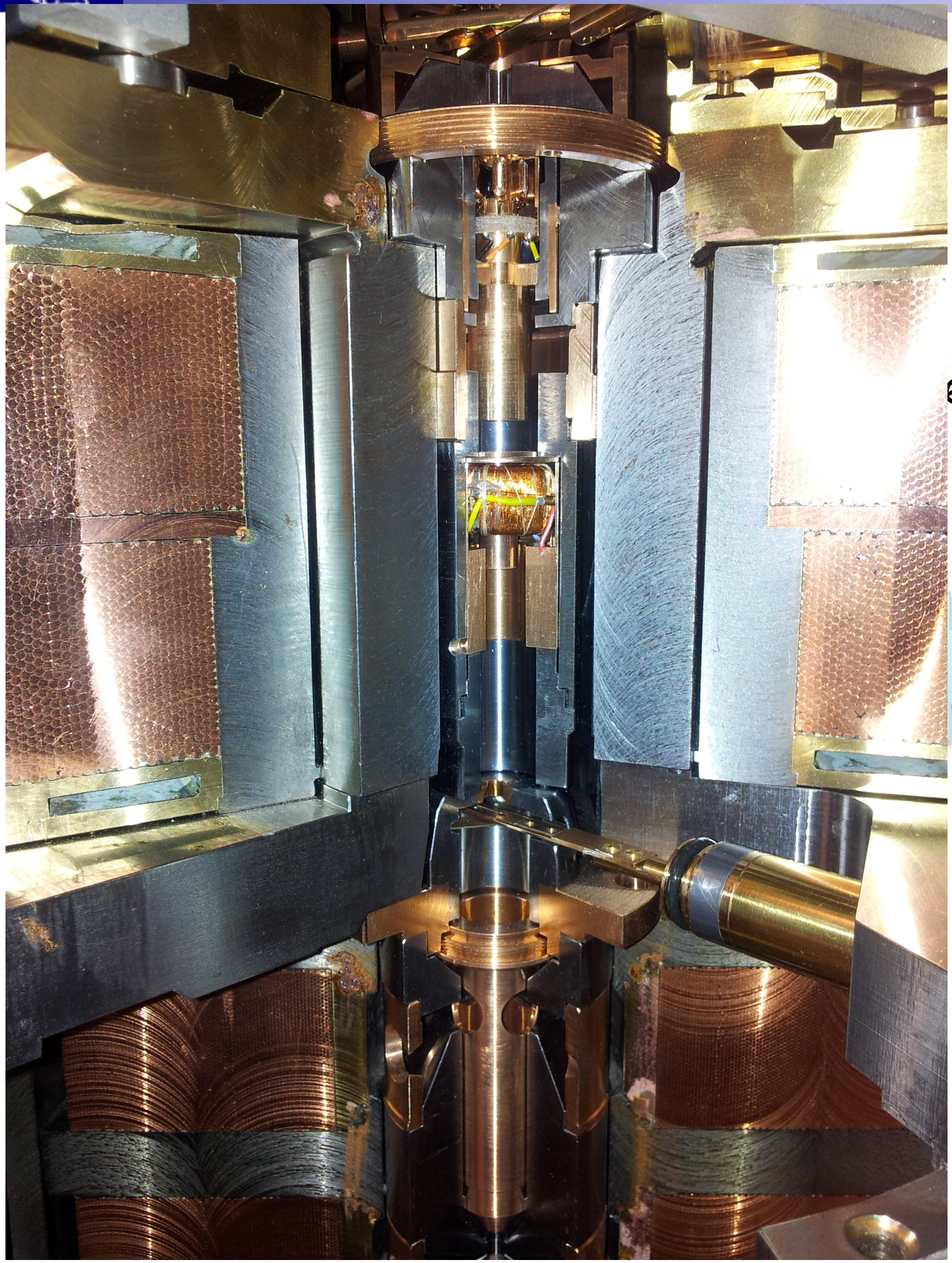
Condenser lens system:



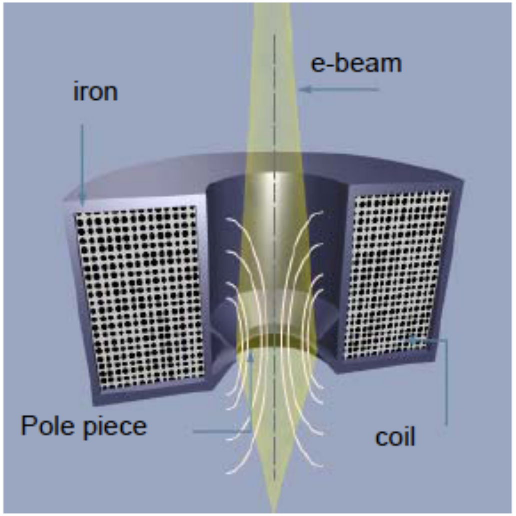
Parallel or converging illumination of the specimen

M. Willinger, FHI

Basic set-up of the TEM



em:

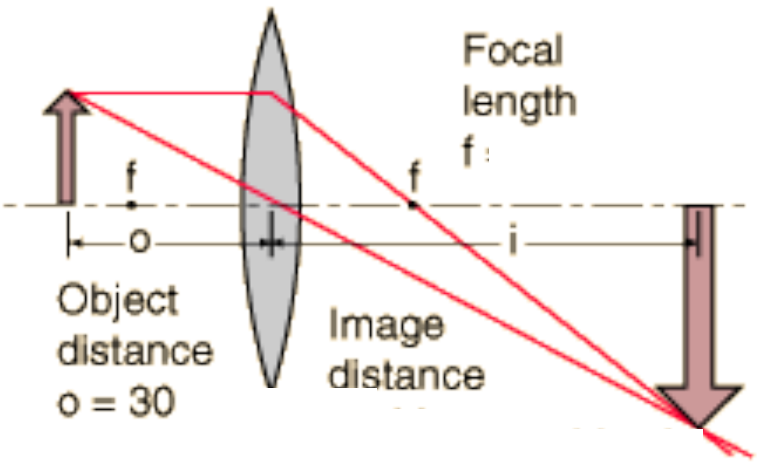


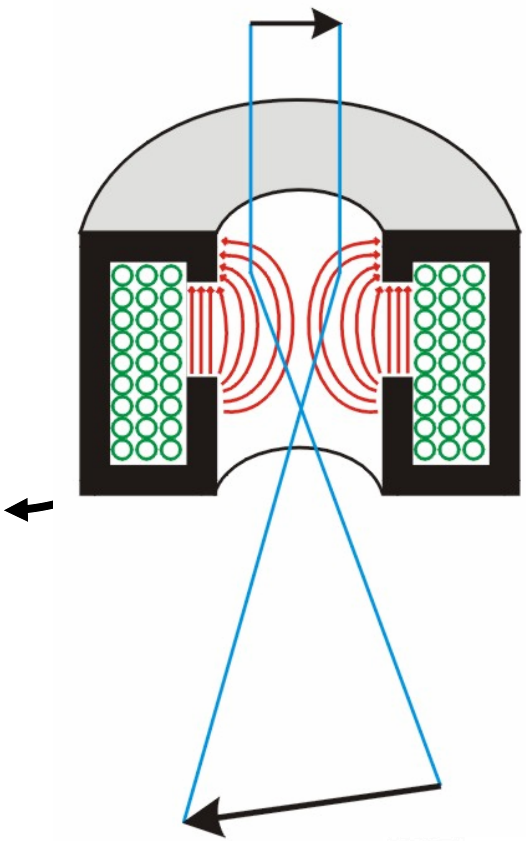
www.x-raymicroanalysis.com

… a few words on this one…

Magnetic Lenses

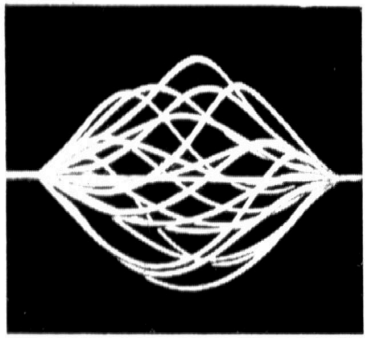
Electron optics was born in 1927, when Hans Busch showed that the elementary lens equation is applicable to short magnetic coils.





$$\frac{1}{d_{object}} + \frac{1}{d_{image}} = \frac{1}{f}$$

$$M = \frac{d_{image}}{d_{object}}$$



Modell der Elektronenbahnen

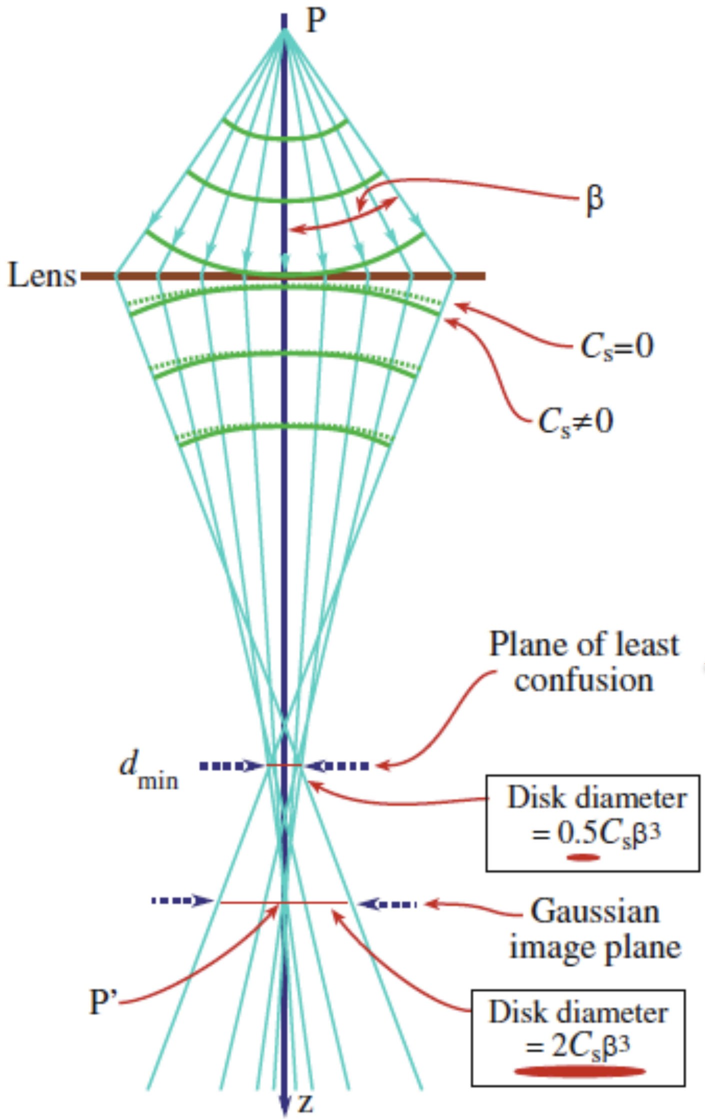
Lens aberrations

Electrons are focused by simple round magnetic lenses which properties resemble the optical properties of a wine glass….

Unlike in light optics the wavelength (2pm for 300kV) is not the resolution limiting factor.

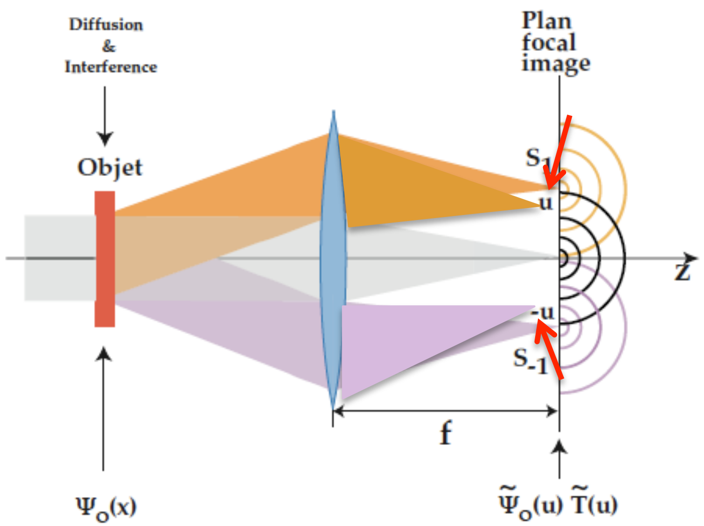
Lens aberrations and instabilities of the electronics (lens currents etc.) limit the resolution of even the best and most expensive transmission electron microscopes to about 50pm.

Lens aberrations:

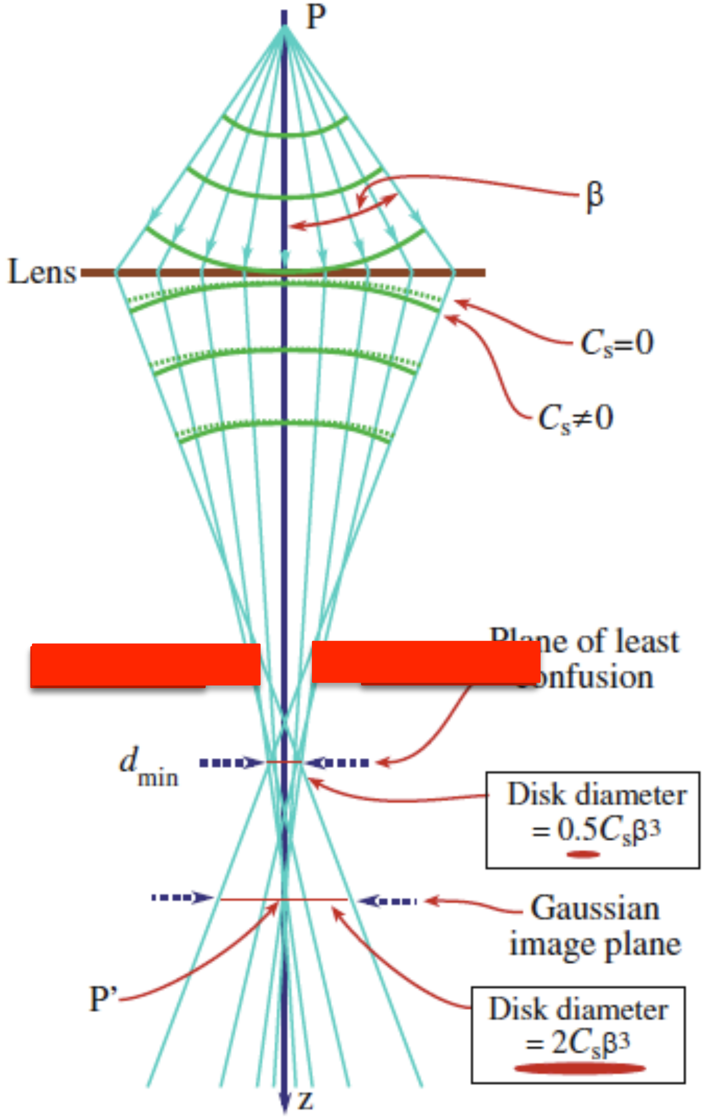


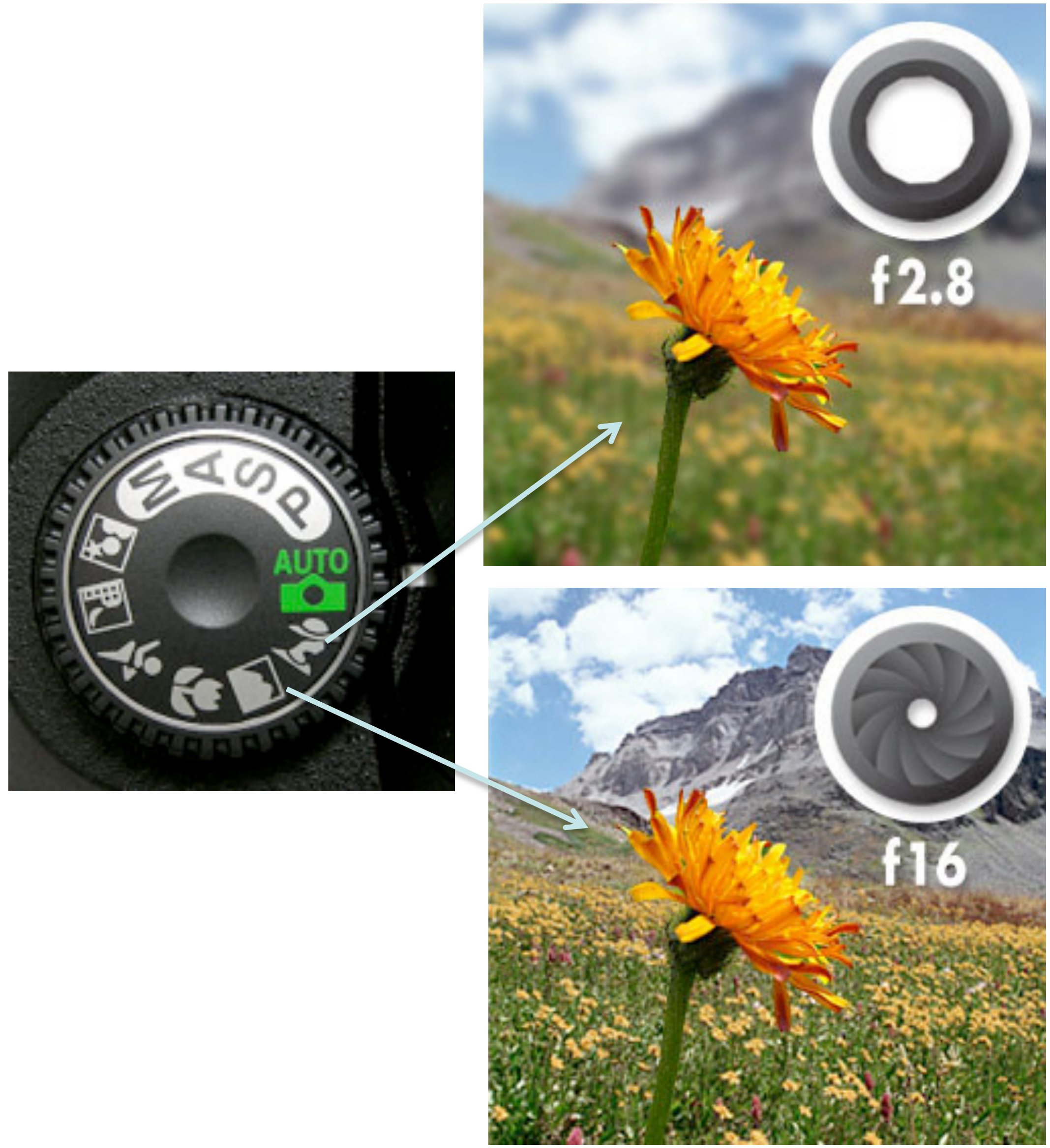
Spherical aberration:

Spherical aberration causes wave fronts to bend more strongly at the outside of the lens than those close to the axis

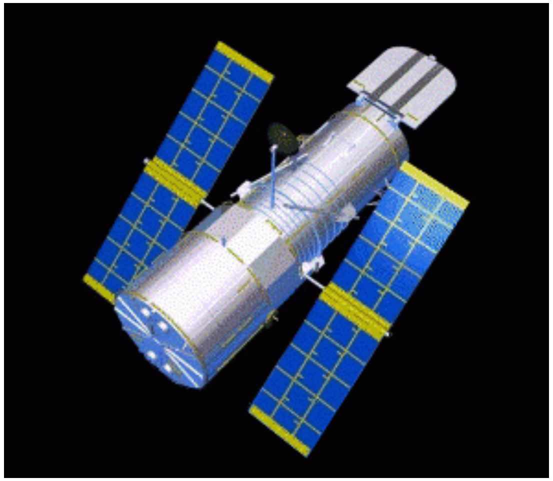


Lens aberrations:





A famous C_s-afflicted instrument

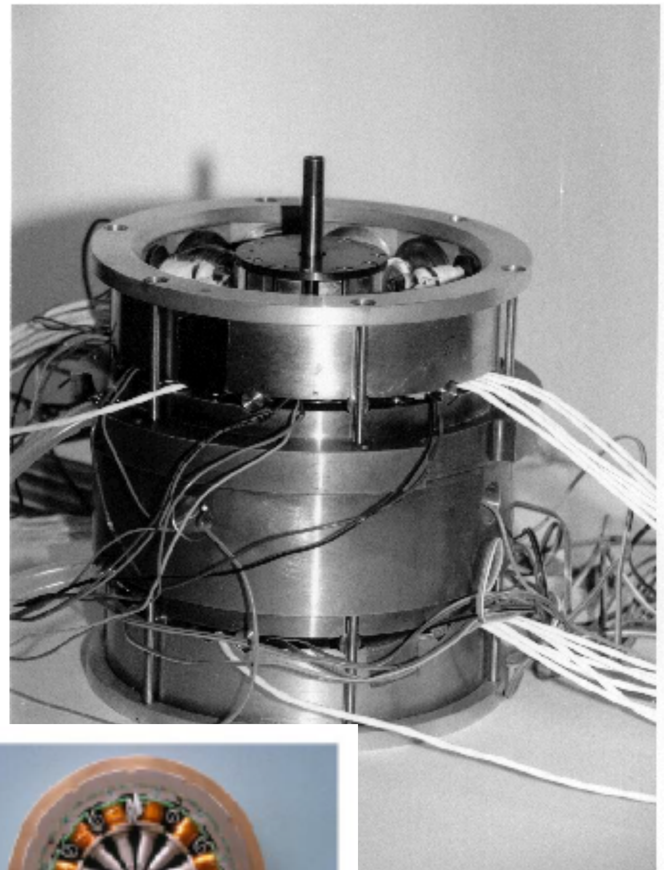


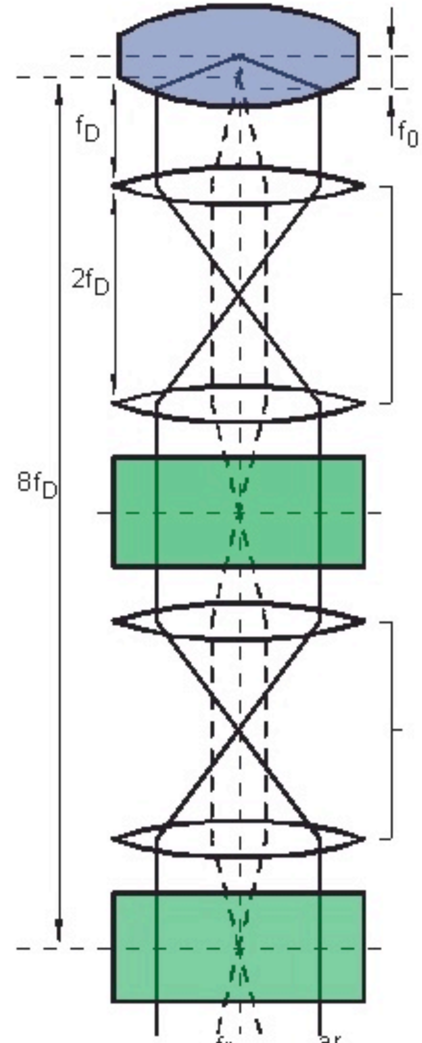
Hubble telescope:
the sides of its Ø 2.5 m primary mirror are 2 μm too low (negative C_s) - the mirror was ground very precisely to the wrong shape. The error was avoidable.

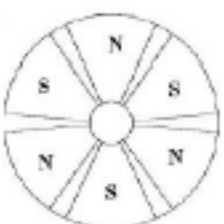
Hubble repair:
a modified camera lens assembly corrected for the too-low phaseshift of marginal rays and resultedin a spectacular improvement of image quality. Primary mirror was not changed.

C_s Corrector:

C_S-Corrector (Rose, Haider and Urban)

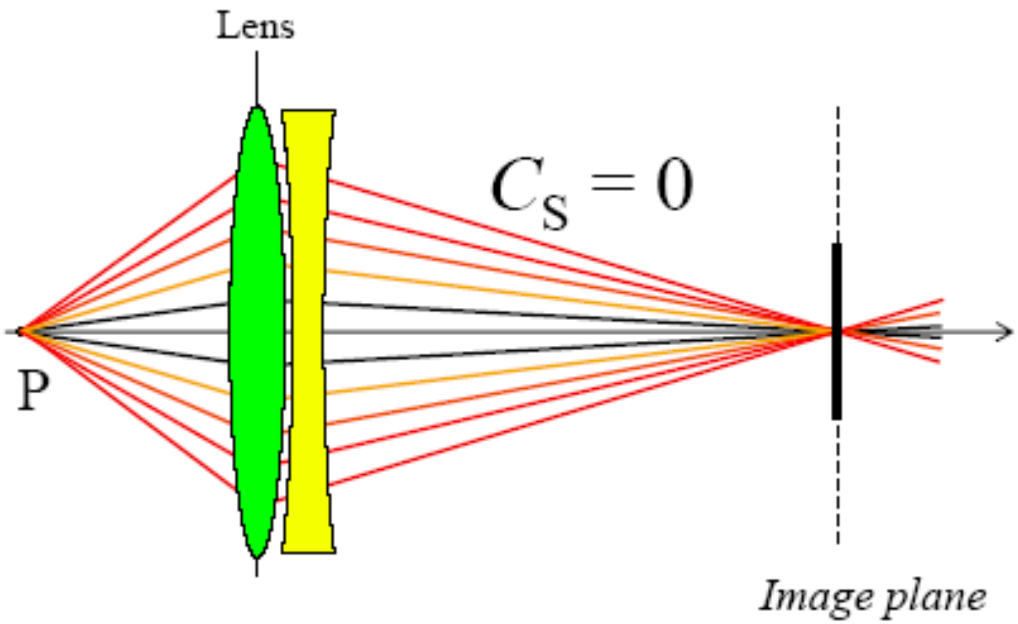






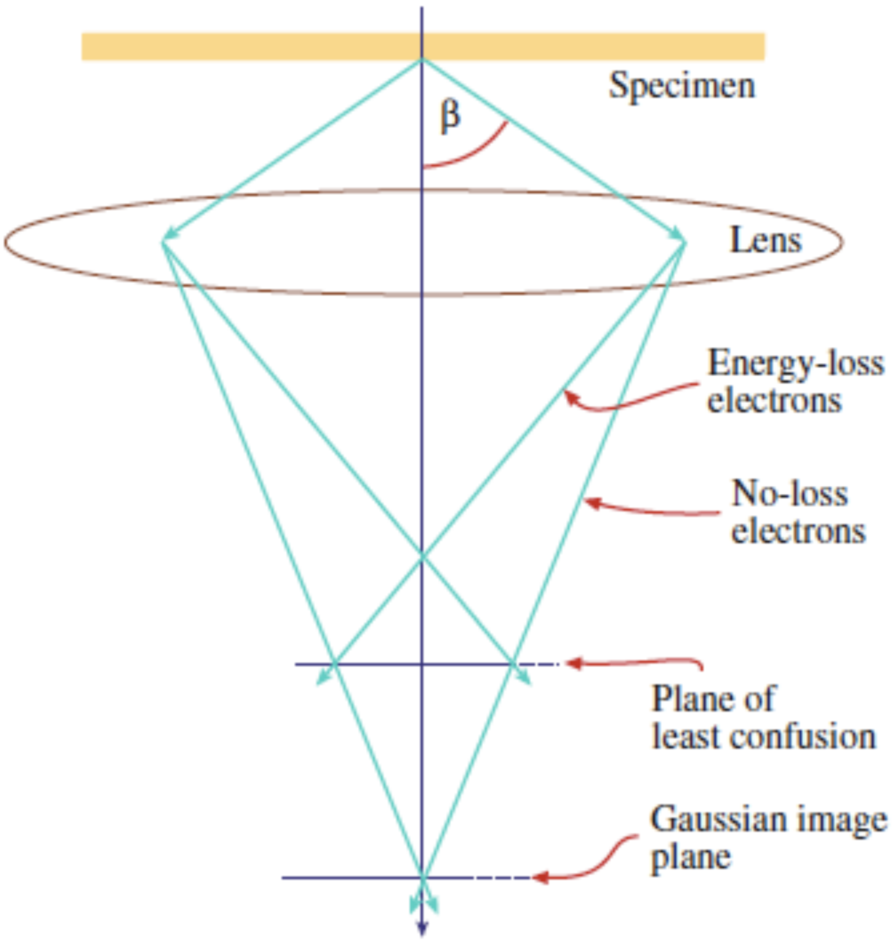
C_s Corrector:

Aberration corrected electron optics
C_s is adjustable!



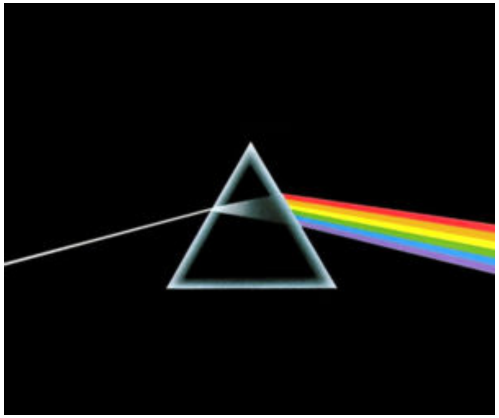
- TU Darmstadt (H. Rose)
- EMBL Heidelberg (M. Haider)
- Forschungszentrum Jülich (K. Urban)

Haider, Rose, Urban et al.
Nature 392, 768 (1998)

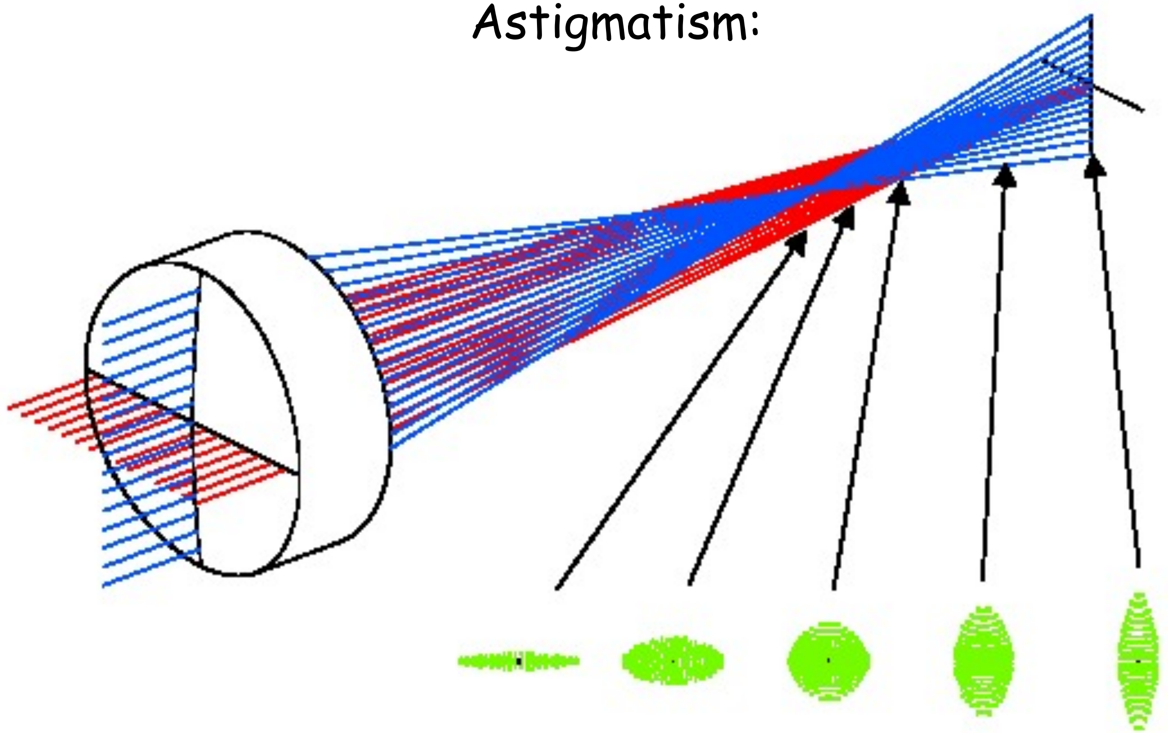


Chromatic aberration:

Chromatic aberration results in electrons with a range of energies being focused in different planes

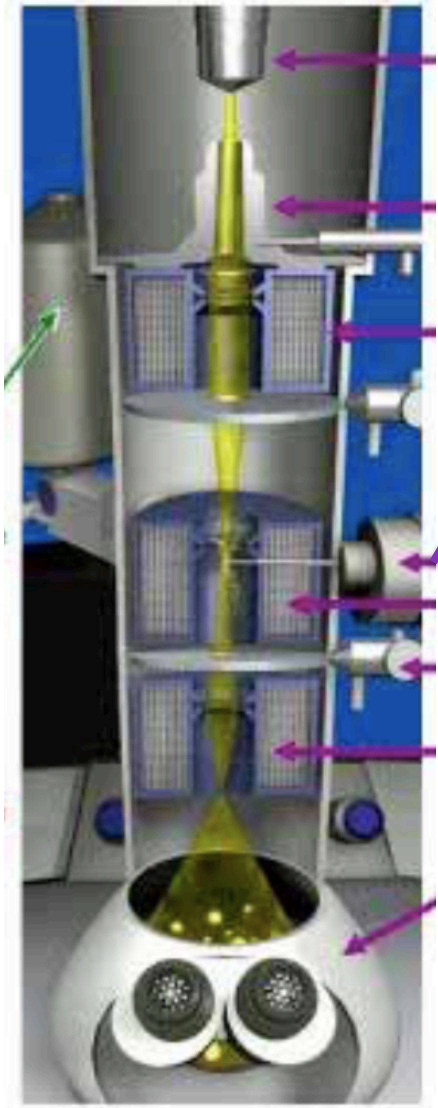


Astigmatism:



Electrons passing at different directions away from the optic axis have different focal lengths.

Basic set-up of the TEM



Electron gun

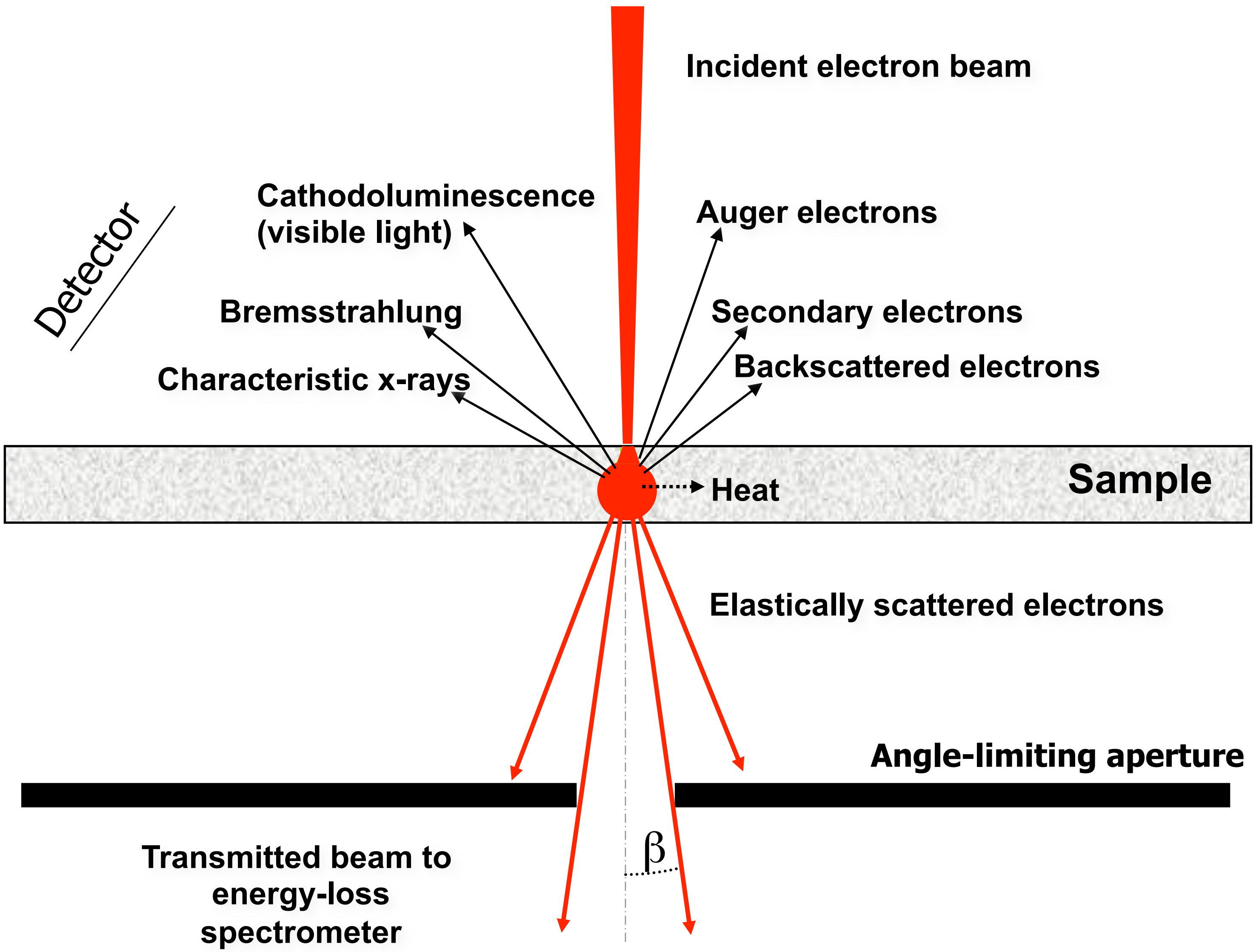
Acceleration stage

Condenser lens system

Specimen stage:

Now things get interesting!

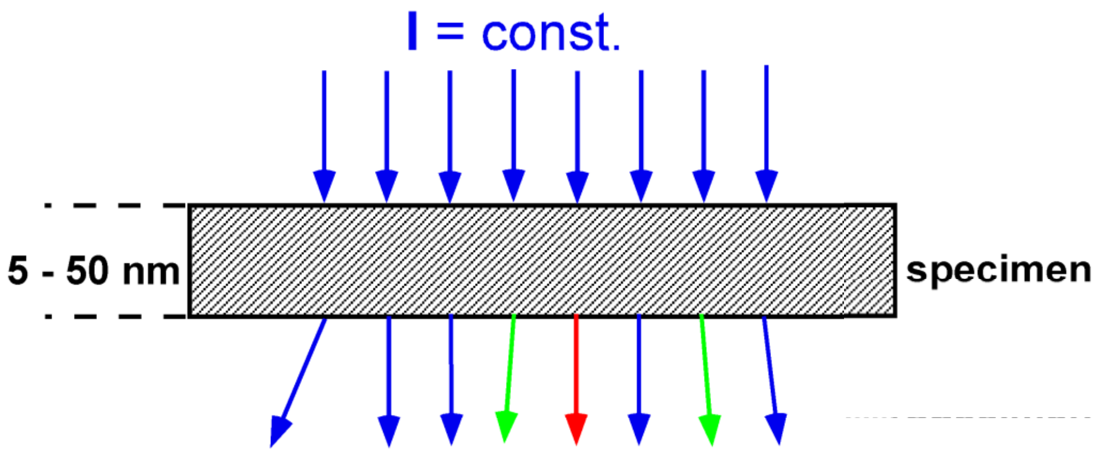
Electron - Sample Interactions



Electron - Sample Interactions

Strahov Stadium in Prague

Electron - Sample Interactions



$$I = I\,(\,x,\ y,\ \theta_x,\ \theta_y,\ \Delta E)$$

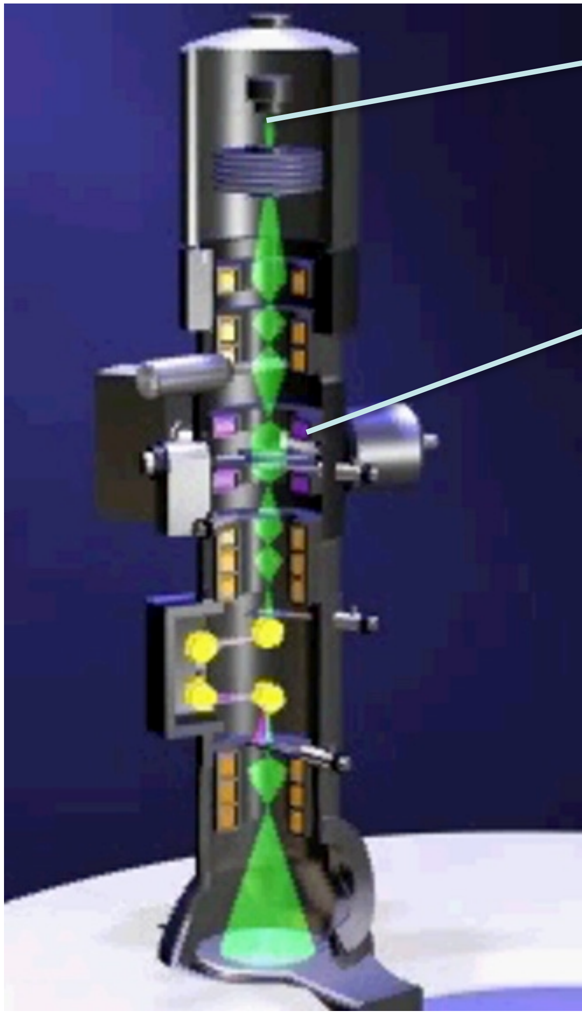
conventional TEM

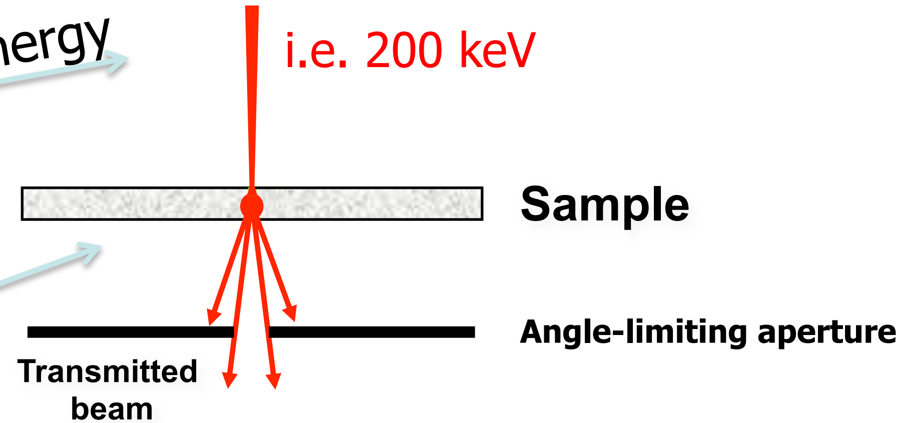
EELS

Electron Spectroscopic
Imaging (ESI)
Diffraction (ESD)

Energy Filtering TEM

Electron - Sample Interactions





Questions you can ask an electron:

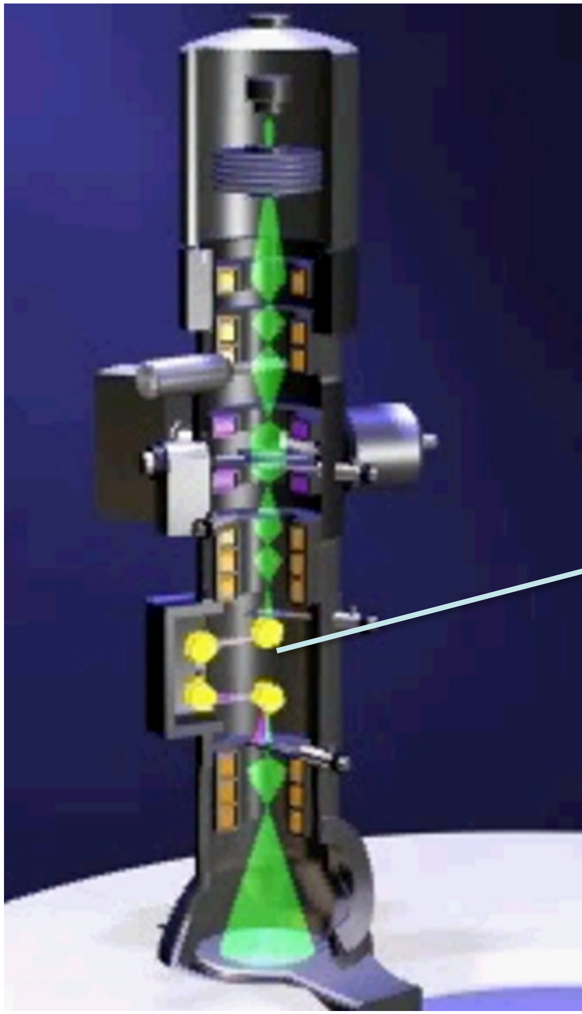
Q1: where are you going to? (→ direction)

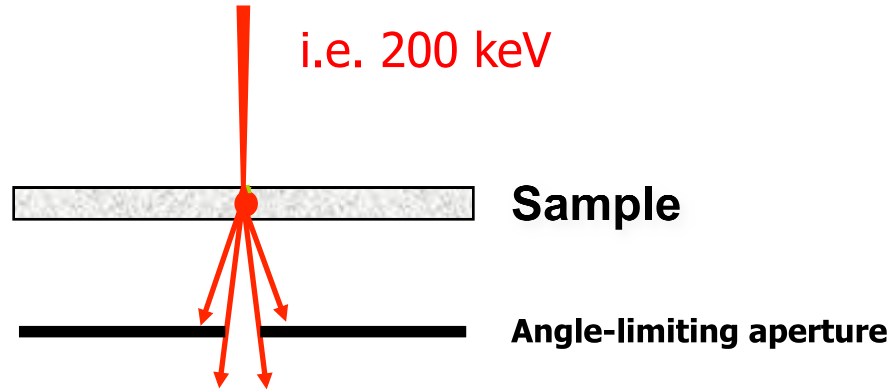
Q2: how is your relation with the others? (→ phase)

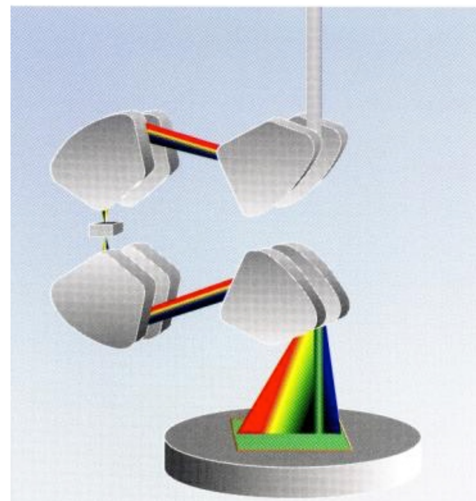
Q3: how fast are you travelling? (→ energy)

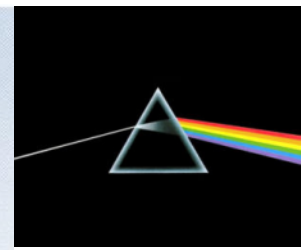
~~Q4: are you up or down? (→ spin)~~

Electron - Sample Interactions

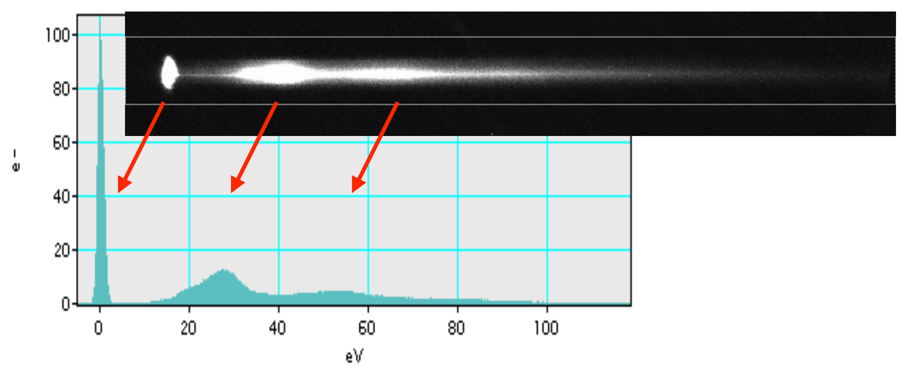








Electron
Energy
Loss
Spectrum



Outline

- Part I: Elastic Interactions
- Part II: Inelastic Interactions
  - the EELS spectrum
  - Spectrometer / Energy Filters
  - What kind of information do I get?

Energy Loss Spectrum

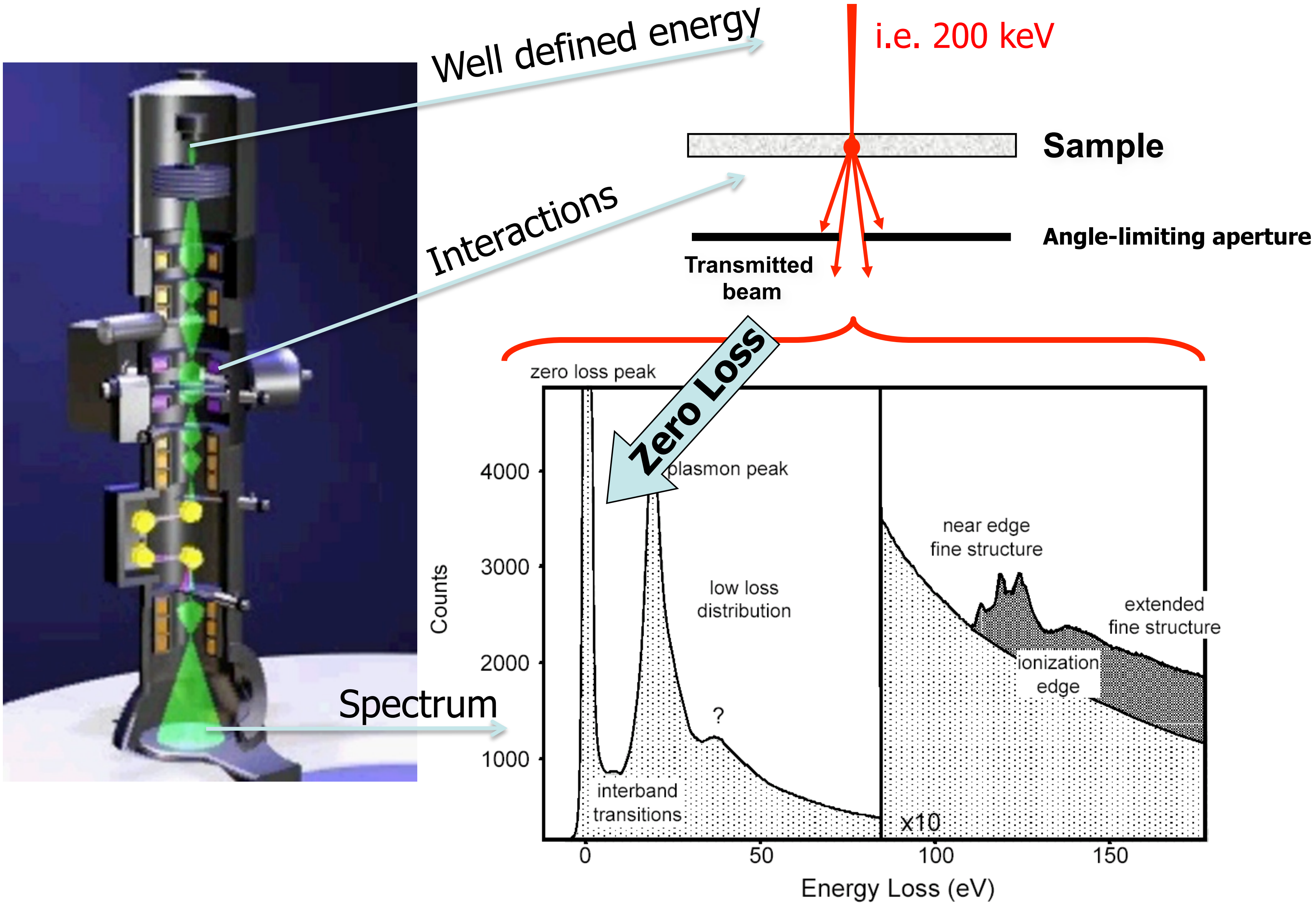
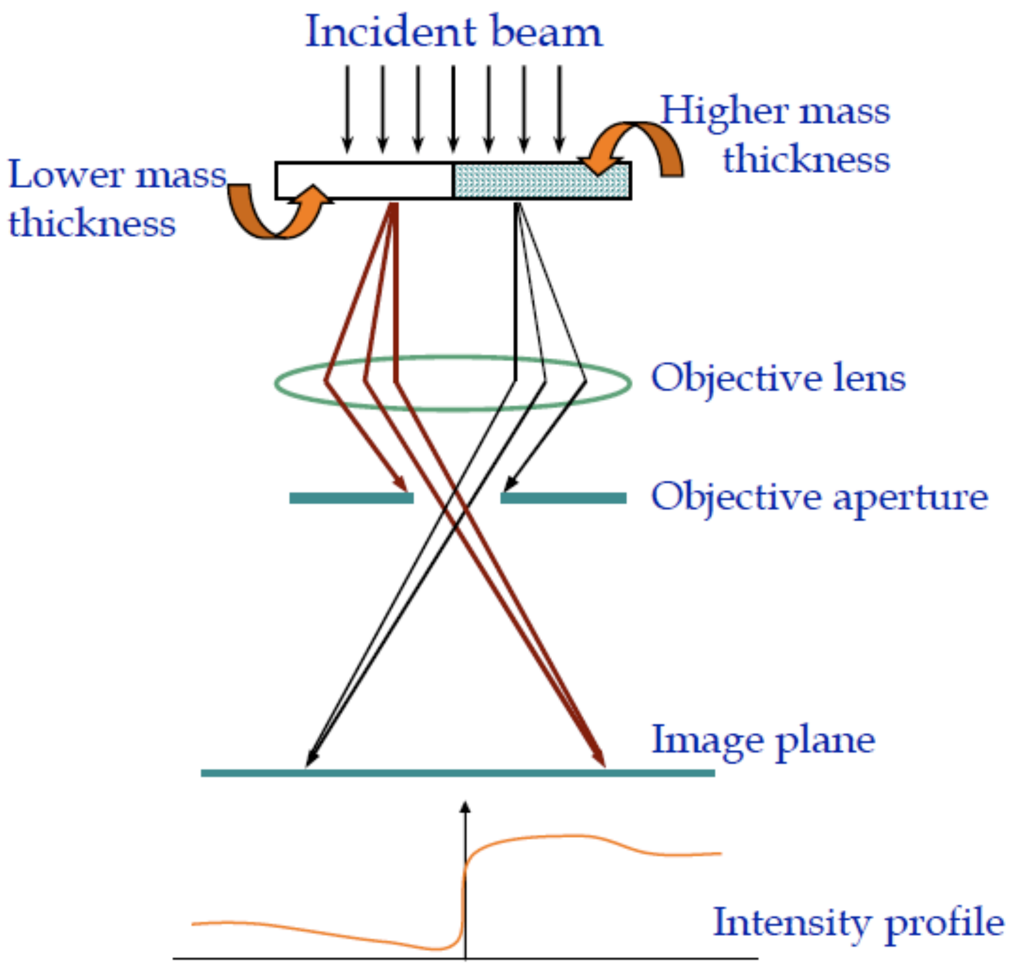
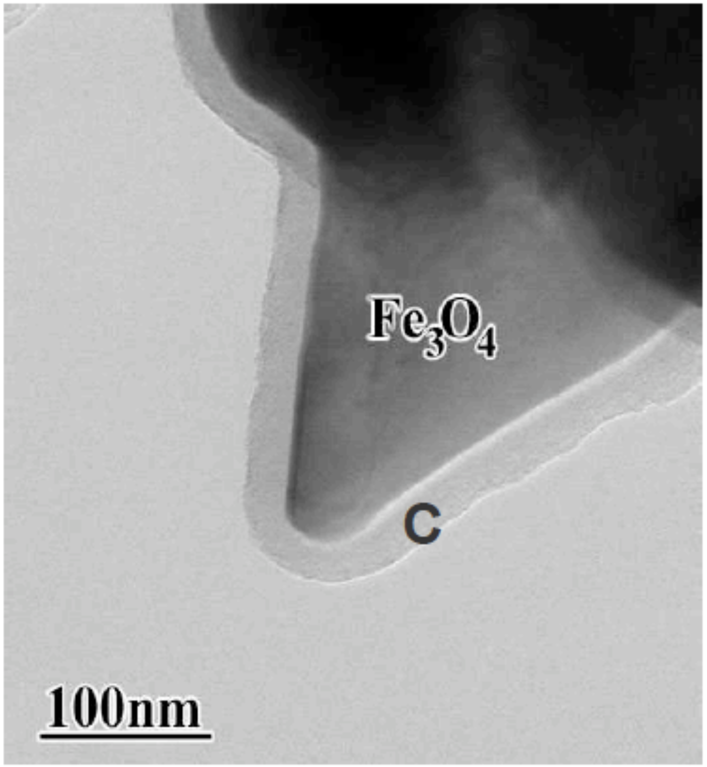


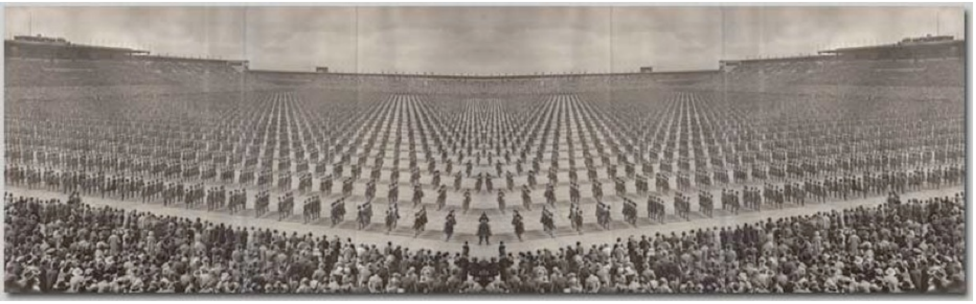
Image Contrast in TEM

I. Mass-thickness contrast

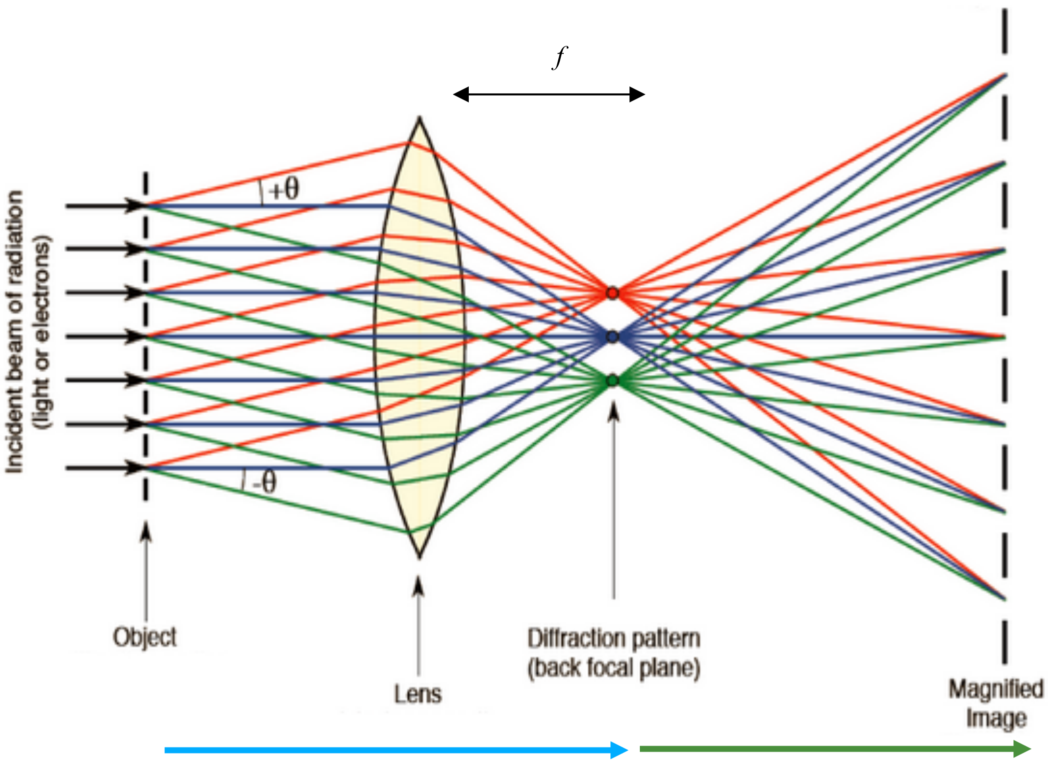


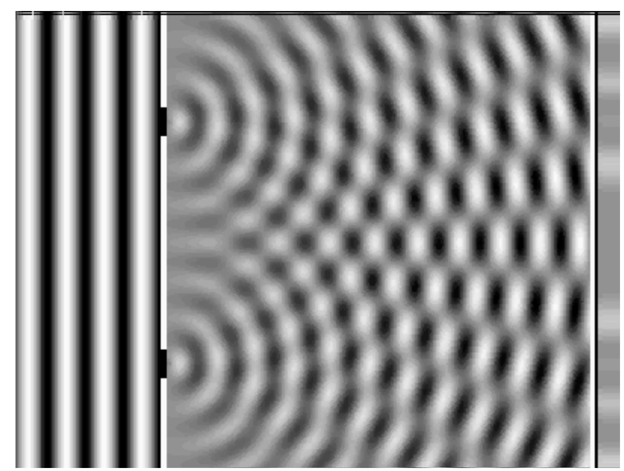


Diffraction Contrast



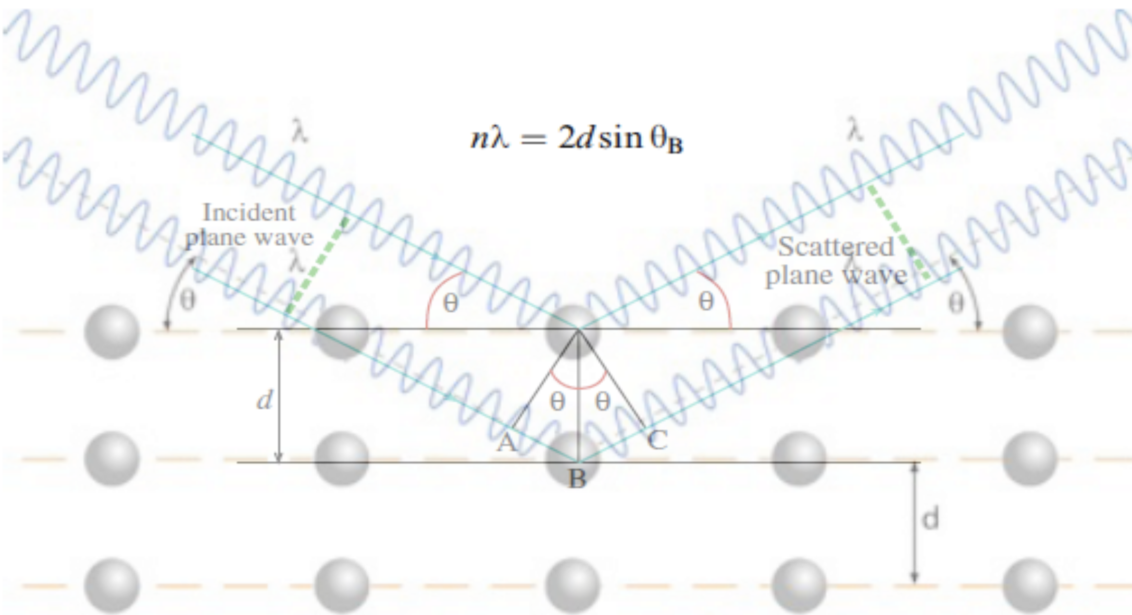
f – focal length of the lens

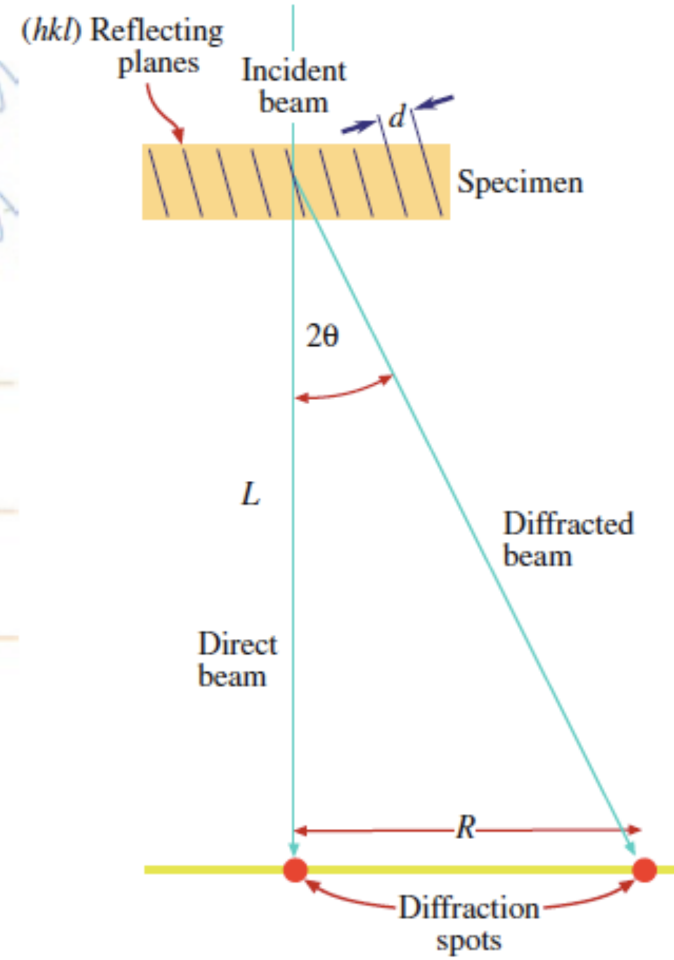




$$\psi(k_x, k_y) \propto F\ \{T(X,Y)\} \qquad T(X,Y) \propto F^{-1}\{\psi(k_x,k_y)\}$$

Coherence & Interference





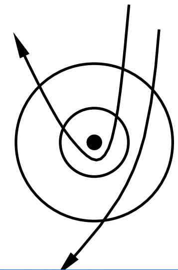
Nothing new… good old Bragg!

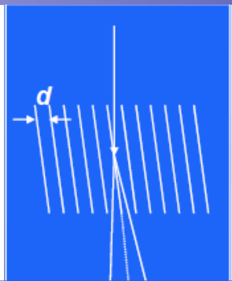
M. Willinger, FHI

Elastic Interactions

Elastic scattering:

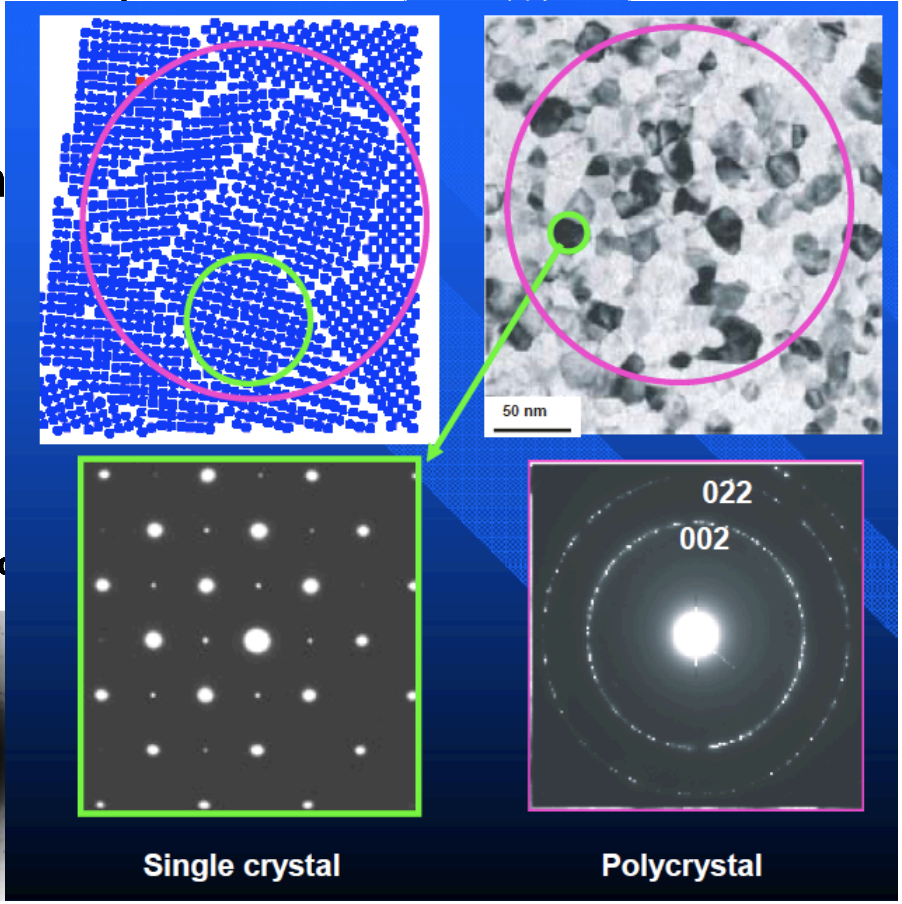
Elastic scattering at low angle is mostly due to Coulomb interactions with the negatively charged electron cloud.





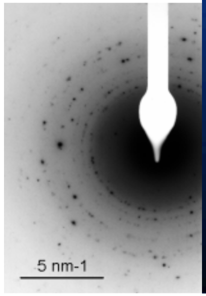
Diffraction:

Interference of (coherently) scattered electron waves from periodically arranged atoms in a crystalline solid.



Diffraction contrast

Diffracti



Elastic scattered electrons are used for image generation in conventional TEM!

Q1: where are you going to?

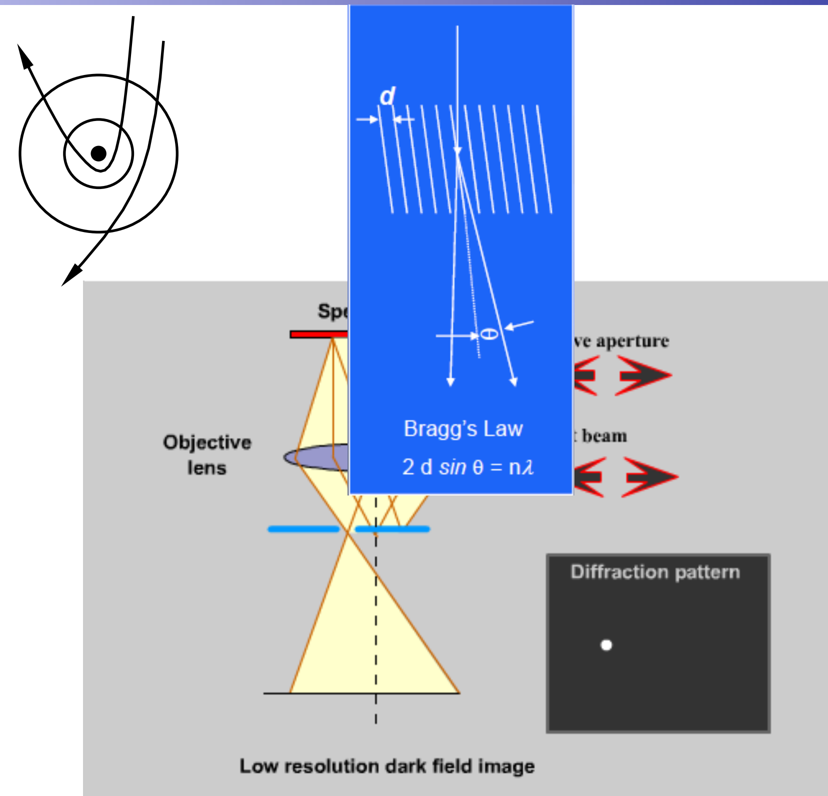
1. Elastic Interactions

Elastic scattering:

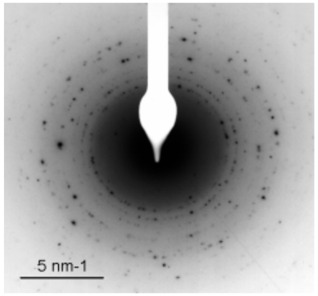
Elastic scattering at low angle is mostly due to Coulomb interactions with the negatively charged electron cloud.

Diffraction:

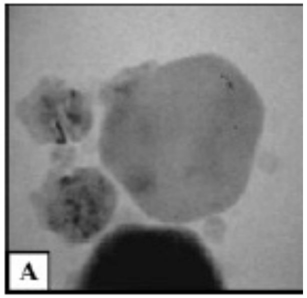
Interference of (coherently) scattered electron waves from periodically arranged atoms in a crystalline solid.



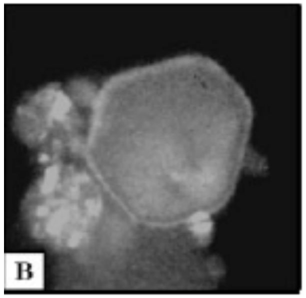
Diffraction



Bright field (BF)



Dark field (DF)



Elastic scattered electrons are used for image generation in conventional TEM!

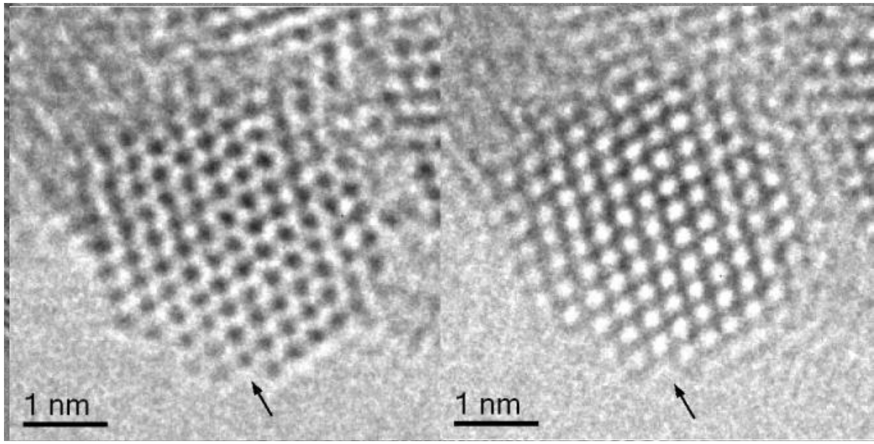
Q1: where are you going to?

Elastic scattering:

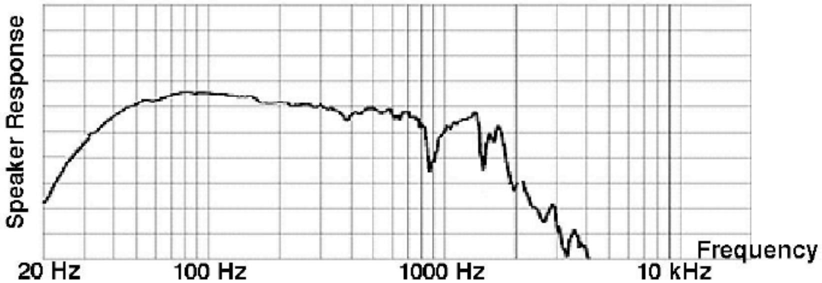
Elastic scattering is also the basis for high resolution imaging, where changes in the phase of the electron waves gives rise to contrast variations:

Phase contrast imaging
(HIGH RESOLUTION TEM, HRTEM)

Coherent, elastic scattering



Transfer Function

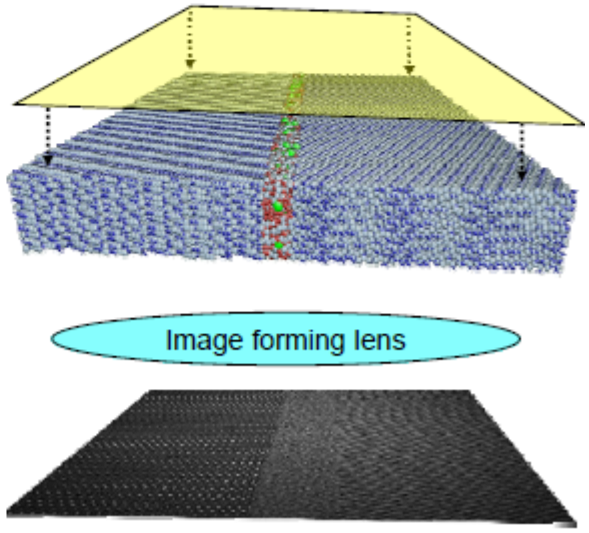


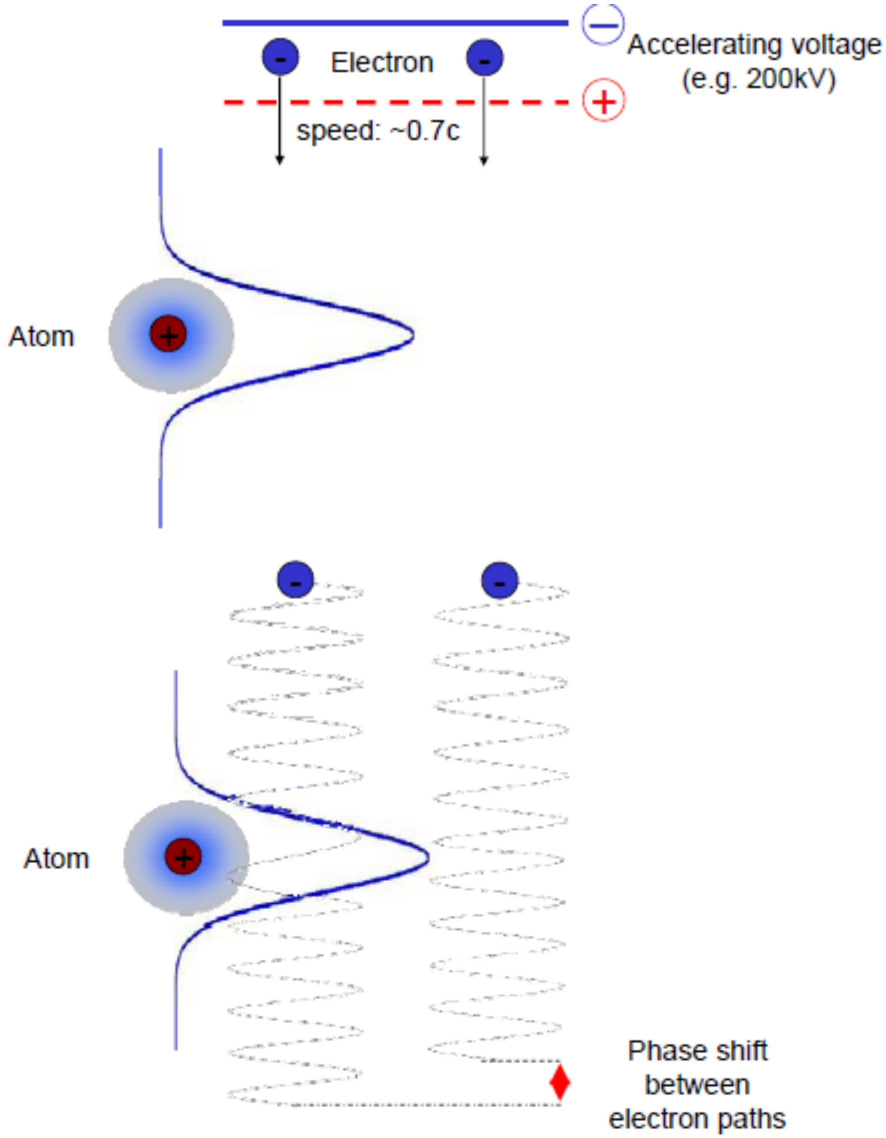
Elastic scattered electrons are used for image generation in conventional TEM!

Q2: how is your relation with the others?

J. Phys. Chem. C 2008, 112, 18815

Contrast transfer function (CTF)





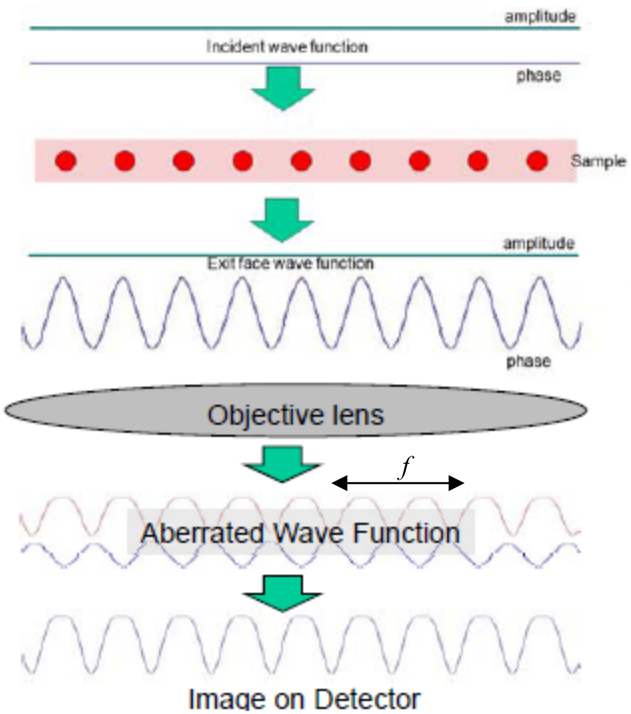
Phase shift $\Delta\phi(r) = \sigma \cdot V_{proj}(r)$

$(\sigma_{200kV} = 0.0026\ V^{-1}Å^{-1})$

Christoph T. Koch

Willinger, FHI

Contrast transfer function (CTF)

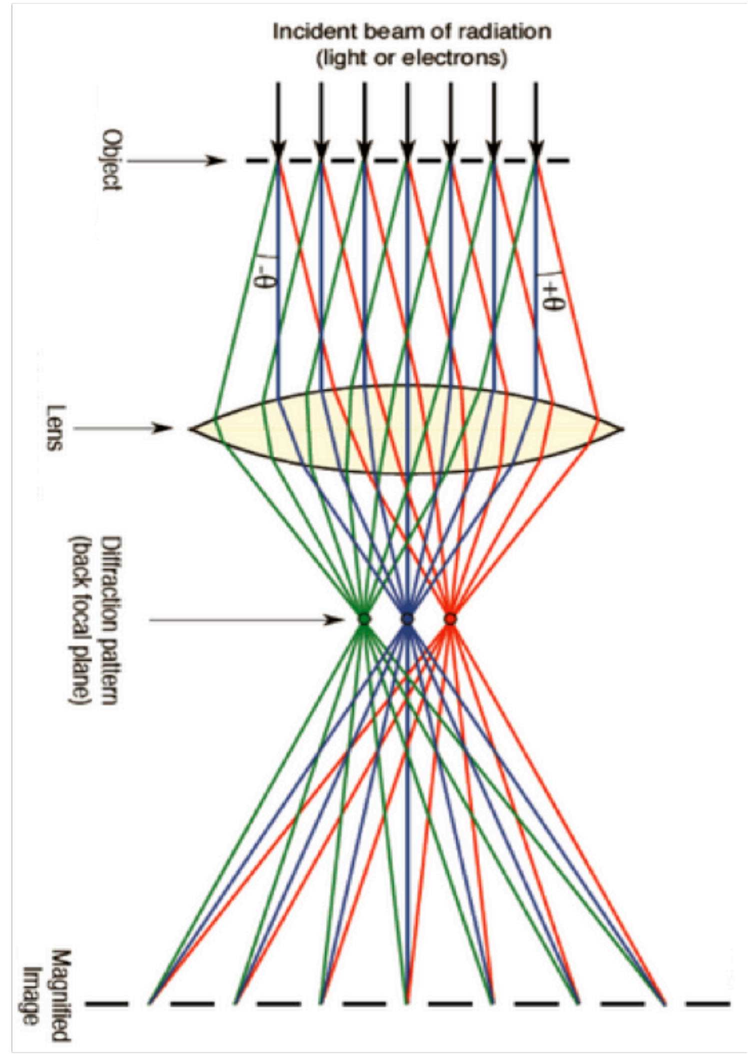


$$\Psi_{inc}(r) = e^{ikz}$$

$$\Psi_{exit}(r) = \Psi_{inc} \cdot e^{i\pi\lambda V_{proj}(r)}$$

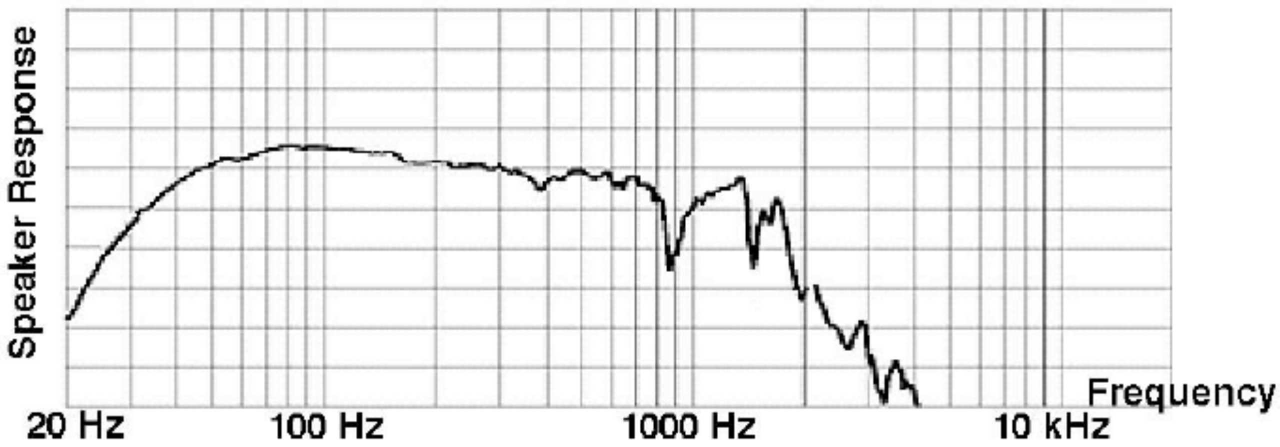
$$\Psi_{ab}(r) = \Psi_{exit} \otimes e^{i\chi(r)}$$

$$I(r) = \left|\Psi_{ab}\right|^2$$



Transfer function

Transfer Function

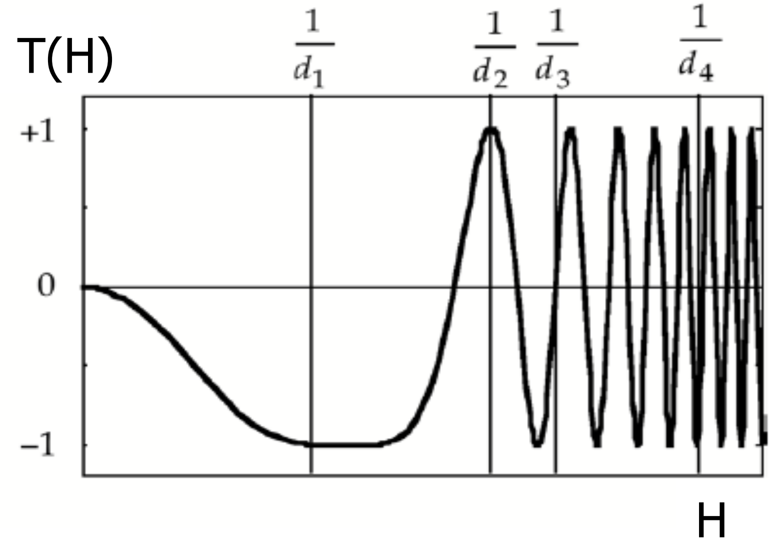


Transfer function

T(H)<0 implies “positive” constrast: atom columns appear dark (in the print, not the negative!).

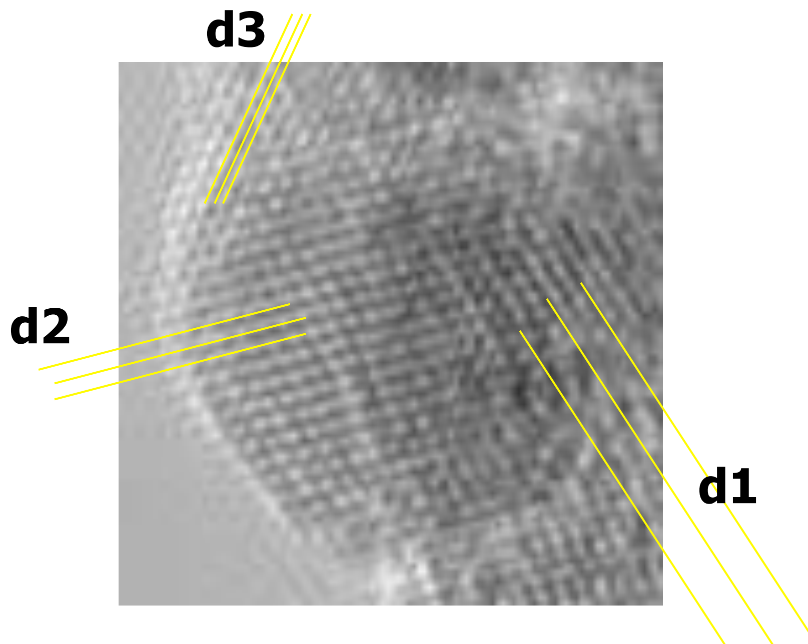
T(H)>0 implies “negative” contrast: atom columns appear bright.

• T(H) = 0 implies no transfer of the respective spatial frequency at all!



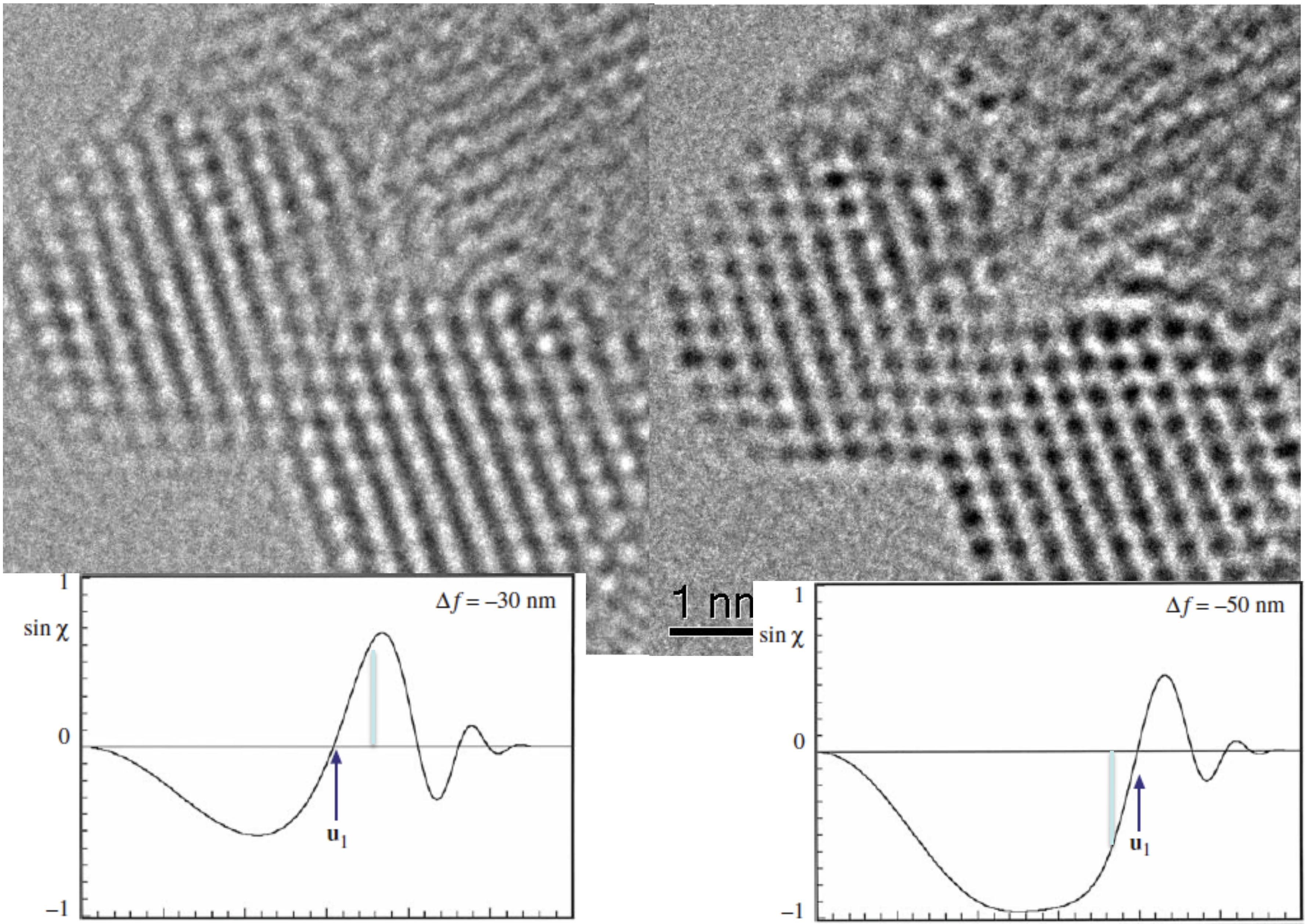
Example: hypothetical crystal with four different sets of planes parallel to the viewing direction

- plane spacing: $d1 > d2 > d3 > d4$
- corresponding spatial frequencies: $1/d1 < 1/d2 < 1/d3 < 1/d4$.
- the planes with spacing $d1$ appear with positive contrast
- the planes with spacing $d2$ appear with negative contrast
- the planes with spacing $d3$ do not appear at all
- it is difficult to predict the contrast of the planes with spacing $d4$. We can avoid these problems by introducing an objective aperture.

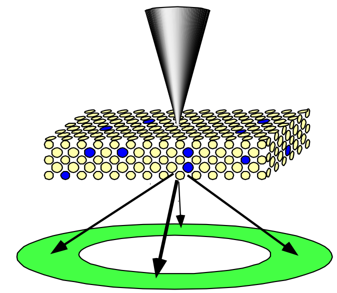


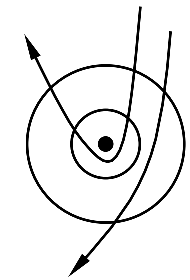
M. Willinger, FHI

Interpretation of TEM images



1. Elastic Interactions





Elastic scattering:

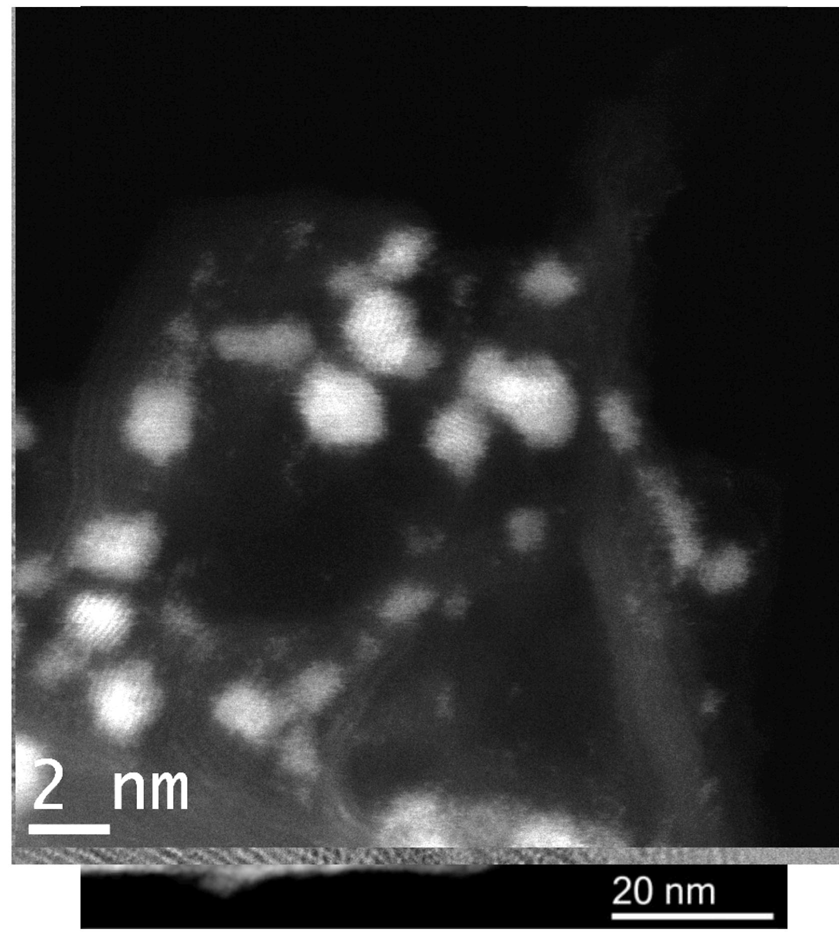
Elastic scattering at higher angles is essentially due to Coulomb interaction with an atomic nucleus.

Rutherford scattering:

Incoherent, elastic scattering to high angle

Intensity is related to atomic number and thickness of specimen

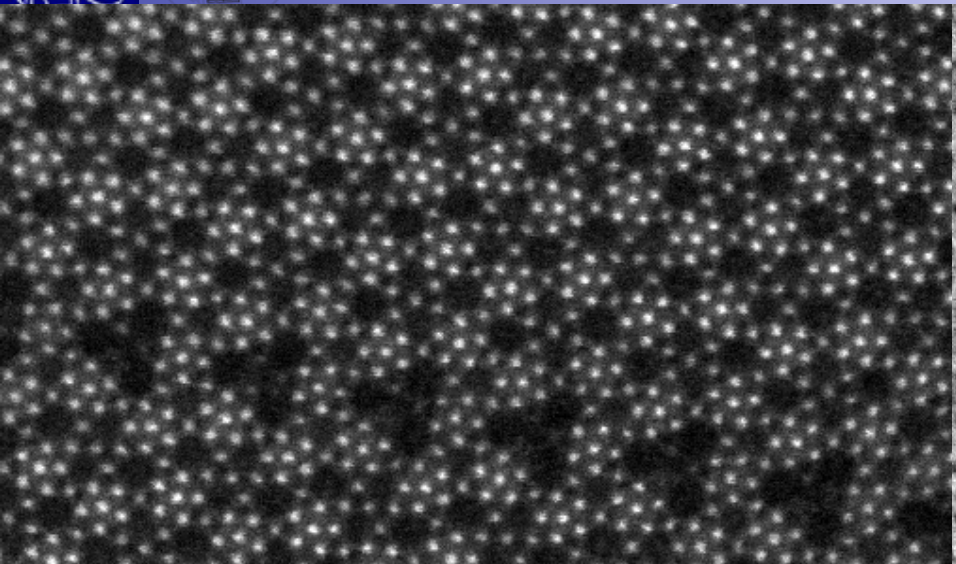
High Angle Annular Dark Field
HAADF - STEM Imaging

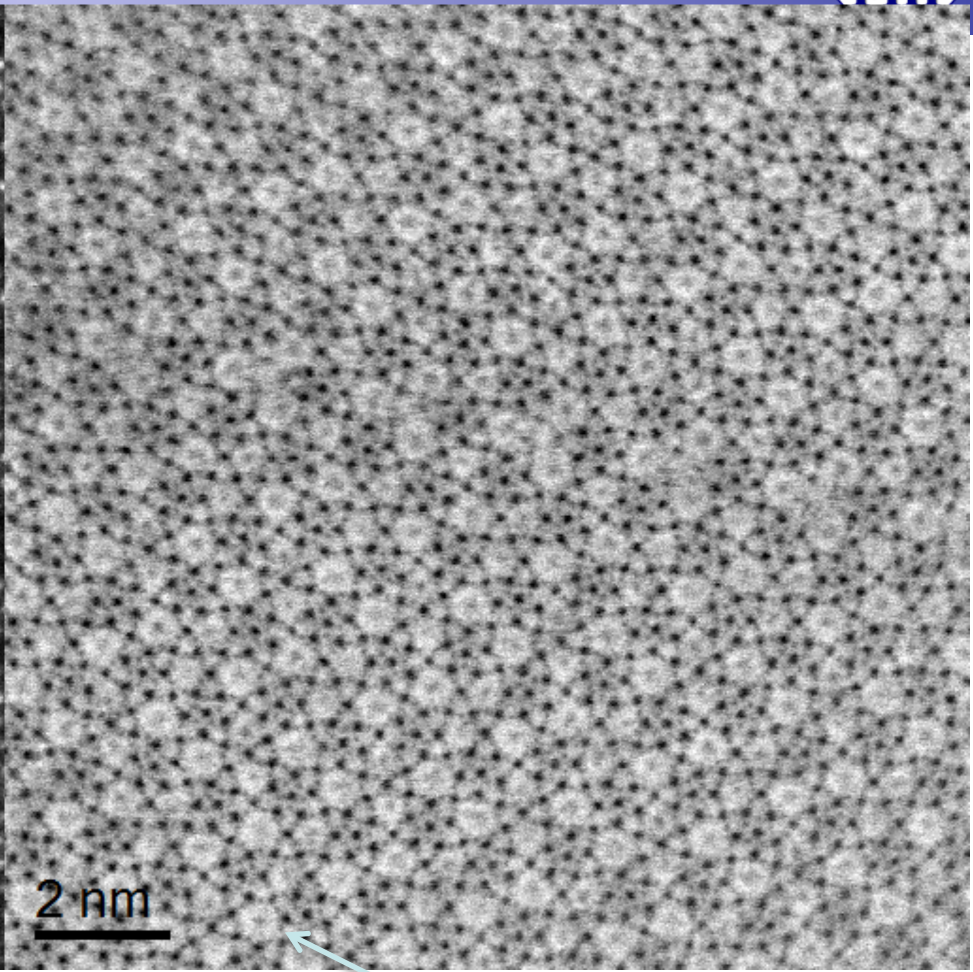


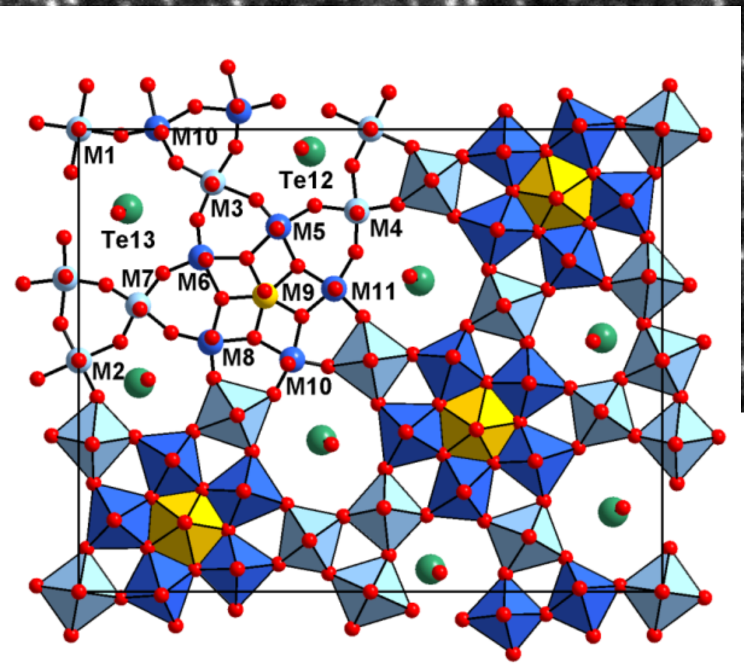
Elastic scattered electrons are used for image generation in conventional TEM!

Q1: where are you going to?

~ 70pm Resolution + Chemical Information





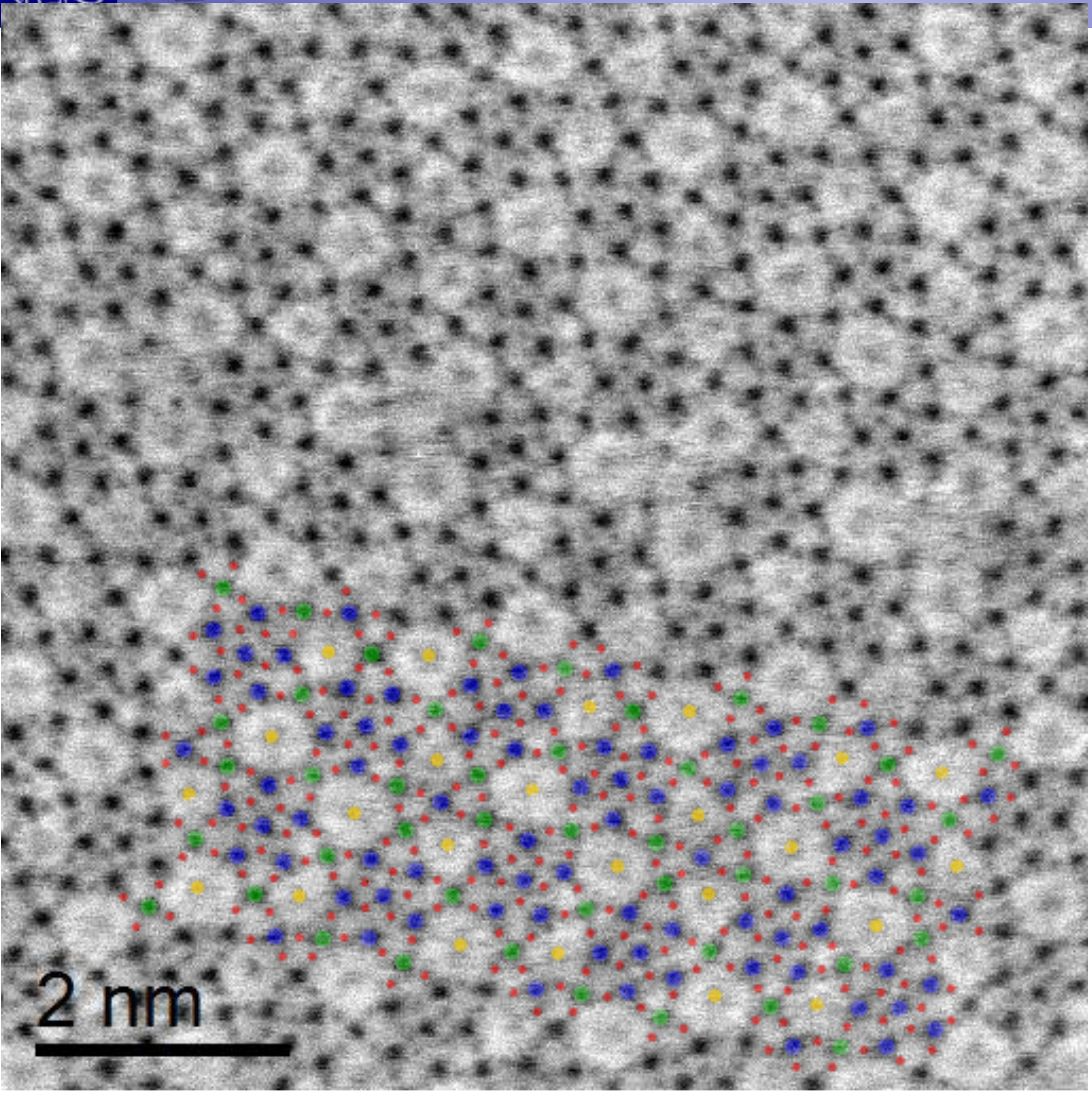


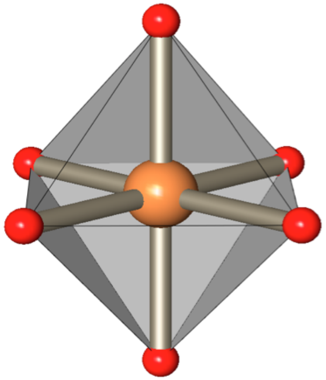
MoVO:
Channels are filled

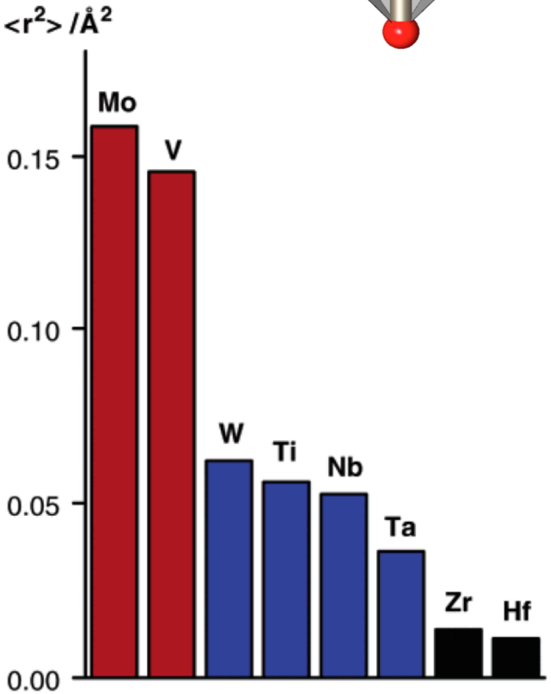
M1 phase $Mo_1V_{0.15}Te_{0.12}Nb_{0.128}O_{3.7}$

M. Willinger, FHI

~ 70pm Resolution + Chemical Information







Ok et al. *Chem.Mater.* **2006**, *18*, 3176-3183.

Out-off-center distortion

Outline

- Part I: Elastic Interactions
- Part II: Inelastic Interactions
  - Spectrometer / Energy Filters
  - The EELS spectrum
  - What kind of information do I get?

NEXT TIME!!!

Interpretation of TEM images

In the TEM we see 2D projections of 3D specimens, viewed in transmission

Our eyes and brain routinely understand reflected light images but are ill-equipped to interpret TEM images and so we must be cautious

This problem is well illustrated by the picture of the two rhinoceros side by side such that the head of one appears attached to the rear of the other

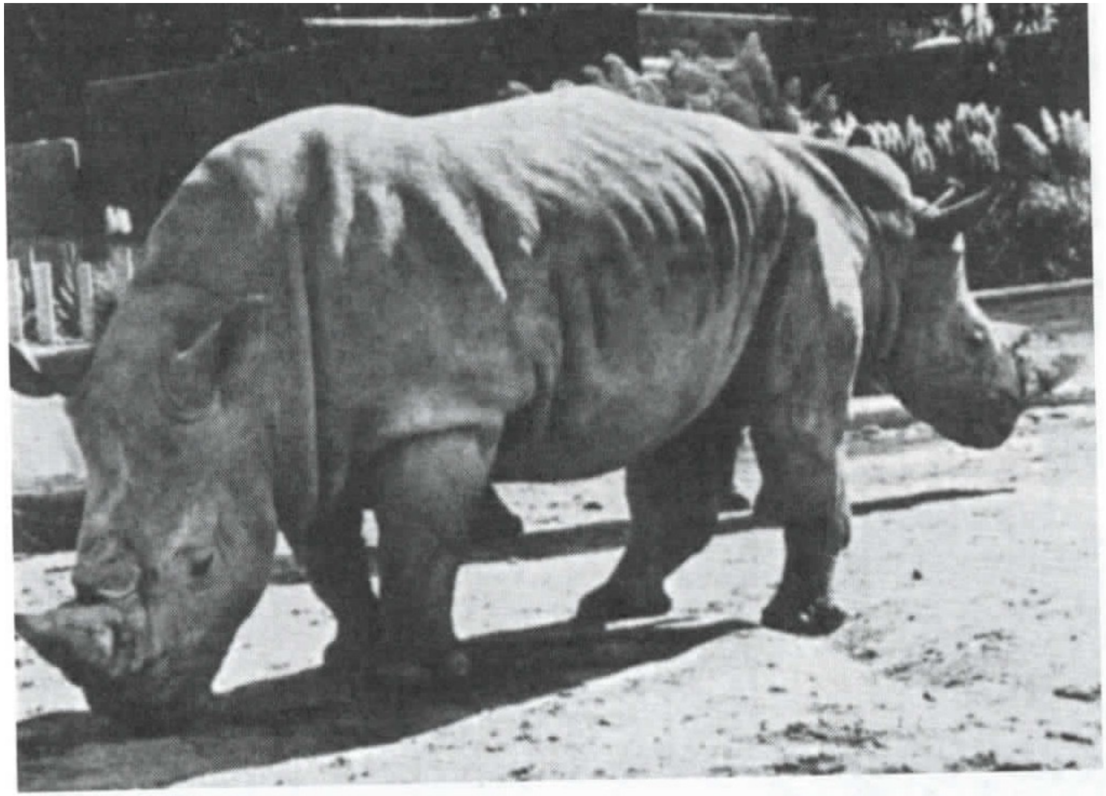
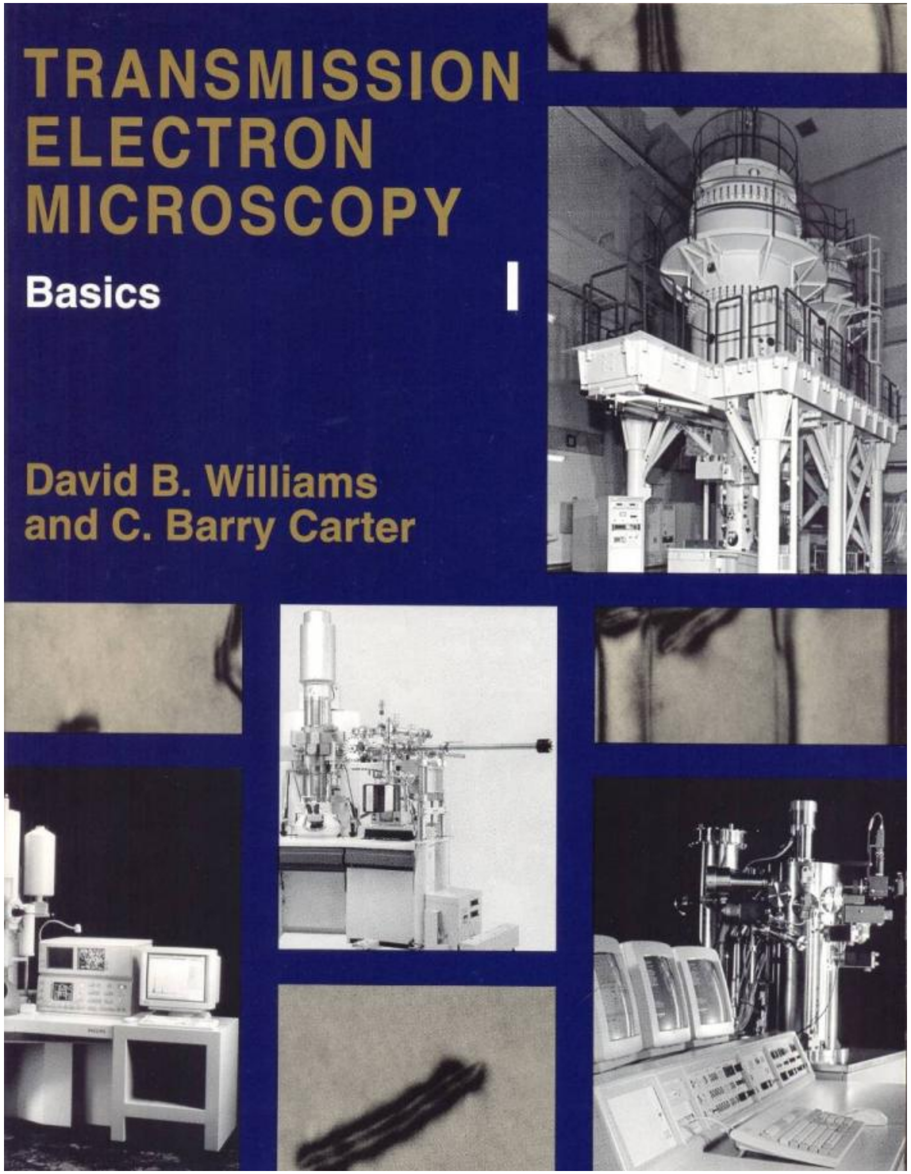
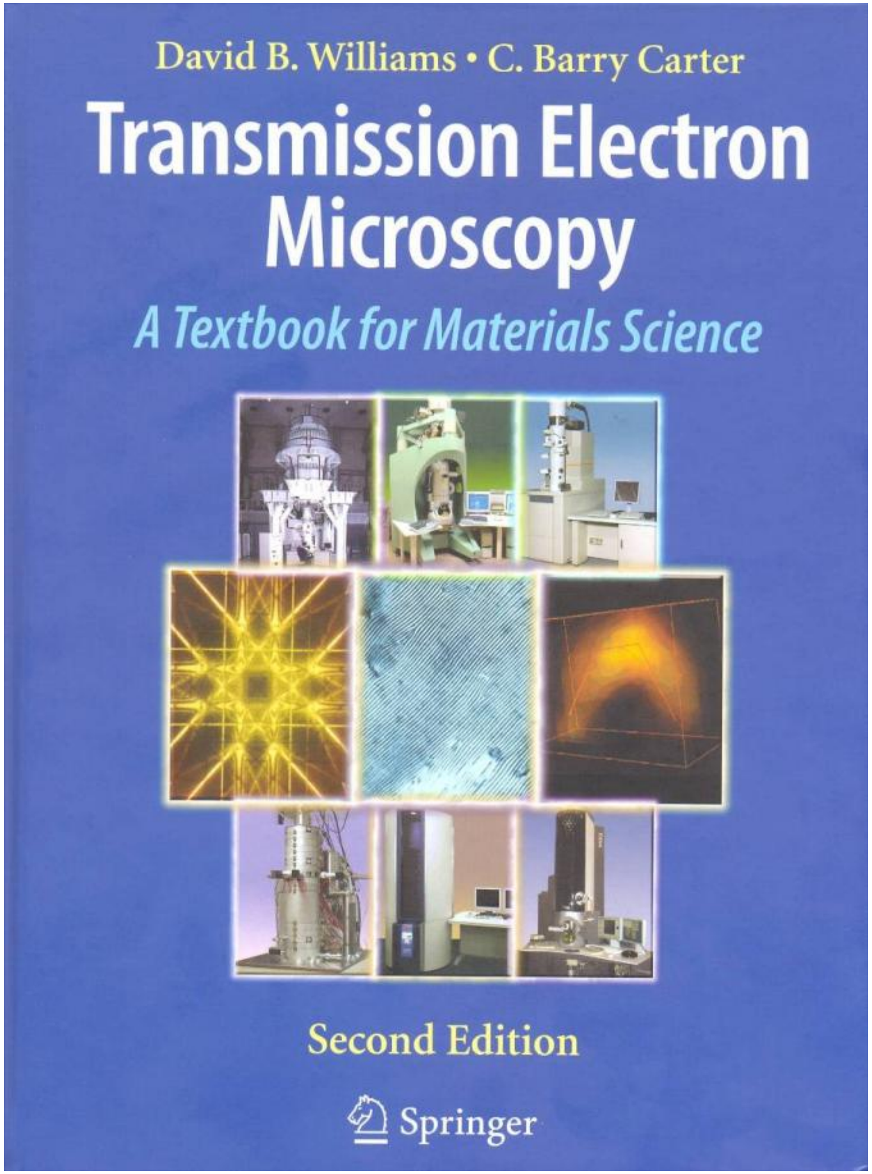


Figure 1.7. Photograph of two rhinos taken so that, in projection, they appear as one two-headed beast. Such projection artifacts in reflected-light images are easily discernible to the human eye but similar artifacts in TEM images are easily mistaken for "real" features.

Literature


TRANSMISSION
ELECTRON
MICROSCOPY
Basics
I
David B. Williams
and C. Barry Carter


David B. Williams • C. Barry Carter
Transmission Electron
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