Electron Microscopy II

- Transmission Electron Microscopy (TEM)
- Scanning Transmission Electron Microscopy (STEM)
- Scanning Electron Microscopy (SEM)

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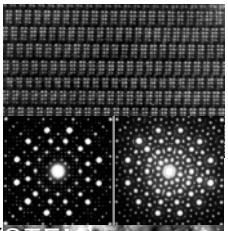
200 nm

Electron Microscopy Methods

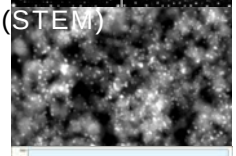
Transmission Electron Microscopy (TEM)

- Bright / Dark Field (BF/DF)
- High-Resolution Transition Electron Microscopy (HRTEM)
- Energy-Filtered (EFTEM)
- Electron Diffraction (ED)



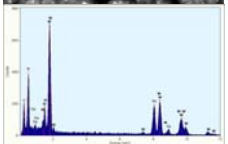
Scanning Transmission Electron Microscopy (STEM)

- Bright / Dark Field (BF/DF-STEM)
- High-Angle Annular Dark Field (HAADF-STEM)



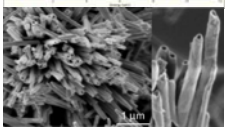
Analytical Electron Microscopy (AEM)

- X-ray Spectroscopy
- Electron Energy-Loss Spectroscopy (EELS)
- Electron Spectroscopic Imaging (ESI)



Scanning Electron Microscopy (SEM)

- Secondary Electrons (SE)
- Back-Scattered Electrons (BSE)

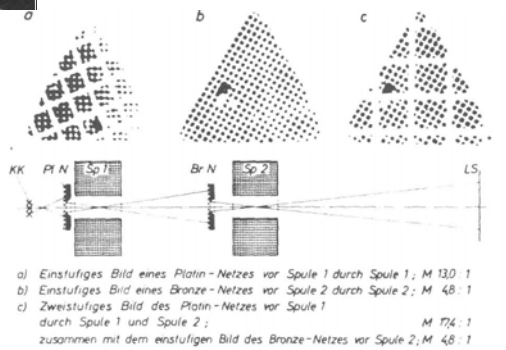


Development of the First Transmission Electron Microscope

1927 *Hans Busch*: Electron beams can be focused in an inhomogeneous magnetic field.

1931 *Max Knoll* and *Ernst Ruska* built the first TEM.

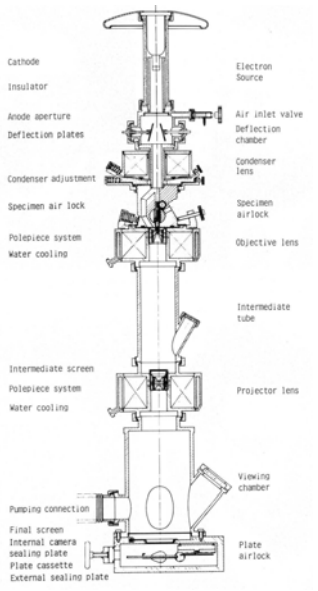
1986 Nobel prize for *Ruska*



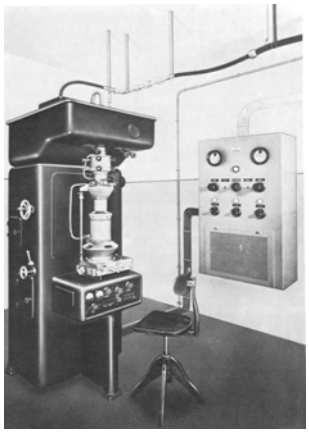
a) Einstufiges Bild eines Platin-Netzes vor Spule 1 durch Spule 1; M 13,0 : 1
b) Einstufiges Bild eines Bronze-Netzes vor Spule 2 durch Spule 2; M 4,8 : 1
c) Zweistufiges Bild des Platin-Netzes vor Spule 1 durch Spule 1 und Spule 2; M 17,4 : 1 zusammen mit dem einstufigen Bild des Bronze-Netzes vor Spule 2; M 4,8 : 1

Knoll, Ruska, *Z. Phys.* **78** (1932) 318

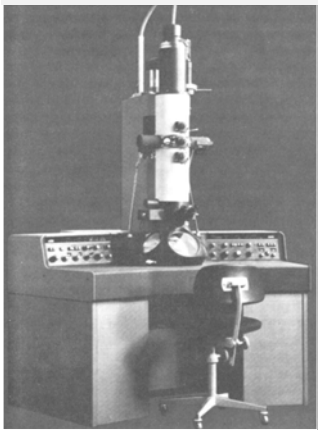
1938 First Siemens Electron Microscope (Resolution ca. 13 nm)



Transmission Electron Microscopes



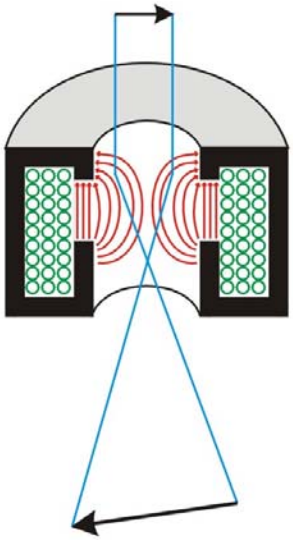
1939: first TEM serially produced by Siemens resolution ca. 7 nm



~1970: HRTEM Philips EM400, V = 120 kV resolution ca. 0.35 nm

~1990 Philips CM30, V = 300 kV resolution ca. 0.2 nm

Magnetic Lens



An electron in a magnetic field (here: inhomogeneous, but axially symmetric) experiences the Lorentz force F:

$$F = -e (E + v \times B)$$

$$|F| = evB\sin(v,B)$$

E: strength of electric field

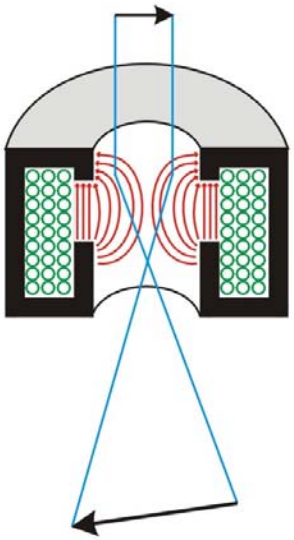
B: strength of magnetic field

e/v: charge/velocity of electrons

Magnetic lenses
- manipulate the electron beam
- form an image of the object

Magnetic Lens

Light optical analogue

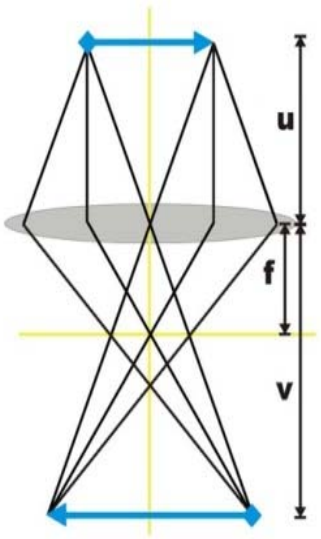


Object plane

Lens

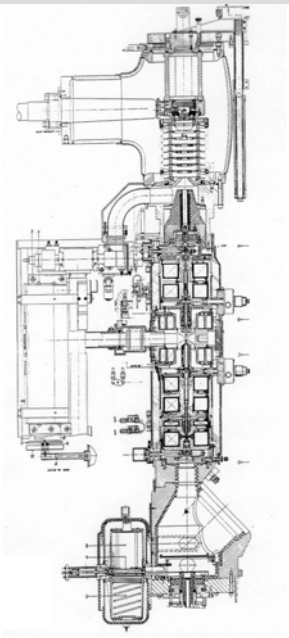
Back focal plane

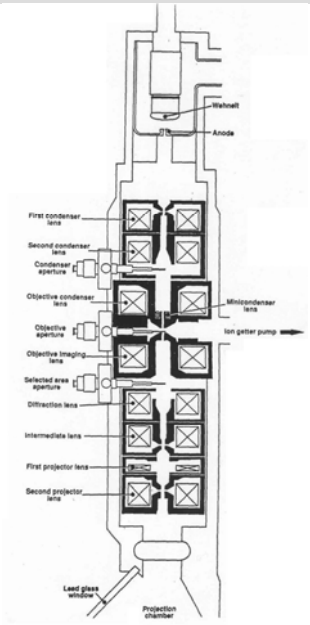
Lens problems:
spherical aberation C_s
chromatic aberation C_c
astigmatism



Lens equation: $1/u + 1/v = 1/f$
Magnification $M = v/u$

Cross-Section of the Column of a CM30 Microscope

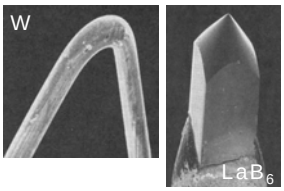




Electron Guns

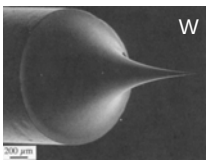
Thermoionic Guns

Electron emission by heating



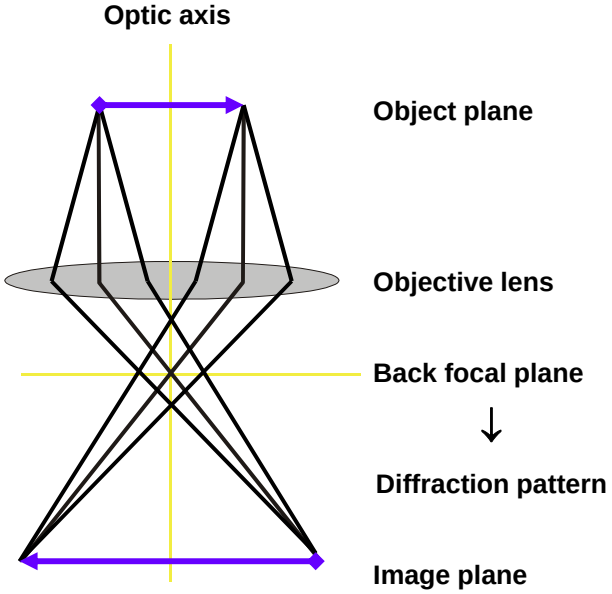
Field Emission Guns (FEG)

Electron emission by applying an extraction voltage

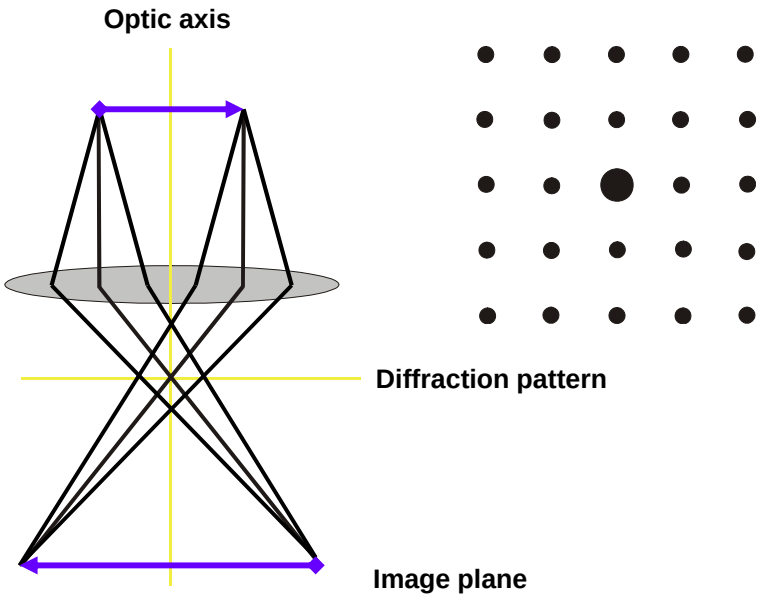


Properties	W	LaB_6	FEG
Work function / eV	4.5	2.4	4.5
Temperature / K	2700	2000	(300-)1800
Energy spread / eV	3-4	1.5-3	0.4-1.5
Source size / nm	30000	5000	3-20
Maximum current / nA	1000	500	(30-)300
Brightness / A/m^2sr	10^9	$5x10^{10}$	10^{13}
Lifetime / h	100	500	>1000

TEM – Imaging and Diffraction

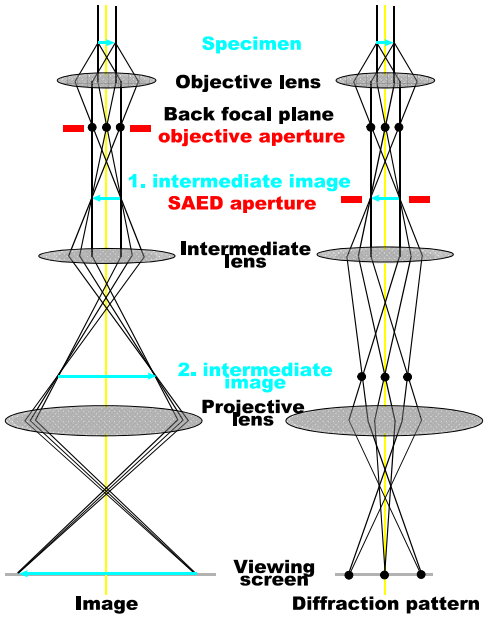


TEM – Imaging and Diffraction



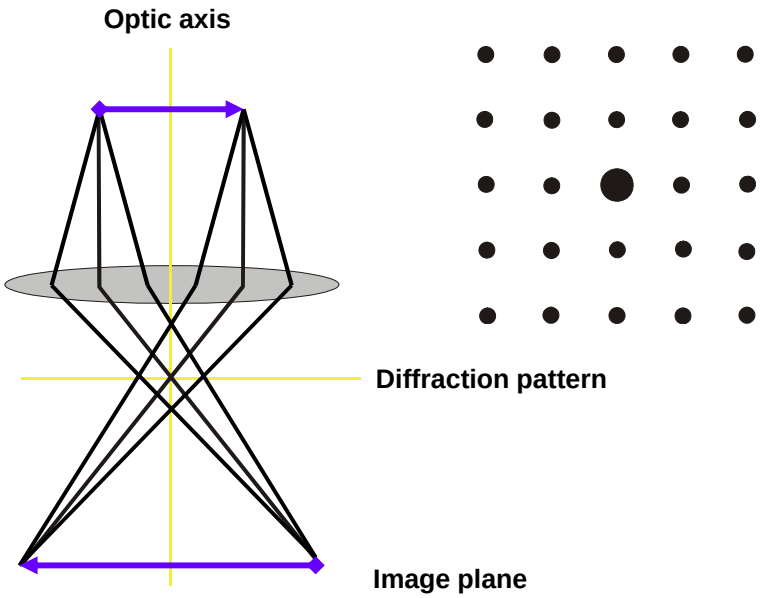
Transmission Electron Microscopy

Diffraction and Imaging Mode

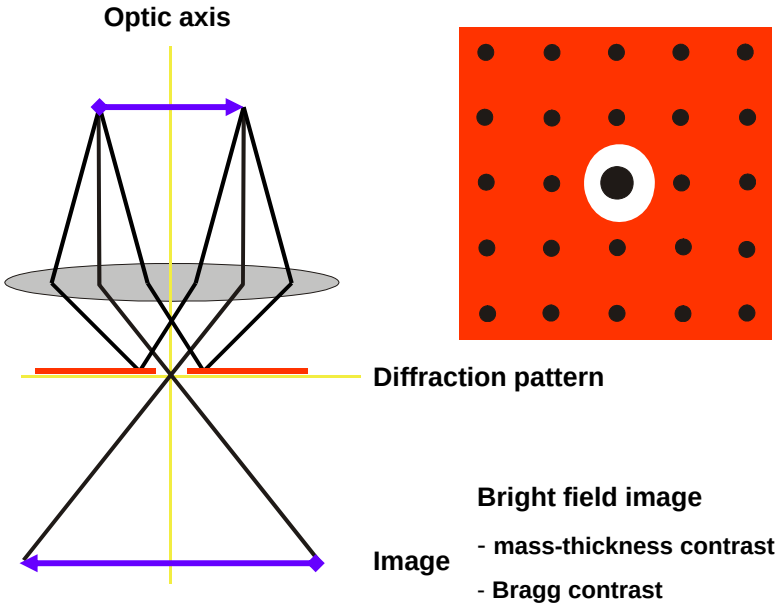


Electron Diffraction

TEM – Imaging and Diffraction



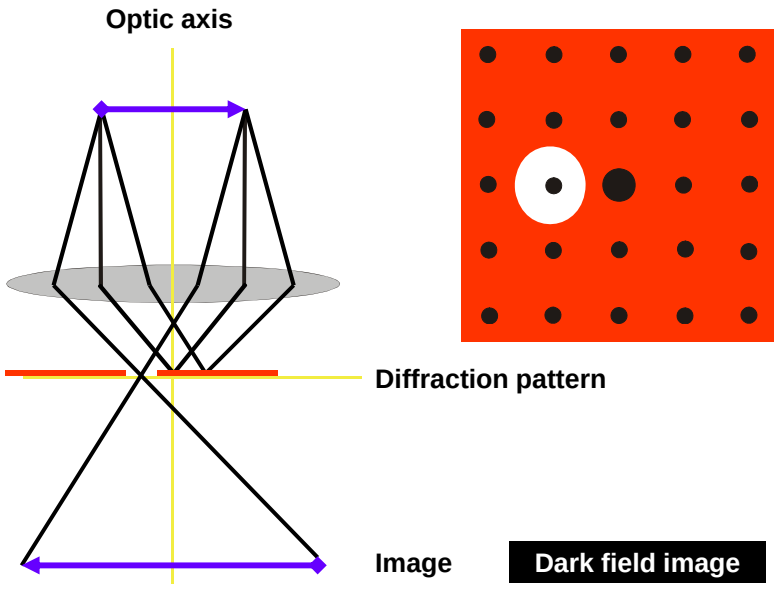
TEM – Imaging and Diffraction



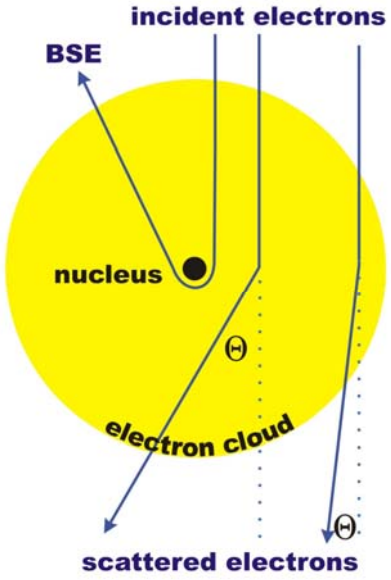
Bright field image

- **mass-thickness contrast**
- **Bragg contrast**

TEM – Imaging and Diffraction



Elastic Scattering of Electrons by an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

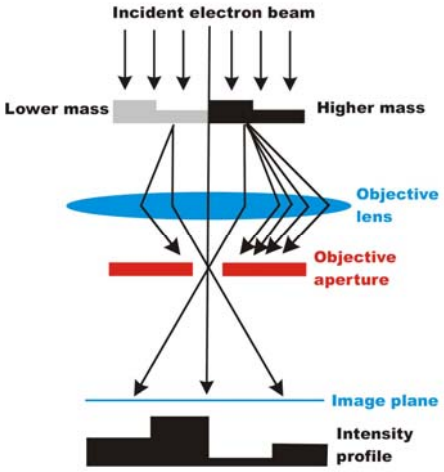
Strong Coulomb interaction with the nucleus

⇒ scattering into high angles or even backwards (Rutherford scattering)

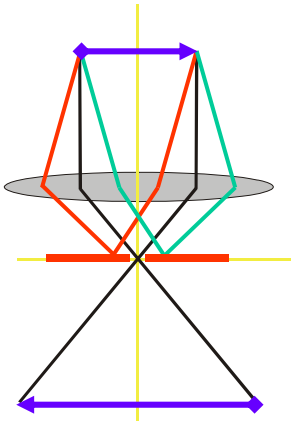
⇒ atomic-number (*Z*) contrast

$$d\sigma/d\Omega \sim Z^2$$

Types of Image Contrast



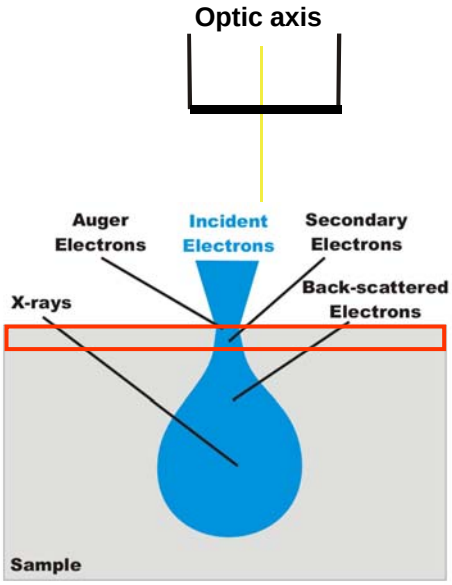
Mass-Thickness contrast

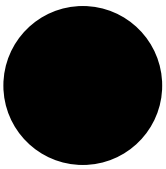


Diffracted beams do not pass through the objective aperture leading to a decreased intensity of crystalline areas

Bragg contrast

BF TEM Image Contrast



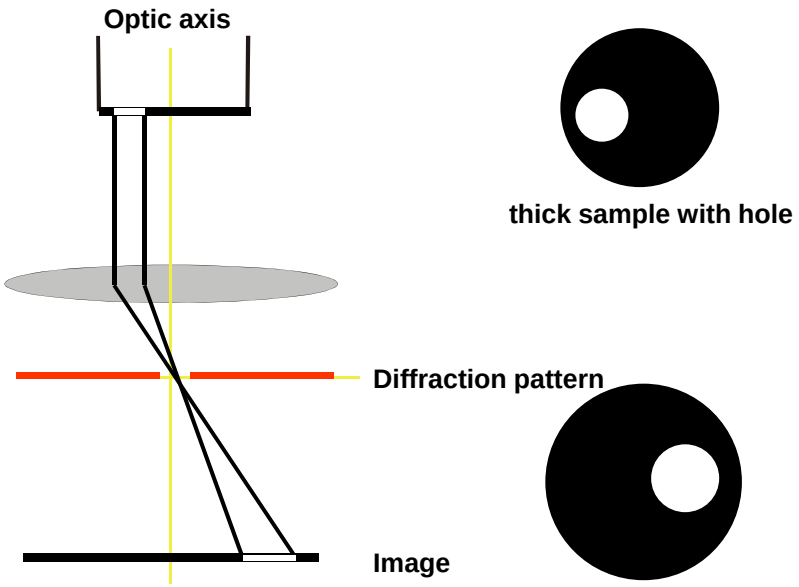


thick sample ⇒ all electrons are absorbed

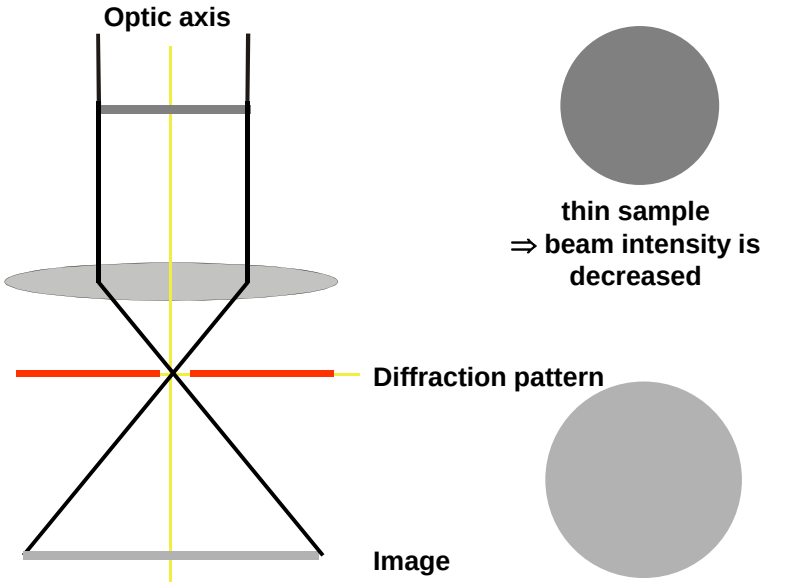
samples for TEM investigation must be thin (<< 100nm)

⇒ often laborious preparation necessary for compact samples!

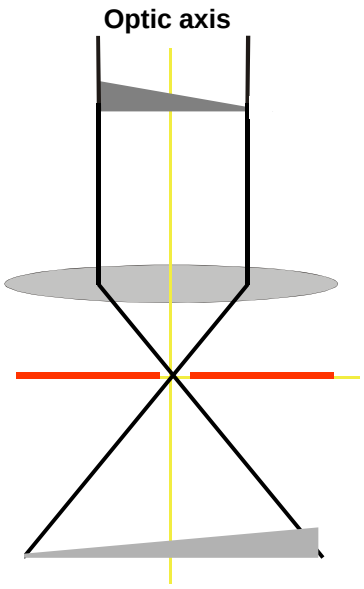
BF Image Contrast



BF Image Contrast

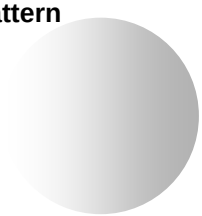


BF Image Contrast

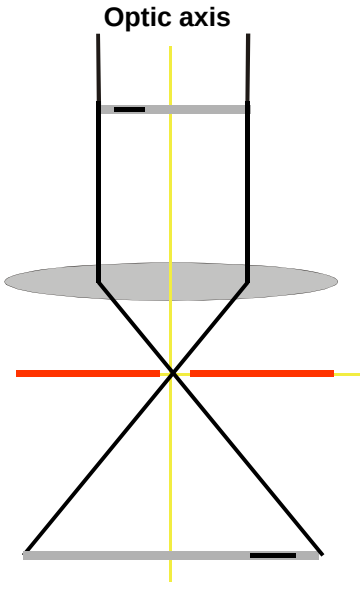


different thickness
⇒ varying image brightness

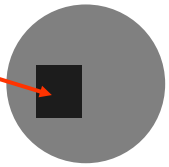
thickness contrast



BF Image Contrast

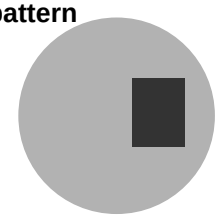


high Z

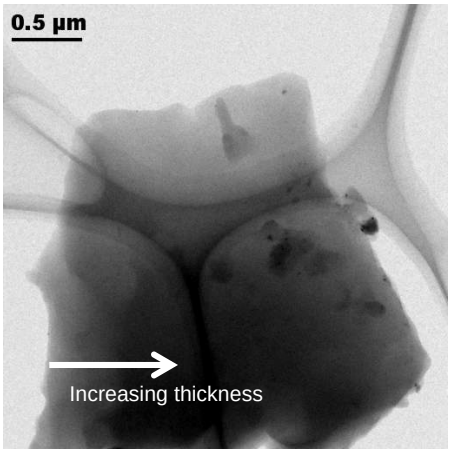


thin sample composed of
different materials
⇒ decrease of beam intensity
depends on scattering potential

mass contrast

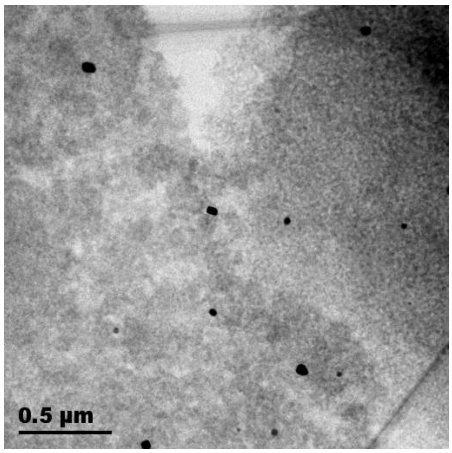


BF Images



Amorphous SiO_2 on C foil

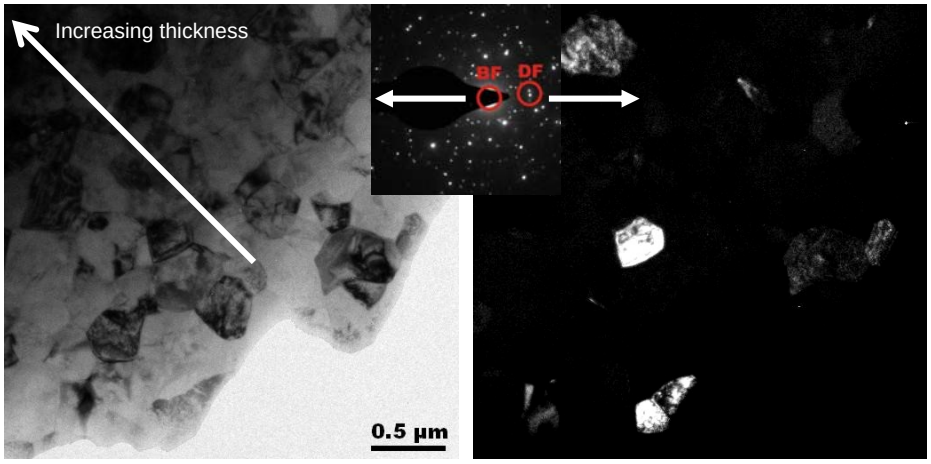
Mainly thickness contrast



Au particles (black) on TiO_2

Mainly mass contrast

BF and DF Images

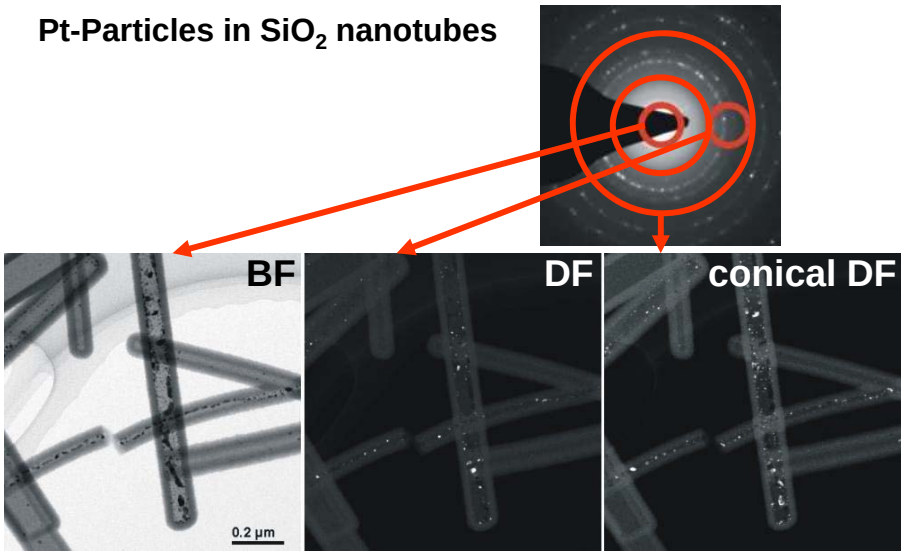


ZrO_2 micro crystals; crystals orientated close to a zone axis appear dark in BF and bright in DF

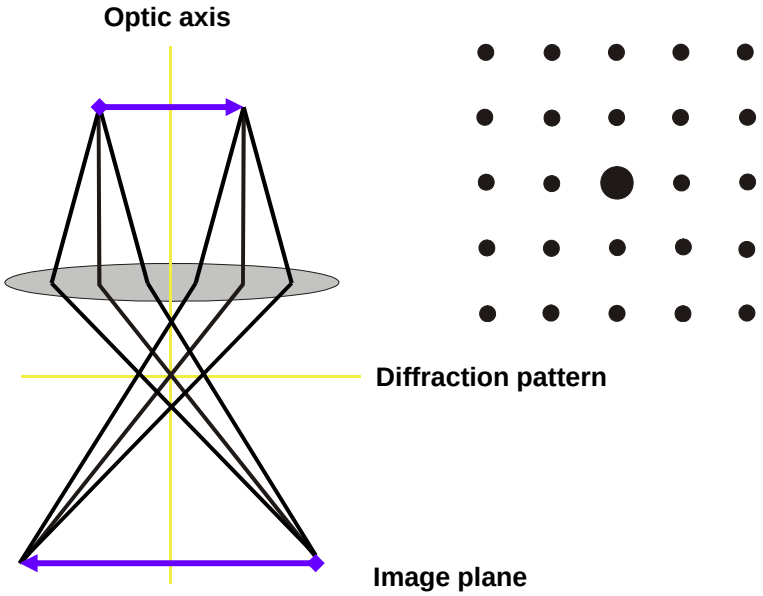
Mainly Bragg contrast

BF and DF Images

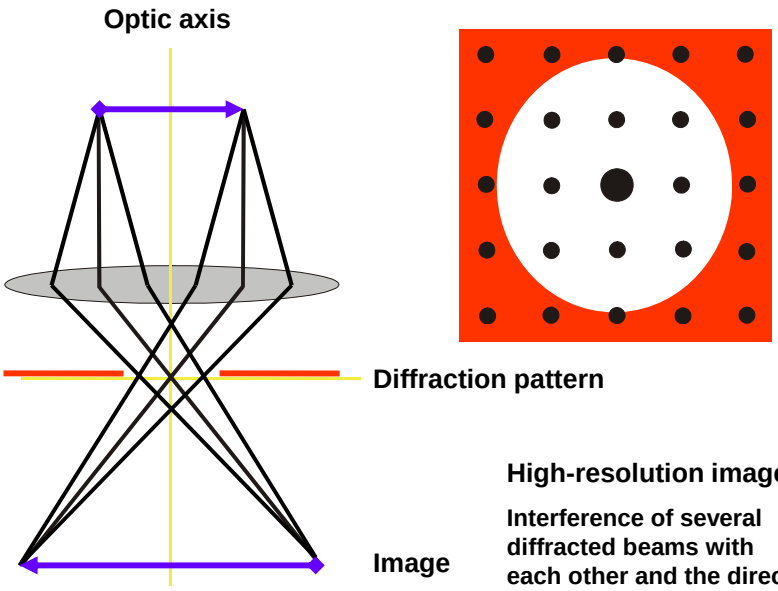
Pt-Particles in SiO_2 nanotubes



TEM – Imaging and Diffraction



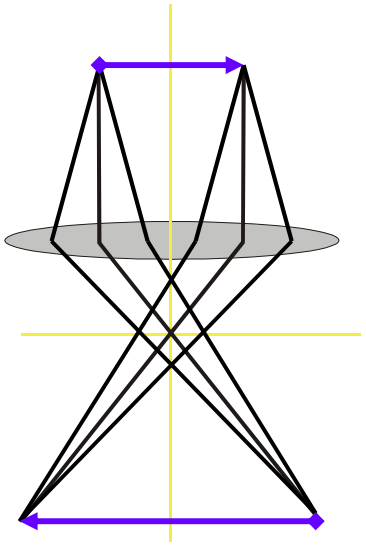
TEM – Imaging and Diffraction



High-resolution image

Interference of several diffracted beams with each other and the direct beam

TEM – Imaging and Diffraction



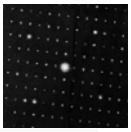
Mathematics

Fourier Transform

$$F\{f(x)\} = \int_{-\infty}^{+\infty} f(x)\, e^{-2i\pi qx}\, dx$$

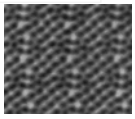
Fourier analysis

Diffraction pattern



Fourier synthesis

Image



TEM – Imaging and Diffraction

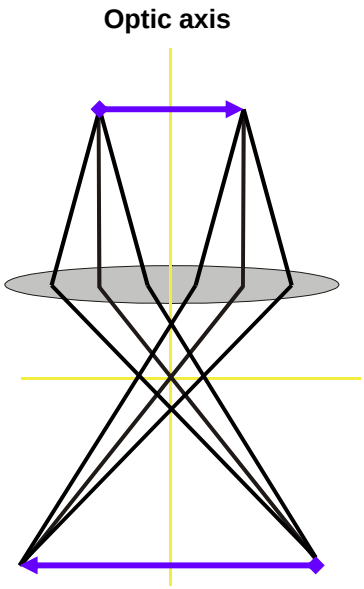


Image Processing

Filtered image

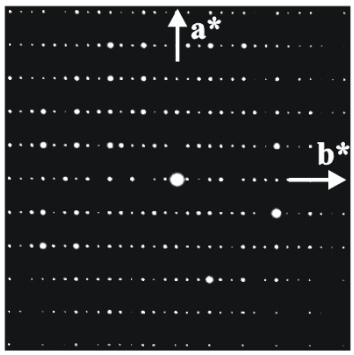
Fourier Transform

Diffraction pattern

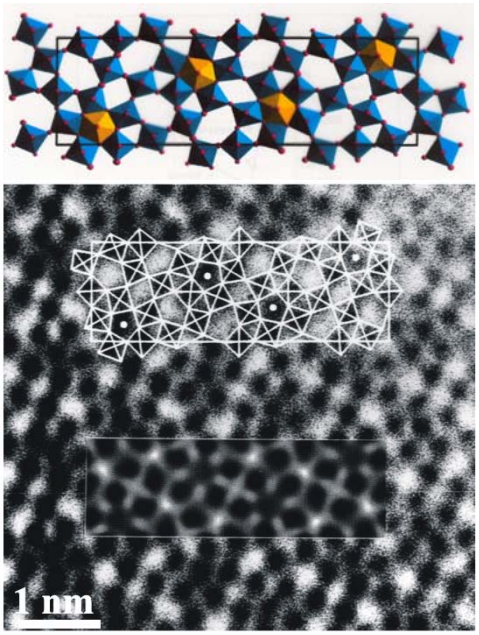
Fourier Transform

HRTEM image

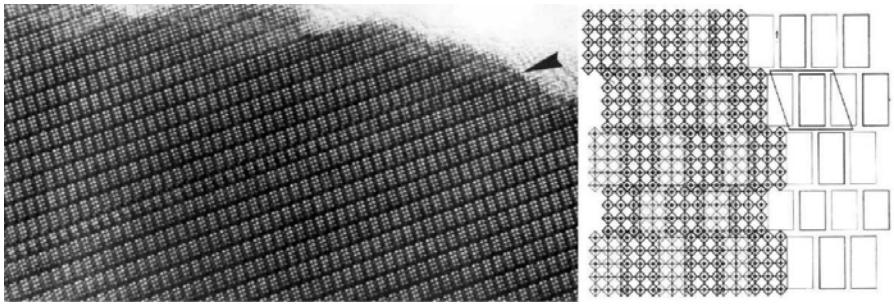
ED + HRTEM



$Nb_7W_{10}O_{47}$ – threefold TTB superstructure



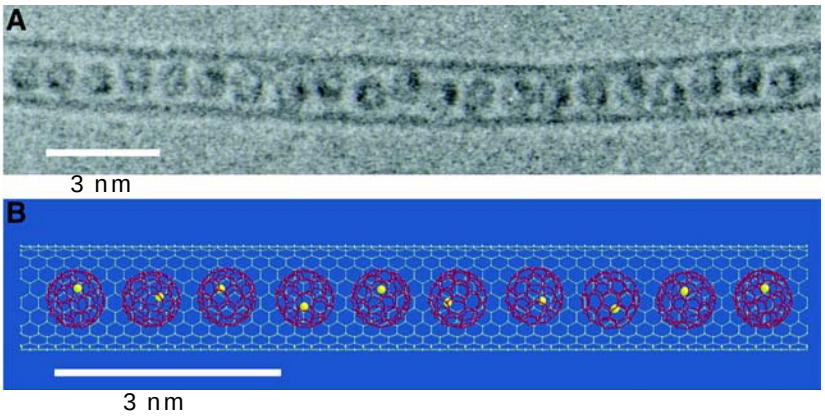
HRTEM: Detection of Defects



Planar defect in $ZnNb_{14}O_{35}F_2$

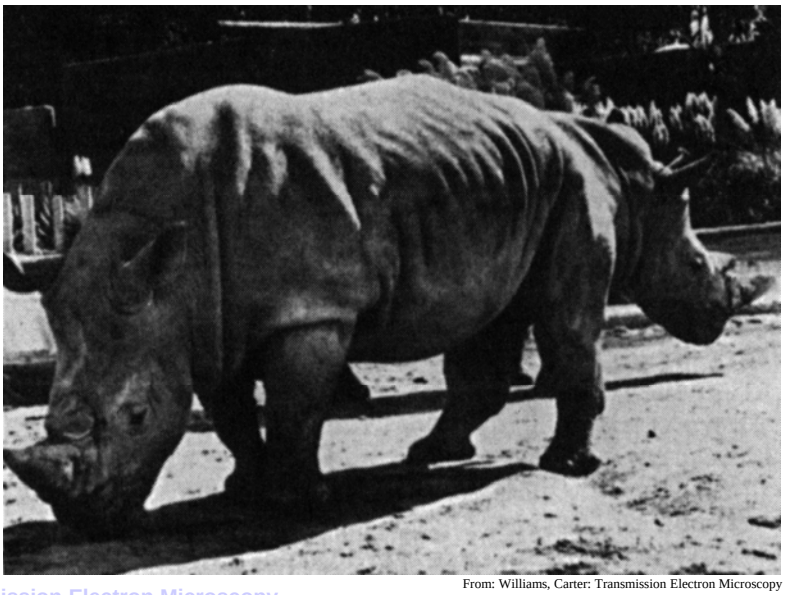
HRTEM: Imaging Single Atoms

$Gd@C_{82}$ in SWCNT



Suenaga et al, *Science* **290** (2000) 2280

Projection Problem: 3D ⇒ 2D



From: Williams, Carter: Transmission Electron Microscopy

Transmission Electron Microscopy

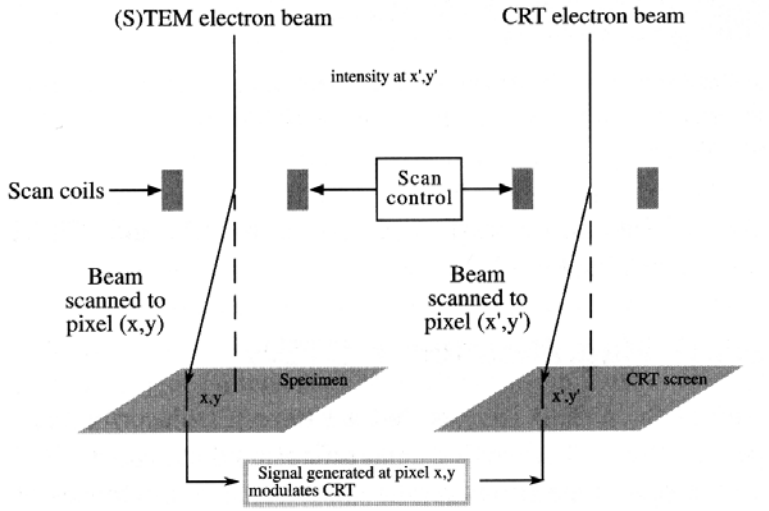
Types of contrast:

- **Mass-thickness (BF/DF)**
- **Bragg (BF/DF)**
- **Phase (HRTEM; resolution limit < 1Å)**

Determination of

- **Structure: HRTEM**
- **Defects: HRTEM, TEM**
- **Lattice constants and symmetry: ED**
- **Particle size: TEM, HRTEM**

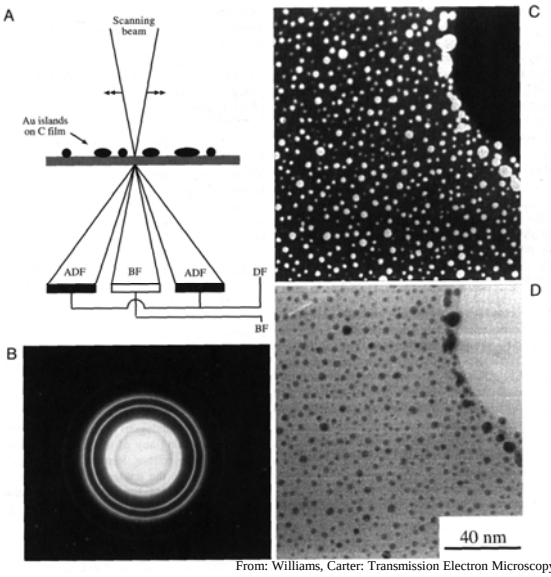
Scanning Transmission Electron Microscopy (STEM)



From: Williams, Carter: Transmission Electron Microscopy

BF and DF Imaging in STEM

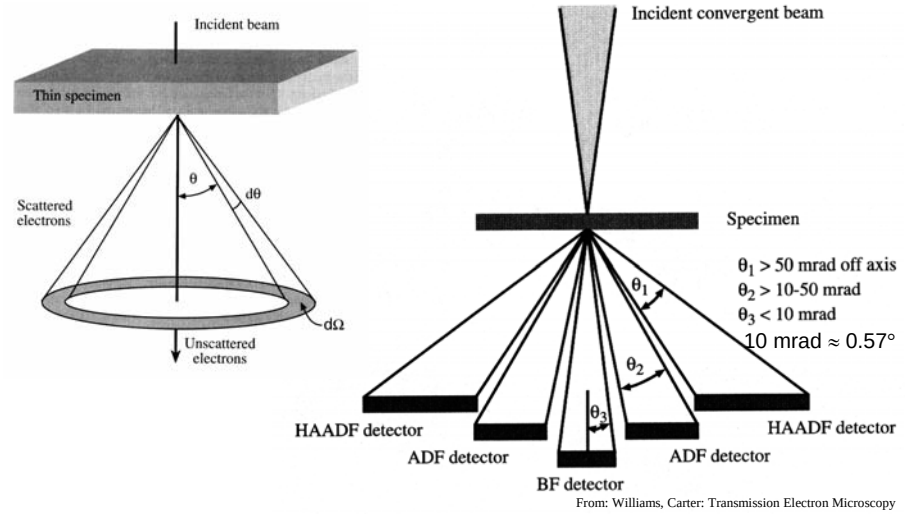
Au islands on a C film



DF image recorded by the annular dark field detector

BF image recorded by the bright field detector

From: Williams, Carter: Transmission Electron Microscopy



From: Williams, Carter: Transmission Electron Microscopy

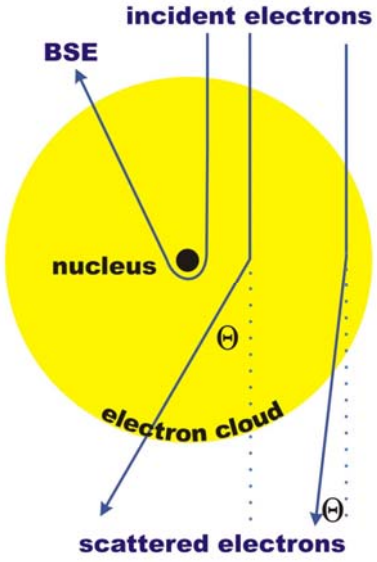
STEM Detectors

BF: Bright Field detector

ADF: Annular Dark Field detector

HAADF: High Angle Annular Dark Field detector

Scattering of Electrons at an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

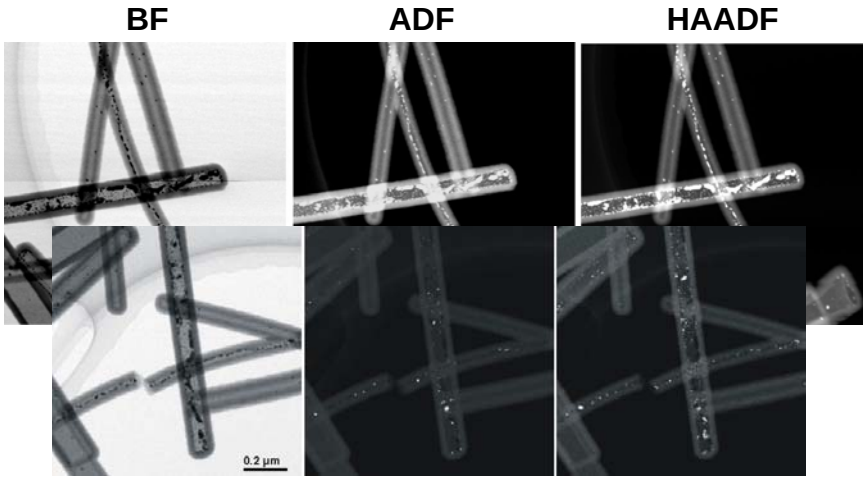
⇒ scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (*Z*) contrast

$$d\sigma/d\Omega \sim Z^2$$

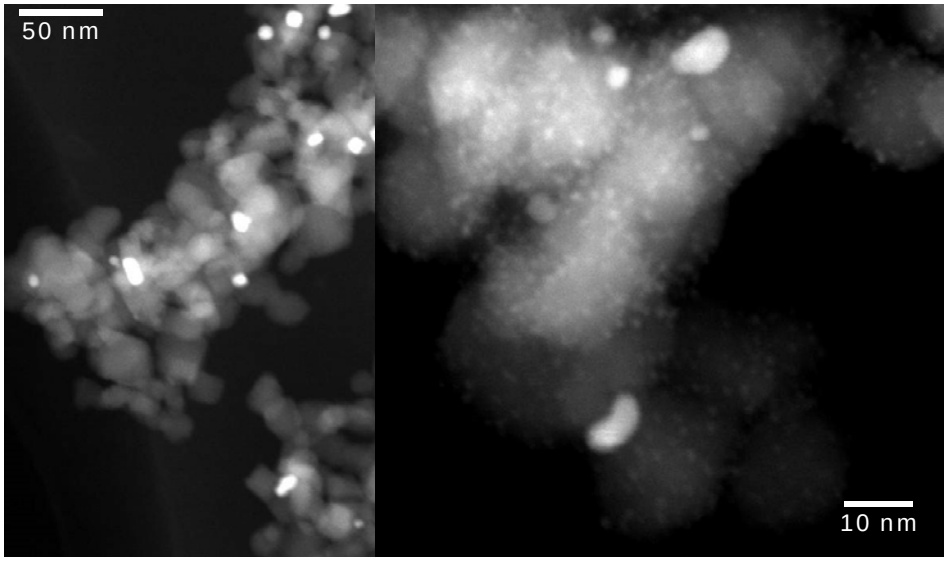
BF and DF Imaging in STEM

Pt particles in SiO_2 nanotubes

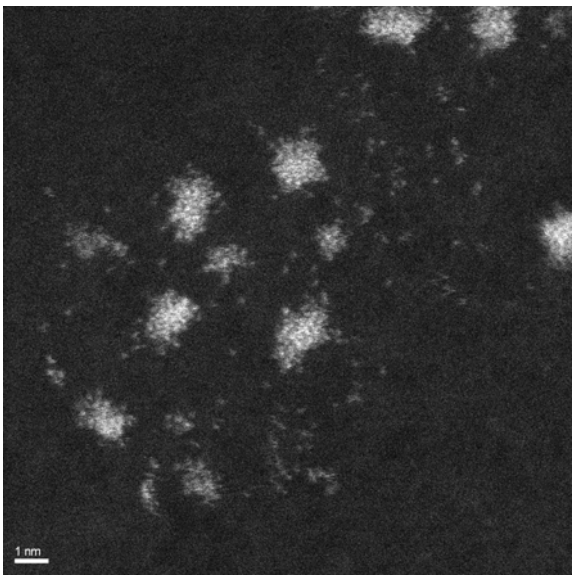


BF DF conical DF TEM

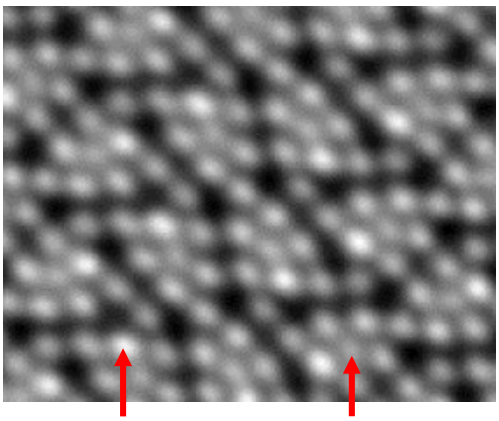
HAADF-STEM or Z contrast Images of Au Particles on Titania



HAADF-STEM or Z contrast Images of Pt Clusters and Atoms on Carbon

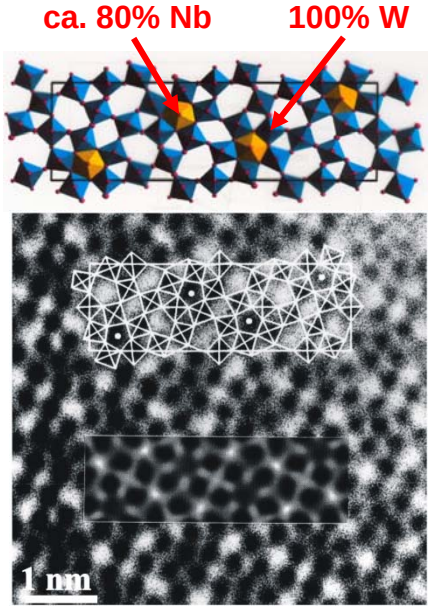


Information about Elemental Distribution in HAADF-STEM or Z contrast images



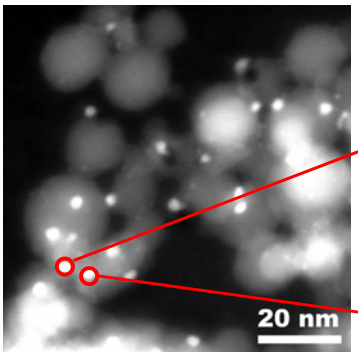
100% W ca. 80% Nb

HAADF-STEM of $Nb_8W_9O_{47}$

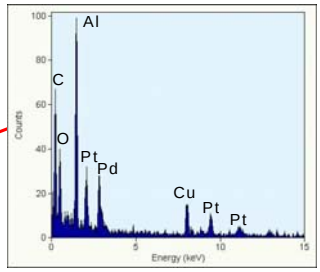


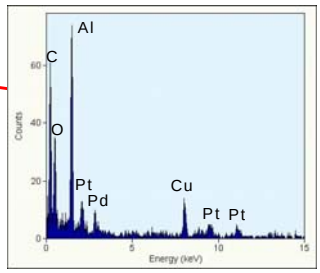
Pd and Pt supported on alumina: Size of the particles? Alloy or separated?

STEM + EDXS: Point Analyses



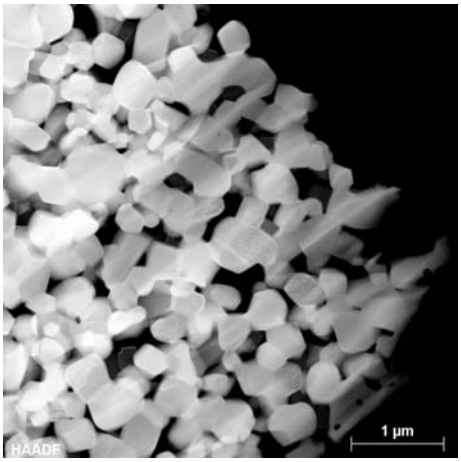
HAADF-STEM image

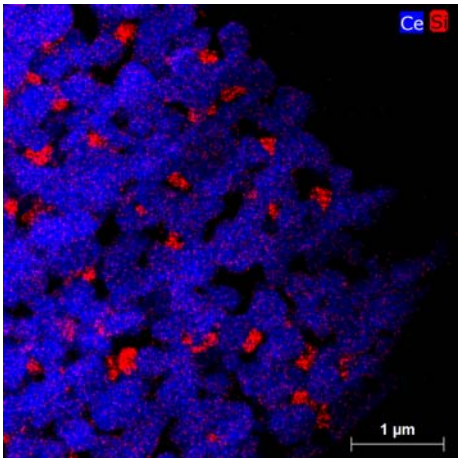




Elemental Mapping

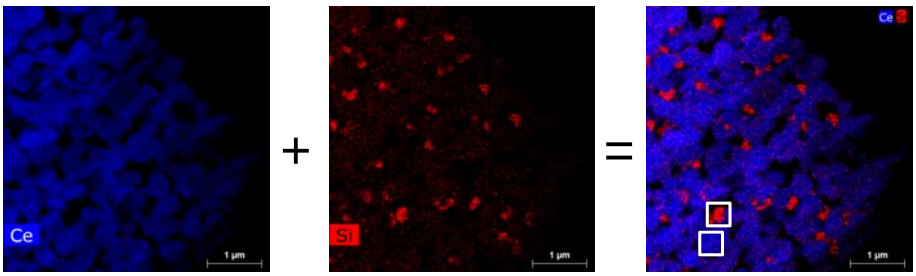
STEM + EDXS: Area Analyses: CeO_2 and zeolite



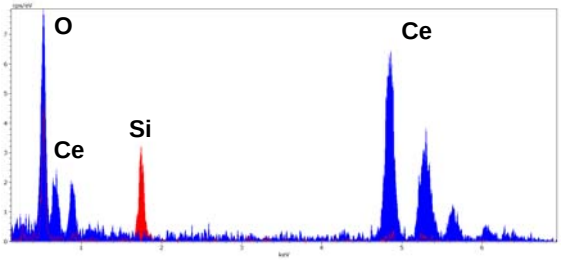


Elemental Mapping

STEM + EDXS: Area Analyses: CeO_2 and zeolite



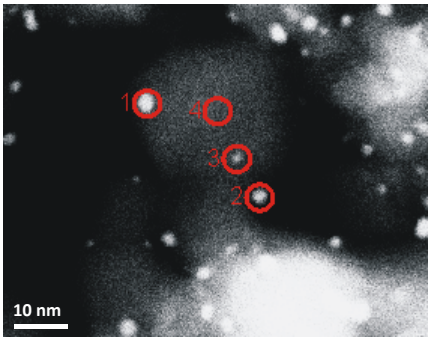
Data cube:
for each pixel in the image, there is an EDX spectrum recorded and stored

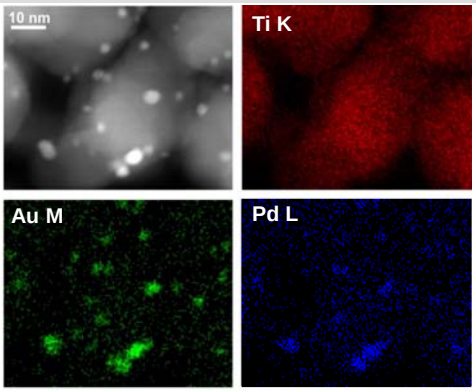


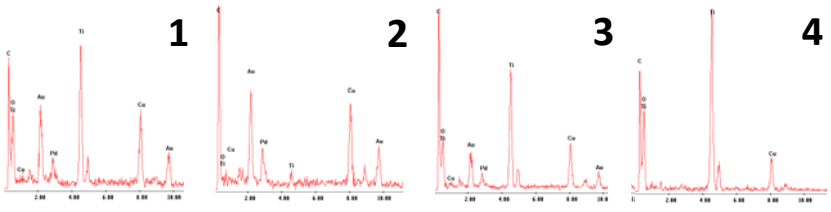
Scanning Transmission Electron Microscopy

STEM+EDXS: spot analyses vs. elemental mapping

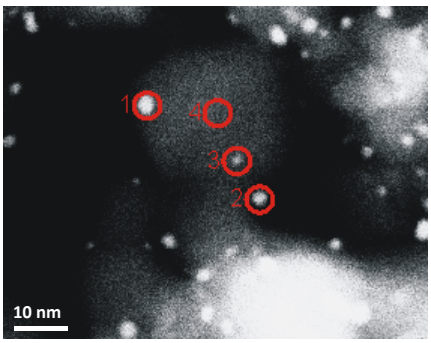
Au and Pd on TiO_2

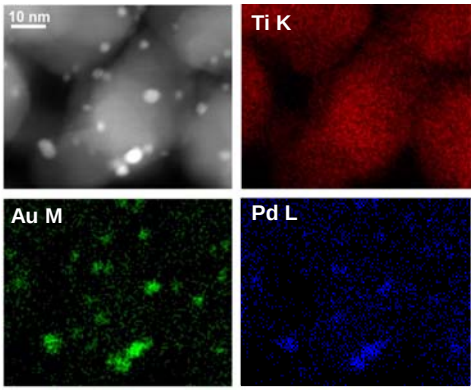






STEM+EDXS: spot analyses vs. elemental mapping





quick and efficient if a clear contrast between the different components appears in STEM

EDX spectra of selected spots with good signal:noise ratio measured in < 1 min

time-consuming but provides the full data cube (1EDXS/pixel)

EDX spectra extracted from selected spots with bad signal:noise ratio

Scanning Transmission Electron Microscopy

Contrast:

- **Mass-thickness (BF/DF)**
- **Bragg (BF/DF)**
- **Z^2 (HAADF)**

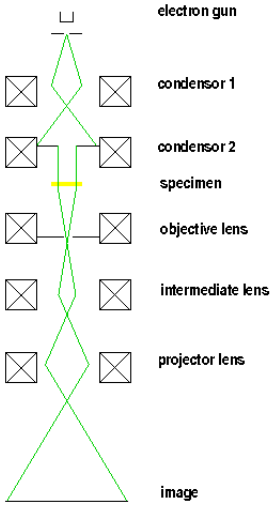
Determination of

- **Particles on support : HAADF**
- **Structure and defects : HR**
- **Chemical information : HAADF**

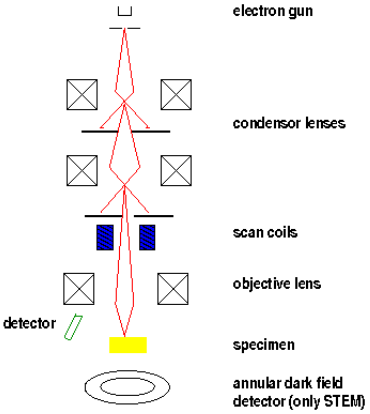
Important: Combination with EDXS or EELS

TEM versus STEM

Transmission (TEM)

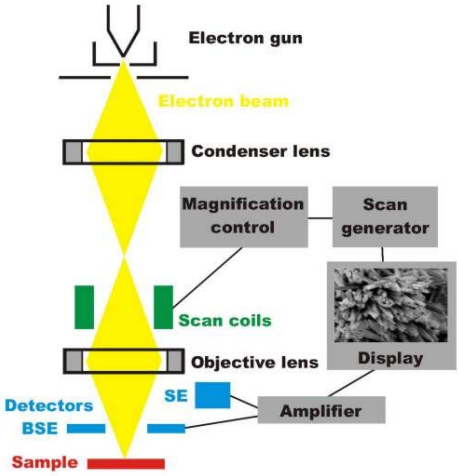


Scanning (SEM or STEM)



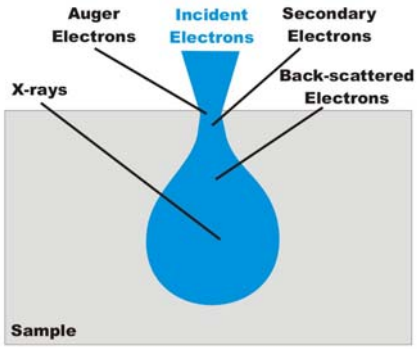
Resolution: $\Delta x = 0.66\ C_s^{1/4}\lambda^{3/4}$ $\quad d = 0.41\ C_s^{1/4}\lambda^{3/4}$

Scanning Electron Microscopy (SEM)



Quanta 200 FEG (FEI)

Signals used in the SEM



Secondary Electrons (SE)

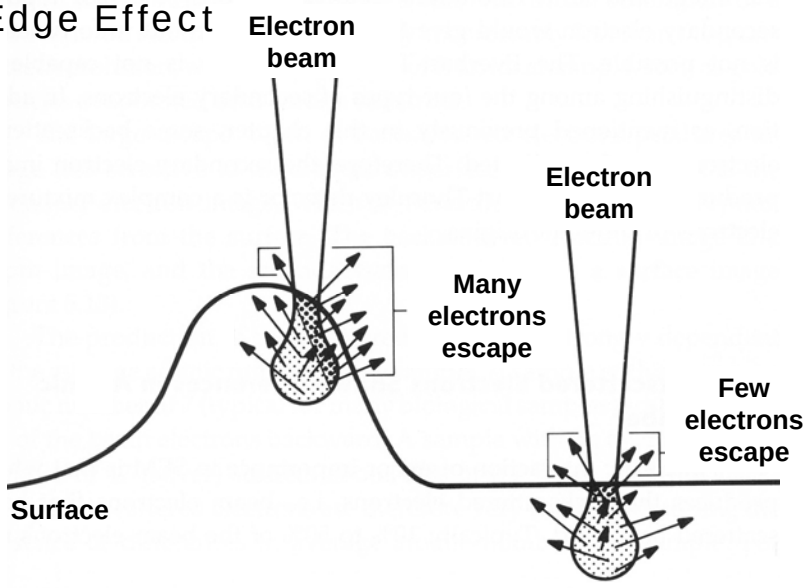
- low energy < 100 eV (result of inelastic interactions)
- information about topography and morphology
- escape only when generated close to the surface

Back-scattered Electrons (BSE)

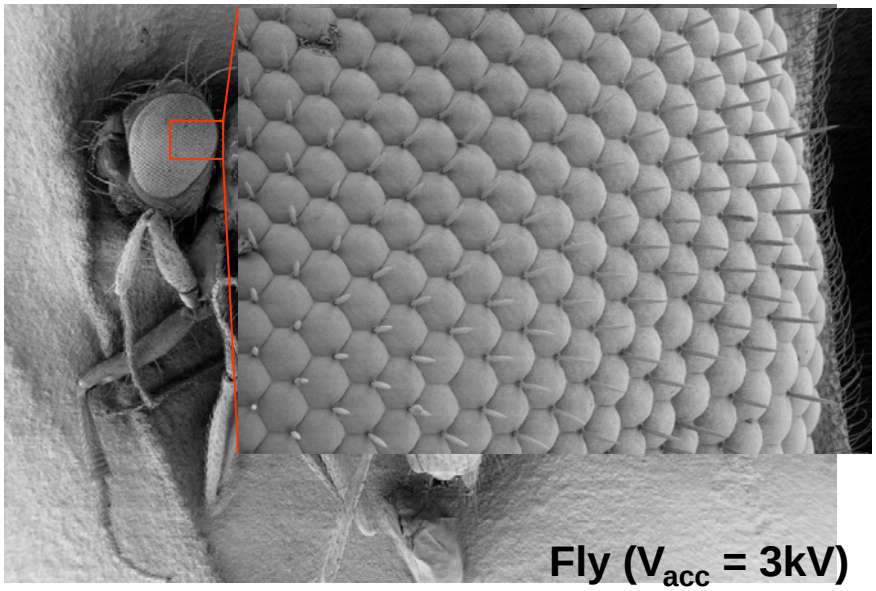
- high energy ≅ E_0 (result of elastic interactions)
- morphology and chemical Information

Topographic Contrast in the SEM

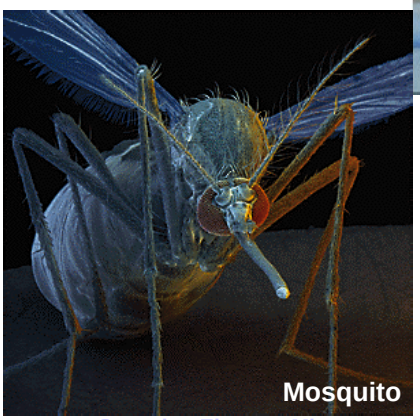
Edge Effect



SEM: Imaging with Secondary Electrons

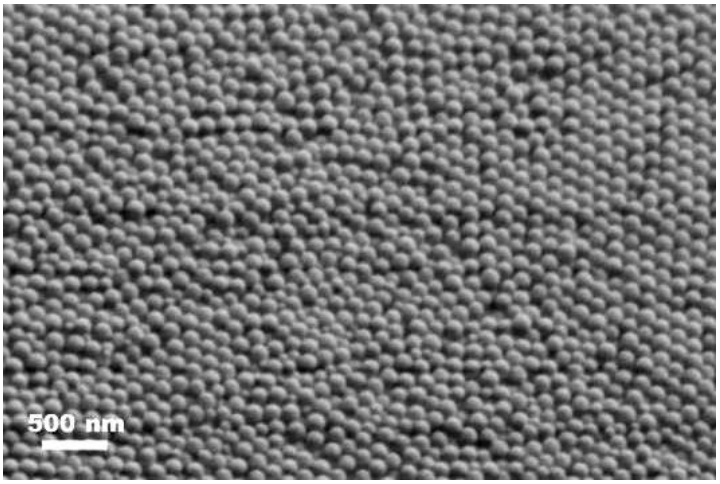


Colorized SEM Images



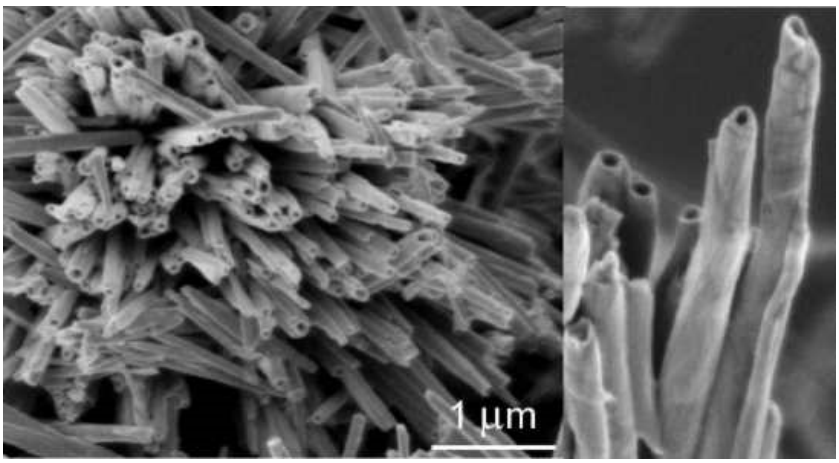
© D. Scharf
www.scharfphoto.com

SEM: Imaging with Secondary Electrons



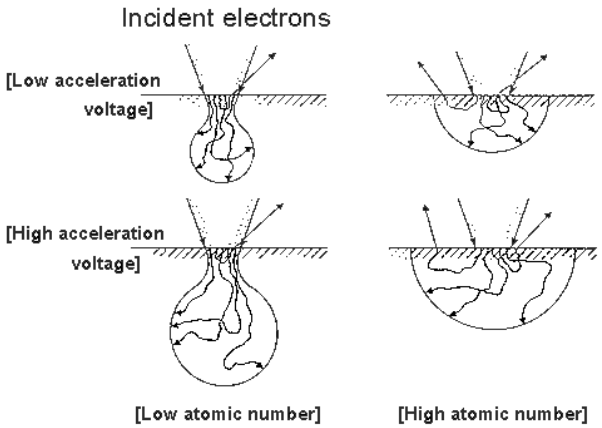
Latex balls (V_{acc} = 1kV)

SEM: Imaging with Secondary Electrons



Vanadium oxide nanotubes (V_{acc} = 1kV)

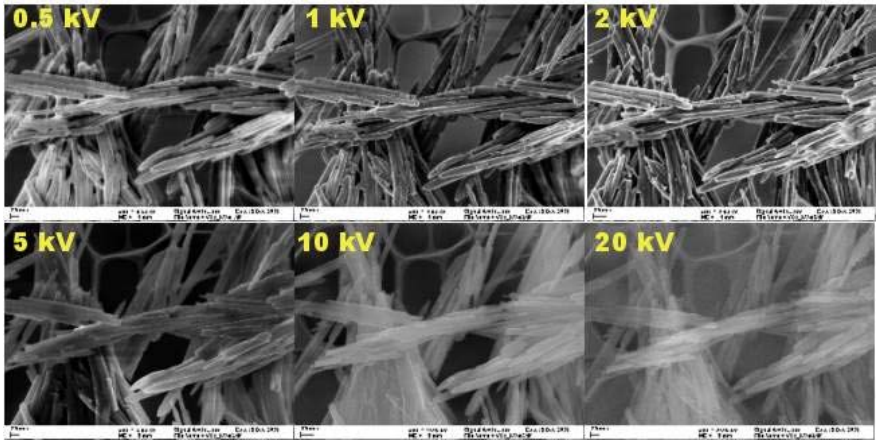
SEM: Dependence on Electron Energy



Penetration depth of electrons in matter

- **increases with increasing V_{acc}**
- **decreases with increasing atomic number**

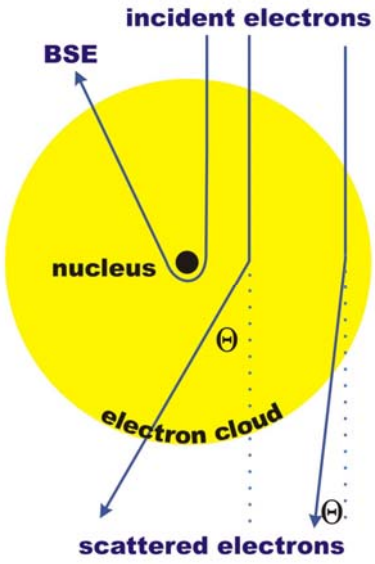
SEM: Dependence on Electron Energy



Resolution (Gemini 1530 FEG):

1 nm at 20 kV 1.5 nm at 10 kV
2.5 nm at 1 kV 5 nm at 0.2 kV

Scattering of Electrons at an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

⇒ scattering into high angles or even backwards (Rutherford scattering)

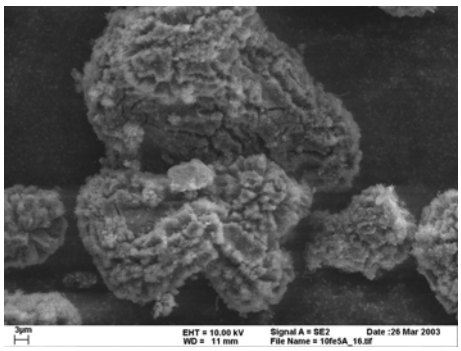
⇒ atomic-number (Z) contrast

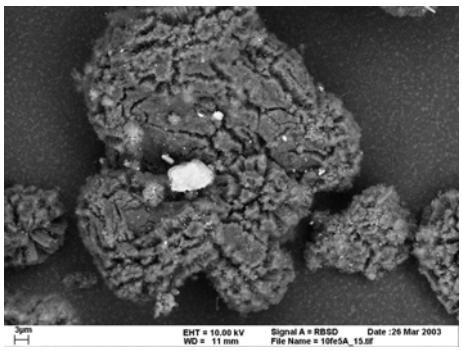
$$d\sigma/d\Omega \sim Z^2$$

c.f. **Z contrast with HAADF-STEM**

SEM: Detection of SE versus BSE

Fe particles in C





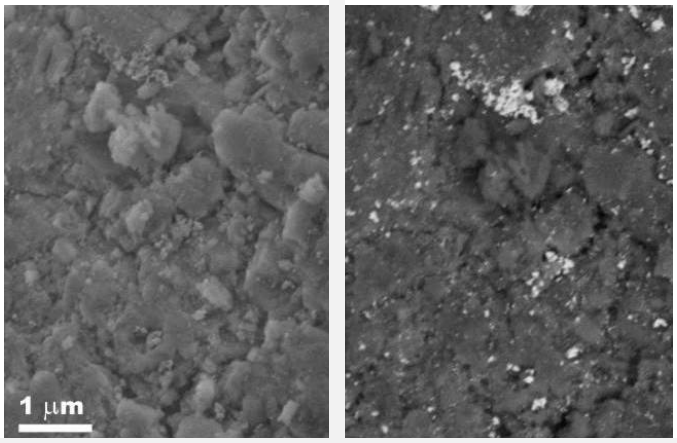
Secondary electron detector

Backscattered electron detector

Fe particles bright (Z contrast)

SEM: Detection of SE versus BSE

Pt particles on alumina



Secondary electron detector **Backscattered electron detector**

Pt particles bright (Z contrast)

Scanning Electron Microscopy (SEM)

Detection of:

- **Secondary electrons**
- **Back-scattered electrons**

Determination of

- **Morphology**
- **Surface topology**
- **Particles of heavy elements**

Combination with EDXS

Script: *Interactions.pdf* on www.microscopy.ethz.ch/downloads

Textbooks:

Williams, Carter, Plenum Press, New York, 1996:
Transmission Electron Microscopy (available in chemistry library)

Thomas, Gemming, Springer, Berlin, 2014:
Analytical Transmission Electron Microscopy – An Introduction for Operators
Analytische Transmissionselektronenmikroskopie – eine Einführung für den Praktiker

Lecture: *Electron Microscopy* (each fall term)