Basics of Transmission Electron Microscopy

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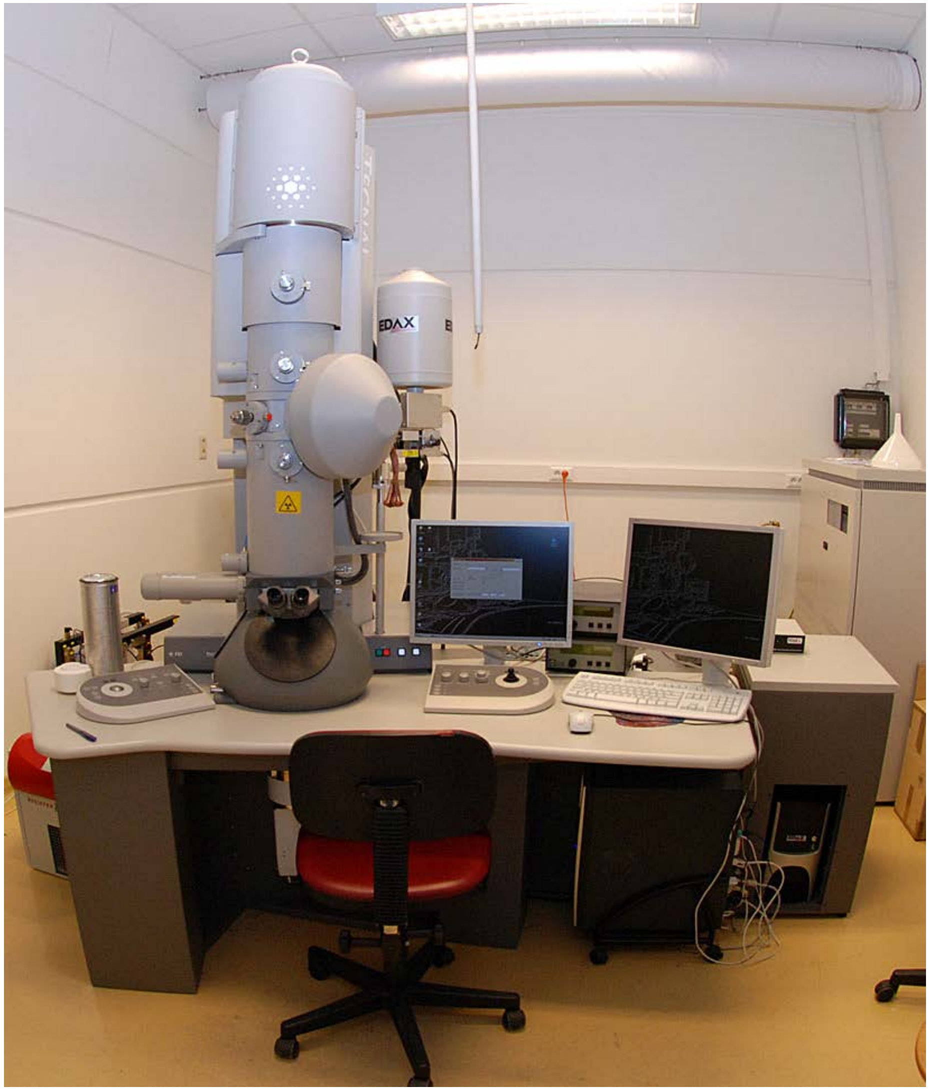
Outline

- TEM column
- Wave properties of electrons
- Sample preparation
- Parallel-beam illumination mode
  - Selected area electron diffraction
  - High-resolution TEM
- Focused-beam mode (STEM)
- Analytical TEM

Examples of transmission electron microscopes



FEI Technai G2, EMAT, Antwerp

FEI Titan Themis Z, Skoltech

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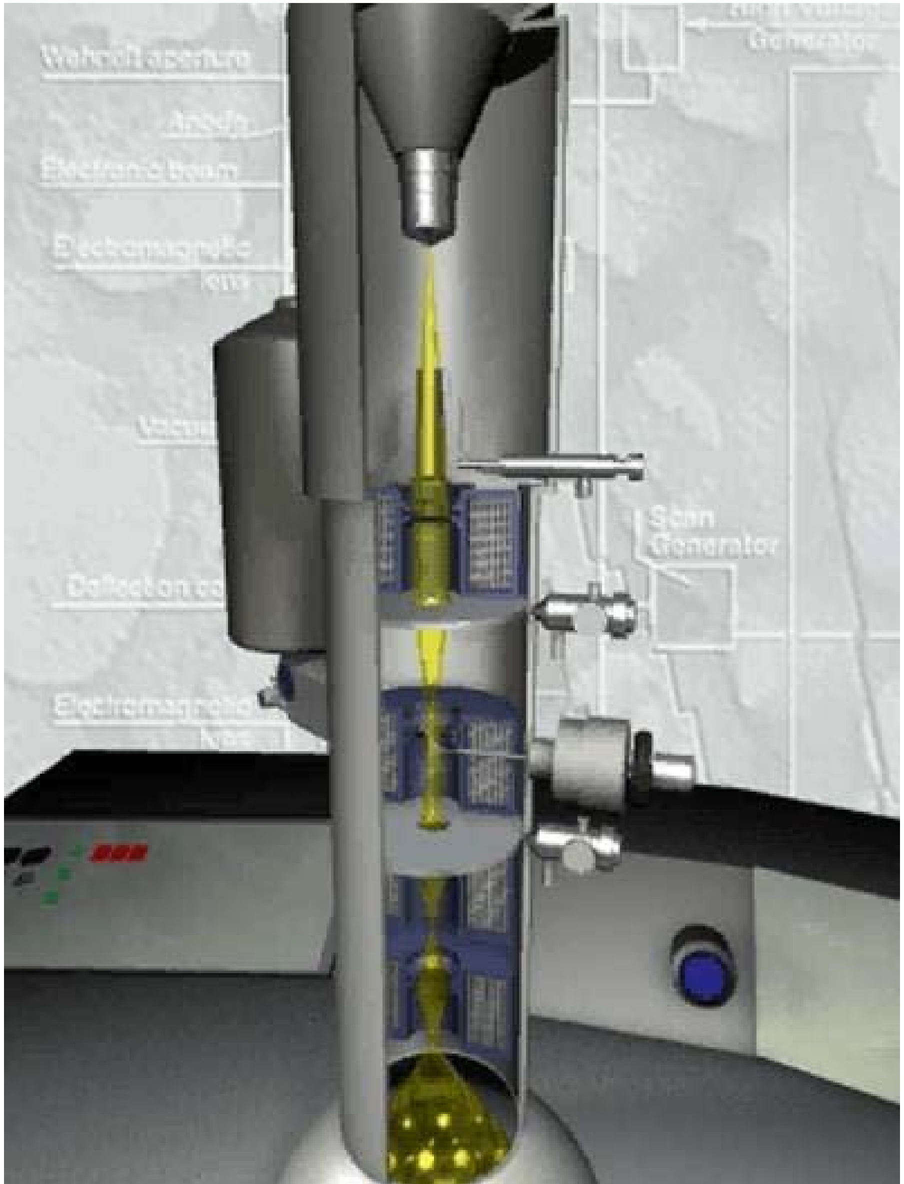
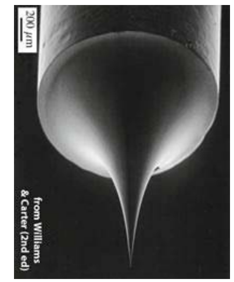
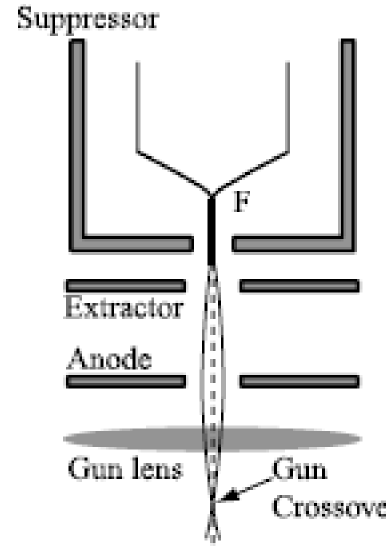
Column of transmission electron microscope



Electron source
(thermionic gun,
Schottky FEG, cold FEG)





Condenser system

Sample stage and objective lenses

Annular detector for STEM mode

Projector and intermediate lenses

CCD or CMOS detector for
image registration

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Wave properties of electron and resolution limit

Energy of electron accelerated in the potential U:

$$E = eU = \frac{m_o v^2}{2} \Rightarrow v = \sqrt{\frac{2eU}{m_o}}$$

Electron energy, kV	Wavelength, Å
100	0.037
200	0.0251
300	0.0197

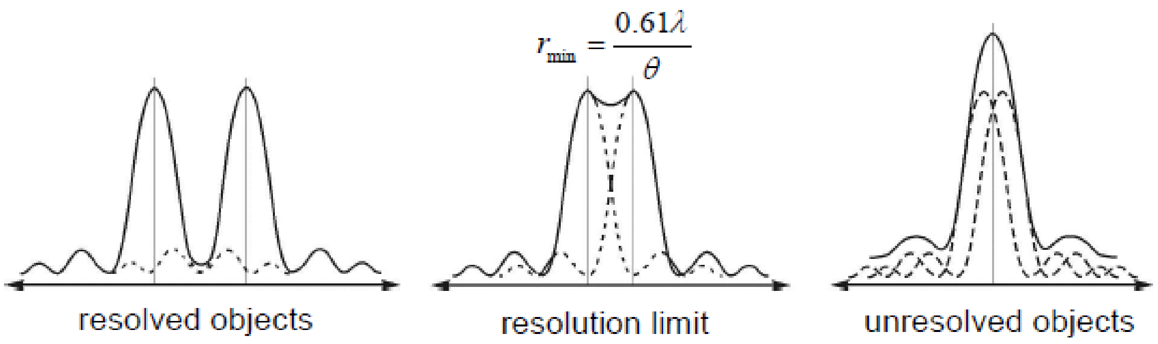
De Broglie equation: $\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{h}{\sqrt{2em_0U}} = \frac{12.26}{\sqrt{U}}$ (U in volts, λ in Å)

Relativistic correction (U > 100 kV): $\lambda = \frac{h}{\sqrt{2m_0eU(1+\frac{eU}{2m_0c^2})}} = \frac{1.226}{\sqrt{U}}(1+9.79.10^{-7}U)^{1/2}$

Resolution limit of optical system

300 kV: $r^{theor} \approx 0.02$ Å

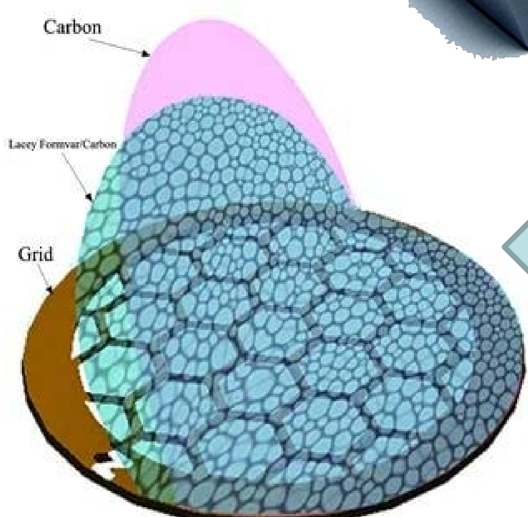
$r^{exper} \approx 0.50$ Å



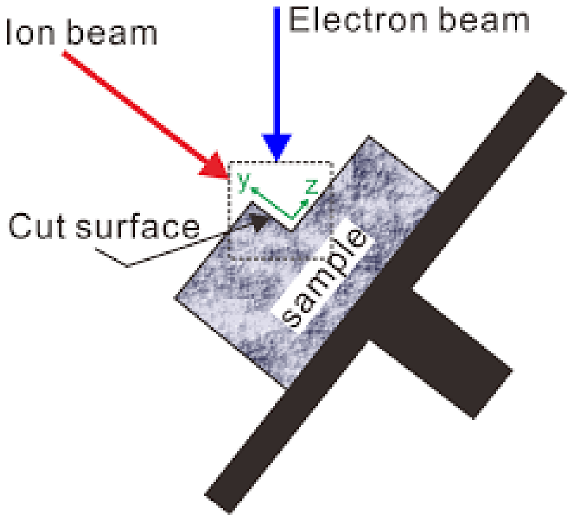
…because of lens aberrations

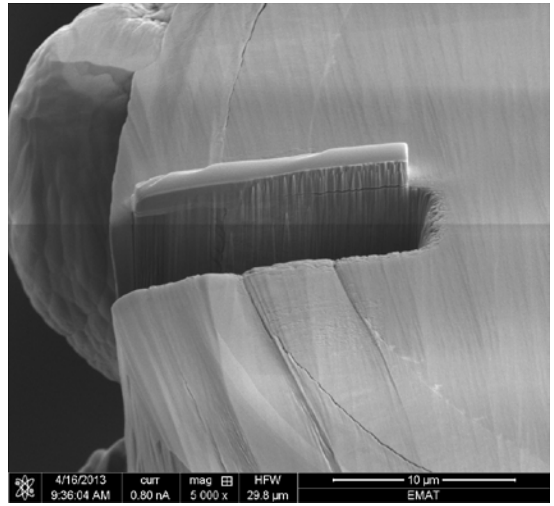
Sample preparation: powders and air sensitive materials

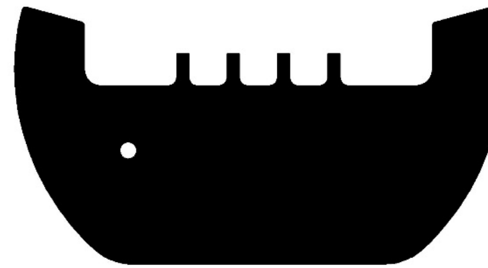
1. Grinding under anhydrous solvent in air or inert atmosphere
2. Dropcasting the suspension onto the holey TEM grid



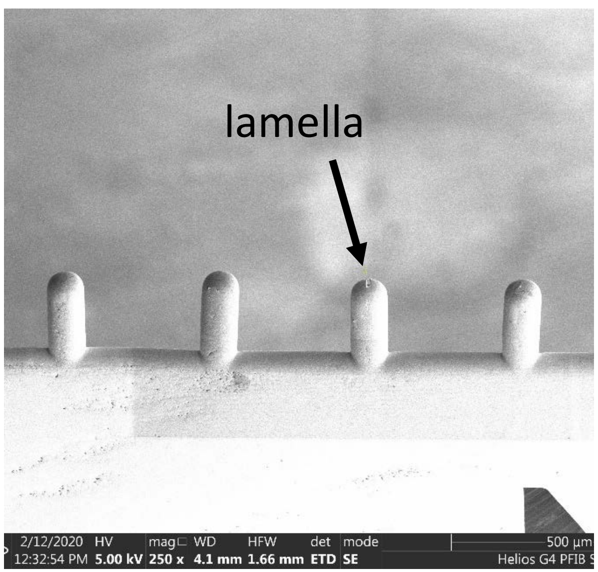
Sample preparation: FIB

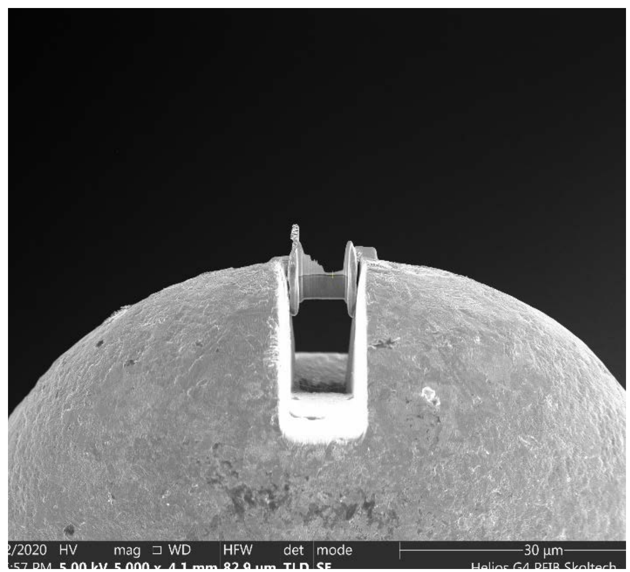


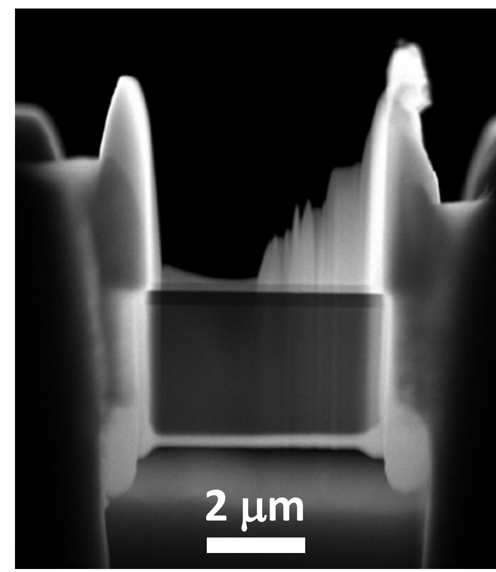




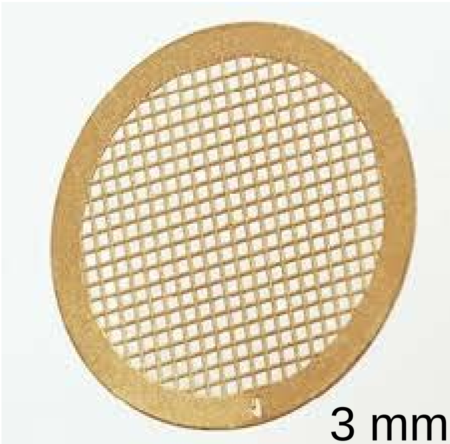
FIB grid

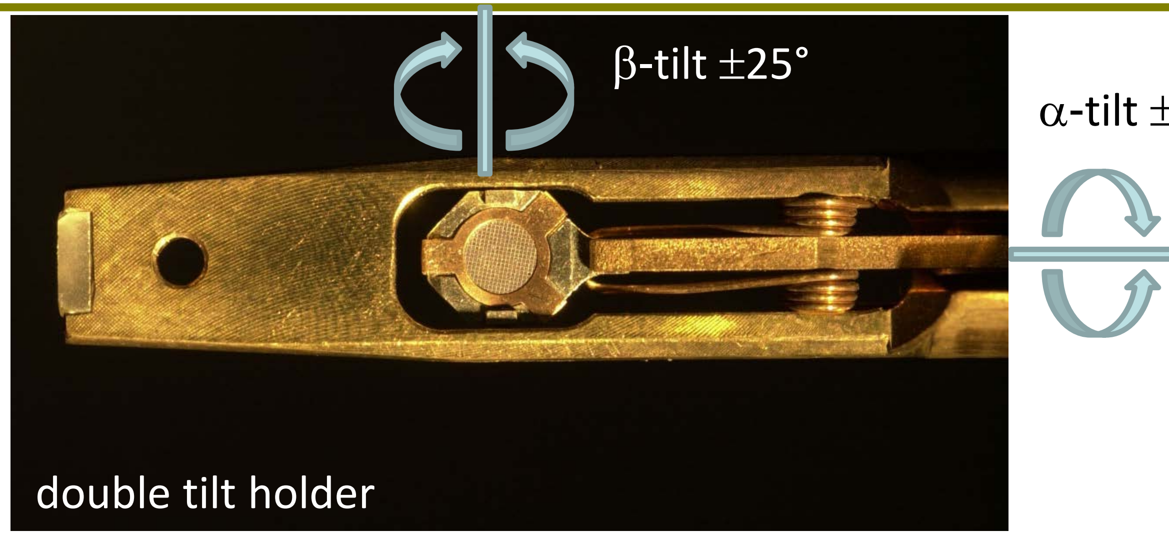




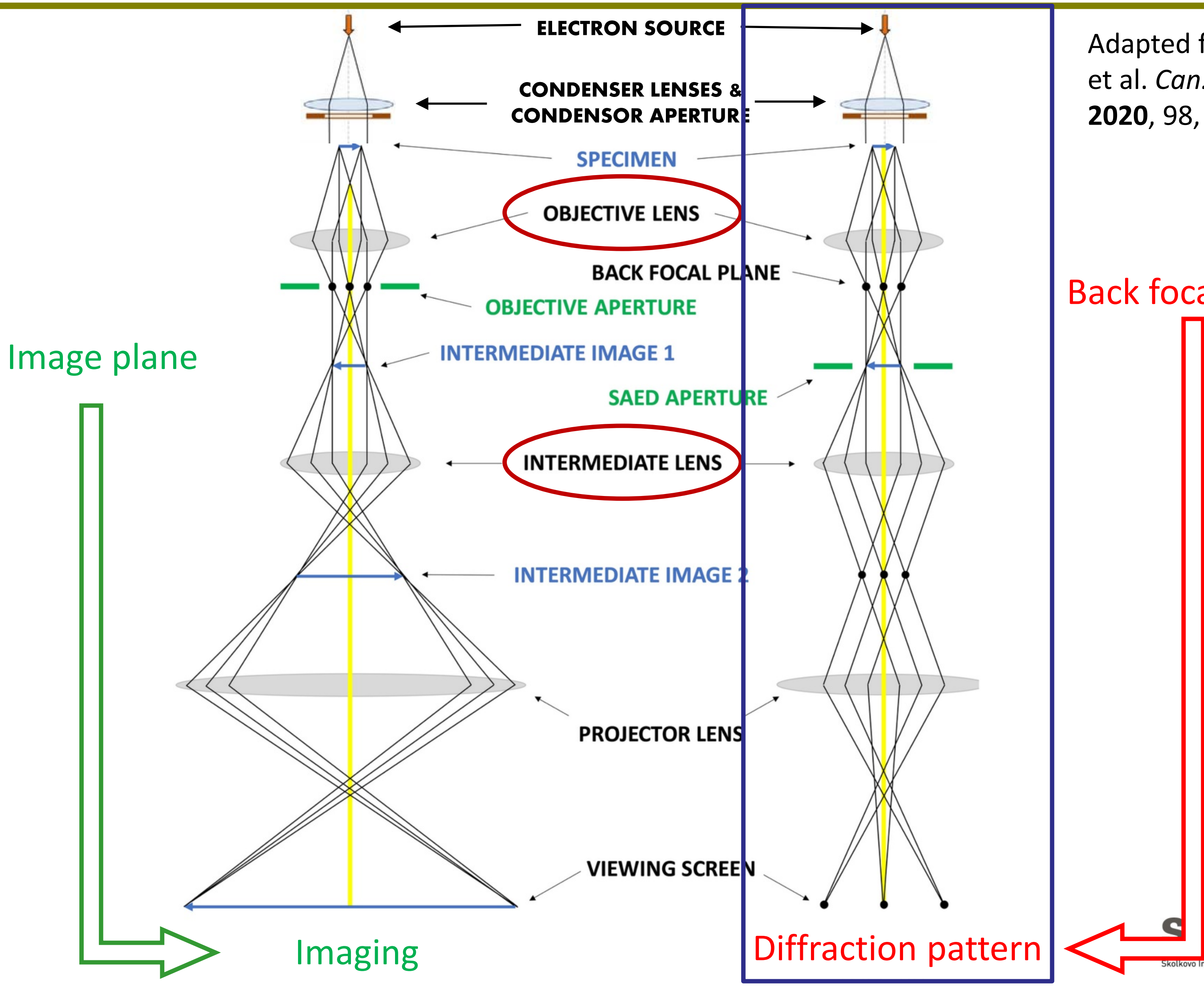


Transferring into TEM column





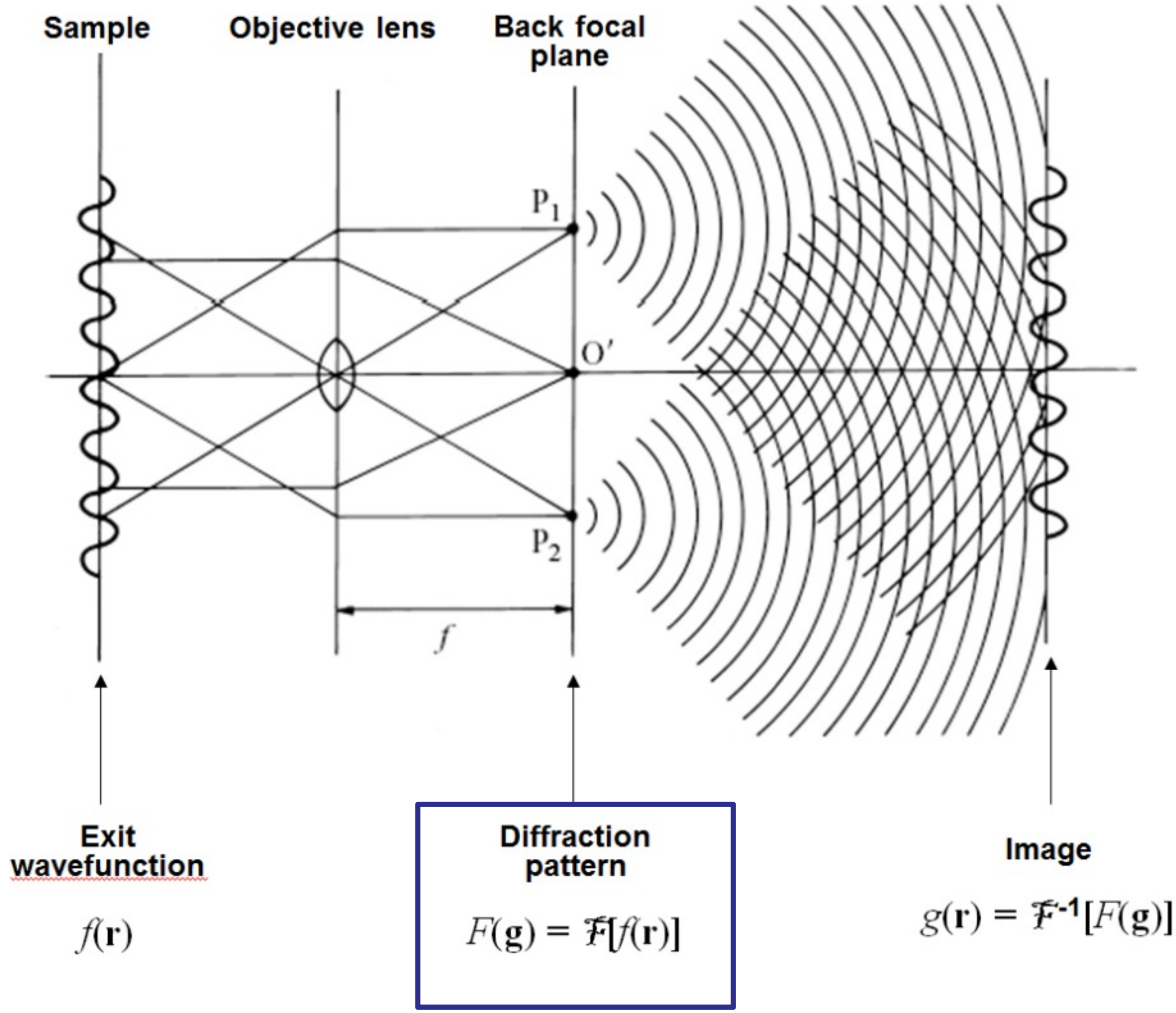
TEM modes with parallel-beam illumination



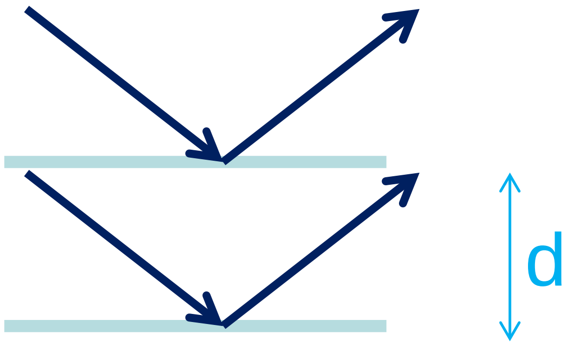
Adapted from N. Braidy et al. *Can. J. Chem. Eng*. **2020**, 98, 628–641

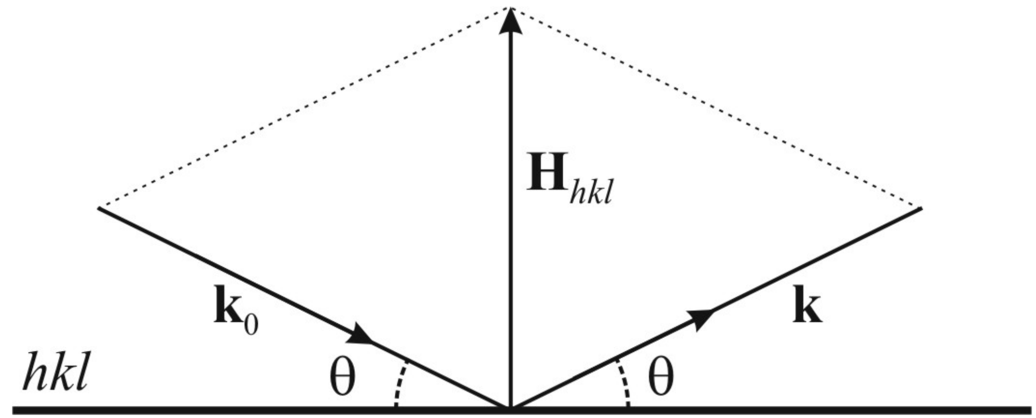
Diffraction mode

Formation of image: direct and Fourier space



Crystallographic planes and reciprocal lattice





Set of the $\mathbf{H}_{hkl}$ vectors form a reciprocal lattice of crystal

$\mathbf{k}_0$ – wave vector of the incident beam, $|\,\mathbf{k}_0\,| = 1/\lambda$

$\mathbf{k}$ – wave vector of the diffracted beam, $|\,\mathbf{k}| = 1/\lambda$

$\mathbf{H}_{hkl} \perp hkl$ plane, $\mathbf{H} = \mathbf{k} - \mathbf{k}_0$

Bragg's condition is satisfied if $|\mathbf{H}| = 2\sin\theta/\lambda = 1/d_{hkl}$

Vectors of reciprocal space:

$\mathbf{a}^* \perp \mathbf{bc}$ plane

$\mathbf{b}^* \perp \mathbf{ac}$ plane

$\mathbf{c}^* \perp \mathbf{ab}$ plane

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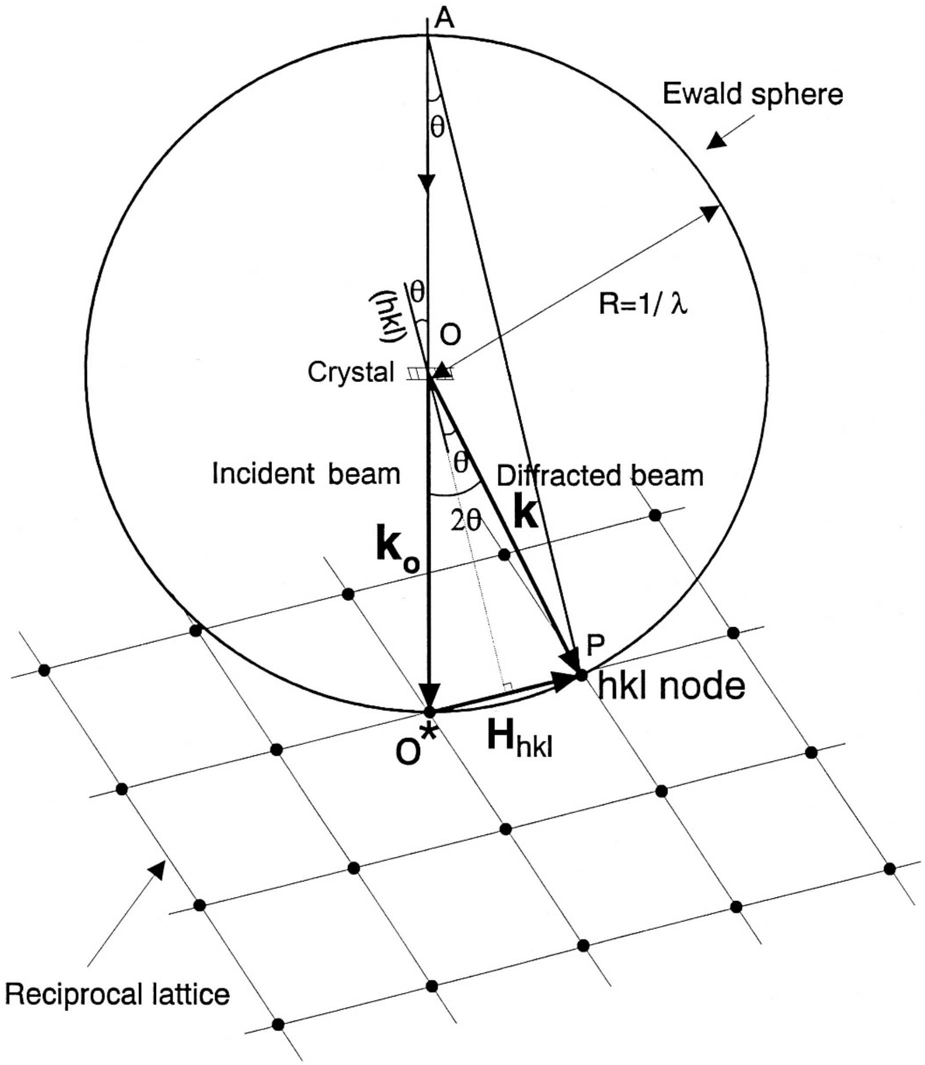
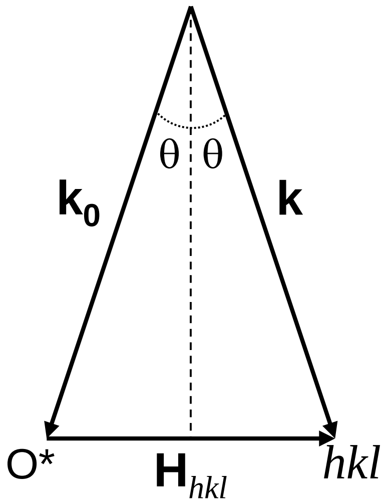
Reciprocal lattice and the Ewald sphere



1. Ewald sphere with the radius of $1/\lambda$
2. Crystal at the center of the sphere
3. Incident beam – wave vector $\mathbf{k}_0$
4. Origin of the reciprocal lattice O* at the intersection of the Ewald sphere and $\mathbf{k}_0$
5. Diffraction condition: when hkl node intersects the Ewald sphere (vector k)

$$|\mathbf{H}_{hkl}| = 2|\mathbf{k}_0| sin\theta$$

$$1/d_{hkl} = 2/\lambda \sin\theta$$



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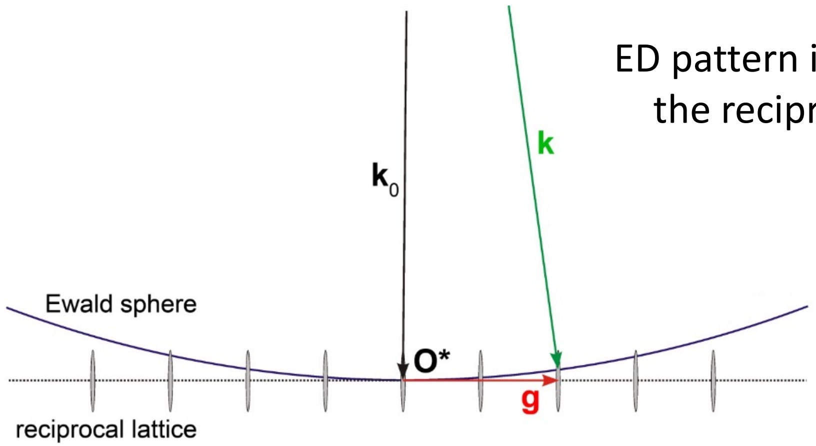
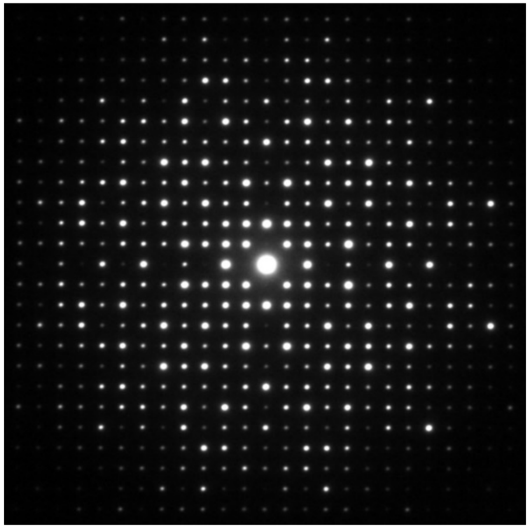
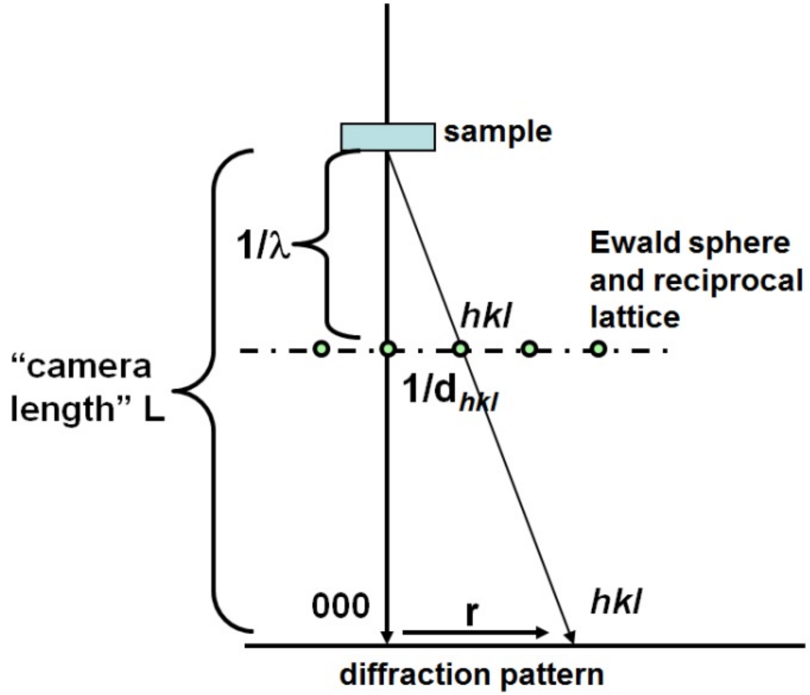
Selected area electron diffraction (SAED)



ED pattern is a **section** of the reciprocal lattice





Bragg equation for electron diffraction:

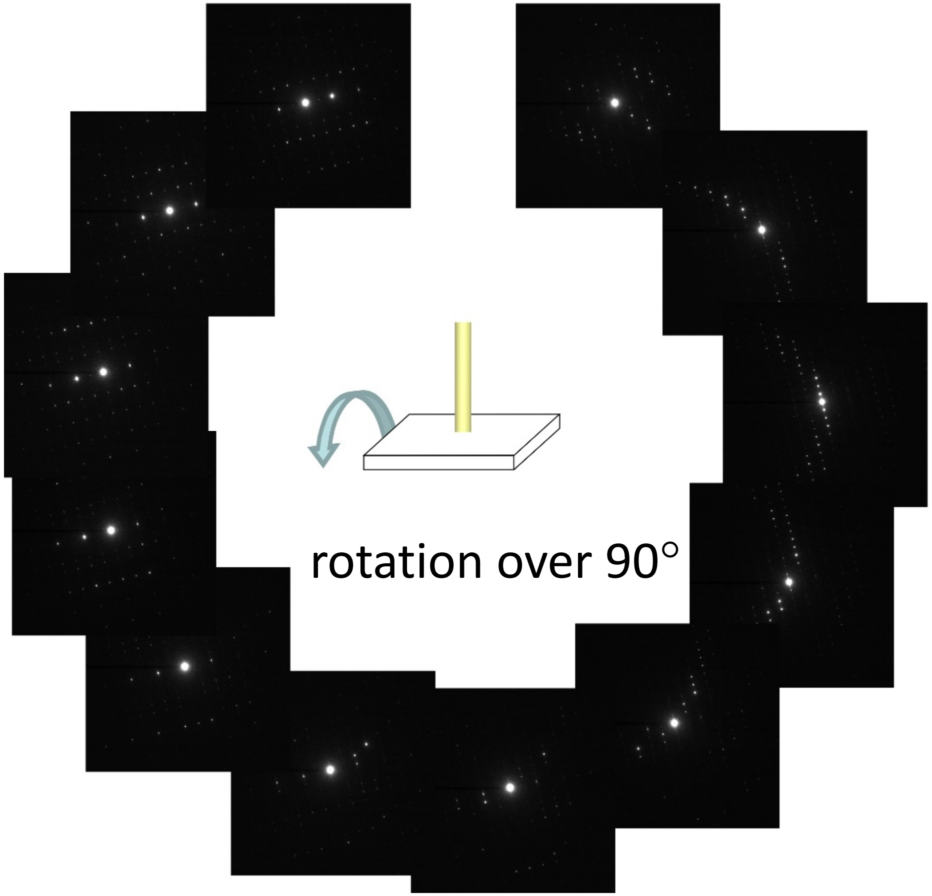
$$2d_{hkl}\sin\theta = \lambda, \theta - \text{small}$$

$$\sin\theta \approx \theta$$

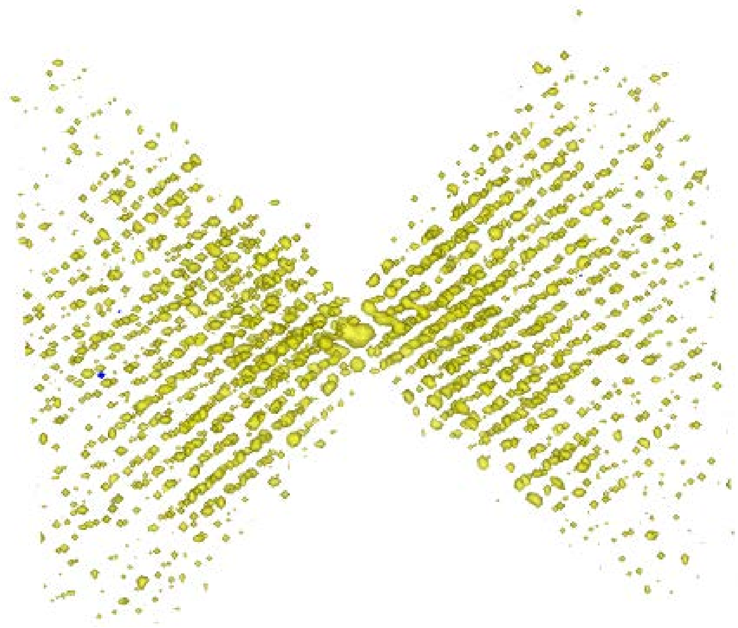
$$d_{hkl} \approx \frac{\lambda}{2\theta} \approx \frac{\lambda}{\tan(2\theta)} = \frac{L\lambda}{r}$$

From single SAED pattern to series of images

Electron diffraction tomography (EDT)



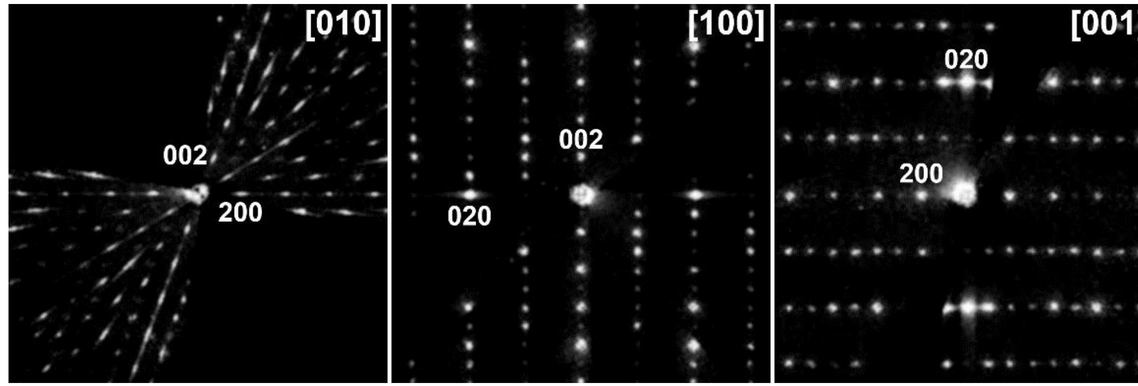
1. Registration of ED pattern each 0.5-1°
2. Data treatment and integration of intensities in quasi-kinematical approximation
3. Reconstruction of 3D reciprocal space
4. Search for structure model by charge flipping or other algorithm



U. Kolb et al. *Ultramicroscopy*, **2007**, 107, 6-7.

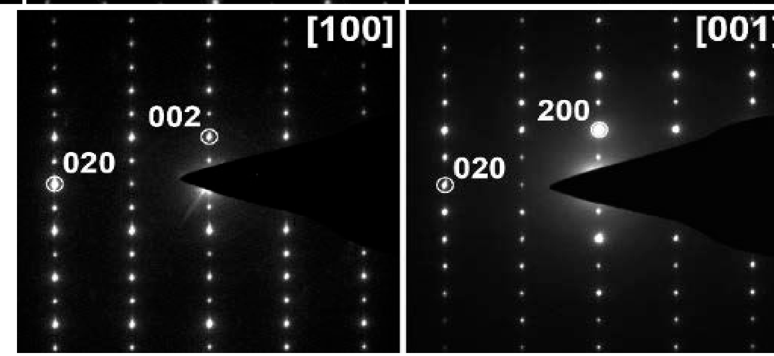
Electron diffraction tomography (EDT)

Reciprocal lattice sections from EDT

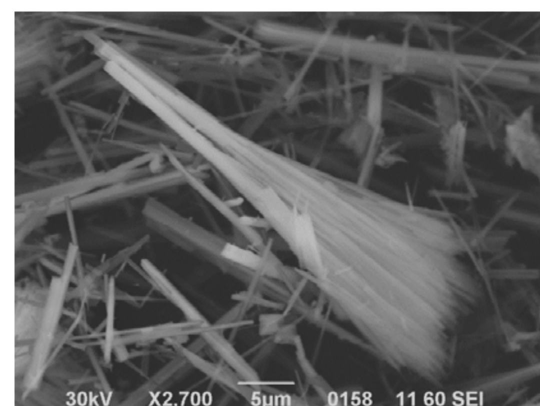


SAED patterns

[010] zone axis is (almost) not possible to observe experimentally!

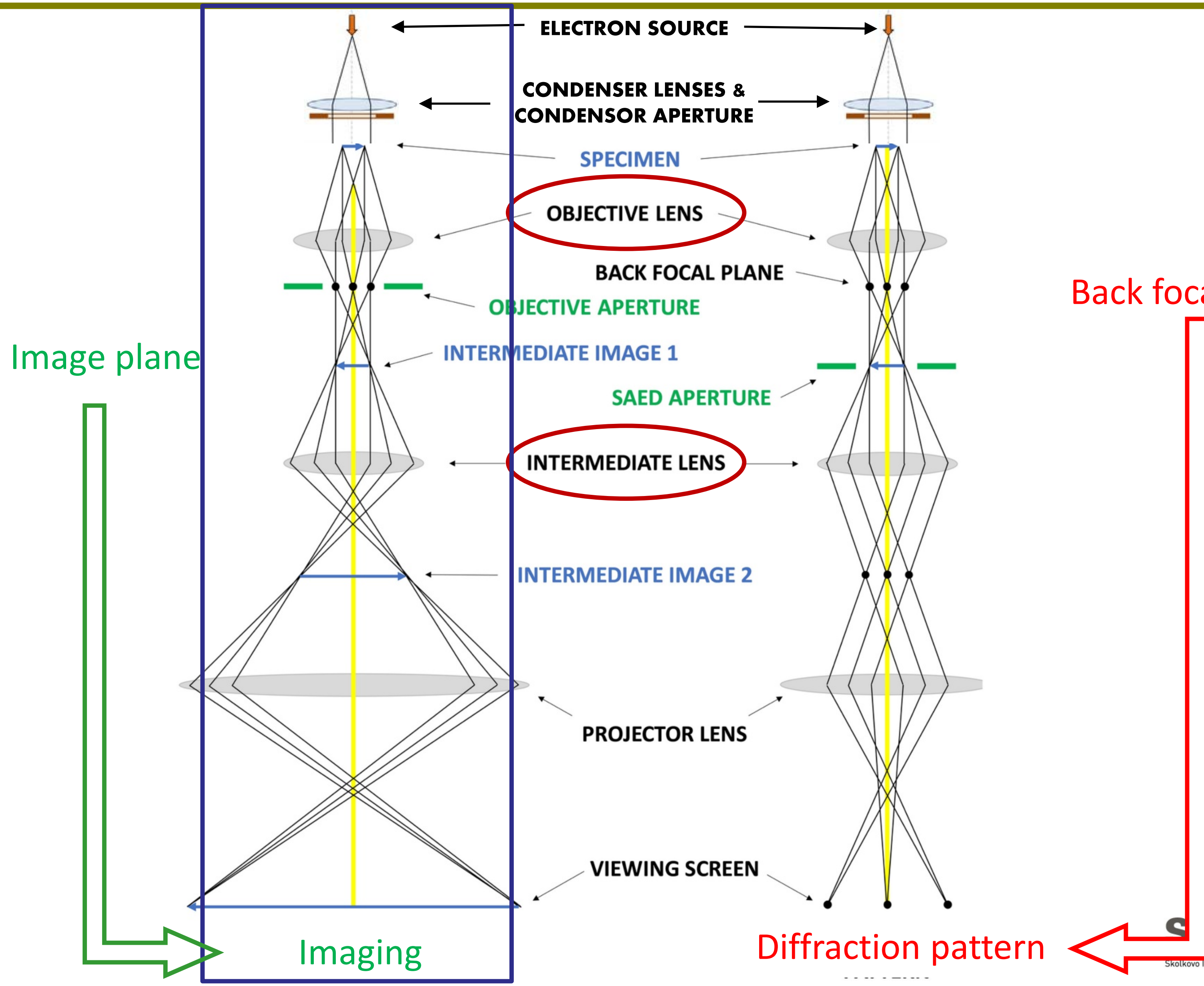


$Na_5Ni_2(PO_4)_3 \cdot H_2O$, $P2_1/n$, a = 14.039 Å, b = 5.185 Å, c = 16.474 Å, β = 110.42°

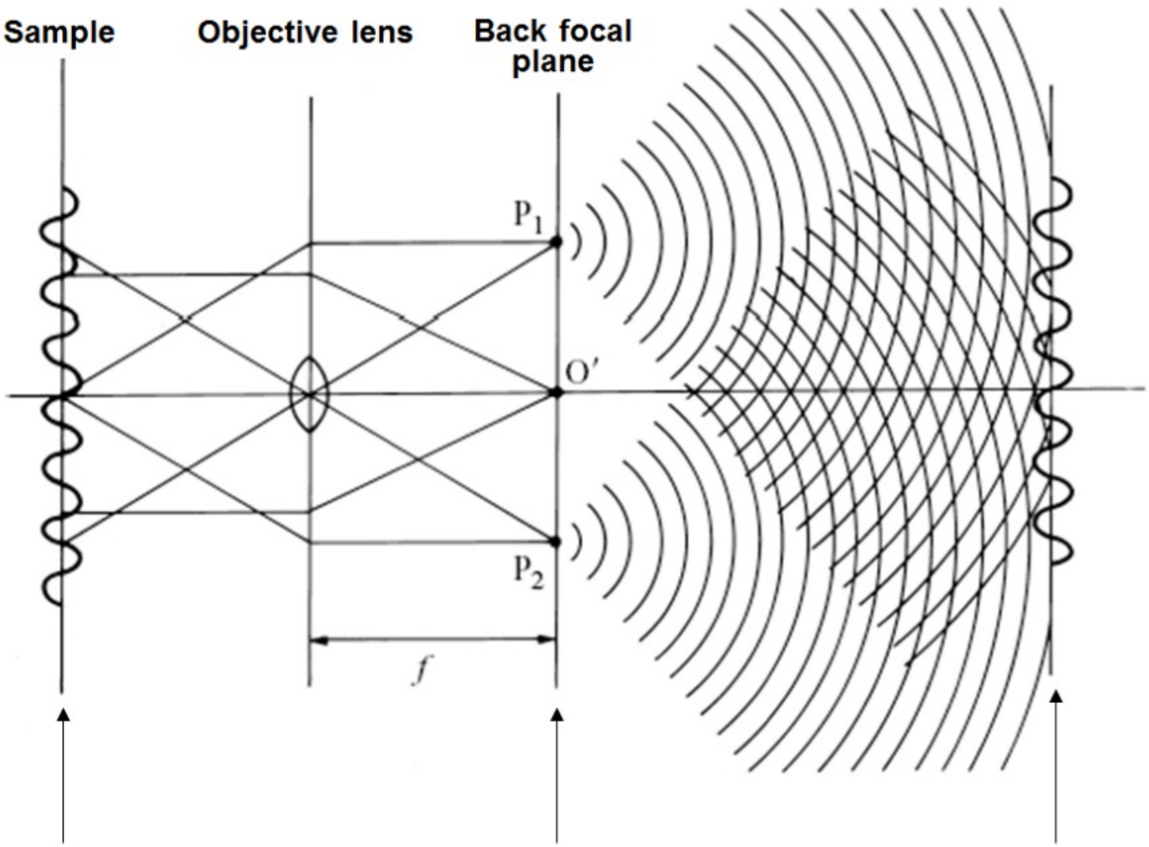


Imaging in parallel beam

TEM modes with parallel-beam illumination



High-resolution TEM imaging



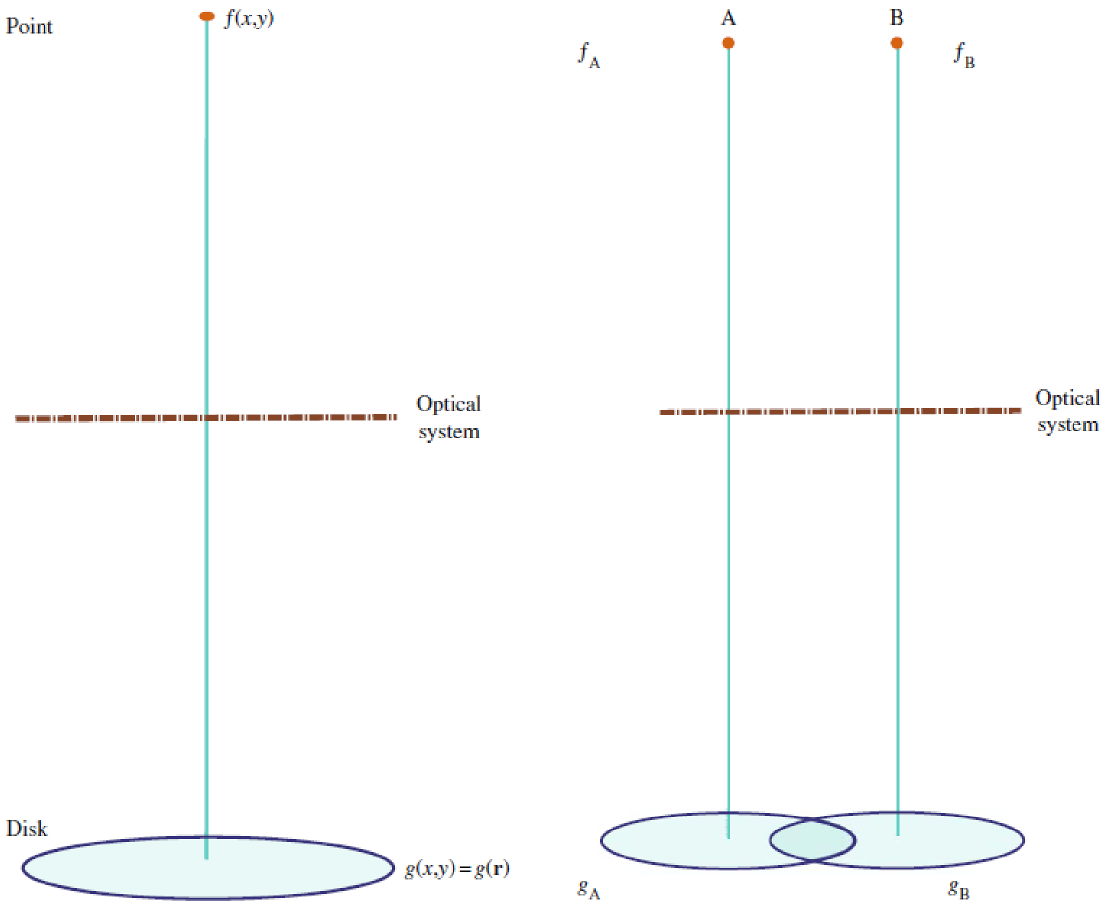
exit wave

diffraction pattern

magnified image of the exit wave (HRTEM)

We can put objective aperture in the BFP

HRTEM image – reality modified by microscope



point $f(\mathbf{r}) \to$ disk $g(\mathbf{r})$

$$g(\mathbf{r}) = \int f(\mathbf{r}')h(\mathbf{r}-\mathbf{r}')d\mathbf{r}' =$$
$$= f(\mathbf{r}) \otimes h(\mathbf{r}-\mathbf{r}')$$

image is a convolution of $f(\mathbf{r})$ with point-spread function $h(\mathbf{r})$

$H(\mathbf{g})$ – contrast transfer function

$$H(\mathbf{g}) = A(\mathbf{g})E(\mathbf{g})e^{-i\chi(\mathbf{g})}$$

$A(\mathbf{g})$ – aperture function
$E(\mathbf{g})$ – incoherent envelope function
$\chi(\mathbf{g})$ – phase shift of the scattered wave

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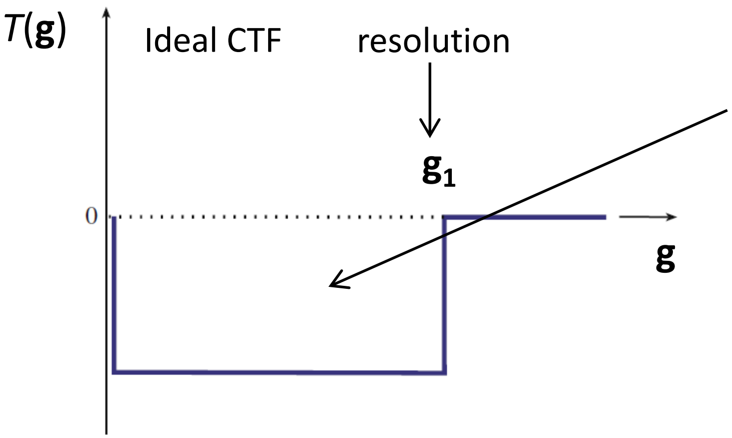
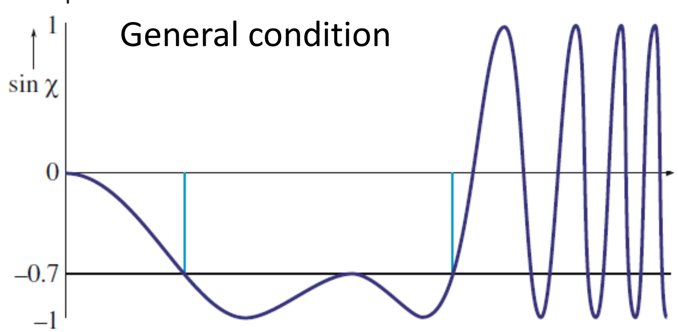
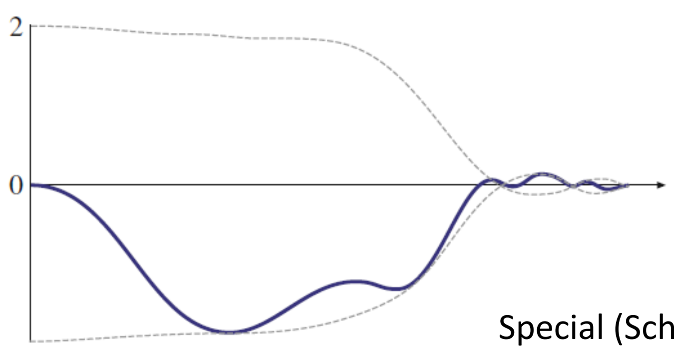
Contrast in HRTEM



$T(\mathbf{g})$ is large, constant and negative
- atoms appear dark





Special (Scherzer) condition

Phase shift of the scattered wave:

$$\chi(g) = \pi \Delta F \lambda g^2 + \frac{\pi C_s \lambda^3 g^4}{2}$$

ΔF – defocus
C_s – spherical aberration coefficient
g – diffraction vector
λ - wavelength

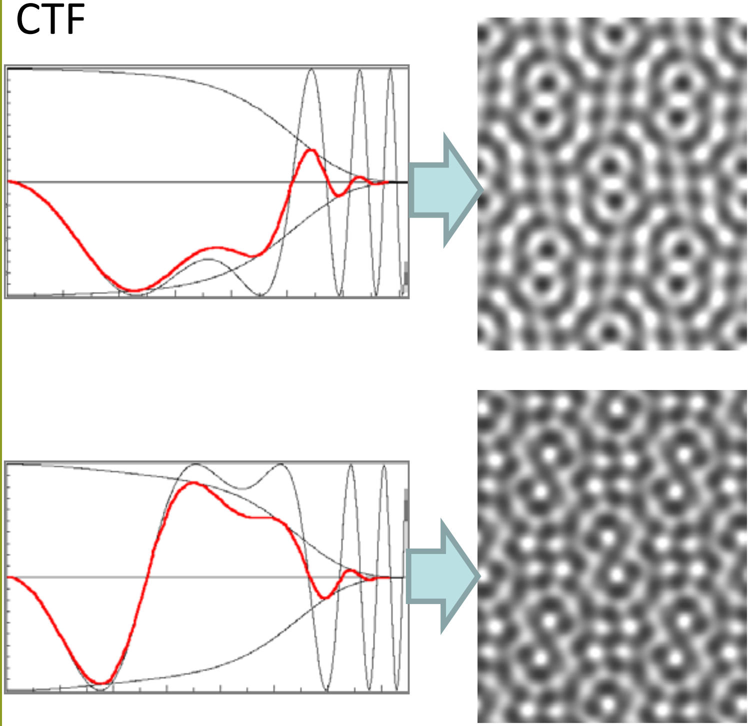
Phase-contrast transfer function (CTF):

$$T(\mathbf{g}) = A(\mathbf{g}) D(\alpha, \Delta) \sin \chi(\mathbf{g})$$

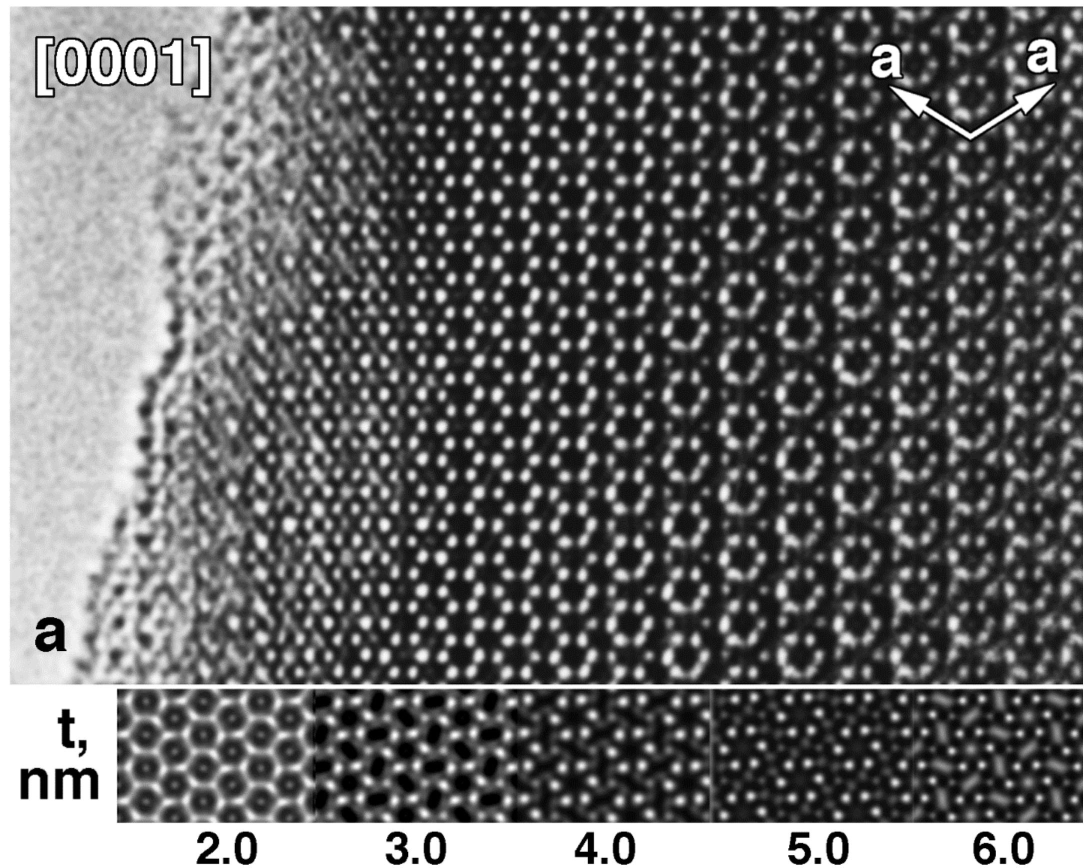
HRTEM: examples

Focus-dependent

CTF

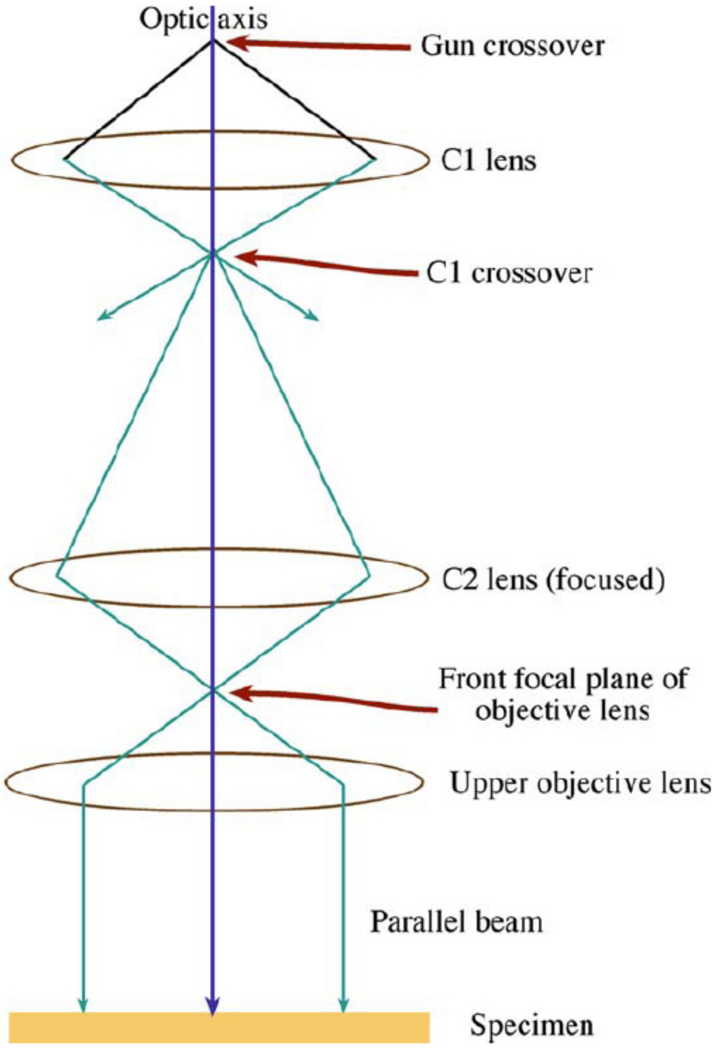


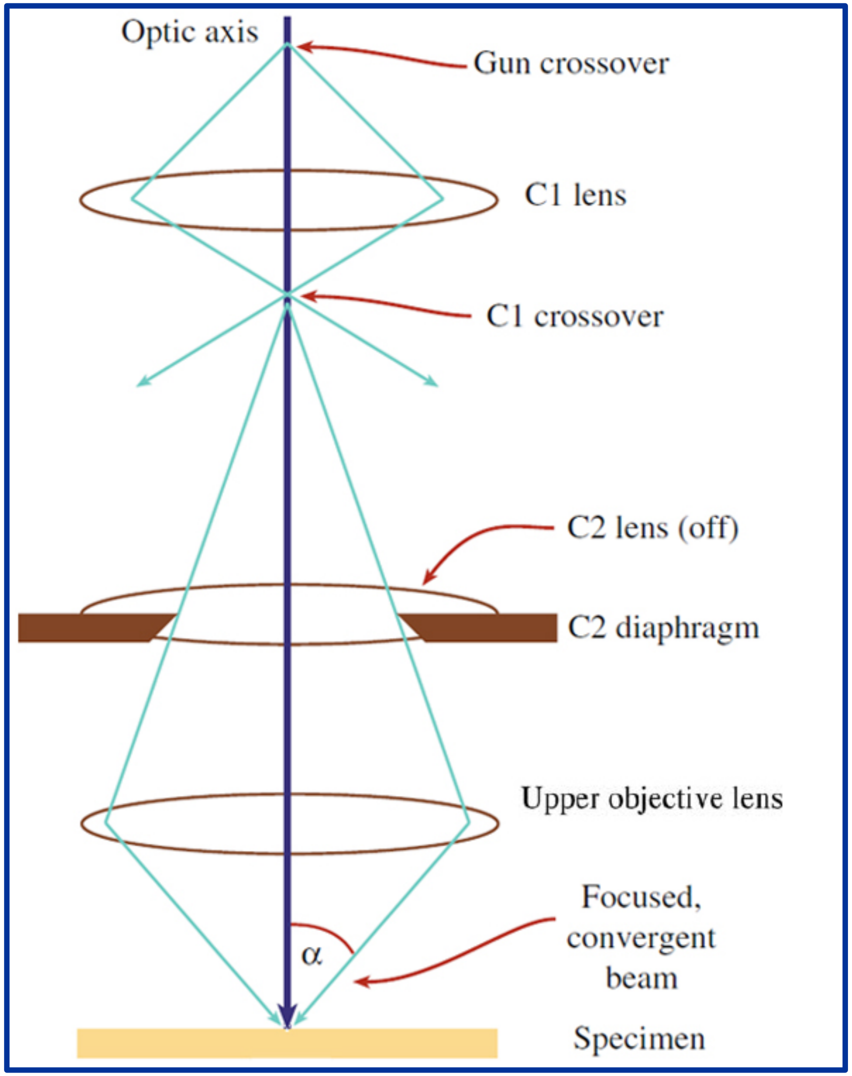
Thickness-dependent



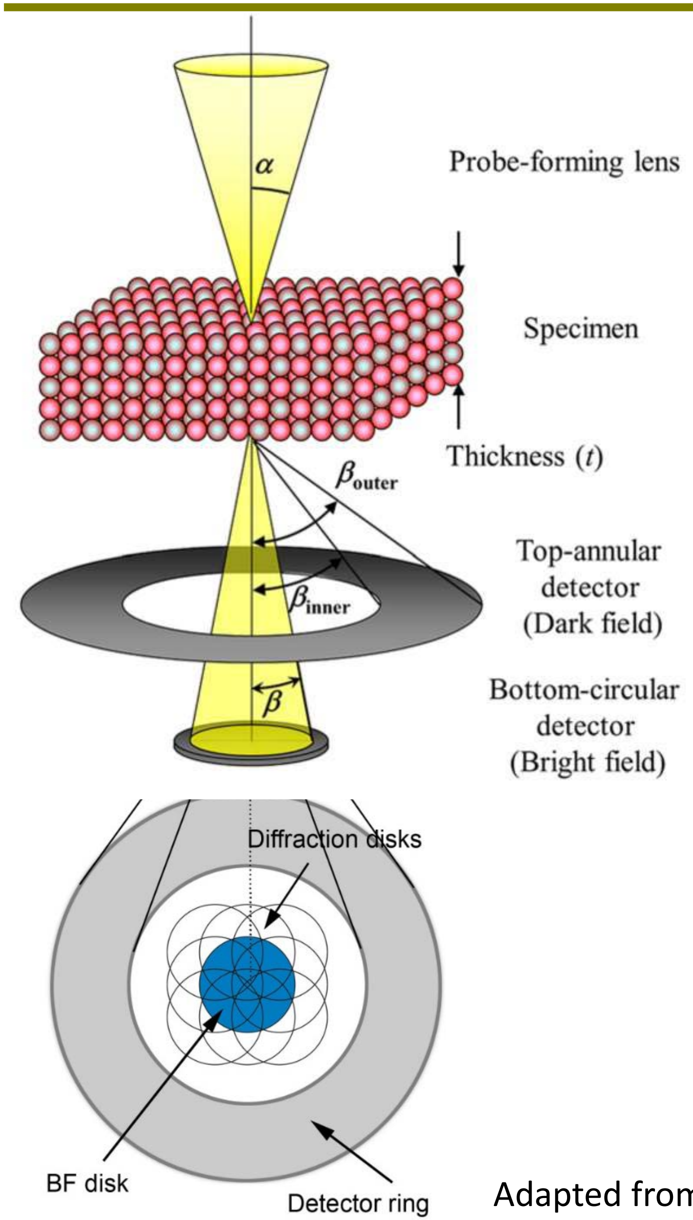
Imaging in focused beam – Scanning Transmission Electron Microscopy (STEM)

Focused beam mode - STEM





HAADF-STEM imaging



HAADF-STEM – High Angle Annular Dark Field Scanning Transmission Electron Microscopy

- Focused probe ~ 1 Å
- ADF detector is located in the diffraction plane
- Intensity of signal is highly dependent on Z number: $I \sim Z^2$

Adapted from Y. Kotaka, *Appl. Phys. Lett*. **2012**, 101, 133107.

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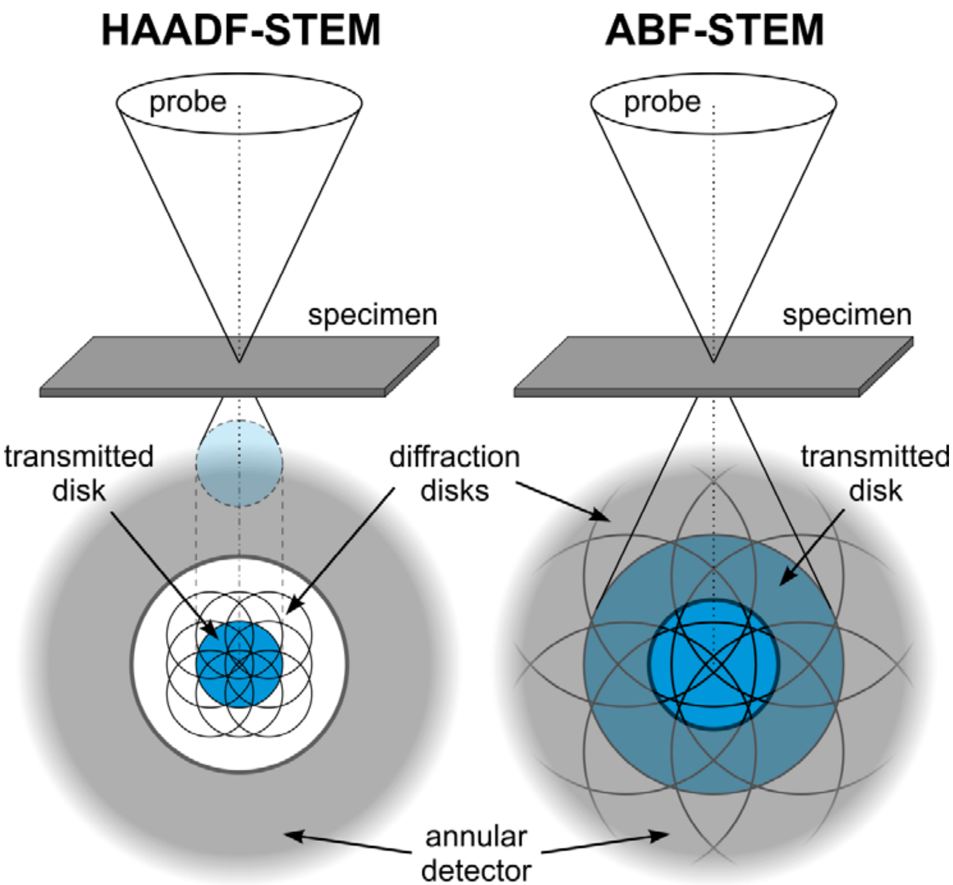
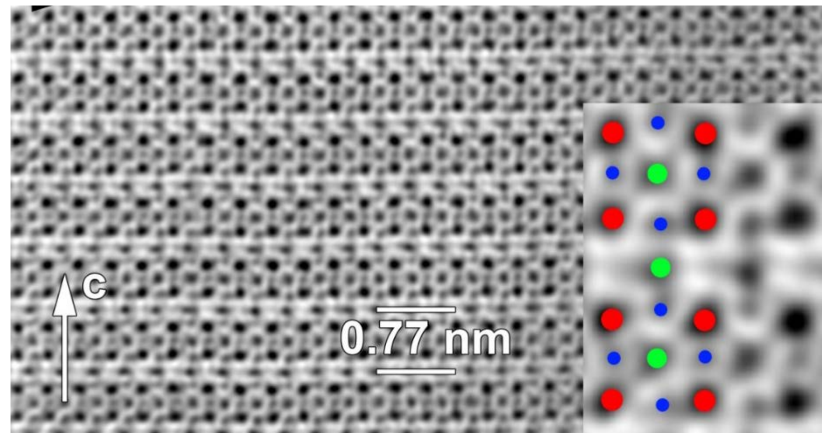
HAADF- vs. ABF-STEM imaging

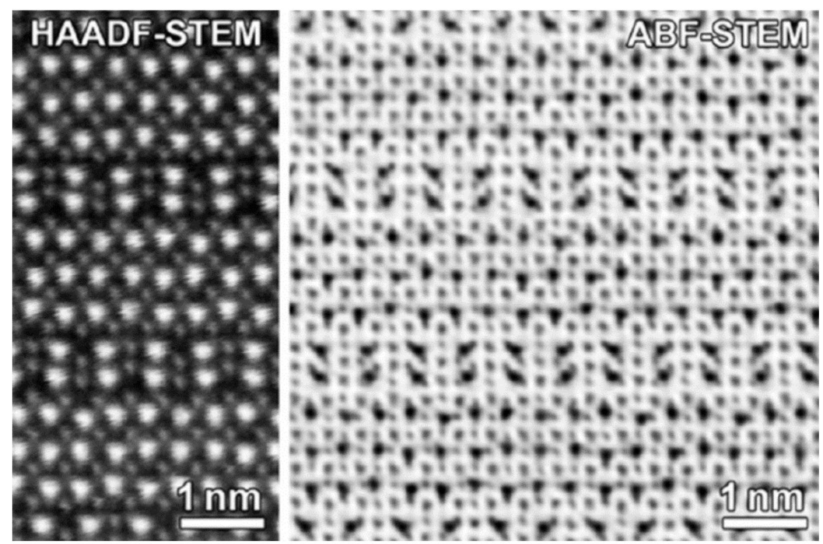
ABF-STEM – Annular Bright Feld Scanning Transmission Electron Microscopy



$I \sim Z^2$

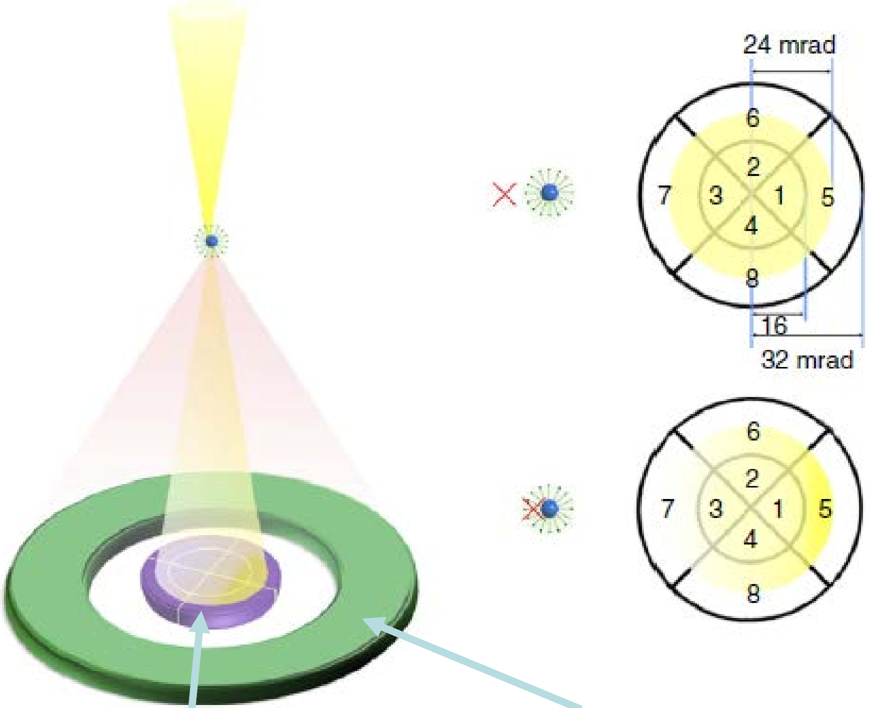
$I \sim Z^{1/3}$





Visualization of light elements (Li, O…)

iDPC and dDPC STEM mapping



(HA)ADF-detector

segmented detector, inserted in the BF-region of the illuminating cone

Registering DPC-maps

Adapted from N. Shibata et al., *Nature Commun.*, **2017**, 8, 15631.

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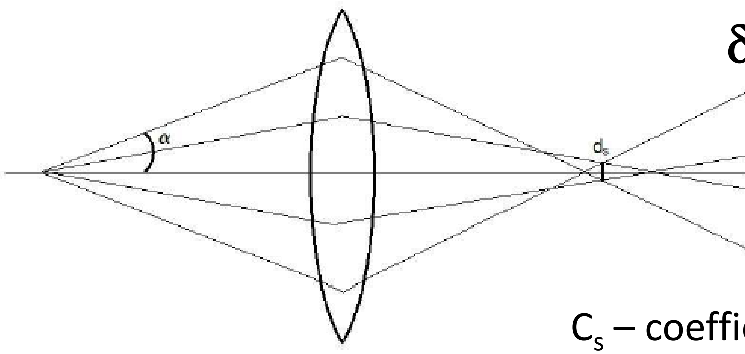
Resolution limit: aberrations of lenses

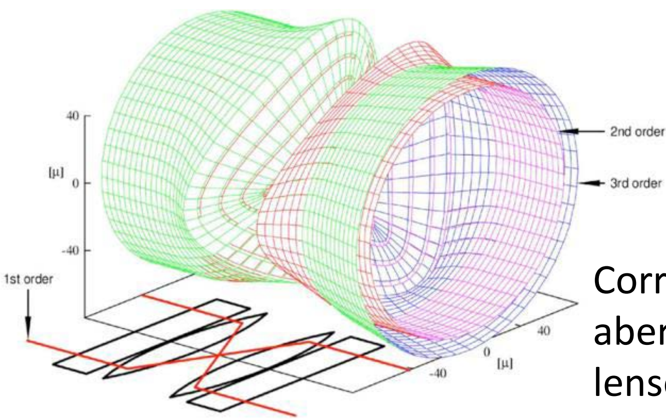
300 kV: $\delta^{theor} \approx 0.02$ Å

$\delta^{exper} \approx 0.50$ Å



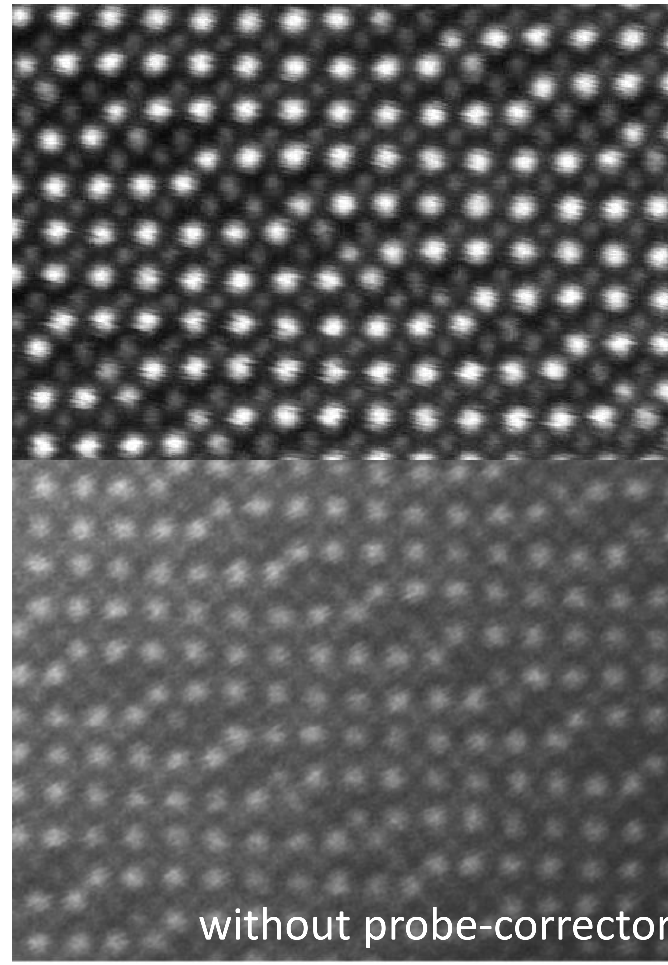
C_s – coefficient of spherical aberration

$$d_s = \frac{1}{2} C_s \alpha^3$$



Corrector of spherical aberrations of condenser lenses

aberration corrected



Principle: non-spherical elements of electron optic create divergent lens

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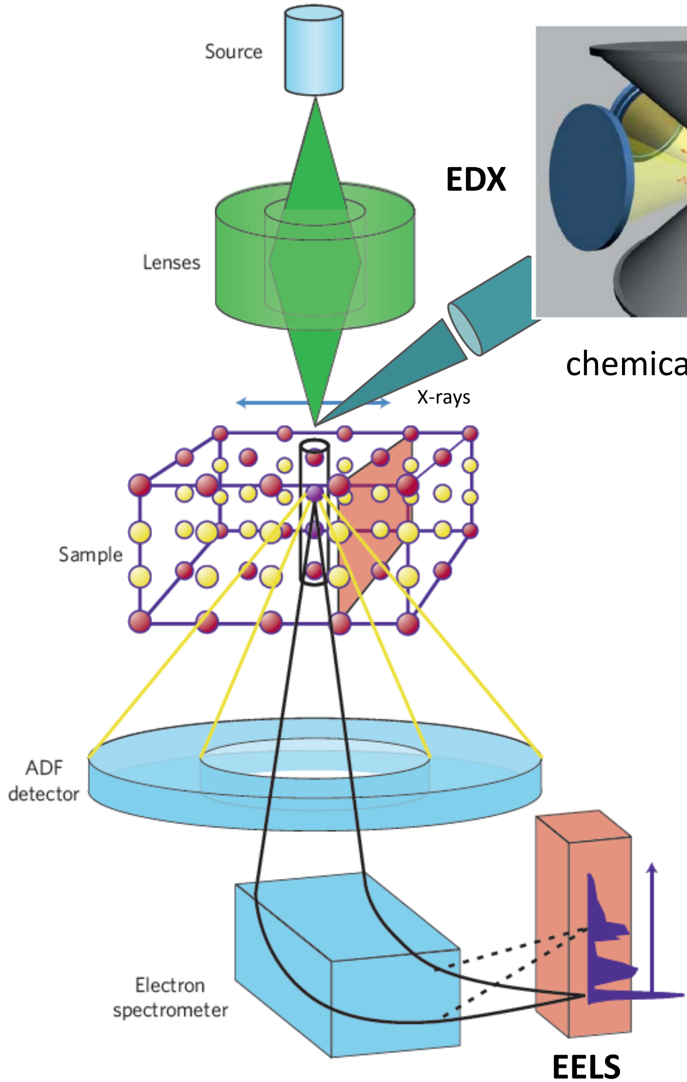
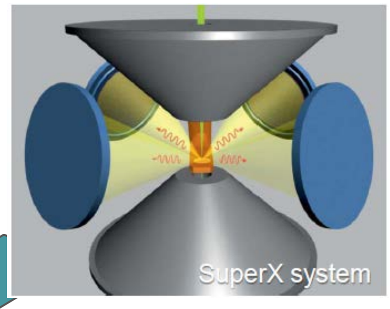
Analytical tools of TEM

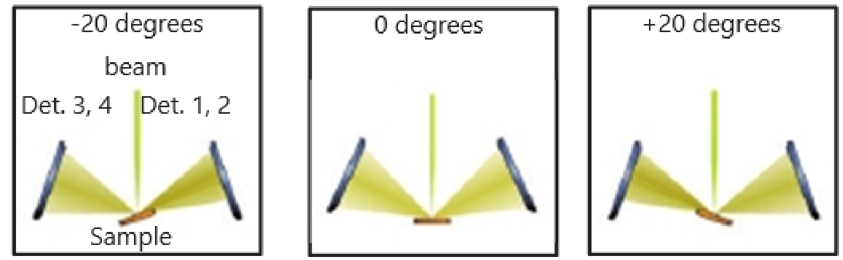
Chemistry at atomic resolution



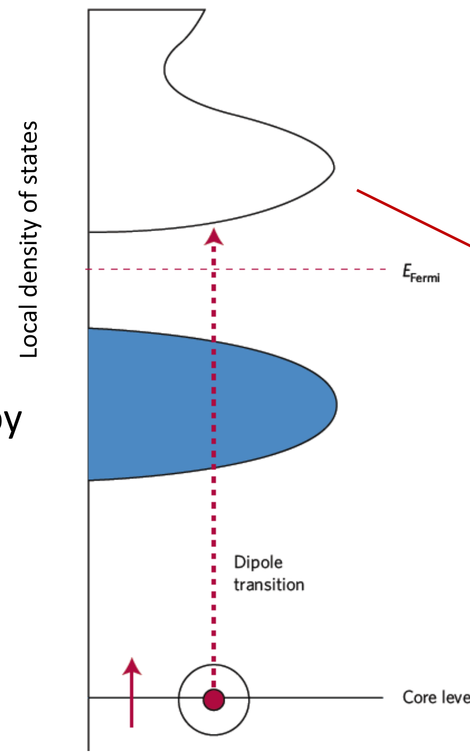


chemical composition

EDX – Energy Dispersive X-ray Spectroscopy

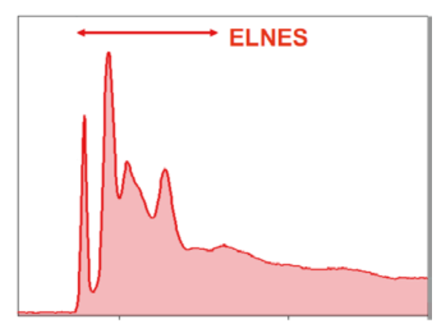


EELS –
Electron
Energy
Loss
Spectroscopy



EELS-mapping of:

- oxidation state
- coordination number



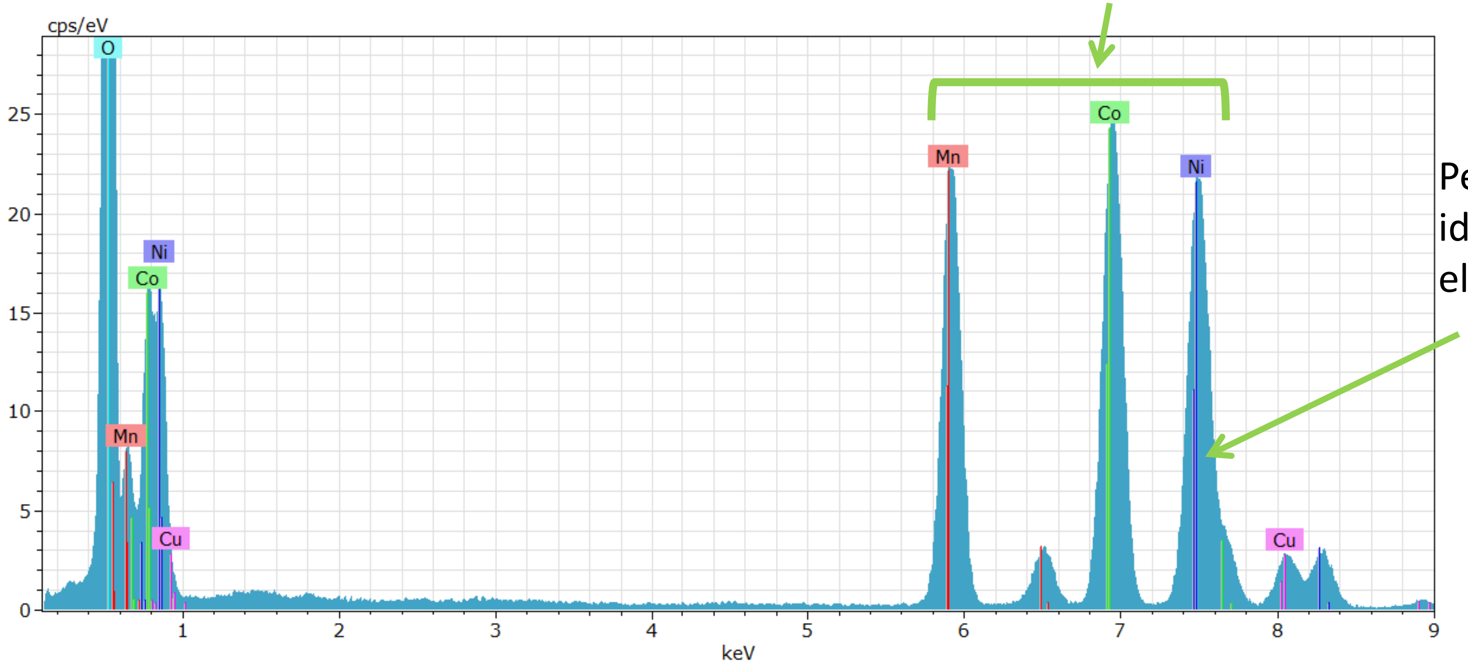
Electron Energy Loss
Near Edge Structure

Adapted from D. Muller, *Nature Mater.*, **2009**, 8, 263.

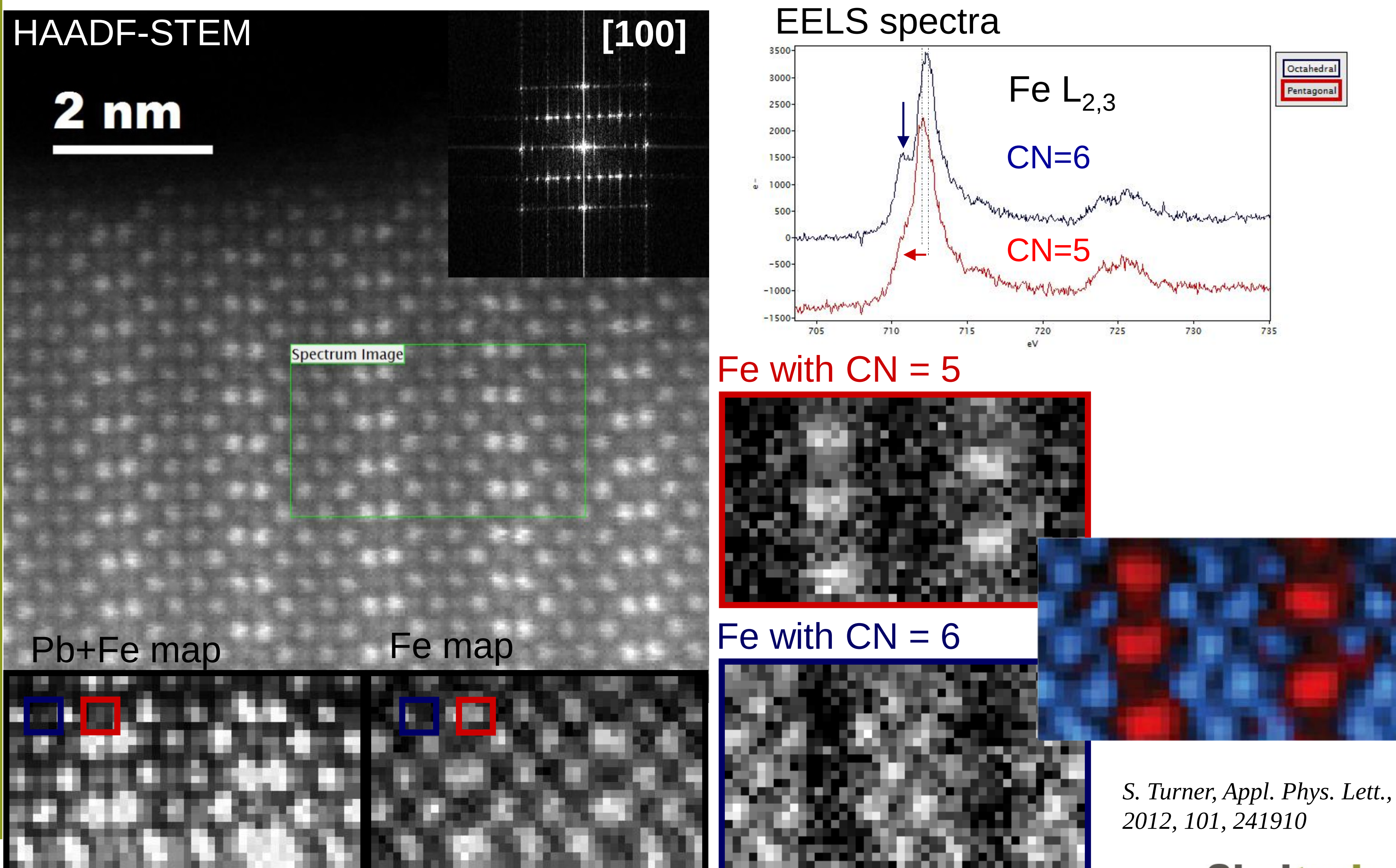
STEM-EDX

Intensity ratio to measure the composition

Peak positions to identify the elements



STEM-EELS



S. Turner, Appl. Phys. Lett., 2012, 101, 241910

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All-round help – Prof. Artem Abakumov

FIB SEM images – courtesy of Dr. Ilya Krupatin